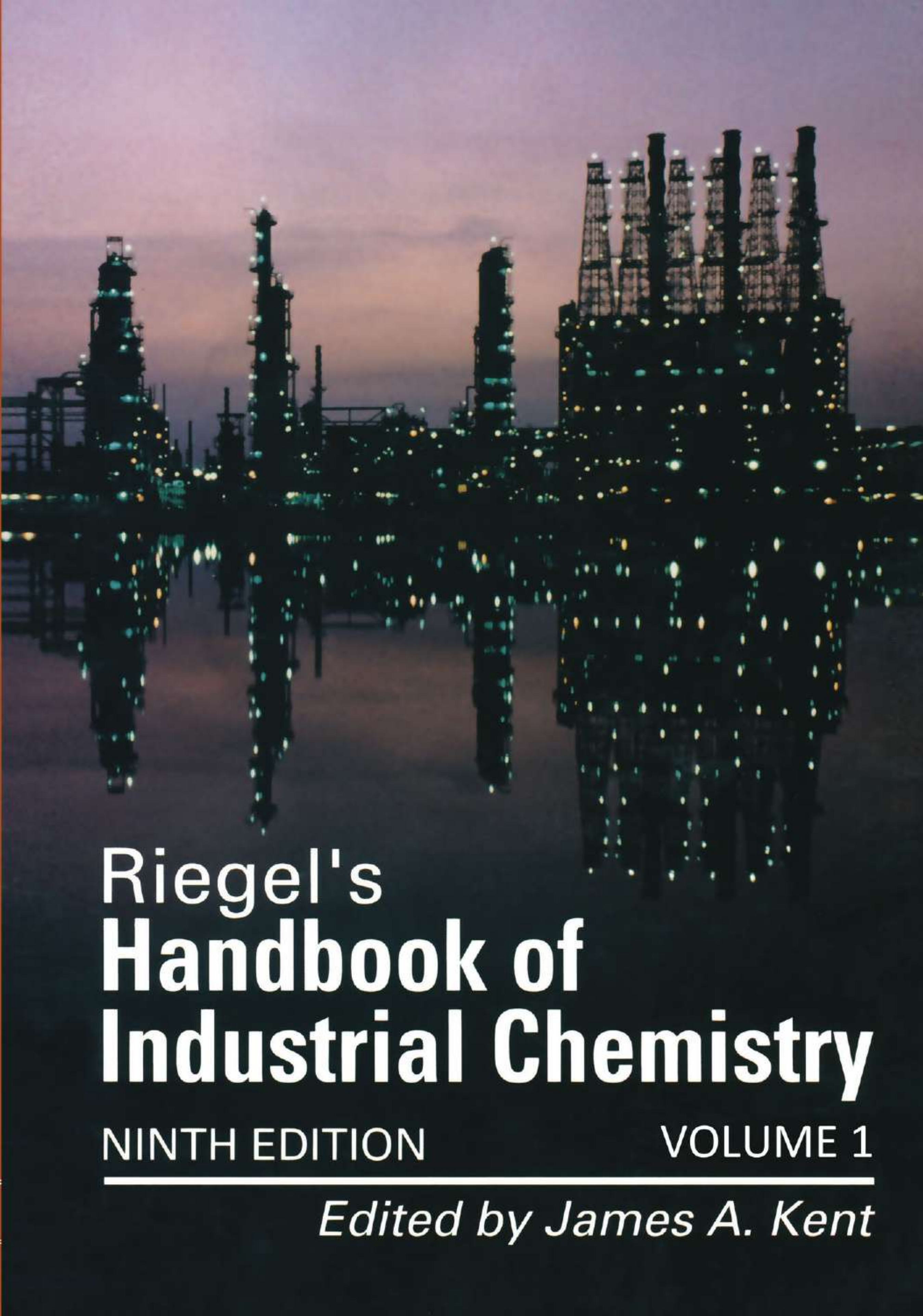

Riegel's
Handbook of Industrial Chemistry

NINTH EDITION VOLUME 1

Edited by James A. Kent

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To my Wife
ANITA

Contents

Preface

The aim of this book is to present in a single volume an up-to-date account of the chemistry and chemical engineering which underlie the major areas of the chemical process industry. This most recent edition includes several new chapters which comprise important threads in the industry's total fabric. These new chapters cover waste minimization, safety considerations in chemical plant design and operation, emergency response planning, and statistical applications in quality control and experimental planning. Together with the chapters on chemical industry economics and wastewater treatment, they provide a unifying base on which the reader can most effectively apply the information provided in the chapters which describe the various areas of the chemical process industries.

The ninth edition of this established reference work contains the contributions of some fifty experts from industry, government, and academe. I have been humbled by the breadth and depth of their knowledge and expertise and by the willingness and enthusiasm with which they shared their knowledge and insights. They have, without exception, been unstinting in their efforts to make their respective chapters as complete and informative as possible within the space available. Errors of omission, duplication, and shortcomings in organization are mine.

Grateful acknowledgment is made to the editors of technical journals and publishing houses for permission to reproduce illustrations and other materials and to the many industrial concerns which contributed drawings and photographs.

Comments and criticisms by readers will be welcome.

James A. Kent
Stevensville, Maryland

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Economic Aspects of the Chemical Industry

F. E. Bailey, Jr.* and J. V. Koleske**

Within the formal departments of science at the traditional university, chemistry has grown to have a unique status because of its close correspondence with an industry and a branch of engineering—the chemical industry and chemical engineering. There is no biology industry, but drugs, pharmaceuticals, and agriculture are closely related disciplines. There is no physics industry although power generation, electricity, and electronics industries do exist. But connected with chemistry, there is an industry. This unusual correspondence probably came about because in chemistry one makes things from basic raw materials—chemicals—and the science and the use of chemicals more or less grew up together during the past century.

Since there is a chemical industry, which serves a major part of all industrialized economies, providing in the end synthetic drugs, fertilizers, clothing, building materials, paints, elastomers, etc., there is also the subject of "chemical economics"; and it is this subject, the economics of the chemical industry, that is the concern of this chapter.

DEFINITION OF THE CHEMICAL INDUSTRY

Early in the twentieth century, the chemical industry was considered to have two parts: the manufacture of inorganic chemicals and the manufacture of organic chemicals. Today, the Standard Industrial Classification (SIC Index) of the United States Bureau of the Census defines "Chemical and Allied Products" as comprising three general classes of products: "(1) basic chemicals such as acids, alkalis, salts, and organic chemicals; (2) chemicals to be used in further manufacture such as synthetic fibers, plastics materials, dry colors, and pigments; and (3) finished chemical products to be used for ultimate consumer consumption as architectural paints, drugs, cosmetics, and soaps or to be used as materials or supplies in other industries such as industrial paints, adhesives, fertilizers, and explosives."[1] An even broader description that is often considered is that of the "chemical

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process industries," major segments of which include: chemical and allied products and petrochemicals; pulp and paper; petroleum refining; rubber and plastics; and stone, clay, and glass products.

THE PLACE OF THE CHEMICAL INDUSTRY IN THE ECONOMY

Because the chemical industry is a major sector of any advanced national economy, a forecast of trends in the chemical industry must fall within certain general guidelines that are established by the national economy. A forecast for the chemical industry in the United States must be within the general boundaries set for the overall social and economic forecasts for the country.

It has been clear for many years that certain demographic and societal issues would have a dominant effect on the U.S. economy of the 1990s. It was evident, for example, that from the late 1980s through the year 2000 there would be a decline in the growth of the work force in the United States. There is a direct relation between the growth of the work force and the growth of the GNP (Gross National Product, the sum of all goods and services produced in a year); the decline in the growth of the work force in this period was determined by the number of women in the usual child-bearing age group (18 to 35) and by family-size decisions made in the 1960s. Therefore, this factor was set and calculable from census data obtained 20 years earlier.

A predicted decline in the growth of the GNP due to a declining work force can be offset if worker productivity increases or if the age of retirement from the work force is extended beyond the usual retirement age of 65. In the United States during the 1980s, there was little overall increase in worker productivity; and, in many industries, there was a move toward retirement before age 65. In many industries, the average age of retirement moved toward 60 from the long-accepted norm of 65. These trends, as well as a marked growth in the service sector of the economy as opposed to such growth in the manufacturing sector, have contributed to a shortage of technically trained chemists and engineers entering the work force. This shortage is expected to become severe in the latter part of the 1990s.

Another factor in the overall economy that must be considered is that the GNP represents a "volume" of goods and services measured in value or "dollars." This "dollar volume" is very sensitive to inflation (or deflation). To remove this sensitivity for forecasting purposes, GNP is expressed in "constant dollars," dollars "deflated" by the annual inflation rate to some base year such as 1982.

Against this brief discussion of the general demographic, societal, and economic factors that govern forecasting, Table 1.1 gives a general picture of the economy of the United States in terms of the GNP and chemical industry production.

The forecast for the early part of the 1990s, which is subject to all the uncertainties and unpredictabilities of social and international events, is for steady growth of the U.S. chemical industry, but growth at a rate lower than that experienced in the mid-1980s and moderated by an average annual inflation rate of about 5 percent per year. This forecast includes a gradual increase in the price of imported oil and petroleum products during the early 1990s compared with lower imported oil costs in the late 1980s. Changes such as that caused by the 1990–91 Persian Gulf crisis have not been considered although such events certainly can have a profound effect on prices. At present the price of oil appears to be fairly stable, at least for the short term.

This forecast is presented to highlight the sensitivity and the place of the chemical industry in the national economy. The importance of the cost of imported raw materials such as petroleum products in both the economy and the forecast highlights two important concerns. One is that the chemical industry is worldwide and interconnected; not only does the United States both import and export a wide variety of raw materials and chemical products, but major United States–based chemical companies have manufacturing and sales facilities abroad, and a large number

TABLE 1.1 U.S. Economy and the Chemical Industry[2]

Year	United States GNP (Current dollars, billions)	United States GNP (1982 dollars, billions)	Percent Change in Chemicals and Allied Products Annual Production Index
1987	4500	3800	6.1
1988	4900	4000	8.5
1989	5200	4100	4.9
1990 (estimate)	5500	4200	2.4
1995 (forecast)	8000	4700	2.8*

*Annual average for 1990–95.

of foreign-based companies have manufacturing and sales facilities in the United States. The other is that the United States economy is dependent on the balance of trade, the difference between the dollar value of exports and that of imports. A negative trade balance means that dollars spent abroad to import goods and services exceed the value of goods and services exported, a circumstance that effectively increases the cost of goods and services purchased in the United States—a net inflationary effect. To a large extent during the 1980s, this potentially inflationary effect was offset by foreign investment in the United States; however, this offsetting of a negative trade balance by investment cannot be depended on to continue through the 1990s. At some point, foreign investors will demand a return on their investment, in effect an export of dollars, with an inflationary result on the domestic economy.

In foreign trade, the performance of the chemical industry of the United States has been outstanding. While the overall balance of trade has been negative, the chemical industry has been one of the truly strong sectors in the U.S. economy; see Table 1.2. If the total world export market for chemicals is considered, that is, the sum of all of the chemicals exported by all the world's national economies, the U.S. chemical industry held about a 15 percent market share during the decade of 1979 to 1989.

Major segments in the U.S. chemical trade balance in 1989 were:

Organic chemicals— + $3.6 billion
Plastics materials— + $4.6 billion
Pharmaceuticals— + $1.6 billion

The less favorable overall trade balance of the United States was due principally to imports of manufactured goods and petroleum products; see Table 1.3.

To support the U.S. chemical economy in 1989, there was a work force of more than one million, 600,000 of whom were occupied in chemical production. The largest single sector of this work force, about 20 percent,

TABLE 1.2 U.S. Balance of Trade

	Total Trade Balance (billions of dollars)			Chemical Trade (billions of dollars)		
Year	Export	Import	Balance	Export	Import	Balance
1979	181	206	−25	17	7	+10
1987	253	406	−153	26	16	+10
1989	364	473	−109	36	20	+16
1990	394	495	−101	39	22	+17

TABLE 1.3 U.S. Trade Balance in 1989 (billions of dollars)

Sector	*Import*	*Export*	*Balance*
Chemicals	20	36	+16
Machinery	206	148	−58
Other manufactured goods	139	60	−79
Fuels and petroleum products	53	9	−44

was involved in the manufacture of ethical drugs and pharmaceuticals. This group was closely followed by those workers involved in the manufacture of plastics and synthetic materials. To back up this immensely important part of the economy, the chemical industry (chemicals and allied products) employed about 75,000 scientists and engineers, which is about 10 percent of the total number of scientist and engineers employed by industry in the United States. On an average, the larger chemical companies (top 15 companies in chemical sales) invested approximately 4 percent of their gross sales in research and development activities to support growth and to maintain their market share.

CHARACTERISTICS OF THE CHEMICAL INDUSTRY

Investment Trends

The chemical industry tends to be a high-investment business. Capital spending by the chemical and allied products industry in the United States has been a sizable percentage of the total spent for all manufacturing. Amounts spent in this industry and in certain facets of it are detailed in Table 1.4. The amount spent for all chemical process industries has been, of course, even larger; it totaled $68.9 billion in 1990, for example, a 5.3 percent increase over the amount spent in 1989. For perspective, annual expenditures for new plant and equipment in the United States for the chemical and allied products industry in recent years have averaged about 2.5 times the amount spent for iron and steel and about half of that invested in the petroleum industry. For the past decade a significant part of these capital investments have been made in pollution control and projects related to the environment.

TABLE 1.4 New Capital Spending in the U.S. Chemical and Allied Products Industry and Comparison with That Spent a Decade Earlier[1]

	Billions of Dollars	
	1986	*1976*
Total chemical and allied products	7.9	7.1
Selected Segments		
Agricultural chemicals	0.52	1.05
Industrial inorganic chemicals	0.81	0.81
Industrial organic chemicals	1.84	2.69
Plastic materials, synthetic resins, and thermoplastic elastomers	1.90	1.37
Soap, detergents, perfumes, cosmetics, and other toilet products	0.74	0.29
Miscellaneous chemicals	0.51	0.32

Much of the capital investment in the chemical industry is spent for facilities used to produce major chemicals (Table 1.4) in truly enormous quantities. The volume produced is reflected in the size of plants being built to achieve the required economies of scale. That such economies are achieved is seen in the more modest increases in the chemical producers' price indices relative to the inflation levels in the general economy. (Economy of scale refers to the relative cost of building a larger plant; a rule of thumb is that the relative cost of building a smaller or a larger plant is the ratio of the productivities of the two plants being considered, raised to the 0.6 power. In other words, the unit cost of producing a chemical markedly decreases as the size of the plant producing it is increased, provided that the plant can be operated near capacity.)

Today, a typical, base petrochemicals plant will consume the equivalent of 30,000 barrels per day of naphtha to produce about one billion pounds of ethylene a year, plus 2.5

TABLE 1.5 Employment in Selected Parts of the Chemical Industry in 1990, 1987, and 1977[2]

Chemical Industry	Thousands of Employees 1977	 1987	 1990
Chemical and allied products	1,074	1,026	1,086
Segments			
Cosmetics, perfumes, etc.	53	70	N/A*
Drugs	181	212	239
Industrial inorganic chemicals	162	135	135
Industrial organic chemicals	166	152	153
Paints	66	63	63
Pharmaceutical preparations	145	169	N/A
Plastic materials	83	76	N/A

*N/A = not available.

billion pounds of coproducts. To be economically feasible, for example, plants for the production of monomers such as vinyl chloride and styrene for plastic products must be scaled in the billion-pound-per-year range.

Along with these very large plants and the associated enormous investment in them, most of the chemical industry is characterized by high investment versus low labor components in the cost of manufacture. The National Industrial Conference Board statistics list the chemical industry as one of the highest in terms of capital investment per production worker. The investment per worker in a base petrochemicals olefins plant may well exceed a quarter of a million dollars. Once again, however, such an index covers a spectrum of operations, and for a profitable chemical specialties manufacturer the investment may be on the order of 25,000 dollars per worker. Employment in selected parts of the chemical industry is given in Table 1.5.

Commercial Development and Competition Factors

In an earlier period of the chemical industry's development, chemical companies were generally production-oriented, exploiting a process to produce a chemical and then selling it in rapidly expanding markets. The plant sizes and investments required for participation were small fractions of what is needed to participate today. Raw materials often were purcharsed to produce chemical intermediates for sale. Small plants operating in small manufacturing complexes did not present the obvious problems of environmental pollution, which everyone has become increasingly aware of during the past decade. A new investment in chemical production today must include a significant proportion of the total outlay for abatement and control of environmental intrusion.

As the industry has grown, there has been a strong tendency toward integration, both forward and back. Petroleum producers have found opportunities based on their raw materials position to move into chemical manufacturing. Chemical companies, on the other hand, have moved to assure their access to low-cost raw materials. Similarly, producers of plastic materials have moved forward to produce fabricated products, such as films, fibers, and consumer items, while fabricators have installed equipment to handle and formulate the plastic materials to provide a supply at the lowest possible cost.

With ever higher investment needs and increasing cross-industry competition, much greater sophistication has been required in marketing analysis and selection of investment opportunity. The enormity of the investment now required for successful participation does not allow multiple approaches for the private investor. Consequently, a high degree of market orientation tends to predominate in the chemical industry, along with increasingly focused research and development programs.

A major trend in industrial chemistry has been an emphasis on improved processes for the production of major chemicals. The need for higher-efficiency, lower-cost processes has been accentuated by relatively slow growth rates in overall production of major industrial chemicals in recent years, as described in Table 1.6 for inorganic chemicals and Table 1.7 for organic chemicals. Thus profitability growth has had to be achieved from higher efficiencies in production.

For plastics materials, there also was relatively slow growth—except for a few bright spots such as high-density polyethylene

TABLE 1.6 U.S. Production of Major Inorganic Chemicals in 1990 and the Average Annual Production Growth Rate, 1980–90[3]

Chemical	*1990 Production Amount, 1980–90 (billion of pounds)*	*Annual Growth Rate (percent per year)*
Sulfuric acid	88.6	0
Nitrogen	57.3	5.1
Oxygen	39.0	0.9
Lime	34.8	−0.9
Ammonia	33.9	−1.5
Phosphoric acid	24.4	1.2
Sodium hydroxide	23.4	0.1
Chlorine	21.9	−0.4
Sodium carbonate	19.9	1.8
Urea	15.8	0.1
Nitric acid	15.5	−1.7
Ammonium nitrate	14.2	−2.5
Carbon dioxide	11.0	6.2
Ammonium sulfate	5.0	1.6
Hydrochloric acid	4.7	−2.1
Potash (K_2O basis)	3.6	−3.1
Carbon black	2.9	1.2
Aluminum sulfate	2.4	−0.6
Titanium dioxide	2.2	4.2
Sodium silicate	1.8	0.9
Sodium sulfate	1.5	−4.3
Calcium chloride	1.4	−3.5

TABLE 1.7 U.S. Production of Major Organic Chemicals in 1990 and Average Annual Growth Rate, 1980–90[3]

Chemical	*1990 Production Amount, 1980–90, (billion of pounds)*	*Annual Growth Rate (percent per year)*
Ethylene	37.5	2.7
Propylene	22.1	4.9
Ethylene dichloride	13.3	1.8
Benzene	11.9	−2.2
Vinyl chloride	10.7	5.1
Ethyl benzene	9.0	1.6
Styrene	8.0	1.6
Methanol	8.0	1.1
Terephthalates	7.7	2.4
Formaldehyde	6.4	1.4
Toluene	6.1	−1.9
Xylene	5.7	−1.4
Ethylene oxide	5.6	0.7
Ethylene glycol	5.0	1.4
Phenol	3.5	3.2
Acetic acid	3.5	2.4
Propylene oxide	3.2	6.1
Butadiene	3.2	1.2
Acetone	2.2	0.7
Vinyl acetate	2.6	2.8
Cyclohexane	2.5	2.3

TABLE 1.8 U.S. Production of Major Plastics Materials in 1990 and Annual Growth Rate, 1980–90[3]

Plastic Material	*Annual Production (billion of pounds) 1990*	*1980*	*Production Growth Rate 1980–90*
Polyethylene			
Low density	11.2	7.3	1.9
High Density	8.3	4.4	6.6
Poly(vinyl chloride)*	9.1	5.5	5.2
Polypropylene	8.3	3.7	8.6
Polystyrene	5.0	3.5	3.6
Unsaturated polyester	1.2	1.0	2.6
Epoxide	0.50	0.32	5.0

*Includes copolymers of vinyl chloride.

and polypropylene—over the decade of 1979–89; see Table 1.8. Toward the end of the 1980s, growth decreased as increasing emphasis was placed on the recycling of packaging materials, and as new construction, a major use area for plastics materials, declined. As the 1990s began, recycling was showing strong growth, and there was no reason to think recycling would decrease during the nineties.

In the plastic and synthetic materials sector, in which useful fabricated articles are produced directly, for example, from polymers such as polyethylene, polypropylene, and poly(vinyl chloride), there is now major emphasis on the reuse of plastic instead of discarding it, particularly as packaging of various sorts, in trash for landfill. The major problems are not so much technical as they are ones of logistics and the development of a new kind of infrastructure to accommodate recycling.

Some 20 years ago, there was a proposal in Germany to reuse "virgin" poly(vinyl chloride) blow-molded beer bottles sold in the larger football (soccer) stadiums by regrinding the plastic bottles and extruding the ground product as pellets for use in flooring applications. The concept was that a large number of empty bottles could be collected at one point and reprocessed essentially "on the spot." This proposal was not successful; but it illustrates the major recycling problems of collection, sorting by material, and reprocessing for reuse. The proposal also presaged many active new ventures being started in the 1990s, such as the Du Pont effort to reprocess polyethylene and polyester polymers into fencing, fence posts, and garden furniture, and the new ventures by Mobil Chemical and Union Carbide to reprocess polyethylene packaging, film, and wrap. American National Can Company has demonstrated, with the help of the Center for Plastics Recycling Research at Rutgers University, that a blow-molded, layered polypropylene bottle could not only be reprocessed into shampoo and detergent bottles but also into automobile bumper fascia. Today supermarkets are collection depots for plastic grocery bags, and many municipalities are requiring separation of trash into recyclable components. Even more desirable are the voluntary separation and proper disposal of selected trash items that have been undertaken by many individuals.

The principal recycling problems that must be overcome to make plastic-material recycling feasible on a significant scale include the development of commercial pathways for consumer disposal, collection, and reprocessing. A technical problem remains in the collection–reprocessing step of sorting by material type. In the examples of the poly(vinyl chloride) bottle for stadium beer in Germany and polyethylene shopping bags and wrap, identification and collection are relatively simple if the collection is done at the point of sale, or if material is collected later at the place of original sale. However, it must be realized that different polymeric materials usually are not compatible with one another. Two incompatible materials generally will not mix or blend together sufficiently to yield a product with any utilizable strength properties, and are useful only for their fuel value. The process of sorting items into separate materials (e.g., poly(vinyl chloride), polyester, polypropylene), by the consumer–home owner or at a community-operated collection center, is still difficult. A recent solution to this problem has been to mark shaped plastic articles with a code that permits easy identification by classification or type.

Technological Orientation

The chemical industry is a high-technology industry, even though it is now more marketing-oriented and competitive than it was in its earlier period of development. This orientation is shown by the number of scientists and engineers employed in research and development in the chemical industry relative to other industries (Table 1.9). In general, the chemical industry is among the largest employers of scientists and engineers, and it puts a sizable percentage of the total U.S. business investment in research and development.

The contemporary scientist or engineer engaged in research and development in the chemical industry represents individually a high-investment occupation. Since the mid-1950s, chemistry has become increasingly an instrumental science. The instruments now routinely used are both highly sophisticated and costly. A major research project would not be undertaken today without access to a variety of spectrophotometers, spectrometers, chromatographs, etc., as well as the necessary physical/chemical instruments for molecular structure determinations and reaction kinetics. Pilot plants are highly automated and instrumented. Both the basic researcher and the pilot plant engineer require access to computer facilities. In 1978, the average annual cost to maintain an operating R&D scientist or engineer in the chemical industry was about $75,000. Today, it may be three or four times that amount. Impressive as these statistics may be in representing the business investment in chemicals R&D in the United States, R&D spending in the chemicals industry as a percent of sales declined from about 4 percent in 1970 to about 2.5 percent in 1980, although today it remains about 4 percent in the largest chemical companies. This relatively low level is a concern because reinvestment in R&D in other industrialized countries, particularly in West Germany and Japan, has remained at a higher level as measured by this index.

TABLE 1.9 Scientists and Engineers in Research and Development in the United States in 1990 and a Decade Earlier[2]

	Thousands of Employees		
	1990	*1987*	*1980*
Chemicals and Allied Products	78.4	75.2	51.4
Segments			
Industrial Chemicals	23.0	22.4	20.9
Drugs	33.0	32.6	21.6
Other Chemicals	22.4	20.2	8.9

Obsolescence and Dependence on Research

The high technology level that characterizes the chemical industry, and which is reflected in heavy investments in R&D, generally concerns discovery and development of new products and improvements in the manufacture of known products. The first area is more conspicuous: the pharmaceutical for a specific disease; the narrow-spectrum, transient pesticide; the new superperformance, composite system for an internal combustion engine; or a thermoset polymer/graphite fiber-composite material for a high-technology military aircraft, such as the "stealth" bomber or fighter. The second area, however, makes viable the circumstances outlined earlier, where increasing investments can be made to produce larger quantities of materials. The development of a new, lower-cost process for a commercial product can permit the development of a profitable opportunity, or can spell disaster for a company with existing investment in a now-obsolete plant. Major reductions in manufacturing cost can be achieved, for example, by reducing the number of reaction steps required, changing to a lower-cost or more available raw material, or eliminating coproducts, costly separations, and environmental intrusions. The ability of a process scheme to contain or avoid a pollutant can be a deciding factor in the continuance of a manufacturing operation. Examples of the above situations will make the economic consequences clear.

Acetic acid production in the United States has increased about eightfold in the last 40 years. From the 1930s, acetic acid was produced by a three-step synthesis from ethylene; acid hydrolysis to ethanol, then catalytic dehydrogenation to acetaldehyde, then direct liquid-phase oxidation to acetic acid and acetic anhydride as coproducts:

$$CH_2{=}CH_2 \xrightarrow{H_2SO_4/H_2O} C_2H_5OH$$

$$\xrightarrow{Cu/Cr} CH_3CHO$$

$$CH_3CHO \xrightarrow{[O],Co}$$

$$CH_3CO{-}O{-}OCCH_3 + CH_3COOH$$

In the 1940s a major process change was introduced—direct oxidation of butane to acetic acid and coproducts (such as methylethylketone):

$$C_4H_{10} \xrightarrow{[O]} CH_3COOH$$

$$+ CH_3COC_2H_5 + \text{others}$$

Having fewer steps in the synthesis was reflected in lower cost and investment. In 1969, another advance was announced, synthesis of acetic acid from methanol and carbon monoxide with essentially no coproducts:[4,5]

$$CH_3OH + CO \xrightarrow{I/Rh} CH_3COOH$$

The absence of coproducts reduces production costs and investment in distillation and other separation systems. These are very attractive process features in an industry where the principally accepted measure of business quality is return-on-investment.

Acetic anhydride is required as a process intermediate in acetylations. To obtain acetic anhydride from acetic acid, acetic acid is first pyrolyzed to ketene, which then reacts with recovered acetic acid to yield the anhydride:

$$CH_3COOH \xrightarrow{Heat} CH_2{=}C{=}O$$

$$CH_2{=}C{=}O + CH_3COOH \longrightarrow$$

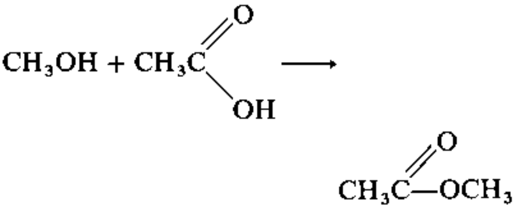
$$CH_3CO{-}O{-}OCCH_3$$

In 1980, the Tennessee Eastman unit of Eastman Kodak announced that it would begin construction of a plant to make acetic anhydride from coal.[6,7] This decision reflected a changing of the raw materials base of much of the chemical industry due to such factors as the rising cost of natural gas and petroleum and the large coal reserves of the United States.

In the new process, synthesis gas (carbon monoxide and hydrogen) is made from coal. Then, methanol is produced from the synthesis gas. (Previously, methanol had been produced chiefly from natural gas methane.)

$$CO + 2H_2 \rightarrow CH_3OH$$

Methanol can then react with acetic acid to give methyl acetate:



$$CH_3OH + CH_3C(=O)OH \longrightarrow CH_3C(=O){-}OCH_3$$

Acetic anhydride is then obtained from the catalytic carbonylation of methyl acetate with carbon monoxide:[5]

$$CH_3COO{-}CH_3 + CO \rightarrow$$

$$CH_3CO{-}O{-}OCCH_3$$

The attractiveness of this process is twofold: (1) the raw materials base of synthesis gas from coal and (2) the avoidance of energy-consuming manufacture of ketene by pyrolyzing acetic acid.

The increase in the production of vinyl chloride, the principal monomer for poly(vinyl chloride) plastics, which are used in vinyl flooring, phonograph records, shower curtains, raincoats, carseat upholstery, house siding, pipe, and so on, has been even more spectacular. Production in the United States has increased from 250 million pounds in 1950 (when it was declared by many industry economic forecasters to be a mature chemical commodity) to over one billion pounds in 1960, to about 3.5 billion pounds in 1970, to over 7 billion pounds in 1980, and to almost 11 billion pounds in 1990.

During the early development period of vinyl polymers in the 1930s, vinyl chloride was produced via catalytic addition of hydrogen chloride to acetylene:

$$CH{\equiv}CH + HCl \xrightarrow{HgCl} CH_2{=}CHCl$$

Later, a so-called **balanced** process was introduced, in which, by addition of chlorine to ethylene, ethylene dichloride was produced:

$$CH_2{=}CH_2 + Cl_2 \xrightarrow{[O]/Cu} CH_2ClCH_2Cl$$

Ethylene dichloride could then be cracked to vinyl chloride and HCl, with the hydrogen chloride recycled to produce vinyl chloride from acetylene:

$$CH_2ClCH_2Cl \xrightarrow{Heat} CH_2{=}CHCl + HCl$$

At that time, vinyl chloride was being produced from chlorine, acetylene, and ethylene. More recently, catalytic oxychlorination has been developed, in which vinyl chloride is produced from ethylene and hydrogen chloride:[8]

$$CH_2{=}CH_2 + HCl \xrightarrow{[O]/Cu} CH_2{=}CHCl + H_2O$$

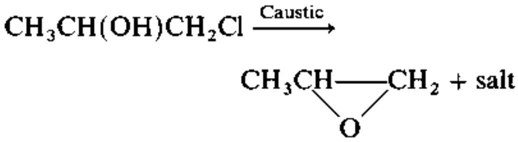
The hydrogen chloride can be obtained via cracking of ethylene dichloride. The oxychlorination process freed vinyl chloride from the economics of the more costly raw material, acetylene. (Deliberate acetylene manufacture is energy-intensive. Although by-product acetylene from gas cracking is less expensive than the raw material, it has not been available in sufficient supply for the large, near billion-pound-per-year, vinyl chloride units.)

During the long period of development of poly(vinyl chloride) into one of the major plastics material, several basic processes for making PVC evolved. In all of these processes vinyl chloride was handled as a liquid under pressure. Despite the relative ease with which it could be polymerized by free radical initiators, the monomer, vinyl chloride, was regarded as an innocuous, relatively inert chemical. A number of producers of PVC resins were caught by total surprise in the 1970s when it was found that long-term (20-year) exposure to vinyl chloride monomer could cause rare forms of tumors.[9]

During the 1960s, vinyl chloride sold in the United States for five to six cents per pound. In the presence of traces of air (oxygen), it would form low concentrations of peroxide, which could collect in compressors and on occasion rapidly decompose to blow out compressor seals. Rather than recover and compress the inexpensive monomer for recycle from stripping and drying operations at the end of the polymerization process, some manufacturers vented it into the atmosphere. After the discovery that vinyl chloride was a carcinogen, venting was not permissible; containment and recovery were mandatory. Some older processes and manufacturing facilities could not be economically modified to incorporate monomer containment, so operations were discontinued. This case is but one example of the impact that necessary environmental controls can have on manufacturing processes and operations.

Propylene oxide is another basic chemical, used in manufacturing intermediates for urethane foams (used in cushioning and insulation) and brake and hydraulic fluids. The volume of propylene oxide produced increased from 310 million pounds in 1960 to 3.2 billion pounds in 1990. The classical industrial synthesis has been the reaction of chlorine with propylene to produce the chlorohydrin, followed by dehydrochlorination with caustic to produce the epoxide, propylene oxide, plus salt. In this case, both the chlorine and the caustic used to effect this synthesis are discarded as a valueless salt by-product:

$$CH_3CH{=}CH_2 + Cl_2 + H_2O \longrightarrow CH_3CH(OH)CH_2Cl$$

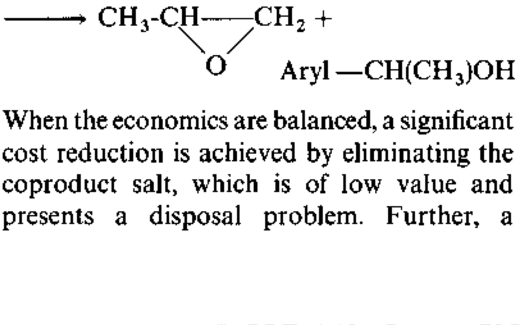


$$CH_3CH(OH)CH_2Cl \xrightarrow{\text{Caustic}} CH_3\underset{\diagdown O \diagup}{CH{-}CH_2} + \text{salt}$$

A more economical process has been commercialized. In one version, a hydroperoxide is produced by catalytic air-oxidation of a hydrocarbon such as ethylbenzene. Reaction of this hydroperoxide with propylene yields propylene oxide as a coproduct. This direct peroxidation can be carried out with other agents to give different coproducts such as t-butanol or benzoic acid.[10,11]

$$\text{Aryl-}C_2H_5 \xrightarrow{[O]/V} \text{Aryl-}CH(CH_3)OOH$$

$$\text{Aryl}{-}CH(CH_3)OOH + CH_3CH{=}CH_2$$



$$\longrightarrow CH_3\text{-}\underset{\diagdown O \diagup}{CH{-}CH_2} + \text{Aryl}{-}CH(CH_3)OH$$

When the economics are balanced, a significant cost reduction is achieved by eliminating the coproduct salt, which is of low value and presents a disposal problem. Further, a process can be designed to produce a coproduct that can be used or sold as a chemical intermediate. In the case of using isobutane as the starting hydrocarbon, the by-product is t-butanol, which can then be converted to methyl t-butyl ether, which is the gasoline additive used to replace lead in "lead-free" gasoline.

If a company is in the business of making and selling products such as acetic acid, vinyl chloride, propylene oxide, or other chemicals and has plans to stay in business and to expand its facilities to serve growing markets, it at least must have economically competitive processes. Today this means being competitive with not only any new processes developed in the United States, but also with any new process technology developed in Western Europe, Japan, and Russia—for the chemical industry is a worldwide industry. This is readily apparent from the data in Tables 1.10, 1.11, and 1.12, which describe the sales for the largest chemical producers in the United States, Western Europe, and Japan, respectively. Further, the processes that are operative must be environmentally compatible—all toxic or carcinogenic by-products or waste must be contained and disposed of harmlessly. Even a relatively innocuous by-product such as salt must be disposed of so as not to intrude on the environment.

The profound effect of environmental concerns on the manufacture of a chemical is

TABLE 1.10 Largest U.S. Chemical Producers[2,12]

	Chemical Sales Millions of Dollars			
Company	*1969*	*1979*	*1989*	*1990*
Du Pont	*3,655*	*12,572*	*15,249*	*15,571*
Dow Chemical	*1,876*	*9,255*	*14,179*	*14,690*
Exxon	*1,004*	*5,807*	*10,559*	*11,153*
Union Carbide	*2,933*	*9,177*	*7,962*	*7,621*
Monsanto	*1,939*	*6,193*	*5,782*	*5,711*
Hoechst Celanese	*1,250*	*3,010*	*5,658*	*5,499*
General Electric	—	—	*4,929*	*5,167*
Occidental Petroleum	—	—	*5,203*	*5,040*
BASF (U.S.A. only)	—	—	*4,461*	*4,366*
Amoco	—	—	*4,274*	*4,087*

reflected in the history of aerosol pressurized products. These products are familiar to the consumer in aerosol spray cans containing hair sprays, deodorants, dessert toppings, or insect sprays (Table 1.13). The market for these products grew enormously in the 1960s, with rapid consumer acceptance of packaged convenience products.[13,14]

The aerosol spray product is a pressurized formulation with a propellant gas. During the rapid growth of these products, the major propellant gases were chlorofluorocarbons. Then, in 1973, the uncontrolled release of chlorofluorocarbons into the atmosphere was linked to possible depletion of the ozone layer in the earth's atmosphere. Since stratospheric ozone provides significant protection at the earth's surface from ultraviolet radiation from the sun, depletion of the ozone layer could be forecast to lead to skin cancers, reductions in seafood and grain crops, and alteration of the carbon dioxide level in the atmosphere. Carbon dioxide is thought to be a potential culprit in "global warming."

Popular concern over "global warming" has now spread from its origin mainly in the large developed economies, which were the principal users of halocarbon propellants, to virtually all countries. The release into the atmosphere of contaminants that can affect the ozone layer, particularly the "ozone hole"

TABLE 1.11 Largest Western European Chemical Producers

		Chemical Sales Millions of Dollars		
Company	*Country*	*1969*	*1979*	*1988*
BASF	Germany	2,430	15,018	24,925
Hoechst	Germany	2,550	15,870	23,275
Bayer	Germany	2,550	15,079	22,993
ICI	United Kingdom	3,250	11,389	20,817
Ciba-Geigy	Switzerland	—	—	12,087
Rhone-Poulenc	France	1,840	7,940	10,962
Montedison	Italy	2,620	8,224	10,846
Norsk Hydro	Norway	—	—	9,207
Akzo	The Netherlands	—	—	8,374
Degussa	Germany	—	—	7,730

1988 data from "Facts and Figures for the Chemical Industry," *Chemical and Engineering News*, p. 81, June 19, 1989.

TABLE 1.12 Largest Japanese Chemical Producers

	Chemical Sales Millions of Dollars	
Company	*1979*	*1988*
Asahi Chemical Industry	2,359	6,384
Mitsubishi Kasei	2,967	6,132
Takeda Chemical Industry	—	4,567
Sumitomo Chemical	2,716	4,341
Toray Industries	2,094	4,317
Sekisui Chemical	1,300	3,936
Showa Denko	1,706	3,679
Dainippon Ink & Chemicals	1,416	3,440
Mitsui Toatsu Chemicals	1,767	3,082
Mitsubishi Petrochemical	1,558	2,654

1988 data from "Facts and Figures for the Chemical Industry," *Chemical and Engineering News*, p. 83, June 19, 1989.

TABLE 1.13 Aerosol, Pressurized Product Sales in the United States in 1978

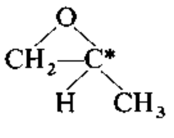
Use	*Percent of Sales*
Personal products and toiletries	33%
Household products	28
Coatings and finishes	14
Automotive	7
Food products	6
Insect sprays	6
Industrialized products	5
Animal products	1
Miscellaneous	0.5

over the Antarctic region, has been identified with the very general use of fire-extinguishing devices, refrigerants, and fabricating processes such as the manufacture of foamed plastic. An international protocol formulated in Montreal in 1988 has now been generally accepted, and plans to phase out the manufacture of ozone-depleting chemicals during the next few years are now in place—an extraordinary example of international agreement and cooperation.[15]

THE NEXT VISTA IN CHEMISTRY

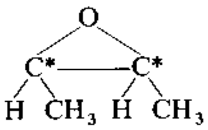
While the major thrust in process development for chemicals in the 1980s was to reduce by-product manufacture, to increase process efficiencies, and by these means to control and reduce the impact that chemical processes and products may have on the environment, the next vista may well involve radically new chemical reaction concepts. Enantiomorphic selectivity, which is the ability to control the stereoisomer produced from a complex organic reaction, will be particularly important in the areas of pharmaceuticals and agricultural chemicals, where it is commonly the case that only one of many possible stereoisomers has the desired bioactivity. In 1992, this area of chemical synthesis is still in its true infancy.

A simple example of enantiomorphic selective synthesis can be taken from polymer chemistry and the polymerization of propylene oxide. Propylene oxide contains an asymmetric carbon atom, C*:



The polymerization of propylene oxide can be induced in a number of ways, two of which can be given in this example.[16] With a caustic initiator such as potassium hydroxide, polymerization does not discriminate between the stereoisomers, and a random distribution of stereoisomers occurs. The resulting polymer is a liquid or a soft, amorphous solid, depending on molecular weight, that softens at about −40°C. This material can be the main structural unit in specialty polyether elastomers and in many flexible urethane foams found in seat cushions, for example.

If, however, a complex initiator based on aluminum or zinc alkyls is used, a product with identical chemical constitution but entirely different physical characteristics results. The reason for this is that the individual polymer chains are produced from either one or the other of the two stereoisomers. The polymer formed from the racemic mixture of *d*- and *l*-propylene oxides is a solid thermoplastic with a crystalline melting point of about +75°C. An even more dramatic result was obtained by Vandenberg[17] with the polymerization of 2,3-epoxybutane:



in which there are two asymmetric carbon atoms, and diestereoisomer selectivity is possible. Vandenberg was able to produce three entirely different polymers from this one monomer, depending on the initiator used:

1. A soft, amorphous rubbery polymer.
2. A crystalline polymer melting at 162°C.
3. A crystalline polymer melting at 100°C.

Examples of this kind of enantiomorphic or chiral selectivity are now being found in organic synthesis. Asymmetric synthesis, for example, has been demonstrated with stereocontrolled Michael addition in the synthesis of beta-lactams using chiral catalysts, where an acyl ligand such as acetyl is bound to cyclopentadiene carbonyl triphenylphosphine.[18] Essentially complete enantiomorphic selectivity has been achieved in this Michael addition synthesis. Another case is enantiomorhic ketone reduction in ethylbenzene reduction in the ethylation of benzaldehyde. Using chiral catalysts, 97% selectivity has been achieved.[19] Closely related research involves the making of catalytic antibodies and hybrid enzymes.[20]

Composites were only briefly mentioned earlier, but this area, which will supply shaped articles to the aircraft/aerospace, industrial, and recreation markets, is expected to grow at a compounded rate of 8 percent from 1988 through the year 2000.[21] In 1988, worldwide consumption of such polymer composites was $2,300 million.

Stereolithography,[22] a new technique for prototyping products, is currently used for modeling and is envisioned as a production tool that will use large quantities of highly upgraded, formulated chemicals. Yet, a few years ago this highly useful technique that couples computers, lasers, or other curing methods and chemistry was unknown, with the first patent being issued in 1986.[23]

It is in areas such as these that the commercial thrusts of the 1990s will have to be aimed if they are to maintain the chemical industry's place in the viable economies of the world.

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2

Pollution Prevention and Waste Minimization

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INTRODUCTION

Pollution prevention offers industry an opportunity, but its exact cost, benefits, and risks are difficult to fully identify or quantify. Pollution prevention represents a significant change in the scope and methodology usually used in waste management. It is a multimedia approach that concentrates on preventing the production of waste in any form in all parts of the plant.

Waste minimization was first introduced as a national policy in the 1984 Hazardous and Solid Waste Amendments (HSWA) to the Resource Conservation and Recovery Act (RCRA). The EPA elaborated on the concept in its 1986 Report to Congress.[1]

The general proposition is this: By practicing pollution prevention, industry can obtain improved environmental protection and increased industrial efficiency, profitability, and competitiveness. Preventing pollution at its source, through modifications in manufacturing processes or product design, is a goal.

There are numerous examples of successful waste-reduction initiatives and some impressive data, usually on a waste stream or plant basis. However, no comprehensive company, industry, or national data thus far available demonstrate broad success at cutting industrial-waste generation. Enormous amounts of wastes, pollutants, and discharges still continue to be generated.

It is not a matter of merely choosing between the traditional end-of-pipe treatment or pollution prevention. Preventing pollution is like preventing disease by changing eating habits and lifestyle; pollution control is like using medicine and surgery to minimize ill effects.

Pollution control can shift pollution around. Air and water pollution-control equipment extracts harmful substances and can generate large amounts of solid and hazardous waste which are disposed of in landfills. Some of these landfills have been linked to groundwater contamination. Regulatory gaps, regulatory noncompliance, the difficulty of responding to newly identified environmental problems, threats from very small residual levels of pollution, and continuing global population

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growth and industrialization all strongly support the goal of environmental protection.

Pollution prevention can help meet the public demand for solutions to urgent and extremely complex environmental problems, such as dealing with the threat of global warming and safely managing toxic and solid waste. This is why many environmentalists advocate pollution prevention as one possible way of addressing environmental problems.

Pollution prevention can also make good economic sense. The costs to government (taxpayers) of developing and enforcing pollution-control regulations and the costs to industry of complying with these regulations have become burdensome. All concerned need a better understanding of the technical means of pollution prevention and of the human, organizational, and social obstacles to applying it. Practicing pollution prevention may very well mean changing the way in which products are made.

To be effective in a given case, waste minimization must become organization or company policy. This policy must span the range from inventory management through equipment and process modification to reuse. Thus, waste minimization must become an integral part of the company's operations. Required actions would include:

- *Inventory management and improved operations*:
  Inventory and trace all raw materials.
  Purchase fewer toxic and more nontoxic production materials.
  Implement employee training and management feedback.
  Improve material receiving, storage, and handling practices.
- *Modification of equipment*:
  Install equipment that produces minimal or no waste.
  Modify equipment to enhance recovery or recycling options.
  Redesign equipment or production lines to produce less waste.
  Improve operating efficiency of equipment.
  Maintain a strict preventive maintenance program.
- *Production process changes*:
  Substitute nonhazardous for hazardous raw materials.
  Segregate wastes by type for recovery.
  Eliminate sources of leaks and spills.
  Separate hazardous from nonhazardous wastes.
  Redesign or reformulate end products to be less hazardous.
  Optimize reactions and raw material use.
- *Recycling and reuse*:
  Install closed-loop systems.
  Recycle on-site for reuse.
  Recycle off-site for reuse.
  Exchange wastes.

INCENTIVES

EPA has found that U.S. industry has the potential to significantly reduce public health and environmental risks by minimizing its hazardous waste production. Such reduction could also lower disposal costs and the nation's need for treatment and disposal facilities. Therefore, EPA is actively encouraging industry to find ways to reduce both the volume and the toxicity of its wastes. EPA is also working closely with the states to help foster waste reduction technologies.

For example, only 4 percent of the total amount of hazardous waste generated in 1981 was recycled, according to a recent Office of Technology Assessment (OTA) study.[2] Most industry efforts at waste minimization have resulted from efforts to decrease manufacturing costs, improve production yields, or comply with government standards. According to the study, federal and state regulations for disposal have increased land disposal costs from $15 per ton to a current cost of $250 per ton. Incineration costs have risen from $500 to $1500 per ton.[2]

WASTE MINIMIZATION TERMS

To ensure that readers of this chapter have a common understanding of the technical terms used, several key terms are defined below. Waste minimization techniques showing

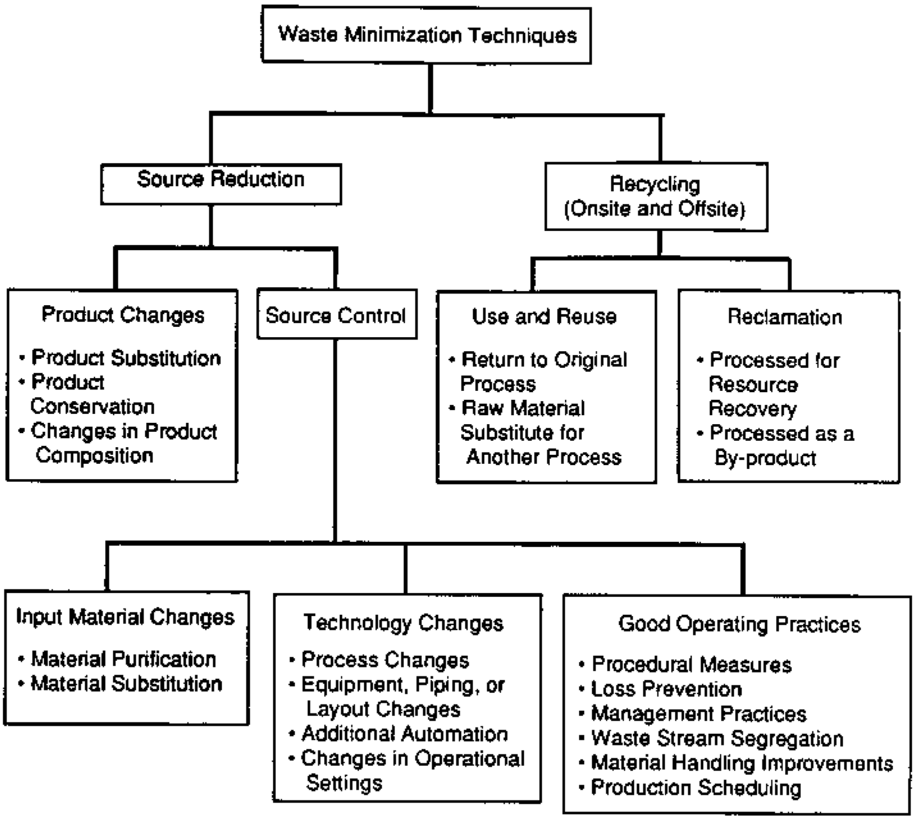

Fig. 2.1. Waste minimization techniques.

source reduction and on-site/off-site recycling are presented in Fig. 2.1.

> *Waste minimization.* The reduction of hazardous waste generated or subsequently treated, stored, or disposed of. This includes source reduction undertaken by a generator to reduce the total volume or quantity of hazardous waste and/or on-site and off-site recycling.
>
> *Source reduction.* The reduction or elimination of waste generation at the source (usually within a process). This includes process changes, feedstock changes, improved housekeeping/management, and in-process recycle.
>
> *Waste reduction.* In-plant practices that reduce, avoid, or eliminate the generation of hazardous waste. OTA states: "Actions taken away from the waste generating activity, including waste recycling or treatment of wastes after they are generated, are not considered waste reduction." Also: "Action that merely concentrates the hazardous content of a waste to reduce waste volume ... is not waste reduction."[3]
>
> *Recycling.* Use or reuse of a waste as a substitute for a commercial product or as a feedstock to an industrial process. This includes on-site or off-site reclamation of useful fractions of a waste or removal of contaminants from a waste to allow its reuse.

Already, some U.S. companies have discovered how waste reduction can offer substantial benefits quickly at low cost. In the past, EPA's Industrial Pollution Control Program emphasized process modification to control industrial effluents.[4-6]

There are a variety of incentives for minimizing waste, including the following:

- Economic benefits, including reduction of the amount of waste to be treated and disposed of and reduction of raw materials costs.
- Reduced liability (including liability for both short- and long-term environmental problems, and for long-term monitoring of health and safety).
- Improved public image and demonstrated environmental concern.

The economics of waste minimization efforts are directly related to the costs of wastewater treatment and waste disposal. As treatment and disposal costs rise, there is added benefit to reducing the volume and toxicity of waste requiring treatment and disposal. Environmental regulations, especially those of RCRA and CWA (Clean Water Act) have had a major effect on treatment and disposal costs.[7]

DEFINITIONS USED BY EPA AND OTA

Table 2.1 shows EPA definitions of several pollution prevention terms and Table 2.2 shows the differences in definitions between the EPA's "Report to Congress: Minimization of Hazardous Waste" and the OTA's "Serious Reduction of Hazardous Waste Report."

ASSESSMENT PROCEDURE

To be able to identify waste minimization opportunities in a given facility or process, it is necessary to use a systematic approach that takes into consideration all of the important factors. The Waste Minimization Assessment Procedure (WMAP) represents such an approach. One part of a larger waste minimization program that is required of hazardous waste generators, the procedure involves a step-by-step approach to (1) understand the facility's wastes and processes, (2) identify options for reducing waste, and (3) determine which of the options exhibit sufficient technical and economic feasibility to justify implementation. Naturally, it is necessary to modify the procedure to fit the specific needs of individual companies. Thus, it should be viewed as a source of ideas and concepts, rather than a vigorous prescription of how to do assessments.

The waste minimization procedure, which is depicted in Fig. 2.2, consists of four phases:[7]

Planning and organization
Assessment
Feasibility analysis
Implementation

These phases are discussed below, and a sample assessment worksheet is presented.

Planning and Organization

Careful planning and organization are necessary to bring about a successful waste minimization program. To start the program and maintain momentum and control, it is necessary that there be strong management commitment from the very beginning. The program should set general goals by which to measure its effectiveness. Selecting a qualified program staff is critical to the ultimate success of the program.

Assessment

The assessment phase serves to identify the best options for minimizing waste through a thorough understanding of the waste-generating processes, waste streams, and operating procedures. Therefore, the initial tasks in the assessment phase include collecting information about the facility's waste streams, processes, and operations.

Information about the facility's waste streams can come from a variety of sources, such as hazardous waste manifests, biennial reports, environmental audits, emission inventories, waste assays, and permits. Mass balances should be developed for each of the important waste-generating operations to identify sources and gain a better understanding of the wastes' origins.

TABLE 2.1 Definitions of Pollution Prevention Terms*

Waste. In theory, the term "waste" applies to nonproduct outputs of processes and discarded products, irrespective of the environmental medium affected. In practice, since the passage of the Resource Conservation and Recovery Act (RCRA), most uses of the term "waste" refer exclusively to the hazardous and solid wastes regulated under RCRA, and do not include air emissions or water discharges regulated by the Clean Air Act or the Clean Water Act. The Toxics Release Inventory, TRI, refers to wastes that are hazardous as well as nonhazardous.

Pollution/Pollutants. In this report, the terms "pollution" and "pollutants" refer to all nonproduct outputs, irrespective of any recycling or treatment that may prevent or mitigate releases to the environment.

Waste Minimization. One of the earliest initiatives in pollution prevention was waste minimization. The initial focus here was on wastes (as defined under RCRA), rather than on a comprehensive evalution of industrial emissions regulated under all environmental statutes. This term become a source of controversy because some considered it to designate approaches to *treating* waste so as to minimize its volume or toxicity, rather than decreasing the quantity of waste at the source of its generation. The distinction became important because some advocates of decreased waste generation believed that an emphasis on waste minimization would deflect resources away from prevention towards treatment (the EPA Office of Solid Waste Source Reduction and Recycling Action Plan (see Chapter 5) will formally define waste minimization). In the current RCRA biennial report, waste minimization refers to source reduction and recycling activities, and now excludes treatment and energy recovery.

Industrial Source Reduction. Industrial source reduction is defined in the recently enacted Federal Pollution Prevention Act as "any practice which 1) reduces the amount of any hazardous substance, pollutant, or contaminant entering any waste [pollutant] stream or otherwise released into the environment (including fugitive emissions) prior to recycling, treatment, and disposal; and 2) reduces the hazards to public health and the environment associated with the release of such substances, pollutants, or contaminants. The term includes equipment or technology modifications, process or procedure modifications, reformulation or redesign of products, substitution of raw materials, and improvements in housekeeping, maintenance, training, or inventory control."

Source reduction does not entail any form of waste management (e.g., recycling and treatment). The Act excludes from the definition of source reduction "any practice which alters the physical, chemical, or biological characteristics or volume of a hazardous substance, pollutant, or contaminant through a process or activity which itself is not integral to and necessary for the production of a product or the providing of a service.

Waste Reduction. This term has been used by the Congressional Office of Technology Assessment and INFORM to mean source reduction. On the other hand, many different groups have used the term to refer to waste minimization. Therefore, care must be employed in determining which of these different concepts is implied when the term "waste reduction" is encountered.

Toxic Chemical Use Substitution. The term "toxic chemical use substitution" describe replacing toxic chemicals with less harmful chemicals, although relative toxicities may be fully known. Examples would include substituting a toxic solvent in an industrial process with a chemical with lower toxicity and reformulating a product so as to decrease the use of toxic raw materials or the generation of toxic byproducts. One such case involves DowBrands, a subsidiary of Dow Chemical Company, which responded to pressure from California public interest groups to reformulate its K2r* Spotlifter, excludes the toxin perchloroethylene.

In this report, this term also includes attempts to reduce or eliminate the use in commerce of chemicals associated with health or environmental risks. Examples include the phase-out of lead in gasoline, the attempt to phase out the use of asbestos, and efforts eliminate emissions of chlorofluorocarbons and halons. Some of these attempts have involved substitution of less hazardous chemicals for compariable uses, but other involve the elimination of a particular process or product from the market without direct substitution.

Toxics Use Reduction. The term "toxics use reduction" refers to the activities grouped under "source reduction," where the intent is to reduce, avoid, or eliminate the use of toxics in processes and/or products so as to reduce overall risks to the health of working consumers, and the environment without shifting risks between workers, consumers, and parts of the environment.

Industrial Pollution Prevention. The terms "industrial pollution prevention" and "pollution prevention" refer to the combination of industrial source reduction and toxic chemical use substitution. It does not include any recycling or treatment of pollutants, nor does it include substitution of a nontoxic product made with *nontoxic* chemicals for a nontoxic product made with *toxic* chemicals.

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*Source: Pollution Prevention 1991, "Progress on Reducing Industrial Pollutants" EPA 21P-3003 (October 1991).

TABLE 2.2 Waste Covered by EPA and OTA Reports

EPA	*OTA*	*HSWA on waste minimization*
Hazardous Waste:		
EPA does not explicitly say which wastes are covered by its use of the term "hazard wastes." An assumption can be made that since the report deals within the context of RCRA and was mandated under RCRA that EPA considers waste minimization to cover only those solid wastes regulated as hazardous waste under RCRA.	"All nonproduct hazardous outputs into all environmental media, even though they may be within permitted or licensed limits. This is much broader than the legal definition of hazardous solid waste in the Resource Conversation and Recovery Act, its amendments, and subsequent regulations. Hazardous refers to harm to human health or the environment as is broader than the term "toxicity." For example, wastes that are hazardous because of their corrosive, flammability, explosiveness, or infectiousness are not normally considered toxic." [p. 31]	The phase used in HSWA was "hazardous wastes." The assumption can be made, therefore, that the waste minimization regulations required by HSWA were intended to cover only those solid wastes regulated as hazardous waste under RCRA. Some ambiguity exists, however, due to the legislative history. Senate Report No. 98-284 on waste minimization provisions in S. 757, voiced concerns about "...pollutants contained in effluents, emission's wastes or other pollution streams."
EPA	*EPA*	*OTA*
Differing views of multimedia approach:		
Waste minimization is RCRA: All incentives/disincentives (barriers) are framed within the RCRA content. The one exception is: "Commercial recycling facilities that wish to increase their operations might be reluctant to do so if the expansion were to require a revision of their NPDES water pollution permit to authorize a change in the composition of their discharges or allow for larger flows." [p. 29] Almost all information/data reviewed for report and assessment of needs for future concerns RCRA hazardous waste generation and management. *Waste minimization is multimedia*: EPA lists protecting human health and the environment as a key role for waste minimization because "... none of EPA's environmental control programs can fully eliminate all the risks that they attempt to control." [p. 9]	"To achieve its purpose, waste minimization like other pollution control measures, must look comprehensively across all environmental media, reduction in hazardous waste must not be made at the expense of increases in air or water pollution.... Waste minimization programs must therefore be carefully designed to avoid cross-media transfers and to protect human health and the environment in a comprehensive sense. The need to design a waste minimization program that addresses both of these goals provides a framework for integrating the objectives of all environmental programs." [p. 10] "EPA believed that the waste minimization must be implemented as a general policy throughout the hazardous waste management system and, ultimately, more broadly throughout all of EPA's pollution control programs." [p. 121]	*Waste reduction is multimedia*: "Reduction—applied to a broad universe of emissions, discharges, and waste—is the best means of achieving pollution prevention." [p. 7] "OTA has concluded that a comprehensive multimedia (air, water, land) definition for hazardous waste is necessary... 1) to avoid creating opportunities for shifting waste from one environmental medium to another possibly unregulated or less regulated medium ... and 2) to include wastes that are not currently regulated, such as most toxic air emissions. If the term hazardous waste is defined or applied narrowly, waste reduction measures can be ineffective." [p. 11]

Sources: Compiled by OTA, 1987. For column 1, U.S. Environmental Protection Agency, Report to Congress: *Minimization of Hazardous Waste*, EPA/530-SW-86-033 (Washington, DC, EPA, Office of Solid Waste and Emergency Response, October 1986), pages as noted. For column 2, U.S. Congress Office of Technology Assessment, Serious Reduction of Hazardous Waste, OTA-ITE-317 (Washington, DC: U.S. Government Printing Office, September 1986), pages as noted.

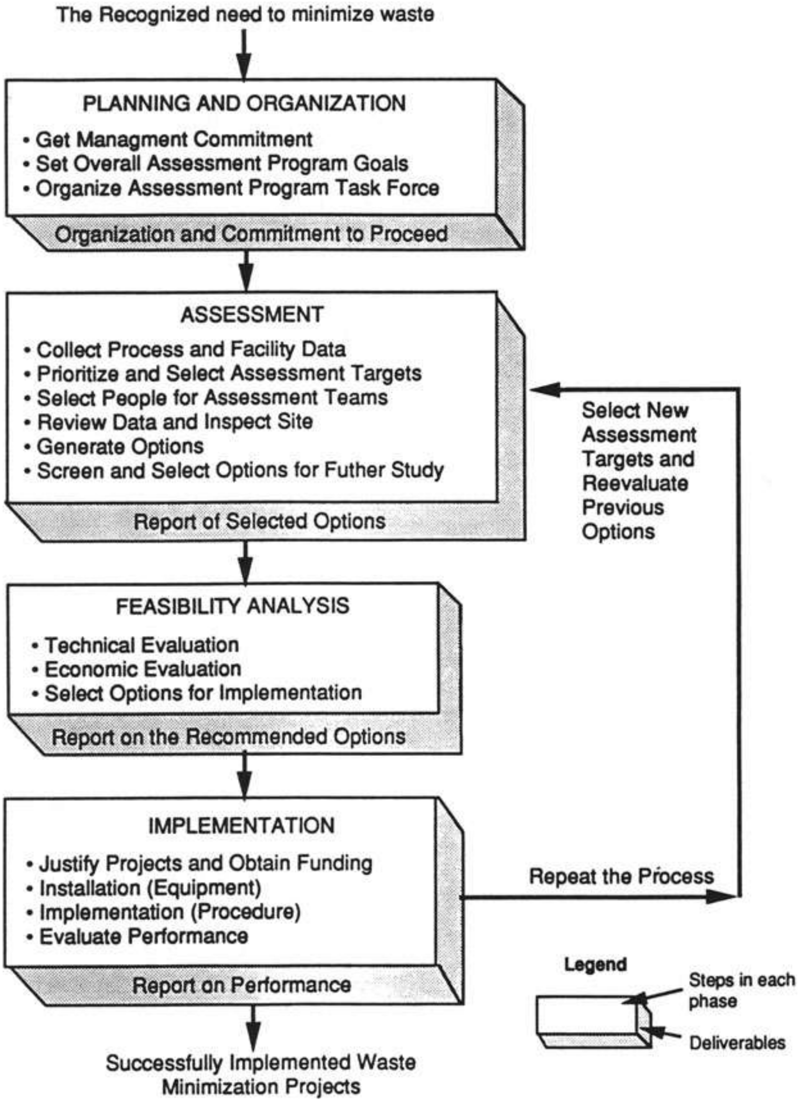

Fig. 2.2. A waste minimization assessment procedure.

Collecting waste-stream data and constructing mass balances will create a basis by which the assessment can track the flow and characteristics of the waste streams over time. This will be useful in identifying trends in waste generation and will also be critical in the task of measuring the performance of implemented waste minimization options later. The result of the activity is a catalog of waste streams that provides a description of each waste, including quantities, frequency of discharge, composition, and cost of management.

In addition to data about waste streams, other information is needed to fully understand the facility's operations, including the following items:

- Process, equipment, and facility design information.
- Raw material production information.
- Operating cost information.
- Policy and organizational information.

Ideally, assessments should be conducted on all of the waste-generating operations in a plant. However, in larger plants this often is not practical, considering the limited resources available. In these cases, a program task force should prioritize the streams. Important criteria to consider in prioritizing waste streams and/or facility areas include the following:

- Compliance with current environmental regulations.
- Disposal cost and/or volume of the waste.
- Hazardous nature of the waste, and other safety considerations.
- Potential for (and ease of) minimization.
- Potential for removing production or waste treatment bottlenecks.
- Available budget and expertise for the waste minimization assessment program.

A practical consideration in determining which waste streams to select is to find those that can be reduced with minimum economic or production impact. A successfully implemented waste minimization project will ensure the acceptance of further waste minimization efforts within the organization.[8]

The assessment team must include people who are familiar with the area of the facility to be assessed (e.g., first line operators and the production supervisors are recommended). These people may or may not already be on the assessment program task force. (In a large facility, the task force should have a broad understanding of the facility's operations, whereas the assessment team should have a specific understanding of the areas to be assessed.) It may be advisable to include people from other parts of the facility that regularly interact with the areas to be assessed.

Although collecting and reviewing data is important in the assessment, the assessment team must be familiar with the actual operation at the site. Therefore, the assessment team should visit the site during various stages or cycles of an operation. If all of the assessment team members work at the facility (or are located relatively close by), it is easy for the team members to visit the site. However, if some members are from outside the facility, it is recommended that a formal site inspection be carried out.

A formal inspection can address many of the questions raised by data collected earlier in the assessment phase. An inspection can also confirm whether the facility is operating in the way it was originally intended to operate. An inspection concentrates on understanding how the wastes are generated.

The assessment team should "walk the line" from the beginning of the process to the point where products and wastes leave the facility. Because waste can be generated in receiving and storage areas as well as the production areas, all areas within the site should be visited. The following guidelines will help in organizing an effective site inspection:

- Prepare an agenda in advance.
- Schedule the inspection to coincide with the particular operation of interest.
- Interview operators, foremen, and supervisors, and assess the operating personnel's awareness of the waste generation aspects of the operation.
- Observe the housekeeping aspects of the operation.
- Assess the overall cleanliness of the site.
- Review the organizational structure and the level of coordination of waste-related activities between the assessed facility area and other related areas.
- Assess the administrative controls.

After collecting data during the assessment preparation step and the site inspection, the members of the assessment team will have begun to identify possible ways of reducing waste in the assessed area. The generation of options is both a creative and an analytical process. Although individual assessment team members may be able to suggest many potential waste minimization options, the process can be enhanced by using group decision techniques such as brainstorming. These techniques allow the team to identify options that the individual members might not have come up with on their own.

Identifying potential options requires the expertise of the assessment team members, much of whose knowledge comes from their education and on-the-job experience. Other sources of background information on potential options include the following:

- Trade associations.
- Published literature.
- Environmental conferences and exhibits.
- Equipment vendors.
- Plant personnel (especially the operators).
- Federal, state, and local government environmental agencies.
- Consultants and/or employees from other facilities.

A successful assessment will result in the proposal of many waste minimization options; so it is necessary to identify those options that offer a real possibility of minimizing waste and reducing costs. The purpose of the screening step is to eliminate those options that are perceived to be impractical. The screening of options may be achieved through an informal decision made by the assessment program manager, a vote of the assessment team, or a weighted sum method that combines relative weights of such factors as operating cost reduction, capital cost requirement, and reduction in the waste hazard.

Some options (such as procedural changes) may involve limited capital costs and may be implemented in a short time frame. The screening step should consider the ease of implementation. If such an option is clearly desirable and indicates a potential cost saving, it should be considered for further study.

In screening the options, the assessment team should address questions that relate to the waste minimization goals and constraints. Examples of questions that should be addressed include the following:

- Does the necessary technology exist to develop the option?
- How much will the option reduce the waste quantity, hazard, and treatment/disposal costs?
- How much will the option reduce the use of raw materials?
- What will the impact be on liability and insurance costs?
- How much does it cost? Is it cost-effective?
- Can the option be implemented within a reasonable amount of time?
- Does the option have a good "track record"? If not, is there evidence that the option can work in this case? What other benefits will occur?

Feasibility Analysis

The waste minimization options that are successfully screened in the assessment phase then undergo a more detailed feasibility analysis. Most important, the feasibility analysis consists of three steps: technical evaluation, economic evaluation, and implementing option selections.

The purpose of the technical evaluation is to ensure that the option will work as intended, given specific facility constraints and product requirements. Typical questions of concern in performing technical evaluation are:

- Will the option work in this application?
- How has it worked in similar applications?
- Is space available? Are utilities available? Must new utility systems be installed?
- Is the new equipment or procedure compatible with the facility's operating procedures, work flow, and production rates?
- How long will production be stopped in order to install the system?
- Will product quality be maintained, improved, or adversely affected?
- Is special expertise required to operate or maintain the new system? What service will the vendor provide? Does the system or procedure create or remove safety hazards?
- Does the system or procedure create other environmental problems?

All affected groups in the facility should contribute to and review the results of the technical evaluation. Prior consultation and review with the affected groups is needed to ensure the viability and the acceptance of the option. If the option calls for a change in production methods, its effects on the quality of the final product must be determined. Only those projects that are judged to be feasible and practical in the technical evaluation go on to an economic evaluation.

An economic evaluation is carried out by using the standard measures of profitability, such as payback period or discounted cash flow techniques (internal rate of return and net present value). Each company uses its own economic evaluation procedures and criteria for selecting projects for implementation. In performing the economic evaluation, planners must consider various costs and savings. As in any project, cost elements can be grouped into capital costs and operating costs.

Capital costs for waste minimization projects include the fixed capital costs for designing, purchasing, and installing equipment as well as costs for working capital, permitting, training, start-up, and financing charges. It is important to realize that some waste minimization options, such as procedural or materials changes, will not have any capital costs. Also, many source reduction options have the advantage of not requiring environmental permitting to be implemented.

Waste minimization projects need to show a savings in operating costs to be economically effective. Operating costs and savings typically associated with waste minimization projects include the following:

- Reduced waste treatment, disposal, and reporting costs.
- Raw material cost savings.
- Insurance and liability savings.
- Increased costs (or savings) associated with product quality.
- Decreased (or increased) utilities, operating, and maintenance costs and overhead costs.
- Increased (or decreased) revenues from changes in production of marketable by-products.

Once the capital and operating cost savings have been determined, a project's profitability can be determined by using profitability measures. These profitability measures are discussed in virtually all financial management, cost accounting, and engineering economics textbooks. Those options that require limited capital costs should be implemented as soon as savings in operating costs can be shown.

An important consideration of waste minimization projects is their potential to reduce the toxicity of a waste stream and thereby to reduce the environmental risk. Although these risks can be qualitatively identified, it is difficult to quantify their financial impact. Also, although the profitability of a waste minimization assessment program is important in deciding whether to implement a project, compliance with environmental regulations must be considered. Violations may ultimately result in shutting down a facility, or carry possible criminal penalties for the company's responsible people.

The product of a feasibility analysis is a report that presents technical and economic information concerning the feasibility of each option. It also contains recommendations to implement the options. The report should include project cost and performance information. Topics covered in the report should include:

- Applicability of the technology.
- Resource requirements (resources available in-house and outside).
- Estimated construction period and production downtime.
- Means to evaluate performance after the project is implemented.
- Environmental and safety liability considerations.

Before the report is completed, the results should be reviewed with the appropriate individuals.

Implementation

Implementation of the waste minimization project requires management's commitment to overcome the natural resistance to change that occurs within an organization. Once the project is implemented and is operating, it is important to evaluate its performance. Is it performing as expected? If not, should it be modified, or is its use still beneficial? What other potential options were identified during the implementation and operation of this option?

The waste minimization program should be viewed as a continuing one. As waste minimization options are implemented, the task force should continue to look for new opportunities, assess other waste streams, and consider options that were not pursued earlier. The ultimate goal is to reduce the toxicity and volume of wastes to the maximum extent practical.

TABLE 2.3 A Waste Minimization Worksheet

Number and Title	*Purpose/Remarks*
Planning and Organization	
1. Management Commitment	Needs top-down approval.
2. Assessment Overview	Summarizes the overall assessment procedure.
3. Program organization	Records key members in the WM program task force and the WM assessment teams. Also records the relevant organization.
4. Assessment Task Force Makeup	Lists names of assessment team members as well as duties. Includes a list of potential departments to consider when selecting the teams.
Assessment Phase	
5. Collects Facility Data	Lists background information about the facility, including location, products, and operations. This is a checklist of useful process information to look for before starting the assessment.
6. Prioritizes and Selects Targets	Identifies hazardous components, production rate, revenues, and other information about products.
7. Selects Personnel Teams	Records information about the personnel who work in the area to be assessed.
8. Collects and Reviews Data	Records input material information for a specific production or process area. This includes name, supplier, hazardous component or properties, cost, delivery and shelf-life information, and possible substitutes.
9a. Inspects Site and Characterizes Waste	Records source, hazard, generation rate, disposal cost, and method of treatment or disposal for each waste stream.
b. Prepares Waste Stream Summary	Summarizes all of the information collected for each waste stream. This sheet is also used to prioritize waste streams to assess.
10a. Generates Option	Records options proposed during brainstorming or nominal group technique sessions. Includes the rationale for proposing each option.
b. Develops Option Description	Describes and summarizes information about a proposed option. Also notes approval of promising options.
11. Screens and Selects Options	Makes evaluation by weighted sum method.
Feasibility Analysis	
12. Technical Evaluation	Provides detailed checklist for performing a technical evaluation of a WM option. This worksheet is divided into sections for equipment-related options, personnel/procedure-related options, and materials-related options.
13. Economic Evaluation	Provides detailed list of capital and operating cost information for use in the economic evaluation of an option.
Implementation	
14. Justifies Projects and Funding for Equipment and Procedures	Summarizes important tasks to be performed during the implementation of an option. This includes deliverable, responsible person, budget, and schedule.
15. Evaluates Performance	Records material balance information for evaluating the performance of an implemented option.

Assessment Worksheet

A sample worksheet used in making waste minimization assessments is shown in Table 2.3. Designed to clarify the assessment procedure, the worksheet includes the phase of each step in the procedure, its number and title, and a brief description of its purpose or other useful remarks.

EXAMPLES OF ECONOMIC BENEFITS[11]

A number of waste minimization efforts have been documented by EPA's Office of Solid Waste. This section presents brief descriptions of 12 cases of waste minimization initiatives taken verbatim from EPA/530-SW-87-026. For additional information readers are referred to that publication, entitled "Waste Minimization, Environmental Quality with Economic Benefits."

> A Texas chemical manufacturer of adiponitrile, a nylon intermediate, recently developed a new process that improves product yield while reducing by 50 percent the amount of aqueous waste generated. The company's original process generated 800 gallons of wastewater per minute, along with nonchlorinated waste solvents that had to be incinerated. The new process enables the firm not only to reduce the amount of wastewater that must be treated, but also to burn the waste solvents in the company's powerhouse. Steam generated by the burning of the waste solvents is used in the manufacturing process, thereby saving the company more than $10 million per year in fuel oil.
>
> A Pennsylvania die manufacturer uses 1,1,1-trichloroethane to clean and degrease machine parts. Prior to installing this solvent recovery unit, the company shipped the contaminated solvent offsite for reclamation and then purchased reclaimed solvent at $0.80 per gallon and virgin 1,1,1-trichloroethane at $4.50 per gallon. Using this solvent recovery unit, the company now reclaims solvent onsite at a cost of $0.04–$0.10 per gallon. In addition, the company's purchase of virgin 1,1,1-trichloroethane has dropped from two 55-gallon drums each month to two 55-gallon drums every 6 months, a savings of nearly $5,000 per year.
>
> In 1986, EPA sponsored a waste minimization assessment at an electric arc furnace steel-making facility. The assessment team examined waste minimization options, including source reduction and resource recovery, for the company's corrosive and heavy metal wastes. The assessment revealed that calcium fluoride (fluorspar) in the sludge generated during the neutralization of the pickling line wastewater could be economically recovered. Previously, the company had disposed of the sludge and purchased 1,000 tons of fluorspar per year as flux material for the steel-making process. The waste minimization option identified by the assessment team will save the company $100,000 per year in costs avoided to purchase fluorspar, and a further $70,000 per year because of a 30 percent reduction in the volume of sludge to be disposed of.
>
> An electronics plant installed an electrolytic metal recovery cell to recover copper from waste generated in the production of telephone switching equipment. The process produces a better quality copper deposit on the cell's cathode plates, where the copper collects in half-inch-thick sheets. The cell recovers 75 pounds of copper per week, which is sold for $0.50 per pound—a total of about $2,000 per year. The use of the cell also has eliminated 1 drum of sludge per week, saving an additional $4,000 per year.
>
> Evaporative recovery systems can minimize the volume of waste from metal-plating baths and recycle plating solutions by recovering 90–95 percent of the plating solution lost through dragout. The operating cost of the recovery system is only $0.08 per gallon, while the dragout sludge hauling and disposal costs are close to $1.00 per gallon. With only 5–10 percent of the dragout requiring waste treatment, waste handling and disposal costs have been reduced significantly.
>
> During standard equipment-cleaning operations, hospitals, universities, and research centers, as well as many small and medium-sized businesses, such as metal finishers and furniture manufacturers, generate small amounts of waste solvents. These waste solvents can be recycled for reuse in cleaning operations using small, commercially available recovery units. Depending on the commercial value and amount of solvent recovered, the pay-back time for recycling equipment can be as short as 1 year. Since

transportation costs can be very high, even businesses that use only low volumes of solvents may find it more economical to recycle their waste solvents onsite rather than ship the wastes offsite for recovery or disposal.

An electric company uses a water-based electrostatic paint system instead of a conventional organic solvent paint system. This has resulted in improved quality of application, decrease of downtime from 3 percent to 1 percent, reduction in the generation of aromatic waste solvent by 95 percent, reduction in paint sludge by 97 percent, and increase of efficiency with up to 95 percent recovery and reuse of paint. The new system reduced hazardous waste disposal costs and decreased personnel and maintenance costs by 40 percent.

Ion exchange metal-recovery units are used to remove heavy metals from aqueous residues generated by electroplating, metal-finishing, electronic manufacturing, and metal-refining processes. Ion exchange systems are commercially available, are relatively compact, and use little energy.

The chemical and pigments department of a major chemical company in Kentucky manufactures freon. Low-quality hydrochloric acid, generated as a manufacturing byproduct, was previously disposed of in injection wells. The company recently installed a new freon manufacturing process that produces high-quality hydrochloric acid. By installing the new process and building an additional acid storage facility, the company now is able to sell approximately 22 million pounds per year of acid that was previously discarded.

A polymer products operation in Arizona uses reverse osmosis to eliminate the discharge of cyanide-containing rinse water from one of the company's four plating units. The process, which concentrates the cyanide and separates it from the rinse water, reduces the environmental impact of the discharge and conserves valuable plating materials and water treatment chemicals.

One of the largest chemical manufacturers in the Netherlands uses waste segregation, removal of solvents in water solutions by distillation, and other source reduction measures to reduce the company's annual wastewater output by 80 percent.

In Sweden, a major pharmaceutical producer initiated a program to recycle approximately 10,000 tons of hazardous waste solvents per year through the company's onsite distillation plant, thereby reducing by 60 percent the amount of solvent waste that was shipped offsite for disposal.

INTERNATIONAL PERSPECTIVE

The waste reduction activities of national governments may be of interest to policymakers for two reasons. First, the choices made by other countries help them in understanding the range of policies available in addressing waste problems. Second, the expertise gained by nations with a relatively long experience in waste reduction can provide important historical trend data. Some Western European governments have actively encouraged waste reduction for many years. To the extent that their experience in waste reduction results in more efficient processes and increased productivity, U.S. firms can benefit from Western Europe's experience. Currently, the competition among waste-reduction vendors favors Western Europe. If a worldwide market for waste-reducing technologies and techniques emerges in the coming decade, U.S. firms may find that European vendors are offering a wide variety of technologies that have been tested over a long period of time.

Some of the earlier initiatives in waste reduction came from international organizations. The United Nations Economic Commission for Europe (ECE) sponsored the first International Conference on Non-Waste Technology in Paris in 1976. In 1979, the ECE adopted a detailed "Declaration on Low and Non-Waste Technology and Reutilization and Recycling of Wastes."[12] In this document, the ECE recommended action on both the national and international levels to develop and promote low and non-waste technologies. International ECE activities resulting from this declaration included:

- Publication of a four-volume compendium on low and non-waste technologies in

	JAPAN	CANADA	GERMANY	SWEDEN	NETHERLANDS	DENMARK
Tax Incentives						
Waste End Taxes			●		●	●
Tax Incentives	●	●	●			
ECONOMICS						
Price Support System for Recycling			●		●	
Government Grants as Subsidies	●	●	●	●	●	●
Low Interest Loans	●		●			
TECHNICAL ASSISTANCE						
Information and Referral Service	●	●	●		●	●
Site Consultation	●	●				
Training Seminars		●	●			●
R&D ASSISTANCE						
Technical Development Labs				●	●	●
Demonstration Projects	●	●	●	●		
Industrial Research			●	●	●	
PERMITS AND PLANS						
National Waste Managements Plans					●	
Waste Reduction Agreements	●					
Waste Reduction as a Part of Permits				●		
WASTE EXCHANGE						
Regional Waste Exchanges	●	●	●		●	●
PUBLIC INFORMATION						
Focus on Corporate Image	●					
Focus on Consumer Practices			●			

Fig. 2.3. Waste minimization practices in other countries. (*"Foreign Practices in Hazardous Waste Minimization," Medford, MA: Center for Environmental Management, Tufts University, 1986.*)

1982, listing over 80 examples of successful pollution prevention efforts by European industrial firms.[12]

- Publication of a compendium of lectures by experts in low and non-waste technology in 1983.[13]
- Holding a European Seminar on Clean Technologies at The Hague in 1980.
- Setting up a Working Party on Low and Non-Waste Technology and Re-utilization and Recycling of Wastes, which has met annually since 1980.[14]
- Setting up an environmental fund for demonstrating innovative technologies that are broadly applicable to reducing pollution. A sum of 6.5 million in European Currency Units (about 6.1 million in U.S. dollars) was set aside for this purpose in 1985.[15]
- Holding an International Solid Waste Association meeting in Geneva, Switzerland in 1989.[16]

Various waste minimization practices used in other countries are shown in Fig. 2.3.

IMPLEMENTATION OPTIONS AND SOURCES OF HELP

After a waste minimization program is implemented, the question is, "How effective are the options?" Means to measure the effectiveness need to be in place. Reduction could be achieved in the volume of waste produced or in the degree of hazard. Another measure could be the ratio of waste quantity to material throughput or product output.[17] This measure is applicable for individual operations or processes. Another option could be implemented at other facilities that utilize the same process or operation within the plant.[18]

As pointed out by Newton,[19] waste minimization must not be a one-time effort. It should be continuous. Areas with lower priorities must be addressed once the higher priorities have been implemented. Assessments should be conducted yearly or when there are:

- Changes in raw material or product requirements.
- Changes in waste management costs.
- New technologies available.
- Changes in regulations.
- Environmental events.

Additional information on waste reduction is available from a wide variety of source materials, including:[20-22]

- Sector or specialized trade associations.
- Consulting/engineering firms that offer assistance in identifying and classifying waste, drum handling, site assessment, and preparation of manifests.
- Hazardous waste management contractors who offer information about costs involved with treatment, disposal, and waste transport.
- Chemical suppliers who offer information on chemical safety and waste management.

Potential opportunities for waste reduction in several industrial areas are listed in Table 2.4.

In conclusion, pollution prevention is one aspect of environmental protection. Prevention

TABLE 2.4 Potential for Waste Reduction Opportunities across Different Industry Types

Company/Industrial Characteristic	*Example Industries*	*Operations Changes*	*In-Process Recycling*	*Process Changes*	*Input Substitution*	*End Product Changes*
Mature process technology, high volume product	Rubber Petroleum Commodity chemicals Paper products Lumber	+	+	−	−	−
Very stringent product specifications or high product quality demands for high cost/high profit products	Pharmaceuticals Weapons Robotics Specialty chemicals	+	−	−	−	−
Frequently changing, high-tech products for industrial use	Electronic components Medical equipment	+	+	+	+	−
Job shop processing of many different industrial products	Electroplating Printing	+	+	+	+	−
	Foundries Machine shops	+	+	−	+	−
Changing production technology for commodity goods	Steelmaking Nonferrous metals Textiles	+	+	+	−	−
Large-scale manufacture of consumer goods	Automobiles Appliances Consumer electronics Paints	+	+	+	+	+

Source: Office of Technology Assessment, J. Hirschhorn (1986).

of pollution at its source by modification of processes, equipment, product design, or utilization of alternative raw materials is the goal. Pollution prevention is a broad term that covers energy conservation, recycle, and reuse, whereas waste minimization, the major theme of this chapter, concentrates on waste streams. The ultimate goal of waste minimization is to reduce the generation of waste to the greatest extent possible.

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3

Industrial Wastewater and Hazardous Materials Treatment Technology

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INTRODUCTION

The gravest water quality issue now facing the nation is the disposal of industrial wastes. Other major environmental problems include medical wastes, hazardous wastes, and toxic contamination of the nation's streams and groundwater. Municipal waste disposal and landfill issues also are very serious concerns.

It has been reported (*Environmental Business Journal*, July 1989) that:

- About 13,600 hazardous substance spills occur outside fixed facilities each year; OSHA reports that an additional 11,000 such spills occur inside the workplace.
- Some $13.1 billion of revenue was generated by firms providing hazardous waste disposal equipment and services in 1987; the figure is expected to double by the year 2000.
- By 1990 there were about 5666 facilities for hazardous waste treatment, storage, disposal, and recycling facilities operating in the United States. The Government Accounting Office estimated that some 2500 facilities will require some corrective action under the Resource Conservation and Recovery Act (RCRA).
- In 1987 9.7 billion pounds of toxic substances were released into streams and other surface waters. In the same year 1.9 billion pounds went to municipal wastewater treatment plants and 2.7 billion pounds to landfills, and 2.7 billion pounds of chemicals were emitted into the air. These figures do not include releases by small quantity generators.

The same journal also reported that:

- Current annual investment in pollution control equipment amounted to $200 billion.
- The estimated cost to clean up hazardous and radioactive waste at 45 DOE sites was $92 billion.
- The market for drinking water purification equipment and services in 1995 is expected to be $7.7 billion.

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- Some 1.2 billion gallons of waste oil are generated each year at gasoline stations, auto dealerships, and industrial facilities.

Figure 3.1 shows estimated market values and predicted annual growth rates for various environmental sectors.

Industrial effluents contain enormous quantities of inorganic and organic chemical wastes, which are steadily becoming more complex and difficult to treat by conventional technologies. The variety and the complexity of inorganic and organic compounds contained in these effluents present a serious liquid wastewater treatment control problem, in that the pollution and toxicity effects of these constituents are of much greater significance than those found in domestic wastewater.

Conventional wastewater treatment technologies, often barely adequate for existing waste types, offer even less promise of providing the type and the degree of treatment that will be required in the near future. Therefore, industrial pollution-control technology must be developed to achieve effective and economical control of pollution from such varied industries as those producing metals and metal products, chemicals and allied products, food and kindred products, textiles, and leather goods.

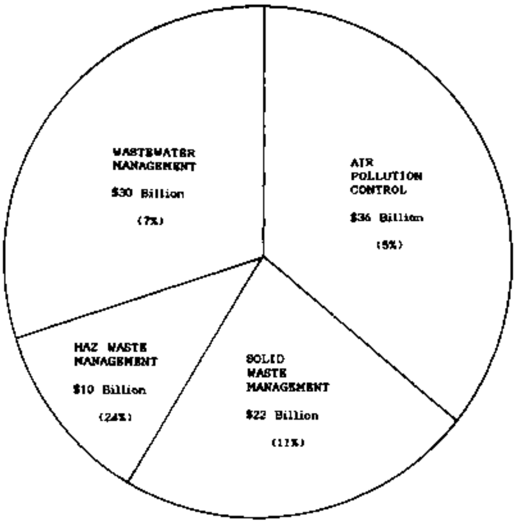

Fig. 3.1. Estimated environmental market values and, in parentheses, estimated annual growth rates for various environmental sectors. Market values do not include remediation. (*Data from R. K. Miller and Assoc.,* Waste Technology News, *Vol. 2, No. 22, July 1990.*)

Federal Laws and Regulations

There are currently 15 key federal laws related to the control and regulation of hazardous and toxic materials. A summary of these laws, their regulatory objectives, and primary responsible federal agencies is shown in Table 3.1. In addition there are many more state laws and regulations, often with more stringent requirements than their federal counterparts. It is important to review these state and federal regulations as part of the risk assessment process. The various laws and regulations provide specific definitions, specific lists of toxic and hazardous materials, requirements for compliance, and methods and standards for compliance.

TREATMENT LEVELS

Presently, there are two basic methods of treating wastewaters; in certain cases additional treatment is required. The processes or methods are referred to as primary, secondary, and tertiary treatment.*

Primary Treatment

As wastewater enters a plant for primary treatment, it flows through a screen that removes large floating objects such as rags and sticks that may clog pumps and pipes. Such screens vary from coarse to fine—from those consisting of parallel steel or iron bars with openings of about a half inch or more to screens with much smaller openings.

Screens are generally placed in a chamber or channel in a position inclined with respect to the flow of the sewage to make cleaning easier. The debris caught on the upstream surface of the screen can be raked off manually

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*The reader is encouraged to consult the glossary of wastewater-treatment terms at the end of this chapter as needed.

TABLE 3.1 Summary of Key Federal Laws and Responsible Agencies Related to the Control and Regulation of Hazardous and Toxic Materials

Regulatory Objectives	*Key Federal Laws*	*Responsible Agencies*
Air pollution control	Clean Air Act (CAA)	EPA
Water pollution control	Clean Water Act (CWA)	EPA
	Safe Drinking Water Act	EPA
	Marine Protection, Research and Sanctuaries Act (MPRSA)	EPA, Corps of Engineers
Regulation of hazardous waste	Resource Conservation and Recovery Act (RCRA)	EPA, DOT
	Comprehensive Environmental Response, Compensation and Liability Act (CERCLA)	EPA
	Hazardous Materials Transportation Act	DOT, EPA
Regulation of the transportation of hazardous materials	Hazardous Materials Transportation Act	DOT
	Dangerous Cargo Act	DOT
	Federal Railroad Safety Act	DOT
	Ports and Waterways Safety Act	DOT
Regulation of the workplace	Occupational Safety and Health Act	OSHA, NIOSH
	Federal Mine Safety and Health Act	MSHA, NIOSH
Regulation of toxic industrial chemicals	Toxic Substances Control Act (TSCA)	EPA
Regulation of pesticides	Federal Insecticide, Fungicide and Rodenticide Act (FIFRA)	EPA
	Federal Environmental Pesticide Control Act	EPA
Update cleanup enforcement activities	Superfund Amendments and Reauthorization Act (SARA)	EPA

Note:
EPA—U.S. Environmental Protection Agency
DOT—U.S. Department of Transportation
OSHA—Occupational Safety and Health Administration
NIOSH—National Institute of Occupational Safety and Health
MSHA—Mine Safety and Health Administration

or mechanically. Some plants use a device known as a comminutor, which combines the functions of a screen and a grinder. These devices catch and then cut or shred the heavy solid material. The pulverized material remains in the sewage flow to be removed later in a settling tank.

After the wastewater has been screened, it passes into a grit chamber, where sand, grit, cinders, and small stones are allowed to settle to the bottom. The unwanted grit or gravel from this process is usually disposed of by land filling near a treatment plant.

In some plants, another screen is placed after the grit chamber to remove any additional material that might damage equipment or interfere with later processes.

With the screening completed and the grit removed, the wastewater still contains suspended solids. These are minute particles of matter that can be removed from the sewage by treatment in a sedimentation tank. When the speed of the flow of wastewater through one of these tanks is reduced, the suspended solids will gradually sink to the bottom. This mass of solids is called raw sludge.

Various methods have been devised for removing sludge from the sedimentation tanks. In older plants it was removed by hand. After a tank had been in service for several days or weeks, the sewage flow was diverted to another tank, and the sludge in the bottom of the out-of-service tank was pushed or flushed with water to a nearby pit and then removed for further treatment or disposal.

Almost all plants built within the past 30 years have included mechanical means for removing the sludge from sedimentation tanks. In some plants it is removed continuously, whereas in others it is at intervals. To complete the primary treatment, the sludge-free effluent may be chlorinated to kill harmful bacteria and then discharged into a stream or river, or it can be sent to a secondary treatment process.

Secondary Treatment

Secondary treatment removes 90-plus percent of the organic matter in wastewater by making use of the bacteria it contains. The two principal processes for secondary treatment are trickling filters and the activated-sludge process. The effluent from the sedimentation tank in the primary treatment stage flows or is pumped to a facility using one or the other of these processes.

Trickling Filter. A trickling filter is simply a bed of stones from 3 to 10 feet deep through which the wastewater passes. Bacteria gather and multiply on these stones until they can consume most of the organic matter in the wastewater. The cleaner water trickles out through pipes in the bottom of the filter for further treatment. The wastewater is applied to the bed of stones in two principal ways. One method consists of distributing the effluent intermittently through a network of pipes laid on or beneath the surface of the stones. Attached to these pipes are smaller, vertical pipes that spray the effluent over the

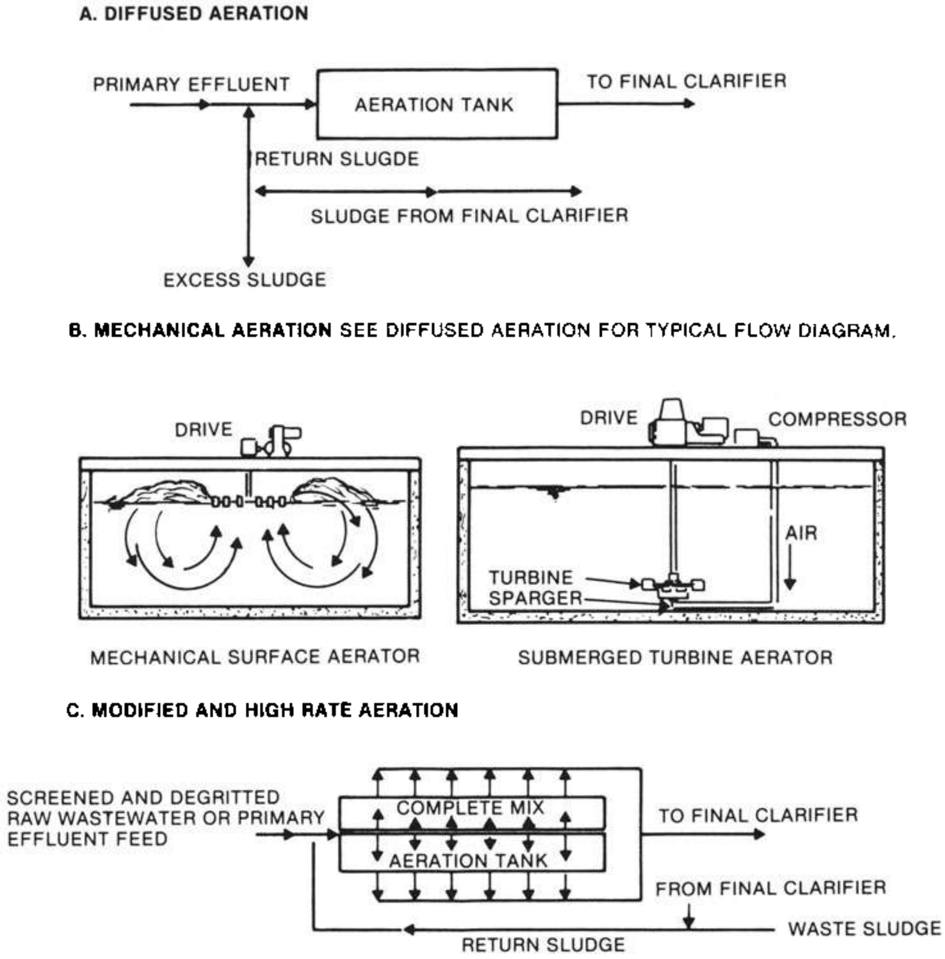


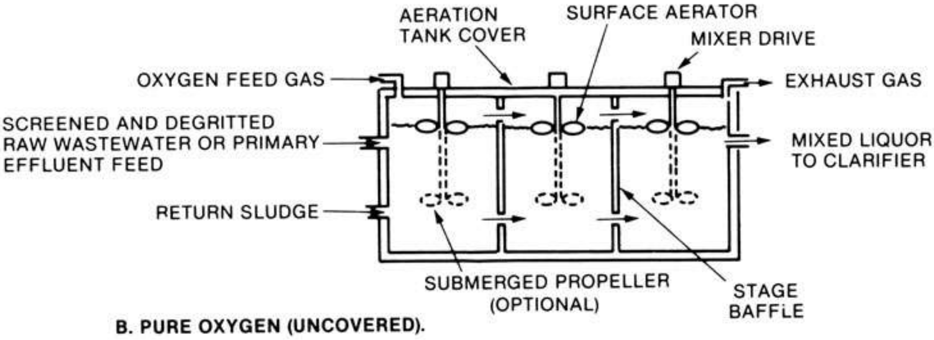
Fig. 3.2. Types of secondary biological treatment methods. (*Courtesy EPA.*)

stones. Another much-used method consists of a vertical pipe in the center of the filter connected to rotating horizontal pipes that spray the effluent continuously upon the stones.

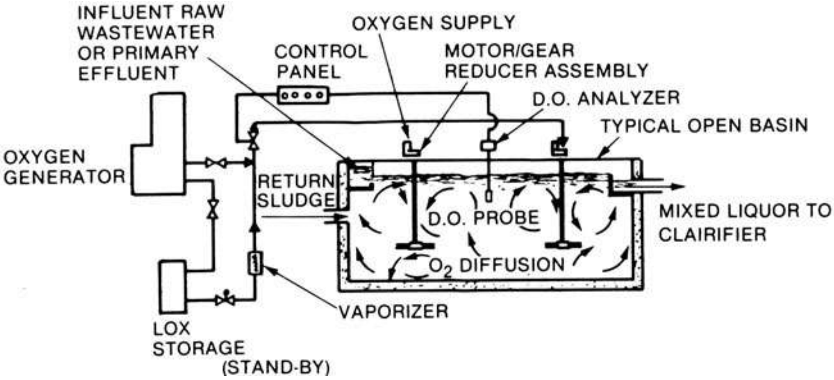
Activated-Sludge Process. The trend today is toward the use of the activated-sludge process instead of trickling filters. The former process speeds up the work of the bacteria by bringing air and sludge heavily laden with bacteria into close contact with the wastewater. (See Fig. 3.2.)

In the activated-sludge process, the wastewater from the sedimentation tank in primary treatment is pumped to an aeration tank where it is mixed with air and sludge loaded with bacteria and allowed to remain for

A. PURE OXYGEN (COVERED).



B. PURE OXYGEN (UNCOVERED).



C. CONTACT STABILIZATION.

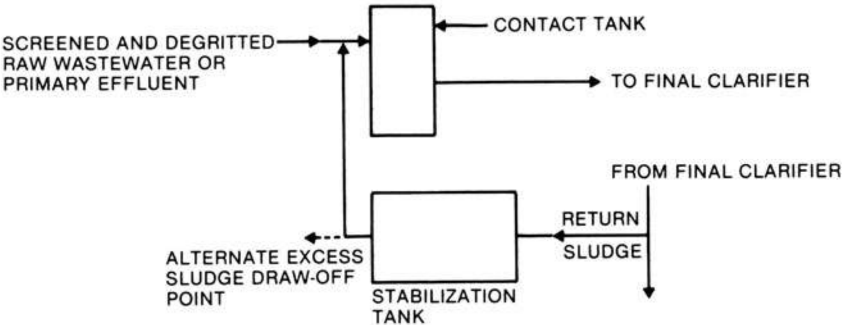


Fig. 3.3. Oxygen and contact stabilization processes for wastewater treatment. (*Courtesy EPA.*)

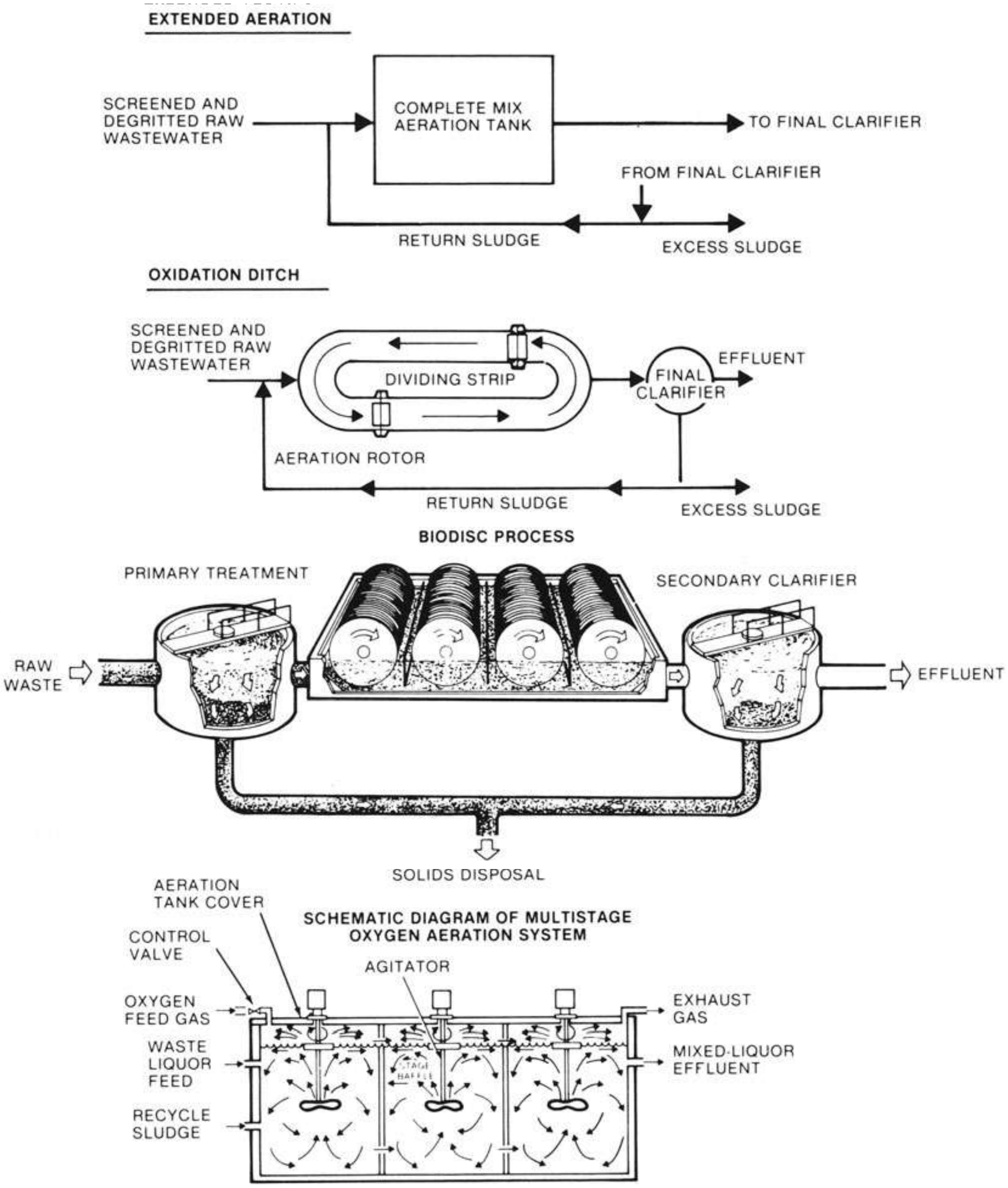


Fig. 3.4. Other types of aeration and biological treatment processes. (*Courtesy EPA.*)

several hours. During this time, the bacteria break down the organic matter. From the aeration tank, the wastewater, now called mixed liquor, flows to another sedimentation tank to remove the solids. Chlorination of the effluent completes the basic secondary treatment. The sludge, now activated with additional millions of bacteria and other tiny organisms, can be used again by returning it to an aeration tank for mixing with new wastewater and ample amounts of air.

The activated-sludge process, like most other techniques, has advantages and limitations. The size of the units needed is small so that they require comparatively little land space. Also, the process is free of flies and odors. But it is more costly to operate than the trickling filter, and it sometimes loses its effectiveness when presented with difficult industrial wastes.

An adequate supply of oxygen is necessary for the activated-sludge process to be effective. Air is mixed with wastewater and biologically active sludge in order for the aeration process to be effective. This mixing can be done using three different methods. The first, mechanical aeration, is accomplished by drawing the wastewater from the bottom of the aeration tank and spraying it over the surface, thus causing the wastewater to absorb large amounts of oxygen from the atmosphere. In the second method, large amounts of air under pressure are piped down into the wastewater and forced out through openings in the pipe. The third method is a combination of mechanical aeration and the forced-air method. (See Figs. 3.3 and 3.4.)

Tertiary Treatment

Tertiary treatment is used when the waste stream must meet strict requirements governing recreational bodies of water, or must approach drinking-water standards. This may require one or several of the following processes: slow filtration; rapid filtration with activated carbon; adsorption by activated carbon; application of ozone; high-rate chlorination or the use of another oxidizing chemical; or lagooning.

At each plant the question may arise of what degree of treatment is actually required. Water-quality criteria imposed by different waste-streams discharges may vary widely. Even within the same state, or for a particular river basin, different limits for each of the contaminants may be set for the section of the river under consideration.

WASTE TREATMENT TECHNOLOGIES

Anaerobic Digestion

Anaerobic digestion is a biodegradation process capable of handling high-strength aqueous waste streams that would not be efficiently treated by aerobic biodegradation processes. Advantages of anaerobic systems over aerobic systems include:

- Ability to break down some halogenated organics.
- Low production of biomass sludges that require further treatment and disposal.
- Low cost.

However, anaerobic systems can be less reliable than aerobic systems. For this reason, aerobic systems are better suited for mobile (truck- or trailer-mounted) unit applications. Disadvantages of anaerobic systems include:

- Potential for shock loading of biomass and termination of biodegradation process due to variation in waste stream characteristics.
- Low throughput due to the slow biodegradation process (two steps).
- Frequent need for further treatment of effluent prior to discharge off-site or to a municipal treatment system.
- Generation of methane gas (a problem if it cannot be readily used on-site for meeting energy requirements).

Careful design and control often can solve these problems, but vendors are reluctant to recommend anaerobic mobile systems. Anaerobic systems are much more susceptible to variation in waste stream characteristics and environmental parameters. Fixed anaerobic systems are widely used in industry for treatment of uniform, concentrated biodegradable waste in aqueous waste streams due to the low-cost, low-residual generation and production of usable methane gas. However, application to variable CERCLA waste streams is relatively infrequent. Anaerobic systems have the best potential as a pretreatment step for an aerobic system that would otherwise be unable to process a high-strength waste such as a leachate.

Figure 3.5 shows schematic diagrams of conventional and high-rate anaerobic digesters.

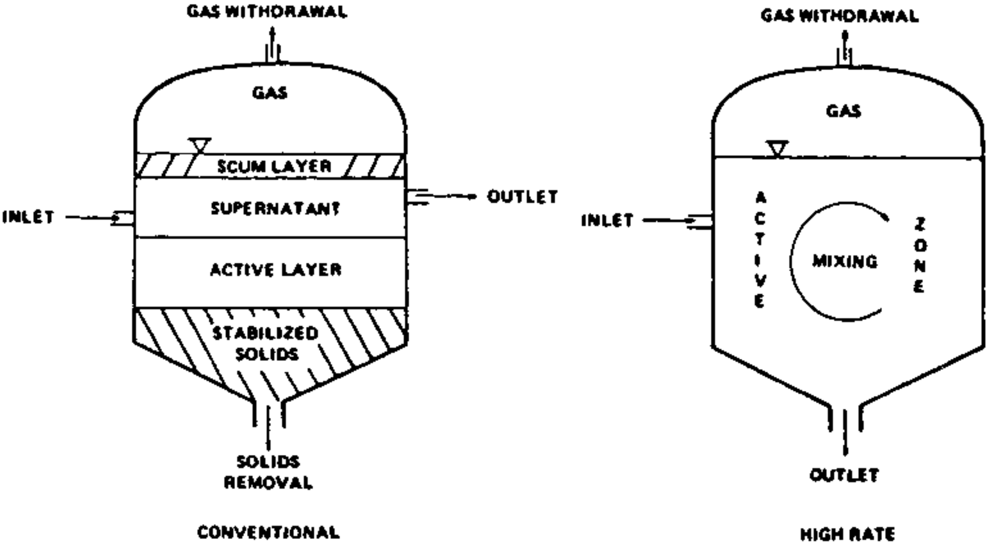


Fig. 3.5. Schematic diagrams of conventional and high-rate anaerobic digesters. (*Courtesy EPA.*)

Waste Types Handled. Anaerobic digesters can handle concentrated waste streams with biodegradable nonhalogenated organics and moderate levels of halogenated organics. The most suitable application may be as a treatment step for landfill leachates where storage, mixing, and flow regulation can be accomplished prior to introduction at the digesters.

Anaerobic digestion can partially break down some halogenated organics unsuitable for aerobic digestion. Also, anaerobic systems can be used as a pretreatment step prior to aerobic biodegradation. Recommended influent characteristics for anaerobic processes are as follows:

BOD: 1000 to 15,000 mg/l
COD: >1500 mg/l

Restrictive Waste Characteristics. As with aerobic systems, the biodegradation process can be slowed or halted by the following:

- Abrupt change in waste stream characteristics.
- Variable environmental conditions (e.g., temperature, pH).
- Elevated levels of heavy metals or halogenated organics toxic to the biomass.
- Inadequate nutrient levels.

Wet Air Oxidation

Wet air oxidation is a thermal treatment technology that breaks down organic materials by oxidation in a high-temperature, high-pressure aqueous environment and in the presence of compressed air. The resulting exothermic reactions are self-sustaining and potentially capable of generating steam as a by-product.

In this process, wastes are mixed with compressed air. The waste–air mixture then is preheated in a heat exchanger before entering a corrosion-resistant reactor where exothermic reactions increase the temperature to the desired level. The exit stream from the reactor is used at the place where the spent process vapors (i.e., noncondensable gases consisting primarily of air and carbon dioxide) are separated from the oxygenated liquid phase.

The reactor or pressure vessel is sized to accommodate a specific waste flow over a certain amount of time. The residence time, temperature, pressure, and possibly a catalyst are based on the characteristics of the waste.

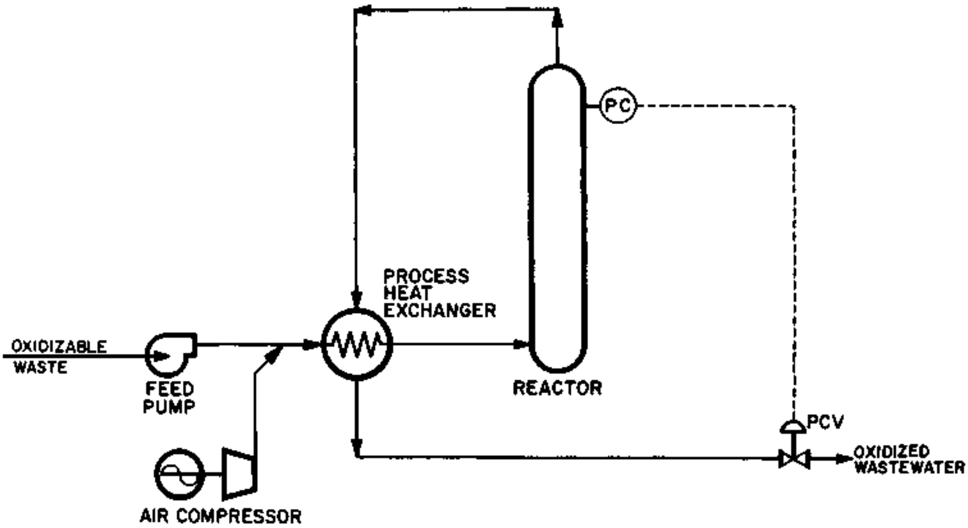


Fig. 3.6. Process flow diagram of wet air oxidation. (*Courtesy Zimpro Passavant Environmental Systems, Inc., Rothschild WI.*)

A process flow diagram for wet air oxidation is shown in Fig. 3.6.

Waste Types Handled. Wet air oxidation can be applied to dissolved or suspended organic substances in the form of liquid wastes and sludges. Particular contaminants and wastes processed include: halogenated organics, inorganic/organic sludges, contaminated groundwater, inorganic and organic cyanides, phenols, and leachates.

Although wet air oxidation technology has been used extensively for industrial applications, its use for hazardous wastes is limited. There are, however, several full-scale fixed wet air oxidation facilities treating hazardous waste.

Restrictive Waste Characteristics. Nonpumpable aqueous wastes and highly halogenated wastes are restricted from this process. Minimum and maximum chemical oxygen demand (COD) concentrations for a feasible application are 10,000 mg/l and 200,000 mg/l, respectively.

Supercritical Water Oxidation

The supercritical water oxidation process is based on the ability of water to perform as an excellent solvent for organics when the water is above its critical temperature (705°F) and critical pressure (3200 psi). When air is mixed with aqueous wastes above the critical temperature and pressure of water, organics are reported to be rapidly and completely oxidized to CO_2 and water. In addition, inorganic salts become almost insoluble above 930°F and precipitate out of the supercritical liquid. The exothermic conditions during the oxidation reactions produce energy in excess of process energy requirements and, in principle, allow for the production of high pressure steam or electricity.

Process operation involves the use of a high pressure pump to bring an aqueous solution or slurry of hazardous wastes up to system pressure before being heated to supercritical conditions in a feed/effluent heat exchanger. Large organic molecules are thus broken down to molecules of low molecular weight. High pressure air then is injected into the reactor, rapidly oxidizing the lower molecular weight compounds. Bases such as sodium hydroxide are added to the waste to neutralize any inorganic acids formed during oxidation.

The supercritical water oxidation process can be adapted to a wide range of feed mixtures and scales of operation, making it a

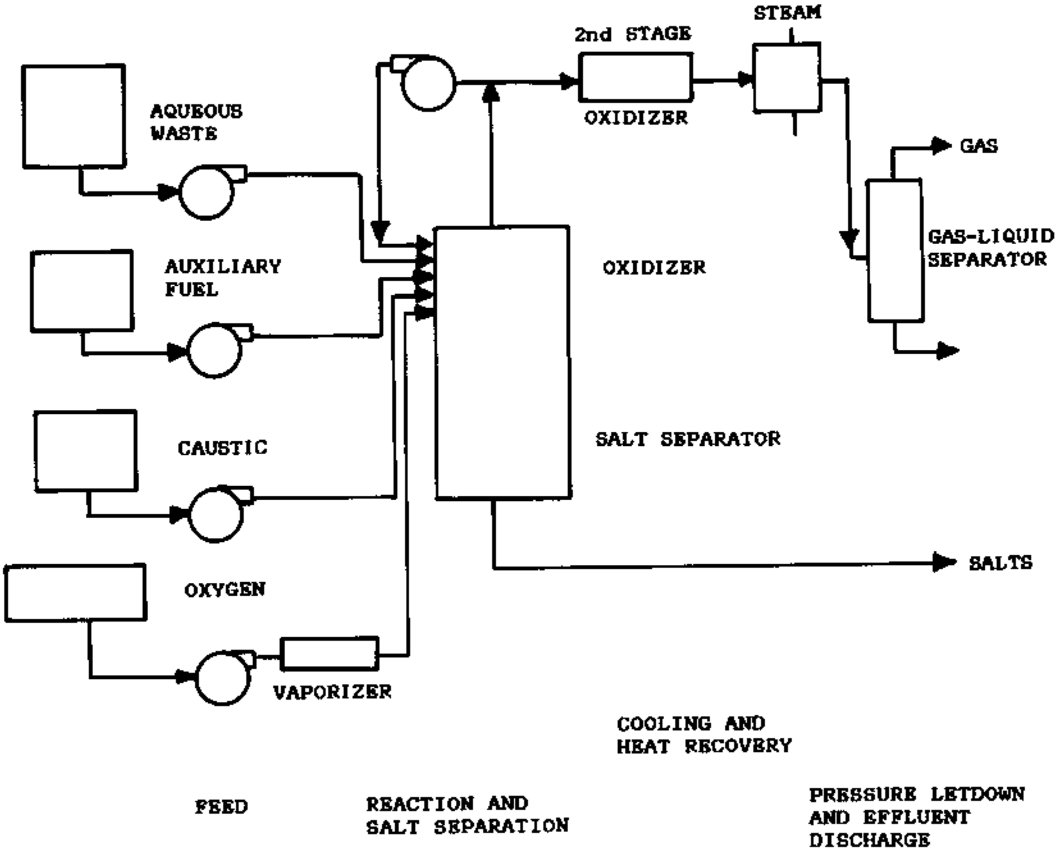


Fig. 3.7. Process flow diagram of supercritical water oxidation process. (*Modar, Inc., Houston, TX; courtesy EPA.*)

potentially feasible mobile technology. However, supercritical water oxidation is a relatively new thermal technology. To date, operating experience has been restricted to bench-scale and pilot-scale systems.

A process flow diagram is shown in Fig. 3.7.

Waste Types Handled. This technology can be applied to aqueous solutions or slurries with organic concentrations from 1 to 100 percent. The actual organic concentration of the waste fed to the process will depend on the heating value of the original waste material. The heat content of waste fed to the process is controlled at 1800 Btu/lb. Therefore, wastes with a heating value below 1800 Btu/lb require the addition of auxiliary fuel, and waste material with a heating value above 1800 Btu/lb requires either the addition of dilution water or blending with a lower-heating-value waste.

Particular contaminants and wastes processed include: PCBs, dioxins, solvents, pesticides, and still bottoms and tank bottoms.

Filtration

Filtration may be used for two primary purposes:

1. Removal of suspended solids from a fluid by passage of the fluid through a bed of granular material.
2. Dewatering of sludges and solids by vacuum, high pressure, or gravity. Granular media filters (typically sand and anthracite) remove suspended solids through straining, physical adsorption, and coagulation–flocculation. These filters may be pressurized or gravity-fed, with loading rates ranging from 2 to 15 gpm/sq ft.

Various filtration methods have been employed to dewater sludges, including:

- Vacuum filtration
- Belt filter press
- Chamber pressure filtration

Vacuum filtration typically is performed using a mechanically supported cylindrical rotating drum covered by a filter medium (cloth, coil springs, or wire mesh fabric). Water is drawn into the center by vacuum while the solids are scraped off the drum.

The belt filter press continuously squeezes the sludge through a series of rollers, which apply increasing pressure and shear force on the sludge.

The chamber pressure filters consist of a collection of cloth-covered plates arranged in parallel and pressed together by pressure up to 200 psi. As the plates are compressed, filtrate exits through the cloth.

Gravity-fed or pressurized granular media filter systems are less energy-intensive than the three systems mentioned above but require highly qualified operators with sufficient experience in backflushing procedures. These systems are not applicable to the removal of dissolved chemical species.

Waste Type Handled. Pressurized and gravity-fed granular media filtration systems are used for waste streams containing suspended solids. Vacuum, belt press, and pressure chamber filtration processes are used primarily to dewater sludges.

Restrictive Waste Characteristics. Energy-intensive filtration operations such as belt press filtration, vacuum rotary filtration, and pressure filters operate at optimal solids content. Sludges that range from 5 to 10 percent solids are generally well suited for these operations.

Ion Exchange

Anions and cations dissolved in a dilute aqueous waste can be removed from solution through the process of ion exchange. As the name implies, one ion, electrostatically attached to a solid resin material, is exchanged for a dissolved toxic ion. The exchange reaction is reversible, allowing for resin regeneration.

The exchange occurs because the divalent and trivalent toxic metal anions or cations have an increased affinity for the charged sites on the surface of the resins, which originally were coated with weakly held monovalent anions or cations such as chloride, hydroxyl, sodium, or hydrogen ions.

Currently, the majority of new ion exchange resins are constructed of synthetic organic materials. These resins are able to withstand a wide range of temperatures and pH, are capable of specific selectivity and a high exchange capacity.

It is possible to remove both dissolved toxic anions and cations by placing a cation exchange column and an anion exchange column in series. This system has the ability, depending upon the choice of resins, to remove a wide range of inorganic and organic dissolved contaminants.

Pressure vessels typically range from 2- to 6-inch-diameter systems up to a custom size of 12 feet in diameter. Corresponding flow rates range from 25 gpm up to a maximum of 1150 gpm. These vessels could easily be truck-mounted and moved from site to site.

Waste Types Handled. Wastes that are suited for anion exchange include:

- All metallic anions and cations such as $Cr_2O_7(-2)$, $SeO_4(-2)$, $AsO_4(-2)$, $Ni(+2)$, $Cd(+2)$, and $Hg(+2)$.
- Inorganic anions such as halides, sulfates, and cyanides.
- Organic acids such as carboxylics, sulfonics, and some phenols.
- Organic bases such as amines.

Restrictive Waste Characteristics. The upper limits of concentration at which ion exchange may be applied are 2500 mg/l for dissolved ions and 50 mg/l for suspended solids. Higher concentration levels of dissolved ion will result in rapid exhaustion of the resin with unusually high regeneration expenses. High concentrations of suspended solids will result in clogged columns. Oxidants in the waste stream also should be avoided.

Membrane Separation

Membrane technologies separate solutes or contaminants from liquids through the use of semipermeable membranes, which function by selectively rejecting contaminants based on pore size, ionic valence, or co-precipitation. Membrane separation processes can be used for volume reduction, purification, concentration, and recovery of the contaminants.

The types of membrane separation technologies include reverse osmosis, hyperfiltration, ultrafiltration, and electrodialysis. At present, reverse osmosis is the only membrane separation technology that has been used as a mobile system and thus is the only such technology discussed in this section.

The reverse osmosis system allows a solvent (such as water) to be removed from a solution containing solutes (such as salts) by use of a pressure-driven membrane process. In this process, the solvent molecules (water) are forced through the microscopic pores of a semipermeable membrane by achieving sufficient hydrostatic pressure to overcome the concentrate osmotic pressure. Operating pressures for a typical reverse osmosis system can range from 200 to 800 psi. As the solvent flows through the membrane, the larger organic and inorganic compounds are rejected.

The effectiveness of RO systems depends on the following factors:

- Temperature of the solution
- Pressure of the system
- pH of the solution
- Chemical and physical structure of the membrane

Waste Types Handled. The reverse osmosis process has typically been used for treatment of brackish waters and aqueous metal wastes (plating baths), but innovative technologies have made it very effective in treating other forms of contaminants such as:

- PCB and chlorinated organics in groundwater
- Waters containing high BOD levels
- Insecticides/herbicides in groundwater
- Organic and inorganic leachate

Concentration levels of organics generally range in the milligram per liter level for the feed, with a permeate in the range of 10 to 50 μg/l.

Reactive Waste Characteristics. To avoid membrane plugging and to ensure a long maintenance-free life, it is important to remove suspended solids and oils with conventional pretreatment.

Mobile Incineration System (MIS)

Development of the EPA Mobile Incineration System began in the mid-1970s as a research effort to demonstrate the ability to incinerate oil and hazardous materials on-site. Following several years of design and construction, a unit was tested in 1981.

The MIS consists of a 16-foot rotary kiln with a dual refractory lining. This is connected to an 18-foot by 50-inch-diameter cyclone, which feeds into a secondary chamber (42 feet long by 52 inches i.d.) and quench sump. The exhaust then enters a wet electrostatic precipitator which is 40 feet high with a cross section that is 84 inches by 84 inches. The final unit is a mass transfer scrubber 8 feet long by 5 feet high.

The entire system can be mounted on over-the-road equipment and transported to a cleanup site. A total of 21 trailers are required to transport this incineration system.

Types of Wastes Handled. During trial burns in 1982 and 1983 the MIS successfully incinerated PCBs and other chlorinated organic liquids. The unit was subsequently modified to handle solid materials and field-tested at Denny Farm in southwestern Missouri. In this test the incinerator was fed with soil contaminated with 2,3,7,8-tetrachlorodibenzo(*p*)dioxin (2,3,7,8-TCDD) and related chemicals. This test was successfully completed in April 1985. Between 1985 and 1989 the incinerator treated over 12,500,000 pounds of solids and 230,000 pounds of liquids (EPA, Sept. 1990).

Phase Separation

Phase separation is used for separating solid/liquid or liquid/liquid suspensions with different specific gravities. It encompasses many different processes, several of which are described below.

Oil Separation. This process employs a number of equipment configurations to remove oil from water, each of which provides surface contact for de-emulsifying the oil particles from the water phase. A coalescer is a flow-through chamber containing metal sheets inclined at an angle, causing the oil droplets to agglomerate and form a continuous oil phase. The lighter oil fraction rises to the top of the chamber and is skimmed off.

Centrifugation. In this process the components of the oil/liquid mixture are separated mechanically by applying centrifugal force. This is done by rapidly rotating the mixture in a confined vessel. The suspended oils will migrate toward the center of the vessel. Centrifuges also may be used for separation of liquid/solid mixtures.

Dissolved Air Flotation (DAF). These processes are used to separate emulsified oils from water by first dissolving air (under high pressure) into the water and then dropping the pressure. This causes tiny air bubbles to be generated throughout the water phase. The oils accumulate at the air–water interface and are carried to the top of the chamber where they are skimmed off. DAF units usually are employed for more complete oil removal, whereas coalescers are used for coarse oil separation.

Operating Parameters. Mobile phase separation units depend on the following parameters:

- Oil concentration
- Detention time
- Surface area
- Skimming rate
- Air pressure
- Revolutions per minute (rpm)
- Treatment chemical needed

Waste Type Handled. The following wastes can be treated with phase separation:

- Immiscible oily liquids in water
- Suspended solids
- Hydrophobic chemicals
- Two-phase leachates

Ozonation

Ozone is an unstable gas that is slightly soluble in water (having about 13 times the solubility of oxygen). Although relatively stable in air, in aqueous solution ozone continues to decompose at increasing rates with increasing concentrations of oxidizable contaminants. Thus, solutions of ozone do not provide long-lasting residuals.

Ozone is the most powerful oxidizing agent/disinfectant readily available for water and wastewater treatment. As a result, it is used for the following purposes:

- Disinfection and viral inactivation
- Chemical oxidation
- Preoxidation in preparation for biological treatment

The amounts of ozone needed to perform each of these functions depend upon a number of factors, but primarily upon the ozone demand of the constituents of the water/wastewater to be ozonized.

During preozonation to prepare solutions or during subsequent biological treatment, only small amounts of ozone are added (1 mg/l of ozone per mg/l of dissolved organic carbon). When it is used to oxidize pollutants that react rapidly with ozone, attainment of measurable ozone concentrations can be taken as achievement of the ozone demand.

A concentration of residual ozone can be achieved and monitored during disinfection and/or viral inactivation of waters that have little extraneous ozone demand (drinking water, swimming pool water, cooling water, etc.). For other drinking water or industrial water treatment applications, and for most wastewater applications, control of ozonation processes must be monitored by a surrogate analytical technique. Such process controls are not based upon the monitoring of dissolved residual ozone.

Lagoons and Septic Tanks

Many well-populated areas in the United States are not served by sewer systems or waste treatment plants. Lagoons and septic tanks are the usual alternatives in such situations.

Lagoons, or, as they are sometimes called, stabilization or oxidation ponds, have several advantages when used correctly. They can provide primary and secondary treatment of sewage, or they can be used to supplement other processes. A lagoon is a specially designed pond, usually 3 to 5 feet deep, in which sunlight, algae, and oxygen interact to restore water to a quality equal to or better than that of the effluent from secondary treatment. Although changes in the weather will affect how well lagoons break down sewage, they can be very effective when used with other waste treatment processes.

Solvent Extraction Process

The Basic Extraction Sludge Treatment (B.E.S.T.®) process developed by the Resources Conservation Company is a solvent extraction process used to treat contaminated soils and sludges. This patented process uses an aliphatic amine to break down suspensions and emulsions and separate a waste into three constituents—dischargeable water, oil and organics, and dry, oil-free solids. Treatment costs vary with feed characteristics but generally have been demonstrated to be lower

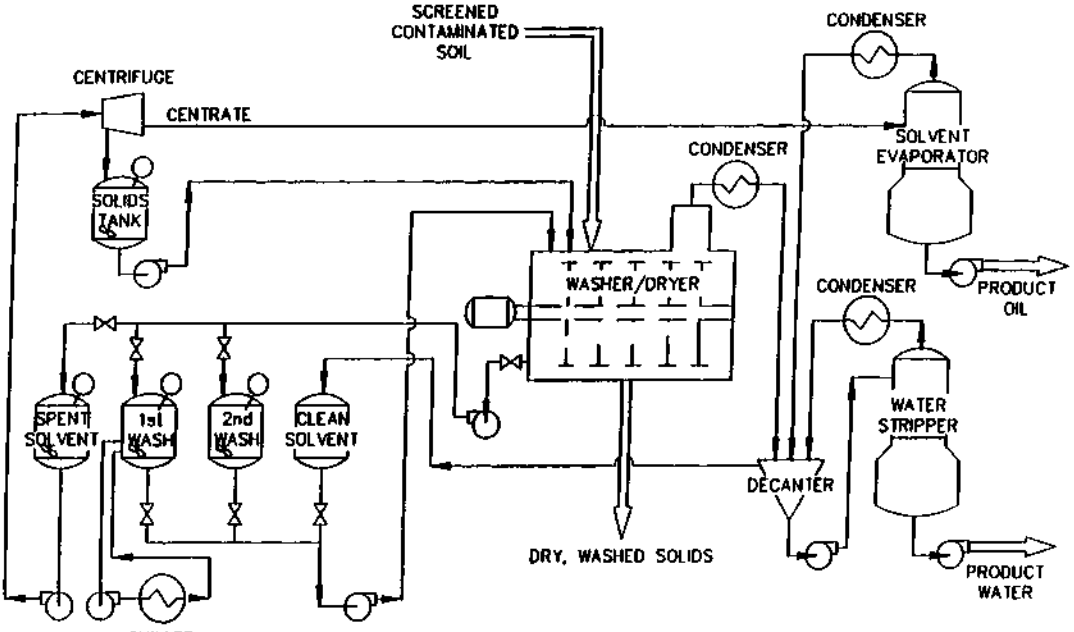


Fig. 3.8. B.E.S.T.® soil cleanup unit schematic. (*Courtesy Resources Conservation Company, Inc., Bellevue, WA.*)

than those for incineration or commercial landfilling. (See Fig. 3.8.)

The process can be used to treat wastes from refineries, petrochemical plants, wood treating operations, wastewater treatment systems, and steel mills. In addition, PCB-contaminated sludges and soils and the RCRA-listed hazardous wastes (shown below) are suitable feed stocks.

K001*—Creosote sludges
K048—OAF float
K049—Slop oils emulsion solids
K050—Heat exchanger sludge
K051—API separator bottoms
K052—Leaded tank bottoms
K062—Ammonia still sludge
K089—Decanter tar sludge
K101—Distillation residues
K044—Water treatment sludges

KPEG Chemical Dechlorination Process

Chemical dechlorination processes that use metallic sodium to treat materials contaminated with polychlorinated biphenyls (PCBs) are considered proven technologies. However, metallic sodium is difficult to handle and dangerous. Dr. L. Pytlowski at the Franklin Institute Research Laboratory is credited with initially discovering that alkaline-glycolate reagents could detoxify chlorinated aroniaties, especially polychlorinated biphenyls.

It is generally accepted that the initial reaction (between, e.g., potassium polyethylene glycolate and PCB) is a nucleophilic substitution that produces an aromatic, as shown in the following equation:

This reaction can be conducted at moderate temperatures and ambient pressure in conventional equipment. Water will slow but not stop the reaction.

Soil decontamination tests have demonstrated that the process can effectively decontaminate soils containing up to 10,000 ppm of PCBs and soils or sludge containing 5 percent or less of organics; soils with higher contaminant concentrations may be more economically treated by incineration. However, this process can treat soils containing more than 5 percent organics. (See Fig. 3.9.)

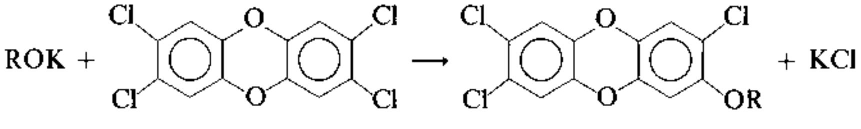
Bioremediation of Wastewater

Various biological materials are found in contaminated wastewaters. The removal mechanisms include adsorption, bioaccumulation, metal reduction, and conversion to insoluble metal sulfides. Normally, most microbial techniques are specific for individual metals.

Researchers have been successful with a microbial strain, *Bacillus megaterium*, that has the ability to adsorb a variety of heavy metals. In its dormant spore form, it has an affinity for many heavy metals. Additionally, this form of the organism does not require nutrients and is resistant to the usual toxic effects of heavy metals.

Tests with *Bacillus megaterium* isolated from sedimentation contaminated with mercury, lead, strontium, and cesium have been conducted on laboratory solutions and electroplating rinse waters. The rinse water pH was adjusted with HCl, and the solution was filtered. Spores were added to give a 0.10 weight ratio (wet) of spores to rinse water, and the mixture was incubated for 24 hours.

$$\text{ROH} + \text{KOH} \longrightarrow \text{ROK} + \text{HOH}$$



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*EPA Office of Solid Waste Code Classification for the named waste type.

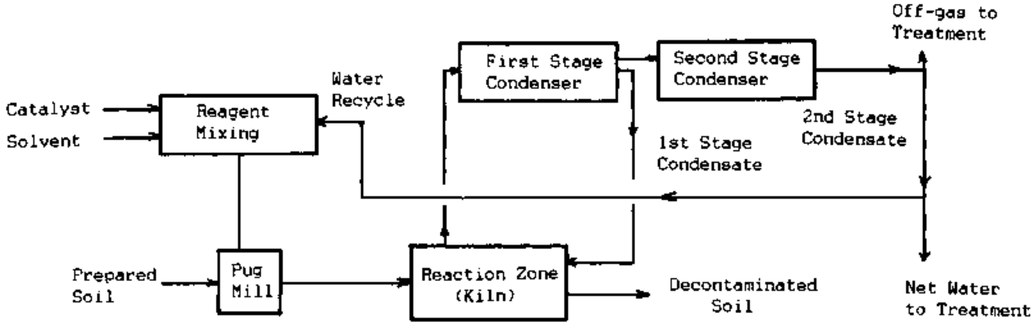

Fig. 3.9. KPEG decontamination process for PCB soils.

The spores then were filtered from the mixture, and HCl was added to adsorb the metals from the spores.

Some competition for the bonding sites between metal species seeking the same type of bonding site have been noted. For example, silver, arsenic, and cadmium appeared to seek similar adsorption sites. When one of these species was added to a solution containing another, adsorption of the latter was correspondingly decreased.

Researchers at Worcester Polytechnic Institute are investigating the feasibility of developing a wastewater treatment technology using a fungus called *P. ochro-chloron*. This fungus, discovered growing in an electroplating wastewater stream in Japan, is obtained from spores grown in petri dishes. The organism produces a cell wall that has the ability to bind large amounts of heavy metals as divalent cations. Heavy metal ions are added to the growth medium to ensure that the fungus grows in colonies that form beadlike structures.

After the fungi beads are grown, they are killed by using ethanol and then treated with a mixture of sodium carbonate and bicarbonate. This treatment prepares the fungal cell walls to exchange sodium ions for heavy metal ions. The fungal beads are packed into a column, and metal-containing water is passed through the column. The adsorbed heavy metals can be retrieved from the biological material by washing the beads with a dilute acid solution. This work is in the early stages of commercialization.[1]

Biological treatment processes have been gaining increasing respect in the hazardous waste industry as viable treatment alternatives. Although the number of these processes commercially available for hazardous waste treatment is still small, a number of new biological treatment processes are on the commercial threshold. One such process utilizes a common white rot fungus, *Phanerochaete chrysosporium*, which has the ability to degrade trichlorophenol, trinitrotoluene (TNT), DDT, lindane, PCBs, benzo[α]pyrene, dioxins, and other chlorinated organics.

Investigation of various biological reactor configurations revealed that a fixed-film reactor is compatible with the fungus. A rotating biological contactor was selected because this design is already in widespread commercial use and thus requires no further development.

The rotating biological contactor is first charged with a concentrated *P. chrysosporium* spore suspension. Typically, the suspension comprises 20 percent of the reactor volume although it has been found that the amount can be reduced by a factor of 100 with no adverse effects. The fungus is allowed to grow in the reactor for 2 to 4 days until the reactor surfaces are completely covered. During this period, nutrient solution is added to promote growth.

At this point, the reactor conditions are altered to force the fungus into a secondary metabolic state. In this state, the fungus excretes enzymes capable of degrading a wide variety of organic compounds by catalyzing oxidation reactions. Because the fungus does not excrete these enzymes unless it is nutritionally stressed, one or more of a variety of nutrients, usually nitrogen, are withheld from the medium to induce the secondary metabolic state.

The optimum temperature for the process appears to be 102°F (39°C), and the pH is typically 4.5. The oxygen concentration should be at least 20 percent in the enclosed space above the liquid in the reactor, and 50 to 100 percent oxygen is preferable.

Once the secondary metabolic state has been induced, the reactor is ready to accept aqueous waste for treatment. The process can be operated in either a batch or a continuous mode. Effluent from the reactor must undergo additional separation and filtration steps prior to reuse or discharge.

Organic compounds are eventually degraded to water, carbon dioxide, and inorganic ions by the process. No significant sludge disposal problems are associated with the process because very little fungal growth occurs after the initial growth period.

In bench-scale tests, pure TNT was degraded from an initial concentration of 90 ppm to 5 ppm in 8 hours. TNT concentrations in both industrial and synthetic "pink water" (i.e., wastewater from the manufacture of TNT munitions) were reduced from 90 ppm to nondetectable levels in less than one day. Other tests indicate that 50 ppm of 2,4,6-trichlorophenol also can be degraded in less than one day.

TYPES OF INDUSTRIAL WASTES

Table 3.2 presents the Standard Industrial Classification (SIC) of industries of significance for water pollution. The great variety of industrial pollutants argues against an attempt to catalog them. However, for the purpose of general description, at least five distinct categories of waste from industrial sources can be recognized:

1. Oxygen-demanding materials.
2. Settleable and suspended solids.
3. Many materials that impart acidity or alkalinity.
4. Heat.
5. Toxic compounds.

Within these general categories of pollutants are included most of the possible sources of recognized water-quality problems. Only bacterial and viral presences fall outside the group of pollutants to which industry contributes materially. (However, even they are not entirely outside the scope of the polluting activities of industry. For example, meat packing plants, and other food processors in lesser measure, contribute to the presence and viability of water-borne bacteria.) Manufacturing must stand near the top of, and very probably leads, any list of potential sources of water pollution. (See Table 3.3.)

Therefore, in any possible strategy of water-pollution control, industrial wastes are of critical importance. Over the last few years, the amount and composition of industrial output has been such that for every new increment of BOD that has been generated directly by population increase, 20 more units have been generated by increased industrial output. Increased per capita production is the essence of improvement in a society's standard of living, and the production of wastes is an inescapable concomitant of the production of goods. So as population and per capita production continue to advance, we can anticipate a continuing and unavoidable advance in the volume of wastes that must be managed.

Fortunately, industry has added rapidly to its inventory of waste-treatment facilities since the mid-1970s, and it appears that provision for waste treatment is routinely designed into new plants and plant additions. Even though additional treatment of municipal wastes has had an undesirable influence on the nation's ability to contain the level of waste discharges, the preponderence of industrial wastes and their extremely rapid rate of increase would have made containment impossible if increases in industrial-waste-treatment effectiveness had not outdistanced production increases.

TABLE 3.2 Standard Industrial Classification of Industries of Significance for Water Pollution

CODE	
20	FOOD AND KINDRED PRODUCTS
201	Meat products
2011	Meat slaughtering plants
2013	Meat processing plants
2015	Poultry dressing plants
202	Dairy products
2021	Creamery butter
2022	Natural and process cheese
2023	Condensed and evaporated milk
2026	Fluid milk
203	Canned and frozen foods
2033	Canned fruits and vegetables
2034	Dehydrated food products
2035	Pickled foods, sauces, salad dressings
2037	Frozen fruits and vegetables
204	Grain mill products
2041	Flour and other grain mill products
2043	Cereal preparations
2046	Wet corn milling
205	Bakery products
206	Sugar
207	Candy and related products
208	Beverage industries
2082	Malt liquors
2084	Wines and brandy
2085	Distilled liquors
2086	Soft drinks
209	Miscellaneous foods and kindred products
2091	Cottonseed oil mills
2092	Soybean oil mills
2094	Animal and marine fats and oils
2096	Shortening and cooking oils
22	TEXTILE MILL PRODUCTS
2211	Weaving mills, cotton
2221	Weaving mills, synthetic
2231	Weaving, finishing mills, wool
225	Knitting mills
226	Textile finishing, except wool
228	Yarn and thread mills
229	Miscellaneous textile goods
24	LUMBER AND WOOD PRODUCTS
2421	Sawmills and planning mills
2432	Veneer and plywood plants
2491	Wood preserving
26	PAPER AND ALLIED PRODUCTS
2611	Pulp mills
2621	Paper mills, except building
2631	Paperboard mills
264	Paper and paperboard products
265	Paperboard containers and boxes
2661	Building paper and building board mills
28	CHEMICALS AND ALLIED PRODUCTS
281	Basic chemicals
2812	Alkalies and chlorine
2818	Organic chemicals, n.e.c.
2819	Inorganic chemicals, n.e.c.
282	Fibers, plastics, and rubbers
2821	Plastics materials and resins
2823	Cellulosic man-made fibers
2824	Organic fibers, noncellulosic
283	Drugs
284	Cleaning and toilet goods
2851	Paints and allied products
2861	Gum and wood chemicals
287	Agricultural chemicals
289	Miscellaneous chemical products
29	PETROLEUM AND COAL PRODUCTS
2911	Petroleum refining
295	Paving and roofing materials
30	RUBBER AND PLASTICS PRODUCTS, n.e.c.
3069	Rubber products, n.e.c.
3079	Plastics products, n.e.c.
31	LEATHER AND LEATHER PRODUCTS
3111	Leather tanning and finishing
32	STONE, CLAY, AND GLASS PRODUCTS
3211	Flat glass
3241	Cement, hydraulic
325	Structural clay products
326	Pottery and related products
327	Concrete and plaster products
3281	Cut stone and stone products
329	Nonmetallic mineral products
33	PRIMARY METAL INDUSTRIES
331	Steel rolling and finishing mills
332	Iron and steel foundries
333	Primary nonferrous metal
3341	Secondary nonferrous metals

The processes that can be used to separate heavy metals from industrial liquid waste streams are given in Table 3.4, processes that can treat various tars or solids are shown in Table 3.5, and processes suitable for treating slurries and sludges are listed in Table 3.6.

The EPA national screening survey of hazardous waste treatment, storage, disposal, and recycling facilities yielded the data shown in Table 3.7. The compounds listed in Table 3.8 are refractory industrial waste compounds.

A summary of potentially suitable industrial wastewater treatment technologies for various waste types is given in Table 3.9. Additionally, there are three basic approaches to land treatment of nonhazardous industrial effluent wastewater, as depicted in Fig. 3.10.

INDUSTRIAL WASTE MANAGEMENT STRATEGIES

Unlike the public sector, where only variations on a single theme of waste treatment are possible, industrial pollutants can be managed through at least four distinct strategies:

1. Installation of waste treatment plants, the most obvious procedure.
2. Discharge of industrial wastes to public sewage systems for treatment. (Industry is estimated to account for half of the current BOD loading to metropolitan area waste treatment plants.)
3. Process modification.
4. Changed product formulations.

Strategies (3) and (4) together comprise the most effective as well as the most efficient means of reducing wastes.

Joint Treatment

Joint treatment is an alternative that can be advantageous both to a publicly owned treatment works (POTW) and to industry. Treatment of industrial wastewaters is incidental to a POTW's primary function of treating domestic sewage. Where the industrial contribution constitutes a significant portion of the total flow and substantially alters the concentration of pollutants normally contained in domestic sewage, the public agency may resort to a joint treatment approach. Then the industry or industries contributing the pollutants are made partners in the design and construction of the system, and the treatment works is designed specifically to remove the industrial pollutants. Both capital costs and operating costs are allocated to the industry and the public agency according to an agreement arrived at through negotiation, or as required by federal regulations if construction grant funds are involved.

Joint treatment of industrial wastewaters with municipal domestic sewage offers the following advantages:

- Increased flow, which can result in reduced ratios of peak to average flows.
- More efficient use of land resources, particularly in cases where available land for treatment facilities is scarce.
- Improved operations (larger plants are potentially better operated than smaller plants).
- Increased number of treatment modules with resultant gains in reliability and flexibility.
- More efficient disposal of sludges resulting from treatment of wastewaters containing pollutants susceptible to treatment in POTWs.
- Utilization of the nutrients available in domestic wastes for biological treatment of industrial wastes that are nutrient-deficient.

There also may be disadvantages to joint treatment:

- Where the pollutants are different from those usually treated in a POTW, a design to treat the combined industrial/domestic waste stream for those pollutants may not be cost-effective.
- Joint treatment by definition implies that the POTW was designed so as not to be interfered with by industrial wastes. However, where it requires design modifications ordinarily not required for domestic

TABLE 3.3 Wastewater Characteristics and Pollutants of Selected Industry

Liquid Waste Characteristic	*Domestic*	*Meat Products*	*Canned and Frozen Foods*	*Sugar*	*Textile Mill Products*	*Paper and Allied Products*
Unit volume	x	x	x	x	x	x
pH		x		x	x	x
Acidity				x	x	
Akalinity		x		x	x	x
Color					x	x
Odor					x	
Total solids		x		x	x	x
Suspended solids	x	x	x	x	x	x
Temperature		x				x
BOD_5/BOD ultimate	x	x	x	x	x	x
COD	x					
Oil and grease		x		x	x	x
Detergents (Surfacants)	x				x	x
Chloride		x				x
Heavy metals						
Cadmium						
Chromium					x	
Copper					x	
Iron						
Lead						
Manganese						
Nickel						
Zinc					x	
Nitrogen						
Ammonia		x		x	x	x
Nitrate					x	
Nitrite					x	
Organic		x		x		x
Total		x			x	x
Phosphorus		x				
Phenols					x	
Sulfide					x	x
Turbidity	x				x	
Sulfate					x	x
Thiosulfate					x	
Mercaptans						x
Lignins						x
Sulfur						x
Phosphates						x
Potassium						x
Calcium						x
Polysaccharides						x
Tannin						x
Sodium						x
Fluorides						
Silica						
Toxicity					x	
Magnesium						
Ammonia						
Cyanide						
Thiocyanate						
Ferrous iron						
Sulfite						x
Aluminum						
Mercury						x

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[a] Source: *The Total Cost of Clean Water*, Volume II, FWPCA, U.S. Department of the Interior,

Basic Chemicals	*Fibers Plastics and Rubbers*	*Fertilizer*	*Petroleum Refining*	*Leather Tanning and Finishing*	*Steel Rolling and Finishing*	*Primary Aluminum*	*Motor Vehicles and Parts*
x	x	x	x	x	x	x	x
x	x	x	x	x	x	x	x
x		x	x	x	x	x	x
x			x	x	x		x
x	x		x				x
x	x		x				x
x	x	x		x	x	x	x
x	x		x	x	x		x
x	x	x			x		x
x	x		x	x	x		x
x	x		x		x		x
x	x		x		x		x
x	x						x
x	x		x	x	x		x
x							x
x							x
x							x
x			x		x		x
x							x
x			x				x
x							x
x							x
x		x	x	x	x		
x							
x							
x			x	x			
x		x		x			
x		x					
x	x		x		x		x
x			x	x	x		
x			x				
x	x		x	x			
x							
x			x				
x							
x		x					x
x			x				
x			x				
x							
				x			
x			x	x			
x		x	x		x	x	
x		x					x
x	x						
			x				
x		x	x		x		
x				x	x		x
x					x		
x					x		
x							
x							
x		x	x				

U.S. Government Printing Office, Washington, DC. Apr. 1, 1968.

TABLE 3.4 Processes That Separate Heavy Metals from Liquid Waste Streams

Process	*Required Feed Stream Properties*	*Characteristics of Output Stream(s)*
Physical Removal		
Ion exchange	Con. <4000 ppm; aqueous solutions, low SS	One concentrated in heavy metals; one purified
Reverse osmosis	Con. >400 ppm; aqueous solutions; controlled pH; low SS; no strong oxidants	One concentrated in heavy metals; one with heavy metal concentrations >5 ppm
Electrodialysis	Aqueous solutions; neutral or slightly acidic; Fe and Mn <0.3 ppm; Cu <400 ppm	One with 1000–5000 ppm heavy metals; one with 100–500 ppm heavy metals
Liquid ion exchange	Aqueous solutions; no concentrations limits; no surfactants; SS <0.1%	Extraction solvent concentrated in heavy metals; purified water or slurry
Freeze crystallization	Aqueous solutions; TDS <10%	Concentrated brine or sludge; purified water, TDS ~100 ppm
Chemical Removal		
Precipitation	Aqueous or low viscosity non-aqueous solutions, no concentration limits	Precipitated heavy metals sulfides, hydroxides, oxides, etc.; solvent With TDS governed by solubility product of precipitates
Reduction	Aqueous solutions; concentrations of heavy metals <1%; controlled pH	Acidic solutions with reagant (Oxidized Na_2PO_4 or Zn); metallic precipitates
Electrolysis	Aqueous solutions; heavy metal concentrations <10%	Recovered metals; solution with 2–10 ppm heavy metal

*Source: *Pollution Engineering*, Feb. 1988.

TABLE 3.5 Processes That Can Treat Tars or Solids

Process	*Required Feed Stream Properties*	*Characteristics of Output Stream(s)*
Calcination	Tars or solids that can be volatilized	Volatile; char and/or metal oxides
Hydrolysis	Tars or solid powders	Hydrolysis products
Steam distillation	Solids contaminated with volatile organics	Purified solids; condensed organics
Dissolution	Tars, solids, or solid powders that will dissolve in some reagant	Liquid solution for further treatment; solid residue
Crushing and grinding	Bulk solid	Powdered solid
Cryogenics	Tar, bulk solid	Reduced particle size

*Source: *Pollution Engineering*, Feb. 1988.

wastes, joint treatment may not be cost-effective.

- If joint treatment results in sludge disposal or utilization problems, it may not be acceptable.

About 16,000 municipal wastewater treatment facilities treating 37 B gallons per day, many commercial establishments, and 160,000 industries discharge their wastes into POTWs; about 39,000 industries discharge directly into waterways.

Wastewater treatment is primarily a local function, with 15,438 systems (*EPA 1988 Needs Survey* data). (See Table 3.10.)

The escalating cost of upgrading, maintaining, and operating the existing wastewater treatment infrastructure, expanding it to support residential and commercial growth, and providing a new infrastructure where it

TABLE 3.6 Processes That Can Treat Slurries or Sludges

Process	*Required Feed Stream Properties*	*Characteristics of Output Stream(s)*
Calcination	Waste stream with components that decompose by volatilization (hydroxides, carbonates, nitrates, sulfites, sulfates)	Solid greatly reduced in volume, volatiles
Freeze crystallization	Low-viscosity aqueous slurry or sludge	Brine sludge; purified water
HGMS	Magnetic or paramagnetic parties in slurry	Particles adsorbed on magnetic filter
Liquid ion exchange	Solvent-extractable inorganic component	Solution in extraction solvent
Flotation	Floatable particles in slurry	Froth
Hydrolysis	Hydrolyzable component	Hydrolysis products
Anaerobic digestion	Aqueous slurry $<7\%$ solids; no oils or greases; no aromatics or long-chain hydrocarbons	Sludges, methane, and CO_2
Composting	Aqueous sludge; $<50\%$ solids	Sludge; leachate
Steam distillation	Sludge or slurry with volatile organics	Volatile, solid residue
Solvent extraction	Solvent-extractable organic	Solution of extracted components; residual sludge

Source: *Pollution Engineering*, Feb. 1988.

TABLE 3.7 Hazardous Waste Managed by Industry

Industry	*Number of Facilities*	*Amount Waste Managed (MMT)**	*General Waste Description*
Chemical	700	218	Contaminated wastewaters, spent solvent residuals, still bottoms, spent catalysts, treatment sludges, and filter cakes
Fabricated metals	200	4	Electroplating wastes, sludges contaminated with metals and cyanides, degreasing solvents
Electrical equipment	240	1	Degreasing solvents
Petroleum refinery	100	20	Leaded tank bottoms, slop oil emulsion solids, API separator sludge, DAF float
Primary metals	150	4	Pickle liquor, sludge with metal contaminates
Transportation equipment	150	3	Degreasing solvents, metals, sludges
National security	100	1	All types of wastes
Other	1360	24	All types of wastes
Total	3000	275	

*Million metric tons.

Source: National Screening Survey of Hazardous Waste Treatment, Storage, Disposal and recycling Facilities, U.S. EPA, Office of Solid Waste, Office of Policy, Planning and Information (1986).

does not exist is creating problems in the United States. Additional requirements for the treatment of toxics, in addition to the conventional pollutants further complicate the issue. Toxic chemical control also dictates that the treatment, handling, and disposal of treatment process sludge or residues receive considerably more attention than they have had in the past.

Sludge Management. Sludge management represents about half of wastewater treatment operation and maintenance (O&M) costs. The ultimate disposal of sludges produced by either pretreatment or joint treatment operations is an important consideration. The POTW must be aware of effects on the environment that may result from sludge disposal. Pretreatment facilities normally

TABLE 3.8 Refractory Industrial Wastes

Nitrobenzene[a]	Bromobenzene
Trichloroethane	Dichlorobenzene
Tetrachloroethylene	Bromochlorobenzene
Chloroethyl ether	Ethylbenzene[a]
Chloromethyl ethyl ether	Chloroform
Chloropyridine	Styrene[a]
Chloronitrobenzene	Isopropylbbenzene
Dichloroethyl ether	Butylbenzene
Benzene[a]	Dibromobenzene
Toluene[a]	Isocyanic acid[a]
Camphor	Methylchloride[a]
Veratrole (1,2-dimethoxy benzene)	Bromophenylphenyl ether
Guaiacol (methoxy phenol)	Dinitrotoluene[a]
Borneol (bornyl alcohol)	Methylbiphenyl
Isoborneol	Acetone
Ethylene dicloride[a]	2-Ethylhexanol
Chlorobenzene	2-Benzothiozole

[a]These compounds also have been found to impart taste and odor to drinking water supplies in trace amounts.

remove incompatible pollutants that may be deposited in the POTW sludge, and their removal can be an advantage in terms of the environmental problems connected with ultimate sludge disposal. Incompatible pollutants in sludges can cause problems with most disposal techniques including incineration, landfills, ocean dumping, and land spreading. Consequently, the removal of incompatible pollutants at their source by pretreatment is advantageous.

However, incompatible pollutants removed by pretreatment still require ultimate disposition. The sludge produced by pretreatment operations may be a source for by-product recovery or recycle; but when this is not economically or technically feasible, disposal of the sludge is necessary. Although the sludges produced by industrial pretreatment may not technically be under municipal regulatory control, their impact on other environmental areas should be noted.

Inhibition of Biological Treatment Processes. Interfering substances are generally categorized as inorganics and organics. Acidity, alkalinity, pH, ammonia, metal ions, sulfate, and sulfide comprise the major inorganic interferences. Organic substances include alcohols, amines, ketones, aldehydes, chlorinated (or halogenated) hydrocarbons, pesticides, herbicides, phenols, surfactants, and miscellaneous (both aromatic and aliphatic) chemicals.

A precipitated pollutant has relatively little inhibitory impact on biological treatment compared to soluble compounds. Settleable solids usually are removed in the primary treatment phase and therefore seldom reach the secondary or biological treatment phase.

Whether or not a substance is inhibitory depends on factors such as concentration and the presence of other chemicals that have synergistic or antagonistic effects. Some substances, such as mercury, even when present in wastewater at a very low concentration can disrupt one or more functions of a biological treatment system. Others, such as chloride ion, are inhibitory only at relatively high concentrations. Special phenomena that may alter the inhibitory nature of a substance include synergism, antagonism, and acclimation. These are described below.

Synergism is characterized as an increase in the inhibiting effect of one substance by the presence of another. Synergism and its opposite, antagonism, are most prevalent in

TABLE 3.9 Potentially Suitable Industrial Wastewater Treatment Technologies

Waste Type	Incineration	Pyrolysis	Wet Oxidation	Neutralization	Precipitation	Distillation	Air Stripping/ Soil Aeration	Activated Carbon	Evaporation/ Dewatering	Phase Separation	Fixation	Extraction/Soil Washing	Membrane Sep./ Ion Exchange	Evaporation	Filtration	Activated Sludge	In situ Biodegradation
Aqueous Wastes:																	
Metals	×	×	×	●	●	×	×	○	×	×	×	○	●	●	●	×	×
Highly toxic organics	○	○	●	○	○	●	×	●	×	●	×	○	●	●	●	○	○
Volatile organics	○	○	●	○	○	●	●	●	×	●	×	○	○	×	×	○	○
Toxic organics	○	○	●	○	○	●	●	●	×	●	×	○	●	●	×	●	●
Radioactive	×	×	×	×	○	×	×	×	×	×	×	×	×	○	●	×	×
Corrosive	×	×	×	●	●	○	×	×	×	×	×	×	×	×	×	×	×
Cyanide	○	○	●	○	○	×	×	×	×	×	×	×	×	×	×	○	×
Pesticide	○	○	●	●	●	●	×	●	×	●	×	○	●	●	●	○	×
Asbestos	×	×	×	○	○	×	×	×	×	×	×	×	○	●	●	×	×
Explosive	○	×	×	×	●	×	×	●	○	●	×	○	●	○	×	○	○
Organic Liquids:																	
Metals	○	○	×	●	●	●	×	×	×	●	○	×	×	●	●	×	×
Highly toxic organics	●	●	●	×	×	●	×	○	×	○	×	×	×	×	×	×	×
Volatile organics	●	●	●	×	×	●	×	×	×	○	×	×	×	×	×	×	×
Toxic organics	●	●	●	×	×	●	×	×	×	○	×	×	×	×	×	×	×
Radioactive	○	×	×	×	○	●	×	×	×	○	○	×	×	○	○	×	×
Corrosive	×	×	×	●	○	●	×	×	×	○	×	×	×	×	×	×	×
Cyanide	●	●	●	×	×	●	×	×	×	○	×	×	×	×	×	×	×
Pesticide	●	●	●	×	×	●	×	×	×	○	×	×	×	×	×	×	×
Sludges/Soils:																	
Metals	×	○	×	○	●	×	×	○	●	×	●	●	×	○	×	×	×
Highly toxic organics	●	●	●	×	×	●	×	●	●	●	●	○	×	●	●	×	○
Volatile organics	●	●	●	×	×	●	●	○	●	○	○	○	×	×	×	×	○
Toxic organics	●	●	●	×	○	○	×	●	●	●	●	○	×	○	○	×	●
Radioactive	×	×	×	×	×	×	×	×	●	●	●	×	×	×	×	×	×
Corrosive	×	×	×	●	×	×	×	×	●	×	●	×	×	×	×	×	×
Cyanide	○	○	●	×	○	○	×	×	●	×	○	×	×	×	×	×	○
Pesticide	●	●	○	×	●	○	×	●	●	○	●	●	×	●	○	×	○
Asbestos	×	×	×	×	×	×	×	×	●	×	●	×	×	×	×	×	×
Explosive	○	○	×	○	×	×	×	●	●	●	●	○	×	×	×	×	○

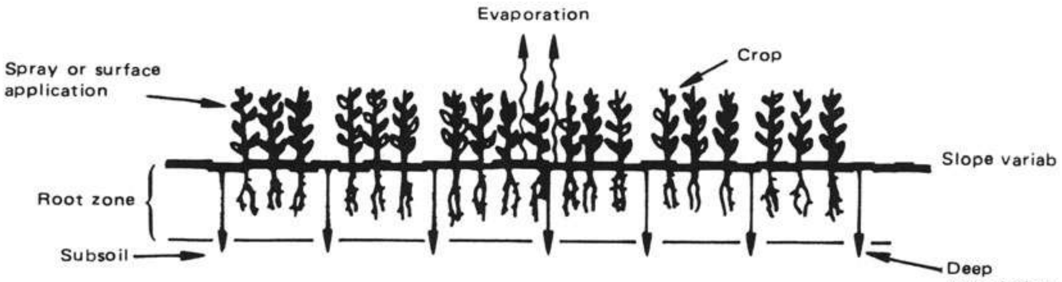
● Applicable ○ Potentially applicable × Not applicable

Source: EPA Office of Solid Waste and Emergency Response, 540/2-86/003(f), Sept. 1986. (*Courtesy EPA.*)

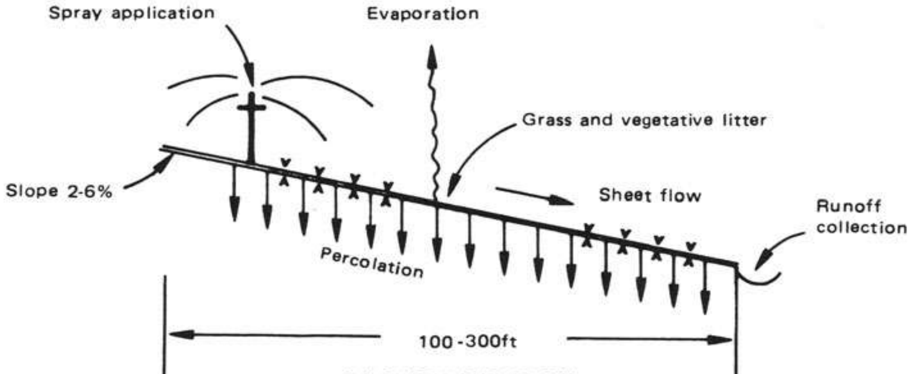
situations involving combinations of transition metals or heavy metals. The inhibitory effects also are enhanced by acidity.

The synergistic effects of such metals in combination with acidity can be understood from the chemistry of these metals. In the usual pH range of sewage influents (somewhat basic), heavy metals tend to be insolubilized by hydrolysis. They precipitate or adsorb on solids, and they interact with polyelectrolytes or various chemical species containing anionic functional groups. Acidity suppresses hydrolysis, keeping the metal ions in solution, and the hydrogen ions compete with the metal ions for adsorption on solids or anionic functional groups in solution.

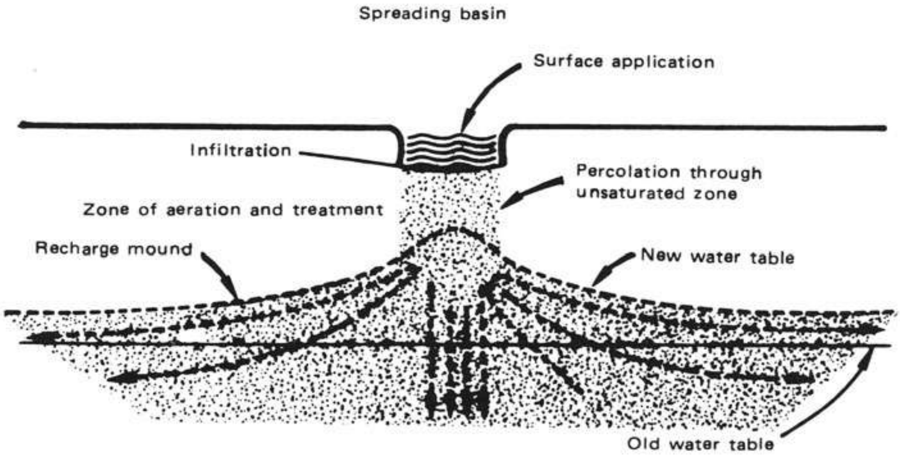
The synergism of cyanide or other complexing substances makes metal wastes more easily biodegradable. It is possible for a microorganism to ingest excessive levels of



(a) IRRIGATION



(b) OVERLAND FLOW



(c) INFILTRATION-PERCOLATION

Fig. 3.10. Three basic approaches to treatment of nonhazardous waste waters. (*Courtesy EPA.*)

TABLE 3.10 Distribution Information; Facilities and Treatment

Size (MGD)	*No. of Municipal Plants*	*Capacity in 10^3 gallons*	*Percent*
0.01– 0.1	4960	251	0.7
0.11– 1.0	7003	2671	7.2
1.01–10.0	2893	9372	25.6
10.01+	577	24,383	66.5
Totals	15,438	36,677	100.0
Treatment			
Less than 2nd	2122	5521	15.1
Secondary	8403	15,714	42.6
More than 2nd	3115	14,373	39.2
No discharge	1762	973	2.7
Unknown	46	88	0.2
Totals	15,438	36,677	100.0

*According to *EPA 1988 Needs Survey* data, wastewater treatment is primarily a local function with 15,438 systems.

complexed metal ion and then to be destroyed by assimilating the complexing substance that shields the microorganism from the metal ion. The subsequent release of an excessive level of the metal within the organism upsets its biological life processes.

Antagonism is the opposite of synergism; it is characterized as a decrease in the inhibitory effect of one substance caused by the presence of another. Antagonistic effects occur with combinations of metallic and anionic pollutants. Chelating agents such as EDTA (disodium salt of ethylenediamine tetraacetic acid) and HEDTA (disodium salt of hydroxyethylenediamine triacetic acid) exhibit antagonistic properties with metals. Chelating agents are used in culturing microorganisms to regulate the level of metals needed to grow bacterial cultures. Bacteria survive in culture solutions containing concentrations of these metals high in the inhibitory range when chelating agents are present.

There is ambiguity in the literature about the inhibitory effects of metals on sludge digestion. This ambiguity may be explained by the antagonistic effect of the sulfide normally present in a digester. Sulfide ion precipitates metals, removing them from solution and thus eliminating their inhibitory effect. Knowledge of this behavior has been used effectively in putting upset digesters back into operation. Additionally, other ions such as hydroxide, chromate, ferricyanide, phosphate, carbonate, and arsenate will tend to precipitate with metals, thereby reducing their inhibitory effects.

One must consider significant biological factors to understand the inhibitory effect of pollutants. In the activated-sludge process, a healthy biomass contains a broad distribution of microorganisms, including many species of bacteria and protozoa. In the absence of sufficient food, reproduction slows, and the microorganisms devour each other. Whenever the environment changes because of the introduction or the omission of a given pollutant, the opportunities for reproduction and growth of different species change.

The history of an activated-sludge biomass affects the way in which it will respond when a new pollutant is introduced; species that cannot tolerate the substance fail to reproduce and grow and tend to die off, whereas more tolerant species consume the food supply and grow and reproduce.

When a biomass becomes accustomed to the presence of a normally inhibitory concentration of a substance, it can be characterized as *acclimated* to that pollutant. But sludge digestion and nitrification do not have the same flexibility of adaptation to changing environmental conditions that other biological processes have. Both nitrification and sludge digestion are biological processes that rely on particular strains of bacteria. Sludge digestion proceeds in two steps, using two specific bacterial strains to achieve digestion. Nitrification is also limited to particular bacterial types. When adverse conditions are encountered in these processes, there is no possibility of another organism taking over for the affected strain of bacteria. Neither nitrification nor sludge digestion is readily acclimated to a new pollutant, and both may be easily upset.

A POTW may contain many thousands of inorganic compounds present as major or minor constituents. Most inorganic substances dissolved in wastewater are present in ionic form, and the number of parameters of interest can be reduced to a few cations and anions and nonionics.

The major cations consist of the ammonium ion and various metal ions. A few metal ions, chiefly sodium, calcium, and magnesium, are prevalent in wastewaters but are not inhibitory except at very high concentrations

SUPERFUND INNOVATIVE TECHNOLOGY EVALUATION (SITE) PROGRAM

The EPA initiated this program to promote and evaluate newly developed techniques that had not been fully demonstrated. The goal of this effort was to find new ways to remediate uncontrolled hazardous waste sites. The technologies accepted for field-scale evaluation represented a wide array of innovative methods, from thermal treatment and bioremediation to soil washing, solvent extraction, and in situ stripping.

The purpose of the SITE Program Applications Analysis Reports is to provide overall assessment of the performance, reliability, and costs of technologies in the Demonstration Program, relative to typical Superfund sites. Reports utilize all available data including the results of the SITE demonstration, the vendor's design and test data, and other laboratory and field applications of the technology. An analysis is given of the advantages, disadvantages, and limitations of the technology. Cost estimates are based on pilot-scale and commercial applications and available data. The report also examines factors, such as site and waste characteristics, that have a major impact on costs and performance. Highlights of Applications Analysis for some of the technologies demonstrated are provided below.

In the solidification/stabilization process developed by Hazcon, Inc., a patented binding agent is mixed with pozzolans in a mobile, truck-mounted blending unit.[2] The resulting concrete mass has been shown to enhance solidification of wastes containing high concentrations of organics and to immobilize heavy metals. TCLP leachate reduction for metals often is achieved in excess of 100 ppm. However, organic contaminants (volatiles and semivolatiles) were not immobilized based on SITE TCLP tests. Tests indicated that the permeabilities of the treated soil were very low, durability tests were good, and no loss of strength was observed after a weathering test. The resulting volume of the treated soil was approximately double that of the undisturbed waste feed. Although the equipment experienced some operating difficulties during the field demonstration, it is expected to operate efficiently with some design changes. The technology is economical, with costs estimated to be between $97 and $207 per ton.[3]

The Electric Infrared Incineration process, originally developed by Shirco Infrared Systems, Inc., is an electric infrared thermal processing system that uses silicone-carbide rods to bring organic wastes to combustion temperatures and then destroys remaiining organics in a gas-fired chamber.[4] The commercial unit is transportable and allows for discontinuous operation. Test results based on ten case studies, which include two full-scale applications at Superfund sites, show that the system can meet RCRA and TSCA incineration standards. Most of the metals in the feed concentrate in the ash. Available data suggest that this process is suitable for solid wastes containing particles from 5 microns to 2 inches in diameter, up to 50 percent moisture content, up to 5 wt. percent chlorine and sulfur, up to 1 wt. percent alkali metals, and heating values up to 10,000 Btu/lb.[5] Based on recent commercial operations, on-line reliability should range from 50 to 75 percent. Excluding waste excavation, feed preparation, profit, and ash disposal costs, costs may be as high as $800/ton. In 1990, three vendors owned and operated commercial, full-scale infrared thermal treatment systems.[6]

American Combustion Technologies developed the Pyretron Oxygen Air Burner system, which employs an oxygen-air-fuel burner for use with a rotary kiln incinerator.[7] The replacement of air with oxygen reduces the heat sink phenomenon of nitrogen in air and reduces the combustion gas volume, which in turn reduces particulate carryover and the load on air pollution control equipment. The primary advantage of the burner system is increased waste throughput, which, based primarily on SITE data, can be twice that of a conventional rotary kiln incinerator. The greatest capacity increases will occur for wastes with a low heating value. During the SITE demonstration, equipment operation was fairly reliable. Representative cost savings over conventional rotary kiln incineration are estimated to be about $30 per ton. Actual savings will depend on site-specific conditions.

Terra-Vac, Inc., developed the In-Situ Vacuum Extraction process, which removes volatile organic constituents (VOCs) from the unsaturated zone of soils through extraction wells.[8] The extracted gases and water proceed to a vapor–liquid separator and an emission control system. The process has been employed at over 60 sites. Four case studies, including three Superfund sites, have been documented.[9] The process represents a viable technology to fully remediate sites contaminated with volatile organics. Considerations for use include contaminent volatility, site-specific cleanup level, and soil properties. The process works well with most soil types. The air-filled porosity of a soil is an important criterion to indicate whether vacuum extraction will work. Soils with low permeability but with adequate air-filled porosity are amenable to treatment by this process. Soils with a high water content may require extensive dewatering before the process being to work. The in situ vacuum extraction process is relatively simple and operates reliably under all weather conditions. It typically costs around $50 per ton, with the cost strongly dependent on whether off-gas treatment is required and whether wastewater is generated by the process at a given site.

International Waste Technologies and Geo-Con, Inc. together demonstrated the In-Situ Soil Stabilization system on PCB-contaminated soil. The system employs a proprietary additive and a specific soil-mixing technology which precludes the need for soil excavation. A hollow-stem auger, offered by Geo-Con, injected the IWT chemicals into the soil and mixed it. Physical properties of the treated soil were generally satisfactory: unconfined compressive strength was high, permeability was low, and little degradation occurred as a result of wet/dry weathering tests. However, many freeze/thaw samples showed marked degradation. Microstructural analysis showed a dense, homogeneous, and low-porosity structure. Overall, the results also indicated a potential for long-term durability. The process appears to immobilize PCBs; however, results near detection limits did not allow a decisive determination. The Geo-Con equipment can operate in virtually all types of soils, although clays, oily sands, and cohesive soil may reduce the treatment rate and the depth. Also, small changes in ground level result from the addition of the reagents. The Geo-Con equipment operated satisfactorily during demonstration runs, and the process is economical. The cost of a commercial, four-auger operations was estimated at $110 per ton.[10]

C.F. Systems Corporation's organic solvent extraction technology was pilot-tested in September 1988 on polychlorinated biphenyl (PCB)–contaminated harbor sediments from the New Bedford, MA Superfund site. The technology extracts organics from contaminated soils based on the solubility of organics in a mixture of liquefied propane and butane.

Sediments were treated with C.F. Systems' trailor-mounted Pit Cleanup Unit (PCU) that has a design capacity of 1.5 gpm or 20 barrels/day. PCB extraction efficiencies of 90 percent were achieved for harbor sediments containing from 350 to 2570 ppm, resulting in clean sediments containing as little as 8 ppm. The cost of applying the technology to a full-scale cleanup effort could vary from $148 and $447 per tone including pre- and post-treatment costs, materials handling, and costs for specialized factors for a full-scale unit.[11]

HAZARDOUS WASTES

General Considerations

A waste is generally thought of as any solid, liquid, or contained gaseous material that is no longer useful to its owner and is to be recycled, disposed of, or stored for later disposal. As a routine result of doing business, a company can generate many wastes, which can, if not handled or disposed of properly, cause injury or death or pollute and damage land, air, and water. Such wastes are considered hazardous and are currently regulated by numerous federal and state public health and environmental safety laws.

There are two ways in which wastes may be brought into the hazardous waste regulatory system: (1) by listing and (2) by identification through their characteristics.

Listed Wastes. A waste is considered hazardous if it appears on any one of the four lists of hazardous wastes contained in RCRA (Resource Conservation and Recovery Act) regulations. The regulations list over 400 hazardous wastes, including discarded commercial products and wastes derived from manufacturing processes.

Some wastes are considered to be "acutely hazardous," having been determined by EPA to be so dangerous in small amounts that they are regulated in the same way as are large amounts of other hazardous wastes.

Characteristic Wastes. Some wastes are considered hazardous even though they do not appear on the EPA lists because they have one or more of the following characteristics:

- They are easily combustible or flammable. Examples of such "ignitable" wastes are paint wastes, certain degreasers, and other solvents.
- They dissolve metals or other materials, or burn the skin. Examples of such "corrosive" wastes include rust removers, waste acid or alkaline cleaning fluids, and waste battery acid.
- They are unstable or undergo rapid or violent chemical reaction with water or other materials. Examples of these "reactive" wastes are waste bleaches, other waste oxidizers, and cyanide plating wastes.
- They exhibit EP (extraction procedure) toxicity. Wastes are EP-toxic if an extract from the waste is tested and found to contain high concentrations of heavy metals (mercury, lead, cadmium) or specific pesticides that could be released into the groundwater.

Hazardous Waste Defined

Defining what constitutes a "hazardous waste" requires consideration of legal and scientific factors. The basic definitions used in this chapter are derived from (a) the Resource Conservation and Recovery Act (RCRA), as amended by the Hazardous and Solid Waste Amendments (HSWA), and (b) the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), as amended by the Superfund Amendments and Reauthorization Act (SARA). These definitions are given below.

Hazardous waste refers to "a solid waste, or combination of solid wastes, which because of its quantity, concentration, or physical, chemical, or infectious characteristics may ... pose a hazard to human health or the environment ..." [RCRA, Section 1004(5)].

Solid waste means "any garbage, refuse, sludge from a waste treatment plant, water supply treatment plant, or air pollution control facility and other discarded material, including solid, liquid, semisolid, or contained gaseous material resulting from industrial, commercial, mining, and agricultural operations and from community activities, but does not include solid or dissolved material in domestic sewage ..." [RCRA, Section 1004(27)].

Hazardous substance means "any substances designated in Section 311 (b) (2) (A) of the Federal Water Pollution Control Act ... any hazardous waste having the characteristics identified in Section 3001 of the Solid Waste Disposal Act ... any toxic pollutant listed under Section 307(a) of the Federal Water Pollution Control Act, any hazardous air pollutant listed under Section 112 of the Clean Air Act, and any imminently hazardous chemical substance or mixture ... listed in Section 7 of the Toxic Substances Control Act" [CERCLA, Section 101(14)].

Under RCRA, a waste is considered hazardous if it is reactive, ignitable, corrosive, or toxic, or if the waste is listed as a hazardous waste in Parts 261.33-33 of the *Code of Federal Regulations* (40CFR). Currently, there are about 400 listed wastes.

In addition to hazardous wastes defined under RCRA, there are "hazardous substances" defined by Superfund.* Superfund's definition of a hazardous substance is broad and grows out of the statutory definitions in the Clean Water Act (CWA), the Clean Air Act (CAA), the Toxic Substances Control Act (TSCA), and RCRA. Superfund considers a hazardous substance to be any air or water pollutant defined as hazardous in the CAA or the CWA, or as a hazardous waste defined in RCRA, that exceeds reportable quantity levels. Superfund encompasses numerous wastes and chemical substances:

- One hundred twenty-six "priority pollutants" and 65 "toxic pollutants" (CWA).
- Sixteen "hazardous air pollutants" and 7 chemicals identified as "criteria pollutants" (CAA).
- Ninety-five chemicals defined as toxic on the basis of production volume, exposure, and biological effects (TSCA).
- Substances identified or listed as hazardous waste under §3001 of RCRA.
- CERCLA Contract Lab List.

There also are other hazardous wastes or toxic substances that are not specifically included. Examples are:

- Wastes from nonpoint sources (e.g., storm or irrigation runoff).
- Wastes that are exempt from RCRA management, such as wastewaters treated in enclosed tanks and discharges subject to NPDES permits.
- Industrial wastewaters discharges to surface waters under NPDES permits or into underground injection systems.
- Wastes from agricultural application of pesticides.
- PCB wastes that are not contaminated with hazardous waste.

Although these wastes are not regulated under RCRA or Superfund, they are covered by other statutory authorities such as the Clean Air Act, the Clean Water Act, the Safe Drinking Water Act, and the Toxic Substances Control Act.

Hazardous Waste Management Overview

The following discussion examines hazardous waste issues from an integrated perspective suitable for addressing various environmental issues; namely:

1. It gives an overview of the hazardous waste system that can serve as a point of reference for continuing, more detailed work.
2. It serves as a starting point for the 20-year state capacity certification efforts required by the Superfund Amendments and Reauthorization Act of 1986 (SARA).
3. It provides an initial vehicle for discussion of possible impacts of various EPA regulatory efforts now under way regarding hazardous waste control.

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*"Superfund" became the common/popular name for CERCLA. Its goal was to clean up abandoned hazardous waste sites. When CERCLA expired, it was reauthorized and expanded under SARA.

The primary focus is on hazardous waste as defined in RCRA and by the Superfund program. However, the hazardous waste system does not exist in isolation. Before dealing with the specific subject of hazardous wastes, it is useful to look at several key elements of the overall waste system. Such an overview is provided in Fig. 3.11. The point of this diagram is to illustrate the relationships among such items as hazardous wastes, municipal and industrial wastewater, and nonhazardous solid wastes. It will be increasingly important to understand "where things go" in dealing with hazardous and solid wastes and wastewaters.

It is also important to note that this overview does not deal with every source or possible exposure route. For example, hazardous air emissions, pesticide applications, and many nonpoint waste sources are not

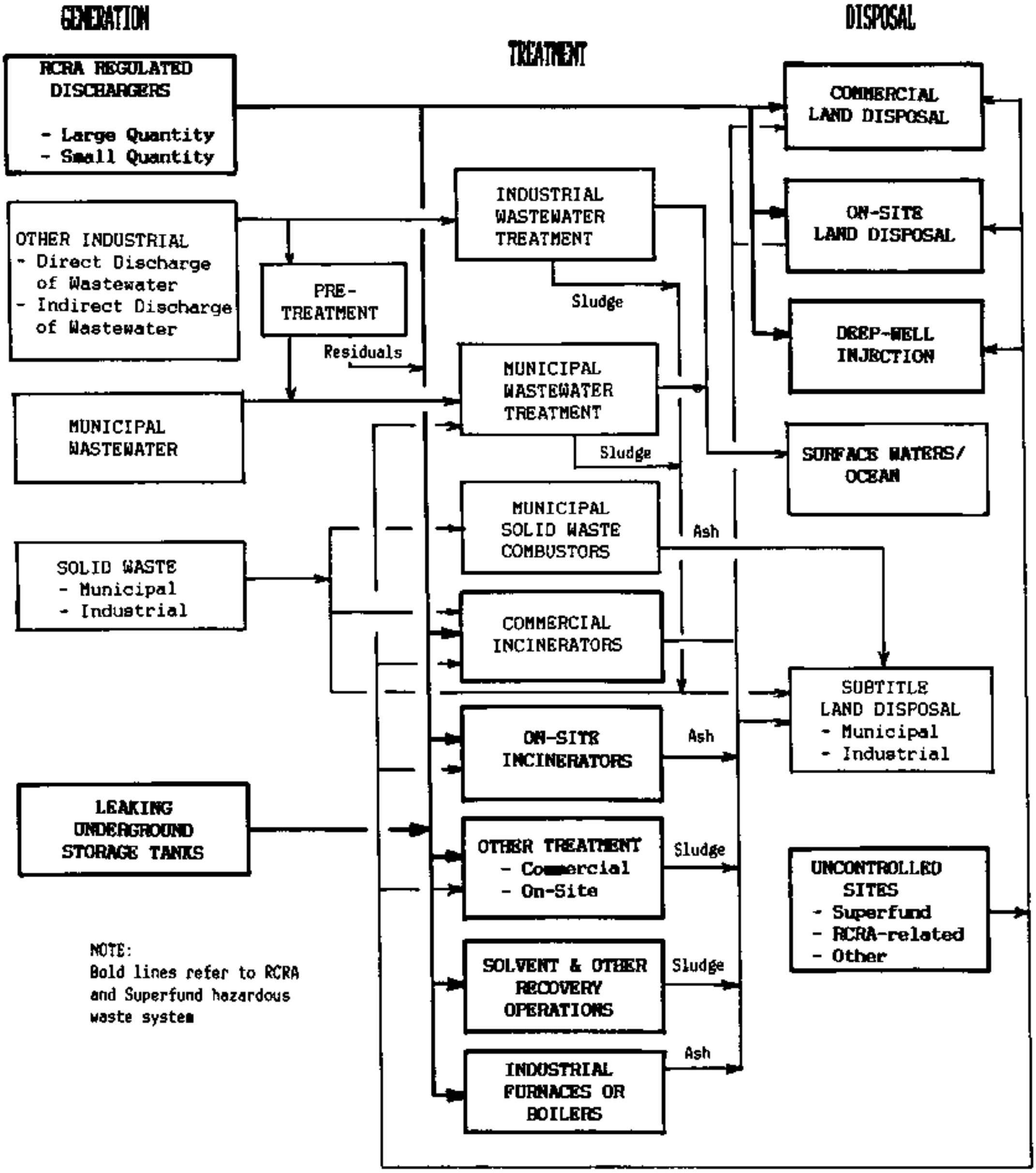

Fig. 3.11. Simplified water system chart. (*Courtesy EPA.*)

TABLE 3.11 Volumes of RCRA Hazardous Waste Treated and Disposed

	On-site at Private Firms (MMT)	*Off-site at Commercial Firms (MMT)*	*Estimated Total (MMT)*
Incineration	1.7	0.4	2.1
Other treatment	204.0	1.6	205.6
Solvent and other recovery	*	*	57.0
Furnaces and boilers	*	*	0.9
Land disposal	8.0	5.0	13.0
Deep-well injection	*	*	~25.0
Total			303.6**

Source: National Screening Survey, U.S. EPA, Office of Solid Waste (1986).
*Breakdown of on-site versus off-site waste volumes is not currently available.
**Total exceeds 275 MMT as deep-well injection, which is covered under the Safe Drinking Water Act, is included.
MMT = million metric wet tons per year.

included in Fig. 3.11. These sources and others such as waste discharges to surface waters through a National Pollutant Discharge Elimination System (NPDES) permit are not discussed in detail in this section.

RCRA and Superfund hazardous wastes from various industries are shown in Table 3.7, which includes the amount of waste, the number of facilities, and a general description. The hazardous wastes managed under RCRA totaled about 275 million metric tons in 1985.* The overwhelming portion of this quantity, well over 99 percent, was managed by "large quantity generators" (over 1000 kilograms per month).

A number of factors could affect the volumes of wastes generated in the future. Factors such as economics and population growth, regulatory decisions, and waste minimization efforts will influence the amount of waste produced. As industrial production increases, the volume of industrial wastes produced could also increase. However, efforts to recycle and reuse wastes, as well as programs to minimize the amount of waste generated, are likely to temper increases in waste volumes.

Hazardous Waste Treatment and Disposal

About 96 percent of all RCRA hazardous wastes are managed on-site by the companies that generate them. The remaining 4 percent goes to off-site commercial treatment and disposal facilities. Table 3.11 provides an overview of the kinds and quantities of hazardous wastes managed by 3000 facilities.

Several different kinds of treatment and disposal technologies are used in managing hazardous wastes. For example, there were over 175 on-site incinerators and 15 commercial incinerators in operation in the late 1980s. In addition to incineration, many other treatment methods are used, including biological wastewater treatment, solidification, steam stripping, and treatment impoundments. Most current systems consist of on-site impoundments handling relatively dilute wastewaters. There are about 430 operating land disposal facilities, approximately 60 of which are commercial facilities that accept a wide range of wastes. Although the majority of deep-well injection systems are located on-site, a few commercial facilities also use deep-well injection systems.

The Hazardous and Solid Waste Amendments of 1984 (HSWA) require that EPA ban the land disposal of over 400 chemicals and waste streams unless the waste streams are

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*Source: National screening survey conducted by the U.S. EPA Office of Solid Waste.

TABLE 3.12 Applicability of Treatment and Disposal Technologies to Categories of Hazardous Waste

	Organic Chemicals		*Hazardous Waste Category*			
	Biodegradable	*Nonbiodegradable*	*Metals Inorganics*	*Nonmetal Caistocs*	*Acid Treatment*	*Pesticides*
Treatment	Dissolved air flotation Aerated lagoons Trickling filter Waste stab. Activated slud. Anaerobic dig. Hydrolysis	Evaporation Distillation Oil/water sep. Reverse osm. Ultrafilt. Hydrolysis Carbon adsorp. sed.	Precip/floc/ sed. Reverse osm. Ultrafilt. Chem. oxid./ red.	Precip/floc/ sed. Filtration Evaporation Chem. oxid./ red. Hydrolysis	Chem. oxid./ red.	Hydrolysis
Solidification	Chemical fixation Encapsulation					
Disposal	Incineration Land disposal Evaporation pond					

Source: SCS Engineers, 11260 Roger Bacon Drive, Reston, VA 22090.

treated, or it can be demonstrated that there will be "no migration as long as the waste remains hazardous." The solvents and dioxin portion of the rules became effective in November 1986, and other rules were promulgated over succeeding years. The major impact of these rules was to significantly increase the degree of treatment required for hazardous wastes.

Treatment Technology, Costs, and Potential risks

This section concerns principally the data and information contained in several tables and figures. Table 3.12 shows the applicability of various treatment and disposal technologies to different hazardous waste categories and is self-explanatory. Table 3.13 contains information on the costs associated with common landfilling of hazardous wastes. It is interesting to note the wide spectrum of costs associated with this simple technology, depending on the hazardous nature of the waste and the form in which it is disposed. Stringent regulations apply to the design and use of hazardous waste landfills, and carefully engineered liners and caps are required. Figure 3.12 shows the

TABLE 3.13 Range of Costs Associated with Landfilling Hazardous Waste

Process	*Cost**
Shipping to out-of-state landfills	\$100–\$300/ton
Landfilling dioxin-contaminated soils	\$70/ton
Landfilling materials with PCB concentrations < 500 ppm	\$0.50–\$1.25/gal
Landfilling low-hazard waste	\$25–\$50/ton
Landfilling high-hazard waste	\$100–\$300/ton
Landfilling drums	\$140–\$230/ton
Landfilling bulk	\$33–\$90/ton

*Source: CDM–FPC Inc. Report to EPA 1989 Superfund (in 1988 dollars).

TABLE 3.14 Range of Costs Associated with Liquid Hazardous Waste Treatment

Activated sludge	\$100,000–\$390,000/mgd
Lagoons	\$80,000–3.4 million/mgd
Rotating biological contractors	\$0.9–\$29.6 million/mgd
Carbon treatment	\$14,132–\$643.000/mgd
Oil/water separator	\$12,720/ton
Deep well injection	\$29–\$120/ton \$0.12–\$0.50/gal
Solvent recovery	\$300–\$624/ton \$1.25–\$2.60/gal
Air stripping	\$607,000–\$7.3 million/mg

*From Federal Programs Corp.–CDM report to EPA 1989 Superfund (based on 1988 dollars).

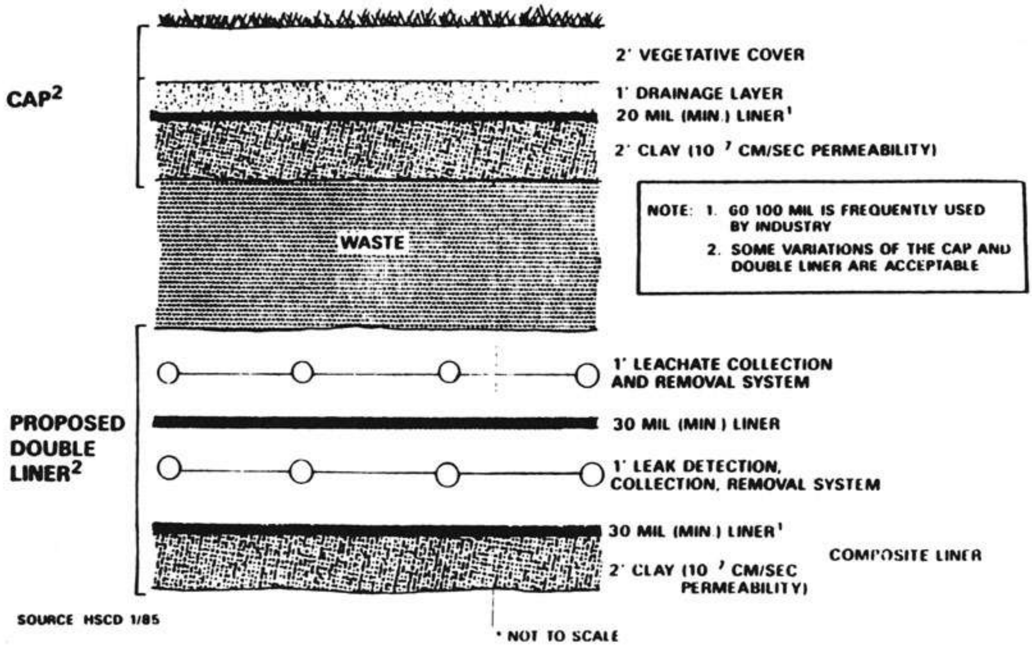

Fig. 3.12. RCRA cap and double liner. (*Land Disposal of Hazardous Waste: Proceedings of 11th Annual Research Symposium, July 1985; courtesy EPA.*)

TABLE 3.15 Range of Costs Associated with Hazardous Waste Cleanup. (In 1988 dollars.)

Surface sealing	\$1.32–\$16.88/sq yd
Grading	\$4,000–\$16,205/acre
Drainage ditches	\$1.27–\$6.04/linear foot
Revegetation	\$1.214–\$8,000/acre
Permeable treatment beds	\$14–\$267/sq ft
Deep well system	\$4,862–\$13,513/well
Extraction/injection well system	\$37.50/vertical foot
Extract wells/seepage basin	\$33,618–\$53,360/system
Excavation, transport and disposal	\$379–\$343/cu yd
Hydraulic dredging	\$1.25–\$3.54/cu yd
Mechanical dredging	\$1.37–\$0.49/cu yd
Drum handling	\$60–\$1,528/drum
Slurry wall construction	\$250,000–\$470,000 +/−50%

*From Federal Programs Corp.–CDM Report to EPA 1989 Superfund.

details of an RCRA-approved double liner placed over a suitable clay soil. Table 3.14 contains information on the costs associated with various treatment options for liquid hazardous wastes, and Table 3.15 shows the cost for hazardous waste cleanup. The latter table is particularly interesting in that it displays the wide range of technologies associated with cleanup operations.

It must be realized that there are potential environmental risks associated with all hazardous waste treatment/disposal alternatives. Some of these are listed in Table 3.16, which compares various technologies with potential impacts on health, surface water pollution, subsurface pollution, air emissions, and production of residual concentrates.

TABLE 3.16 Potential Environmental Risks Associated with Hazardous Waste Treatment/Disposal Alternatives

Technology	*Potential for Health Impacts*	*Potential for Surface Water Pollution*	*Potential for Subsurface Pollution*	*Potential for Air Emissions*	*Ash/Sludge/ Concentrate Production*
Precipitation/flocculation/ sedimentation	0	+	–	–	+
Filtration	0	+	–	–	+
Evaporation	0	0	–	+	+
Distillation	0	0	–	+	+
Flotation	0	+	–	0	+
Reverse osmosis	0	–	–	–	+
Ultrafiltration	0	–	–	–	+
Chemical oxidation/reduction	0	+	–	–	0
Hydrolysis	0	0	–	–	0
Aerated lagoon	+	+	+	+	–
Trickling filter	+	+	0	+	+
Waste stabilization pond	+	+	+	+	–
Anaerobic digestion	0	0	0	0	+
Activated sludge	0	+	0	0	+
Carbon adsorption	0	+	–	–	0
Incineration	+	–	–	+	+
Land disposal	+	+	+	+	–
Chemical fixation	–	–	0	–	–
Encapsulation	–	–	0	–	–
Evaporation pond	+	+	+	+	+

+ = Possible Impact. 0 = Variable. – = No possible Impact.
Source: SCS Engineers, 11260 Roger Bacon Drive, Reston, VA 22090.

RECYCLE–REUSE

Before proceeding with this discussion, it is necessary to define the terms recycle, multiple use, and reuse. Recycle as used here means using water over and over for the same application. An examplenwould be in the use of steam to drive a turbine where the condensate is returned to the boiler. Reuse or multiple use means using water more than once, but always for a different and successively dirtier application until it is no longer fit for use. The objective of all these methods of water use is to reduce water intake and the discharge of wastewater.

In the plant depicted in Fig. 3.13, the three major water uses are in processing, cooling, and steam generation. Assumed in constructing this hypothetical situation is the suitability of the process waste water for cooling functions, as well as the acceptability of cooling water blowdown for making boiler feed. The average gross water use is taken as 15 units. In the once-through system, the water intake is obviously the same as the gross water use, that is, 15 units. In the case of multiple use and reuse, although the gross water use remains the same, the intake and discharge requirements are less—how much less depending on the technology used.

In order to reduce wastewater discharge through reuse or recycle, it is necessary continually to remove waste materials that accumulate in the water. In practice, it is the accumulation of wastes or impurities that limits the extent to which reuse is feasible. Such factors as salinity, alkalinity, organic matter, and suspended solids must be controlled so that the process in which the water is used is not compromised. In the example being discussed, the boiler feed water is made acceptable by evaporation, the alkalinity is controlled by addition of chemicals, and organic and suspended solids are removed by traditional methods. If the ratio of gross water

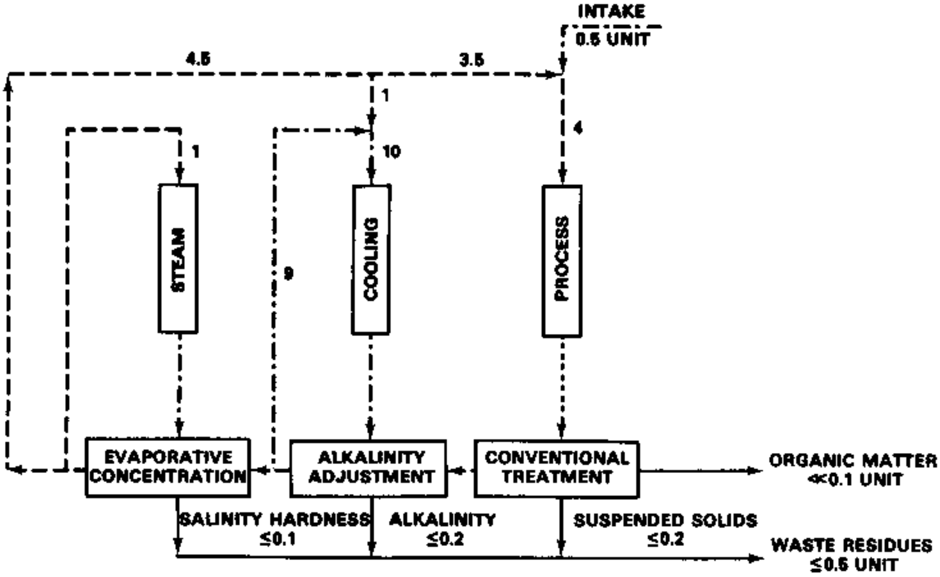

Fig. 3.13. Reuse-recycle industrial water system. (Lacy, W. J., "The Closed-Loop Cycle for Industrial Wastewater: The Future Pollution Solution," *Environ-ment International*, 2, 3–8 (1979)).

to water intake is an index of reuse, the once-through system would have a reuse ratio of 1.0, the multiple use system in the example would have a ratio of 1.5, and the reuse–recycle system would have a ratio of 15.0. If total reuse could be achieved—a practical impossibility because of losses from evaporation, leaks, etc.—the ratio would be infinite. It will always be necessary to provide some makeup water to the system.

INDUSTRIAL WATER USE

The total water intake by U.S. industries in 1983, according to a U.S. Department of Commerce survey, was more than 10 trillion gallons (U.S. Department of Commerce, 1986). This represented 96 percent of the total water use estimated for manufacturers. Those companies reporting water intake of 20 million gallons or more represent only 3 percent of the total manufacturing establishments, 32 percent of the total number of persons employed in manufacturing, and 46 percent of the value added by manufacturers.

Approximately 84 percent of the 10 trillion gallons of water used by manufacturing establishments in 1983 was accounted for by four major industry groups: SIC 28, Chemicals and Allied Products; SIC 33, Primary Metals; SIC 26, Paper and Allied Products; and SIC 29, Petroleum and Coal Products. Of the total water intake for manufacturing, 60 percent was used for cooling and condensing operations, such as steam for electric power generation, air conditioning, and other uses. Approximately 59 percent of the total water intake was from company surface water systems. Of the total 8.9 trillion gallons of water discharged, 45 percent was treated.

Approximately 75 percent of the water used in manufacturing industries was concentrated in six water resource regions: Great Lakes, South Atlantic–Gulf, Middle Atlantic, Ohio, Lower Mississippi, and Texas–Gulf.

Industrial Water Quality

Water use and needs in the manufacturing industries can be divided among three major functions: cooling; process use; and use in boiler feedwater for steam production. Table 3.17 shows water intake by industry, source, and kind, for all manufacturing and for selected industrial groups. These are the requirements for intake and consumption and

TABLE 3.17 Water Intake by Source and Kind for Industry Groups for 1983 (in billion gallons)

		Source								
			Public Water	Company				Kind		
SIC Code	*Industry*	*Total*	*System*	*Surface*	*Ground*	*Tidewater*	*Other*	*Fresh*	*Brackish**	*Salt***
	All manufacturing	10,039	1,311	5,927	1,234	1,199	369	8,522	739	777
20	Food & Kindred Products	648	219	129	232	37	31	568	62	18
26	Paper & Allied Products	1,900	257	1,212	350	62	18	1,766	115	19
28	Chemical & Allied Prod.	3,400	211	2,162	314	592	123	2,665	202	539
29	Petroleum & Coal Prod.	818	138	286	62	297	35	491	223	104
33	Primary Metals	2,363	109	1,821	149	[D]	[D]	2,211	[D]	[D]

(1) U.S. Department of Commerce, 1982 Census of Manufacturers Water Use, MC 82-5-6 (Mar. 1986).
(2) Standard Industrial Classification.
*1000 to 10,000 ppm dissolved salts.
**More than 100 ppm dissolved salts.
[D] Withheld to avoid disclosing data for individual companies; data are included in higher level totals.

TABLE 3.18 Industrial Water Quality in Use[a]

			Process and General Industrial Water						
			Iron and Steel			Pulp and Paper			Boiler Feedwater (150 psig)
Water Quality Charracteristics (ppm)	*Cooling Water (once thru) Fresh*	*Brackish*	*Quench and Gas Clean*	*DM Rinse*	*Chemical and Allied Products*	*Kraft Unbleached*	*Fine*	*Petro Refin.*	*Prior to Chem Cond.*
Temperature, °F	(b)	(b)	100	100	(b)	—	—	—	(b)
pH (units)	5–8.3	6–8.3	5–9	—	5–5.9	—	—	6–9	7–10
S.S.	5,000	2,500	100	0.1	10,000	100 (c)	10 (c)	5,000	10
D.S. (e)	1,000	35,000	(b)	0.1	2,500	500	200	3,600	700
Chloride	600	19,000	(b)	0.1	500	—	—	1,600	(b)
Sulfate	630	2,700	—	—	850	—	—	900	(b)
Silica	50	25	—	—	(b)	100	20	85	30
Iron	(b)	(b)	—	—	10	1	0.1	15	1
Hardness	850	6,260	(b)	0.1	1,000	200	100	900	360
Alkalinity	500	115	(b)	0.5	500	150	75	500	360
C.O.D.	75	75	—	—	(b)	—	—	1000	5
Oil	(f)	(f)	(b)	0.02	—	—	—	—	—
Color (units)	—	—	—	—	500	100	5	25	—
D.O.	some	some	some	some	(b)	—	—	—	2.5

Notes: (a) Reference: Based on EDA former water quality criteria reports; (b) accepted as received; (c) suspended solids; (d) as turbidity; (e) dissolved solids; (f) no floating oil.

reflect the extent of internal water reuse that occurs within the industry. Cooling water needs are largest, followed by process demands and boiler feed makeup. This is a fortunate situation, as the water-quality requirements are generally less critical for cooling than for process or boiler feed.

Table 3.18 summarizes water-quality characteristics of the various water functions for major industrial users. It shows that industry has a use for low-quality water and could use waters of various qualitites. It further shows that if one excludes the bacterial consideration, then the quality criteria parameters are less stringent than those for desirable potable water. These are important considerations in planning an industrial water management system, as they would allow the reuse of water in a countercurrent manner for successively dirtier applications. Combining reuse with a water recycle system can close an industrial water circuit to the point where there is essentially zero discharge of pollutants. Table 3.19 is a summary of the water discharged, treated and untreated, by point of discharge for various industrial groups.

TABLE 3.19 Summary of Water Use Statistics for Industry Groups and Industries: 1983

SIC Code	Industry group and industry	Establishments reporting water intake of 20 million gallons or more during 1982	Gross water used[1]					Water discharged		
			Total		Water intake					
			Quantity (billion gallons)	Percent of all manufacturing industries	Quantity (billion gallons)	Percent of all manufacturing industries	Water and reused (billion gallons)	Total (billion gallons)	Untreated (billion gallons)	Treated (billion gallons)
	All manufacturing industries[2]	10,262	33,835.2	100	10,038.9	100	23,796.3	8,913.7	4,889.8	4,023.9
20	Food and kindred products	2,656	1,406.2	4	647.7	6	758.6	552.0	355.8	196.1
26	Paper and allied products	600	7,435.8	22	1,899.3	19	5,536.5	1,768.1	479.0	1,289.1
28	Chemicals and allied products	1,315	9,630.1	28	3,400.7	34	6,229.4	2,979.8	1,996.3	983.6
29	Petroleum and coal products	260	6,177.3	18	818.4	8	5,358.9	699.3	323.4	375.9
33	Primary metal industries	776	5,885.2	17	2,362.5	24	3,522.8	2,112.0	1,227.9	884.1

*U.S. Department of Commerce, 1982 Census of Manufacturers Water Use, MC 82-5-6 (Mar. 1986).

Rather than discuss economics with typical costs based on the amount of water treated or on the specific processes employed, it may be simpler to look at the total water treated, amount of suspended solids, alkalinity, hardness, organic matter, and dissolved salts removed.

In poor-water-quality areas the total water recycle method may provide a minimum cost for pollution control, as these water supplies bring into a plant several of the same materials whose removal is required for use or discharge. The net effect is that more suspended solids, organic materials, and dissolved salts would be handled on a once-through basis than if only net increases due to internal (closed-loop) plant functions were to be treated.

In 1990, manufacturing plants spent over $6 billion for pollution abatement capital expenditures, according to the Bureau of the Census, U.S. Department of Commerce. Of this total, about $2.5 billion was spent for air pollution abatement, $2.6 billion for water pollution abatement, and $817 million for solid waste management. In addition, industrial firms spent about $17 billion for pollution abatement operating costs. A breakdown by different industry groups is given in Table 3.20. A graph showing expenditures for pollution abatement and control over the period from 1972 to 1989 is shown in Fig. 3.14.

Research and Development Needs

Much research and development is needed to achieve a realistic zero discharge of water pollutants for the wide variety of industrial

TABLE 3.20 Pollution Abatement Capital Expenditures and Operating Costs, by Form of Abatement and major Industry Group: 1990

(Value figures in millions of dollars)

		Pollution abatement capital expenditures (PAGE)				*Pollution abatement gross annual cost (GAC) including payment to government units*				*Standard error of estimate (percent)*	
SIC Code	*Industry*	*Total*	*Air*	*Water*	*Solid waste*	*Total*	*Air*	*Water*	*Solid waste*	*PAGE*	*GAC*
	All industries	6,029	2,562	2,650	817	17,104	5,027	6,414	5,663	2	2
20	Food	249	65	163	21	1,109	146	693	271	11	4
21	Tobacco	6	4	1	1	45	16	13	16	30	17
22	Textile	46	19	25	2	198	26	115	58	25	8
24	Lumber	105	58	10	37	259	86	37	136	25	12
25	Furniture	24	19	2	2	141	51	23	67	35	16
26	Paper	1,075	414	510	152	1,607	398	788	421	3	4
27	Printing	68	56	4	7	241	71	31	140	23	10
28	Chemicals	1,851	596	994	261	3,948	858	1,797	1,293	4	2
29	Petroleum	917	426	401	90	2,705	1,472	702	531	3	4
30	Rubber	94	69	11	14	428	97	113	218	15	10
31	Leather	8	1	7	1	49	7	26	16	25	25
32	Stone	128	94	20	14	498	248	93	157	10	5
33	Primary metals	499	279	167	54	2,054	944	565	545	4	3
34	Fabricated metals	171	53	61	57	814	114	344	356	9	8
35	Machinery	107	46	41	20	577	78	159	320	10	7
36	Electric	178	93	58	26	788	113	370	304	12	14
37	Transportation	395	207	143	46	1,232	247	373	612	10	4
38	Instruments	92	58	26	8	248	37	69	142	10	7
39	Miscellaneous	18	7	7	4	185	19	103	63	19	59

Note: Totals may not agree with detail because of independent rounding.
Source: Government Printing Office: 1992 – 311-899/40231

water problems. If the approach taken to zero discharge of pollutants is related to integrated supply and wastewater management, major areas for R and D can be identified, as shown in Fig. 3.15. The figure also shows various ways to reuse–recycle water and to manage sludges, and general areas where research and development may lead to a better way to reduce water pollution outside an industrial plant.

The major industrial water use and handling activities (i.e., cooling, process operations, water treatment, and steam production) should be viewed individually for opportunities to improve pollution control performance and reduce pollutants, as well as in an integrated fashion to conserve energy and avoid duplication in treatment. For example, in process operations improved housekeeping, revised operating procedures, and process changes in themselves can produce significant gains in reducing water management costs while improving pollution control. As most industrial water is used for cooling purposes, research and development efforts in cooling techniques, water quality limitations, corrosion control, and the effectiveness of the cooling process itself as a method of treating pollutants (other than heat) should be strongly pursued.

The challenge of achieving zero discharge of pollutants from the major water use generally is best left to the chemical engineering profession. The problems of the four large industrial water users are not sanitary in the classical sense but instead are chemical, or, more specifically, they involve chemical separation of pollutants in water to a desired level that will allow reuse or discharge.

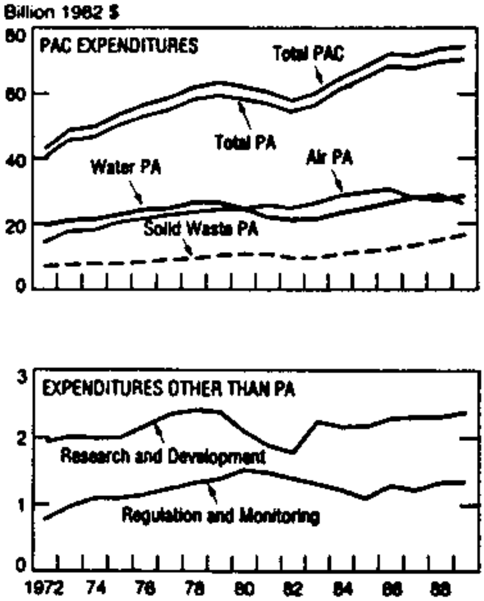

Fig. 3.14. Real expenditures for pollution abatement and control, 1972–89. (Rutledge, G. L. and Leonard, M. L., U.S. Department of Commerce, Bureau of Economic Analysis.) (Note: Pollution Abatement and Control (PAC) expenditures consist of expenditures for the direct abatement of pollution (PA), for regulation and monitoring, and for research and development.)

Another problem is that of optimizing and integrating water conditioning and treatment steps to achieve a minimum number of operations.

The system described here also includes consideration of environmental concerns other than water pollution control, namely, the use of wastewater for air and thermal pollution control functions and waste residue usage for heat and power production and/or water treatment (ash and sludges). However, even an ideal plant system will have a net discharge of some waste material. The system described in Fig. 3.14 includes excess ash from thermal power production and wastewater blowdown of high salinity, hardness, and toxicity. These wastes may be blended for some beneficial purpose, to ease proper handling, or for controlled assimilation by the environment in appropriate disposal sites. These concerns will have to be given consideration as industry proceeds to meet future environmental demands.

The industrial water management concept of closed-cycle operation to achieve zero discharge of pollutants appears to be a

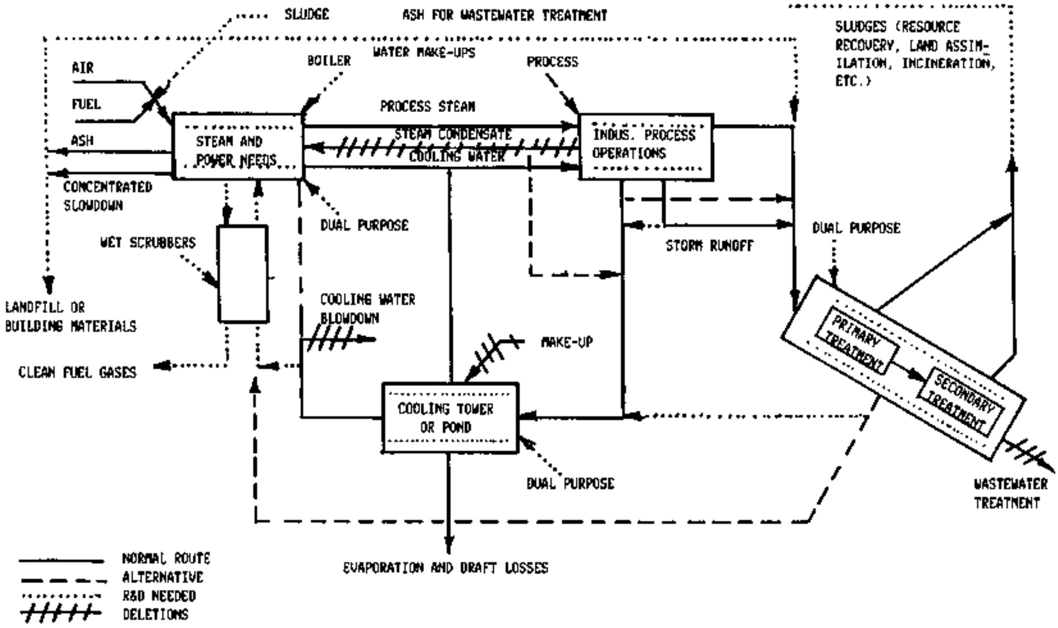

Fig. 3.15. Industrial wastewater management R and D needs.

historically, economically, and theoretically sound approach to industrial wastewater pollution control. Comments about excessive or unreasonable energy demands for industrial water pollution control may be more conjecture than fact. It is difficult to conceive how a water conservation approach to pollution control, properly developed, would not also be energy-conserving.

Future Demands

Closed-loop industrial wastewater and water systems are vitally necessary to maintain continuity in future industrial expansion. The huge water demands and high water usage growth rate of U.S. industry cannot continue to rely on traditional water supply sources. Even in water-abundant areas, intake water supplies for industrial use are fast becoming restricted.

Current and future environmental standards for wastewater discharges are expected to increase the pressure on industry to reduce both the pollution discharge loads and the magnitude of effluent volumes in order to minimize environmental impact. Industrial water-quality requirements for reuse are less demanding, as a general rule, than are municipal requirements. Accordingly, industrial water reuse should be technically and economically achievable earlier than comparable municipal water reuse systems.

Wastewater reuse is not only a resource conservation measure, but also a method of pollution control—a step in tune with future demands. Adequate research and development activity in this area is crucial to accelerating the implementation of extensive wastewater reuse systems and, eventually, the total closed-loop cycle. The latter, with no effluent discharge, would comply with any quality standards, now or in the future.

TERMINOLOGY

Many of the more common terms encountered in wastewater-treatment technology are given below to assist the reader in developing a vocabulary in this field and in understanding what follows.

Abatement. The method of reducing the degree of intensity of pollution; also the use of such a method.

Absorption. The penetration of a substance into or through another; for example, in air pollution control, absorption in a liquid from which it then can be extracted.

Acclimation. The physiological and behaviorial adjustments of an organism to changes in its immediate environment.

Acclimatization. The acclimation or adaptation of a particular species over several generations to a marked change in the environment.

Activated carbon. A highly adsorbent form of carbon, used to remove odors and toxic substances from gaseous emissions. In advanced waste treatment, activated carbon is used to remove dissolved organic matter from wastewater.

Activated sludge. Sludge that has been aerated and subject to bacterial action, used to remove organic matter from sewage.

Activated-sludge process. The process of using biologically active sewage sludge to hasten breakdown of organic matter in raw sewage during secondary waste treatment.

Acute toxicity. Any poisonous effect produced within a short period of time, usually from 24 to 96 hours, resulting in severe biological harm and often death.

Adaption. A change in structure or habit of an organism that allows it to exist in a changed environment.

Adsorption. The adhesion of a substance to the surface of a solid or a liquid. Adsorption often is used to extract pollutants by causing them to be attached to such adsorbents as activated carbon or silica gel. Hydrophobic, or water-repulsing, adsorbents are used to extract oil from waterways in oil spills.

Advanced waste treatment. Wastewater treatment beyond the secondary or biological stage that includes removal of nutrients such as phosphorus and nitrogen and removal of a high percentage of suspended solids. Advanced waste treatment, known as tertiary treatment, is the "polishing stage" of wastewater treatment and produces a high-quality effluent.

Aeration. The process of being supplied or impregnated with air. Aeration is used in wastewater treatment to foster biological and chemical purification.

Aerobic. Term referring to life or processes that can occur only in the presence of oxygen.

Agricultural pollution. The liquid and solid wastes from all types of framing, including runoff from pesticides, fertilizers, and feedlots; water and wind erosion and dust from plowing; animal manure; carcasses; and crop residues and debris. It has been estimated that agricultural pollution in the United States has amounted to more than 2½ billion tons per year.

Air stripping. A treatment system that removes, or "strips," volatile organic compounds (VOCs) from contaminated groundwater of surface water by forcing an airstream through the water and causing the compounds to evaporate.

Anaerobic. Term referring to life or processes that occur in the absence of oxygen.

Anti-degradation clause. A provision in air quality and water quality laws that prohibits deterioration of air or water quality in areas where the pollution levels are presently below those allowed.

Aquaculture project. A controlled discharge of pollutants to enhance growth or propagation of harvestable freshwater, estuarine, or marine plant or animal species.

Aquatic plants. Plants that grow in water, either floating on the surface, growing up from the bottom of the body of water, or growing under the surface of the water.

Aquifer. An underground bed or stratum of gravel or porous stone that contains water.

Assimilation. Conversion or incorporation of absorbed nutrients into protoplasm. The term also refers to the ability of a body of water to purify itself of organic pollution.

Autotrophic. Self-nourishing; term denoting those organisms capable of constructing organic matter from inorganic substances.

Bacteria. Single-celled microorganisms that lack chlorophyll. Some bacteria are capable of causing human, animal, or plant diseases; others are essential in pollution control because they break down organic matter on the air and in the water.

Baghouse. An air pollution abatement device used to trap particulates by filtering gas streams through large fabric bags, usually made of glass fibers.

Baling. A means of reducing the volume of solid waste by compaction.

Bar screen. In wastewater treatment, a screen that removes large floating and suspended solids.

Benthic region. The bottom of a body of water. This region supports the benthos, a type of life that not only lives upon but contributes to the character of the bottom.

Benthos. The plant and animal life whose habitat is the bottom of a sea, lake, or river.

Bioassay. The employment of living organisms to determine the biological effect of some substance, factor, or condition.

Biochemical oxygen demand (BOD). A measure of the amount of oxygen consumed in the biological processes that break down organic matter in water. Large amounts of organic waste use up large amounts of dissolved oxygen; thus the greater the degree of pollution is, the greater the BOD.

Biodegradable. Capable of decomposing quickly as a result of the action of microorganisms.

Biological oxidation. The process by which bacterial and other microorganisms feed on complex organic materials and decompose them. Self-purification of waterways, activated sludge, and trickling filter wastewater treatment processes depend on this principle. The process is also called biochemical oxidation.

BOD_5. The amount of dissolved oxygen consumed in 5 days by biological processes breaking down organic matter in an effluent. (See *Biochemical oxygen demand.*)

Boom. A floating device that is used to contain oil on a body of water.

Carcinogen. A substance that causes cancer.

Carbon adsorption. A treatment system where contaminants are removed from groundwater or surface water when the water is forced through tanks containing activated carbon, a specially treated material that attracts the contaminants.

Channelization. The straightening and deepening of streams to permit water to move faster, to reduce flooding, or to drain marshy acreage for farming. Channelization also reduces the organic waste assimilation capacity of the stream and may disturb fish breeding and destroy the stream's natural beauty.

Chemical oxygen demand (COD). A measure of the amount of oxygen required to oxidize organic and oxidizable inorganic compounds in water. The COD test, like the BOD test, is used to determine the degree of pollution in an effluent.

Chlorination. The application of chlorine to drinking water, sewage, or industrial waste for disinfection or oxidation of undesirable compounds.

Chlorinator. A device for adding a chlorine-containing gas or liquid to drinking water or wastewater.

Chlorine-contact chamber. A chamber in a waste treatment plant in which effluent is disinfected by chlorine before it is discharged to the receiving waters.

Clarification. In wastewater treatment, the removal of turbidity and suspended solids by settling, often aided by centrifugal action and chemically induced coagulation.

Clarifier. In wastewater treatment, a settling tank that mechanically removes settleable solids from wastes.

Coagulation. The clumping of particles in order to settle out impurities; often induced by chemicals such as lime or alum.

Coliform index. An index of the purity of water based on a count of its coliform bacteria.

Coliform organism. Any of a number of organisms common to the intestinal tract of humans and animals whose presence in wastewater is an indicator of pollution and of potentially dangerous bacterial contamination.

Combined sewers. A sewerage system that carries both sanitary sewage and stormwater runoff. During dry weather, combined sewers carry all wastewater to the treatment plant. During a storm, only part of the flow is intercepted, because of plant overloading; the remainder goes untreated to the receiving stream.

Combustion. Burning; technically, a rapid oxidation accompanied by the release of energy in the form of heat and light. It is one of three basic contributing factors causing air pollution; the others are attrition and vaporization.

Comminution. Mechanical shredding or pulverizing of waste; a process that converts waste into homogeneous and more manageable material. It is used in solid waste management and in the primary stage of wastewater treatment.

Comminutor. A device that grinds solids to make them easier to treat.

Compaction. Reducing the bulk of solid waste by rolling and tamping.

Compost. Relatively stable decomposed organic material.

Composting. A controlled process of degrading organic matter by microorganisms.

(1) Mechanical—a method in which the compost is continuously and mechanically mixed and aerated. (2) Ventilated cell—method where compost is mixed and aerated by being dropped through a vertical series of ventilated cells. (3) Windrow—an open-air method in which compostable material is placed in windrows, piles, or ventilated bins or pits and occasionally turned or mixed. The process may be anaerobic or aerobic.

Decomposition. Reduction of the net energy level and a change in chemical composition of organic matter brought about by the actions of aerobic or anaerobic microorganisms.

Diatomaceous earth (Diatomite). A fine siliceous material resembling chalk used in wastewater treatment plants to filter sewage effluent in order to remove solids. It also may be used as an inactive ingredient in pesticide formulations applied as dust or powder.

Digester. In a wastewater treatment plant, a closed tank that decreases the volume of solids and stabilized raw sludge by bacterial action.

Digestion. The biochemical decomposition of organic matter. Digestion of sewage sludge takes place in tanks where the sludge decomposes, resulting in partial gasification, liquefaction, and mineralization of pollutants.

Dissolved oxygen (DO). The oxygen dissolved in water or sewage. Adequately dissolved oxygen is necessary for the life of fish and other aquatic organisms and for the prevention of offensive odors. Low dissolved oxygen concentrations generally are due to the discharge of excessive organic solids having a high BOD, the result of inadequate waste treatment.

Dissolved solids. The total amount of dissolved material, organic and inorganic, contained in water or wastes. Excessive dissolved solids make water unpalatable for drinking and unsuitable for industrial uses.

Effluent. A discharge of pollutants into the environment, partially or completely treated or in its natural stage. Generally the term is used in regard to discharges into waters.

Electrodialysis. A process that uses electrical current and an arrangement of permeable membranes to separate soluble minerals from water. Often it is used to desalinize salt or brackish water.

Enrichment. The addition of nitrogen, phosphorus, and carbon compounds or other nutrients into a lake or other waterway in order to greatly increase the growth potential of algae and other aquatic plants. Most frequently, enrichment results from the inflow of sewage effluent or from agricultural runoff.

Environment. The sum of all external conditions and influences affecting the life, the development, and, ultimately, the survival of an organism.

Environmental impact statement. A document prepared by a federal agency on the environmental impact of its proposals for legislation and other major actions significantly affecting the quality of the human environment. Environmental impact statements are used as tools for decision making and are required by the National Environmental Policy Act.

Eutrophication. The normally slow aging process by which a lake evolves into a bog or marsh and ultimately assumes a completely terrestrial state and disappears. During eutrophication the lake becomes so rich in nutritive compounds, especially nitrogen and phosphorus, that algae and other microscopic plant life become superabundant, thereby "choking" the lake and eventually causing it to dry up. Eutrophication may be accelerated by many human activities.

Eutrophic lakes. Shallow lakes, weed-choked at the edges and very rich in nutrients. The water is characterized by large amounts of algae, low transparency, low dissolved oxygen, and high BOD.

Evaporation ponds. Shallow, artificial ponds where sewage sludge is pumped, permitted to dry, and either removed or buried by more sludge.

Fecal coliform bacteria. A group of organisms common to the intestinal tracts of humans and of animals. The presence of fecal coliform bacteria in water is an indicator of pollution and of potentially dangerous bacterial contamination.

Filtration. In wastewater treatment, the mechanical process that removes particulate matter by separating water from solid material, usually by passing it through sand.

Floc. A clump of solids formed in sewage by biological or chemical action.

Flocculation. In wastewater treatment, the process of separating suspended solids by chemical creation of clumps or flocs.

Fly ash. All solids, including ash, charred paper, cinders, dust, soot, or other partially incinerated matter, that are carried in a gas stream.

Groundwater. The supply of freshwater under the earth's surface in an aquifer or soil that forms a natural reservoir for human use.

Groundwater runoff. Groundwater that is discharged into a stream channel as spring or seepage water.

Habitat. The sum total of environmental conditions of a specific place that is occupied by an organism, a population, or a community.

Hazardous substance. Any material that poses a threat to public health and/or the environment. Typical hazardous substances are materials that are toxic, corrosive, ignitable, explosive, or chemically reactive.

Heavy metals. Metallic elements with high molecular weights, generally toxic in low concentration to plant and animal life. Such metals are often residual in the environment and exhibit biological accumulation. Examples include mercury, chromium, cadmium, arsenic, and lead.

Hydrology. Science dealing with the properties, movement, and effects of water on the earth's surface, in the soil and rocks below, and in the atmosphere.

Incineration. Burning of certain types of solid, liquid, or gaseous materials under controlled conditions to destroy hazardous waste.

Infiltration/inflow. Total quantity of water entering a sewer system. Infiltration means entry through such sources as defective pipes, pipe joints, connections, or manhole walls. Inflow signifies discharge into the sewer system through service connections from such sources as the area of foundation drainage, springs and swamps, storm waters, street wash waters, or sewers.

Interceptor sewers. Sewers used to collect the flows from main and trunk sewers and carry them to a central point for treatment and discharge. In a combined sewer system, where street runoff from rains is allowed to enter the system along with sewage, interceptor sewers allow some of the sewage to flow untreated directly into the receiving stream, to prevent the plant from being overloaded.

Lagoon. In wastewater treatment, a shallow pond—usually artificial—where sunlight, bacterial action, and oxygen interact to restore wastewater to a reasonable state of purity.

Leachate. Liquid that has percolated through solid waste or some other medium and has extracted dissolved or suspended materials from it.

Leaching. The process by which soluble materials in the soil, such as nutrients, pesticides, chemicals, or contaminants, are washed into a lower layer of soil or are dissolved and carried away by water.

Monitoring wells. Special wells drilled at specific locations on or off a hazardous wastes site where groundwater can be sampled at selected depths and studied to determine such things as the direction in which the groundwater flows and the types and amounts of contaminants present.

NTA. Nitrilotriacetic acid, a compound once used to replace phosphates in detergents.

Nutrients. Elements or compounds essential as raw materials for organism growth and development; for example, carbon, oxygen, nitrogen, and phosphorus.

Oligotrophic lakes. Deep lakes that have a low supply of nutrients and thus contain little organic matter. Such lakes are characterized by high water transparency and high dissolved oxygen.

Outfall. The mouth of a sewer, drain, or conduit where an effluent is discharged into the receiving waters.

Oxidant. Any oxygen-containing substance that reacts chemically in the air to produce new substances. Oxidants are the primary contributors to photochemical smog.

Oxidation. A chemical reaction in which oxygen unites or combines with other elements. Organic matter is oxidized by the action of aerobic bacteria; thus oxidation is used in wastewater treatment to break down organic wastes.

Oxidation pond. An artificial lake or pond in which organic wastes are destroyed by bacterial action. Often oxygen is bubbled through the pond to speed the process.

Packed tower. An air pollution control device in which polluted air is forced upward through a tower packed with crushed rock or wood chips while a liquid is sprayed downward on the packing material. The pollutants in the air stream either dissolve or react chemically with the liquid.

Pathogenic. Causing or capable of causing disease.

PCBs. Polychlorinated biphenyls, a group of organic compounds used in the manufacture of plastics. In the environment, PCBs exhibit many of the same characteristics as DDT and may, therefore, be confused with that pesticide. PCBs are highly toxic to aquatic life; they persist in the environment for long periods of time, and they are biologically accumulative.

Percolation. Downward flow or infiltration of water through the pores or spaces of a rock or soil.

Polyelectrolytes. Synthetic chemicals used to speed flocculation of solids in sewage.

Pretreatment. In wastewater treatment, any process used to reduce the pollution load before the wastewater is introduced into a main sewer system or before it is delivered to a treatment plant for substantial reduction of the pollution load.

Primary treatment. The first stage in wastewater treatment, in which substantially all floating of settleable solids are mechanically removed by screening and sedimentation.

Quality assurance/quality control (QA/QC). A system of procedures, checks, audits, and corrective actions used to ensure that field work and laboratory analysis during the investigation and cleanup of Superfund sites meet established standards.

Resource recovery. The process of obtaining or energy, particularly from solid wastes.

Removal action. An immediate action taken over the short term to address a release or threatened release of hazardous substances.

Resource Conservation and Recovery Act (RCRA). A federal law that established a regulatory system to track hazardous substances from the time of generation to disposal. The law requires safe and secure procedures to be used in treating, transporting, storing, and disposing of hazardous substances. RCRA is designed to prevent the creation of new, uncontrolled hazardous waste sites.

Response action. A CERCLA-authorized action at a Superfund site involving either a short-term removal action or a long-term remedial response that may include, but is not limited to, the following activities:

- Removing hazardous materials from a site to an EPA-approved licensed hazardous waste facility for treatment, containment, or destruction.
- Containing the waste safely on-site to eliminate further problems.
- Destroying or treating the waste on-site by using incineration or other technologies.
- Identifying and removing the source of groundwater contamination and halting further movement of the contaminants.

Runoff. The portion of rainfall, melted snow, or irrigation water that flows across the ground surface and eventually is returned to streams. Runoff can pick up pollutants from the air or the land and carry them to the receiving waters.

Sanitation. Control of all the factors in humans' physical environment that exercise or can exercise a deleterious effect on their physical development, health, and survival.

Sanitary landfilling. An engineered method of solid-waste disposal on land in a manner that protects the environment. Waste is spread in thin layers, compacted to the smallest practical volume, and covered with soil at the end of each working day.

Screening. The removal of relatively coarse floating and suspended solids by straining with racks or screens.

Scrubber. An air pollution control device that uses a liquid spray to remove pollutants from a gas stream by absorption or chemical reaction. Scrubbers also reduce the temperature of the emission.

Secondary treatment. Wastewater treatment, beyond the primary stage, in which bacteria consume the organic parts of the wastes. This biochemical action is accomplished by the use of trickling filters or the activated-sludge process. Effective secondary treatment removes virtually all floating and settleable solids. Customarily, disinfection by chlorination is the final stage of the secondary treatment process.

Sedimentation tanks. In wastewater treatment, tanks where the solids are allowed to settle or to float as scum. Scum is skimmed off, and settled solids are pumped to incinerators, digesters, filters, or other means of disposal.

Septic tank. An underground tank used for the deposition of domestic wastes. Bacteria in the wastes decompose the organic matter, and the sludge settles to the bottom. The effluent then flows through drains into the ground. Sludge is pumped out at regular intervals.

Settleable solids. Bits of debris and fine matter heavy enough to settle out of wastewater.

Settling tank. In wastewater treatment, a tank or basin in which settleable solids are removed by gravity.

Sewage. The total of organic waste and wastewater generated by residential and commercial establishments.

Sewerage. The entire system of sewage collection, treatment, and disposal. The term also applies to all the effluent carried by sewers, whether it be sanitary sewage, industrial wastes, or storm-water runoff.

Sludge. The construction of solids removed from sewage during wastewater treatment. Sludge disposal is handled by incineration, dumping, or burial.

Solid waste. Useless, unwanted, or discarded material with insufficient liquid content to be free-flowing. (Also see *Waste.*) (1) Agricultural—solid waste that results from the raising and slaughtering of animals, as well as the processing of animal products and orchard and field crops. (2) Commercial—waste generated by stores, offices, and other activities that do not actually turn out a product. (3) Industrial—waste that results from industrial processes and manufacturing. (4) Institutional—waste originating from educational, health care, and research facilities. (5) Municipal—residential and commercial solid waste generated within a community. (6) Pesticidal—the residue from the manufacturing, handling, or use of chemicals intended for killing plant and animal pests. (7) Residential—waste that normally originated in a residential environment; sometimes called domestic solid waste.

Sorption. A term including both adsorption and absorption. Sorption is basic to many processes used to remove gasous and particulate pollutants from an emission and to clean up oil spills.

Stabilization. The process of converting active organic matter in sewage sludge or solid wastes into inert, harmless material.

Suspended solids (SS). Small particles of solid pollutants in sewage that contribute to turbidity and that resist separation by conventional means. The examination of suspended solids and the BOD test constitute the main determinations for water quality performed at wastewater treatment facilities.

Synergism. The cooperative action of separate substances so that the total effect is greater than the sum of the effects of the substances acting independently.

Tertiary treatment. Wastewater treatment beyond the secondary or biological stage that includes removal of nutrients such as phosphorus and nitrogen and removal of a high percentage of suspended solids. Also known as advanced waste treatment, tertiary treatment produces a high-quality effluent.

Thermal pollution. Degradation of water quality by the introduction of a heated effluent. It is primarily a result of the discharge of cooling waters from industrial processes, particularly from electrical power generation. Even small deviations from normal water temperatures can affect aquatic life. Thermal pollution usually can be controlled by cooling towers.

Toxic pollutants. A combination of pollutants including disease-carrying agents that, after discharge and upon exposure, ingestion, inhalation, or assimilation into any organism can cause death or disease, mutations, deformities, or malfunctions in such organisms or their offspring.

Trace metals. Metals found in small quantities or traces, usually because of their insolubility.

Trickling filters. A device for the biological or secondary treatment of wastewater, consisting of a bed of rocks or stones that support bacterial growth. Sewage is trickled over the bed, enabling the bacteria to break down organic wastes.

Urban runoff. Storm water from city streets and gutters, which usually contains a great deal of litter and organic and bacterial wastes.

Waste. (Also see *Solid waste.*) (1) Bulky waste—items whose large size precludes or complicates their handling by normal collection, processing, or disposal methods. (2) Construction and demolition waste—building materials and rubble resulting from construction, remodeling, repair, or demolition operations. (3) Hazardous waste—waste that requires special handling to avoid illness or injury to persons or damage to property. (4) Special wastes—those wastes that require extraordinary management. (5) Wood pulp waste—wood or paper fiber residue resulting from a manufacturing process. (6) Yard waste—plant clippings, prunings, and other discarded material from yards and gardens (also known as yard rubbish).

Water pollution. The addition of sewage, industrial wastes, or other harmful or objectionable material to receiving water at concentrations or in sufficient quantities to result in measurable degradation of water quality.

Water quality criteria. The levels of pollutants that affect the suitability of water for a given use. Generally, water use classification includes: public water supply, recreation, propagation of fish and other aquatic life, agriculture, and industrial use.

Water quality standard. A plan for water quality management containing four major elements: (1) the uses (recreation, drinking water, fish and wildlife propagation, industrial, or agricultural) to be made of the water, (2) criteria to protect those uses, (3) implemented plans (for needed industrial–municipal waste treatment improvements), and (4) enforcement plans and an antidegradation statement to protect existing high-quality waters.

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4

Applied Statistical Methods and the Chemical Industry

Robert Kasprzyk* and Stephen Vardeman**

INTRODUCTION

The discipline of statistics is the study of effective methods of data collection, data summarization, and (data based, quantitative) inference making in a framework that explicitly recognizes the reality of nonnegligible variation in many real-world processes and measurements.

The ultimate goal of the field is to provide tools for extracting the maximum amount of useful information about a noisy physical process from a given investment of data collection and analysis resources. It is clear that such a goal is relevant to the practice of industrial chemistry. The primary purposes of this chapter are to indicate in concrete terms the nature of some existing methods of applied statistics that are particularly appropriate to industrial chemistry, and to provide an entry into the large and detailed statistical literature for those readers who find in the discussion here reasons to believe that statistical tools can help them be effective in their work. A secondary purpose is to indicate the relation of applied statistical methodology to modern quality philosophy in the chemical industry.

This chapter will begin with some simple ideas of modern descriptive statistics, including numerical and graphical data summarization tools, and the notions of fitting equations to data and using theoretical distributions. Next, some tools for routine industrial process monitoring and capability assessment, concentrating primarily on the notion of control charting, will be presented. This will be followed by a more extensive discussion of common statistical data collection strategies and data analysis methods for multi-factor experimental situations met in both laboratory and production environments. This section will touch on ideas of partitioning observed variation in a system response to various sources thought to influence the response, factorial and fractional factorial experimental designs, sequential experimental strategy, screening experiments, and response surface fitting and representation. Next come brief discussions of two types of special statistical tools associated specifically with chemical applications, namely, mixture techniques and

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nonlinear mechanistic model building. A short exposition of chemical industry implications of relationships between modern quality philosophy and the discipline of statistics follows. The chapter concludes with a reference section listing sources for further reading.

SIMPLE TOOLS OF DESCRIPTIVE STATISTICS

Statisticians have developed a variety of data summarization or description methods whose purpose is to make evident the main features of a data set. (Their use, of course, may be independent of whether or not the data collection process actually employed was in any sense a "good" one.) To illustrate some of the simplest of these methods, consider the data listed in Table 4.1. These numbers represent aluminum impurity contents (in ppm) of 26 bihourly samples of recycled PET plastic recovered at a Rutgers University recycling pilot plant.

A simple plot of aluminum content against time order, often called a *run chart*, is a natural place to begin looking for any story carried by a data set. Figure 4.1 shows such a plot for the data of Table 4.1, and in this case reveals only one potentially interesting feature of the data. That is, there is perhaps a weak hint of a downward trend in the aluminum contents that might well have been of interest

TABLE 4.1 Twenty-six Consecutive Aluminum Contents (ppm)[a]

291,	222,	125,	79,	145,	119,	244,	118,	182,	63,	30,	140,	101
102,	87,	183,	60,	191,	119,	511,	120,	172,	70,	30,	90,	115

[a]Based on data in Albin.[1]

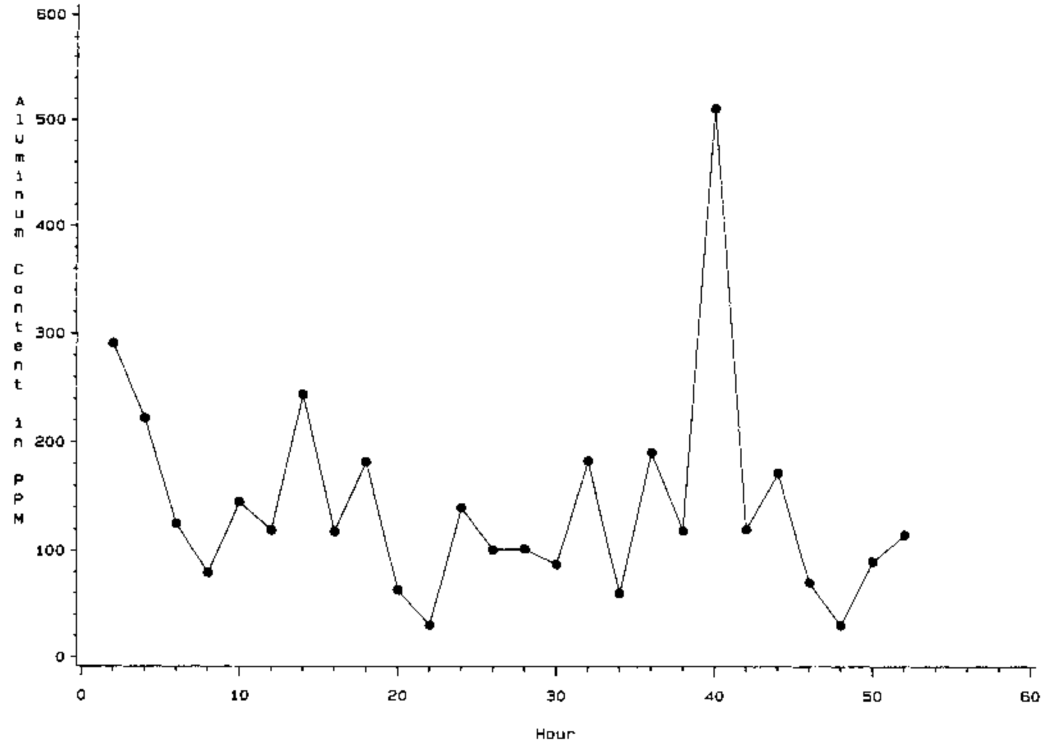

Fig. 4.1. A run chart for 26 consecutive aluminum contents.

to the original researchers. (If indeed the possible slight decline in aluminum contents is more than "random scatter," knowledge of its physical origin, whether in actual composition of recycled material or in the measurement process, presumably would have been helpful to the effective running of the recycling facility. We will save a discussion of tools for rationally deciding whether there is more than random scatter in a plot like Fig. 4.1 until the next section.)

The run chart is a simple, explicitly dynamic tool of descriptive statistics. In those cases where one decides that there is in fact little information in the time order corresponding to a data set, there are a variety of simple, essentially static, statistical tools that can be used in describing the pattern of variation in a data set. Figures 4.2 through 4.5 show graphical representations of the data of Table 4.1 in, respectively, *histogram*, *stem and leaf plot*, *dot plot*, and *box plot* forms.

The histogram/bar chart idea of Fig. 4.2 is likely familiar to most readers, being readily available, for example, through the use of commercial spreadsheet software. It shows how data are spread out or distributed across the range of values represented, tall bars indicating high frequency or density of data in the interval covered by the base of the bar. Figure 4.2 shows the measured aluminum contents to be somewhat asymmetrically distributed (statistical jargon is that the distribution is "skewed right"), with a "central" value perhaps somewhere in the vicinity of 120 ppm.

Histograms are commonly and effectively used for final data presentation, but as working data analysis tools they suffer from several limitations. In one direction, their

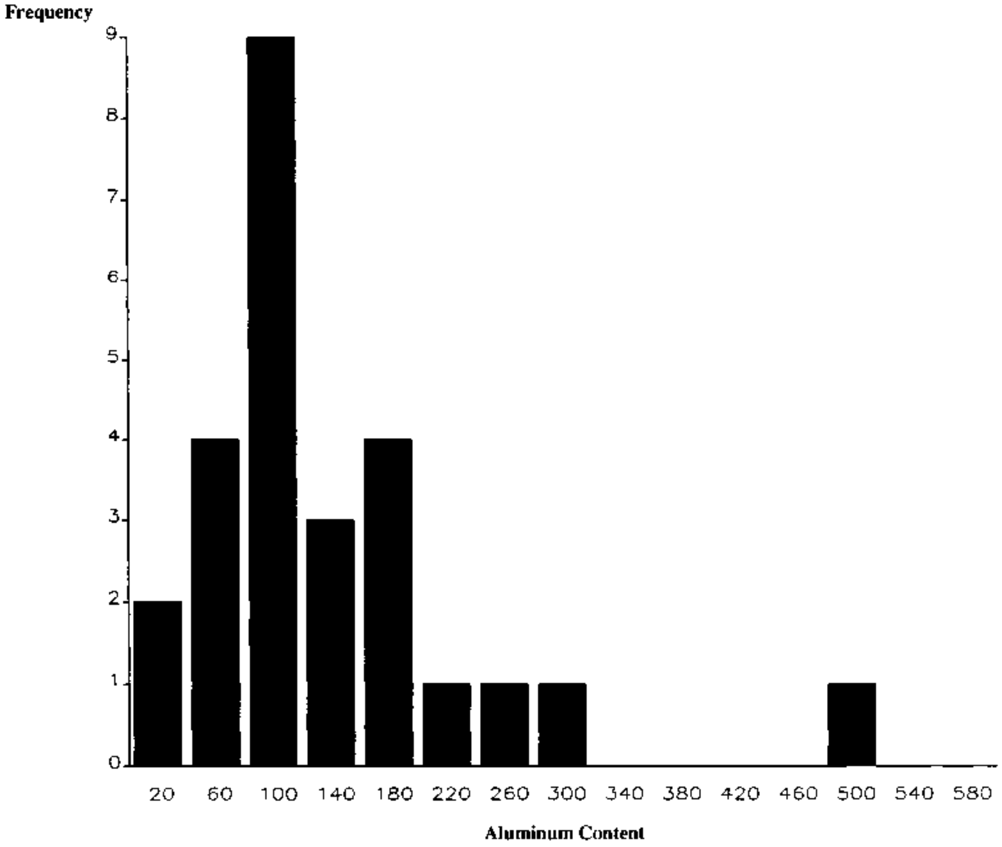

Fig. 4.2. A histogram for 26 aluminum contents.

appearance is fairly sensitive to the data grouping done to make them, and it is usually not possible to recover from a histogram the exact data values used to produce it, should one wish to try other groupings. In another direction, histograms are somewhat unwieldy, for example, not being particularly suitable to the comparison of, say, 10 or 12 data sets on a single page. The graphical devices of Figs. 4.3 through 4.5 are less common than the histogram, but address some of these shortcomings.

5	11
4	
4	
3	
3	
2	91
2	22,44
1	72,82,83,91
1	01,02,15,18,19,19,20,25,40,45
0	60,63,70,79,87,90
0	30,30

Fig. 4.3. A stem and leaf plot for 26 aluminum contents.

The stem and leaf diagram of Fig. 4.3 and the dot plot of Fig. 4.4 carry shape information about the distribution of aluminum contents in a manner very similar to the histogram of Fig. 4.2. But the stem and leaf and dot diagrams do so without losing the exact identities of the individual data points. The box plot of Fig. 4.5 represents the "middle half" of the data with a box divided at the 50th percentile (or in statistical jargon, the median) of the data, and then uses so-called whiskers to indicate how far the most extreme data points are from the middle half of the data.

Box plots preserve much of the shape information available from the other displays (e.g., portraying lack of symmetry through differing sizes of box "halves" and/or whisker lengths), but do so in a way that is conducive

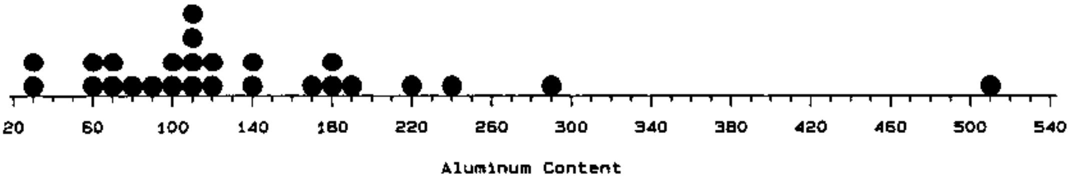

Fig. 4.4. A dot plot for 26 aluminum contents.

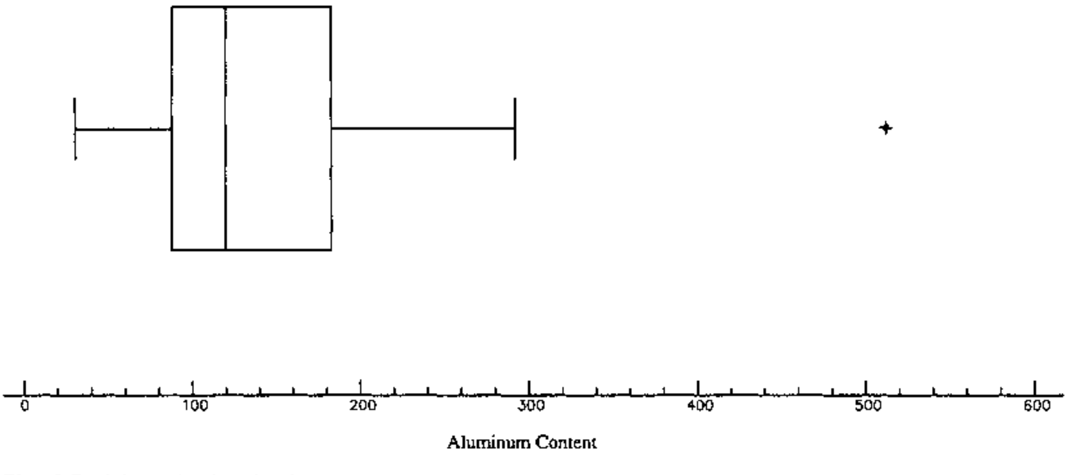

Fig. 4.5. A box plot for aluminum contents.

to simultaneous representation and comparison of many data sets on a single graphic, through the placement of box plots side by side. Figure 4.6 illustrates this point with a graphical comparison of three laboratory test methods to a standard.

A total of 75 samples of a stock solution known to contain 25 parts per million of an impurity were analyzed by a single lab team (25 of the samples being allocated to each of the three methods), and the box plots in Fig. 4.6 portray the measured impurity levels for the different methods. The figure shows quite effectively that Method A is neither precise nor accurate, Method B is quite precise but not accurate, and Method C is somewhat less precise than B but is accurate. This kind of knowledge can form the basis of an informed choice of method.

Figures 4.2 through 4.6 give only a hint of the spectrum of tools of statistical graphics that are potentially helpful in data analysis for industrial chemistry. For more details and much additional reading on the subject of modern statistical graphics, the reader is referred to the book by Chambers et al.[2] listed in the references section.

Complementary to graphical data summaries are *numerical summarizations*. For the simple case of data collected under a single set of conditions, the most commonly used measures deal with the location/center of the data set and the variability/spread of the data. The (*arithmetic*) *mean* and the *median* are the most popular measures of location, and the *variance* and its square root, the *standard deviation*, are the most widely used measures of internal variability in a data set.

For n data values $y_1, y_2, \ldots, y_n$ the median is

$$\tilde{y} = \text{the "middle" or } \frac{n+1}{2}\text{th ordered data value} \quad (4\text{-}1)$$

and the mean is

$$\bar{y} = \frac{1}{n}\sum_{i=1}^{n} y_i \quad (4\text{-}2)$$

The reader is invited to check that upon ordering the $n = 26$ values in Table 4.1, the 13th smallest value is 119 and the 14th smallest value is also 119, so that the only sensible interpretation of (4-1) for the aluminum content data is that

$$\tilde{y} = \text{the 13.5th ordered data value} = \frac{119 + 119}{2} = 119 \text{ ppm}$$

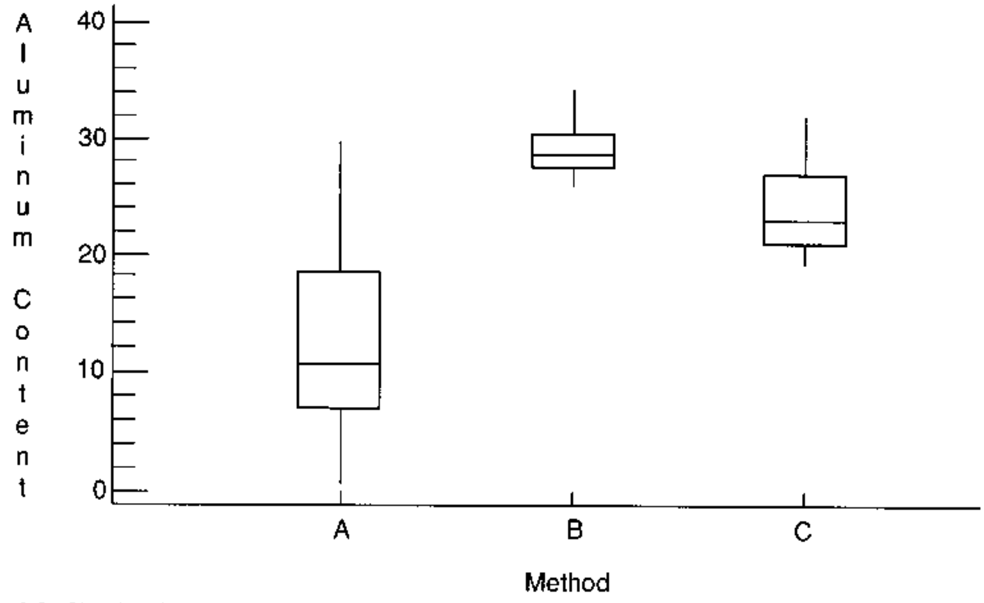

Fig. 4.6. Side-by-side box plots for three laboratory test methods.

On the other hand, from (4-2) the mean of the aluminum contents is

$$\bar{y} = \frac{1}{26}(291 + 222 + 125 + \cdots + 30 + 90 + 115)$$

$$\approx 142.7 \text{ ppm}$$

The media and mean are clearly different measures of location/center. The former is in the middle of the data in the sense that about half of the data are larger and about half are smaller. The latter is a kind of "center of mass," and for asymmetrical data sets like that of Table 4.1 is usually pulled from the median in the direction of any "skew" present, that is, is pulled in the direction of "extreme" values.

The variance of n data values $y_1, y_2, \ldots, y_n$ is essentially a mean squared deviation of the data points from their mean. In precise terms, the variance is

$$s^2 = \frac{1}{n-1}\sum_{i=1}^{n}(y_i - \bar{y})^2 \qquad (4\text{-}3)$$

and the so-called standard deviation is

$$s = \sqrt{s^2} = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(y_i - \bar{y})^2} \qquad (4\text{-}4)$$

For the example of the aluminum contents, it is elementary to verify that

$$s^2 \approx \frac{1}{26-1}((291 - 142.7)^2 + (222 - 142.7)^2 + \cdots + (115 - 142.7)^2)$$

$$\approx 9{,}644 \text{ (ppm)}^2$$

so that

$$s = \sqrt{s^2} \approx 98.2 \text{ ppm}$$

An appropriate interpretation of s is not completely obvious at this point, but it does turn out to measure spread of a data set, and to be extremely useful in drawing quantitative inferences from data. (In most, but not all, circumstances met in practice, the *range* or largest value in a data set minus the smallest value is on the order of four to six times s.) The variance and standard deviation are time-honored and fundamental quantifications of the variation present in a single group of measurements and, by implication, the data-generating process that produced them.

When data are collected under several different sets of conditions, and those conditions can be expressed in quantitative terms, effective data summarization often takes the form of *fitting an approximate equation* to the data. As the basis of a simple example of this, consider the data in Table 4.2. The variable x, hydrocarbon liquid hourly space velocity, specifies the conditions under which information on the response variable y, a measure of isobutylene conversion, was obtained in a study involving the direct hydration of olefins.

For purposes of economy of expression, and perhaps some cautious interpolation between values of x not included in the original data set, one might well like to fit a simple equation involving some parameters $\underset{\sim}{b}$, say,

$$y \approx f(x|\underset{\sim}{b}) \qquad (4\text{-}5)$$

to the data of Table 4.2. The simplest possible form for the function $f(x|\underset{\sim}{b})$ that accords with the "up then back down again" nature of the conversion values y in Table 4.2 is the quadratic form

$$f(x|\underset{\sim}{b}) = b_0 + b_1 x + b_2 x^2 \qquad (4\text{-}6)$$

and a convenient method of fitting such an equation (that is linear in the parameters b) is *the method of least squares*. That is, to fit a parabola through a plot of the seven (x, y) pairs specified in Table 4.2 it is convenient to choose b_0, b_1, and b_2 to minimize the sum of squared differences between the observed conversion values y and the corresponding fitted values of y on the parabola. In symbols, the least squares fitting of the approximate

TABLE 4.2 Seven Liquid Hourly Space Velocity/Mole % Conversion Data Pairs[a]

Liquid Hourly Space Velocity, x	*Mole % Isobutylene Conversion*, y
1	23.0, 24.5
2	28.0
4	30.9, 32.0, 33.6
6	20.0

[a] Based on a graph in Odioso *et al.*[3]

relationship specified by (4-5) and (4-6) to the data of Table 4.2 proceeds by minimization of

$$\sum_{i=1}^{7} (y_i - (b_0 + b_1 x_i + b_2 x_i^{\,2}))^2$$

over choices of the coefficients b. As it turns out, use of standard statistical "regression analysis" software shows that the fitting process for this example produces the approximate relationship

$$y \approx 13.64 + 11.41x - 1.72x^2$$

and Fig. 4.7 shows the fitted (summarizing) parabola sketched on the same set of axes used to plot the seven data points of Table 4.2.

The least squares fitting of approximate functional relationships to data with even multidimensional explanatory variable x typically goes under the (unfortunately obscure) name of *multiple regression* analysis, and is given an introductory treatment in most engineering statistics textbooks, including, for example, the ones by Devore[4] and Vardeman[5] listed in the references. A lucid and rather complete treatment of the subject can also be found in the book by Neter, Wasserman, and Kutner.[6]

A final notion that we wish to treat in this section on descriptive statistics is that of representing a distribution of responses and/or the mechanism that produced them (under a single set of physical conditions) by a *theoretical distribution*. That is, there are a number of convenient theoretical distributional shapes, and it is often possible to achieve great economy of expression and thought by seeing in a graphical representation such as Figs. 4.2 through 4.5 the possibility of henceforth describing the phenomenon portrayed via some one of those theoretical distributions. Here we will concentrate on only the most commonly used theoretical distribution, the so-called *Gaussian* or *normal* distribution.

Figure 4.8 is a graph of the function of x

$$g(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2} \right) \qquad (4\text{-}7)$$

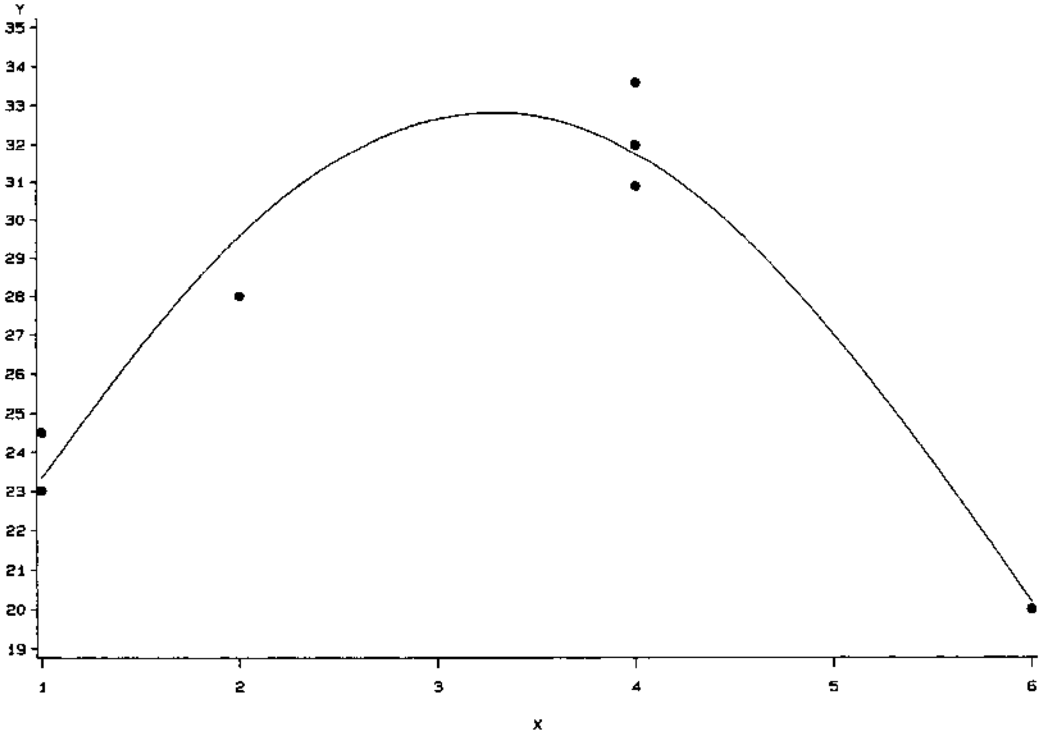

Fig. 4.7. A scatterplot of seven space velocity/mole % conversion data pairs and a fitted parabola.

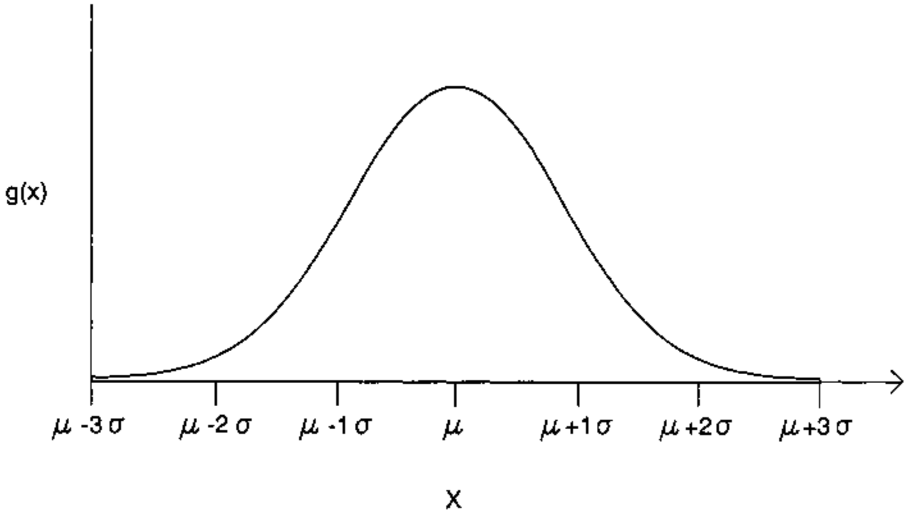

Fig. 4.8. The Gaussian probability density with mean μ and standard deviation σ.

where $g(x)$ specifies the archetypical "bell-shaped curve" centered at the number μ, with spread controlled by the number σ (and is in fact usually called the Gaussian probability density with mean μ and standard deviation σ).

Figure 4.8 can be thought of as a kind of idealized histogram. Just as fractional areas enclosed by particular bars of a histogram correspond to fractions of a data set with values in the intervals represented by those bars, areas under the curve specified in (4-7) above particular intervals might be thought of as corresponding to fractions of potential data points having values in those intervals. (It is possible to show that the total area under the curve represented in Fig. 4.8, namely, $\int_{-\infty}^{\infty} g(x)\,dx$, is 1.) Simple tabular methods presented in every elementary statistics book avoid the need to regularly use numerical integration in evaluating such areas. These methods can, for example, be used to show that roughly 68% of a Gaussian distribution lies between $\mu - \sigma$ and $\mu + \sigma$, roughly 95% lies between $\mu - 2\sigma$ and $\mu + 2\sigma$, and roughly 99.7% lies between $\mu - 3\sigma$ and $\mu + 3\sigma$. Part of the convenience provided when one can treat a data-generating process as approximately Gaussian is that, given only a theoretical mean μ and theoretical standard deviation σ, predictions of fractions of future data values likely to fall in intervals of interest are thus easy to obtain.

At this point let us return to the aluminum content data of Table 4.1. The skewed shape that is evident in all of Figs. 4.2 through 4.5 makes a Gaussian distribution inappropriate as a theoretical model for (raw) aluminum content of such PET samples. But as is often the case with right skewed data, considering the *logarithms* of the original measurement creates a scale where a normal distribution is more plausible as a representation of the phenomenon under study. Thus, Table 4.3 contains the natural logs of the values in Table 4.1, and the corresponding stem and leaf plot in Fig. 4.9 shows the transformed data to be much more symmetrically distributed than the original data. The possibility opened up by this kind of transformation idea is one of

TABLE 4.3 Twenty-six Logarithms of Aluminum Contents

5.67,	5.40,	4.83,	4.37,	4.98,	4.78,	5.50,	4.77,	5.20,	4.14,	3.40,	4.94,	4.62
4.62,	4.47,	5.21,	4.09,	5.25,	4.78,	6.24,	4.79,	5.15,	4.25,	3.40,	4.50,	4.74

6 | .24
5 | .50,.67
5 | .15,.20,.21,.25,.40
4 | .50,.62,.62,.74,.77,.78,.79,.79,.83,.94,.98
4 | .09,.14,.25,.37,.47
3 |
3 | .40,.40

Fig. 4.9. A stem and leaf plot for the logarithms of 26 aluminum contents.

using statistical methods based on the normal distribution to reach conclusions about ln*y* and then simply exponentiating to derive conclusions about the original response *y* itself. The applicability of statistical methods developed for normal distributions is thereby significantly broadened.

In addition to providing convenient conceptual summarizations of the nature of response distributions, theoretical distributions such as the normal distribution form the mathematical underpinnings of methods of formal quantitative *statistical inference*. It is outside our purposes in this chapter to provide a complete introduction to such methods, but thorough and readable accounts are available in engineering statistics books such as those of Devore[4] and Vardeman.[5] Here, we will simply say that, working with a Gaussian description of a response, it is possible to quantify in various ways how much information is carried by data sets of various sizes. For instance, if a normal distribution describes a response variable y, then in a certain well-defined sense, based on $n = 26$ observations producing a mean $\bar{y}$ and a standard deviation s, the interval with end points

$$\bar{y} - 2.060s\sqrt{1 + \frac{1}{26}}$$

and (4-8)

$$\bar{y} + 2.060s\sqrt{1 + \frac{1}{26}}$$

has a 95 percent chance of predicting the value of an additional observation. For instance, applying formula (4-8) to the log values in Table 4.3, the conclusion is that the interval from 3.45 ln(ppm) to 6.10 ln(ppm) has in some sense a 95 percent chance of bracketing an additional log aluminum content produced (under the physical conditions of the original study) at the recycling plant. Exponentiating, the corresponding statement about raw aluminum content is that the interval from 31 ppm to 446 ppm has in some sense a 95 percent chance of bracketing an additional aluminum content. Methods of statistical inference like that represented in (4-8) are called *prediction interval* methods. The book by Hahn and Meeker[7] provides a thorough discussion of such methods, based not only on the Gaussian distribution but on other theoretical distributional shapes as well.

TOOLS OF ROUTINE INDUSTRIAL PROCESS MONITORING AND CAPABILITY ASSESSMENT

Probably the two most basic generic industrial problems commonly approached using statistical methods are those of (1) monitoring and maintaining the stability/consistency of a process and (2) assessing the capability of a stable process. This section provides a brief introduction to the use of tools of "control" charting in these enterprises.

Working at Bell Labs during the 1920s and 1930s, Walter Shewhart developed the notion of routinely plotting data from an industrial process in a form that allows one to separate observed variability in a response into two kinds of variation. The first is that variation which appears to be inherent, unavoidable, short-term, baseline, and characteristic of the process (at least as currently configured). This variation Shewhart called *random* or *common cause variation*. The second kind of variability is that variation which appears to be avoidable, long-term, and/or due to sources outside of those seen as legitimately impacting process behavior. This variation he called *assignable* or *special cause variation*.

Shewhart reasoned that by plotting summary statistics from periodically collected data sets against time order of collection, one would be able to see interpretable trends or other evidence of assignable variation on the plots, and could intervene to eliminate the physical causes of that variation. The intention was thereby to make process output stable or consistent to within the inherent limits of process precision. As a means of differentiating plotted values that should signal the need for intervention from those that carry no special message of process distress, he suggested drawing so-called control limits on the plots. (The word "control" is something of a misnomer, at least as compared to common modern engineering usage of the word in referring to the active, moment-by-moment steering or regulation of processes. The nonstandard and more passive terminology "monitoring limits" would actually be far more descriptive of the purpose of Shewhart's limits.) These limits were to separate plausible values of the plotted statistic from implausible values when in fact the process was operating optimally, subject only to causes of variation that were part of standard conditions.

By far the most famous implementations of Shewhart's basic logic come where the plotted statistic is either the mean, the range, or, less frequently, the standard deviation. Such charts are commonly known by the names *x-bar charts*, *R charts*, and *s charts*, respectively. As a basis of discussion of Shewhart charts, consider the data given in Table 4.4. These values represent melt index measurements of specimens of extrusion grade polyethylene, taken four per shift in a plastics plant.

TABLE 4.4 Measured Melt Indices for Ten Groups of Four Specimens[a]

Shift	*Melt Index*	$\bar{y}$	R	s
1	218, 224, 220, 231	223.25	13	5.74
2	228, 236, 247, 234	236.25	19	7.93
3	280, 228, 228, 221	239.25	59	27.37
4	210, 249, 241, 246	236.50	39	17.97
5	243, 240, 230, 230	235.75	13	6.75
6	225, 250, 258, 244	244.25	33	14.06
7	240, 238, 240, 243	240.25	5	2.06
8	244, 248, 265, 234	247.75	31	12.92
9	238, 233, 252, 243	241.50	19	8.10
10	228, 238, 220, 230	229.00	18	7.39

[a] Based on data from page 207 of Wadsworth, Stephens, and Godfrey.[8]

Figure 4.10 shows plots of the individual melt indices, means, ranges, and standard deviations from Table 4.4 against shift number. The last three of these are the beginnings of so-called Shewhart $\bar{x}$, R, and s control charts.

What remain to be added to the plots in Fig. 4.10 are appropriate control limits. In order to indicate the kind of thinking that stands behind control limits for Shewhart charts, let us concentrate on the issue of limits for the plot of means. The fact is that mathematical theory suggests how the behavior of *means* $\bar{y}$ ought to be related to the distribution of *individual* melt indices y, provided the data-generating process is stable, that is, subject only to random causes. If individual responses y can be described as normal with some mean μ and standard deviation σ, mathematical theory suggests that averages of n such values will behave as if a different normal distribution were generating them, one with a mean $\mu_{\bar{y}}$ that is numerically equal to μ and with a standard deviation $\sigma_{\bar{y}}$ that is numerically equal to $\sigma/\sqrt{n}$. Figure 4.11 illustrates this theoretical relationship between the behavior of individuals and the behavior of means.

The relevance of Fig. 4.11 to the problem of setting control chart limits on means is that if one is furnished with a description of the typical pattern of variation in y, sensible exceptations for variation in $\bar{y}$ follow from simple normal distribution calculations. So Shewhart reasoned that since about 99.7 percent (most) of a Gaussian distribution is within 3 standard deviations of the center of the distribution, means found to be farther than 3 theoretical standard deviations (of $\bar{y}$) from the theoretical mean (or $\bar{y}$) could be safely attributed to other than chance causes. Hence, furnished with standard values for μ and σ (describing individual observations), sensible control limits for $\bar{y}$ become

$$\text{Upper Control Limit for } \bar{y} = \mu_{\bar{y}} + 3\sigma_{\bar{y}}$$

$$= \mu + 3\frac{\sigma}{\sqrt{n}}$$

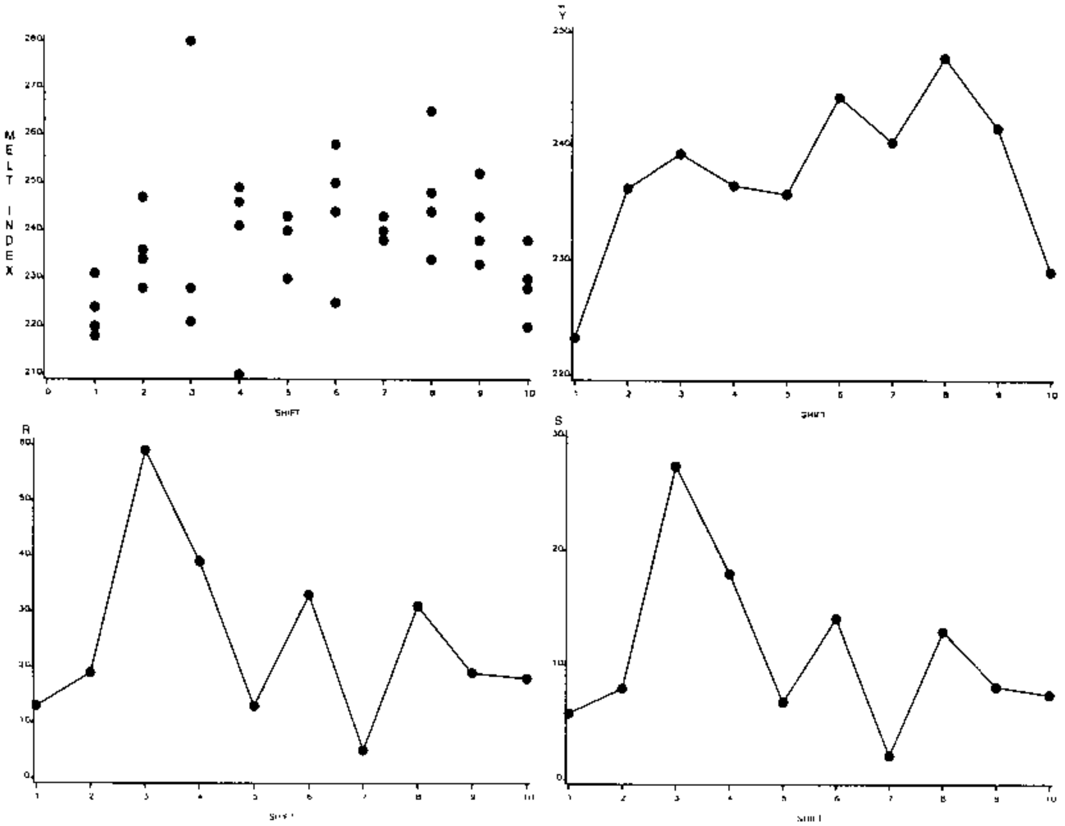

Fig. 4.10. Plots of melt index, $\bar{y}$, R, and s against shift number.

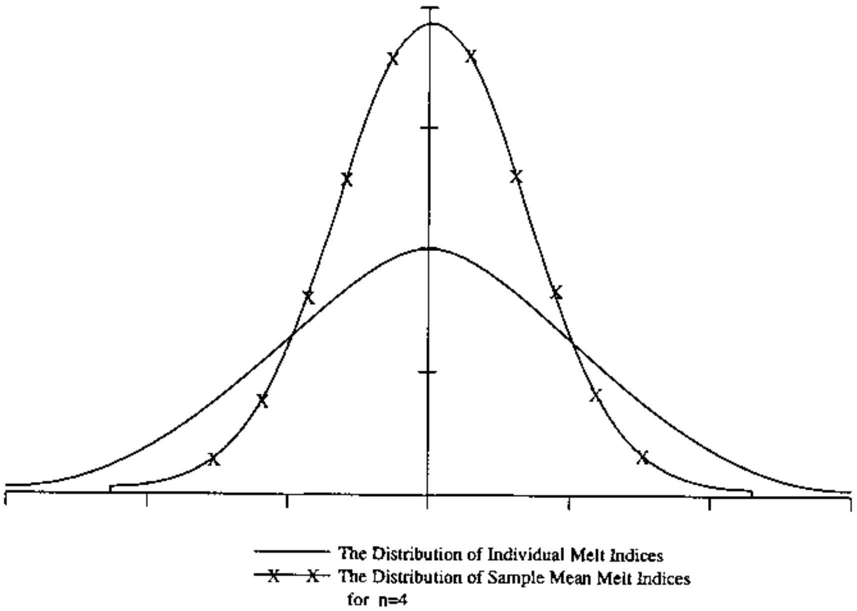

Fig. 4.11. The distributions of individuals, y, and sample means, $\bar{y}$.

and

$$\text{Lower Control Limit for } \bar{y} = \mu_{\bar{y}} - 3\sigma_{\bar{y}}$$

$$= \mu - 3\frac{\sigma}{\sqrt{n}} \quad (4\text{-}9)$$

Returning to the context of our example represented by the data of Table 4.4, Wadsworth et al.[8] state that the target value for melt index in the original application was in fact 235. So if standard process behavior is "on target" behavior, the value $\mu = 235$ seems appropriate for use in (4-9). No parallel value for σ was provided by the authors. Common practice in such situations is to use the data in hand (the data of Table 4.4) to produce a plausible value for σ to use in (4-9). There are many possible ways to produce such a value, but to understand the general logic behind the standard ones, it is important to understand what σ is supposed to measure. The variable σ is intended as a theoretical measure of baseline, short-term, common cause variation. As such, the safest way to try to approximate it is to somehow use only measures of variation *within* the groups of four values in Table 4.4 *not* influenced by variation *between* groups. (Measures of variation derived from considering all the data simultaneously, e.g., would reflect variation between shifts as well as the shorter-term variation within shifts.) In fact, the most commonly used ways of obtaining from the data in hand a value of σ for use in (4-9) are based on the averages of the (within-group) ranges or standard deviations. For example, the 10 values of R given in Table 4.4 have a mean

$$\bar{R} = \frac{1}{10}(13 + 19 + 59 + \cdots + 19 + 18) = 24.9$$

and some standard mathematical theory suggests that because the basic group size here is $n = 4$, an appropriate multiple of $\bar{R}$ for use in estimating σ is

$$\frac{\bar{R}}{2.059} \approx 12.1 \qquad (4\text{-}10)$$

(The divisor above is a tabled factor commonly called d_2, which increases with n.)

Finally, substituting 235 for μ and 12.1 for σ in (4-9) produces numerical control limits for $\bar{y}$:

$$\text{LCL} = 235 - 3\frac{(12.1)}{\sqrt{4}} = 216.9$$

and

$$\text{UCL} = 235 + 3\frac{(12.1)}{\sqrt{4}} = 253.1$$

Comparison of the $\bar{y}$ values in Table 4.4 to these limits reveals no "out of control" means, that is, no evidence in the means of assignable process variation. Figures 4.12 and 4.13 show control charts for all of $\bar{y}$, R, and s, where control limits for the last two quantities have been derived using standard calculations not shown here.

The R and s charts in Figs. 4.12 and 4.13 are related representations (only one is typically made in practice) of the shift-to-shift behavior of melt index *consistency*. It is seen that on both charts, the shift #3 point plots above the upper control limit. The strong suggestion thus is that melt index consistency was detectably worse on that shift than on the others, so that from this point of view the process was in fact *not stable* over the time period represented in Table 4.4. In practice, physical investigation and hopefully correction of the origin of the instability typically would follow, as well as some reconsideration of our earlier assessment of 12.1 as a plausible figure to represent the inherent short-term variability of melt index. (If shift #3 could be treated as a special case, explainable as an unfortunate but correctable situation that was not expected to reoccur, there might be reason to revise $\bar{R}$ downward by deletion of shift #3 from the calculation, and thereby to reduce one's view of the size of baseline process variability. Notice that, in general, such a downward revision of $\bar{R}$ might well also have the effect of causing one to need to rethink his or her assessment of the constancy of the melt index *mean*.)

There is a variation on the basic "$\bar{x}$ and R chart" idea that we wish to illustrate here next, because of its frequent usefulness in

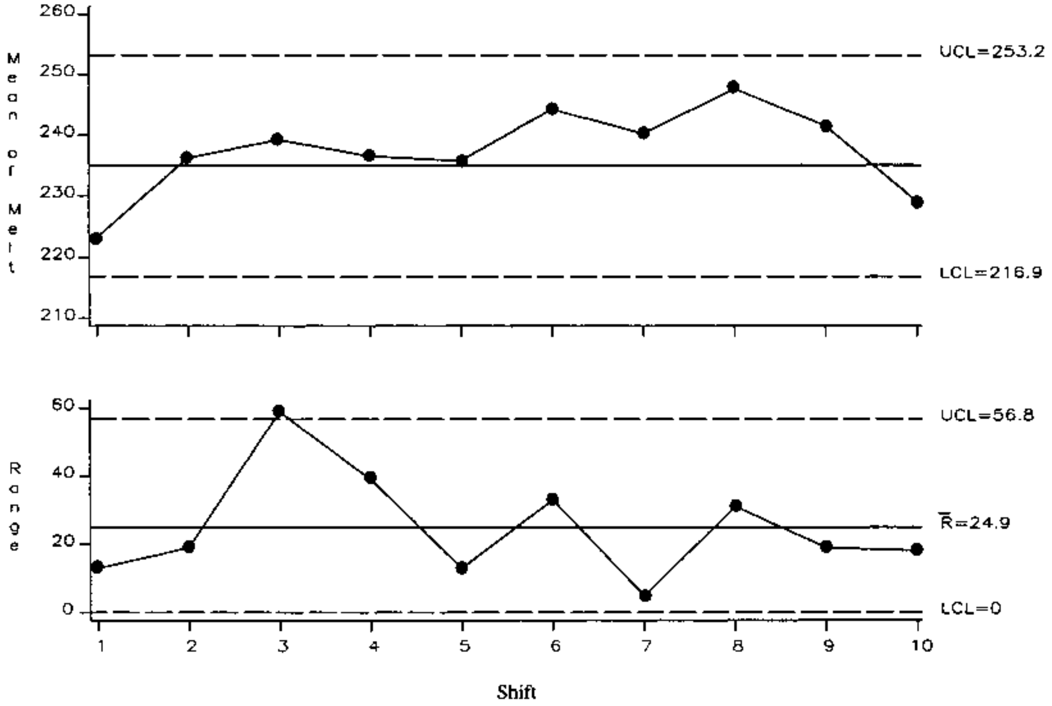

Fig. 4.12. Control charts for $\bar{y}$ and R based on melt indices.

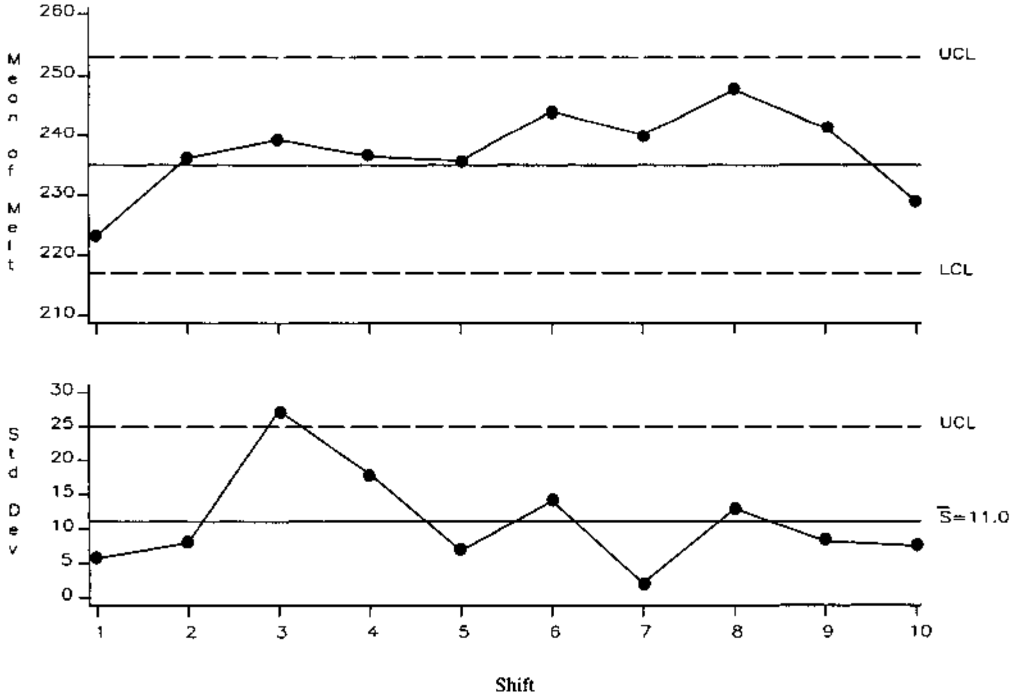

Fig. 4.13. Control charts for $\bar{y}$ and s based on melt indices.

chemical industry applications. That is the making of a so-called x and MR chart pair. The motivation for this modification of the ideas outlined thus far in this section is that in many chemical process monitoring contexts the natural "group size" is $n = 1$. A mean of $n = 1$ observation(s) is simply that observation itself, and the limits of (4-9) make perfectly good sense for the case of $n < 1$. That is, the analog of an $\bar{x}$ chart for $n = 1$ cases is clear, *at least if one has an externally provided value for* σ. But what, if anything, to do for an $n = 1$ counterpart of the R chart and how to develop an analog of (4-10) in cases where σ is not a priori known are perhaps not so obvious. Table 4.5 contains data representing moisture contents in 0.01 percent of bihourly samples of a polymer, and the question at hand is what besides simply the bihourly y values might be plotted in the style of a Shewhart control chart for such data.

The final column of Table 4.5 gives 19 so-called moving ranges of pairs of successive moisture contents. It is often argued that although these MR values are actually affected not only by variation within a 2-hour production period but by some variation between these periods as well, they come as close to representing purely short-term variation as any measure available from $n = 1$ data. Accordingly, as a kind of $n = 1$ analog of an R chart, moving ranges are often charted in addition to individual values y. Further, the average moving range is used to estimate σ in cases where information on the inherent variability of individuals is a priori lacking, according to the formula

$$\text{estimated } \sigma = \frac{\overline{MR}}{1.128}$$

where $\overline{MR}$ is the mean of the moving ranges (and plays the role of $\bar{R}$ in (4-10)), and 1.128 is the $n = 2$ version of the factor d_2 alluded to immediately below (4-10).

In the case of the data of Table 4.5,

$$\overline{MR} = \frac{1}{19}(16 + 4 + 5 + \cdots + 16 + 18) \approx 8.2$$

so that a (possibly somewhat inflated due to between period variation) data-based estimate of within-period variability σ for use, for example in limits (4-9) is

$$\frac{8.2}{1.128} \approx 7.2$$

Figure 4.14 shows both an x (individuals) chart and an MR (moving range) chart based on these calculations. As no standard value of moisture content was provided in Burr's text,[9] the value $\bar{y} = 28.55$ was used as a substitute for μ in (4-9). The MR chart limits are based on standard $n = 2$ (because ranges of "groups" of two observations are being plotted) r chart control limit formulas. Figure 4.14 shows no evidence of assignable variation in the moisture contents.

The use of Shewhart control charts is admirably documented in a number of statistical quality control books, including those by Wadsworth et al.,[8] Duncan,[10] Burr,[9] Grant and Leavenworth,[11] and Ott and Schilling.[12] Our purpose here is not to provide all details necessary for their use, but only to give the reader an introduction to the overall function that they serve. It should be said, however,

TABLE 4.5 Moisture Contents for 20 Polymer Samples[a]

Sample	*Moisture*, y	*Moving Range*, MR
1	36	—
2	20	16
3	16	4
4	21	5
5	32	11
6	34	2
7	32	2
8	34	2
9	23	11
10	25	2
11	12	13
12	31	19
13	25	6
14	31	6
15	34	3
16	38	4
17	26	12
18	29	3
19	45	16
20	27	18

[a] Based on data from page 190 of Burr.[9]

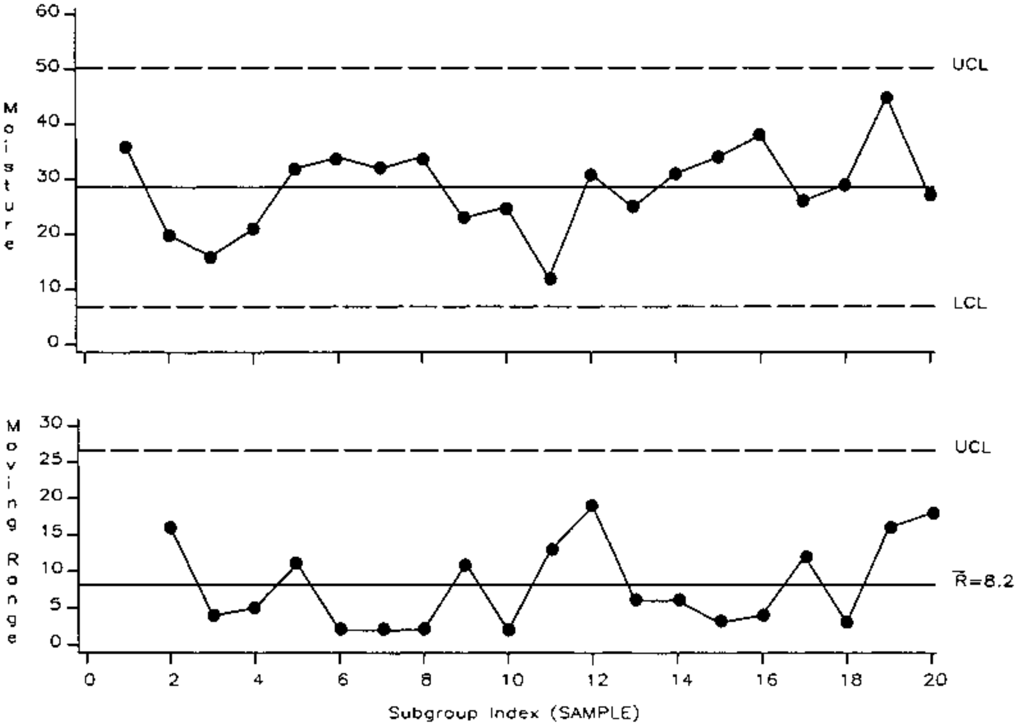

Fig. 4.14. Control charts for *y* and *MR* based on moisture contents of 20 polymer samples.

that in recent years other statistical process monitoring tools such as the so-called CUmulative SUM (CUSUM) schemes and Exponentially Weighted Moving Average (EWMA) schemes have been developed as competing methodologies, and can in some circumstances be practically more effective than the original Shewhart charts. Indeed, many computerized controllers for real-time chemical process monitoring and adjustment now employ some form of CUSUM or EWMA logic. For more on these topics, including their integration with model-based process controllers, the reader is referred to Lucas,[13,14] Lucas and Crosier,[15] Lucas and Saccucci,[16] Crowder,[17,18] Hunter,[19] and, in particular, Vander Wiel et al.[20]

Shewhart's basic conceptualization of common and special cause variation not only leads to control charts as quantitative, rational tools to guide one in knowing when (and when not!) to intervene in an industrial process to correct potential ills, but it also provides a framework for considering the question of what is the best/most consistent performance one can hope for from a particular version of a process. That is, it provides a framework for discussing process capability assessment.

If $\hat{\sigma}$ is some (standard deviation type) estimate of the baseline variation inherent in an industrial process (obtained, e.g., from a calculation such as (4-10) or from data taken from the process after eliminating all physical sources of assignable variation), it essentially specifies what is possible in terms of consistency of process output. There are, however, several common ways of using such an estimate to produce related measures of process capability.

For one thing, remembering again the fact that an interval from $\mu - 3\sigma$ to $\mu + 3\sigma$ (i.e., of length 6σ) will bracket about 99.7 percent of a normal distribution, the figure $6\hat{\sigma}$ is sometimes stated as "the process capability." This usage would say that in the context of the polyethylene melt index example of Table 4.4 the $\hat{\sigma} = 12.1$ figure from (4-10) implies a melt index process capability of $6 \cdot (12.1) \approx$

72.6. If properly monitored, the process appears capable of producing almost all individual melt indices in a 73-point range.

Where there are stated specifications for individual measurements y, $\hat{\sigma}$ is sometimes turned into a kind of index comparing it to the difference in upper and lower engineering specifications. For example, one such *process capability index* is

$$C_p = \frac{\text{USL} - \text{LSL}}{6\hat{\sigma}}$$

where USL − LSL is the difference in specifications. Fairly obviously, the larger the value of C_p, the more comfortably (properly targeted) process output values will fit in an interval from LSL to USL.

Another process capability measure that is frequently used in the industrial chemistry sector is

$$C_{pk} = \text{minimum} \left\{ C_{pu} = \frac{\text{USL} - \hat{\mu}}{3\hat{\sigma}}, \quad C_{pl} = \frac{\hat{\mu} - \text{LSL}}{3\hat{\sigma}} \right\}$$

where $\hat{\mu}$ is an estimated overall process average for an in-control/stable/predictable process, and $\hat{\sigma}$ is as before. This measure is clearly similar to C_p, but it takes into account the placement of the process mean in a way that is ignored by C_p. A large value of C_{pk} indicates that not only is the process short-term variation small enough for the process output values to potentially fit comfortably between LSL and USL, but that the process is currently so targeted that the potential is being realized.

STATISTICAL METHODS AND INDUSTRIAL EXPERIMENTATION

Probably the most important area of opportunity for the new application of statistical methods in the chemical industry during the 1990s is that of increasing the effectiveness of industrial experimentation. That is, it is one thing to bring an existing industrial process to stability (a state of "statical control"), but it is quite another to determine how to make fundamental changes in that process that will improve its basic behavior. This second activity almost always involves some form of experimentation, whether it be in the laboratory or in a plant. As we indicated in the introduction, efficient methods and strategies of such data collection (and corresponding analysis) are a central concern of applied statistics. In this section, we hope to give the reader some insight into the kinds of statistical tools that are available for use in chemical industry experimentation.

We will here take as our meaning of the term "experimentation" the observation of a (typically noisy) physical process under more than one condition, with the broad goal of understanding and then using knowledge of how the process reacts to the changes in conditions. In most industrial contexts, the "conditions" under which the process is observed can be specified in terms of the settings or so-called levels chosen for several potentially important process or environmental variables, the so-called factors in the experiment. In some cases, the hope is to identify those (often largely unregulated) factors and combinations of factors that seem to most influence an observed response variable, as a means of targeting them for attention intended to keep them constant or otherwise to eliminate their influence, and thereby to improve the consistency of the response. In other situations the hope is to discover patterns in how one or more critical responses depend on the levels of (often tightly controlled) factors, in order to provide a road map for the advantageous guiding of process behavior (e.g., to an increased mean reaction yield) through enlightened changing of those levels.

This section is organized into two subsections. In the first, we will illustrate the notion of variance component estimation through an example of a nested or hierarchical data collection scheme. In the second, we will discuss some general considerations in the planning of experiments to detail the pattern of influence of factors on responses, consider so-called factorial and fractional factorial experimental designs, illustrate response surface fitting and interpretation tools and the data requirements they imply, and, in the process, discuss the integration of a number of statistical tools in a sequential learning strategy.

Identifying Major Contributors to Process Variation

A statistical methodology that is particularly relevant where experimentation is meant to identify important unregulated sources of variation in a response is that of variance component estimation, based on so-called ANalysis Of VAriance (ANOVA) calculations and random effects models. As an example of what is possible, consider the data of Table 4.6. Shown here are copper content measurements for some bronze castings. Two copper content determinations were made on each of two physical specimens cut from each of 11 different castings.

The data of Table 4.6 were *by design* collected to have a "tree type" or so-called hierarchical/nested structure. Figure 4.15 shows a diagram of a generic hierarchical structure for *balanced* cases like the present one, where there are equal numbers of branches leaving all nodes at a given level (there are equal numbers of determinations for each specimen and equal numbers of specimens for each casting).

An important goal in most hierarchical studies is determining the size of the contributions to response variation provided by the different factors, that is, the different levels of the tree structure. (In the present context, the issue is how variation between castings compares to variation between specimens within a casting, and how they both compare to variation between determinations for a given specimen. If the overall variability observed were considered excessive, such analysis could then help guide efforts at variation reduction by identifying the largest contributors to observed variability.) The structure portrayed in Fig. 4.15 turns out to enable an appealing statistical analysis, providing help in that quantification.

TABLE 4.6 Forty-four Copper Content Measurements From 11 Bronze Castings[a]

Casting	*Specimen*	*Determination*	*Copper Content*, y (%)
1	1	1	85.54
1	1	2	85.56
1	2	1	85.51
1	2	2	85.54
2	1	1	85.54
2	1	2	85.60
2	2	1	85.25
2	2	2	85.25
3	1	1	85.72
3	1	2	85.77
3	2	1	84.94
3	2	2	84.95
4	1	1	85.48
4	1	2	85.50
4	2	1	84.98
4	2	2	85.02
5	1	1	85.54
5	1	2	85.57
5	2	1	85.84
5	2	2	85.84
6	1	1	85.72
6	1	2	85.86
6	2	1	85.81
6	2	2	85.91
7	1	1	85.72
7	1	2	85.76
7	2	1	85.81
7	2	2	85.84
8	1	1	86.12
8	1	2	86.12
8	2	1	86.12
8	2	2	86.20
9	1	1	85.47
9	1	2	85.49
9	2	1	85.75
9	2	2	85.77
10	1	1	84.98
10	1	2	85.10
10	2	1	85.90
10	2	2	85.90
11	1	1	85.12
11	1	2	85.17
11	2	1	85.18
11	2	2	85.24

[a] Based on data taken from Wernimont.[21]

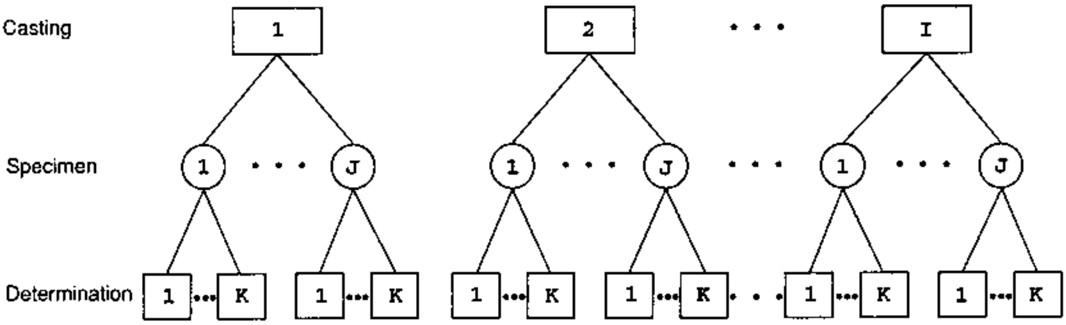

Fig. 4.15. A balanced hierarchical data structure.

If one lets

y_{ijk} = the copper content from the kth determination of the jth specimen from casting i

$\bar{y}_{ij\cdot} = \frac{1}{2}\sum_k y_{ijk}$ = the mean copper content determination from the jth specimen from casting i

$\bar{y}_{i\cdot\cdot} = \frac{1}{2}\sum_j \bar{y}_{ij\cdot}$ = the mean copper content determination from the ith casting

and

$\bar{y}_{\cdot\cdot\cdot} = \frac{1}{11}\sum_i \bar{y}_{i\cdot\cdot}$ = the overall mean copper determination

it is possible to essentially break down the variance of all 44 copper contents (treated as a single group) into interpretable pieces, identifiable as variation between $\bar{y}_{i\cdot\cdot}$'s (casting means), variation between $\bar{y}_{ijk\cdot}$'s (specimen means) within castings, and variation between y_{ijk}'s (individual measurements) within a specimen. That is, it is an algebraic identity that for 44 numbers y_{ijk} with the same structure as those in Table 4.6

$$\begin{aligned}(44-1)s^2 &= \sum_{i,j,k}(y_{ijk}-\bar{y}_{\cdot\cdot\cdot})^2\\ &= \sum_{i,j,k}(\bar{y}_{i\cdot\cdot}-\bar{y}_{\cdot\cdot\cdot})^2+\sum_{i,j,k}(\bar{y}_{ij\cdot}-\bar{y}_{i\cdot\cdot})^2\\ &\quad+\sum_{i,j,k}(y_{ijk}-\bar{y}_{ij\cdot})^2 \qquad (4\text{-}11)\end{aligned}$$

The sums indicated in (4-11) are over all data points; so, for example, the first summand on the right is obtained for the copper content data by summing each $(\bar{y}_{i\cdot\cdot}-\bar{y}_{\cdot\cdot\cdot})^2$ a total of $2\cdot 2 = 4$ times, one for each determination on a given casting. With the obvious meaning for the $\bar{y}$'s and the substitution of the total number of data values for 44, the identity in (4-11) applies to any balanced hierarchical data structure. It is a so-called ANOVA identity, providing an intuitively appealing partitioning of the overall observed variability in the data, an *analyzing of the (observed) variation.*

Some tedious arithmetic "by hand," or by use of nearly any commercially available statistical package that includes an ANOVA program, shows that for the copper content data of Table 4.6 the numerical version of (4-11) is approximately

$$5.1385 = 3.2031 + 1.9003 + .0351 \qquad (4\text{-}12)$$

Although we will not provide any details here, the reader is alerted to the fact that it is common practice to present the elements of an identity such as (4-12) in a tabular form called an "ANOVA table." The use for the elements of (4-12) that we wish to illustrate here is their role in estimating casting, specimen, and determination "variance components."

That is, if one models an observed copper determination as the sum of a *random* casting-dependent *effect* whose distribution is described by a variance σ_c^2, a *random* specimen-dependent *effect* whose distribution is described by a variance σ_s^2, and a *random* determination-dependent *effect* whose distribution is described by a variance σ_d^2, the elements of (4-12) lead to estimates of the *variance components* σ_c^2, σ_s^2, and σ_d^2 in the model. Note that in such a random effects model of the data-generating process, copper measurements from the same casting share the same casting effect, and copper measurements from the same specimen share the both same casting and the same specimen effects. The individual σ^2 values are conceptually the variances that would be seen in copper contents if only the corresponding sources of variation were present. The sum of the σ^2 values is conceptually the variance that would be seen in copper contents if single determinations were made on a number of different castings.

Standard statistical methodology for estimation of the variance components (which we will not detail here, but can, e.g., be found in Chapter 11 of Hicks[22] produces

$$\hat{\sigma}_d^2 = \frac{.0351}{11 \cdot 2 \cdot (2-1)} \approx .0016\,(\%)^2$$

as an estimate of σ_d^2,

$$\hat{\sigma}_s^2 = \frac{1}{2}\left(\frac{1.9003}{11 \cdot (2-1)} - .0016\right) \approx .0856\,(\%)^2$$

as an estimate of σ_s^2, and

$$\hat{\sigma}_c^2 = \frac{1}{2 \cdot 2}\left(\frac{3.2031}{(11-1)} - \frac{1.9003}{11 \cdot (2-1)}\right)$$
$$\approx .0369\,(\%)^2$$

as an estimate of σ_c^2. Figure 4.16 is a pie chart representation of these three estimated variance components as fractions of their sum (the variance predicted if single determinations were made on single specimens from each casting), and graphically identifies inhomogeneity between specimens cut from a single casting as the biggest contributor to observed variation.

On the standard deviation scale the estimates translate to $\hat{\sigma}_d \approx 0.04\%$, $\hat{\sigma}_d \approx 0.29\%$, and $\hat{\sigma}_c \approx 0.19\%$. So, for example, the data of Table 4.6 indicate that even if castings and specimens were all exactly alike, it would still be reasonable to expect measured copper contents to vary according to a standard deviation of about .04 percent, presumably due to unavoidable measurement error.

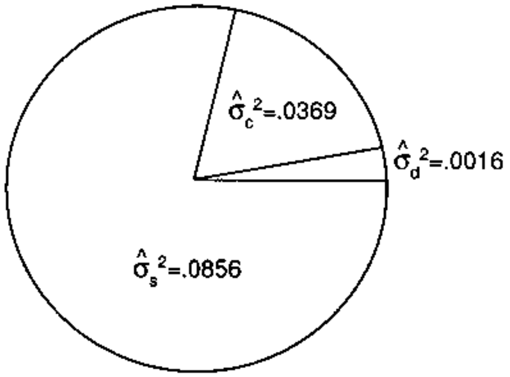

Fig. 4.16. Three estimated variance components for copper contents.

Variance component estimation methodology is not limited to balanced hierarchical experiments, but they do provide an important and straightforward context in which to introduce the technology. More detailed information on the case discussed here and extensions to other kinds of data structures can be found in books by Vardeman,[5] Neter et al.,[6] Mason, Gunst, and Hess,[23] and Hicks.[22]

Discovering and Exploiting Patterns of Factor Influence on Responses

Having discussed statistical methodology particularly appropriate to studies whose primary purpose is simply to identify factors with the largest influence on a response, we will now consider methods aimed more directly at detailed experimental quantification of the pattern of factor influence on one or more responses. As an example, we will use a "sanitized" account of some statistical aspects of a highly successful and economically important process improvement project. (Data presented here are not the original data, but resemble them in structure. Naturally, details of the project not central to our expository purposes and those of a proprietary nature will be suppressed.)

The process monitoring, capability assessment, and variance source identification ideas discussed thus far are almost logical prerequisites for industrial experimentation to detail the nature of dependence of response variables on factors of interest. When an industrial process has been made to operate in a stable manner, its intrinsic variability reduced to the extent practically possible, and that baseline performance quantified and understood, the prospects of success are greatly enhanced in subsequent efforts to understand the effects of potential fundamental process changes.

Preliminary work by various groups left a project team with a batch production process behaving in a stable but unsatisfactory fashion. Obvious sources of variation (both in the process itself and "upstream") has been identified and, to the degree practically possible, eliminated. The result was a process with an average output *purity* of 88 percent and an associated purity standard deviation of around 5 percent, and an average *yield* of 43 percent and an associated yield standard deviation of around 5 percent as well. The project team was charged with finding ways to increase the purity and yield means to, respectively, 95 percent and 59 percent while hopefully also further reducing the standard deviations. To accomplish this, the team recognized the need for an improved understanding of how various process variables under their control influenced purity (which we will call y_1) and yield (which we will call y_2). Experimentation to provide this was authorized, and, in particular, attention was focused on four factors consisting of three reactant concentrations and the process run time. We will call the Reactant A mole ratio x_1, the Reactant B mole ratio x_2, the Reactant C mole ratio x_3, and the run time (in hours) x_4.

The choice of experimental factors (what to vary in data collection) is a nontrivial matter of fundamental importance that is best handled by people with firsthand process knowledge. There are a number of popular techniques and tools (such as so-called cause and effect diagrams, discussed for instance in the book by Wadsworth et al.[8]) for helping groups brainstorm and reach a consensus on such matters. Further, in cases where a priori knowledge of a process is scarce, relatively small preliminary screening experiments can help reduce a large list of potential factors to a smaller list apparently worthy of more detailed study. (The fractional factorial plans that will be illustrated shortly often are recommended for this purpose.)

Once a particular set of experimental factors has been identified, questions about exactly how they should be varied must be answered. To begin with, there is the choice of levels for the factors, the matter of how much the experimental factors should be varied. Particular experimental circumstances usually dictate how this is addressed. Widely spaced (substantially different) levels will in general lead to bigger changes in responses, and therefore clearer indications of how the responses depend upon the experimental factors, than will closely spaced (marginally different) levels. But they may do so at the expense of potentially creating unacceptable or even disastrous process conditions or output. Thus, what may be an acceptable strategy in a laboratory study might be completely unacceptable in a production environment and vice versa.

Given a set or range of levels for each of the individual experimental factors, there is still the question of exactly what combinations of levels actually will be used to produce experimental data. For example, in the process improvement study, standard process operating conditions were $x_1 = 1.5$, $x_2 = 1.15$, $x_3 = 1.75$, and $x_4 = 3.5$, and the project team decided on the ranges

$$1.0 \leqslant x_1 \leqslant 2.5,\ 1.0 \leqslant x_2 \leqslant 1.8,\ 1.0 \leqslant x_3 \leqslant 2.5, \text{ and } \qquad (4\text{-}13)$$

$$2.0 \leqslant x_4 \leqslant 5.0$$

as defining the initial limits of experimentation. But the question remained as to exactly what sets of mole ratios and corresponding run times were appropriate for data collection.

A natural, but largely discredited, strategy of data collection is the one-variable-at-a-time experimental strategy of picking some base of experimental operations (such as standard operating conditions) and varying the level of only one of the factors away from that base at a time. The problem with such a strategy is that sometimes two or more factors act on responses jointly, doing things in concert that neither will do alone. For example, in the process improvement study, it might well have been that an increase in either x_1 or x_2 alone would have affected yield very little, whereas a simultaneous increase in both would have caused an important increase. Modern strategies of industrial experimentation are conceived with such possibilities in mind, and attempt to spread out observations in a way that gives one some ability to identify the nature of the response structure no matter how simple or complicated it turns out to be.

There are several issues to consider when planning the combinations of levels to include in an experiment. We have already said that it is important to "vary several factors simultaneously." It also is important to provide for some replication of at least a combination or two in the experiment, as a means of getting a handle on the size of the experimental error or baseline variation that one is facing. The replication both verifies the reproducibility of values obtained in the study and identifies the limits of that reproducibility. Also, one must balance the urge to "cover the waterfront" with a wide variety of combinations of factor levels against resource constraints and a very real law of diminishing practical returns as one goes beyond what is really needed in the way of data to characterize response behavior. In addition, the fact that real-world learning is almost always of a sequential rather than a "one shot" nature suggests that it is in general wise to spend only part of an experimental budget on early study phases, leaving resources adequate to follow up directions suggested by what is learned in those stages.

It is obvious that a minimum of two different levels of an experimental factor must appear in a set of experimental combinations if any information is to be gained on the effects of that factor. So one logical place to begin thinking about a candidate design for an industrial experiment is with the set of all possible combinations of two levels of each of the experimental factors. If there are p experimental factors, statistical jargon for such an arrangement is to call it a (complete) $2 \times 2 \times \cdots \times 2$ or 2^p factorial plan. For example, in the process improvement situation, an experiment consisting of the running of all 16 possible combinations of

$$x_1 = 1.0 \text{ or } x_1 = 2.5$$

$$x_2 = 1.0 \text{ or } x_2 = 1.8$$

$$x_3 = 1.0 \text{ or } x_3 = 2.5$$

and

$$x_4 = 2.0 \text{ or } x_4 = 5.0$$

would be called a complete $2 \times 2 \times 2 \times 2$ or 2^4 factorial experiment. Notice that in geometric terms, the (x_1, x_2, x_3, x_4) points making up this 2^4 structure amount to the 16 "corners" in four-dimensional space of the initial experimental region defined in (4-13).

A complete factorial experimental plan is just that, in some sense "complete." It provides enough information to allow one to assess (for the particular levels used) not only individual but also joint or interaction effects of the factors on the response or responses. But when in fact (unbeknownst to the investigator) a system under study is a relatively simple one, principally driven by only a few individual or low-order joint effects of the factors, fewer data actually are needed to characterize those effects adequately. So what is often done in modern practice is initially to run only a carefully chosen part of a full 2^p factorial, a so-called fractional factorial plan, and to decide based on the initial data whether data from the rest of the full factorial appear to be needed in order adequately to characterize and understand response behavior. We will not here discuss the details of how so-called 2^{p-q} fractional factorials are intelligently chosen, but there is accessible reading material on the subject in books by Box, Hunter, and Hunter,[24] and by Vardeman.[5]

In the process improvement study, what was actually done in the first stage of data collection was to gather information from one-half of a full 2^4 factorial (a 2^{4-1} fractional factorial) augmented by four observations at the "center" of the experimental region (thereby providing both some coverage of the interior of the region, in addition to a view of some of its corners, and important replication as well). The data in Table 4.7 are representative of what the group obtained.

The order in which the data are listed is simply a convenient systematic one, not to be confused with the order in which experimental runs were actually made. The table order is far too regular for it to constitute a wise choice itself. For example, the fact that all $x_3 = 1.0$ combinations precede the $x_3 = 2.5$ ones might have the unfortunate effect of allowing the impact of unnoticed environmental changes over the study period to end up being confused with the impact of x_3 changes. The order in which the 12 experimental runs were actually made was chosen in a "completely randomized" fashion. For a readable short discussion of the role of randomization in industrial experimentation, the reader is referred to Box.[25]

For purposes of this discussion, attention is focused on the yield response variable, y_2. Notice first that the four y_2 values from the center point of the experimental region has $\bar{y} = 53.2$ and $s = 1.13$ (which incidentally already appear to be an improvement over typical process behavior). As a partial indication of the logic that can be used to investigate whether the dependence of yield on the experimental factors is simple enough to be described adequately by the data of Table 4.7, one can compute some estimated "main effects" from the first eight data points. That is, considering first the impact of the variable x_1 (alone) on yield, the quantity

$$\bar{y}_{\text{high}\,x_1} - \bar{y}_{\text{low}\,x_1} = \tfrac{1}{4}(45.9 + 46.0 + 51.2 + 52.8) - \tfrac{1}{4}(35.1 + 4.0 + 41.4 + 10.0) = 26.35$$

is perhaps a sensible measure of how a change in x_1 from 1.00 to 2.50 is reflected in yield. Similar measures for the other variables turn out to be

$$\bar{y}_{\text{high}\,x_2} - \bar{y}_{\text{low}\,x_2} = -15.20$$

$$\bar{y}_{\text{high}\,x_3} - \bar{y}_{\text{low}\,x_3} = 6.10$$

and

$$\bar{y}_{\text{high}\,x_4} - \bar{y}_{\text{low}\,x_4} = 0.45$$

These measures provide some crude insight into the directions and magnitudes of influence of the experimental variables on y_2. (Clearly, by these measures $x_1 = 2.50$ seems preferable to $x_1 = 1.00$, and the run time variable x_4 seems to have little impact on yield.) But they also provide strong evidence that the nature of the dependence of yield on the experimental factors is too complicated to be described by the action of the factors individually. For example, if it *were* the case that the separate actions of the experimental factors were adequate to describe system behavior, then standard statistical theory and the data indicate that the mean response for the $x_1 = 1.00$, $x_2 = 1.0$, $x_3 = 1.00$, and $x_4 = 2.0$ set of conditions would be around

$$\hat{y} = \bar{y}_{\text{corners}} - \tfrac{1}{2}(26.35) - \tfrac{1}{2}(-15.20) - \tfrac{1}{2}(6.10) - \tfrac{1}{2}(0.45) = 27.45$$

(where $\bar{y}_{\text{corners}}$ is standing for the mean of the first eight yields in Table 4.7). But the observed yield of 35.1 is clearly incompatible

TABLE 4.7 Data from an Initial Phase of a Process Improvement Study

x_1	x_2	x_3	x_4	*Purity,* y_1(%)	*Yield,* y_2(%)
1.00	1.0	1.00	2.0	62.1	35.1
2.50	1.0	1.00	5.0	92.2	45.9
1.00	1.8	1.00	5.0	7.0	4.0
2.50	1.8	1.00	2.0	84.0	46.0
1.00	1.0	2.50	5.0	61.1	41.4
2.50	1.0	2.50	2.0	91.6	51.2
1.00	1.8	2.50	2.0	9.0	10.0
2.50	1.8	2.50	5.0	83.7	52.8
1.75	1.4	1.75	3.5	87.7	54.7
1.75	1.4	1.75	3.5	89.8	52.8
1.75	1.4	1.75	3.5	86.5	53.3
1.75	1.4	1.75	3.5	87.3	52.0

with such a mean and the standard deviation value (of $s = 1.13$) derived from the repeated center point. Also, other simple evidence that (at least linear and) separate action of the four factors is not enough to describe yield adequately is given by the large difference between $\bar{y}_{\text{corners}} = 35.8$ and the observed mean from the center point $\bar{y} = 53.2$. (As it turns out, calculations that we will not show here indicate the *possibility* that individual action of the factors *plus joint action* of the Reactant A and Reactant B mole ratios is sufficient to describe yield. But in any case, the point is that the data of Table 4.7 provide evidence that the pattern of dependence of yield on the experimental variables is not simple, and thus that completion of the 2^4 factorial is in order.)

After a complete analysis of the first round of experimental data, the project team "ran the second half fraction" of the 2^4 factorial, and data similar to those in Table 4.8 were obtained. (Again, no significance should be attached to the order in which the observations in Table 4.8 are listed. It is not the order in which the experimental runs were made.)

The data from the second phase of experimentation served to complete the project team's 2^4 factorial picture of yield and confirm the tentative understanding drawn first from the initial half fraction. It is seen that the combinations listed in Table 4.8 are in the same order as the first eight in Table 4.7 as regards levels of experimental variables x_1, x_2, and x_3, and that the corresponding responses are very similar. (This, by the way, has the happy practical implication that run time seems to have little effect on final purity or yield, opening the possibility of reducing or at least not increasing the standard run time.) Thorough data analysis of a type not shown here left the project team with a clear (and quantified version of the) understanding that Reactant A and B mole ratios have important individual and joint effects on the responses, and that, acting independently of the other two reactants, Reactant C also has an important effect on the responses. However, it did *not* yet provide a solution to the team's basic problem, which was to reach a 59 percent mean yield goal.

TABLE 4.8 Data from a Second Phase of a Process Improvement Study

x_1	x_2	x_3	x_4	Purity, $y_1(\%)$	Yield, $y_2(\%)$
1.00	1.0	1.00	5.0	64.0	35.3
2.50	1.0	1.00	2.0	91.9	47.2
1.00	1.8	1.00	2.0	6.5	3.9
2.50	1.8	1.00	5.0	86.4	45.9
1.00	1.0	2.50	2.0	63.9	39.5
2.50	1.0	2.50	5.0	93.1	51.6
1.00	1.8	2.50	5.0	6.8	9.2
2.50	1.8	2.50	2.0	84.6	54.3

The data of Table 4.7 and 4.8 do hold out hope that conditions producing the desired purity and yield can be found. That is, though none of the 16 corners of the experimental region nor the center point appeared to meet the team's yield goal, the data do show that there is substantial *curvature* in the yield response. (The joint effect of x_1 and x_2 amounts to a kind of curvature, and the nonlinearity of response indicated by a large difference between $\bar{y}_{\text{corners}} \approx 35.8$ and $\bar{y} = 53.2$ at the center of the experimental region also is a kind of curvature.) If one could "map" the nature of the curvature, there is at least the possibility of finding favorable future operating conditions in the interior of the initial experimental region defined in (4-13).

It ought to be at least plausible to the reader that 2^4 factorial data (even supplemented with center points) are not really sufficient to interpolate the nature of a curved response over the experimental region. More data are needed, and a standard way of augmenting a 2^p design with center points to one sufficient to do the job is through the addition of so-called star points to produce a central composite design. Star points are points outside the original experimental region whose levels of all but one of the p experimental factors match those of the center point. Figure 4.17 shows graphical representations of central composite designs in $p = 2$ and $p = 3$ factors.

The project team conducted a third phase of experimentation by adding eight star points to their study and obtained data similar to those in Table 4.9.

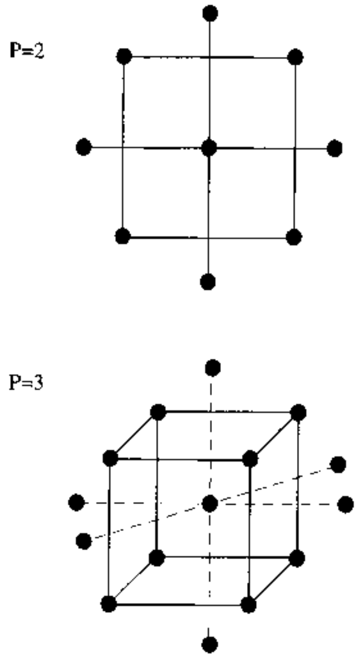

Fig. 4.17. $p = 2$ and $p = 3$ central composite designs.

The data in Tables 4.7, 4.8, and 4.9 taken together turn out to provide enough information to enable one rather thoroughly to quantify the "curved" nature of the dependence of y_2 on x_1, x_2, x_3, and x_4. A convenient and often successful method of accomplishing this quantification is through the least squares fitting of a general *quadratic response surface.* That is, central composite data are sufficient to allow one to fit an equation to a response that involves a constant term, linear terms in all the experimental variables, quadratic terms in all of the experimental variables, and cross-product terms in all pairs of the experimental variables. Appropriate use of a multiple regression program with the project data represented here produces the fitted equation

$$
\begin{aligned}
y_2 \approx\ & 15.4 + 37.9x_1 - 66.2x_2 + 48.8x_3 \\
& + 0.97x_4 - 16.1x_1^2 - .03x_2^2 \\
& - 13.6x_3^2 - .046x_4^2 + 26.5x_1x_2 \\
& + 0.344x_1x_3 - .217x_1x_4 \\
& + 1.31x_2x_3 - .365x_2x_4 + .061x_3x_4
\end{aligned}
$$

This may not seem to the reader to be a particularly helpful data summary, but standard multiple regression tools can be used to deduce that an essentially equivalent, far less cluttered, and more clearly interpretable representation of the relationship is:

$$
\begin{aligned}
y_2 \approx\ & 13.8 + 37.8x_1 - 65.3x_2 + 51.6x_3 \\
& - 16.2x_1^2 - 13.6x_3^2 + 26.5x_1x_2 \qquad (4\text{-}14)
\end{aligned}
$$

Equation (4-14), provides an admirable fit to the data in Tables 4.7, 4.8, and 4.9, is in perfect agreement with all that has been said thus far about the pattern of dependence of yield on the experimental factors, *and* allows one to do some intelligent interpolation in the initial experimental region. Use of an equation like (4-14) ultimately allowed the project team to determine that an increase of x_1 only would, with minimal change in the existing process, allow them to meet their yield goal. (In fact, the single change in x_1 proved to be adequate to allow them to meet all of their yield *and* purity goals!)

Graphical representations similar to those in Figs. 4.18 and 4.19 for (4-14) with $x_3 = 1.75$

TABLE 4.9 Data from a Third Phase of a Process Improvement Study

x_1	x_2	x_3	x_4	*Purity, y_1(%)*	*Yield, y_2(%)*
0.6895	1.4	1.75	3.5	20.8	13.0
2.8105	1.4	1.75	3.5	95.9	54.3
1.75	0.8344	1.75	3.5	99.9	62.4
1.75	1.9656	1.75	3.5	65.9	41.2
1.75	1.4	0.6895	3.5	64.4	32.7
1.75	1.4	2.8105	3.5	64.8	40.3
1.75	1.4	1.75	1.379	88.1	52.7
1.75	1.4	1.75	5.621	88.9	50.5

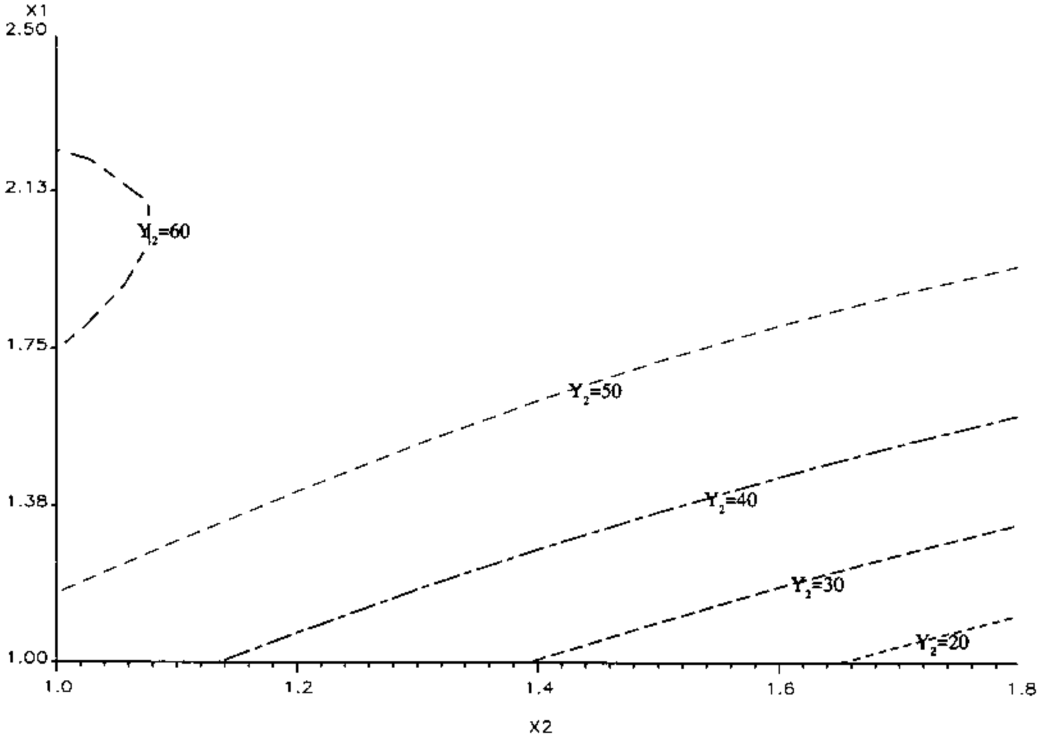

Fig. 4.18. A contour plot of fitted yield when $x_3 = 1.75$.

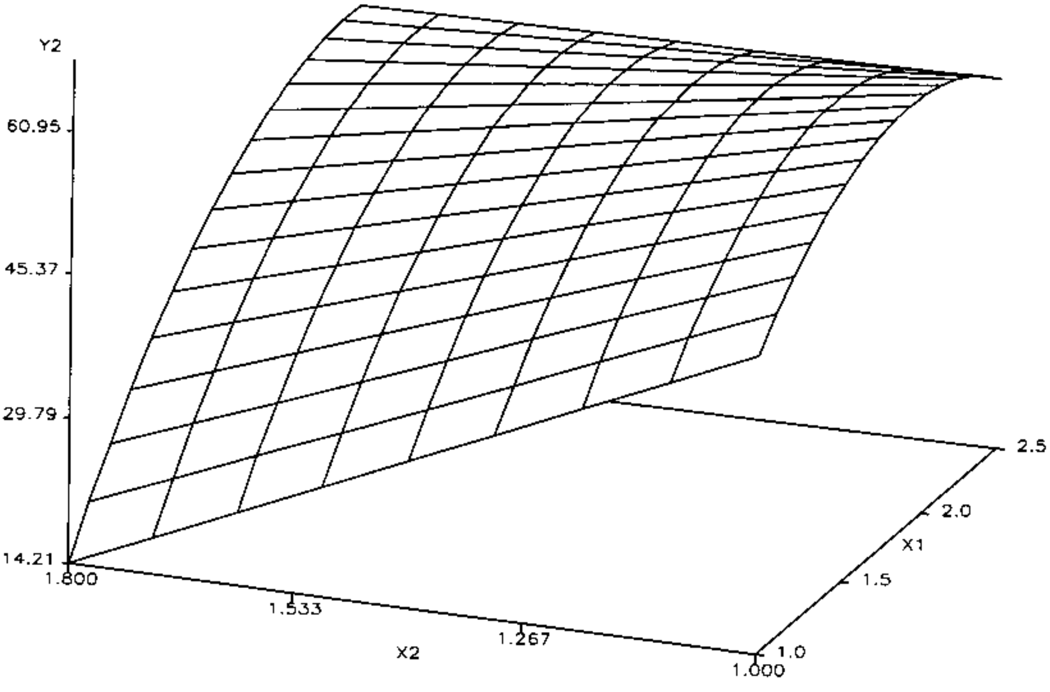

Fig. 4.19. A perspective graph of fitted yield when $x_3 = 1.75$.

(the standard operating value for x_3) were instrumental in helping the team understand the message carried by their data and how yield could be improved. Figure 4.18 is a so-called contour plot (essentially a topographic map) of the fitted equation, and Fig. 4.19 is a more three-dimensional–looking representation of the same surface. Both types of display are commonly used tools of modern statistical experiment design and analysis. The contour plot idea is particularly helpful where several responses are involved, and by overlaying several such plots one can simultaneously picture the various implications of a contemplated choice of process conditions.

SPECIAL STATISTICAL TOOLS FOR CHEMICAL APPLICATIONS

The statistical methods discussed thus far are of a quite general nature, routinely finding application beyond the bounds of the chemical industry. In this section, we will briefly highlight two statistical methodologies whose most important applications are to chemical problems. That is, we will touch on some of the ideas of mixture experiments and the role of statistics in mechanistic modeling.

Mixture Experiments

In many situations in industrial chemistry, some important measured property of a product is a function of the proportions in which a set of p ingredients or components is represented in a mixture leading to the product. For example, case studies in the literature have covered subjects ranging from octanes of gasoline blends, discussed by Snee;[26] to strengths of different formulations of ABS pipe compound, treated in Koons and Wilt;[27] to aftertaste intensities of different blends of artificial sweeteners used in an athletic sport drink, discussed by Cornell;[28] to moduli of elasticity of different rocket propellant formulations, considered by Kurotori.[29] For experimenting in such contexts, special statistical techniques are needed. These tools have been discussed at length by Cornell,[30,31] and our purpose here is not to attempt a complete exposition, but only to whet the reader's appetite for further reading in this area.

The goal of mixture experimentation is to quantify how proportions $x_1, x_2, x_3, \ldots, x_p$ of ingredients 1 through p affect a response y. Usually, the hope is to fit some kind of approximate equation involving some parameters $\underset{\sim}{b}$, say

$$y \approx f(x_1, x_2, \ldots, x_p | \underset{\sim}{b})$$

to a set of n $(x_1, x_2, \ldots, x_p, y)$ data points, for the purpose of using the fitted equation to guide optimization of y, that is, to find the "best" blend. The logic of data collection and equation fitting is complicated in the mixture scenario by the fact that

$$x_1 + x_2 + \cdots + x_p = 1 \qquad (4\text{-}15)$$

The linear constraint (4-15) means that (p way) factorial experimentation is impossible, and that special measures must be employed in order to use standard regression analysis software to do least squares equation fitting. We will briefly describe in turn some approaches to experimental design, equation fitting, and presentation of results for the mixture problem under its fundamental constraint (4-15).

In the case of $p = 3$ (a three-component mixture problem), the set of all possible combinations of values for x_1, x_2, and x_3 satisfying (4-15) can be conveniently represented as an equilateral triangular region. Figure 4.20 shows such a region and the so-called simplex coordinate system on the region. The corners on the plot stand for cases where the "mixture" involved is actually a single pure component. Points on the line segments bounding the figure represent two-component mixtures, and interior points represent genuine three-component mixtures. For example, the center of the simplex corresponds to a set of conditions where each component makes up exactly one-third of the mixture.

One standard mixture (experimental) design strategy is to collect data at the extremes (corners) of the experimental region along with collecting data on a regular grid in the

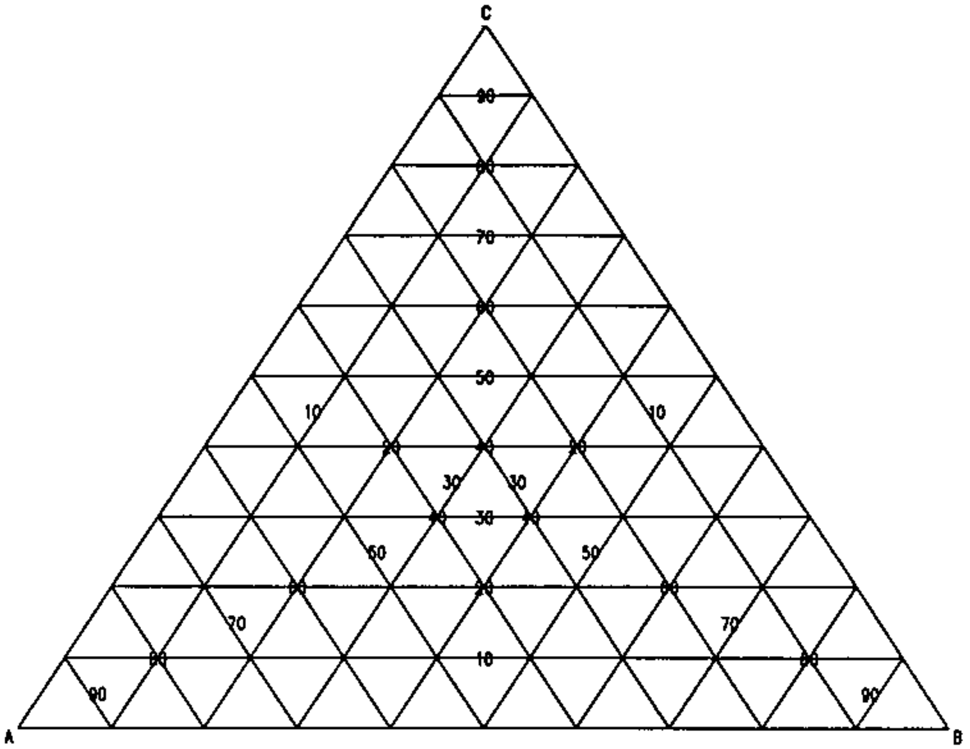

Fig. 4.20. The set of points with $x_1 + x_2 + x_3 = 1$ and a simplex coordinate system.

experimental region. Figure 4.21 shows a $p = 3$ example of such a so-called simplex lattice design, and Table 4.10 lists the (x_1, x_2, x_3) points involved. (As in the cases of the data in tables 4.7, 4.8, and 4.9, the order used in the listing in Table 4.10 is not one that would be used in sequencing data collection runs. Instead, a randomly chosen order often is employed.)

Another standard mixture experiment strategy is the so-called simplex centroid design, where data are collected at the extremes of the experimental region and for every equal-parts two-component mixture, every equal-parts three-component mixture,

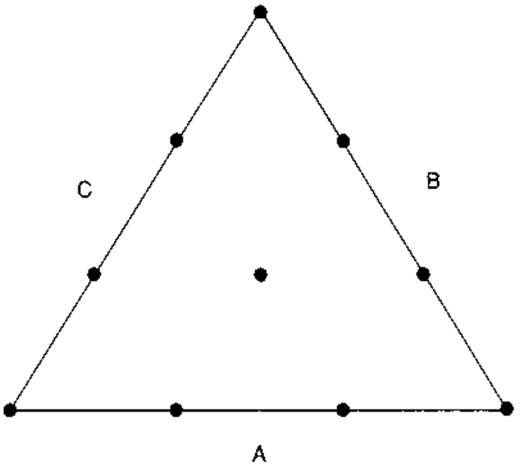

Fig. 4.21. A $p = 3$ simplex lattice.

TABLE 4.10 (x_1, x_2, x_3) Points in a Particular $p = 3$ Simplex Lattice Design

x_1	x_2	x_3
1	0	0
0	1	0
0	0	1
$\frac{1}{3}$	$\frac{2}{3}$	0
$\frac{2}{3}$	$\frac{1}{3}$	0
$\frac{1}{3}$	0	$\frac{2}{3}$
$\frac{2}{3}$	0	$\frac{1}{3}$
0	$\frac{1}{3}$	$\frac{2}{3}$
0	$\frac{2}{3}$	$\frac{1}{3}$
$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$

and so on. Figure 4.22 identifies the blends included in a $p = 3$ simplex centroid design.

Often, the space of practically feasible mixtures is smaller than the entire set of $x_1, x_2, \ldots, x_p$ satisfying (4-15). (For example, in many contexts, "pure" mixtures do not produce viable product. Concrete made using only water and no sand or cement obviously is a useless building product. One common type of constraint on the proportions $x_1, x_2, \ldots, x_p$ that produces quite simple experimental regions is that of lower bounds on one or more of the individual proportions. Cornell,[30] for example, discusses a situation where the effectiveness in grease stain removal of a $p = 3$ bleach mixture was studied; and past experience with the product indicated that the proportions by weight of bromine, x_1, of powder, x_2, and of HCl, x_3, needed to satisfy the following constraints:

$$x_1 \geqslant .30,\ x_2 \geqslant .25,\ \text{and}\ x_3 \geqslant .02 \qquad (4\text{-}16)$$

for effective action of the product (i.e., the mixture needed to be at least 30 percent bromine, at least 25 percent powder, and at least 2 percent HCl by weight.)

The effect of adding the lower bound constraints (4-16) to the basic mixture constraint (4-15) can be pictured as in Fig. 4.23. There, a triangular subregion of the basic $p = 3$ simplex depicts the feasible (x_1, x_2, x_3) points. The choice of experimental mixtures for such an experimental region can be made by direct analogy to or rescaling of designs such as the simplex lattice and simplex centroid designs illustrated above to cover the entire simplex. (It is common to refer to the rescaling process as the use of pseudo-components.)

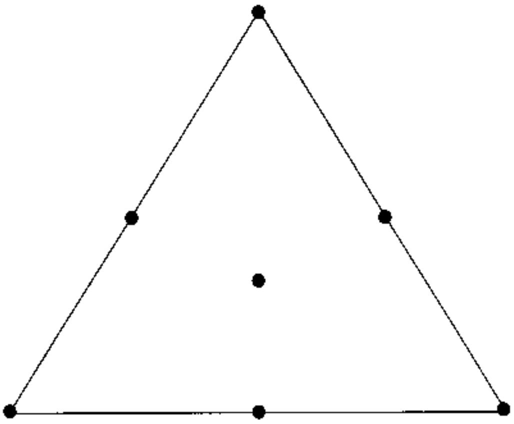

Fig. 4.22. A $p = 3$ simplex centroid design.

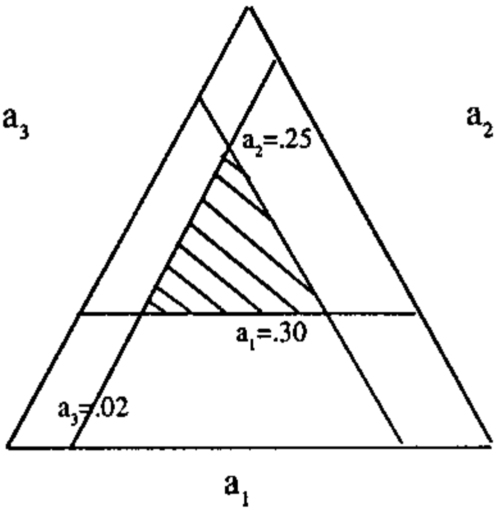

Fig. 4.23. The $p = 3$ simplex and a set of feasible bleach mixtures.

Constraint systems more complicated than simple lower bounds produce irregularly shaped experimental regions and less obvious methods of choosing $(x_1, x_2, \ldots, x_p)$ points to cover the experimental region. When $p = 3$, it is possible to sketch the region of feasible points on a simplex plot and use it to help guide the choice of mixture experiment strategy. Figure 4.24 illustrates the kind of region that can arise with other than exclusively lower bound constraints.

When more than three components are involved in a mixture study, such plots are, of course, no longer possible, and other more analytic methods of identifying candidate experimental mixtures have been developed. For example, McLean and Anderson[32] presented an algorithm for locating the vertices of an experimental region defined by the basic constraint (4-15) and any combination of upper and or lower bound constraints

$$0 \leqslant a_i \leqslant x_i \leqslant b_i \leqslant 1$$

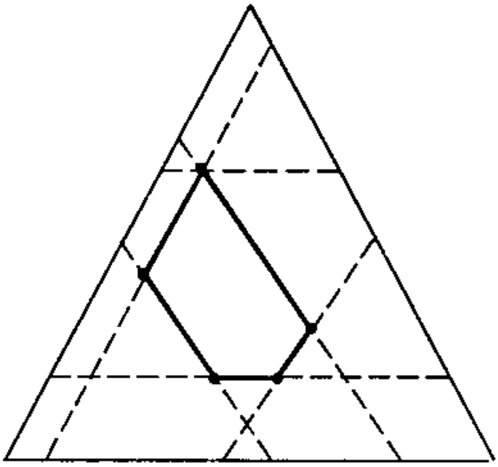

Fig. 4.24. An irregularly shaped experimental region in a $p = 3$ mixture study.

on the proportions x_i. Cornell[30,31] discusses a variety of algorithms for choosing good mixture experiment designs under constraints, and many of the existing algorithms for the problem have been implemented in the MIXSOFT software package developed by Piepel.[33]

Empirical polynomial descriptions of (approximately) how a response y depends upon proportions $x_1, x_2, \ldots, x_p$ are popular mixture analysis tools. The process of fitting polynomials to mixture experiment data in principle uses the same least squares notion illustrated in the fitting of a parabola to the data of Table 4.2. However, the mechanics of using standard multiple regression analysis software in the mixture context is complicated somewhat by the basic constraint (4-15). For example, in view of (4-15) the basic ($p + 1$ parameter) linear relationship

$$y \approx b_0 + b_1x_1 + b_2x_2 + \cdots + b_px_p \quad (4\text{-}17)$$

is in some sense "overparameterized" in the mixture context, in that it is equivalent to the (p parameter) relationship

$$y \approx b_1x_1 + b_2x_2 + \cdots + b_px_p \quad (4\text{-}18)$$

if one identifies the coefficients in (4-18) with the sums of the corresponding coefficients in (4-17) and the coefficient b_0. As a result, it is the "no intercept" relationship (4-18) that is typically fit to mixture data when a linear relationship is used. In a similar way, when a second-order or (multivariable) quadratic relationship between the individual proportions and the response variable is used, it has no intercept term and no pure quadratic terms. For example, in the $p = 3$ component mixture case, the general quadratic relationship typically fit to mixture data is

$$y \approx b_1x_1 + b_2x_2 + b_3x_3 + b_4x_1x_2 + b_5x_1x_3 + b_6x_2x_3 \quad (4\text{-}19)$$

(Any apparently more general relationship involving an intercept term and pure quadratic terms can by use of (4-15) be shown to be equivalent to (4-19) in the mixture context.) Relationships of the type of (4-19) are often called Scheffé models, after the first author to treat them in the statistical literature. Other more complicated equation forms are also useful in some applications, but we will not present them in this chapter. The interested reader is again referred to Cornell[30,31] for more information on forms that have been found to be tractable and effective.

We should point out that the ability to fit equations of the form (4-18) or like (4-19), or of an even more complicated form, is predicated on having data from enough different mixtures to allow unambiguous identification of the parameters $\underset{\sim}{b}$. This requires proper data collection strategy. Much of the existing statistical research on the topic of mixture experiment design has to do with the question of wise allocation of experimental resources under the assumption that a particular type of equation is to be fit.

One's understanding of fitted polynomial (and other) relationships often is enhanced through the use of contour plots made on coordinate systems like that in Fig. 4.25. (This is even true for $p \geqslant 3$ component mixture scenarios, but the use of the idea is most transparent in the three-component case.) A plot like Fig. 4.25 can be a powerful tool to aid one in understanding the nature of a fitted equation and finding regions of optimum fitted response.

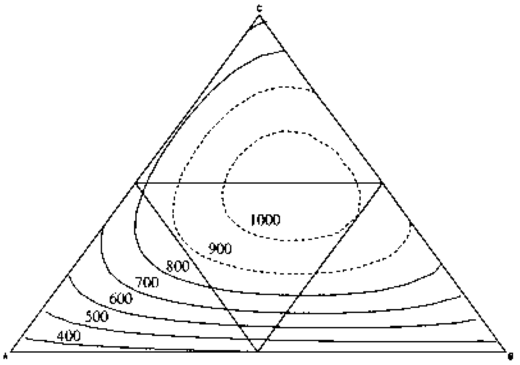

Fig. 4.25. A contour plot made on the $p = 3$ simplex.

The mixture experiment counterpart to conventional screening/fractional factorial experimentation also is possible. So-called axial designs have been developed for the purpose of providing screening-type mixture data for use in rough evaluation of the relative effects of a large number of mixture components on a response variable. The same kind of sequential experimental strategy illustrated in the process improvement example is applicable in mixture contexts, as well as contexts free of a constraint such as (4-15).

Mechanistic Model Building

The kinds of equations most easily fit to multi-factor data using standard (least squares) regression analysis techniques are polynomial equations such as (4-6), (4-14), (4-18), and (4-19). These are particularly convenient because they are linear in their parameters, b. But they are probably best thought of as empirical "mathematical French curve" descriptions of the relation of a response, y, to the explanatory variables, x. Polynomials equations function as extremely useful summaries of observed patterns in one's data, but they do not typically provide direct insight into chemical mechanisms that produce those patterns, and the fitted parameters, b, do not often have direct physical meanings. Their use is particularly appropriate where there is little a priori knowledge of mechanisms involved in a process that might aid in its description, and/or no such knowledge is really essential to achieving one's goals.

Sometimes, however, it is desirable (on the basis of possible reaction kinetics or for other reasons) to posit theoretical descriptions of process outputs in terms of explanatory variables. That is, physicochemical principles often lead (through differential or integral equation descriptions of a system) to equation forms for a response that, like the following

$$y = \frac{K_1 K_A K_B P_A P_B}{(1 + K_A P_A + K_B P_B)^2}$$

$$y = C_0 \exp(-Kt)$$

and

$$y = \frac{K_1 x}{1 + K_2 x}$$

are nonlinear in the parameters. Although such equations or models may be less tractable than empirical polynomial equations, the parameters involved more often than not *do have* direct physical interpretations. Further, when such a model can be verified as being an adequate description of a process (thereby confirming scientific understanding) and the parameters involved are estimated from process data, such mechanistic models can provide much safer extrapolations beyond an experimental region than the cruder empirical polynomial models.

The process of research in chemical systems is one of developing and testing different models for process behavior. Whether empirical or mechanistic models are involved, the discipline of statistics provides data-based tools for discrimination between competing possible models, parameter estimation, and model verification for use in this enterprise. In the case where empirical models are used, techniques associated with "linear" regression (linear least squares) are used, whereas in mechanistic modeling contexts "nonlinear" regression (nonlinear least squares) techniques most often are needed. In either case, the statistical tools are applied most fruitfully in iterative strategies such as that outlined in Fig. 4.26.

Reilly and Blau[34] and Chapter 16 of Box et al.[24] provide introductions to the general philosophy of using statistical methods in

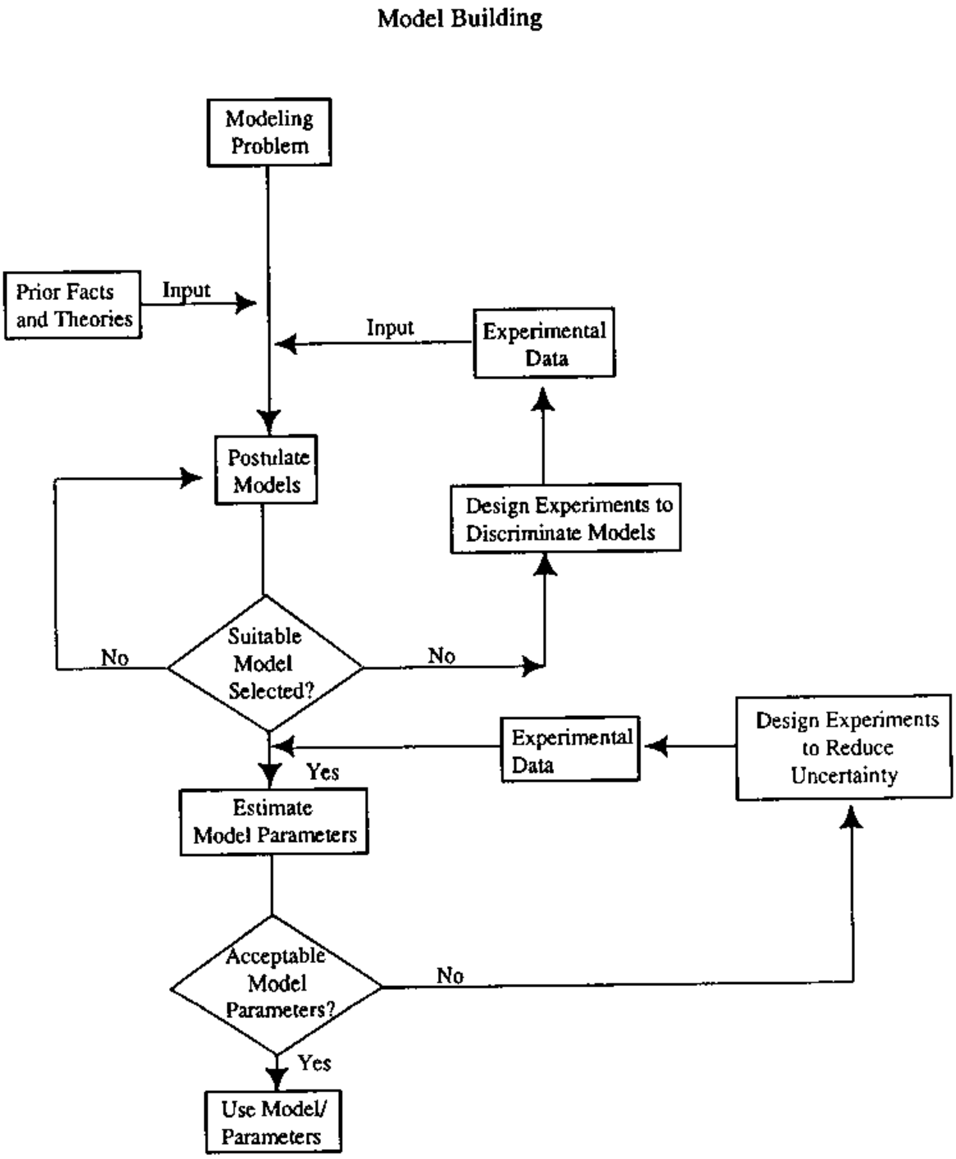

Fig. 4.26. An iterative model-building strategy. (*From "Simusolv, a Computer Program for Building Mathematical Models," G. Blau and K. Kuenker,* CAST Communications, *12, 1, 10–21 (1989). By permission.*)

mechanistic modeling contexts, as well as a number of useful references for further reading.

Fairly sophisticated and specialized statistical software is needed in the practical application of nonlinear regression methods to mechanistic modeling for industrial chemistry applications. The techniques implemented in such software are best discussed in Bates and Watts,[35] Bard,[36] and Reilly and Blau.[34]

MODERN QUALITY PHILOSOPHY AND THE DISCIPLINE OF STATISTICS

It is widely recognized that the well-being of modern business concerns, both within and outside the chemical sector, is closely related to corporate attitudes toward quality. The writing and corporate seminars of respected experts such as Deming,[37] Juran,[38,39] Crosby,[40] and Feigenbaum[41] all promote a modern business paradigm based on the importance of product and process quality and emphasizing the importance of continuous improvement. These emphases are applied not only to the creation of new products and delivery of existing products, but to all internal and external aspects of business and interaction with suppliers and customers. Such a *total quality* emphasis gives organizations the ability to compete in a global marketplace, and its proponents all point to the important role of management's leadership in the integration of quality and continuous improvement emphases into corporate life.

The discipline of statistics plays an important role in the total quality approach. Perhaps most fundamentally, the conceptual framework that it provides for recognizing and quantifying variation (itself almost a synonym for lack of quality), for using data to give insight into the operation of processes, and for experimentally probing for ways of improving processes is essential to the success of total quality management. Also, the regular enlightened use of the tools of statistical methods of data collection and analysis is the surest known path to the efficient implementation of total quality goals.

The whole gamut of statistical methods, from the simple to the highly sophisticated, is potentially applicable to the implementation of total quality objectives. See, for example, the books of Juran and Gryna,[42] Duncan,[10] Montgomery,[43] Feigenbaum,[41] and Scherkenbach[44] in this regard. The simplest methods, of course, have seen the most widely used. Ishikawa[45] and Kane[46] present some of the simplest of statistically related quality improvement tools, which have been widely embraced and have appeared as key components of many corporate quality improvement success stories. In addition to the run charts, histograms, and control charts illustrated earlier in this chapter, Ishikawa helped popularize the use of *Pareto charts, cause and effect* (or *fishbone*) *diagrams, flow charts,* and *scatterplots* in quality improvement projects.

Figure 4.27 illustrates a Pareto chart, which is a kind of bar graph intended to help distinguish the "important few" causes of quality problems from the "trivial many."

Cause and effect diagrams such as Fig. 4.28 are helpful tools in organizing a discussion of possible causes of waste and variation.

Flow charts such as Fig. 4.29 are another tool for looking at the steps involved in a work flow, and for stimulating and organizing a discussion of possible causes of variation and waste.

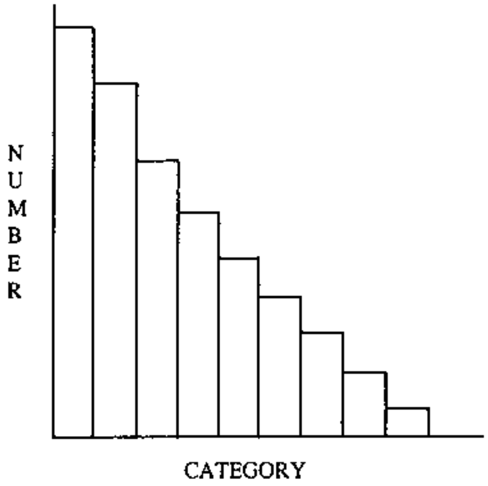

Fig. 4.27. A Pareto chart.

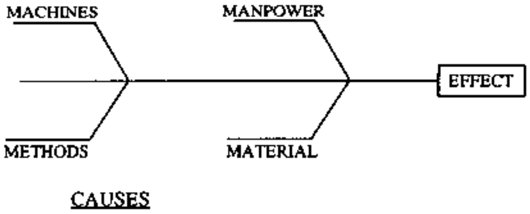

Fig. 4.28. A cause and effect diagram.

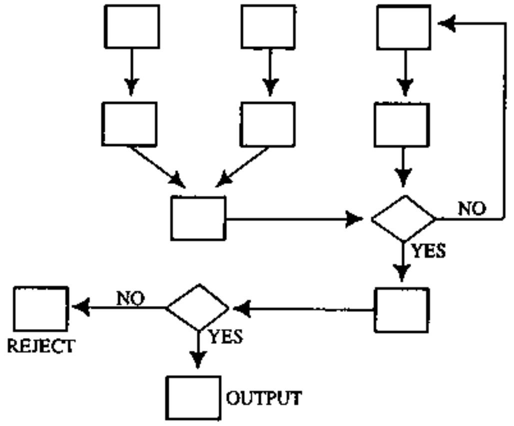

Fig. 4.29. A flow chart.

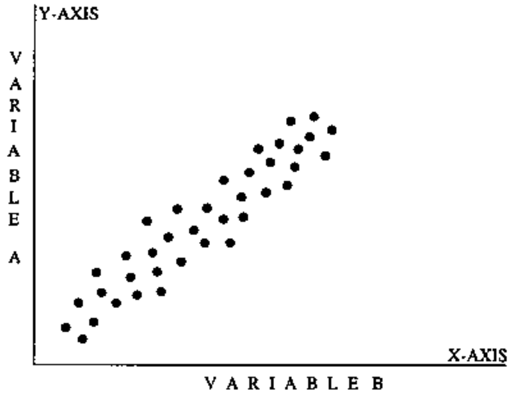

Fig. 4.30. Two scatterplots.

Scatterplots such as Fig. 4.30 provide an initial graphical look at the relationship between two variables, and can provide suggestions of possible patterns of causality (either between the two plotted variables or from a third one, potentially influencing both of the ones plotted).

It should be emphasized that although statistical methods like these simple tools may traditionally be most strongly associated with manufacturing applications, they have in recent years been shown to be highly effective in a variety of service and managerial decision-making applications as well. See, for example, Nolan and Provost[47] and Wheeler and Chambers.[48]

The adoption of statistically based corporate total-quality thinking and tools is, of course, easier said than done. The goal must be embraced by the entire organization. To be effective, the approach must be a part of all employees' daily work process. Such widespread cooperation in a total quality endeavor requires more than simple attendance at a training class on statistical methods. The total quality philosophy must be promoted at all levels of the organization, and proper use of appropriate tools must be guided and nurtured. The books of Scholtes,[49] Hradeskey,[50] Scherkenbach,[44] and Feigenbaum[41] discuss issues and approaches in the implementation of total quality programs.

CONCLUSION

We have tried in this chapter to give the reader the flavor of modern applied statistical methods and to illustrate their usefulness in the chemical industry. Details of their implementation have of necessity been reserved for further, more specialized reading, for which the interested reader is encouraged to consult the references given in this chapter. The bibliographies in Vardeman and Cornell,[51] Vardeman and David,[52] and Hahn and Meeker[53] provide an effective additional source of references for the topics discussed here in general terms.

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5

Safety Considerations in the Chemical Process Industries

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INTRODUCTION

In recent years there has been an increased emphasis on chemical process safety as a result of a number of serious accidents. Public awareness of these accidents has provided a driving force for industry to improve its safety record. Local and national governments are taking a hard look at safety in industry as a whole and the chemical industry in particular, and there has been an increasing amount of government regulation.

Although the chemical industry is one of the safest industries, its safety image in the eyes of the public is dismal, perhaps because sometimes when there is an accident in a chemical plant, it is spectacular and receives a great deal of attention. For many reasons, the public often associates the chemical industry with environmental problems and safety problems; and, unfortunately, all too often the negative image that goes with the problems is deserved.

Hazards from combustion and runaway reactions play a leading role in many chemical process accidents. Knowledge of these reactions is essential for the control of process hazards. Much of the damage and loss of life in chemical accidents results from a sudden release of material at high pressures, which may or may not result from fire; so it is important to understand how sudden pressure releases can occur. They can be due, for example, to ruptured high pressure tanks, runaway reactions, flammable vapor clouds, or pressure developed from external fire. Fires can cause severe damage from thermal radiation. Chemical releases from fires and pressure releases can form toxic clouds that can be dangerous to people over large areas. Static electricity often is a hidden actor in accidents. It is important to understand the reactive nature of the chemicals involved in a chemical facility.

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Chemical process safety involves both the technical and the management aspects of the chemical industry, and this chapter addresses both. It is not enough to be aware of how to predict the effect of process hazards and how to design systems to reduce the risks of these hazards. It also is important to consider how chemical process safety can be managed. Technical people at all levels have a degree of management responsibility, and can contribute to the overall management of safe plants.

Loss of containment due to mechanical failure or misoperation is not a major cause of chemical process accidents. The publication *One Hundred Largest Losses: A Thirty Year Review of Property Damage Losses in the Hydrocarbon-Chemical Industry*[1] cites loss of containment as the leading cause of property loss in the chemical process industries.

The term, "inherent" means "belonging by nature, or the essential character of something." An "inherently safe" plant is safe by its nature and by the way it is constituted.

No facilities can be completely "inherently safe," but they can be made "inherently safer" by careful examination of all aspects of plant design and management. It is possible to identify "inherently unsafe" equipment and management practices and try to avoid them. It has been found that the basic or root cause of most chemical process accidents can be traced to some failure of a management system. Human error plays an important role in many process accidents and is often closely related to problems with management systems. Major efforts are under way to address the potential problems of human error. By being aware of modern advances in design and management techniques, and putting these techniques into practice, it is possible to have facilities that are safer than ever.

The term "intrinsic" has a meaning similar to that of "inherent," but the common usage of "intrinsic" in the chemical industry usually means a protection technique related to electricity. Intrinsic safety is based on the restriction of electrical energy to a level below which sparking or heating effects cannot ignite an explosive atmosphere (Lees,[2] p. 513).

CONSIDERATIONS IN THE DESIGN AND OPERATION OF INHERENTLY SAFER PLANTS*

The design of chemical plants to be more nearly "inherently safe" has received a great deal of attention in recent years. This is due in part to the worldwide attention to safety issues in the chemical industry brought on by the gas release at the Union Carbide plant in Bhopal, India, in December 1984. This and the fairly frequent occurrence of other chemical plant incidents has raised the issue of chemical plant safety to a very high level of visibility and concern. The major factors which should be considered in the planning, design, and operation of chemical plants are described below. The reader is referred to the list of recommended supplementary reading at the end of the chapter for more detailed information.

Responsibility for Safety in Design and Operation

It is very important that responsibility for the safe design and operation of a plant be clearly defined in the early stages. This means that competent and experienced people should be made responsible and held accountable for decisions made from the start of plant design on through plant start-up and operation.

Review of Design Alternatives

Hazards should be considered and eliminated in the process development stage where possible. This would include considerations of alternative processes, reduction or elimination of hazardous chemicals, site selection, etc. By the time the process is developed, the process designers already have major constraints imposed on them.

Hazards should also be identified and removed or reduced early in the design.

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Adding protective equipment at the end of the design or after the plant is operating can be expensive and not entirely satisfactory.

Allowing time in the early stages of design for critical reviews and evaluation of alternatives would involve studies such as an early hazard and operability (HAZOP) study, using flowsheets, before final design begins.[4] Fault tree analysis," QRA (quantitative risk assessment), checklists, audits, and other review and checking techniques can also be very helpful. These techniques are extensively discussed in the technical literature and will not be discussed in detail here.

Emergency Planning

Emergency planning is primarily for the protection of plant personnel and people in nearby areas and the environment that could be affected by plant problems. It should be considered early in the design and should be coordinated with the existing site emergency plan.

Emergency planning includes tornado and storm shelters, flood protection, earthquakes, proximity to public areas, and safe exit routes. It also includes the effect that an emergency in the "new process" would have on other plants, and the effect that an emergency in another plant would have on the new process. The effects of potential spills on waterways and aquifers should be considered.

Emergency response planning is discussed fully in Chapter 6.

Placement of Process and Storage Areas

The Bhopal plant of Union Carbide was built originally 1.5 miles from the nearest housing (see below under "Case Histories"). Over time, a residential area grew up next to the plant. This demonstrates the need to prevent hazardous plants from being located close to residential areas and to prevent residential areas from being established near such plants.[4] If possible, the cost of a plant should include an adequate buffer zone unless other means can be provided to ensure that the public will not build adjacent to the plant. The nature and size of this buffer zone depend on many factors, including the amount and type of chemicals stored and used.

Storage of Hazardous Materials

The best way to minimize releases of a hazardous or flammable material is to have less of it around. In the Flixborough disaster[2] on June 1, 1974, the process involved the oxidation of cyclohexane to cyclohexanone by air (with added nitrogen) in the presence of a catalyst (see below under "Case Histories"). The cyclohexanone was converted to caprolactam, which is the basic raw material for Nylon 6. The reaction product from the final reactor contained approximately 94 percent unreacted cyclohexane at 155°C and over 200 psig. The holdup in the reactors was about 240,000 lb, of which about 80,000 lb escaped. It is estimated that about 20,000 to 60,000 lb actually was involved in the explosion. The resulting large unconfined vapor cloud explosion (or explosions—there may have been two) and fire killed 28 people and injured 36 at the plant and many more in the surrounding area, demolished a large chemical plant, and damaged 1821 houses and 167 shops. The very large amount of flammable liquid well above its boiling and flash points contributed greatly to the extreme severity of the disaster (Lees,[2] p. 863).

The results of the Flixborough investigation make it clear that the large inventory of flammable material in the process plant contributed to the scale of the disaster. It is concluded that "limitations of inventory (of flammable materials) should be taken as specific design objectives in major hazard installations." It should be noted that reduction of inventory may require more frequent and smaller shipments, and this would entail more chances for errors in connecting and reconnecting. These possibly "negative" benefits should also be analyzed. Quantitative risk analysis of storage facilities has revealed solutions that may run counter to intuition.[5]

For example, contrary to popular opinion, reducing inventories in tanks of hazardous materials does little to reduce risk in situations where most of the exposure arises from the number and extent of valves, nozzles, and lines connecting the tank. Removing tanks from the service altogether, on the other hand, helps.

A large tank may offer greater safety than several small tanks of the same aggregate capacity because there are fewer associated nozzles and lines. Also, a large tank is inherently more robust, or can economically be made more robust by deliberate overdesign, than is a small tank and therefore is more resistant to external damage. On the other hand, if the larger tank has larger connecting lines, the relative risk may be greater if release rates through the larger lines increase the risk more than the tank's inherently greater strength reduces it. In transportation of hazardous materials, the benefits of head shields and shelf couplers have been shown through quantitative risk assessment. Maintaining tank car integrity in a derailment is often the most important line of defense in transportation of hazardous materials.

Liquefied Gas Storage

Usually, leaks of liquefied gases are much less serious if such gases are stored refrigerated at low temperatures and pressures than if they are stored at ambient temperatures under pressure. A leak of a volatile liquid held at atmospheric temperature and pressure results in only a relatively slow evaporation of the liquid. Escape of a refrigerated liquefied gas at atmospheric pressure gives some initial flashoff, and then it evaporates at a rate which is relatively slow but faster than the first case, depending on weather conditions.

Loss of containment of a liquefied gas under pressure and at atmospheric temperature, however, causes immediate flashing of a large proportion of the gas, followed by slower evaporation of the residue. This is usually a more serious case than if a refrigerated tank is used. The hazard from a gas under pressure is normally much less in terms of the amount of material stored, but the physical energy released if a confined explosion occurs at high pressure is large.

Use of Open Structures

There are many examples of serious fires and explosions that probably resulted in part from handling moderate to large quantities of flammable or combustible liquids and liquefied flammable gases inside of enclosed structures. If a sufficient quantity of flammable mixture should ignite inside an ordinary chemical processing building, it is highly probable an explosion will occur that will seriously damage the building. For this reason, processing equipment is often installed in a structure without walls, usually called an "open structure." This permits effective ventilation by normal wind currents and aids the dispersion of any vapors that do escape. If ignition of gas occurs within the structure, the absence of walls minimizes the pressure developed from the combustion and the probability of flying shrapnel from a shattered structure.[6]

Substantial explosion damage will be done to a building by combustion of a surprisingly small quantity of a flammable gas–air mixture. If there is an explosion of a flammable gas–air mixture in a building where the flammable gas mixture occupies a space equal to only one or two percent of the building volume, the building may be seriously damaged if it does not have adequate explosion venting. This is because most buildings will suffer substantial structural damage from an internal pressure appreciably less than 1 psi (0.07 bar). Thus, a building does not need to be "full" or even close to "full" of a flammable mixture for a building explosion to occur that can cause considerable damage.

In 1950 a serious hydrocarbon explosion occurred in an enclosed chemical processing unit of The Dow Chemical Company. It was instrumental in causing Dow to establish a policy of using open structures for chemical processes which use substantial quantities of flammable liquids and liquefied flammable gases, and combustible liquids above their flash points.

Need to Understand Reactive Chemicals Systems

The main business of most chemical companies is to manufacture products through the control of reactive chemicals. The reactivity that makes chemicals useful can also make them hazardous. Therefore, it is essential that a process designer understand the nature of the reactive chemicals involved in his or her process.

Usually reactions are carried out without mishaps, but sometimes chemical reactions get out of control for many reasons, including:

1. Wrong raw material used.
2. Operating conditions changed.
3. Time delays unanticipated.
4. Equipment failure.
5. Reactants contaminated.
6. Materials of construction wrong.
7. Misoperation.
8. External fire.

Such mishaps can be worse if the chemistry is not fully understood. A chemical plant can be "inherently safer" only if knowledge of the reactive chemicals systems is carefully used in its design.

Reactive Hazard Evaluations. Reactive hazard evaluations should be made on all new processes, and on all existing processes on a periodic basis. There is no substitute for experience, good judgment, and good data in evaluating potential hazards. Reviews should include:

- Process chemistry:
  Reactions
  Potential pressure buildup
  Intermediate streams
  Side reactions
  Heat of reaction
- Reactive chemicals test data for evidence of:
  Flammability characteristics
  Shock sensitivity
  Exotherms
  Other evidence of instability
- Planned operation of process, especially:
  Upsets
  Delays
  Critical instruments and controls
  Mode of failure
  Redundancy
  Worst credible case scenarios

Worst-Case Thinking. At every point in the operation, the process designer should conceive of the *worst* possible combination of circumstances that could *realistically* exist, such as:

Air leakage
Deadheaded pumps
Instrument failure
Loss of agitation
Loss of compressed air
Loss of cooling water
Plugged lines
Power failure
Raw material impurities
Wrong combination or amount of reactants
Wrong valve position

An engineering evaluation should then be made of the worst-case consequences, with the goal that the plant will be safe even if the worst case occurs. A HAZOP study could be used to help accomplish "worst-case thinking." When the process designers know what the worst-case conditions are, they should:

- Try to avoid worst-case conditions.
- Be sure adequate redundancy exists.
- Identify and implement lines of defense:
  Preventive measures.
  Corrective measures.
  Sometimes, as a last resort, containment or, possibly, abandoning the process if the hazard is unacceptable.

It is important to note that the worst case should be something that is realistic, not something that is conceivable but which may be unreasonable, such as a chemical plant far from any airport being struck by a large airplane.

Reactive Chemicals Testing. Much reactive chemical information involves thermal stability and the determination of:

- The temperature at which an exothermic reaction starts.
- The rate of reaction as a function of temperature.
- Heat generated per unit of material.

The information can be obtained by a variety of types of laboratory tests and by thermodynamic calculations, although reliable kinetic data cannot usually be obtained solely by calculations.

Losses from Dust Explosions

Most organic solids, most metals, and some combustible inorganic salts can form explosive dust clouds. In order to have a dust explosion, it is necessary to satisfy certain conditions:

- Suitably sized dust particles.
- Sufficient source of ignition energy.
- Dust concentration within explosive limits.
- Explosible dust.

If an explosive dust in air that meets the above criteria occurs in a process, an explosion should be considered as inevitable. The process designer should take into account the possibility of dust explosions and design accordingly.

In dust explosions the combustion process is very rapid. The flame speed is high compared to that in gas deflagrations. Detonations normally do not occur in dust explosions in industrial plants.

The sequence of events in a serious industrial dust explosion is often as follows:

1. A primary explosion occurs in part of a plant, causing an air disturbance.
2. The air disturbance disperses dust and causes a secondary explosion which is often more destructive than the primary explosion.

If the occurrence of a flammable (explosive) dust is inevitable in a particular process, several design alternatives or combinations of alternatives are available:

- Containment (maximum pressure of a dust explosion is usually below 120 to 150 psig).
- Explosion venting to a safe place.
- Inerting (most organic dusts are nonflammable in atmospheres containing less than about 10% oxygen).
- Suppression.

A fundamental solution to the dust explosion problem is to use a wet process so that dust suspensions do not occur at all. However, the process must be wet enough to be effective. Some dusts with a high moisture content can still be ignited.

Dust concentrations in major equipment may be designed to be below the lower flammable limit, but this often cannot be depended on in actual operation. Dust concentrations cannot be safely designed to be above an upper flammable limit because such a limit is ill-defined.[2]

For a large number of flammable dusts, the lower explosion limit lies between 0.02 and 0.06 kg/m.[3] The upper explosion limit is in the range of 2 to 6 kg/m,[3] but this number is of limited importance.

A small amount of flammable gas or vapor mixed in with a flammable dust can cause an explosive mixture to be formed even if both are at concentrations below the explosive range by themselves. These mixtures are called "hybrid" mixtures. The ignition energy to ignite a hybrid mixture is often less than that required for the flammable dust by itself.

Venting is only suitable if there is a safe discharge for the material vented. Whenever an explosion relief venting device is activated, it may be expected that a tongue of flame containing some unburned dust will first be ejected. The unburned dust will be ignited as it flows out the vent and can produce a large fireball that will extend outward, upward, and downward from the vent. It is essential for protection of personnel that venting is to an open place not used by people. If a duct must be used, the explosion pressure in the enclosure will be increased considerably. Therefore, particular attention must be paid to the design of the enclosure in which the explosion could take place.

The NFPA 68 guide issued in 1988[7] has nomographs which can be used to select relief areas required for combustible dusts when test data on the dusts are available. The nomographs in NFPA 68 are by far the preferred way to design dust exlosion relief devices.

Relief venting to reduce dust explosion pressure requires the equipment to be protected to have a certain minimum strength. If the enclosure strength is too low, the enclosure will be damaged or destroyed before the explosion relief device can function. NFPA 68[7] states that the strength of the enclosure should exceed the vent relief pressure by at least 0.35 psi. For industrial equipment such as dryers and baghouses, it is often desirable to have considerably more strength built into the structure to reduce the size of the vent area required. Also, the supporting structure for the enclosure must be strong enough to withstand any reaction forces developed as a result of operation of the vent.

Inerting is a very good preventive measure against dust explosions. The maximum oxygen concentration at which dust explosions are "just not possible" cannot be predicted accurately, as it depends on the nature of the combustible material; testing is usually required. It has been found that in an atmosphere of 10 percent oxygen and 90 percent nitrogen, most combustible organic dusts are no longer explosive. To allow a safety margin, it is good industrial practice to maintain oxygen concentrations below 8 percent. For metal dusts, the allowable oxygen content is about 4 percent.[7]

Inerting leads to the possibility of asphyxiation by operating personnel if they should be exposed to the inert gas. Strict precautions must be taken to prevent exposure of personnel to inerting atmospheres.

Explosion suppression systems are designed to prevent the creation of unacceptably high pressure by explosions within enclosures that are not designed to withstand the maximum explosion pressure.[8] They can protect process plants against damage and also protect operating personnel in the area. Explosion suppression systems restrict and confine the flames in a very early stage of the explosion. Suppression systems require more maintenance than do relief venting devices. Explosion suppression systems are made by only a few manufacturers and are quite expensive. This may be the reason why this type of safeguard has not been as widely used in industry as one might expect, although its effectiveness has been proved by much practical experience.

Explosion suppression is a proven technology and should be considered as a candidate for explosion protection. The NFPA has published a standard reference on explosion-suppression protection.[9] Manufacturers should be consulted on design, installation, and maintenance.

Even with explosion suppression, it is common for the explosion pressure to reach one atmosphere before it is suppressed. The added pressure surge from the injection of the suppressing agent must also be considered. Therefore, sufficient mechanical strength is always required for enclosures protected by explosion suppression.

Substitution of Less Hazardous Materials

It may be possible to substitute a less hazardous material for a hazardous product. For example, bleaching powder can be used in swimming pools instead of chlorine.[4] Benzoyl peroxide, an initiator used in polymerization reactions, is available as a paste in water, which makes it much less shock-sensitive than the dry form. Other substitutions that have been used to make transportation, storage, and processing safer include:

- Shipping ethylene dibromide instead of bromine.
- Shipping ethyl benzene instead of ethylene.
- Storing and shipping chlorinated hydrocarbons instead of chlorine.

- Storing and shipping methanol instead of liquefied methane.
- Replacing flammable refrigerants by halogenated hydrocarbons that are known to have acceptable environmental effects.
- Storing and shipping carbon tetrachloride instead of anhydrous hydrochloric acid. The CCl_4 is burned with supplemental fuel to make HCl on demand at the user's site.
- Using magnesium hydroxide slurry to control pH instead of concentrated sodium hydroxide solutions, which are corrosive to humans and relatively hazardous to handle.
- Using pellets of flammable solids instead of finely divided solids to reduce dust explosion problems.

The use of substitutes may appear to be more costly. The added safety provided by substitutes may make their use worthwhile and can in some cases actually lower the true cost of the project when the overall impact on the process, surrounding areas, and shipping is considered.

Substitutes should be employed only if it is known that overall risk will be reduced. Inadequately tested processes may introduce unrecognized health, safety, and environmental problems.

Catastrophic Failure of Engineering Materials[10–12]

Uniform corrosion of metals can usually be predicted from lab tests or experience. Corrosion allowances which will require thicker metal can be called for in the design of equipment when uniform corrosion rates are expected.

The most important materials failure to avoid in the design of metal equipment is *sudden catastrophic failure*. This occurs when the material fractures under impulse instead of bending. Catastrophic failure can cause complete destruction of piping or equipment, and can result in explosions, huge spills, and consequent fires. Causes of some of the more common types of catastrophic failures are:

- Low temperature brittleness.
- Stress corrosion cracking.
- Hydrogen embrittlement.
- High penetration rates involving pitting and corrosion.
- Fatigue failure.
- Creep.
- Mechanical shock.
- Thermal shock.
- High rates of temperature change in brittle materials.
- Zinc embrittlement of stainless steel.
- Caustic embrittlement.
- Nitrate stress corrosion.

Redundant Instrumentation and Control Systems[13]

Computer-controlled chemical plants are becoming the rule rather than the exception. As a result, it is possible to measure more variables and get more process information than ever, and chemical plants can be made "inherently safer" than ever before. However, it must be kept in mind that instruments and control components *will* fail. It is not a question of *if* they will fail, but *when* they will fail, and what the consequences will be. Therefore, the question of redundancy must be thoroughly considered. *The system must be designed so that when failure occurs, the plant is still safe.*

Redundant measurement means obtaining the same process information with two like measurements or two measurements using different principles. Redundant measurements can be *calculated* or *inferred* measurements. Two like measurements would be two pressure transmitters, two temperature measurements, two level measurements, and so on. An example of inferred measurement would be measuring temperature in a boiler and, using a pressure measurement and vapor pressure tables, determining the pressure to check an actual temperature measurement.

A continuous analog signal that is continuously monitored by a digital computer is generally preferable to a single point or single switch such as a high level switch or high pressure switch. A continuous analog measurement can give valuable information about what the value is *now* and can be used to compute values or compare with other measurements. Analog inputs may be visual, and one can see what the set point is and what the actual value is. The software security system should determine who changes set points, and should not be easy to defeat.

A single point (digital) signal only determines whether switch contacts are open or not. It can indicate that something has happened, but not that it is going to happen. It cannot provide information to anticipate a problem that may be building up or a history about why the problem happened. Single point signals are easy to defeat. Some single point measurements are necessary, such as fire eyes, backup high level switches, and so on.

As a rule, it is best to avoid:

- Both pressure transmitters on the same tap.
- Both temperature measuring devices in the same well.
- Both level transmitters on the same tap or equalizing line.
- Any two measurements installed so that the same problem can cause a loss of both measurements.

It is a good idea to use devices that use different principles to measure the same variable, if possible.

An alarm should sound any time redundant inputs disagree. In many cases, the operating personnel will have to decide what to do. In some cases the computer control system will have to decide by itself what to do if redundant inputs disagree.

The more hazardous the process, the more it is necessary to use multiple sensors for flow, temperature, pressure, and other variables.

Since it must be assumed that all measuring devices will fail, they should fail to an alarm state. If a device fails to a non-alarm condition, there can be serious problems. If a device fails to an alarm condition, but there is really not an alarm condition, it is also serious, but generally not as serious as if it fails to a non-alarm condition, which can provide a false sense of security.

Usually it is assumed that two devices measuring the same thing will not fail independently at the same time. If this is assumed, one can consider the effects of different levels of redundancy:

Number of Inputs	*Consequence*
One	Failure provides no information on whether there is an alarm condition or not.
Two	Failure of one device shows that there is a disagreement, but without more information, it cannot be determined whether there is an alarm condition or not. More information is needed; the operator could "vote" if there is time.
Three	Failure of one device leaves two that work; there should be no ambiguity on whether there is an alarm condition or not.

Pressure Relief Systems

The design of relief systems involves, in general, the following steps:

1. Generate scenario. What could reasonably happen that could cause high pressures? This could be fire, runaway reactions, phase changes, generation of gases or vapors, leaks from high pressure sources, etc.
2. Calculate the duty requirements—the lb/hr of material that has to be vented, and its physical condition (temperature, pressure, ratio of vapor to liquid, physical properties). This is a rather involved calculational procedure.
3. Calculate the relief area required based on the duty, inlet and outlet piping, and downstream equipment. This is also a rather involved calculational procedure.
4. Choose the relief device to be specified from vendor information.

A group of chemical companies joined together in 1976 to investigate emergency relief systems. This later resulted in the formation of The Design Institute for Emergency Relief Systems (DIERS), a consortium of 29 companies under the auspices of the AIChE. DIERS was funded with $1.6 million to test existing methods for emergency relief system design and to "fill in the gaps" in technology in this area, especially in the design of emergency relief systems to handle runaway reactions.[14] DIERS completed contract work and disbanded in 1984.

Huff was the first to publish details of a comprehensive two-phase flow computational method for sizing emergency relief devices, which, with refinements, has been in use for over a decade.[15–18] The most significant theoretical and experimental finding of the DIERS program was the ease with which two-phase vapor–liquid flow can occur during an emergency relief situation. *The occurrence of two-phase flow during runaway reaction relief almost always requires a larger relief system than does single-phase flow vapor venting.* The required area for two-phase flow venting can be from two to much more than two times larger to provide adequate relief than if vapor-only venting occurs.[15] Failure to recognize this can result in drastically undersized relief systems that will not provide the intended protection.

Two-phase vapor–liquid flow of the type that can affect relief system design occurs as a result of vaporization and gas generation during a runaway reaction or in many liquid systems subjected to fire (especially tanks that are nearly full). Boiling can take place throughout the entire volume of liquid, not just at the surface. Trapped bubbles, retarded by viscosity and the nature of the fluid, reduce the effective density of the fluid and cause the liquid surface to be raised. When it reaches the height of the relief device, two-phase flow results. Fauske and Leung[19] described test equipment that can be used to help determine the design of pressure relief systems for runaway reactions that often result in two- or three-phase flow.

Safe and Rapid Isolation of Piping Systems and Equipment

It should be possible to easily isolate fluids in equipment and piping when potentially dangerous situations occur. This can be done using emergency block valves, or EBVs. An EBV is a manually or remotely actuated protective device which should be used to provide manual or remote shutoff of uncontrolled gas or liquid flow releases. EBVs can be used to isolate a vessel or other equipment, or an entire unit operation. Manual valves are often used on piping at block limits where it is unlikely that there would be a hazard to personnel if an accident occurs. Remotely controlled EBVs are recommended on tanks and on piping in areas where it may be hazardous for personnel in case of an accident, or where quick response may be necessary.

EBVs used on tanks should be as close as possible to the tank flange and not in the piping away from the tank. In cases where EBVs may be exposed to fire, the valve and valve operating mechanism must be fire-safe.

In one design case involving large quantities of highly flammable materials, a HAZOP showed that suitably located EBVs were one of the most important features that could be installed to reduce the possibility of loss of containment and serious fire and explosions.

Piping, Gaskets, and Valves

Piping.[20] All-welded pipe and flanges should be used in "inherently safer" chemical plants. Since flanges are a potential source of leaks, as few flanges as possible should be used. One, of course, has to be realistic: if it is necessary to clean out pipes, flanges must be provided at appropriate places to make it possible. Also, enough flanges must be provided to make maintenance and installation of new equipment reasonably easy.

Threaded piping should be avoided for toxic and flammable materials. It is very difficult to make threaded fittings leakproof, especially with alloys such as stainless steel. Where threaded piping is necessary, use schedule 80 pipe as a minimum. Pipe nipples should never be less than schedule 80.

Pipe support design should be given special attention. It may be desirable to increase pipe diameter to provide more pipe strength and rigidity and make it possible to have greater distance between supports. Normally, in chemical plants, it is not desirable to use piping less than one-half inch in diameter and preferably not less than one inch in diameter, even if the flow requirements permit a smaller pipe, except for special cases. Pipe smaller than one-half inch has insufficient strength and rigidity to be supported at reasonable intervals. Tubing, properly supported, should normally be used for anything smaller than one-half inch. Tubing is not as fragile as pipe in small sizes. It can be bent so that the number of fittings required is reduced. If it is necessary to use smaller pipe, or small tubing, special provisions should be made for its support and mechanical protection. Also, consideration should be given to using schedule 80 or schedule 160 pipe if small pipe is required to provide extra mechanical strength, even if the fluid pressure does not require it.

Gaskets.[21] Gaskets are among the weakest elements of most chemical plants. Blown-out or leaky gaskets have been implicated in many serious incidents. A leak at a flange can have a torch effect if it is ignited. A fire of this type was considered as a possible cause of the Flixborough disaster.[2] (See below under "Case Histories.")

Modern technology makes it possible to greatly reduce the incidence of gasket failure by the use of spiral wound gaskets. These are sold by several manufacturers, including Flexitallic, Parker Spirotallic, Garlock, and Lamons. A spiral wound gasket is considered the safest gasket type available because of the metal inner and outer rings which contain the filler material at the ID and OD. This sturdy construction of a spiral wound gasket does not permit blowout of the gasket material, which is the potential for gaskets made of sheet material.

Bolting with spiral wound gaskets is very important. *Use of plain carbon steel bolts (such as A307 Grade B) with spiral wound gaskets is not permitted.* They are not strong enough. High strength alloy bolts such as A193-B7 (contains Cr and Mo) with A194 heavy hex nuts should be used. To properly seal spiral wound gaskets, it is necessary to tighten the bolts to specified torque limits, which are generally higher than those of conventional gaskets. Compared to conventional gaskets, spiral wound gaskets require better flange finish, heavier flanges, and better flange alignment.

Valves. It is desirable and "inherently safer" to use firesafe valves whenever it is necessary to isolate flammable or combustible fluids in a pipeline or a tank or other type of equipment. Firesafe valves should be considered for handling most fluids that are highly flammable, highly toxic, or highly corrosive and that cannot be allowed to escape into the environment.

Firesafe valves should be used to isolate reactors, storage vessels, and pipelines. They can be used wherever EBVs are required. With the increase in popularity of automated plants, quarter-turn valves are very popular and are used in most installations. The only common quarter-turn valves that are available as completely firesafe valves are ball valves and high-performance butterfly valves. For special purposes, there are other special firesafe valves.

Plastic Pipe and Plastic-Lined Pipe. Plastic-lined pipe is excellent for many uses, such as highly corrosive applications, or where sticking is a problem, and where ease of cleaning is a factor. It is often the cheapest alternative. However, if there is a fire, there may be "instant holes" at each flange because the plastic will melt away, leaving a gap. Therefore, plastic-lined pipe should not ordinarily be used for flammable materials that must be contained in case of a fire. An exception to this is a firesafe plastic-lined pipe system such as that made by the Resistoflex Corp., which provides a metal ring between each flange that will make plastic-lined pipe firesafe. The pipe will probably have to be replaced after a fire, but the contents of the pipe will be contained during a fire.

In general, all types of solid plastic or glass-reinforced plastic pipe should be avoided, if possible, with flammable liquids. Compared to metal, plastic piping:

- Will melt and burn easier.
- Is more fragile and can be easily mechanically damaged.
- Is harder to support adequately.

Plastic pipe should be used with appropriate judgment.

Avoidance of Inherently Unsafe Equipment

Some equipment items can be regarded as "inherently unsafe" for use in flammable or toxic service and should be avoided if possible. These items include a variety of devices.

Glass and transparent devices, such as sight glasses, bull's-eyes, sightports, rotameters, and glass and transparent plastic piping and fittings, may be hazardous. Glass devices are sensitive to heat and shock. Transparent plastic devices may be resistant to shock, but are not resistant to high temperatures. If they fail in hazardous service, severe property damage and personnel injury can result. The guidelines to follow are:

1. If broken, would they release flammable material?
2. If broken, would they expose personnel to toxic or corrosive materials?

Flexible or expansion joints in piping should be eliminated wherever possible. Flexible joints and expansion joints are any corrugated or flexible transition devices designed to minimize or isolate the effects of:

- Thermal expansion
- Vibration
- Differential settling
- Pumping surges
- Wear
- Load stresses
- Other unusual conditions

The need for flexible joints sometimes can be eliminated by proper design so that solid pipe will be able to handle misalignment, thermal expansion, and so on, by bending slightly. In many cases electronic load cells can be used to accurately weigh large reactors and process tanks that may have pipes attached to them, with no flexible or expansion joints. This is done by cantilevering the pipes to the equipment using sufficient runs of straight horizontal unsupported pipe with 90° elbows to take up movements and vibration without interfering significantly with the operation of the load cells.

Flexible joints should not be used as a correction for piping errors or to correct misalignment.

Pumps for Hazardous Service

A wide variety of excellent pumps are available in the chemical industry. It is sometimes a problem to choose the best from the large number available. This discussion will be limited to centrifugal pumps. Assuming that one has sized the pump, decided on a centrifugal pump, and chosen a suitable list of vendors, the main choices involve (1) metallurgy (2) seal-less pumps versus conventional centrifugal pumps, and (3) type of seals for conventional pumps.

Metallurgy.[22] Cast iron should not be used for flammable or hazardous service. The minimum metallurgy for centrifugal pumps for hazardous or flammable materials is cast ductile iron, type ASTM A 395, having an ultimate tensile strength of about 60,000 psi.

Seal-less Pumps.[23] The most common maintenance problem with centrifugal pumps is with the seals. Seals can be essentially eliminated with seal-less pumps. Seal-less pumps are manufactured in two basic types: canned motor and magnetic drive. Magnetic drive pumps have thicker "cans," which hold in the process fluid and the clearances between the internal rotor and "can" are greater compared to canned motor pumps. Seal-less pumps are becoming very popular and are widely used in the chemical industry. Mechanical seal problems account for most of the pump repairs in a chemical plant, with bearing failures a distant second. The absence of an external motor (on canned pumps) and a seal is appealing to those experienced with mechanical seal pumps. However, it cannot be assumed that just because there is no seal, seal-less pumps are always safer than pumps with seals, even with the advanced technology now available in seal-less pumps. Seal-less pumps must be used with considerable caution when handling hazardous or flammable liquids. A mistreated seal-less pump can rupture with potentially serious results. The "can" can fail if valves on both sides of the pump are closed, and the fluid in the pump expands because of heating up from a cold condition with the pump off, or if the pump is started up under these conditions. If the pump is run dry for even a short time, the bearings can be ruined. Seal-less pumps, especially canned motor pumps, produce a significant amount of heat because nearly all the electrical energy lost in the system is absorbed by the fluid being pumped. *If this heat cannot be properly dissipated, the fluid will heat up with possibly severe consequences.* Considerable care must be used in installing a seal-less pump to be sure that misoperations cannot occur.

Properly installed and maintained, seal-less pumps, especially magnetic drive pumps, offer an economical and safe way to minimize hazards and leaks of hazardous liquids.

TECHNICAL MANAGEMENT OF CHEMICAL PROCESS SAFETY

Although understanding and using sound technology is important in designing and operating safe process plants, technology is not enough. As the chemical process industries have developed more sophisticated ways to improve process safety, safety management systems have been introduced to make process safety engineering activities more effective. The following is a brief summary of a recent approach to the technical management of chemical process safety.[24]

Twelve process safety elements have been identified as important in the context of plant design, construction, start-up, operation, maintenance, modification, and decommissioning. This does not include personnel safety, transportation issues, chronic releases to the environment, or community response, which are separate and important issues. Process safety management must deal with each element. Even the best companies, with the best safety records, have room for improvement.

1. *Accountability.* Accountability begins with a clear, explicit and reasonably specific statement of a company's expectations, objectives, and goals. Example: "Process safety audits must be conducted based on the relative risk involved."

2. *Process Knowledge and Documentation.* Capturing process knowledge is a foundation upon which many aspects of a process safety program are built. This is sometimes referred to as "company memory." Preserving this knowledge and making it available within a company are important for process safety for a number of reasons, including:

- Keeping a record of design conditions and materials of construction to help ensure that operations remain faithful to the original intent.
- Providing a basis for understanding how and why the process should be operated a certain way.
- Making it possible to pass information from older to younger workers.
- Providing a baseline for process changes.
- Recording causes of incidents and accidents and corrective action for future guidance.

3. *Process Safety Reviews for Capital Projects.* The need for process safety reviews of capital projects, whether new or revised facilities, has been a recognized feature of engineering organizations. These reviews must be comprehensive and systematic. It is best to do reviews early to avoid costly modifications later. Not only do process hazards need to be identified and addressed by the design, but broader issues should be considered, such

as:

- Is the company prepared to accept the hazards and risks of this project?
- Is the location appropriate?

4. *Process Risk Management.* Process risk management involves the systematic identification, evaluation, and control of potential losses that may arise in existing operating facilities from events such as fires, explosions, toxic releases, runaway reactions, or natural disasters. If risks are not identified, they cannot be considered. Whether resulting losses are measured in terms of direct costs, impacts on employees and/or the public, property or environmental damage, lost business, or various liabilities, the possibility of experiencing such losses is considered a risk. When risks have been identified, it is possible to plan for their reduction, and it can be determined whether the remaining, or residual, risk is acceptable. Risk can never be entirely eliminated. It is the purpose of this component of risk management to manage the risks that remain after implementation of risk controls.

5. *Management of Change.* Changes to process facilities are necessary for many reasons. Change includes all modifications to equipment, procedures, and organizations that may affect process safety. Normal operation of a process should be within defined safe limits; operation outside of these limits should require review and approval. Replacement personnel should be trained before moves of people are made. There should be no difference between things to consider for changes intended to be permanent and changes that have a limited life, that is, are "temporary" in nature. A hazard will proceed to an incident whether the change is permanent or temporary. In any operation, situations arise that were not foreseen. To assure that these deviations from normal practice do not create unacceptable risks, it is important to have a variance procedure incorporated into the management system.

6. *Process and Equipment Integrity.* Equipment used to handle or process hazardous materials should control the risk of releases and other accidents. Management systems should ensure that equipment is designed properly and constructed and installed according to the design. Components of the process and equipment integrity element include: reliability engineering, materials of construction, inspection procedures, installation procedures, preventive maintenance, and maintenance procedures. It is very important that a program of tests and inspections be available to detect impending failures and mitigate their potential before they can develop into more serious failures.

7. *Incident Investigation.* Incidents can be defined broadly as unplanned events with undesirable consequences. Incident investigation is the management process by which the underlying causes of incidents are uncovered and steps are taken to prevent similar incidents. Almost always, it has been found that process safety incidents are a result of some failure of the management system, which, had it functioned properly, could have prevented the incident. Incident investigations should identify all underlying causes and management system failures. It is not enough to discover the immediate cause, such as operator error, but the investigation should go deeper and find out why the operator made the error and possibly discover training and equipment deficiencies. The incident investigation should report facts and conclusions and make recommendations.

8. *Training and Performance.* Training is an essential part of any process safety management program. Proper training of personnel is an absolute requirement for keeping complex process equipment and machinery operating safely. Good training programs tell the student not just what to do, but also how to do it and why it is important. Teaching should be a high-priority task. There should be specific criteria for instructor selection. It is not enough to know the subject, although that is important; the teacher should have good presentation skills. The effectiveness of training should be evaluated regularly to determine the effectiveness of the instructors and the performance of the students.

9. *Human factors (Ergonomics).* Human factors or ergonomics refers to human characteristics that must be considered in designing technical systems and equipment so that they can be used safely and efficiently. Anything that increases the difficulty of an operator's job may result in errors if shortcuts are taken. Such shortcuts may work under normal conditions, but unacceptable in upset or abnormal conditions. The process safety management system should address the human–hardware interface, in both automated and manual processes. Safety reviews and HAZOP studies should include exmination of the human–hardware interface. Even in a nearly perfectly designed situation, operators will make occasional errors. Consideration should be given to involving specialized experts in human error assessment, especially in processes involving high potential risks and extensive operator control.

10. *Company Standards, Codes, and Regulations.* Company standards, codes, and regulations are intended to communicate minimum acceptable safe practice and to assure that all operating locations within the company share a common approach to process safety. All U.S. chemical plants are also subject to federal government regulations, and in some states there are specific environmental and toxic laws that apply. Plants in many countries outside the U.S. have specific laws that apply to those countries. Many companies also have internal standards and guidelines to ensure consistency in decision-making by design engineers and plant personnel. There should be clear documentation so that it is known which codes, standards, and guidelines are to be followed.

11. *Audits and Corrective Actions.* Audits are methodical, independent, and usually periodic examinations of local installations, procedures, and practices. Audits help assure compliance with a sound process safety program and that risks are being properly managed. The frequency of audits should be determined by the hazards of the facility. Corrective actions are the steps taken by a company in response to recognition of a process safety deficiency, either through an audit or by other means. It is important that an audit team have expertise in facility operations, safety disciplines such as fire protection, and management systems. Corrective action includes the process of addressing identified deficiencies, weaknesses, or vulnerabilities. It also includes processes for corrective action planning and follow-up.

12. *Enhancement of Process Safety Knowledge.* Organizations with strong process safety programs can contribute to advancing the latest process safety technology. They should share nonproprietary results of safety research and support process safety–oriented research and development programs of professional and trade associations and colleges. Improved process safety knowledge can produce a competitive advantage by improved yields, better quality, increased productivity, and less downtime. Consideration should be given to encouraging technical staff participation in professional and trade association programs. The Center for Chemical Process Safety of the American Institute of Chemical Engineers, which is supported by many large chemical and chemical-related companies, is an example of a technical group that sponsors conferences, training programs, and publications in the area of chemical process safety.

COMBUSTION HAZARDS

Introduction

The enchanting flame has held a special mystery and charm the world over for thousands of years. According to Greek myth, Prometheus the Titan stole fire from the heavens and gave it to mortals—an act for which he was swiftly punished. Early people made use of it anyway. Soon the ancients came to regard fire as one of the basic elements of the world. It has since become the familiar sign of the hearth and a mark of youth and blood, as well as the object of intense curiosity and scientific investigation.

Suitably restrained, fire is of great benefit; unchecked or uncontrolled, it can cause immense damage. We respond to it with a powerful fascination coupled with an inbred respect and fear. A good servant but a bad master is Thoreau's "most tolerable third party."[25]

Fire[26]

Fire or combustion is normally the result of fuel and oxygen coming together in suitable proportions and with a source of heat. The consumption of a material by a fire is a chemical reaction in which the heated substance combines with oxygen. Heat, light, smoke, and products of combustion are generated. The net production of heat by a fire involves both heat-producing and heat-absorbing reactions, with more heat being produced than is absorbed. Energy in the form of heat is required:

1. To produce vapors and gases by vaporization or decomposition of solids and liquids. Actual combustion usually involves gases or vapors intimately mixed with oxygen molecules.
2. To energize the molecules of oxygen and flammable vapors into combining with one another and so initiating a chemical reaction.

The amount of energy required to cause combustion varies greatly. Hydrogen and carbon disulfide can be ignited by tiny sparks, or simply may be ignited by static generated as the gases or vapors discharge from pipes into air. Other materials, such as methylene chloride, require such large amounts of energy to be ignited that they sometimes are considered nonflammable. Fire also can result from the combining of such oxidizers as chlorine and various hydrocarbon vapors; oxygen is not required for a fire to take place.

There are exceptions to the general rule that a solid must vaporize or decompose to combine with oxygen; some finely divided materials such as aluminum powder and iron power can burn, and it is generally accepted that they do not vaporize appreciably before burning.

Products of Combustion. Heat, light, smoke, and asphyxiating toxic gases are produced by fire. In a hot, well-ventilated fire, combustion usually is nearly complete. Nearly all the carbon is converted to carbon dioxide, and all the hydrogen to steam, and oxides of various other elements such as sulfur and nitrogen are produced.

This is not the case in most fires, where some of the intermediate products, formed when large complex molecules are broken up, persist. Examples are hydrogen cyanide from wool and silk; acrolein from vegetable oils; acetic acid from timber or paper; and carbon or carbon monoxide from the incomplete combustion of carbonaceous materials. As the fire develops and becomes hotter, many of these intermediates, which are often toxic, are destroyed (e.g., hydrogen cyanide is decomposed at a significant rate at 538°C).

Small airborne particles of partially burnt carbonaceous materials form smoke, which is often thickened by steam, when there is only partial combustion of fuel.

Solids. Ordinarily, combustible solids do not combine directly with oxygen when they burn. They give off vapor and gaseous decomposition products when they are heated, and it is the vapors or gases that actually burn in the characteristic form of flames. Thus, before a solid can be ignited, it usually must be heated sufficiently for it to give off flammable concentrations of vapors. Glowing, which is combustion in the solid state, is characteristic of materials in the final stages of a fire's decay when flammable gases have been burned away, or when the production of gases and vapors has been suppressed.

Solids with larger surface areas, in relation to their volume, burn more readily than those that are more compact when exposed to heat and oxygen in the air. Common materials such as textiles in the form of fibers or fabrics, foamed rubber, foamed plastics, thin sheets of plastic, paper, corrugated cardboard, combustible dusts, dry grass and twigs, and wood shavings are examples of materials with large surface areas in relation to their volume. In a well-established fire, materials with relatively small surface areas, such as chunks of coal or logs, burn readily.

Combustion is self-propagating; burning materials produce heat which causes more of the solid to produce flammable vapors until either the fuel or oxygen is exhausted, or until the fire is extinguished in some other way.

Dusts. Most combustible solids can produce combustible dusts. Combustible dusts are particularly hazardous; they have a very high surface area to volume ratio. When finely divided as powders or dusts, solids burn quite differently from the original material in the bulk. Dust and fiber deposits can spread fire across a room or along a ledge or roof beam very quickly. Accumulations of dust can smoulder slowly for long periods, giving little indication that combustion has started until the fire suddenly flares up, possibly when no one suspects a problem.

Many combustible dusts produced by industrial processes are explosible when they are suspended as a cloud in air. Even a spark may be sufficient to ignite them. After ignition, flame spreads rapidly through the dust cloud as successive layers are heated to ignition temperature. The hot gases expand and produce pressure waves that travel ahead of the flame. Any dust lying on surfaces in the path of the pressure waves will be thrown into the air and could cause a secondary explosion more violent and extensive than the first.

Liquids. A vapor has to be produced at the surface of a liquid before it will burn. Many common liquids give off a flammable concentration of vapor in air without being heated, sometimes at well below room temperature. Gasoline, for example, gives off ignitable vapors above about −40°C, depending on the blend. The vapors are easily ignited by a small spark or flame. Other liquids, such as fuel oil and kerosene, need to be heated until sufficient vapor is produced.

Many liquids can be formed into mists that will burn at temperatures where the vapor pressure is insufficient to produce a flammable mixture of the vapor and air.

For any flammable vapor there are maximum and minimum concentrations of the vapor in air beyond which it cannot burn. When the mixture of vapor in air is too weak, there is insufficient fuel for burning; when the mixture is too strong, there is insufficient oxygen for burning.

If the density of a flammable vapor is greater than that of air, as is normally the case, flammable concentrations may collect at low levels, such as at floor level or in basements, and can travel a considerable distance to a source of ignition, from which flames will then flash back.

Gases. Flammable gases usually are very easily ignited if mixed with air. Flammable gases often are stored under pressure, in some cases as a liquid. Even small leaks of a liquefied flammable gas form relatively large quantities of gas, which is ready for combustion.

The Fire Triangle. The well-known "fire triangle" (see Fig. 5.1) is used to represent the three conditions necessary for a fire:

1. Fuel.
2. Oxidizer: oxygen or other gaseous oxidizer such as chlorine; or liquid oxidizer such as bromine; or solid oxidizer such as sodium bromate.
3. Energy, usually in the form of heat.

If one of the conditions in the fire triangle is missing, fire does not occur; if one is removed, fire is extinguished. Usually a fire

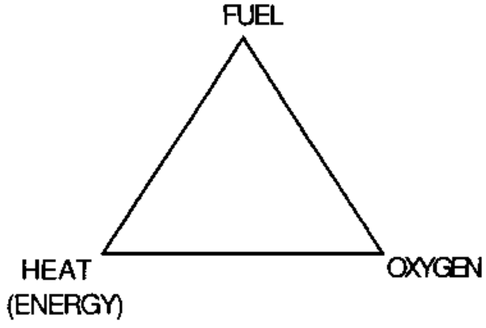


Fig. 5.1. The fire triangle.

occurs when a source of heat contacts a combustible material in air, and then the heat is supplied by the combustion process itself.

The fire triangle indicates how fires may be fought or prevented:

1. Cut off or remove the fuel.
2. Remove the heat or energy—usually by putting water on the fire.
3. Remove the supply of oxygen—usually by foam or inert gas.

Flammability

No single factor defines flammability, but some relevant parameters include:

1. Flash point—often considered the main index of flammability; low flash points usually mean increased flammability.
2. Flammability limits; wide limits mean increased flammability.
3. Autoignition temperature; low temperature means increased flammability.
4. Ignition energy; low ignition energy means increased flammability.
5. Burning velocity; high velocity means increased flammability.

A combustion process is an exothermic reaction initiated by a source of ignition that produces more energy than it consumes. The speed at which the reaction proceeds through the mixture of reactants depends on the concentration of the flammable gas or vapor. This speed is lower at higher ("rich") as well as at lower ("lean") concentrations of the flammable gas than at the stoichiometric mixture. There are lower and upper limits beyond which the reaction cannot propagate through the gas mixture on its own. Some definitions follow:

> *Flammability limits.* The range of flammable vapor–air or gas–air mixtures between the upper and lower flammable limits. Flammability limits are usually expressed in volume percent. Flammability limits are affected by pressure, temperature, direction of flame propagation, oxygen content, type of inerts, and other factors. The precise values depend on the test method.
>
> *Upper flammability limit.* The maximum concentration of vapor or gas in air above which propagation of flame does not occur on contact with a source of ignition.
>
> *Lower flammability limit.* The minimum concentration of vapor or gas in air or oxygen below which propagation of flame does not occur with a source of ignition.

The concentrations at the lower and upper flammability limits are roughly 50 percent and 200 to 400 percent, respectively, of the stoichiometric mixture. The maximum flammability usually (not always) occurs at the stoichiometric mixture for combustion.[2,27]

> *Flammable limits for mixtures of flammable gases and vapors.* For mixtures of several flammable gases and vapors, the flammable limits can be estimated by application of Le Chatelier's equation, if the flammable limits of the components are known.[2]

$$L = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{L_i}} \qquad U = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{U_i}}$$

where:

L = lower flammability limit of the fuel mixture, vol. %.
L_i = lower flammability limit of fuel component i, vol. %.
U = upper flammability limit of the fuel mixture, vol. %.
U_i = upper flammability limit of fuel component i, vol. %.
y_i = concentration of fuel component i, vol. %.

This equation is empirical and is not universally applicable, but is useful and a reasonable approximation when actual mixture data are not available.

It is possible for a mixture to be flammable even though the concentration of each constituent is less than its lower limit.

Methods of measurement. Flammability limits are determined by measuring the volume percent of a flammable gas in an oxidizing gas that will form a flammable mixture, thus identifying the lower and upper flammable limits as well as the critical oxygen concentration (the minimum oxidizer concentration that can be used to support combustion).

Uniformity of lower limits on a mass basis. Concentrations of vapors and gases usually are reported in volume percent. As molecular weight increases, the lower limit usually decreases. On a mass basis, the lower limits for hydrocarbons are fairly uniform at about 45 mg/L at 0°C and one atm. Many alcohols and oxygen-containing compounds have higher values; for example, on a mass basis, ethyl alcohol in air has a lower limit of 70 mg/L.[27]

Effect of temperature on flammable limits. The higher the temperature is at the moment of ignition, the more easily the combustion reaction will propagate. Therefore, the reference temperature (initial temperature) of the flammable mixture must be stated when flammable limits are quoted. There are not a lot of data for flammable limits under different conditions of initial temperature. The behavior of a particular mixture under different conditions of initial temperature usually must be determined by tests.

Burning in atmospheres enriched with oxygen. The flammability of a substance depends strongly on the partial pressure of oxygen in the atmosphere. Increasing oxygen content affects the lower flammability limit only slightly, but it has a large effect on the upper flammability limit. Increasing oxygen content affects the lower flammability limit only slightly, but it has a large effect on the upper flammability limit. Increasing oxygen content has a marked effect on the ignition temperature (reduces it) and the burning velocity (increases it).

At the lower explosive limits of gas–air mixtures, there is already an excess of oxygen for the combustion process. Replacing nitrogen by additional oxygen will influence this limit very little.[8]

Burning in chlorine. Chemically, oxygen is not the only oxidizing agent, though it is the most widely recognized and has been studied the most. Halogens are examples of oxidants that can react exothermically with conventional fuels and show combustion behavior. The applicability of flammability limits applies to substances that burn in chlorine. Chlorination reactions have many similarities to oxidation reactions. They tend not to be limited to thermodynamic equilibrium and often go to complete chlorination. The reactions are often highly exothermic. Chlorine, like oxygen, forms flammable mixtures with organic compounds.

Example. A chlorine–iron fire occurred in a chlorine pipeline, causing a chlorine gas release. Chlorine had liquefied in the lines because of the very cold weather, and the low spot was steam-traced. Steam had been taken from the wrong steam line, using 400 psig steam instead of 30 psig steam. The 400 psig steam was hot enough to initiate the reaction. This serves as a reminder that steel and chlorine can react. The allowable temperature for safe use depends upon the state of subdivision of the iron.

Burning in other oxidizable atmospheres. Flames can propagate in mixtures of oxide of nitrogen and other oxidizable substances. For example, Bodurtha[27] reports that the flammability limits for butane in nitric oxide are 7.5 percent (lower) and 12.5 percent (upper).

Flame quenching. Flame propagation is suppressed if the flammable mixture is held in a narrow space. There is a minimum diameter for apparatus used for determination of flammability limits. Below this diameter the flammable range measurements are narrower and inaccurate.

If the space is sufficiently narrow, flame propagation is suppressed completely. The largest diameter at which flame propagation is suppressed is known as the quenching diameter. For an aperture of slotlike cross section there is critical slot width.

The term "quenching distance" sometimes is used as a general term covering both quenching diameter and critical slot width, and sometimes it means only the latter.

There is a maximum safe gap measured experimentally that will prevent the transmission of an explosion occurring within a container to a flammable mixture outside the container. These data refer to a stationary flame. If the gas flow is in the direction of the flame propagation, a smaller gap is needed to quench the flame. If the gas flow is in the opposite direction, a larger gap will provide quenching. If the gas velocity is high enough, the flame can stabilize at the constriction and cause local overheating. These quenching effects are important in the design of flame arrestors.

Heterogenous mixtures.[28] In industry, heterogeneous (poorly mixed) gas phase mixtures can lead to fires that normally would be totally unexpected. It is important to recognize that heterogeneous mixtures can ignite at concentrations that normally would be nonflammable if the mixture were homogeneous. For example, one liter of methane can form a flammable mixture with air at the top of a 100-liter container although the mixture only would contain 1.0 percent methane by volume if complete mixing occurred at room temperature, and the mixture would not be flammable. This is an important concept because "layering" can occur with any combustible gas or vapor in both stationary and flowing mixtures.

Heterogenous gas phase mixtures can lead to unexpected fires if a relatively small amount of flammable gas is placed in contact with a large amount of air without adequate mixing, even though the average concentration of flammable gas in the mixture is below the flammable limit. *Heterogeneous mixtures are always formed at least for a short time when two gases or vapors first are brought together.*

Effect of pressure. Flammability is affected by initial pressure. Normal variations of atmospheric pressure do not have any appreciable effect on flammability limits.

A decrease in pressure below atmospheric usually narrows the flammable range. When the pressure is reduced low enough, a flame or an explosion no longer can be propagated throughout the mixture.

An increase in pressure above atmospheric usually (not always) widens the flammability range, especially the upper limit.

Explosions in the absence of air. Gases with positive heats of formation can be decomposed explosively in the absence of air. Ethylene reacts explosively at elevated pressure, and acetylene reacts explosively at atmospheric pressure in large-diameter piping. Heats of formation for these materials are +52.3 and +227 kilojoules/g mol, respectively. Explosion prevention can be practiced by mixing decomposable gases with more stable diluents. For example, acetylene can be made nonexplosive at a pressure of 100 atmospheres by including 14.5 percent water vapor and 8 percent butane.

Ethylene oxide vapor will decompose explosively in the absence of oxygen or air under certain conditions when exposed to common sources of ignition if heated to high enough temperatures. One way to prevent the decomposition reaction is to use methane gas to blanket the ethylene oxide liquid. It has also been found that liquid ethylene oxide will undergo a deflagration in the absence of oxygen with a very rapid pressure increase if ignited at a temperature and pressure above a certain level. Fortunately, the conditions required for propagation of the decomposition of liquid phase ethylene oxide are outside the current normal handling and processing ranges for the pure liquid. Propagation has not been observed below 80°C at from 14 to 100 atm pressure.[29] Ethylene oxide also can undergo explosive condensation when catalyzed by a small amount of caustic.[30]

Inert Gases

The addition of inert gases to a mixture of flammable gases and air affects flammability limits. Carbon dioxide causes a greater narrowing of the flammable range than does nitrogen. Water vapor is an acceptable inert gas if the temperature is high enough to exclude much of the oxygen, which requires a temperature of 90 to 95°C. Because water vapor and carbon dioxide have a higher heat capacity than nitrogen, they are somewhat more effective as inerting agents than nitrogen. Some halogen-containing compounds also can be used for inerting materials at relatively low concentrations. An example of this is the use of Freon-12 (CCl_2F_2). Caution must be used with halohydrocarbons because of the possibility of the halocarbons themselves burning, especially at high pressures. Environmental considerations are making the use of halogenated hydrocarbons for inerting increasingly undesirable. Materials are being developed that are considered environmentally acceptable. Figures 5.2 and 5.3[28] show flammability envelopes for methane and *n*-hexane for various air–inert mixtures at 25°C and one atmosphere. All flammable envelopes are similar to Figs. 5.2 and 5.3 except in minor detail. The lower limit is virtually insensitive to added inerts. The upper limit, however, decreases linearly with added inert until the critical concentration of inert is reached beyond which no compositions are flammable. In these graphs, C_{st} means the stoichiometric composition.

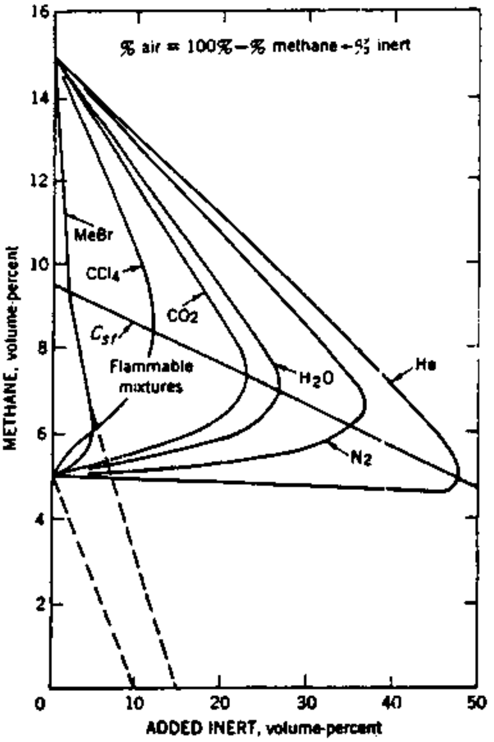


Fig. 5.2. Limits of flammability of various methane-inert gas–air mixtures at 25°C and atmospheric pressure. (*Courtesy Bureau of Mines.*)

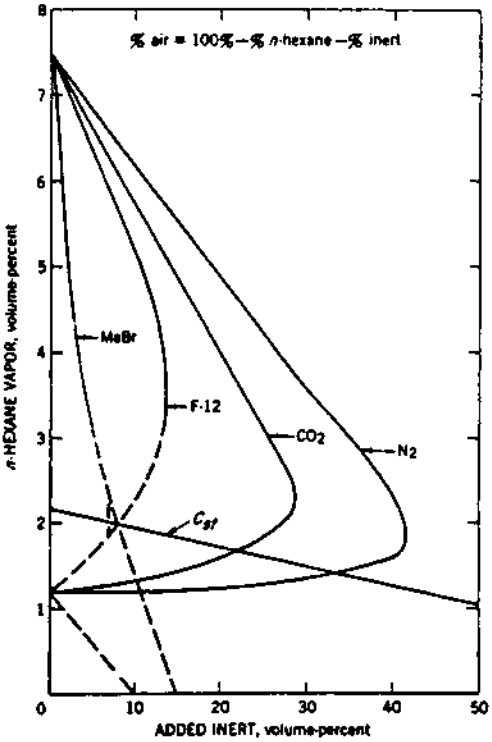


Fig. 5.3. Limits of flammability of various *n*-hexane-inert gas–air mixtures at 25°C and atmospheric pressure. (*Courtesy Bureau of Mines.*)

Figure 5.4 shows the minimum amount of nitrogen or carbon dioxide that must be added to air to suppress flammability of some common hydrocarbons.

Figure 5.5 shows the minimum oxygen content for combustion for some common flammable materials. The limits of flammability are dictated by the ability of a system to propagate a flame front. Propagation does not occur until the flame front reaches about

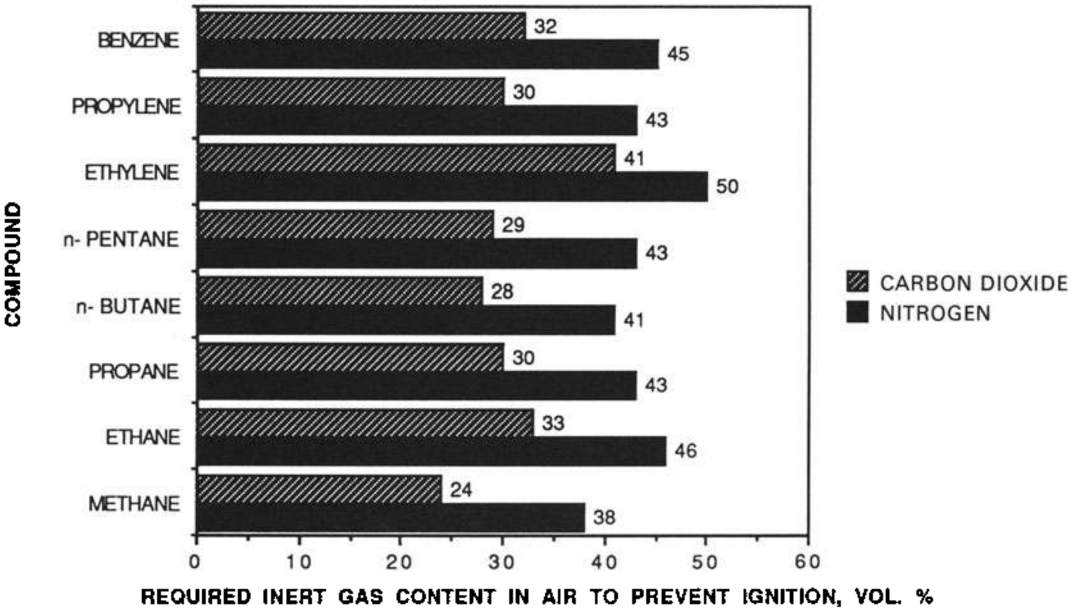


Fig. 5.4. Minimum inert gas content for suppression of flammability of selected substances in air. (*Data from Zabetakis 1965.*[28])

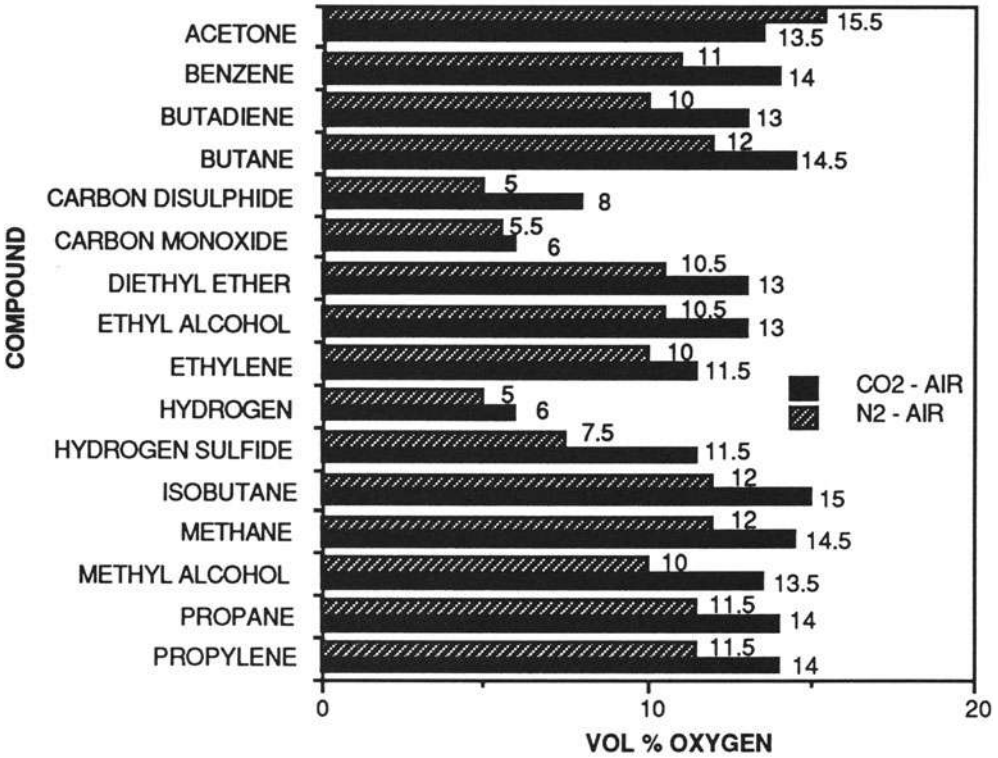


Fig. 5.5. Minimum oxygen content for combustion of selected substances. (*Data from Frank Bodurtha 1980.*[27])

1200 to 1400 K. As the typical terminal temperature for hydrocarbons at stoichiometric conditions is about 2300 K, it can be seen that having only one-half the fuel or oxidizer present will produce about one-half the flame temperature, which is too low to propagate flame.

A useful rule to remember is that the lower flammable limits of most flammable vapors are close to one-half the stoichiometric composition, which can be calculated. Another easy rule to remember is that about 10 percent oxygen or less in air (assuming the rest is mostly nitrogen) will not support combustion of most flammable hydrocarbon vapors.

The flammability limits of hydrocarbon type fuels in oxygen and inert gas atmospheres are a function of the inert gas and any fuel or oxygen in excess of that required by the stoichiometry of the combustion process. In systems where fuel content is fixed, inert material having a high heat capacity will be more effective at flame suppression than inert material having low heat capacity.

Many of the flammable limits reported in the literature are somewhat too narrow, and certain gas compositions regarded as being nonflammable are in fact flammable when given the proper set of circumstances. *In other words, take data on flammability limits from the literature with a grain of salt.* It is best not to design closely on the basis of most available data on flammability limits.

The use of inert gases can cause some serious hazards that must be recognized if inerts are to be used effectively and safely. Considerations in the use of inert gases include:

1. *An inert atmosphere can kill if a person breathes it.* Precautions should be taken to assure that personnel cannot be exposed to the breathing of inert atmospheres.

2. *Some products need at least a small amount of oxygen to be stored safely.* This includes styrene and some other vinyl monomers, which must have some oxygen in them to make the usual polymerization inhibitor for styrene (*t*-butyl catechol, or TBC), effective. If pure nitrogen, for example, is used to blanket styrene, the inhibitor will become ineffective. TBC customarily is added to styrene monomer to prevent polymer formation and oxidation degradation during shipment and subsequent storage; it functions as an antioxidant and prevents polymerization by reacting with oxidation products (free radicals in the monomer). If sufficient oxygen is present, polymerization is effectively prevented (at ambient temperatures); but in the absence of oxygen, polymerization will proceed at essentially the same rate as if no inhibitor were present. The styrene may polymerize and can undergo an uncontrolled exothermic reaction, which may generate high temperatures and pressures that can be very hazardous. The inhibitor level of styrene must be maintained above a minimum concentration at all times. The minimum concentration of TBC in styrene for storage is about 4 to 5 ppm.

3. *To be effective, inert atmospheres must be maintained within certain composition limits.* This requires the proper instrumentation and regular attention to the system.

4. *Inerting systems can be quite expensive and difficult to operate successfully.* Before the use of inert systems, alternatives should be explored, such as the use of nonflammable materials or operating well outside, preferably below, the flammability range.

Mists and Foams

If the temperature of a liquid is below its flash point, flammable concentrations of vapor cannot exist, but conditions still can exist for flammability if mists or foams are formed. A suspension of finely divided drops of a flammable liquid in air has many of the characteristics of a flammable gas–air mixture and can burn or explode. A mist may be produced by condensation of a saturated vapor or by mechanical atomization. Normally, the diameter of drops in a condensed mist is less than 0.01 mm, whereas in a mechanical spray it usually is greater than 0.1 mm.

The commonly accepted fallacy that liquids at temperatures below their flash points cannot give rise to flammable mixtures in air has led to numerous accidents. Flash points are measured under stagnant conditions in carefully controlled laboratory experiments, but in the real world one works with a wide variety of dynamic conditions that can produce mists and foams.

Flammable mist–vapor–air mixtures may occur as the foam on a flammable liquid collapses.[28] Thus, when ignited, many foams can propagate flame. An additional hazard can arise from the production of foams by oxygen-enriched air at reduced pressures. Air confined over a liquid can become oxygen-enriched as pressure is reduced because oxygen is more soluble than nitrogen in most liquids. Thus, the presence of foams on combustible liquids is a potential explosion hazard.

The lower flammability limit for fine mists (<0.01 mm diameter) of hydrocarbons below their flash point, plus accompanying vapor, is about 48 grams of mist/cubic meter of air at 0°C and one atmosphere. Mist can occur in agitated vessels under some conditions, especially when an agitator blade is at or near the liquid–vapor interface in the vessel.

Work on condensed oil mists (drop diameter mostly less than 0.01 mm) has demonstrated that they have flammability characteristics similar to those the mixture would have if it were wholly in the vapor phase at the higher temperature necessary for vaporization. The flammability characteristics are affected by drop size. For larger drop sizes (above 0.01 mm) the lower limit of flammability decreases as drop diameter increases. For mists, the amount of inert gas needed to suppress flammability is about the same as that needed to suppress an equivalent vapor–air mixture of the same material if it were vaporized at a somewhat higher temperature.

A useful rule is that mists of flammable or combustible liquids in air can burn or explode at temperatures below their flash points.

Ignition

Flammable gases and vapors can be ignited by many sources. In the design and operation of processes, it is best not to base fire and explosion safety on the presumption that ignition sources have been excluded. Bodurtha[27] reported that of 318 natural gas fires and explosions, the sources of ignition of 28 percent were unknown. All reasonable measures should be taken to eliminate possible sources of ignition in areas in which flammable materials are handled.

Autoignition. If the temperature of a flammable gas–air mixture is raised in a uniformly heated apparatus, it eventually reaches a value at which combustion occurs in the bulk gas. This temperature is defined as the spontaneous ignition temperature (SIT) or autoignition temperature (AIT). The gas–air mixture that has the lowest ignition temperature is called by various names, such as minimum autoignition temperature, minimum spontaneous ignition temperature, and self-ignition temperature.[27] Usually the AIT reported in the literature is the minimum autoignition temperature.

The autoignition temperature of a substance depends on many factors, such as:

- Ignition delay
- Energy of ignition source
- Pressure
- Flow effects
- Surfaces
- Concentration of vapors
- Volume of container
- Oxygen content
- Catalytic materials
- Flow conditions

Thus, a specific autoignition temperature applies only to the experimental conditions employed in its determination. Usually the values quoted are obtained in clean laboratory equipment.

The autoignition temperature of a substance may be reduced below ideal laboratory conditions by as much as 100 to 200°C for surfaces that are insulated with certain types of insulation, or are contaminated by dust.

Mixtures that are fuel-rich or fuel-lean ignite at higher temperatures than do those of intermediate compositions. Also, in a homologous series of organic compounds,

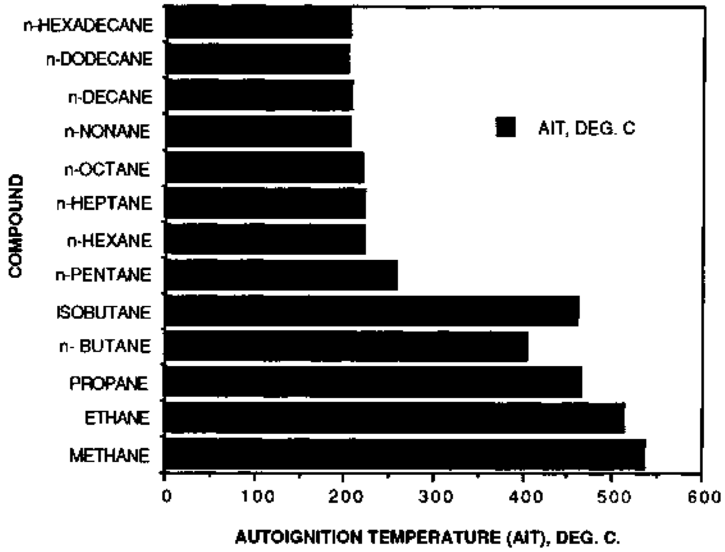


Fig. 5.6. Autoignition temperatures of paraffin hydrocarbons at one atmosphere. (*Data from Bodurtha 1980.*[27])

the autoignition temperature decreases with increasing molecular weight, as shown in Fig. 5.6. (Data from Bodurtha[27]).

Ignition Delay. Ignition of a flammable mixture raised to or above the temperature at which spontaneous combustion occurs is not instantaneous; the time delay between the moment of exposure to high temperature and visible combustion is called the ignition delay. This time delay decreases as the ignition temperature increases. The time delay may be as little as a fraction of a second at higher temperatures, or several minutes close to the autoignition temperature.

Environmental Effects. It has been found that the AIT becomes lower with increasing vessel size in the range of 35 ml to 12 liters. An increase in pressure usually decreases AITs, and a decrease in pressure raises AITs. Usually oxygen enrichment of the air tends to decrease the minimum AIT, and a decrease in oxygen content increases the minimum AIT. Low-temperature oxidation can result in "cool flames," which may grow into ignition.

Catalytic Materials. Ignition may occur where the temperature is less than the minimum AIT. Catalytic materials, such as metal oxides, can promote oxidation on their surfaces, leading to a high local temperature and subsequent ignition. There is a recorded reactive chemical case[31] in which a solvent at 80°C was being pressurized with a gas phase consisting of a high oxygen concentration. The solvent has a flash point in oxygen of greater than 130°C and normally is considered not to be a flammability hazard. There was an ignition, causing the vessel to rupture its main gasket with major damage to the facility. It was found that a mist had been formed in the vessel by the agitator, and that the source of ignition probably was a trace of palladium catalyst remaining from a previous run.

From this incident, several important lessons can be learned:

1. Ignition of a flammable mixture can result from totally unexpected contamination by trace amounts of catalysts if the oxidizer and fuel are present.
2. Mists of oxidizable liquids may form that can burn or explode at temperatures outside the "normal" flammable range.

3. It can be dangerous to perform experiments with pure oxygen, or air enriched with oxygen, especially under pressure and at elevated temperatures, when oxidizable materials are present.
4. The real criterion regarding flammable mixtures in air should be whether a flammable atmosphere can exist under the given process conditions, rather than whether a flammable liquid is at a temperature below its flash point.

Cleaning Up Spills of Flammable or Combustible Liquids. It is customary to clean up small spills of many liquid materials with sand or other noncombustible absorbent material. Some absorbing agents, such as untreated clays and micas, will cause an exothermic reaction with some liquids, especially monomers, which might ignite the liquid if it is flammable or combustible. Before any material is provided to be used to soak up spills of oxidizable material, tests should be made to determine if the material can cause fires with potential spills.

Ignition Caused by Insulation. Ignition of combustible materials that have been absorbed into commonly used insulating materials is possible at temperatures lower than the AIT for nonabsorbed material. All oxidizable materials oxidize to some extent in air at ambient temperatures, usually at a very low rate. When an absorbent material is absorbed into insulation, it is "spread" over a large area, increasing its access to oxygen. Because the absorbent is an insulator, heat from oxidation is retained rather than dissipated, and the temperature will rise if the heat is produced faster than it can be dissipated. The rate of oxidation increases as the material temperature increases, which produces more heat, compounding the hazard. If the temperature rises enough, the material will ignite ("spontaneous combustion"). This is similar to the classic oily rag and wet haystack phenomenon, which has caused many fires in homes and on farms. In the wet haystack phenomenon, fermentation by microorganisms will create heat. Some air is necessary; too much air will remove too much heat to allow the combustion temperature to be reached. For equipment operating above about 200°C containing combustible liquids with high boiling points, insulation should be impervious to the material handled. To date, only a closed cell foamed glass provides the required degree of protection where oxidizable liquid materials are used above 200°C. Insulation based on glass fiber, silicate, or alumina materials is known to cause hazardous situations and should not be used in this service.

Laboratory tests and actual fires show that Dowtherm A® (a heat-transfer fluid consisting of a eutectic mixture of biphenyl oxide and biphenol) can be ignited if it is soaked in glass fiber insulation and in contact with air at temperatures considerably below the normal AIT. This is also true for stearic acid soaked in glass fiber insulation. Table 5.1 shows the reduction in AIT of Dowtherm A® and of steric acid soaked in glass fiber insulation.

Ignition of this type generally occurs only with materials having a high boiling point. Usually materials with low boiling points will vaporize and cannot remain soaked in hot insulation. There are exceptions. For example, ethylene oxide has a fairly low boiling point, but if it leaks into insulation, a polymer can be formed that has a high boiling point and can autoignite insulation at low temperatures.

Ignition Caused by Impact. Solids and liquids can be ignited by impact. Impact tests are made by having a weight fall freely through a known distance and impacting the sample. Impact can occur, for example, if containers are accidentally dropped. The

TABLE 5.1 Reduction in Autoignition Temperatures Caused by Liquids Soaking in Glass Fiber Insulation

Material	*Normal Autoignition Temperature, °C*	*Ignition Temp. in Glass Fiber Insulation, °C*
Dowtherm A®	621	260 to 290
Stearic acid	395	260 to 290

interpretation of the data from impact tests can be difficult.

Ignition Caused by Compression of Liquids. Liquids can be ignited by sudden compression. This can happen when there is water hammer caused by the pressure surge from quick-acting valves and from the compression in liquid pumps. Sudden compression can occur with liquids, for example, if a tank car is bumped rapidly and the liquid goes to one end very quickly, possibly trapping some vapor bubbles that compress and create local hot spots that can cause ignition.

Ignition Caused by Rubbing Friction. Solids can be ignited by frictional sources when rubbed against each other or against another material. The frictional heat produced may be enough to ignite other materials, such as lubricants, that are nearby. A common example of this occurs when bearings run hot, causing oil or grease to vaporize and possibly ignite.

Ignition Caused by Glancing Blows. Friction can cause ignition in other ways. Sparks may occur when two hard materials come in contact with each other in a glancing blow (the blows must be glancing to produce friction sparks). These kinds of sparks are not directly related to frictional impact. Hand and mechanical tools are the most likely sources of friction sparks that occur outside of equipment. The need for nonsparking tools is somewhat controversial; Bodurtha[27] states that it is extremely unlikely that anyone would be using tools in a flammable atmosphere, and it is usually more prudent to control the atmosphere than the tools. Sparkproof tools are not really sparkproof in all situations.

Ignition Caused by Static Electricity. Static electricity is a potential source of ignition wherever there is a flammable mixture of dusts or gases (see next section).

Ignition Caused by Compression of Gases. If a gas is compressed rapidly, its temperature will increase. Autoignition may occur if the temperature of the gas becomes high enough (this is more or less the principle of diesel engines).

An advancing piston of high-pressure gas can compress and heat trapped gas ahead of it. For a perfect gas, the temperature rise due to adiabatic compression is given by:

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k}$$

where T_1 and T_2 are the initial and final gas absolute temperatures, P_1 and P_2 are the initial and final absolute pressures, and k is the ratio of heat capacity at constant pressure to the heat capacity at constant volume. For air and many other diatomic gases, $k = 1.4$. Many hydrocarbons have k values of between 1.1 and 1.2. The value of k is a function of temperature and pressure.

Energy Levels for Ignition. If a flammable gas mixture is to be ignited by a local source of ignition, there is a minimum volume of mixture required to cause a continuing flame throughout the mixture.

For example, to ignite a methane–air mixture in a cold container, a hot patch of 18 mm^2 at 1000 to 1100°C is required in order to heat enough volume of gas to produce a continuing flame,[2] even though the autooxidation temperature for methane is 540°C. Ignition of a flammable gas–air mixture by electrical discharge can occur only if the electrical discharge is of sufficient energy.

Minimum Ignition Energy. There is a minimum ignition energy, which usually occurs near the stoichiometric mixture. The minimum ignition energy for some representative substances in air is shown in Fig. 5.7.[2] The energy required to cause ignition frequently is reported in millijoules (mJ). One joule is 0.24 calorie, so 1 mJ is 0.00024 calorie, which is a very small amount of energy.

A person typically has a capacitance of 200 picofarads, and if charged to 15 kilovolts could initiate a discharge of 22.5 mJ. This is enough to ignite many flammable mixtures. The energy in ordinary spark plugs is 20 to 30 mJ.

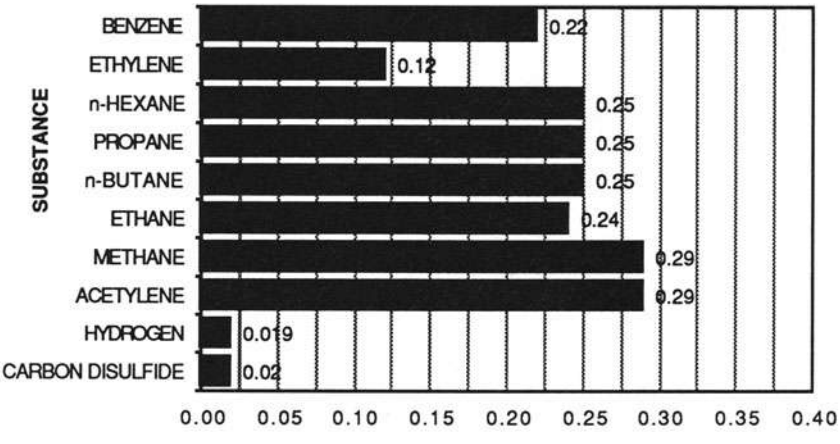


Fig. 5.7. Minimum ignition energy for selected substances. (*Lees 1980.*[2])

The hazard of an explosion should be minimized by avoiding flammable gas–air or dust–air mixtures in a plant. It is bad practice to rely solely on elimination of sources of ignition, as it is nearly impossible to ensure this.

Effect of Oxygen-Enriched Atmospheres. The minimum spark energy to cause ignition varies greatly with the amount of oxygen in oxygen-enriched air. Stull[30] showed that with a composition of 10 percent methane in air, about 0.5 mJ of spark energy is required to initiate a reaction at the lower flammable limit. If the air is enriched with oxygen, the minimum spark energy decreases. If the flammable material is combined with 100 percent oxygen, the spark energy required is only about one percent of the required energy in air at 21 percent oxygen! This demonstrates the extremely small amount of energy required to initiate the reaction, as well as the additional ease with which oxygen-enriched atmospheres are initiated. Table 5.2 compares initiation energies of some common substances in air and in pure oxygen.

Effect of pressure. An increase of pressure decreases the amount of energy required to cause ignition. In a mixture of propane, oxygen, and nitrogen, doubling the pressure decreases the minimum energy required to cause ignition by a factor of about 5.

TABLE 5.2 Comparison of Initiation Energies of Some Common Substances in Air and Pure Oxygen[32]
(Taken from Mackenzie, Ref. 32)

Flammable Substance	*Relative Amount of Energy Required to Initiate Combustion, millijoules*	
	In Air	*In Pure Oxygen*
Methane	0.3	0.003
Hydrogen	0.019	0.0012
Acetone	1.15	0.0024
Diethyl ether	0.2	0.0013

If no other data are available for determination of hazards, minimum ignition energies at ambient temperatures and pressures should be considered as approximately:

- 0.1 mJ for vapors in air
- 1.0 mJ for mists in air
- 10.0 mJ for dusts in air

STATIC ELECTRICITY

Introduction

Many apparently mysterious fires and explosions have eventually been traced to static. In spite of the large amount of information about static electricity, it remains a complex phenomenon not often understood and appreciated. Static electricity is a potential source of ignition whenever there is a flammable mixture of gas or dust.

When two different or similar materials are in contact, electrons can move from one material across the boundary and associate with the other. If the two materials in contact are good conductors of electricity and are separated, the excess electrons in one material will return to the other before final contact is broken. But if one or both of the materials are insulators, this flow will be impeded. If the separation is done rapidly enough, some excess electrons will be trapped in one of the materials. Then both materials are "charged." Electric charges can build up on a nonconducting surface until the dielectric strength is exceeded and a spark occurs. The residual charge could ignite flammable mixtures.

The two materials or phases in initial contact may be:

- A single liquid dispersed into drops
- Two solids
- Two immiscible liquids
- A solid and a liquid
- A solid and a vapor or gas
- A liquid and a vapor or gas

The important thing to keep in mind is that whenever there is contact and separation of phases, a charge may be developed that could be disastrous. Three conditions must be met before an explosion caused by static electricity can take place:

1. An explosive mixture must be present.
2. An electric field must have been produced due to the electrostatic charge that had been generated and accumulated in a liquid or solid.
3. An electric field must be large enough to cause a spark of sufficient energy to ignite the mixture.

In designing preventive measures, all three factors should be controlled.

Static electricity is essentially a phenomenon of low current but high voltage and high resistance to current flow. A low-conductivity liquid flowing through a pipeline can generate a charge at a rate of 10^{-9} to 10^{-6} ampere (A). A powder coming out of a grinding mill can carry a charge at a rate of 10^{-8} to 10^{-4} A. At a charging rate of 10^{-6} A, the potential of a container insulated from earth can rise at a rate of 1000 volts/sec, and a voltage of 10,000 volts or higher can readily be obtained in this way.

Several electrostatic voltages and energies commonly encountered are typified by the following examples:

1. A person walking on dry carpet or sliding across an automobile seat can generate up to 5000 volts in dry weather. An individual having a capacitance of 100 pF (picofarads), a reasonable figure, could generate a spark energy of 1.25 mJ. This is far more than is needed to ignite some flammable vapor–air mixtures.
2. A person can accumulate dangerous charges up to about 20,000 volts when humidity is low.
3. A truck or an automobile traveling over pavement in dry weather can generate up to about 10,000 volts.
4. Nonconductive belts running over pulleys generate up to 30,000 volts. The voltage generated by a conveyor belt can be as high as 10^6 volts; the system can in effect act as a Van der Graaf generator.
5. The energy in the spark from an ordinary spark plug is 20 to 30 mJ.

The capacitance and the energy for ignition of people and of common objects are important. The capacitance of a human being is sufficient to ignite various flammable gas mixtures at commonly attained static voltages.

Hazard Determinants

Capacitance. The capacitance of an object is the ratio of the charge of the object to its potential. The capacitance gets larger as the object gets larger. With a given charge, the voltage gets higher as the capacity of the object gets smaller. For a sphere, capacitance is given by:

$$C = Q(10^{-3})/V$$

The energy stored in a capacitor is:[27]

$$W = 0.5CV^2(10^{-3}) = 500Q^2/C$$

where:

C = capacitance, pF (1 pF = picofarad = 10^{-12} farad)
Q = charge, microcoulombs (1 coulomb = 1A/sec = charge on 6.2×10^{18} electrons)
V = voltage in kilovolts
W = energy, millijoules (mJ)

This energy may be released as a spark when the voltage gets high enough. The minimum sparking potential for charged electrodes is about 350 volts and occurs at a spacing of 0.01 mm. Sparks from an equally charged nonconductor are less energetic and may contain only part of the stored energy. These comparatively weak sparks are not likely to ignite dust clouds but can ignite flammable gases.

The energy that can be stored by capacitance of an object can be compared to the minimum ignition energies of flammable gas–air mixtures and of dust–air mixtures to determine the probability that a spark discharge may have sufficient energy to cause ignition. If the charged object is a poor conductor, the calculation of energy available to produce a spark may not be possible because the charge often is not uniformly distributed, and the resistance to flow of current is high. Figure 5.8 shows some typical values of electrical capacitance.[33]

Relaxation Time. When a liquid is flowing in closed metal pipes, static electricity is not a hazard. When the liquid enters a tank, it may become a hazard. Charges caused by liquid separation during pumping, flow, filtration, and other effects such as splashing and agitation can accumulate on the surface of the liquid in the tank and cause sparking

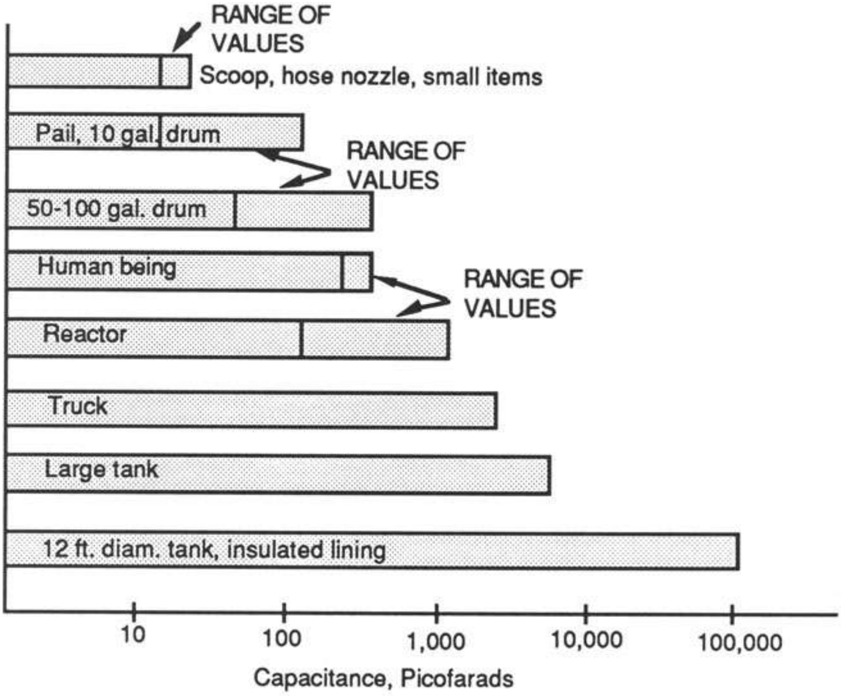


Fig. 5.8. Some typical values of electrical capacitance. (*Data from Eichel 1967.*[33])

between the liquid surface and the tank or conducting objects in the tank. The charge thus generated can be dissipated by relaxation or via discharge through a spark or corona discharge. The relaxation time is the time required for 63 percent of the charge to leak away from a charged liquid through a grounded conductive container. The half-time value is the time required for the free charge to decay to one-half of its initial value. Half-time is related to relaxation time by the relationship:

$$T_h = T_r \times 0.693$$

where:

T_h = half-time
T_r = relaxation time

Relaxation times vary from small fractions of a second up to minutes and even hours for some highly purified hydrocarbons that have very low conductivity.

It is important to recognize that a large charge can accumulate in the liquid even in a grounded container. In fact, it was reported that the majority of accidents attributed to static electricity in the petroleum industry have been with liquid in grounded containers.[2]

Relaxation time can be calculated as follows:

$$T_r = E(E_0/k)$$

where:

T_r = the relaxation time, in seconds; the time for 63% of the charge to leak away
E = relative dielectric constant, dimensionless
E_0 = absolute dielectric constant in a vacuum, $= 8.85 \times 10^{-14}$ to less than 1×10^{-18}
K = liquid conductivity, Siemens/cm

Siemens (S) are also called mhos.

Example: Benzene in a large tank could have a specific conductivity as low as 1×10^{-18} mho/cm and as high as 7.6×10^{-8} S/cm. The corresponding relaxation times for the two conductivities can be calculated as follows. Pure benzene has a dielectric constant of 2.5 to less than 1×10^{-18}. Using the above equation:

$$\text{(1)}\quad T_r = (8.85 \times 10^{-14}) \times (2.5)/(7.6 \times 10^{-8})$$
$$= 2.91 \times 10^{-6}\ \text{sec}$$

$$\text{(2)}\quad T_r = (8.85 \times 10^{-14}) \times (2.5)/(1 \times 10^{-18})$$
$$= 2.21 \times 10^{5}\ \text{sec}$$ (This is in excess of 60 hours.)

Benzene typically contains some water and has a higher conductivity than in the above example and has a much lower relaxation time.

The purity of a liquid has a great effect on its relaxation time, and thus its static hazard potential. In actual practice, relaxation times of a few seconds to an hour are encountered, depending on purity and dryness of the liquid. This emphasizes the dangers of open sampling of tank contents soon after filling. If it is likely that the liquid being used has a low conductivity, it is important that enough time elapse between activities that can produce a static charge, such as loading a tank, and any activity that could cause a spark, such as sampling from the top of the tank.

In case (2) in the above example, a conductivity of 10^{-18} S/cm is so low that there may be little charge separation and little charge formation, and there may be no hazard even though the calculated relaxation time is extremely long. Materials with a half-time value of less than 0.012 sec have been reported not to cause a hazard. A useful rule to remember is that the concept of relaxation is very important because it is possible for liquid in a tank to retain an electric charge for a long time if the liquid is a poor conductor, even if the tank is grounded. The specific conductivity, and therefore the relaxation time, is greatly affected by impurities. For example, the specific conductivity of benzene can vary from as long as 1×10^{-18} to about 7.6×10^{-8} S/cm, depending on its purity. It can vary significantly with the amount of water or other materials dissolved in the benzene.[27]

Resistivity. The extent of charge separation is dependent on the resistivity of the liquid.

Some materials have a sufficiently high conductivity to render them safe in terms of static buildup. If the resistivity is low, charge separation is easy, but so is charge recombination through the liquid. If the resistivity is high, there may be appreciable charge separation without immediate recombination, leading to a high charge. If the resistivity is extremely high, there may be no charge separation, and there is no buildup of a charge. If the conductivity of a liquid falls in the hazardous range, it is possible to modify it by the use of a very small amount of an additive. Additives usually are a combination of a polyvalent metal salt of an acid such as carboxylic or sulfonic acid and a suitable electrolyte. Additives of this type can impart a conductivity of 10^{-8} S/m (Siemens per meter) in a 0.1 percent solution in benzene.[2]

A useful rule to remember is that when the resistivity of a liquid exceeds 10^{15} ohm centimeters, or is less than 10^{10} ohm centimeters, static generation or accumulation is negligible. Between these limits, the net generation of charges increases with the *maximum charge generation at* 10^{13} *ohm centimeters*. Styrene, for example, a commonly used monomer, has a resistivity of 4×10^{13} at 20°C,[34] and therefore is capable of building up a potentially hazardous charge.

Static Charge Development. Static electrification of solids can occur in various ways. Different operations will produce the percentages of the theoretical maximum charge density shown in Fig. 5.9.[33]

It should be noted that pure gases do not generate significant static electricity in transmission through pipes and ducts. Gases contaminated with rust particles or liquid droplets produce static, but this is not a problem in a closed, grounded piping system. *If these gases impinge on an ungrounded, conductive object, dangerous charges can accumulate on that object*. Wet steam, which contains water droplets, can develop charges. *If the water droplets contact an ungrounded conductor, that object can develop a static charge*.

Flammable gases may ignite when discharged to air during thunderstorms, even without a direct lightning hit. Dry hydrogen and occasionally other gases may ignite when they are discharged to air in normal weather. This may be so because the electric field

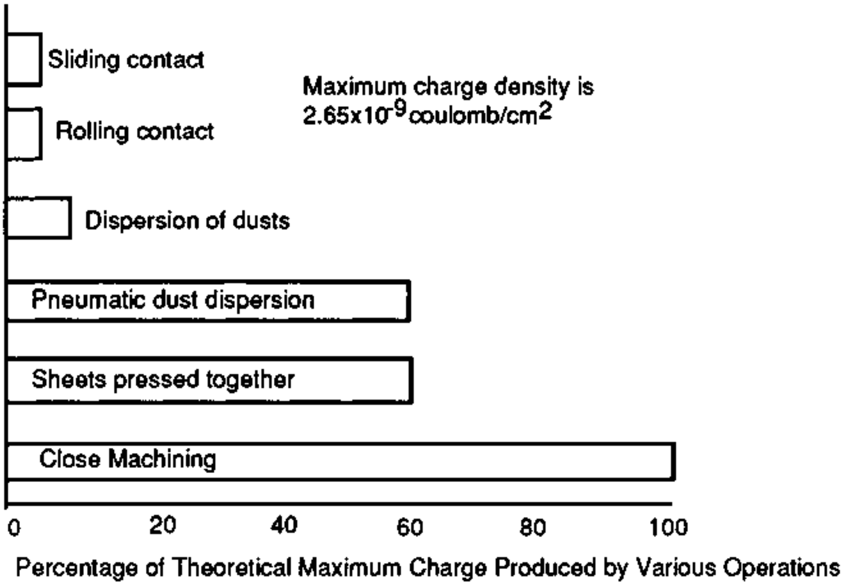


Fig. 5.9. Percentage of theoretical maximum charge produced by various operations. (*Data from Eichel 1967.*[33])

developed by the ejected gases can develop a corona discharge which can cause ignition. The minimum ignition energy of hydrogen is only 0.02 mJ. A toroidal ring developed by NASA (National Aeronautics and Space Administration) is reported to prevent unwanted discharge and subsequent ignition of a vent-stack outlet.[27]

Humidification. The conductivity of electrical nonconductors, such as plastics, paper, and concrete, depends on their moisture content. Relatively high moisture in these materials increases conductivity and therefore increases dissipation of static electricity. With relative humidity of 60 to 70 percent or higher, a microscopic film of moisture covers surfaces, making them more conductive.

Humidification can and often should be practiced to reduce the hazard of static electricity, but should not be relied on entirely to remove all possibility of static discharge.

In winter, cold air brought into a building and heated to normal room temperature is extremely dry, often less than 5 to 10 percent relative humidity. When processing solid materials that can develop a static charge, this air should be humidified to reduce static hazards as well as improve the comfort of personnel.

Filling Liquid Containers. A fire during top loading of a flammable liquid into a tank constitutes a serious problem if there can be a flammable mixture in the vapor space. Static electricity can be generated by splashing if the liquid is top-loaded, so it is normal practice to fill with a dip pipe positioned so the tip of the dip pipe is near the bottom of the tank. This may not be sufficient to prevent static charge buildup, as a charge may be generated in the bottom of the tank before the pipe tip is fully submerged, and it is possible for the liquid to acquire a charge before it reaches the tank.

Product filters using cotton, paper, felt, or plastic elements are prolific generators of static electricity. It is considered that at least 30 sec is necessary to dissipate this charge, although with dry nonconductive liquids, it may require as long as 500 sec.

Loading a less volatile liquid into a tank where there was previously a more volatile liquid is particularly hazardous because the more volatile liquid may form a flammable mixture, and the less flammable material is often a poor conductor and will not readily dissipate static charge. This type of loading accounts for 70 to 80 percent of severe losses at terminals.[2] This appears to occur most often when the compartments are one-fourth to one-third full, and when the temperature is close to $-1°C$.

Inerting the tank while it is being filled will reduce the possibility of ignition by static electricity and is highly recommended when it is possible and practical. However, this is not always practical. In any case, if inerts are to be used, they must be added carefully, as the following example illustrates. Two firemen were fatally injured when an explosion occurred as they were attempting to use portable CO_2 fire extinguishers to inert a tank truck. The source of ignition was believed to be a spark from the horn of the extinguisher to the latch on the tank truck. It was found that the voltage on the horn increased as the carbon dioxide "snow" passed down the horn to the outlet side.

Grounding and bonding lines, although very important, will not immediately dissipate the charge on the surface of a nonconducting liquid in a tank. A relaxation time for charge to be a dissipated should be allowed after filling or other operations to permit static charge on the liquid surface to dissipate to the dip pipe or tank shell. *The minimum time is one minute, but longer periods are advisable with some liquids that have extremely low conductivity. Bottom loading may reduce the static electricity hazard but does not eliminate it.*[35]

EXPLOSIONS

Development of Pressure

Exothermic reactions can lead to high temperatures and in the case of large fires to large loss of property and severe damage from radiant energy. However, in many plant accidents it is the sudden generation of pressure that leads to severe damage, injury, and deaths. Hence, it can be stated that "pressure blows up plants, not temperature." Of course, temperature and pressure are closely related, but it is the pressure effect that is of concern in this section.

The word "deflagration" can be defined in several ways. One definition is "a reaction which propagates to the unreacted material at a speed less than the speed of sound in the unreacted substance."[27] Another definition of deflagration is from Latin, meaning "to burn down, or to burn rapidly with intense heat and sparks given off."[30] A deflagration may be an explosion, but not all deflagrations are explosions (a violently burning fire may be a deflagration, but that is not an explosion). On the other hand, not all explosions are deflagrations (a steam boiler may explode, but that is not a deflagration).

An explosion is a sudden and violent release of energy. Usually it is the result, not the cause, of a sudden release of gas under high pressure. The presence of a gas is not necessary for an explosion. An explosion may occur from a physical or mechanical change, as in the explosion of a steam boiler, or from a chemical reaction. The explosion of a flammable mixture in a process vessel may be either a deflagration or a detonation, which differ fundamentally. Both can be very destructive. Detonations are particularly destructive, but are unlikely to occur in vessels.

A detonation is a reaction that propagates to unreacted material at a speed greater than the speed of sound in the unreacted material; it is accompanied by a shock wave and extremely high pressures for a very short time. It is debatable whether the flammable range is the same as the detonable range. Detonation limits normally are reported to be within the flammable limits, but the view is widely held that separate detonation limits do not exist.

Unconfined vapor clouds can both deflagrate and detonate, with a deflagration being much more likely. A detonation is more destructive, but a deflagration also can produce a damaging pressure wave. A deflagration can undergo transition to a detonation in a pipeline, but this is most likely in vessels.

If a flammable mixture may be present in process equipment, precautions should be taken to eliminate ignition sources. However, it is prudent to assume that, despite these efforts, a source of ignition will at some time occur.

Deflagration

The conditions for a deflagration to occur are that the gas mixture is within the flammable range and that there is a source of ignition or that the mixture is heated to its autoignition temperature.

For the burning of hydrocarbon–air mixtures:

$$\frac{P_{2\mathrm{MAX}}}{P_1} = \frac{N_2 T_2}{N_1 T_1} = \frac{M_1 T_2}{M_2 T_1}$$

where:

T = absolute temperature
M = molecular weight of gas mixture
N = number of moles in gas mixture
P = absolute pressure
1,2 = initial and final states
2MAX = final state maximum value

The maximum pressure rise for a deflagration of flammable mixtures is approximately as follows for initial absolute pressures of 1 to 40 bar, for initial temperatures of 0 to 300°C, and for relatively small volumes of a few cubic meters:

$$\frac{P_2}{P_1} = \text{approx. 8 for hydrocarbon–air mixtures}$$

$$\frac{P_2}{P_1} = \text{approx. 16 for hydrocarbon–oxygen mixtures}$$

For conventionally designed pressure vessels:

$$\frac{P_b}{P_1} = \text{approx. 4 to 5}$$

where:

P_b = vessel bursting pressure
P_1 = normal design pressure
P_2 = pressure caused by deflagration

Therefore, in the absence of explosion relief, the deflagration explosion of a hydrocarbon–air mixture is easily capable of bursting a vessel if it is operating near its design pressure when the deflagration takes place. For reactions operating at or near atmospheric pressure, such as many drying and solids processing operations, it may be practical to construct facilities that will withstand the maximum explosion pressure of most dust–air and flammable gas–air mixtures.

Detonations

Detonation of a gas–air mixture may occur by direct initiation of detonation by a powerful ignition source or by transition from deflagration. This transition occurs in pipelines but is most unlikely in vessels. Two useful rules are:

1. Almost any gas mixture that is flammable is detonable if initiated with a sufficiently energetic source.
2. Detonation of a gas–air mixture is possible in pipelines but is unlikely in vessels.

Bartknecht[8] states that the range of detonability is narrower than the range of flammability. For example, the range of detonability of hydrogen in air is 18 to 59 vol. %, compared with the flammability of 4 to 75 vol. %. With flammable gases in air, if the length-to-diameter ratio of a pipe or vessel is more than about 10:1, and the pipe diameter is above a critical diameter, 12 to 25 mm, a detonation is possible.

Detonation Pressure. In the case of the burning of a flammable mixture of gases in a pipe with one end closed, a series of pressure waves traveling at the speed of sound moves through the unburned gas. Later waves traveling through the unburned gas, which has been heated by compression from the earlier waves, speed up because of the higher temperature and overtake the first wave, and a shock wave develops. Flame follows the shock wave and catches up with it, forming a detonation wave. A stable detonation wave may develop, which moves with supersonic speed relative to the unburned mixture, and peak incident (side-on) pressures are of the order of *30 times* the initial absolute pressure.

TABLE 5.3 Overpressure from Detonations[36]

	Pressure MPa	*Pressure lb/in²*
Incident overpressure	3.5	510
Maximum reflected pressure (wave strikes surface head-on)	28	4100
Load the structure feels (due to acceleration)	56	8100

(MPa means pressure in megapascals.)

Reflected Pressure. Reflected pressure increases the pressure on a rigid surface if the shock wave impinges on the surface at an angle to the direction of the propagation of the wave. The maximum ratio of reflected pressure to incident (side-on) pressure when a strong shock wave strikes a flat surface head-on is 8:1. Furthermore, acceleration from a suddenly applied force of the detonation wave can double the load that a structure "feels." Table 5.3 shows overpressure that can be expected from typical detonations.[36]

Thus, the stable detonation wave may cause enormously high pressures at closed ends of pipes, bends, and tees, where the greatest destruction from a gaseous detonation may occur.

Geometry. The following are some factors to consider when detonation is possible:

- Large length-to-diameter ratios promote the development of detonations; vessels should be designed with the lowest length-to-diameter ratio practicable if a detonation is possible.
- Equipment such as tanks (not including pipelines) designed to withstand 3.5 MPa (about 500 psig) usually will be adequate to contain a detonation, with other safeguards, for flammable gases in air at atmospheric pressure.

- Dished heads survive detonations better than do flat heads because of the more unfavorable incidence of flat heads.
- If turns in a process line are necessary, two 45° bends or a long sweep elbow will greatly reduce reflected pressure compared to a single 90° elbow.
- Restrictions such as orifices in pipelines may intensify a detonation by promoting pressure piling, which results when there are interconnected spaces such that the pressure rise in one space causes a pressure rise in a connected space. The enhanced pressure in the latter then becomes the starting pressure for a further explosion.
- Detonation may be extinguished when it enters a wider pipe from a smaller one, but the detonation may be regenerated somewhere along the longer pipe.
- Flame arrestors, if properly designed, can arrest detonations.

Explosion Violence

The *rate of pressure rise* is a measure of the violence of an explosion. The maximum rate of pressure rise for confined explosions is greatly affected by the volume of the vessel, with the influence of vessel volume on the rate of pressure rise being given by the following equation:

$$(dp/dt)_{\max}(V^{1/3}) = \text{a constant} = K_G$$

where:

$(dp/dt)_{\max}$ = maximum rate of pressure rise, bar/sec

V = vessel volume, cubic meters

K_G = a specific material constant, (bar)(m)(sec)$^{-1}$

This is the *cubic law*, which states that for a given flammable gas, the product of the maximum pressure rise and the cube root of the vessel volume is a specific material constant, K_G.

The cubic law allows the prediction of the course of an explosion of a flammable gas or vapor in a large vessel, based on laboratory tests. It is valid only for the following conditions:

1. The same optimum concentration of the gas–air mixture.
2. Same shape of reaction vessel.
3. The same degree of turbulence.
4. The same ignition source.

Thus, to characterize an explosion, it is not enough to quote the maximum rate of pressure rise: the volume, vessel geometry, turbulence, and ignition energy must also be stated. Table 5.4 lists the K_G values for some common flammable gases measured under laboratory conditions.

It can be seen that the violence of an explosion with propane is about 1.5 times higher than one with methane, and one with hydrogen is about 10 times higher than one with methane. The explosive behavior of propane is representative of many flammable organic vapors in air. Some important relationships among pressure, temperature, turbulence, and vessel shape are discussed below.

1. *Explosion pressure is primarily the result of temperature reached during combustion, not a change in moles.* With complete combustion of propane in air there is a negligible change in moles of gas:

$$\overbrace{}^{\text{\{----air----\}}}$$

$$C_3H_8 + \overbrace{5O_2 + 18.8N_2}^{\text{air}} = 3CO_2 + 4H_2O + 18.8N_2$$

Number of moles at start = 24.8.
Number of moles after complete combustion = 25.8.

TABLE 5.4 K_G Values of Gases, Spark-Ignited with Zero Turbulence, Ignition Energy ~10 Joules, $P_{\max}$ = 7.4 bar[8]
(From Bartknecht, *Explosion Course, Prevention Protection*, Ref. 8, by Permission.)

Flammable Gas	K_G *(bar)(meter)/sec*
Methane	55
Propane	75
Hydrogen	550

Therefore, explosion pressure usually develops principally from an increase in temperature, not an increases in gas moles, during the combustion process of many materials.

Peak explosion pressure at constant volume occurs near the stoichiometric concentration in air. If only a small part of the total volume of a container is filled by an explosive gas–air mixture at atmospheric pressure, and the remainder of the vessel contains air, an explosion of this mixture can create enough pressure to severely damage containers that are designed to withstand only slight pressure —such as buildings and low-pressure storage tanks.

2. *Initial pressure affects maximum explosion pressure and rate of pressure rise.* If the initial pressure is increased above atmospheric pressure, there will be a proportional increase in the maximum explosion pressure and in the rate of pressure rise. Reducing the initial pressure will cause a corresponding decrease in maximum explosion pressure until finally an explosion reaction can no longer be propagated through the gas mixture.

3. *Initial temperature affects maximum explosion pressure and rate of pressure rise.* The maximum explosion pressure decreases when the starting temperature increases at the same starting pressure because of the lower density and thus smaller mass of material within a confined volume at higher temperatures. The maximum rate of pressure rise, $(dp/dt)_{\max}$, increases as the initial temperature rises because the burning velocity increases with an increase in initial temperature.

4. *Initial turbulence increases rate of pressure rise.* Initial turbulence greatly increases the rates of explosion-pressure rise.[8,27] It has been found that with pentane and methane mixtures in air, $(dp/dt)_{\max}$ can be five to nine times more with high initial turbulence than with no turbulence. The maximum explosion pressure is raised by about 20 percent. The course of explosions of flammable gases with a low normal speed of combustion, such as methane, is influenced by turbulence to a much higher degree than is the course of explosions with a high speed of combustion, such as hydrogen. Test data usually are obtained in equipment with a high degree of turbulence.

5. *Effect of vessel shape and increased initial pressure.* The maximum explosion pressure in confined vessels is not significantly affected by the volume or shape of the vessel in confined explosions for vessels that approximate the "cubic shape," that is, with a ratio of diameter to length (or vice versa) of about 1:1 to 1:1.5. In closed elongated vessels with central ignition, spherical ignition of the flame front will cause the flame to proceed swiftly in an axial direction. In the process, it compresses the unburned gases ahead of it, causing the violence of the explosion to increase, and pressure oscillations may occur.

DAMAGE ESTIMATES[37]

Damage estimates deal with the consequences of explosions and thermal radiation to both people and property. Physical models for explosions and thermal radiation generate a variety of incident outcomes: shock wave overpressure estimates, fragment velocities, and radiant flux. These models rely on the general principle that severity of outcome is a function of distance from the source of release. In addition to estimating the damage resulting from an explosion, it is also necessary to estimate how the consequences of these incident outcomes depend on the object of the study. To assess effects on human beings, damage estimates may be expressed as deaths or injuries. If physical property is the object, the damage estimates may be expressed as monetary losses.

Explosion Consequences

A principal parameter characterizing an explosion is the overpressure. Explosion effect modeling generally is based on TNT explosions to calculate the overpressure as a function of distance. Although the effect of a TNT explosion differs from that of a physical or a chemical explosion (particularly in the near-field), the TNT model is the most popular because a large data base exists for

TNT explosions. Several kinds of energy may be released in an explosion; three basic types are: (1) physical energy, (2) chemical energy, and (3) nuclear energy. Nuclear energy is not considered here. Physical energy may take such forms as pressure energy in gases, strain energy in metals, or electrical energy. Chemical energy derives from a chemical reaction. Examples of explosions involving chemical energy are runaway exothermic reactions, including decomposition and polymerization.

Table 5.5 summarizes the effects of explosion overpressure on structures. With respect to human casualties, heavy building damage usually is equated to a fatal effect, as the people inside the buildings probably would be crushed. People outside of buildings or structures are susceptible to direct blast injury (blast overpressure) and indirect blast injury (missiles or whole body transition).

Relatively high blast overpressures (>15 psig) are necessary to produce a human fatality from a direct blast. Instead, the major threat is produced by missiles or by whole body translation. Fatalities arising from whole body translation are mainly due to head injury from decelerative impact. Injury to people due to fragments usually results from either penetration by small fragments or blunt trauma from large fragments. TNO[39] suggested that projectiles with a kinetic energy of 100 Joules can cause fatalities. Table 5.6 shows damage to people (physiological damage) as a function of overpressure.

TABLE 5.5 Effect of Explosion Overpressure on Structures
(Courtesy of Center for Chemical Process Safety, American Institute of Chemical Engineers[38]

Pressure psi	*Damage*
0.02	Annoying noise (137 dB if of low, 10–15 Hz frequency).
0.03	Breaking of large glass windows under strain.
0.04	Loud noise (143 dB), sonic boom, glass failure.
0.10	Breakage of small glass windows under strain.
0.15	Typical pressure for glass breakage.
0.30	"Safe distance" (probability 0.95 of no serious damage below this value); projectile limits; some damage to house ceilings; 10% window glass broken.
0.40	Limited minor structural damage.
0.5–1.0	Large and small windows usually shattered; occasional damage to window frames.
0.70	Minor damage to house structures.
1.00	Partial demolition of houses; made uninhabitable.
1–2.00	Corrugated asbestos shattered; corrugated steel or aluminum panels, fastenings fail, followed by buckling; wood panel fastenings of standard housing fail; panels blown in.
1.30	Steel frames of clad buildings slightly distorted.
2.00	Partial collapse of walls and roofs of houses.
2–3.00	Concrete or cinder blocks shattered if not reinforced.
2.30	Lower limit of serious structural damage.
2.50	50% destruction of brickwork of houses.
3.00	Heavy machines (300 lbs), industrial buildings suffered little damage; steel frame buildings distorted and pulled away from foundation.
3–4.00	Frameless, self-framing steel panel building demolished; rupture of oil storage tanks.
4.00	Cladding of light industrial buildings ruptured.
5.00	Wooden utility poles snapped.
5–7.00	Nearly complete destruction of houses.
7.00	Loaded railcars overturned.
7–8.00	Brick panels, 8–12 in. thick, not reinforced, fail by shearing or flexure.
9.00	Loaded train boxcars completely demolished.
10.00	Probable total destruction of buildings; heavy machine tools (7,000 lb) moved and badly damaged; very heavy machine tools (12,000 lb) survive.
300.00	Limit of crater lip.

TABLE 5.6 Physiological Damage as a Result of Overpressure

Effect	*Peak Overpressure, psi*
Knock down	1.0
Ear drum damage	5.0
Lung damage	15
Threshold for fatalities	35
50% fatalities	50
99% fatalities	65

Radiation Consequences

The effect of thermal radiation on people and objects is determined by one of two approaches:

1. Simple tabulations based on experimental results.
2. Theoretical models based on the physiology of the skin burn response.

Data on time to pain threshold[40] are summarized in Table 5.7. For comparison, solar radiation intensity on a clear, hot summer day is about 320 Btu/hr ft^2 (1 kW/m^2). Other criteria for thermal radiation damage are shown in Table 5.8.[38]

The effect of thermal radiation on structures depends on whether they are combustible or not, and the nature and duration of the exposure. Thus, wooden materials will fail because of combustion, whereas steel will fail because of thermal lowering of the yield stress.

TABLE 5.7 Time to Pain Threshold for Varying Levels of Radiation[40]
(Courtesy American Petroleum Institute)

Radiation Intensity (Btu/hr ft^2)	*Radiation Intensity (kW/m^2)*	*Time to Pain Threshold (s)*
500	1.74	60
740	2.33	40
920	2.90	30
1500	4.73	16
2200	6.94	9
3000	9.46	6
3700	11.67	4
6300	19.87	2

TABLE 5.8 Effects of Thermal Radiation
(Courtesy of Center for Chemical Process Safety, American Institute of Chemical Engineers[38]

Radiation Intensity (kW/m^2)	*Observed Effect*
37.5	Sufficient to cause damage to process equipment.
25.0	Minimum energy required to ignite wood at indefinitely long exposures.
12.5	Minimum energy required for piloted ignition of wood, melting of plastic tubing.
9.5	Pain threshold reached after 6 seconds; second-degree burns after 20 seconds.
4.0	Sufficient to cause pain to personnel if unable to reach cover within 20 seconds; however, blistering of the skin (second degree burns) is likely; 0% lethality.
1.6	Will cause no discomfort for long exposure.

Unconfined Vapor Cloud Explosions (UVCE)

When a large amount of volatile material is released rapidly to the atmosphere, a vapor cloud forms and disperses. If the cloud is ignited before it is diluted below its lower flammability limit, an uncontrolled vapor cloud explosion will occur. This is one of the most serious hazards in the process industries. Both shock waves and thermal radiation will result from the explosion, with the shock waves usually the more important damage producers. UVCEs usually are modeled by using the TNT model.[38] The energy of the blast wave generally is only a small fraction of the energy available from the combustion of all the material that constitutes the cloud; the ratio of the actual energy released to that available frequently is referred to as the "explosion efficiency." Therefore, the TNT weight equivalent of a UVCE includes an explosion efficiency term, which typically is an empirical factor ranging from 1 to 10 percent. The explosion effects of a TNT charge are well documented.

Physical Explosions

A physical explosion usually results from the production of large volumes of gases by nonchemical means. The gases necessary for a physical explosion may be those already existing, such as compressed nitrogen released suddenly from a ruptured cylinder, or steam released explosively from a crack in a steam drum.

The following are some settings and situations in which physical explosions have been known to take place:

- Steam boilers.
- Hydraulic overfill of tanks or pipes with external applied pressure (as in pressure testing).
- Compressed air tanks.
- Deadheaded pumps.
- Thermal expansion of tanks or pipes.
- Liquid cryogenic fluids on water (such as liquid methane on water).
- Water suddenly mixed with sulfuric acid (also may cause a chemical explosion).
- BLEVE (Boiling Liquid Expanding Vapor Explosion) with superheated liquid (flammable or nonflammable) (see next section).
- Explosion of grinding wheel at too high a speed.
- Liquid water in molten $MgCl_2$ solution at high temperatures.
- Implosions due to vacuum.
- Overpressured refrigerant systems.
- Molten metals exploding violently on contact with water.
- Some molten metals exploding when mixed with each other.
- The mixing of two immiscible liquids whose boiling points are not widely separated.

Steam boilers are commonly used in power plants and industries of all kinds. They generally are taken for granted now, but in the second half of the nineteenth century boilers blew up with alarming regularity. Records indicate that from 1870 to 1910 there were at least 10,000 boiler explosions in the United States and adjacent areas of Canada and Mexico; that is, more than one recorded explosion every 36 hours! By 1910, the rate had jumped to between 1300 and 1400 per year. On October 8, 1894, in the Henry Clay Mine in Shamokin, Pennsylvania, 27 boilers disintegrated almost simultaneously! Mainly because of the incorporation of the ASME Boiler Code into laws, boiler explosions have decreased dramatically.[41]

When a pressurized vessel ruptures, the resulting stored energy is released. This energy can cause a shock wave and accelerate vessel fragments. If the contents are flammable, ignition of the released gas could produce additional effects. There is a maximum amount of energy in a bursting vessel that can be released, and it is released in the following proportions:[36]

	Distribution of Energy When Vessel Ruptures		
Type of Failure	*Strain Energy*	*Kinetic Energy of Fragments*	*Shock Wave Energy*
Brittle Failure	< 10%	~20%	up to 80%
Plug Ejection	small	up to 60 to 80%	20 to 40%

The relative distribution of these energy components will change over the course of the explosion, but most of the energy is carried by the shock wave with the remainder going to fragment kinetic energy. To estimate the damage resulting from the shock wave from a physical explosion, the TNT model is used widely. To determine the TNT equivalent of a physical explosion, the total energy in the system must be estimated. For a physical explosion, if the expansion occurs isothermally, and ideal gas laws apply, then the TNT equivalent of the explosion can be calculated. This energy then can be used to estimate overpressure at any distance from the explosion. The analogy of the explosion of a container of pressurized gas to a point source explosion of TNT is not appropriate in the near-field. Prugh[42] suggests a correction method using a virtual distance R_v from an explosion center.

In addition to shock wave effects, a major hazard of a ruptured gas-filled vessel is from projectiles. To estimate damage from projectiles, both the initial velocity and the range are required. A simplified method for calculating the initial velocity uses the following equation:[43]

$$u = 2.05(PD^3/W)^{0.5}$$

where:

u = initial velocity, ft/sec
P = rupture pressure psig
D = fragment diameter, inches
W = weight of fragments, pounds

Clancey[44] gives the following values for initial velocity for the majority of fragments from a TNT explosion:

- Thin case: 8000 ft/sec
- Medium case: 6000 ft/sec
- Thick case: 4000 ft/sec

Once the initial velocity has been determined, the maximum range of the fragment, ignoring air resistance, can be estimated from:

$$R_{\max} = \frac{u^2}{g}$$

If the above values for typical velocities are substituted into the above equation, a maximum range of 5×10^5 feet is possible. Therefore, it is clearly necessary to include air resistance. To include air resistance, a value of C_D, the drag coefficient, must be estimated. The drag coefficient ranges from 0.48 for a sphere to 2 for flow perpendicular to a flat strip, and for most fragments ranges from 1.5 to 2.0.

If one knows the air density, drag coefficient, exposed area of the fragment, mass of the fragment, and the initial velocity, the maximum range R can be calculated with the aid of Fig. 5.10.[45] Although this technique gives the maximum range, most fragments do not travel the maximum distance but fall at distances between 0.3 and 0.8 of the maximum.

The energy required to impart an initial velocity of u to a fragment is:

$$E = \tfrac{1}{2}mu^2$$

where:

m is the mass of the fragment (lb)
u the initial velocity (ft/sec)

Example. A high pressure vessel containing air at 600 bar has ruptured, leading to 15 fragments of approximately equal mass (85 lb), one of which was found as far as 400 feet from the vessel. This fragment has a drag coefficient of 1.5 and an exposed area of 3 ft.^{2} Assuming that 20 percent of the explosion energy went to energy of the fragments, estimate the energy of the explosion in weight equivalent TNT. The air density is 0.081 lb/ft.^{3}

Procedure. Assuming that the fragment found at 400 feet is at the maximum range for the fragments, the scaled fragment range R_s can be calculated:

$$R_s = \frac{r_0 C_D A_D R}{M} = \frac{0.081 \times 1.5 \times 3 \times 400}{85} = 1.7$$

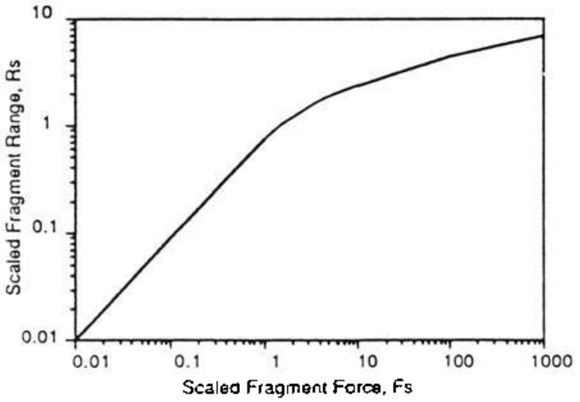
From Fig. 5.10, we obtain a scaled force (F_s) of approximately 5. The initial velocity of the fragment then can be calculated as:

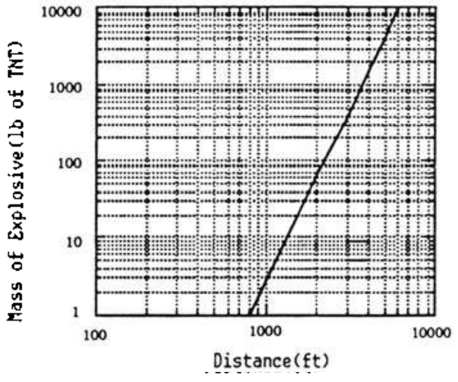
$$u = \sqrt{\frac{MgF_s}{r_0 C_D A_D}} = \sqrt{\frac{85 \times 32.17 \times 5}{0.081 \times 1.5 \times 3}} = 194 \text{ ft/sec}$$

The energy required to give the fragment this initial velocity is:

$$E = \tfrac{1}{2}(85)(194)^2 = 1.6 \times 106 \text{ lb ft}^2/\text{sec}^2 = 64 \text{ Btu}$$

Since there were 15 fragments, the total energy of the explosion that went into





where: $F_s = \dfrac{r_o C_D A_D u^2}{Mg}$ $R_s = \dfrac{r_o C_D A_D R}{M}$

and: r_o = density of air lb/cu ft C_D = drag coefficient

A_D = exposed area of fragment, ft2   R = max range of fragment, ft

M = mass of fragment, lb   U = fragment initial velocity, fps

$g = 32.17 \text{ ft. lb}_m/\text{lb}_f\text{s}^2$

Fig. 5.10A. Scaled fragment range vs. scaled force. (*Baker et al. 1983.*[45])

Fig. 5.10B. Maximum horizontal range of blast fragments. (*Clancy*[44].)

fragment kinetic energy is 15 × 635.8 Btu = 9537 Btu. If only 20 percent of the explosion energy went into fragment kinetic energy, then the total explosion energy is 47,680 Btu, which is the equivalent of 23.8 lb of TNT. Using the method of Clancy[44], 2.4 lb TNT can provide a maximum range of 950 ft for projectiles (Fig. 5.10B).

BOILING LIQUID EXPANDING VAPOR EXPLOSIONS (BLEVEs)

Among the most damaging of accidents is a Boiling Liquid Expanding Vapor Explosion (BLEVE, pronounced BLEV-ee). This occurs when a pressure vessel containing liquid is heated so that the metal loses strength and ruptures. Typically, this happens when the vessel failure results from overheating upon exposure to fire. The failure usually is in the metal contacting the vapor phase; the metal in this area heats to a higher temperature because there is no liquid heat sink to keep the metal temperature from rising rapidly, as there is where metal contacts a liquid phase. A BLEVE can occur with both flammable materials and nonflammable materials, such as water. In all cases the initial explosion may generate a blast wave and missiles. If the material is flammable, it may cause a fire or may form a vapor cloud that then gives rise to a secondary explosion and fireball. Kletz states that BLEVEs can cause as many casualties as can unconfined vapor cloud explosions.[2]

The best known type of BLEVE involves LPG (liquefied petroleum gas). Once a fire impinges on the shell above the liquid level, the vessel usually fails within 10 to 20 minutes. In the case of a BLEVE involving a flammable material, the major consequences are, in order of decreasing importance:

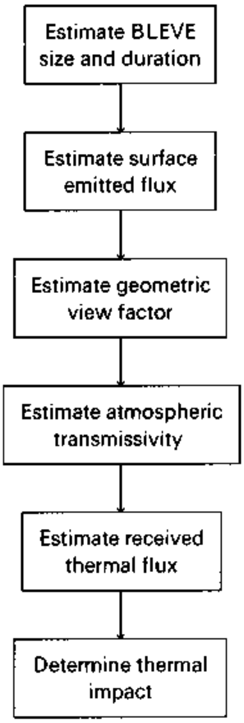
1. Thermal radiation from the resultant fireball.
2. Fragments produced when the vessel fails.
3. Blast wave produced by the expanding vapor/liquid.

For example, a BLEVE of a propane sphere with a diameter of 50 feet, holding about 630,000 gallons, could cause damage as far away as 13,600 feet, and radiation damage and fragmentation damage would each extend to about 3000 feet.

In a fire, a tank containing liquid is most vulnerable in the shell at the vapor space because very little heat can be absorbed by the vapor, and the metal in the vapor space can heat up rapidly to a temperature where it will weaken rapidly. The metal contacting the liquid phase will heat up much less rapidly because the liquid can absorb significant amounts of heat, keeping the shell temperature down in that area for a significant amount of time. Thus, there is a dilemma: a partly full vessel may BLEVE sooner than will a full vessel, but a full vessel will have more fuel for the resulting fireball and fire than will a partly empty vessel.

Significant equipment and building damage frrom radiation is possible from a BLEVE. Wooden structures may be ignited if the radiant heat density at the structure's location exceeds the threshold value for ignition of wood. Severe damage from fragmentation can be expected in the area where 50 percent or more of the fragments may fall, or typically about 300 feet from the vessel.

A BLEVE can lead to shock waves, projectiles, and thermal radiation. The effects of a shock wave and projectiles were dealt with earlier; by far the most serious consequence of a BLEVE is the radiation received from the fireball. The following calculational procedure is used to determine thermal impact (details are available in reference 38):



MECHANICAL HEAT

Mechanical motion in fluids becomes kinetic energy and may become heat in devices with rotating parts. Mechanical heat input from rotating agitators, pump impellers, and other mechanical equipment must be taken into account in the design of process equipment, particularly in systems containing reactive chemicals. This section will provide some guidelines for the analysis of individual cases involving pumps and agitated tanks.[46–48]

Some useful rules are as follows:

1. A deadheaded pump is a pump operating full of liquid and with inlet and outlet valves closed.
2. Almost all deadheaded centrifugal pumps with motors of three horsepower or larger are headed for trouble if left deadheaded. (Depending on the horsepower, a few minutes may be too long.)

3. The heat input from the rotating impeller in a deadheaded centrifugal pump is always a large value relative to the heat sink of the fluid and the pump.
4. It is not necessary for there to be a chemical reaction in a pump for an explosion to take place. Deadheaded pumps containing only water or brine have blown up.
5. An agitator or a circulating pump left on in a vessel of a reactive chemical may heat up the contents enough to cause a runaway reaction.
6. All centrifugal pumps with motors larger than three horsepower should be protected in some way to prevent deadheading. A temperature alarm in the casing is a minimum form of protection. A better way may be to have the high-temperature alarm wired to the process control computer, to both alarm and shut off the pump. Other systems are available and may be used; they may include (but are not limited to) a relief valve on the pump, a minimum flow valve, and a flow orifice in the recirculating line. A relief valve on a pump relieving back to the pump inlet may not eliminate the problem of heat buildup in a deadheaded pump and usually should be avoided unless other protective measures are used such as a high-temperature device.
7. An ammeter on the pump motor usually is not a reliable means of detecting deadheaded conditions. The low power factors often experienced with pump motors, and the nature of pump curves, often make it difficult to distinguish between normal running and deadheaded conditions using an ammeter.
8. For mechanical heat equivalent, the following is recommended: (a) For pumps, use 50 percent of the connected motor horsepower for centrifugal pumps that are deadheaded, unless better information is available. (b) For agitators, use 100 percent of the vendor rated shaft input horsepower for the input shaft (total power less drive and bearing inefficiencies) for the actual material in the vessel.

VACUUM[49]

Ask any chemical engineers who have had some plant experience what they know about vacuum, and they probably will smile and tell a tale about some piece of equipment that tried to turn itself inside out. Usually no one was hurt, and often there is no massive leakage—but not always!

The design for the internal pressure condition of vessels usually is straightforward and well understood. Under vacuum conditions, equipment is subject to external pressure from the atmosphere; and the design for external pressures is more difficult than that for internal pressures. The devious ways in which external pressure can be applied often may be overlooked.

The following are some obvious causes of vacuum collapse:

1. Liquid withdrawal by pump or gravity draining.
2. Removal of gas or vapor by withdrawing with a blower, fan, or jet.
3. Siphoning of liquids.

Less obvious causes include:

1. Condensation of vapor.
2. Cooling of hot gas.
3. Combination of cooling and condensation of a mixture of gas and condensable vapor.

Sometimes obscure causes of vacuum collapse include:

1. Absorption of a gas in a liquid; for example, ammonia in water, carbon dioxide in water, hydrogen chloride in water.
2. Reaction of two or more gases to make a liquid or solid; for example, ammonia plus hydrogen bromide to form ammonium bromide.
3. Reaction of a gas and a solid to form a solid; for example, corrosion in a tank, air plus Fe or FeO forming Fe_2O_3 in the presence of water.

4. Reaction of a gas and a liquid to give a liquid; for example, chlorination, hydrogenation, ethylation.
5. Sudden dropping of finely divided solids in a silo, creating a momentary vacuum that can suck in the sides of the silo.
6. Flame arrestors plugging; for example:
    (a) In styrene service, vapor may condense in flame arrestors, and the liquid formed is low in inhibitor; the liquid may polymerize and plug off the arrestor. Possible solutions: clean the arrestor frequently or use a PVRV (pressure-vacuum-relief valve).
    (b) Liquid service in cold weather: vapor may condense in a flame arrestor and the liquid formed may freeze and plug the arrestor. Possible solution: heat and insulate the arrestor to prevent condensation.
7. Maintenance and testing. It is not a good idea to apply vacuum on a vessel during maintenance or testing without full knowledge of the external pressure rating unless a suitable vacuum relief device is in place and operable.

Protective Measures for Equipment

If equipment may be subject to vacuum, consideration should be given to designing the equipment for full vacuum. This may eliminate the need for complicated devices such as vacuum relief valves and instruments; if they are used, designing the equipment for full vacuum will prevent collapse of the vessel if the instruments or relief valves fail or plug.

A disadvantage of this approach is that it usually is expensive. However, when the total cost of a suitably instrumented vessel not designed for vacuum is compared with the cost of a vessel designed for vacuum but without the extra equipment, the difference may be small or negligible, and the vessel designed for vacuum will be inherently safer. If a vessel is designed for vacuum, precautions should be taken to ensure that internal or external corrosion will not destroy the integrity of the vessel.

PROCESS SAFETY MANAGEMENT SYSTEMS

The public, customers, employees, and local and federal government regulatory agencies all demand that companies take the actions needed to reduce the possibility of the release of hazardous materials. From 1975 to 1991, a number of major chemical or chemical-related incidents had major impacts on the chemical industry and on many communities as well. As the chemical process industries have developed better ways to improve process safety, safety management systems have been introduced to help implement improvements in process safety engineering activities. Management systems for chemical process safety are comprehensive sets of policies, procedures, and practices designed to ensure that barriers to major incidents are in place, in use, and effective.[24,38] Following are some definitions that are useful in discussions on managing process safety.

Definitions

Accident. An unplanned event with undesirable consequences.

Consequences. Damage from a scenario; for example, the number of people exposed to a chemical cloud.

Event. The most elementary action in an accident; for example, an operator response or action.

Hazard. Result of combining a scenario and a consequence; for example, a chemical cloud is formed, and people are exposed. Also, the inherent potential of a material or activity to harm people, property, or the environment.

Incident. An occurrence that may be either an accident or a near miss.

Near miss. Extraordinary event that could have resulted in an accident but did not.

Probability. The likelihood of the occurrence of events or a measure of degree of belief, the values of which range from 0 to 1.

Quantitative Risk Analysis (QRA). The systematic development of numerical estimates of the expected frequency and/or consequence of potential accidents associated with a facility or an operation. Often used interchangeably with "quantitative risk assessment."

Risk. Result of combining scenario, consequence, and likelihood, for example, likelihood (probability) of cloud being formed and people being exposed, given the process specifics. Or, a measure of potential economic loss or human injury in terms of the probability of the loss or injury occurring and the magnitude of the loss or injury if it occurs. Or, combination of the expected frequency (events/year) and/or consequence (effects/event) of a single accident or a group of accidents.

Risk assessment. The systematic evaluation of the risk associated with potential accidents at complex facilities or operations. Or, the process by which the results of a risk analysis are used to make decisions, either through relative ranking of risk reduction strategies or through comparison with risk targets. The terms "risk analysis" and "risk assessment" often are used interchangeably in the literature.

Risk management. A part of chemical process safety management. Risk analysis (often used interchangeably with risk assessment) is a part of risk management.

Scenario. End result of a series of events, for example, release of a chemical cloud.

Some Tools for Evaluating Risks and Hazards

Dow Fire and Explosion Index. The Dow Fire and Explosion Index (F&EI), developed by The Dow Chemical Company, is an objective evaluation of the potential of a facility for a fire, an explosion, or a reactive chemical accident. Its purpose is to quantify damage from incidents, identify equipment that could contribute to an incident, and suggest ways to mitigate the incident; it also is a way to communicate to management the quantitative hazard potential. It is intended for facilities handling flammable, combustible, or reactive materials whether stored, handled, or processed. The goal of the F&EI evaluation is to become aware of the loss potential and identify ways to reduce the potential severity in a cost-effective manner. It does not address frequency (risk) except in a general way. The number is useful mainly for comparisons and for calculations of damage radius, maximum probable property damage, and business interruption loss, and to establish frequency of reviews. The method of carrying out an F&EI evaluation is available to the public from the American Institute of Chemical Engineers, 345 E. 47th St., New York, NY 10017.

Failure Modes and Effects Analysis (FMEA). FMEA is a systematic, tabular method for evaluating the causes and effects of component failures. It represents a "bottom-up" approach in contrast with fault tree, where the approach is "top-down." In large part, HAZOP is a well-developed form of FMEA.[2]

Fault Tree. A fault tree is a logical model that graphically portrays the combinations of failures that can lead to a particular main failure or accident of interest. A fault tree starts with a top event, which is usually a hazard of some kind. The possibility of the hazard must be foreseen before the fault tree can be constructed. A fault tree helps reveal the possible causes of the hazard, some of which may not have been foreseen.[2]

Safety Audit. A safety audit is a method of reviewing the actual construction and operation of a facility. Often safety audits are conducted by a small interdisciplinary team. At least some of the members of the team are not connected with the plant. The audit may be carried out before startup and also is repeated later at intervals of, typically, one to five years.

Chemical Exposure Index. The Chemical Exposure Index is a technique for estimating the relative toxic hazards of chemicals, developed by The Dow Chemical Company. It provides for the relative ranking of toxic chemicals in a given facility, including factors relating to toxicity, quantity volatilized, distance to an area of concern, and physical properties. A description of the method is found in *Guidelines for Safe Storage and Handling of High Toxic Hazard Materials*, Center for Chemical Process Safety, American Institute of Chemical Engineers.[50]

EVALUATION OF HAZARDS AND RISKS

HAZOP[2,50–53]

HAZOP stands for "Hazard and Operability Studies," a set of formal hazard identification and elimination procedures designed to identify hazards to people, process, plants, and the environment. The techniques aim to stimulate the imagination of designers and operations people in a systematic way so they can identify potential hazards. In effect, HAZOP studies assume that there will be mistakes, and provide a systematic search for these mistakes. In some European countries, HAZOP studies are mandatory and attended by observers from regulatory authorities to ensure that the studies are carried out correctly. The examination of accidents[52] during 1988 at a large U.S. chemical company revealed that the accidents could be classified as follows:

Spills: 52 percent
Emissions: 30 percent
Fires: 18 percent

Of the fires, about 50 percent occurred during construction, 25 percent were due to pump seal failure, and the remaining 25 percent resulted from engineering and operational oversights that a HAZOP study possibly could have prevented.

Of the emissions, 37 percent were due to piping failure, with lined pipe being the largest contributor. Operational and procedural issues accounted for 53 percent of the remainder.

Of the spills, 11 percent were due to equipment failures. Piping failures (especially lined pipe and gaskets) accounted for 30 percent, and 56 percent were caused by various types of operational errors, noncompliance with procedures, or nonexistent procedures.

Material handling was a factor in many spills and emissions.

The most frequent type of operational error was a valve being left in an improper position, either open or closed.

HAZOP studies probably could have reduced the number and the seriousness of the problems experienced.

Some investigations have shown that a HAZOP study will result in recommendations that are 40 percent safety-related and 60 percent operability-related. Thus, HAZOP is far more than a safety tool; a good HAZOP study also results in improved operability of the process or plant, which can mean greater profitability.

The HAZOP technique can be used to identify human error potential. From a practical point of view, human error and its consequences can occur at all levels of a management structure as well as in the operation of a particular plant or process. Carried out correctly, Technica[54] states that a HAZOP study will identify at least 70 to 75 percent of potential operational and safety problems associated with a particular design process, including human error.

The HAZOP technique also can be used for the evaluation of procedures. Procedures may be regarded as a "system" designed to "program" an operator to carry out a sequence of correct actions. Deviations from intent are developed, with the emphasis on "operator action deviation" rather than "physical property deviation." It is the procedure, not the hardware, that is the object of study, but hardware modifications may be recommended to cover potential problems identified from procedure deviations.

Operating Discipline

HAZOP can be an important part of establishing the operating discipline of a plant, which can be defined as the total information required to understand and operate the facility. By recording recommendations and actions in detail on all parts of the process, the rationale behind the way the process is designed and intended to operate and key details of the process will be available, which are rarely on record from other sources. This can be especially helpful when plant changes are made, and when new plants based on the same design are built.

Risk Analysis and Assessment

Risk is defined (see above) as the combination of expected frequency (events/year) and consequence (effects/event) of accidents that could occur as a result of an activity. Risk analysis evaluates the likelihood and consequence of an incident. Risk assessment is an extension of risk analysis that includes making judgments on the acceptability of the risk. It may be qualitative or quantitative, or it can range from simple, "broad brush" screening studies to detailed risk analyses studying large numbers of incidents and using highly sophisticated frequency and consequence models. Throughout the published literature, the terms "risk analysis" and "risk assessment" are used interchangeably.

Quantitative Risk Analysis (QRA)

Quantitative Risk Analysis (QRA) models the events, incidents, consequences, and risks, and produces numerical estimates of some or all of the frequencies, probabilities, consequences, or risks.[38,55] QRA can be done at a preliminary level or a detailed level, and in all cases may or may not quantify all events, incidents, consequences, or risks.[56] QRA is the art and science of developing and understanding numerical estimates of the risk associated with a facility or an operation. It uses highly sophisticated but approximate tools for acquiring risk understanding.

QRA can be used to investigate many types of risks associated with chemical process facilities, such as the risk of economic losses or the risk of exposure of members of the public to toxic vapors. In health and safety applications, the use of QRA can be classified into two categories:

1. Estimating the long-term risk to workers or the public from chronic exposure to potentially harmful substances or activities.
2. Estimating the risk to workers or the public from episodic events involving a one-time exposure, which may be acute, to potentially harmful substances or activities.

This discussion will focus on the use of QRA in the assessment of acute hazards and episodic events only.

QRA is fundamentally different from many other chemical engineering activities (e.g., chemistry, heat transfer), whose basic property data are capable of being theoretically and empirically determined and often established experimentally. Some of the basic "property data" used to calculate risk estimates are probabilistic variables with no fixed values, and some of the key elements of risk must be established by using these probabilistic variables. QRA is an approach for estimating the risk of chemical operations by using the probabilistic approach; it is a fundamentally different approach from those used in many other engineering activities because interpreting the results of QRA requires an increased sensitivity to uncertainties that arise primarily from the probabilistic character of the data.

The underlying basis of QRA is simple in concept. It offers methods to answer the following four questions:

1. What can go wrong?
2. What are its causes?
3. What are its consequences?
4. How likely is it?

It has been said that QRA attempts to answer the question, "Does this plant have the potential to cause another Bhopal incident?" (This incident is described below.) Although the application of QRA might not have prevented the Bhopal incident, it is at least possible that the proper application of QRA could have made this incident extremely unlikely.

Methods of Showing Results of Risk Studies

F–N curves are used for societal risks; risk contours show individual risk. Figure 5.11 shows various contours illustrating the probability of a particular impact on an individual located on the contour line. Figures 5.12 and 5.13 illustrate two of the more commonly used methods for displaying societal risk results: an *F–N* curve and a risk profile. The *F–N* curve plots the cumulative frequencies of events causing *N* or more impacts, with the number of impacts (*N*) shown on the horizontal axis. With the *F–N* curve it is easy to see the expected frequency of accidents that could harm more than a specified number of people. The *F–N* curve is a cumulative illustration.

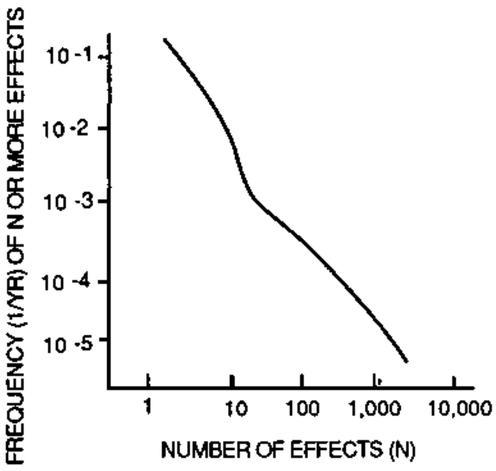


Fig. 5.12. Example of an *F–N* curve (societal risk).

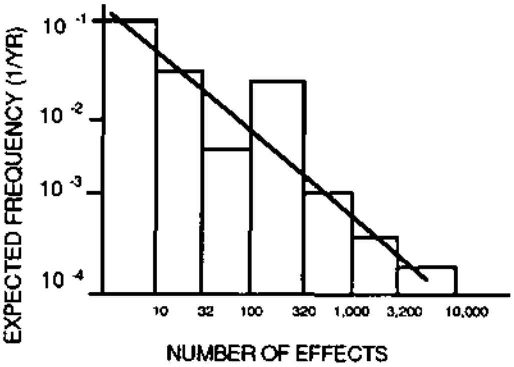


Fig. 5.13. Risk profile—expected frequency of accidents of a particular category.

The risk profile shows the expected frequency of accidents of a particular category or level of consequence. The diagonal line is a line of constant risk defined such that the product of expected frequency and consequence is a constant at each point along the line. As the consequences of accidents go up, the expected frequency should go down in order for the risk to remain constant. If a portion of the histogram sticks its head above the line (i.e., if a particular type of accident contributes more than its fair share of the risk), then that risk is inconsistent with the risk presented by other accident types.

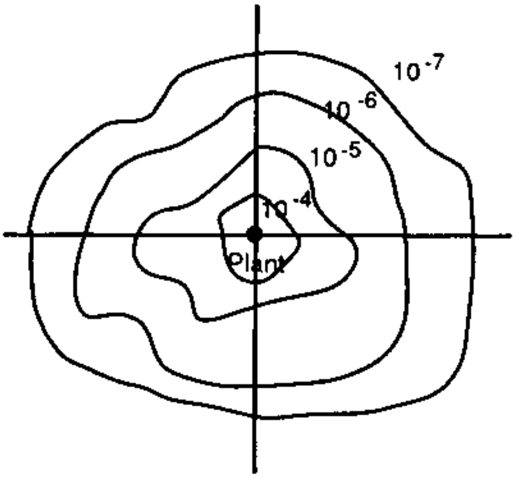


Fig. 5.11. Risk contour (individual risk). Probability per year of an average individual being severely injured.

A method for graphically displaying individual risk results is use of the risk contour, or risk isopleth. If individual risk is defined as the likelihood of someone suffering a specified injury or loss, then individual risk can be calculated at particular geographic locations around the vicinity of a facility or an operation. If the individual risk is calculated at many points surrounding the facility, then points of equal risk can be connected to create a risk contour map showing the geographic distribution of the individual risk.

THE PRINCIPAL REASON FOR MOST CHEMICAL PROCESS ACCIDENTS

Ask any group of people experienced in chemical plant operations what causes most chemical process accidents, and you will get a variety of answers including: operator error, equipment failure, poor design, act of God, and bad luck. However, in the opinion of representatives of many of the large chemical and oil companies in the United States, these answers are generally incorrect. The Center for Chemical Process Safety, an organization sponsored by the American Institute of Chemical Engineers, includes representatives of many of the largest chemical and oil companies in the United States, and states that "It is an axiom that process safety incidents are the result of *management system failure.*" Invariably, some aspect of a process safety management system can be found that, had it functioned properly, could have prevented an incident (or reduced the seriousness of it). "It is a rare situation where an 'Act of God' or other uncontrollable event is the sole cause of an incident. Much more common is the situation where an incident is the result of multiple causes, including management system failures. Therefore, it is more appropriate to presume that management system failures underlie every incident so that we may act to uncover such failures and then modify the appropriate management systems, rather than presume that if an 'Act of God' appears to be the immediate cause, investigation should cease because there is nothing that can be done to prevent such future incidents."[24]

For example, consider a case where a small amount of hazardous material is spilled while a sample is being taken from a process line. It is not enough to look into the situation and conclude that this is an example of an operator error where procedures were not followed, and then simply to recommend that the employee be instructed to follow procedures in the future. Further investigation may reveal deficiencies in the training system or in the equipment. Still more investigation may reveal deficiencies in the management system that plans resources for training or that provides for proper equipment for sampling. It then may be appropriate to change the management system to prevent repetition of the incident.

Levels of Causes

There are several levels of causes of accidents, usually (1) the immediate cause, (2) contributing causes to the accident or to the severity of the accident, and (3) the "root cause." The root cause is what really caused the accident, and when this is determined, it may be possibly to *prevent* future similar accidents. With the 20–20 hindsight that is available after an accident, the root cause usually can be found. The purpose of the discussion in the next section is to illustrate how knowledge about the root causes of some important accidents can help to keep them from happening again. It will be noted that the root cause is rarely the fault of one person, but instead is the result of a management system that does not function properly.

Following are brief analyses of several case histories that have been of landmark importance in the industrial world, and that have affected the chemical industry all over the world.

CASE HISTORIES

Flixborough, England, 1974[2]

On June 1, 1974, an accident occurred in the Nypro plant in Flixborough, England, in a process where cyclohexane was oxidized to cyclohexanone for the manufacture of caprolactam, the basic raw material for the production of Nylon 6. The process consisted of six reactors in series at 155°C and 8.8 bar (130 psig) containing a total of 120 tons of cyclohexane and a small amount of cyclohexanone. The final reactor in the process contained 94 percent cyclohexane. There was a massive leak followed by a large unconfined vapor cloud explosion and fire that killed 26, injured 36 people, destroyed 1821 houses, and damaged 167 shops. It was estimated that 30 tons of cyclohexane was involved in the explosion. The accident occurred on Saturday; on a working day, casualties would have been much higher.

The accident happened when the plant had to replace one of six reactors and rushed to refit the plant to bypass the disabled reactor. Scaffolding was jerry-rigged to support a 20-inch pipe connecting reactor four with reactor six, which violated industry and the manufacturer's recommendations. The reactor that failed showed stress crack corrosion. The only drawings for the repair were in chalk on the machine shop floor. Both ends of the 20-inch pipe had expansion joints where they attached to the reactors. The pipe was supported on scaffolding-type supports and was offset with a "dog-leg" to fit the reactors, which were at different levels to promote gravity flow. The safety reviews, if any, were insufficient.

Immediate Cause. A pipe replacing a failed reactor failed, releasing large quantities of hot cyclohexane forming a vapor cloud that ignited.

Contributing Causes to the Accident and the Severity of the Accident:

1. The reactor failed without an adequate check on why (metallurgical failure).
2. The pipe was connected without an adequate check on its strength and on inadequate supports.
3. Expansion joints (bellows) were used on each end of pipe in a "dog-leg" without adequate support, contrary to the recommendations of the manufacturer.
4. There was a large inventory of hot cyclohexane under pressure.
5. The accident occurred during start-up.
6. The control room was not built with adequate strength, and was poorly sited.
7. The previous works engineer had left and had not been replaced. According to the Flixborough Report, "There was no mechanical engineer on site of sufficient qualification, status or authority to deal with complex and novel engineering problems and insist on necessary measures being taken."
8. The plant did not have a sufficient complement of experienced people, and individuals tended to be overworked and liable to error.

Root Cause. Management systems deficiencies resulted in:

1. A lack of experienced and qualified people.
2. Inadequate procedures involving plant modifications.
3. Regulations on pressure vessels that dealt mainly with steam and air and did not adequately address hazardous materials.
4. A process with a very large amount of hot hydrocarbons under pressure and well above its flash point installed in an area that could expose many people to a severe hazard.

This accident resulted in significant changes in England and the rest of the world in the manner in which chemical process safety is managed by industry and government. One of the conclusions reached as a result of this accident, which has had wide effect in the chemical industry, is that "limitations of inventory (or flammable materials) should be taken as specific design objectives in major hazard installations."

The use of expansion joints (bellows, in this case) which were improperly installed may have been a principal reason for the accident. This provides additional reasons not to use expansion joints (except in special exceptional circumstances).

Bhopal, 1985 (C&EN Feb. 11, 1985; Technica 1989[54])

On December 3 and 4, 1985, a chemical release causing a massive toxic gas cloud occurred at the Union Carbide India, Ltd., plant in

Bhopal, India. The process involved used methyl isocyanate (MIC), an extremely toxic chemical, to make Sevin, a pesticide. According to various authoritative reports, about 1700 to 2700 (possibly more) people were killed, 50,000 people were affected seriously, and 1,000,000 people were affected in some way. The final settlement may involve billions of dollars. It was one of the worst industrial accidents in history. The accident occurred when about 120 to 240 gallons of water were allowed to contaminate an MIC storage tank. The MIC hydrolyzed, causing heat and pressure, which in turn caused the tank rupture disk to burst.

Equipment designed to handle an MIC release included a recirculating caustic soda scrubber tower and a flare system designed for 10,000 lb/hr, which would be moderate flows from process vents. It was not designed to handle runaway reactions from storage. The design was based on the assumption that full cooling would be provided by the refrigeration system. The actual release was estimated to be 27,000 lb over 2 hours, with the tank at 43°C. At the time of the release the refrigeration had been turned off. The flare tower was shut down for repairs. A system of pressurized sprinklers that was supposed to form a water curtain over the escaping gases was deficient, in that water pressure was too low for water to reach the height of the escaping gas.

There have been conflicting stories of how the water got into the tank, including operator error, contamination, and sabotage.

Immediate Cause. The immediate cause was hydrolysis of MIC due to water contamination. The exact source of the water has not been determined.

Contributing Causes:

1. Flare tower was shut down for repair.
2. Scrubber was inadequate to handle a large release.
3. Chilling system was turned off. (It also was too small.)
4. MIC tank was not equipped with adequate instrumentation.
5. Operating personnel lacked knowledge and training.
6. The inventory of MIC was large.
7. There was a lack of automatic devices and warning systems; it has been reported that safety systems had to be turned on manually.
8. When the plant was built, over 20 years before the accident, there were very few people near it. At the time of the accident, a shanty town had grown up near the plant with a density of 100 people per acre, greatly increasing the potential exposure of people to toxic releases. There was no emergency action plan to notify neighbors of the potential for toxic releases or of what to do if there was a release, nor was there a functioning alarm system.

Root Cause. The root cause of the accident appears to be a management system that did not adequately respond to the potential hazards of MIC. There was probably a greater inventory of MIC than was needed. The main process expertise was in the United States. Local management does not appear to have understood the process or the consequences of changes made. This includes plant design, maintenance and operations, backup systems, and community responsibility. The legal problems of Union Carbide are likely to continue for a long time. There appears to be enough blame to go around for all those involved in any way in the plant, including government units.

This accident has become widely known. It is an objective of many chemical process safety programs and government actions to "avoid another Bhopal"—that is, to avoid a severe release of toxic chemicals (usually referring to toxic chemicals in the air). Almost every chemical company in the world has been affected by this incident in one way or another, in the design and operation of chemical plants, in community action programs, and in the activities of such organizations as the American Institute of Chemical Engineers, the Chemical

Manufacturers Association, and many governmental units.

Phillips Explosion, 1989[57]

On October 23, 1989, at approximately 1300, an explosion and fire ripped through the Phillips 66 Company's Houston Chemical Complex in Pasadena, Texas. At the site, 23 workers were killed, and more than 130 were injured. Property damage was nearly $750 million. Business interruption cost is not available but is probably a very large figure.

The release occurred during maintenance operations on a polyethylene reactor. Two of the six workers on the maintenance crews in the immediate vicinity of the reactor leg where the release occurred were killed, together with 21 other employees of the facility. Debris from the plant was found 6 miles from the explosion site. Structural steel beams were twisted like pretzels by the extreme heat. Two polyethylene production plants covering an area of 16 acres were completely destroyed.

The Phillips complex produces high-density polyethylene, which is used to make milk bottles and other containers. Prior to the accident, the facility produced approximately 1.5 billion lb of the material per year. It employed 905 company employees and approximately 600 daily contract employees. The contract employees were engaged primarily in regular maintenance activities and new plant construction.

The accident resulted from a release of extremely flammable process gases that occurred during regular maintenance operations on one of the plant's polyethylene reactors. It is estimated that within 90 to 120 seconds, more than 85,000 pounds of flammable gases were released through an open valve. A huge unconfined flammable vapor cloud was formed that came into contact with an ignition source and exploded with the energy of 4800 lb of TNT. The initial explosion was equivalent to an earthquake with a magnitude of 3.5 on the Richter scale. A second explosion occurred 10 to 15 minutes later when two isobutane tanks exploded. Each explosion damaged other units, creating a chain reaction of explosions. One witness reported hearing ten separate explosions over a 2-hour period.

In the process used by Phillips at this site to produce high-density polyethylene, ethylene gas is dissolved in isobutane and, with various other chemicals added, is reacted in long pipes under elevated pressure and temperature. The dissolved ethylene reacts with itself to form polyethylene particles that gradually come to rest in settling legs, where they are eventually removed through valves at the bottom. At the top of these legs, there is a single ball valve (DEMCO® brand) where the legs join with other reactor pipes. The DEMCO valve is kept open during production so that the polyethylene particles can settle into the leg. A typical piping settling leg arrangement is shown in Fig. 5.14.

In the Phillips reactor, the plastic material frequently clogged the settling legs. When this happened, the DEMCO valve for the blocked leg was closed, the leg disassembled, and the block removed. During this particular maintenance process was going on, the reaction

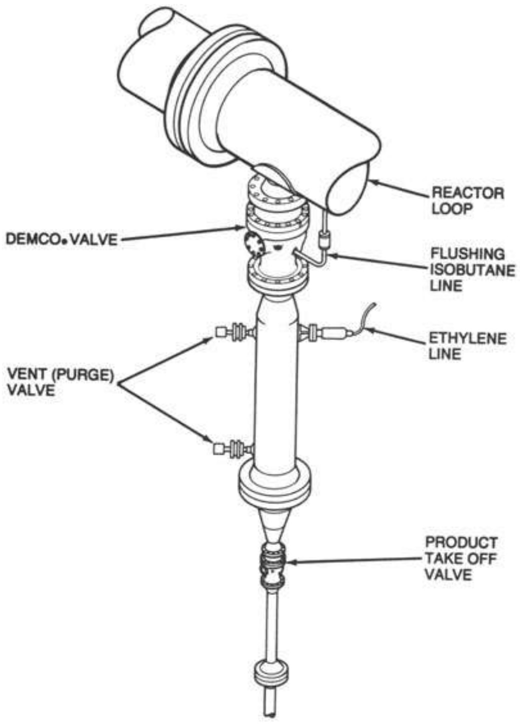


Fig. 5.14. Typical piping settling leg arrangement.

block removed. During this particular maintenance process, the reactor settling leg was disassembled and the block of polymer removed. While this maintenance process was going on, the reaction continued, and the product settled in the legs that remained in place. If the DEMCO valve were to open during a cleaning-out operation, there would be nothing to prevent the escape of the gas to the atmosphere.

After the explosion it was found that the DEMCO valve was open at the time of the release. The leg to be cleaned had been prepared by a Phillips operator. The air hoses that operated the DEMCO valve were improperly connected in a reversed position such that a closed DEMCO valve would be opened when the actuator was in the closed position. In addition, the following unsafe conditions existed:

1. The DEMCO valve did not have its lockout device in place.
2. The hoses supplied to the valve actuator mechanism could be connected at any time even though the Phillips operating procedure stipulated that the hoses should never be connected during maintenance.
3. The air hoses connecting the open and closed sides of the valve were identical, thus allowing the hoses to be cross-connected and permitting the valve to be opened when the operator intended to close it.
4. The air supply valves for the actuator mechanism air hoses were in the open position so that air would flow and cause the actuator to rotate the DEMCO valve when the hoses were connected.
5. The DEMCO valve was capable of being physically locked in the open position as well as in the closed position. The valve lockout system was inadequate to prevent someone from inadvertently opening the DEMCO valve during a maintenance procedure.

Established Phillips corporate safety procedures and standard industry practice require backup protection in the form of a double valve or blind flange insert whenever a process or chemical line in hydrocarbon service is opened. According to OSHA, Phillips had implemented a special procedure for this maintenance operation that did not incorporate the required backup. Consequently, none was used on October 23.

The consequences of the accident were exacerbated by the lack of a water system dedicated to fire fighting, and by deficiencies in the shared system. When the process water system was extensively damaged by the explosion, the plant's water supply for fighting fires was also disrupted. The water pressure was inadequate for fire fighting. The force of the explosion ruptured waterlines and adjacent vessels containing flammable and combustible materials. The ruptured water lines could not be isolated to restore water pressure because the valves to do so were engulfed in flames. Of the three backup diesel pumps, one had been taken out of service and was unavailable, and another soon ran out of fuel. It was necessary to lay hoses to remote sites—settling ponds, a cooling tower, a water treatment plant, and so on. Electric cables supplying power to regular service pumps were damaged by fire, and those pumps were rendered inoperable. Even so, the fire was brought under control within 10 hours.

In the months preceding the explosion, according to testimony, there had been several small fires, and the alarm had sounded as many as four or five times a day. There had been a fatality at the same plant doing a similar operation about three months before this incident. Some of the employees in the area where the release occurred may not have heard the siren because of the ambient noise level, and may not have known of the impending disaster. Employees in the immediate area of the release began running as soon as they realized the gas was escaping.

The large number of fatalities was due in part to the inadequate separation between buildings in the complex. The site layout and the proximity of normally high-occupancy structures, such as the control and finishing building, to large-capacity reactors and hydrocarbon vessels contributed to the severity of the event.

The distances between process equipment were in violation of accepted engineering practices and did not allow personnel to leave the polyethylene plants safely during the initial vapor release; nor was there sufficient separation between reactors and the control room to carry out emergency shutdown procedures. The control room, in fact, was destroyed by the initial explosion. Of the 22 victims' bodies recovered at the scene, all were located within 250 feet of the vapor release point.

OSHA's investigation revealed that a number of company audits had identified unsafe conditions but largely had been ignored. Thus, a citation for willful violations of the OSHA "general duty" clause was issued to Phillips with proposed penalties of $5,660,000. In addition, proposed penalties of $6,200 were issued for other serious violations. A citation for willful violations with proposed penalties of $724,000 was issued to Fish Engineering and Construction, a Phillips maintenance contractor. Other financial penalties have been proposed. In the investigation it became apparent that Fish had become accustomed to tolerating safety and health violations at the site by its personnel and Phillips personnel, as well as participating in those violations by knowing about them and not taking direct positive action to protect its employees.

Since 1972, OSHA has conducted 92 inspections in the Dallas region at various Phillips locations; 24 were in response to a fatality or a serious accident. OSHA determined that Phillips had not acted upon reports by its own safety personnel and outside consultants who had pointed out unsafe conditions. OSHA also had conducted 44 inspections of the Fish Company, seven of them in response to a fatality or a serious accident.

One of the major findings by OSHA was that Phillips had not conducted a process hazard analysis or equivalent (such as HAZOP) in its polyethylene plants.

Immediate Cause. There was a release of flammable process gases during the unplugging of Number 4 Reactor Leg on Reactor 6 while undergoing a regular maintenance procedure by contractor employees. The unconfined flammable vapor cloud was ignited and exploded with devastating results.

The immediate cause of the leak was that a process valve was opened by mistake while the line was open. The valve was open to the atmosphere without a second line of defense such as another valve or a blind flange.

Contributing Causes to the Accident and the Severity of the Accident:

1. Procedures to require backup protection in the form of a double valve or a blind flange insert were not used. The lockout system was inadequate.
2. Air hoses were improperly connected in the reversed position.
3. The air hoses for the open and closed side of the valve were identical, allowing the hoses to be cross-connected.
4. The DEMCO valve actuator mechanism did not have its lockout device in place.
5. There was not a water system dedicated to fire fighting, and there were deficiencies in the system shared with the process.
6. The site layout and proximity of high-occupancy structures contributed to the severity.
7. There was inadequate separation of buildings within the complex. Especially, there was inadequate spacing between the reactors and the control room.

Root Causes. The root causes of the accident and its extreme severity appear to be failures of the management system, as shown by the following:[57]

1. According to OSHA, Phillips had not conducted a process hazard analysis or equivalent (such as HAZOP) in its polyethylene plants.
2. It was found by OSHA that the contractor, Fish Engineering, had a history of serious and willful violations of safety standard, which Phillips had not acted upon. The same contractor also had been

involved in a fatal accident at the same facility three months earlier.

3. A report by OSHA stated that Phillips had not acted upon reports issued previously by the company's own safety personnel and outside consultants. Phillips had numerous citations from OSHA since July 1972. OSHA discovered internal Phillips documents that called for corrective action but which were largely ignored.
4. Safe operating procedures were not required for opening lines in hazardous service.
5. An effective safety permit system was not enforced with Phillips or contractor employees, especially line opening and hot work permits.
6. Buildings containing personnel were not separated from process units in accordance with accepted engineering principles, or designed with enough resistance to fire and explosion.
7. The fire protection system was not maintained in a state of readiness:
   - (a) One of the three diesel-powered water pumps had been taken out of service.
   - (b) Another of the three diesel-powered water pumps was not fully fueled, and it ran out of fuel during the fire fighting.
   - (c) Electric cables supplying power to regular service fire pumps were not located underground and were exposed to blast and fire damage.

SUMMARY

As the tragic case histories unfold, the significance of the process safety consideration presented in this chapter becomes chillingly apparent, and the necessity for inherently safe process design is revealed. The case histories also reveal significant flaws in management systems, which tends to be true for most chemical process accidents. Even an ideally safe process can be transformed into one with a high potential for disaster if a valid system is not in place to ensure that the inherently safe process design retains its integrity.

Because there is always risk when equipment, instrumentation, and human activity are involved, there is no method of making a plant completely safe. However, facilities can be made "inherently safer" by careful examination of all aspects of design and management, using modern techniques that are now available. If we are to improve our process safety performance and our public image, "inherently safe" process design coupled with "inherently safe" process management is imperative.

In addition to the information presented in this chapter and in the publications it has cited, references 58 through 72 are recommended as appropriate source material.

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6

Managing an Emergency Preparedness Program

Thaddeus H. Spencer*

INTRODUCTION

Prevention, Prediction, and Preparation

The preceding chapter explored many technical aspects of chemical process safety and some safety management systems that form the foundation of a comprehensive emergency preparedness program. Clearly, the first step in preparing for emergencies is to identify and mitigate the conditions that might cause them. This process starts early in the design phase of a chemical facility, and continues throughout its life. The objective is to *prevent* emergencies by eliminating hazards wherever possible.

Although hazard elimination is the goal, experience has taught us that guaranteed, failure-free designs and devices have so far eluded human kind, despite astonishing advances in knowledge and technology. Even the most "inherently safe" chemical facility must prepare to control potentially hazardous events that are caused by human or mechanical failure, or by natural forces such as storms or earthquakes.

The process of careful, structured analysis and evaluation used to eliminate hazards during design and construction will also allow a chemical facility to accurately *predict* unplanned events that may create emergencies, and to effectively *prepare* to manage them should they occur. A comprehensive emergency preparedness program has all of these elements: *prevention, prediction*, and *preparation.*

The fundamental need to predict and prepare for a failure of some kind is familiar to everyone. Fortunately, most of the failures that we encounter create little more than inconveniences in our lives. Others have much more serious potential. Such a failure can trigger an emergency, a term that Webster defines as "an unforeseen combination of circumstances or the resulting state that calls for immediate action." If the immediate action is ineffective, the emergency will escalate to a full-blown crisis.

Certainly most if not all of us in our personal experiences have had many opportunities to reconfirm the wisdom of the admonition,

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"Plan for the best, but prepare for the worst." As a result, we prepare ourselves for human and mechanical failure in a variety of ways, some so simple and familiar that we scarcely are aware that we are managing a personal emergency preparedness program.

To varying degrees, each of us has assessed our personal vulnerability to a specific emergency and the potential consequences to family and property. In some cases the required immediate action may be minor, but elsewhere the same combination of circumstances will demand significant resources to avoid a crisis of major proportions. The loss of household electric power in an urban condominium may only turn out the light, but on a farm, where electricity pumps the well water, milks the cows, refrigerates the produce, and irrigates the land, loss of power can bring disaster to the unprepared.

In an industrial environment, the consequences of human or mechanical failure can be far greater, even threatening the lives of employees and neighbors. Therefore, emergency prevention and preparedness efforts must have high priority, receiving continuous attention from every employee, including those in every level of management and supervision.

In the chemical industry, emergency preparedness programs have long been recognized as vital elements in protecting people, property, and the environment from harm. Few chemical facilities are without an emergency response plan. Still, when the alarms sound and the emergency is real, the response often does not proceed as planned. Too often, preparation for the unlikely event has been inadequate. As a result, most chemical facility managers are taking a fresh and critical look at their existing emergency preparedness programs in cooperation with their communities, and placing a still higher priority on being truly prepared for emergencies. This is consistent with the aggressive approach to other aspects of safety management that has made the chemical industry one of the safest industries.

Although the commitment to *prevent* the events that lead to injuries and emergencies of all kinds remains the first priority in safety management, we must "prepare for the worst." In this chapter we will explore how chemical facilities and their neighbors can better *predict* and *prepare* for unplanned events that threaten lives, property, and the environment—events that call for immediate and coordinated action.

Need for Emergency Preparedness Programs

The need for more effective management of emergency preparedness programs by chemical facilities and their host communities became painfully clear to the world in the 1980s—a decade marred by tragic events linked to the manufacture and distribution of chemical products. These events revealed serious deficiencies, not only in training people to react effectively during an emergency, but also in managing the systems employed to identify, evaluate, and mitigate hazards that may cause an emergency.

The chemical industry has vigorously responded to these problems in a variety of ways. In some cases well before the crisis of the 1980s, individual chemical units took aggressive action to increase the reliability of their operations, to communicate these actions to their neighbors, and to involve the communities in the process of emergency response planning. This proactive interaction at the local level proved fruitful in promoting the active partnership needed to solve mutual problems and to respond to public concerns. In 1986, these individual initiatives were institutionalized by the industry in the Chemical Manufacturers Association's "Community Awareness/Emergency Response (CAER)" program, which has in turn become a major element of the more recent "Responsible Care" program.

The proven success of these activities provides a powerful reason for giving high priority to open and cooperative management of an emergency preparedness program. By implementing such a program, a chemical facility builds important bridges to its neighbors and fosters positive perceptions. Involving the host community provides an opportunity to demonstrate a sincere commitment to the protection of people and the environment, and a route to the mutually profitable solution of real problems through meaningful two-way communication with the public.

Much of what had been voluntary prior to 1986 became law in the United States with the enactment of the Superfund Amendments and Reauthorization Act (SARA). The Emergency Planning and Community Right-to-Know portions of the Act (known as Title III, or EPCRA) place specific organizational, planning, communication, and training responsibilities on the public and private sectors, as do the accidental release provisions of the Clean Air Act amendments enacted in 1990. Other laws also require emergency response plans. In addition various state and local regulations must be considered, understood, and reflected in a complete emergency preparedness program.

These laws and regulations, which will be covered later in this chapter, should be viewed as describing only the minimum requirements. Beyond the legal and self-protective reasons for chemical facilities to improve their management of emergency response programs lie other important driving forces. One of these is the moral and ethical responsibility to employees and the public to work toward elimination of events destructive to the quality of life. In practice, full recognition of this responsibility requires actions in prevention, prediction, and preparation that go beyond the letter of the law.

The financial benefits of good emergency preparedness program management are important as well. Emergencies are always expensive. Uncontrolled emergencies can become financially devastating crisis. Nervous communities, fearful of the dangers dimly perceived through industrial fences, can and have put some chemical operations out of business. Creating and maintaining a comprehensive emergency preparedness program does not come free. However, the investment is proving to be money well spent by most chemical facilities.

PREVENTING AND PREDICTING EMERGENCIES: GETTING STARTED

The objective of a comprehensive emergency preparedness program is the protection of people, property, and the environment from unplanned hazardous events. Organizations handling hazardous materials recognize that the process of creating an effective program starts with the identification, evaluation, reduction, and control of hazards (commonly called risk management), and proceeds through the preparation, drilling, and maintenance of plans and procedures designed to contain an emergency situation should one occur.

To assure an effective emergency preparedness program, chemical facilities need to make periodic, formal assessments of their vulnerability to and preparedness for emergencies. Managers must be involved in developing and monitoring key indicators that will help in assessing an organization's ability to prevent or deal with an emergency. Awareness of any program weaknesses revealed by examining these indicators leads to corrective action to ensure that the potential for incidents decreases, and emergency preparedness improves. Sample checklists including some of these key indicators are shown in Fig. 6.1.

Central to all emergency preparedness programs is a written emergency response plan (ERP). An ERP obviously is a key element of emergency preparedness, yet it is only one procedural part of a systematic process that includes the following sequential steps:

- Identify and evaluate hazards.
- Mitigate hazards wherever possible.
- Identify and evaluate remaining hazards.
- Identify and evaluate resources.
- Develop emergency procedures and ERP.
- Train facility personnel.
- Communicate plans to public.
- Integrate with community ERPs.
- Conduct and critique drills.
- Review and revise ERPs.
- Do it again.

EMERGENCY PREVENTION	EMERGENCY RESPONSE PLANNING
1. Frequent management presence in operating areas.	1. Emergency manual that documents the areas or processes with emergency potential and describes the emergency response plan.
2. Proper storage and identification of hazardous materials.	2. Regular emergency response plan training, and drills each quarter.
3. Formal and systematic inspections of key equipment, safety devices, and safety interlocks.	3. Liaison with the community for response coordination.
4. Audits for compliance with safety rules and procedures.	4. Emergency response management organization with documented functional tasks and assigned personnel.
5. Periodic critical reviews of existing operating and maintenance procedures.	5. Systems to recognize and report an emergency in a timely manner.
6. Training programs updated to meet current needs.	6. Documentation of hazardous chemicals with potential to leave the site, and evacuation plan for affected areas.
7. Control systems for maintenance hot work and changes in process and equipment.	7. Adequate emergency response equipment.
8. Systematic process hazards reviews during design, start-up, and routine operations.	8. Proper method to account for personnel during and after an emergency.
9. Formal reviews all of events that could or did cause serious process incidents.	9. Procedures to review and modify the emergency plan following drills or actual emergencies.

Fig. 6.1. Emergency preparedness checklists.

The creation and maintenance of an ERP requires the allocation of valuable resources, as well as strong leadership from a manager. No one else in the organization has the authority to commit the resources required. Only the power of the manager's office can overcome the organizational inertia that is often encountered.

Many people do not like to "prepare for the worst." They may harbor sincere doubts about the value of planning for events that they consider unlikely to occur. Some people are complacent after years free of serious accidents, and honestly believe that "It can't happen here." Others may be concerned that an open discussion of potentially disastrous events will needlessly upset employees and neighbors. These and other "start-up" problems could make trouble for a manager initiating (or reviving) an emergency preparedness program.

Managers need to find ways to stimulate employee interest and enthusiasm in the planning process. This is best done through the involvement of employees. One strategy that minimizes problems is the early involvement of those employees who serve as emergency responders in their communities.

Some of them have witnessed the tragic consequences of failing to heed early danger signs and being unprepared for events. Thus, they can be willing and able catalysts in the emergency response planning process.

Open communication with all employees early in the process also is important. Sharing objectives and encouraging contributions stimulates thoughtful discussion, leads to more complete hazard recognition and mitigation, and ensures a greater chance of effective action when the emergency alarms do sound. Armed with facts, employees acting as informal ambassadors to the community can reduce the potential for public alarm over a facility's preparations to deal with serious but low-probability events.

HAZARD IDENTIFICATION AND MITIGATION

As shown in Fig. 6.2, emergency preparedness begins with the identification and mitigation of hazards. When properly done, the systematic analysis and evaluation of chemical process hazards stimulate actions that eliminate the potential for many emergency situations and pinpoint the situations that remain. The direction of these analytical and corrective efforts is an integral part of managing

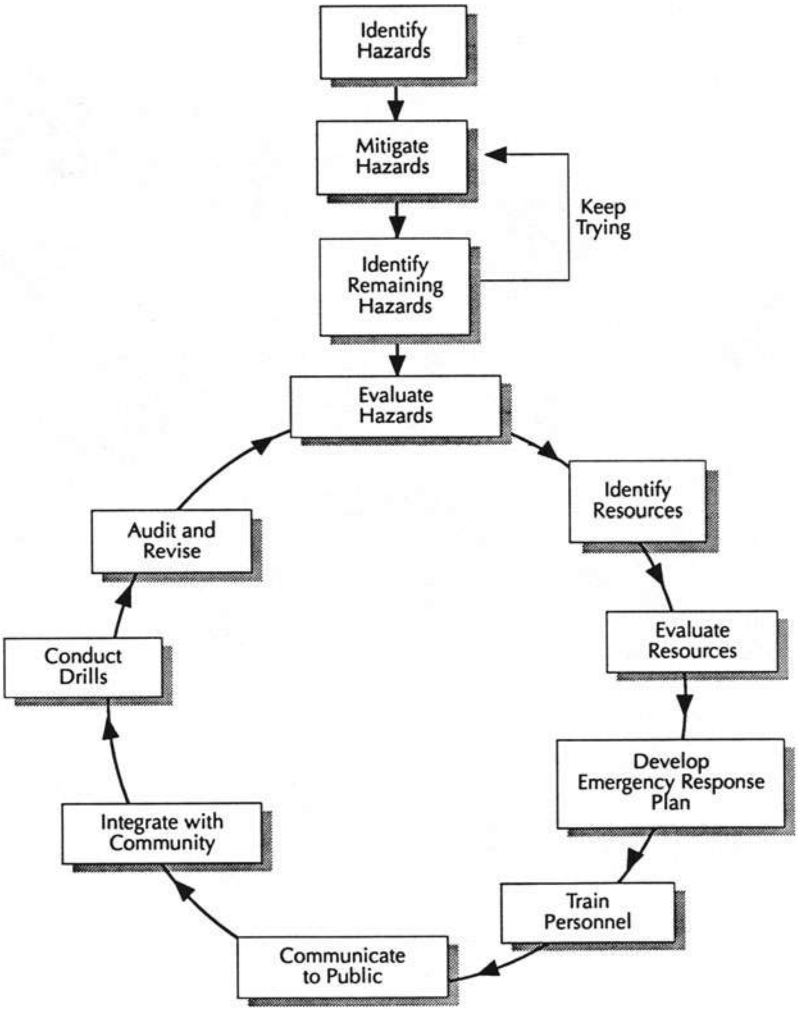

Fig. 6.2. Elements of a comprehensive emergency preparedness program.

a comprehensive emergency preparedness program.

Process Safety Management Team

Hazard identification and mitigation are the responsibility of a facility's line organization—the same people who are responsible for all other organizational performance parameters. However, a line organization often needs support in identifying and mitigating complex chemical process hazards, support that can be effectively provided through the formation of a standing team functioning under the manager's direction. This team, called a Process Safety Management Team (PSMT), includes representatives of each unit of a facility from various levels of the organization. They meet on a regular basis (usually monthly) and report frequently to the manager on the status of their activities.

Identifying Hazards: PSR Teams

Supported by the PSMT, the line organization develops a structured approach for performing process hazard analyses on a repetitive basis. One effective way to do this is to organize knowledgeable facility personnel into ad hoc Process Safety Review (PSR) teams. These teams, supplemented by outside specialists as required, are responsible for studying all processes, identifying all potential hazards, and recommending appropriate corrective or control measures.

The makeup of a PSR team is critical to the success of this process. The effectiveness of the team depends on the skills, knowledge, and cooperative effort of its members, and the leadership ability of its chairperson. Each member must be familiar with the process being studied, and have at least a working knowledge of the basic engineering principles and chemistry involved. The team should include supervisors from operations and maintenance and a technical support person. Knowledgeable process operators and maintenance personnel would be valuable team members as well. Others who could contribute to the team's work include design engineers, specialists in electrical and instrument systems, safety engineers, reaction kinetics consultants, and equipment vendors.

The selection and training of PSR team members must be carefully monitored. Most managers make this the responsibility of the standing PSMT, which also may assist a PSR team in choosing the most appropriate hazards evaluation method for a specific process.

Review Methods

There are many structured methods for carrying out effective reviews of process hazards. The four most commonly used methods are:

- What if/checklist
- Failure mode and effect analysis
- Hazard and operability study (HAZOP)
- Fault tree analysis

What If/Checklist. The most frequently used method of process hazard review, the what if/checklist, is effective in reviews of relatively uncomplicated processes from raw materials to final product. The team formulates and answers "What if?" questions at each handling or processing step to evaluate the effects of component failures or procedural errors. They use a checklist to ensure that all important subjects are addressed. This method should be used as the first step in all process hazard reviews.

Failure Mode and Effect Analysis. When the team studies a specific item of equipment, such as a reaction vessel, they often use the failure mode and effect analysis method. Its semi-quantitative approach assists in prioritizing hazards.

Hazard and Operability Study (HAZOP). The HAZOP procedure systematically questions every part of a process to discover how deviations from the intention of the design can occur, and to determine if the consequences of such deviations are hazardous.

Fault Tree Analysis. Fault tree analysis, the most complex of the commonly used methods, is employed to determine the possible causes of a preselected undesired event. Through the use of logic diagrams and failure rate data, the team can make a quantitative evaluation of the frequency of the undesired event.

For additional information on such methods, refer to Chapter 5.

Recommendations and Reports

Regardless of the method used, the PSR team's most important responsibility is to alert management to serious hazards that may have been overlooked or given inadequate attention. To fulfill this responsibility, a PSR team must take the following steps:

1. Identify the hazards that could cause explosion, fire, release of toxic materials, serious injury, or inappropriate exposure to chemicals.
2. Evaluate the magnitude of the hazards for the areas of probable involvement; the consequences of an event in terms of injuries, environmental harm, and property damage; and, qualitatively or quantitatively, the probability of the hazards' occurrence.
3. Develop practical recommendations to eliminate or control the hazards identified.

The PSR team reviews in detail up-to-date reference material such as:

- Architectural drawings.
- Equipment layout drawings.
- Process schematics.
- Instrument diagrams.
- Chemical and physical characteristics of process materials.
- Equipment design specifications.
- Operating procedures.
- Process conditions.
- Emergency shutdown procedures.

When a facility has more than one chemical process, the PSMT develops a priority order for reviews and recommends a review frequency to the facility manager. The frequency usually ranges from once every two to three years for high-hazard-class processes such as explosives manufacture or acetylene purification to once every five to seven years for low-hazard-class processes such as alcohol purification, steam generation, and operations involving combustible materials.

Changes not anticipated in the original design of equipment often pose serious problems. Some examples of such changes are:

- Introduction of different raw materials.
- Changes in temperatures, pressures, speeds.
- Deterioration of equipment.

At the completion of each PSR, the team prepares a written report that defines needs, makes recommendations to remedy problems, and recommends priorities for the correction of deficiencies. Following review and acceptance of the report, the facility manager assigns responsibility for corrective action to the appropriate operating personnel. The PSMT then assists the manager in monitoring the status of the recommendations from all PSRs.

Mitigating Hazards: Release Detection and Mitigation

The release of flammable or toxic chemicals from uncontrolled pressure relief vents or as a result of equipment failure may present a serious threat to employees or neighbors who fail to guard against exposure. Every chemical facility must address this potential problem and prepare to protect people from these hazards by working toward reducing the potential hazard and its consequences. Typically, the line organization and PSR teams are responsible for hazard mitigation. They conduct a hazard study that includes the following activities:

- Detailed appraisal of the potential for accidental release of toxic gas or vapor.
- Evaluation of instruments and other methods for detecting such leaks.

- Provisions for rapid alerting of threatened personnel, and for communicating with emergency responders.
- Identification of buildings in which people might be trapped by such a release.
- Assessment of the capability of buildings or rooms to prevent the infiltration of gas or vapor.
- Evaluation of plans for building evacuations, including the provision and maintenance of appropriate personal protective equipment.

Early *detection* of a chemical leak is necessary in order to limit its effect on people and the environment. The most fundamental method for detecting a chemical release is the systematic patrol of operating units by personnel trained to recognize potentially hazardous vapors using odor or visual observations. The frequency and scope of the patrols will vary with the nature of the process equipment and materials; however, every facility should have documented patrol procedures in place.

When particularly hazardous vapors are present, the patrol procedures should include special provisions to protect the patrollers from the fumes. For example, in facilities producing or consuming hydrogen sulfide, operators may carry emergency respiratory equipment to escape any unexpected fumes that they may encounter, and patrol in pairs or individually, under constant surveillance.

Many chemical facilities supplement operator patrols with an instrumented detection system. Such a system may be a necessary resource when a hazards study concludes that the system will substantially increase the available escape or emergency response time, or where:

- The harmful substance is odorless or deadens the sense of smell at hazardous concentrations.
- The harmful substance is toxic at concentrations undetectable by smell.
- Large numbers of people may be exposed quickly.
- Ventilation systems might draw toxic fumes into a building before other means of detection could trigger protective action.

At the core of an instrumented leak detection system is a gas detector. There are many kinds of detectors on the market with varying degrees of sensitivity and selectivity. All require careful regular testing and maintenance. An engineering study of many site-specific factors is required before one makes a choice and designs an appropriately instrumented system. Some generally accepted guidelines are:

- Early warning of a leak is enhanced if the sensors can be placed near the process equipment subject to leakage.
- Air movement characteristics are critical in achieving reliable detection.
- Most detectors respond to several gases or fumes, so the possible presence of all airborne substances affecting the detection system must be considered.
- When it is necessary to monitor work areas or the intakes to ventilation systems, a highly sensitive system is desirable.

Most detection systems are designed not only to report the presence of hazardous fumes through instrument readouts but to sound an alarm and automatically initiate corrective or protective action. In an office or shop, for example, the system can be designed to shut down all ventilating fans and close exterior air inlet dampers.

When process safety reviews have identified chemical releases as potential sources of facility emergencies, the organization must provide the training and materials needed to ensure a prompt and appropriate reaction to *mitigate* the hazards. Some countermeasures that are effective in limiting the spread of a hazardous material spill or release should be included in the design of chemical process equipment, and described in emergency response procedures. The following discussion of release mitigation is largely excerpted from

Guidelines for Vapor Release Mitigation, prepared by R. W. Prugh and R. W. Johnson for the Center for Chemical Process Safety of the AIChE (copyright 1988 by the American Institute of Chemical Engineers, reproduced by permission of the Center for Chemical Process Safety of the AIChE).

"Water, steam, and air curtains and water sprays are primarily effective in dispersing and/or diluting vapors with air to reduce the severity of effects of a hazardous vapor release. In some cases, vapors can be partially 'knocked down' or absorbed after release."

"Ignition source control and deliberate ignition are also possible vapor release countermeasures." "For areas around processes handling flammable vapors, ignition source control is practiced to reduce the probability of vapor ignition if a leak occurs." "Administrative controls are exercised on plants where flammable materials are processed. Such controls may include hot work permits, restricted smoking areas, not allowing lighters or matches on the site, and electrical grounding and bonding procedures."

"Deliberate ignition is a countermeasure against spills of highly toxic materials which are also flammable, such as hydrogen sulfide, hydrogen cyanide, and methyl mercaptan. Igniting nontoxic flammable materials such as hydrocarbons may present hazards outweighing possible advantages." In any case, deliberate ignition must be carefully planned and executed so that the resulting fire is truly controllable.

"Practical methods for combating vapor from liquid leaks are dilution, neutralization, or covering. All three reduce the vaporization rate of the pool. Water dilution is effective for spills of water-miscible or water-soluble material. Spraying water into the spill reduces the vapor pressure by reducing the concentration of the liquid." "For acidic spills, limestone or soda ash is often used" to react with the spilled liquid to produce a less volatile salt or ester. "A foam cover can be effective in reducing vaporization from spills," and "dense liquids can be covered with lighter immiscible nonreactive liquids" to accomplish the same thing.

PREPARING FOR EMERGENCIES: IDENTIFYING AND EVALUATING RESOURCES

The process of hazard identification, evaluation, and mitigation, when sustained over a period of time and coupled with other good safety management practices, can prevent most process-related emergencies. However, the potential for various low-probability process-related events will remain. Should one occur, there must be resources available to promptly bring the event under control. These resources include designated personnel, plans, systems, and facilities that are needed for effective action and communication. The facility line organization is responsible for providing and maintaining these resources.

Personnel

Emergency Preparedness Team. As with the PSMT and the PSR team, the efforts of the line will benefit from the support of a standing emergency preparedness team functioning under the direction of the facility manager. This team, which includes representatives of each unit of the facility, leads the development and maintenance of an emergency response plan (ERP) for the facility, and monitors specific procedures and training for handling emergency situations of all kinds. It should meet on a regular basis (usually monthly), and report frequently to the manager on the status of its activities.

Emergency Management Organization. Emergencies demand rapid, well-coordinated decisions, communications, and action to bring them under control as swiftly as possible. There must be a formal emergency management organization (EMO) whose purpose is to achieve this objective. The structure of the organization is not critical as long as it is capable of rapid assembly, carried out its assigned responsibilities, and meets the needs of the facility. A generic EMO is shown in Fig. 6.3; the EMO is described below, in the section on "Developing an Emergency Response Plan."

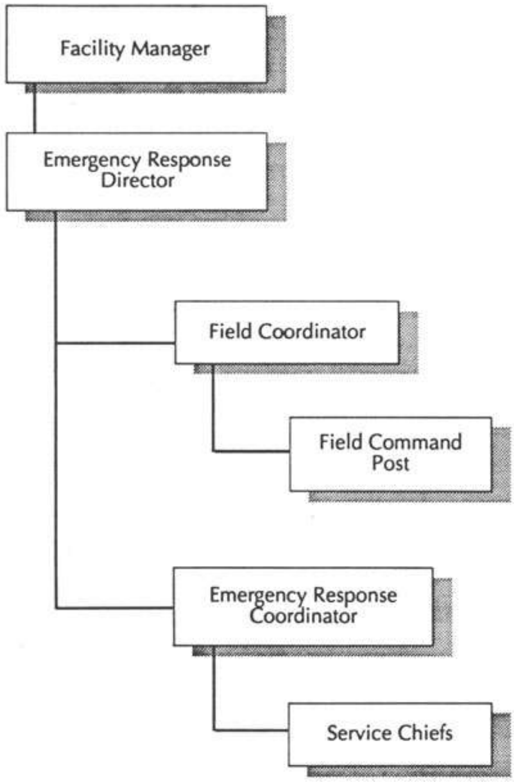

Fig. 6.3. Generic emergency management organization.

Fire Brigades. Most chemical facilities of any size have established fire brigades as a key resource in their emergency preparedness programs. By virtue of its training and familiarity with the equipment and the physical layout of a site, the brigade can be a major factor in *preventing* incidents as well as in minimizing injuries and property damage due to fire, explosion, or other causes.

The size and the structure of a fire brigade vary, depending upon the hazards present, the size of the facility, and the level of internal fire-fighting capability desired; and large, multi-process facilities usually have several unit or area brigades. Each brigade has a designated captain and an alternate. The training of brigade members must be commensurate with the duties and the functions that they are expected to perform, and thus depends on the fire prevention plan option selected by site management. (Fire prevention plans are discussed later in this section.)

It is best to have a written statement establishing the brigade and its duties, specifying its size and organizational structure, and outlining the type, amount, and frequency of training provided. In the United States, OSHA has promulgated minimum standards for fire brigades, which may be found in 29 CFR 1910.156.

Plans

Work Unit Plans. In a large facility, each work unit has emergency procedures for its own area of operations, and these work unit plans form the foundation of the facility emergency response plan (ERP). Thus, the facility's emergency response can be no more effective than the recognition and response capabilities of the employees in the facility work units.

The primary objectives of these unit plans are (1) to control and contain any emergency condition within the unit, and (2) to provide protection for unit personnel and equipment from events originating outside the unit. Unit plans specify who has authority to take emergency action, and how escalation to a full facility emergency occurs. Subjects that must be covered include:

- Unit emergency command and coordination.
- Communications within the unit.
- Communications with other units.
- Emergency assessment.
- Unit evacuation and personnel accounting.
- Emergency shutdowns.
- Communications with the facility management.
- Criteria and procedures for securing resources from outside the unit.

Unit plans clearly assign primary responsibility for initial emergency assessment and reaction to the lead unit employee on site at the time of the event. Among the factors to be considered by that individual in making the initial assessment are:

- Previous experience with similar situations.
- How long the situation has existed.
- What might occur "If...."
- Properties and hazards of materials involved.
- Other complicating situations.

Using the information gained from the assessment, unit personnel take whatever immediate action is required to protect people and property on and off the site.

Work unit plans should contain guidelines for assuring uniformity in the assessment of and reaction to unusual events. An effective approach is to develop an emergency classification system that includes criteria for classification and guidance for the appropriate response actions for each level of emergency that is defined.

For example, an emergency judged to be controllable within the unit, with no evacuation outside the unit and no impact in the community, is a Level One Emergency. Small releases of hazardous materials usually fall into this category. Appropriate response items to consider would include:

- Protection of unit personnel.
- Shutdown or isolation of affected equipment.
- Notification on- and off-site.
- Containment and cleanup.

Similarly, other events are categorized by their potential or actual severity. Preplanned response checklists are prepared for each one. An incident that requires response by facility personnel outside the affected unit but has no impact on the community is a Level Two Emergency. A Level Two Emergency requires activation of the facility ERP. If some community impact becomes probable, the emergency is a Level Three Emergency. That level of emergency triggers additional response requirements, including interaction with the community.

The unit plan must be formal and in writing. Because the emergency procedures of each individual operating area or work unit form the foundation of the facility ERP, they should be reviewed by the emergency preparedness team for completeness and consistency across the site before they are included in the facility ERP.

Fire Prevention Plan. One of the most basic resources that all chemical facilities must have is a fire prevention plan. To be fully effective, this plan must be in writing, and it must be reviewed with all employees on an established schedule.

A comprehensive fire prevention plan includes the following subjects:

- Major facility fire hazards.
- Storage and handling practices for combustible and flammable materials.
- Identification of potential ignition sources.
- Procedures to maintain systems and equipment installed to control ignition sources.
- Names and titles of those responsible for the system and equipment maintenance and the control of fuel source hazards.
- Procedures to minimize accumulations of flammable and combustible waste materials.
- Plans for communicating to all employees the fire hazards and their specific responsibilities in the event of fire.

Fire response options open to facility managers range from a plan to evacuate all employees without attempting fire fighting on any scale, to full involvement of an established fire brigade in fighting advanced-stage structural fires. The fire prevention plan must specify which option applies to the facility. The option selected determines the type and extent of education and training required, as well as the type of equipment needed on the site.

Fire prevention and response information may be covered in other written facility documents (such as job descriptions, rules, or procedures) and communicated to employees on the same schedule as the fire prevention plan.

Evacuation Plans. Many emergency events require the evacuation of at least some facility personnel, if only for precautionary reasons. This presents other needs, which must be addressed in the evacuation plan. Personnel who are directed to evacuate their normal work stations need visible wind direction indicators to help them move away from a dangerous gas cloud drifting downwind of the release point. If the building is enveloped in the cloud, however, they will need personal protective equipment in order to evacuate it safely. When there are processes that must be rapidly shut down and/or isolated as evacuation proceeds, the plan must include written procedures and appropriate means to ensure incident-free action.

Headcount Plan. The evacuation plan also must establish gathering points for all personnel in order to identify those who are missing. The procedure for accounting for personnel, called the headcount, must work effectively and rapidly in the first minutes of the emergency to determine if anyone is missing or known to be injured. Communications to the personnel chief or another designated member of the facility EMO must be quick and accurate so that search and rescue operations and medical aid can be successfully implemented.

Each work unit in a facility must have its own plan for headcounts as a part of its emergency preparedness program. This plan must be in writing, and it must be practiced frequently enough to ensure good execution in a time of real emergency. It should include:

- A designated assembly point for each employee.
- An alternate assembly point, should the primary location be inaccessible.
- A procedure for counting at each assembly point.
- A designated unit headcount coordinator and backup.
- Primary and alternate phone numbers where coordinator may be reached.
- Phone numbers for reaching the personnel chief, who coordinates and summarizes the site-wide accounting.

Headcount procedures must include guidelines for accounting for visitors to the facility at the time of the emergency. These visitors may include truck drivers, vendors, and contractors. Some guidelines are:

- All visitors must sign in and out, preferably at one designated gate.
- Visitors will have a designated host employee responsible for their safety whenever possible.
- Everyone temporarily on the facility must report to the assembly point of the unit he or she is in at the time of the emergency.
- Unit procedures must include reporting these "extra" people by name to headcount headquarters.
- The personnel chief of the EMO must have access to the log at the visitors' gate.

Alarm Systems

Another essential resource that every chemical facility must have is an effective alarm system, which initiates action by endangered personnel and emergency responders and serves the needs of people off as well as on the site.

A satisfactory facility emergency alarm system must meet four additional requirements. It must, at a minimum, immediately alert *all* the people on the site. (A single signaling device should be adequate for small sites; however, large facilities may require many devices placed to reach all occupied areas of the site.) The system must function even when the facility has a general power failure. Alarm activation controls should be located so that an emergency condition is unlikely to prevent access to them. Finally, an emergency warning system must be integrated with the surrounding community, and must be designed with the participation of local officials and special-needs groups.

On most older chemical facilities, the basic component of the emergency warning system is the fire alarm. It is essential that there be different signals to distinguish between an actual fire and other threatening events, as the action taken in response to a toxic gas release, for example, may be quite different from that taken in response to a fire. On multi-process sites, the signals also should identify the work unit involved.

Depending upon the number of people at a facility and their familiarity with response and evaculation procedures, it may be necessary to supplement signals with verbal instructions delivered by public address equipment, radios, or automated telephone systems. For reliability at any time of day, a system using verbal instructions must be located in a regularly manned job station such as a control room or gate house.

Any alarm system used must communicate clearly the nature of the emergency event and its severity. In a Level One Emergency some people may have to be evacuated in order to ensure their safety, but by and large the emergency can be contained within the unit. In that case, information usually may be given to unaffected employees through normal telephone communications.

In the event of a Level Two or a Level Three Emergency, each facility must have an easily recognizable signal that clearly communicates that a major incident has occurred. Some facilities have alarm boxes that will automatically sound this signal when pulled. Others have boxes that require manual operation. Still others rely on a telephone message to trigger the signal.

In some facilities, the "major" emergency alarm is a steady blast on the facility steam whistle. Others use sirens or special bells. Whatever is chosen, the alarm must reach everyone on the site, triggering activation of the facility ERP and the initiation of a headcount procedure.

It is essential that every every employee on a chemical facility know how, where, and when to turn in an appropriate and effective emergency alarm. The specifics will vary considerably, but the procedure for turning in an alarm is similar in all cases.

Employees first need to know how to report a fire. On most facilities, this is done by using a fire alarm box or by telephoning a central station such as a guard house from which the fire alarm can be sounded. Chemical facilities need to have well-developed training and drill programs in place to be sure that response procedures and equipment are maintained.

When fire alarms are supplemented by verbal instructions, the facility personnel who are contacted need to know the location and the nature of the fire, the action under way to control it, and the actions required (if any) by those not involved. There are many commercially available communications systems that deliver this information efficiently, even on large sites.

Facilities for Protection and Communication

Safe Havens. When accidental releases of a toxic gas occur or threaten to occur, the immediate protection of on-site personnel is of paramount importance. One resource available for this purpose is a building or room that by the nature of its construction and its heating and ventilating characteristics can prevent the infiltration of intolerable concentrations of the toxic substance. The best location for a safe haven is determined by an engineering study. That location then is documented in the work unit and facility emergency response plans.

Safe havens may be rare on some sites; however, many buildings can provide personnel with temporary protection until the incident has been analyzed and a decision made on the need for evacuation. To qualify as a designated temporary safe haven, a building must be reasonably well sealed against air infiltration, with adjustable ventilation systems that can reduce or close off exhaust vents and outside makeup air. Emergency procedures should state how long a building can be considered a safe haven under specified exposure conditions.

Main Emergency Control Center. Using a list of safe havens developed by the work units the emergency preparedness team helps management select one building or room to be used as a control center in case of a major emergency. This Main Emergency Control Center (MECC) should be as remote from potential hazards as possible in order to serve as a reasonably safe haven to those involved in directing, coordinating, and communicating activities for the duration of an emergency.

MECCs need to have basic information readily available and maintained in an up-to-date, standby condition. Such a collection would include:

- Copies of the facility ERP.
- Facility maps and diagrams.
- Process material isolation points.
- Fire control maps and diagrams.
- Maps of the surrounding area.
- Aerial photos of the facility and the surrounding area.
- Names, addresses, phone numbers for:
    - All facility employees.
    - Off-site company people to be notified.
    - Groups and organizations who may be notified.
    - Community officials who may be notified.
- MSDS (material safety data sheets) for facility materials.
- MSDSs for the materials of neighboring chemical facilities.
- Copies of mutual aid agreements.
- Highlights of the facility's history, products, and performance.

The MECC should have the following basic equipment:

- Adequate telephones and lines.
- Unlisted telephone and/or a hotline.
- Two-way radios.
- Fume path projector.
- FAX machine.
- Regular radio with tape recorder.
- Regular television with recorder and playback video cassette recorders.
- Chart pads and stands.
- Battery-powered lighting.
- Personal protective equipment.
- Hand-held tape recorders.

Alternate Control Centers. Recognizing the unpredictable nature of a developing emergency, it is advisable to select at least one alternate on-site main control center. Both the MECC and the alternate on-site center should have backup power supplies.

The presence of substantial quantities of explosive or toxic materials on-site may justify establishing yet a third location off-site, in case of a complete evacuation of the facility. This could be a fixed location in the nearby community, or a mobile unit such as a truck or van properly equipped for managing an emergency. Some of the supplies and equipment for the alternate off-site main control center may have to be packed in a readily transported kit rather than being on standby at the alternate off-site location.

Media Headquarters. In an emergency, it is essential to maintain regular contact with the public and the media. A separate location for communications will allow that contact to continue without interfering with the operations of the MECC or overloading its communications system. There, the public affairs chief and the facility manager can receive media representatives and provide periodic updates on the emergency situation. The media headquarters should be equipped with several direct outside telephones and the facilities to make the reporters comfortable for the duration of the emergency. Permanently mounted facility plot plans or aerial photographs are helpful resources, as are handouts describing in general terms the facility and its products.

DEVELOPING AN EMERGENCY RESPONSE PLAN

Following the identification and evaluation of the resources available to the facility, the emergency preparedness team, under the direction of the manager, develops the written emergency response plan (ERP) for the entire facility. The emergency preparedness team is responsible for ensuring that the written facility ERP informs all employees of their roles in an emergency and the hazards to which they may be exposed.

An ERP must be tailored to a specific facility, reflecting its unique conditions and individual needs. Among the variables that affect the details of a plan are:

- Materials used, produced, or stored.
- Nature of the operations.
- Available employee skills.
- Geographic location.
- Proximity to other facilities.
- Available emergency resources.
- Mutual aid agreements.

No two ERPs will be exactly alike, nor is there one best outline. The plan of a production facility will differ from that of a warehouse. However, every plan must include:

- Initial alarm procedures.
- Emergency escape procedures and routes.
- Emergency operating and shutdown procedures for critical operations.
- Accounting procedures for all on-site personnel.
- rescue and medical duties for specified personnel.
- Procedures for communicating the emergency inside and outside the organization.
- Structure, duties, and resources of the EMO, including names or titles of people with detailed knowledge of the plan and its assigned duties.
- Reference material.

Plan Design

The ERP is a working plan, applicable to any event with emergency potential occurring at any time and at any location on the facility. It should be written concisely, with diagrams and checklists used wherever possible, so that it may be effectively used for guidance during an actual emergency. To accomplish this, it is helpful to divide the ERP into several major sections, which are in turn divided by subject.

For example, an ERP may be broken down into three sections: the Emergency Management Organization, Action Plans, and Reference Material.

The first section documents the structure, duties, resources, and communications systems for the facility Emergency Management Organization (EMO), and the conditions that will trigger the EMO's response. It includes plans for site-wide notification and response.

The second section includes detailed action plans for each particular type of emergency. This section includes summaries or outlines of the emergency procedures developed by each work unit of a facility, and may contain considerable process-oriented information.

The third section consists of reference material on plan philosophy, training, plan maintenance, drills, and similar supportive data that usually are not needed at the time of an emergency. Members of the EMO and others with assigned response duties should be able to quickly locate and refer to the appropriate action guidelines, to determine that key functions are being performed.

Using this approach, the outline of an ERP for a multi-process chemical facility would look like this:

Section I
  A. Table of Contents
  B. EMO Structure and Tasks
  C. Notification: On-Site
  D. Accounting for Personnel
  E. Headcount Center
  F. EMO Center
  G. Emergency Scene
  H. Notification: Off-site
Section II
  A. Table of Contents
  B. Work Unit 1
    1. Emergency types
    2. Action checklists
    3. Responsibilities
    4. Communications
    5. Shutdown procedures
  C. Work Unit 2 (same as above)
Section III
  A. Table of Contents
  B. Plan Philosophy and Objectives
  C. Training Programs
  D. Drills and Tests
  E. Return to Normal
  F. Appendices
    1. Special situations (e.g., bomb threats)
    2. Hazardous material data
    3. (Others as required)

Emergency Management Organization Structure

Perhaps the most essential element of an ERP is the establishment of the organization that will manage emergency response once the event has developed beyond a Level One Emergency. The EMO must be capable of rapid assembly, and must be able to carry out all of its assigned responsibilities.

The EMO is composed of the facility manager, the emergency response coordinator, the field coordinator, and various service chiefs. The number of service chiefs and their duties will vary. There need not be a separate individual in charge of each service, and small facilities may combine two or more services under one individual, as long as each function is performed.

The facility manager, in cooperation with the emergency preparedness team, assigns people, by their title or function at the facility, to the EMO, with designated alternates for each EMO function. The duties and responsibilities of each EMO function are defined and documented in the ERP. Because there must be a functional EMO in place regardless of when a facility emergency occurs, designated shift personnel take specific EMO responsibilities until the primary members can reach the site.

All of the positions established for the EMO should have written position descriptions, which may be placed in the third section of the ERP as an appendix to the plan. In the first section of the ERP, the EMO summary need only include a concise checklist for each position, with diagrams showing relationships and major communication flow paths.

Facility Manager. In the EMO, the facility manager has the overall responsibility for protecting people on-site, facility property, the environment, and the public during and after an emergency. With the assistance of the public affairs and communications chiefs, the manager usually serves as the spokesperson for the facility and the company, communicating with representatives of the media and other concerned audiences.

Emergency Response Coordinator. The designated emergency response coordinator, who may also serve as the chairperson of the emergency preparedness team, directs all emergency control activities from the MECC. All other service chiefs on the EMO report to the coordinator. Using information from the emergency scene and from the service chiefs, the coordinator makes the key decisions on what should be done, and coordinates activities on and off the site. The coordinator reports to the manager, who should be available nearby for overall guidance and counsel.

Field Coordinator. The job of the field coordinator is to correct the emergency situation as rapidly as possible with minimum risk to those in or near the affected area. He or she establishes a field command post as close to the scene of the emergency as can be safely done. The post often is in or near a radio-equipped building or vehicle, thus permitting rapid establishment of communications between the command post and the emergency response coordinator.

Ideally, the field coordinator is familiar with the operations and materials involved in the emergency; so she or he often is the highest-ranking supervisor of the affected area who is available at the time of the event. That supervisor may remain as field coordinator for the duration of the emergency, or may be relieved by another designated member of management. In the latter case, the area supervisor may become a service chief with greater hands-on involvement, with the field coordinator concentrating on marshaling required resources and maintaining effective communications. The choice depends to a great extent on the size and complexity of the facility, and the resources available for the EMO.

Public Affairs Chief. Working in close coordination with the facility manager, the public affairs chief releases appropriate information to the news media, regulatory personnel, government officials, and other public groups and individuals. No information is to be made public by anyone other than the facility manager without specific direction from the public affairs chief. The objective is to provide full and accurate statements in a timely fashion, so that public attention is focused on facts and useful information rather than on rumors and speculation.

The public affairs chief also establishes and monitors the media headquarters, which is isolated from the EMCC to avoid interference with operations there. The public affairs chief's function includes assisting the manager in the preparation of formal statements and background information to be distributed to reporters. It also may include arranging with local radio and television stations to make periodic announcements during an emergency so that the public and the employees not on the site are properly informed. The public affairs chief also arranges to monitor and perhaps record the broadcasts of local radio and television stations in order to determine what additional statements or clarifications to the public may be required.

Communications Chief. The communications chief establishes and maintains communications capability with appropriate people on and off the site. This chief must be familiar with the various communicating systems available, including telephones, public address systems, two-way radios, and messengers. The job includes recommending and coordinating revisions or additions to the communicating systems during an emergency, and assisting the facility manager and the public affairs chief with any communications as needed.

Engineering Chief. The engineering chief's primary responsibility is to maintain electrical power for vital services. These services include on-the-scene portable lighting, continuous fire pump operation, and a steady supply of nitrogen, steam, and process cooling water. Another key duty is to assemble repair groups capable of isolating damaged sections of pipelines, electrical lines, and other necessary equipment in order to contain problems and maintain or restore operations outside the affected area. Because these repair groups must be drawn largely from site personnel such as electricians, welders, riggers, and pipefitters, the position of engineering chief should be filled by someone from the facility maintenance organization.

Rescue Chief. The rescue chief's immediate concern is to direct the rescue of trapped and/or injured people on the site. He or she identifies any outside resources needed to conduct the rescue, and coordinates their efforts when they are on the facility. The work requires good communications and coordination with the field coordinator and other chiefs, particularly the engineering chief, because rescue may involve material handling and temporary construction skills. For this reason, the rescue function is sometimes part of the engineering chief's responsibilities.

Emergency and Fire Chief. The emergency and fire chief is responsible for fire-fighting and fume control activities. The best person for this job has good knowledge of and access to the fire-fighting and fume control resources available on and off the site. On a small facility this may be the captain of the fire brigade. The job includes direction of designated facility personnel, and coordination with any outside forces brought in to bring the fire or fume condition under control. The environmental chief may assist in determining optimum courses of action based upon actual or threatened adverse effects on air and water emissions from the facility.

Medical Chief. The medical chief ensures that the proper medical care is provided to people on the facility who have been injured or exposed to toxic materials. When facilities have medical professionals on the site, one of them carries out this function. This chief's responsibilities include establishing field stations to treat affected personnel, and, in cooperation with the transportation chief, providing transportation for injured people to other medical facilities.

The medical chief also participates in discussions with community officials and appropriate facility personnel regarding actual or potential medical problems for people outside the site boundaries. Representatives from nearby local hospitals, ambulance services, fire departments, police forces, and emergency management groups also may be involved in these discussions. The medical chief communicates any action or contingency plans developed in the discussions to the emergency response coordinator and the public affairs chief.

Environmental Chief. The environmental chief oversees all activities designed to minimize adverse effects upon the quality of air and water as a result of an emergency. The function includes coordinating air and water quality monitoring on and off the site during and after the emergency, and assisting the emergency and fire chief in selecting the optimum approach to abating a fire or fume condition. The environmental chief also provides assistance in projecting the path and concentration of a fume release, using computer modeling (if available) or maps with plastic overlays and developing an effective plan of action.

Personnel Chief. The personnel chief is responsible for accounting for all personnel on the facility at the time of the emergency. Unit emergency programs must include training on how this is accomplished. Unit supervisors initiate the process with headcounts at designated rally points. The success of rescue and medical activities depends on how quickly and thoroughly this information is obtained and reported to the personnel chief.

The personnel chief also coordinates communication with relatives of injured or deceased employees, and makes certain that this is completed before any names are released publicly. This requires close coordination with the public affairs chief and the manager.

The personnel chief need not be located at the MECC, but it is imperative that the personnel chief be in close touch with other members of the EMO. Telephones in the headcount center should have answering and message recording equipment to capture any unit reports arriving before the headquarters is staffed.

Protection Chief. The protection chief makes sure that entry to and egress from the facility are properly controlled. This involves securing gates; limiting entry to authorized personnel; registering all who pass through gates; meeting visitors, including representatives of the media, and escorting them to proper locations; and controlling all traffic on the site. The function also includes communicating with local police so that access to the facility is maintained, and crowd control procedures are enforced. Usually, the individual serving as protection chief at the time of the emergency also is responsible for initiating procedures to summon key facility personnel and urgently needed outside agencies.

Transportation Chief. The transportation chief coordinates and controls all transportation on the facility. This includes directing the assembly of available vehicles and crews, and identifying needs beyond site capabilities such as cranes, trackmobiles, and bulldozers that must be obtained from outside organizations. The function also includes providing suitable transportation for facility employees who monitor the effects of emergencies beyond site boundaries, or interact with community officials at an off-site location.

TRAINING PERSONNEL

Having a written facility ERP that is supported by established work unit emergency plans and procedures is an important part of the manager's job of ensuring that unplanned events will be promptly controlled with minimum risk to people, property, and the environment. There is much important work to be done, however, before the ERP is anything more than a valuable resource. Facility personnel must be trained to use the ERP effectively. There must be frequent drills to test the plan and the people against the standards established by management as well as those established by law.

Within the facility, there are three groups of people who require training. First, there are members of the fire brigade, who must be trained to fight fires at the level specified by facility management. Next are the employees who have been assigned active roles in controlling emergencies of all types. This group includes members of the EMO and their alternates, plus designated support people such as headcount coordinators, guards, and emergency repair personnel. Finally, everyone else on the facility must have a basic understanding of the ERP, and must know how to respond when specific alarms sound.

The facility manager is responsible for ensuring that the appropriate training and retraining are done in a timely and effective manner. An employee should be trained when he or she is hired, at least annually thereafter, and when the employee's work area changes or the plan is revised. Most managers make this primarily a line organization function. They expect facility supervisors to use all available resources and means of education to accomplish the tasks. Some specialized training assistance, however, must be provided, particularly for the members of a fire brigade.

Fire Brigade Training

Training programs for fire brigades have two major objectives. One is to inform the brigade members of new hazards at their facility and innovations in fire-fighting techniques and equipment. The other objective is to provide hands-on training for developing skills in emergency operations and using equipment, including:

- Portable fire extinguishers
- Hoses and accessories
- Portable lighting
- Forcible entry tools
- Ladders
- Salvage equipment
- First-aid supplies
- Replacement parts
- Personal protective equipment
- Transportation equipment

A comprehensive training program for fire brigades must include classroom and hands-on training.

Outside resources can provide valuable assistance in the education and training of brigade members. Local fire departments and state fire schools are usually enthusiastic partners in such efforts. Often they are the key to securing adequate resources at a reasonable cost. In industrialized communities, mutual aid agreements may include cooperative training provisions with other chemical facilities, which provide opportunities for even more effective use of available resources. All mutual aid agreements should require cross-training in special hazards at the other facilities.

EMO Training

Training for personnel assigned to the facility EMO can be led by the emergency response coordinator, who meets periodically with each member of the EMO to review and refine position descriptions and the associated functional checklists. An example of such a checklist is shown in Fig. 6.4. The meetings may be followed by limited drills involving only the people and responsibilities included in the individual EMO function. Some facility managers assign specific emergency response training duties to each member of the EMO. For example, the engineering chief organizes, equips, and trains the repair groups who will be called on to physically stabilize a situation at the time of an emergency. The emergency and fire chief could be given the responsibility for maintaining a trained force of fire and fume fighters, which includes competent leadership on all shifts.

Employee Training

There are many ways to be sure that all employees understand the ERP. The emergency preparedness team can assist in the

____ 1. Personnel Chief and aides report to head count room at the MECC.

____ 2. Replay audio counts already received.

____ 3. Record work unit head counts as they are received.

____ 4. Obtain copy of visitors' log and employee with area head counts.

____ 5. Monitor attempts to locate missing personnel.

____ 6. Report to Emergency Response Coordinator as personnel are confirmed as missing.

____ 7. Issue final report to Emergency Response Coordinator after all work unit head counts are received.

____ 8. Determine from Emergency Response Coordinator names of any injured people.

____ 9. Coordinate communications with families of those missing or injured.

Fig. 6.4. Personnel chief functional checklist.

assessment of existing training programs, alerting the organization to training weaknesses and suggesting or providing creative ways to overcome those deficiencies. Unit supervisors must periodically review the ERP in scheduled group safety meetings or with individuals. Key plan elements can be reproduced on wallet-size cards, desktop displays, or telephone stick-ons. Individual or group discussions of how to react in given situations can detect weaknesses in procedures, training, or understanding.

Training programs for the three groups of employees discussed here should be documented, reviewed regularly, and included in a reference section of the facility ERP. But no matter how comprehensive the training programs may be, their effectiveness is unknown until a drill of the ERP is conducted and its systems and procedures are tested.

Facility Drills

To evaluate the effectiveness and completeness of an ERP, a facility must conduct periodic announced and unannounced Level Two and Level Three emergency drills. These are in addition to the more frequent Level One unit drills that are held to ensure that the more limited response procedures of a work unit are complete and well understood. Major internal emergency drills should be held at least four times each year, and scheduled to involve each working shift at least once a year.

To gain the maximum benefit from the drills, assigned observers should witness all aspects of response activity, and gather soon after to participate in a verbal evaluation of actions taken. These observers should include members of the emergency preparedness team. This process is enhanced by capturing on-scene action on videotape or in still photographs. Critiquing can be extremely valuable in identifying necessary plan changes, training needs, and resource deficiencies of all kinds. The process of critiquing must be controlled and managed. The leader must be sure to identify the strengths as well as the weaknesses that were revealed in the drill. The objective is to stimulate actions for positive change, not to assign blame.

Drills should be held on weekends and at night occasionally to test segments of the organization that work at times when all of the specialized resources of the facility are not immediately available. Initially, limited scale drills can test segments of the ERP, such as manning the MECC with the shift personnel that are available and carrying out a headcount without involving daytime employees.

As the proficiency of the organization increases, drill scenarios can become more complex. Complicating factors approaching worst real-life conditions should be introduced periodically, including:

- Telephone switchboard overload.
- Absence of key EMO members.
- Arrival of major TV network anchorperson.
- Simulated mass casualties.
- Two-way radio failure.
- Evacuation of primary and backup MECCs.
- Major community impact.

The emergency preparedness team, with approval of the manager, designs the drill scenarios, monitors the organization's performance, provides leadership for critiquing, and recommends corrective actions. The team also develops and monitors a plan for involving the community in the important task of integrating a facility's ERP into the public emergency preparedness programs of the region.

INVOLVING THE COMMUNITY

Of major concern to the chemical industry is the public perception that facility managers have little concern for the welfare of their neighbors. Managers themselves have contributed to such false impressions by failing to interact with their communities in a consistent and meaningful way.

The public clearly wants to know more about the risks presented by a chemical facility. Increasingly, the public wants to help decide which risks are acceptable and which are not.

Recognizing that industrial facilities exist only with the consent of their host communities, most industrial organizations are assigning a high priority to building stronger bridges with their neighbors. The chemical industry in particular is finding that the involvement of the community in the process of emergency preparedness planning presents an excellent opportunity for constructive two-way communications. This has proved particularly productive if these communications are part of an aggressive and continuous risk communications process.

Communications

Each chemical facility needs to create opportunities for sharing information with its surrounding community; it should not wait for these opportunities to occur. Facility managers in particular should be active in the process, and should monitor the performance of their organizations. Some items that should be on a manager's checklist for risk communications are shown in Fig. 6.5.

The process should start with employee communications. In its employees, a facility has an important, informal communication link with its community that is often ignored. Employees deserve to know at least as much about their facility as their neighbors, and they deserve to know it first. They should be aware through communications (if not through actual involvement) of the facility's entire emergency preparedness program, from

1. Open communications up and down the line organization.
2. Scheduled two-way communications with all employees at least twice per month.
3. Newsletter for employees, pensioners, and key community leaders.
4. Regular meetings with local media reporters and editors.
5. Facility open house at least once every three years.
6. MSDS available to appropriate organizations in the community.
7. Meetings with political leaders and activists at their locations and at the facility.
8. Leadership and participation in local emergency planning committee.
9. Leadership in community projects such as wildlife protection, public land-use designation, etc.
10. Participation in school programs for children.

Fig. 6.5. Risk communication checklist.

prevention to preparation. The employees also should be familiar with the products made and their end uses. They should understand the potential hazards of the processes and materials with which they work, and how to protect themselves and the public from those hazards.

Other communication channels should be developed and regularly used. Scheduled meetings with representatives of community emergency service groups are useful for exchanging information and objectives concerning emergency preparedness, for promoting the sharing of resources, for gaining familiarity with one another's physical facilities and people, for identifying problems, and for recommending action for their solution.

In the 1980s, some chemical facilities and their communities formalized this approach and broadened participation in their meetings to include public officials and representatives of regulatory agencies and the media. Operating as Hazardous Material Advisory Councils (HMACs) and meeting regularly with established leadership and agendas, these groups quickly became key resources in organizing a community's efforts to better understand the potential for hazardous material incidents and to protect against them. Typically the responsibilities of an HMAC include coordinating a regional risk assessment, assisting the development of a community response plan specific to hazardous materials, and assisting with educational programs for various segments of the public.

The Responsible Care program of the Chemical Manufacturers Association embraces HMACs as one good way to communicate relevant and useful information that responds to public concerns for safety, health, and the environment. However, managers are finding many other ways to interact with the public to achieve a fuller measure of community awareness and involvement in affairs of mutual interest. Among the many options from which a manager may choose are the following:

- Hosting facility tours featuring emergency prevention and mitigation procedures.
- Speaking at community meetings (service clubs, schools, governing bodies, etc.).
- Sending newsletters to selected neighbors.
- Preparing informative brochures or newspaper inserts.
- Appearing on local TV or radio.

An open and sincere comprehensive risk communication process led by the facility manager creates a better-informed public that is able to understand real risks (vs. perceptions) and is likely to respond effectively in case of an actual emergency.

Integrating Plans

Most communities have long had written emergency response plans designed for natural events such as floods and windstorms; some communities have had written plans dealing with emergencies created by people, such as bomb threats and civil disturbances; but, until recently, few had specific plans for responding to emergencies involving hazardous materials. As a result, the consequences of accidental chemical releases have been in many cases tragically magnified by the undisciplined reactions of people near the release source. It has been reported, for example, that when the alarms sounded at Bhopal, residents of the nearby homes ran toward the plant rather than taking action to protect themselves from the enveloping fumes.

It is not enough to train the personnel of a chemical facility to implement an ERP effectively. Appropriate people in the community, especially near neighbors, need to understand the elements of an ERP that are designed to protect them and the role they play in making the plan work. There must be a continuous effort to integrate the facility ERP into community emergency planning at local and district levels. Drills involving external resources that test all of the plan elements against the standards mutually established with the community and those imposed by laws and regulations are necessary to ensure successful implementation of the plan.

Off-site Warning

Designing an effective off-site warning system presents some major challenges. Despite excellent ongoing communications between a chemical facility and its neighbors, there is no positive way to ensure that the general public will respond quickly and appropriately to a warning alarm of any kind. Thus, it is essential that the selected warning system be developed with the close cooperation of the community. Even then, it is difficult to predict such factors as the inclination of people to be warned and the degree of public confidence in the validity of an alarm.

No off-site warning system will assure complete coverage of the intended audience. Best results are achieved by combining two or more systems for sequential alerting—the first to trigger preplanned immediate action by the public at greatest risk, followed by other communications that provide further information and guidance to a larger audience. Some of the systems most commonly used are:

- Facility fixed-sound sources, such as sirens and whistles.
- Mobile alerting by police or fire personnel, either from vehicles with loudspeakers or door-to-door.
- Fixed public address systems in the community or in the facility.
- Automated telephone calling.
- Alert radios energized by a special signal to produce a warning tone followed by broadcast messages.
- Strobe lights in situations where the noise level is a problem.
- Local radio stations and the emergency broadcast system.
- Local TV stations.

More sophisticated and less commonly used warning systems include helicopters equipped with loudspeakers, modified cable TV installations, and computer networks between a chemical facility and community emergency response groups.

Local Emergency Plans

Existing plans for a coordinated response to emergencies in a community vary greatly in content and organization, but the plans have two common objectives. They are to:

- Define authority and responsibilities of various emergency service participants.
- Describe the interaction between those participants, government, and industry.

In creating their plans, most communities draw on the Integrated Emergency Management System (IEMS) developed by the Federal Emergency Management Agency (FEMA).

A local plan has many of the same elements as a chemical facility ERP. It includes:

- An emergency management organization, with designated functional responsibilities.
- The location of the emergency operating center and its resources.
- Guidelines for classifying emergencies.
- Activation and declaration checklists.
- Communications requirements and available systems.
- Evacuation and sheltering plans.
- Methods for securing added resources.
- Descriptions of local hazards.

Most local plans are written to be nonspecific as to the cause of the emergency, with various appendices describing the details of response to specific events. These appendices are based upon the results of risk assessments made by the community with the cooperation of industry.

One such appendix should relate to emergencies caused by fixed facility or transportation incidents in which hazardous materials are involved. Chemical facilities must provide substantial support to the community in preparing this portion of the local emergency plan, and provide resources and training leadership that are not available elsewhere in the community. Where a Hazardous Material Advisory Council exists, there is an effective forum for doing this. In any case, a chemical facility manager should seek ways to help the community prepare for and recover from incidents of this nature.

Local Emergency Planning Committees

An important contribution to community and industry cooperation in emergency preparedness was the passage in 1986 of the Superfund Amendments and Reauthorization Act (SARA), which contained an emergency planning and community right-to-know provision. Title III, or EPCRA, as this portion of SARA is commonly called, is intended to encourage and support hazardous materials emergency planning efforts at the state and local level, and to provide citizens and local agencies with appropriate information concerning potential hazards in their communities.

The major portions of Title III require:

- A statewide organization for planning emergency action and receiving hazardous chemical information.
- Notification to the community of emergency releases of chemicals.
- Reports of hazardous chemical inventories and copies of MSDSs to be furnished to the community.
- An annual inventory of hazardous chemical releases to the environment.

Drills and Critiques

The optimum frequency of major drills involving personnel outside a chemical facility is dependent upon a number of variables:

- Location of the facility.
- Dependence upon community emergency agencies.
- Size and complexity of the facility.
- Site and off-site risk assessments.
- Population patterns.

An important element of emergency preparedness is the establishment of an appropriate major drill frequency in cooperation with off-site agencies. A reasonable goal is to hold one such drill each year. The scenario might include an on-site, internally generated hazardous material emergency one year and a transportation emergency somewhere in the adjacent community the following year.

For facilities and communities just beginning to test their plans, desktop or simulated drills are effective for identifying procedural problems that need to be corrected before they proceed to full-scale drills. In these simulations, staffing of the appropriate emergency center would occur, but the emergency service groups would not actually mobilize at the scene of the incident.

As people gain confidence in the completeness and the effectiveness of the emergency response plan, it becomes important to measure the performance of all who are involved. Monitors record and later report on all aspects of response actions, including:

- Elapsed times before critical actions occur.
- Actions and coordination of responding groups.
- Actions of uninvolved personnel.
- Alarm and communication effectiveness.
- Emergency control center management.
- Control at the emergency scene.
- Accounting for personnel.
- Medical aid for simulated casualties.
- Off-site notifications.
- Handling media representatives—real or simulated.

Following each drill there must be an organized critique that provides the information needed to strengthen the plan and/or its implementation. All of the people actively involved should be represented at the critique, and a written report of conclusions and recommendations should be widely distributed. It then is the responsibility of the facility emergency preparedness team and the local emergency planning committee to coordinate and assist in solving any problems identified—a process that begins emergency preparedness activities again: identifying hazards; evaluating and strengthening resources; modifying the emergency plan; training people; communicating and integrating plans; and testing them once again.

LAWS, REGULATIONS, AND SUPPORT

Laws

A number of legal requirements must be incorporated in a facility's emergency response program. Emergency prevention, preparedness, and response planning are regulated at the federal, state, and, occasionally, local levels. At the federal level, these laws include

- Clean Air Act (CAA)
- Clean Water Act (CWA)
- Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)
- Emergency Planning and Community Right-to-Know Act (EPCRA, or SARA Title III)
- Energy Reorganization Act (Nuclear Regulatory Commission)
- Hazardous Materials Transportation Act (HMTA)
- Occupational Safety and Health Act (OSHA)
- Resource Conservation and Recovery Act (RCRA)
- Toxic Substances Control Act (TSCA)
- U.S. Coast Guard requirements

A list of these laws and their *Code of Federal Regulations* (CFR) citations appears in the bibliography at the end of the chapter. States may have their own laws and regulations that also govern emergency response planning. References to these laws may be found in the Bureau of National Affairs (BNA) *Environment Reporter*.

These laws and their regulations are enforced by all levels of governmental agencies. A knowing or willful violation has serious implications for both companies and individuals, who may be held civilly or criminally liable for noncompliance. The penalties can be severe, ranging from daily-assessed fines to imprisonment. Thus, it is prudent to know the regulations that apply to the facility, and to ensure that the regulatory requirements are met.

The regulations regarding emergency planning and response are comprehensive, covering every aspect from prevention to reporting. RCRA's regulations cover the entire process, from planning to training to formal reports on the facility's response to an emergency involving hazardous waste. Other regulations focus on a specific aspect of emergency response, or part of the facility's operations. For example, TSCA requires that spills or releases that contaminate the environment be reported orally and in writing within a certain time frame. All but one of the laws put the burden of planning on the facility. EPCRA, the exception, requires state and local agencies to prepare an emergency response plan for the community. Facilities that meet criteria specified in EPCRA regulations have to assist in the development of the plan; however, they are not responsible for creating it.

Inevitably, some of the regulations and requirements overlap. Most chemical facilities are subject to more than one law, and could be expected to prepare separate plans for specific parts of their facility. RCRA's Contingency Plan, for example, must be developed and maintained apart from other emergency response plans. The key to managing all of the requirements and satisfying the regulations in an efficient, coordinated manner is first to understand the requirements and how they apply to the facility, and then to look for the common denominators among the requirements. The finished product, or master plan, will satisfy all of the common denominators that apply, and will avoid duplication of effort. It also can be used as the basis for plans that must be maintained separately or that have requirements in addition to the common denominators.

Meeting the Requirements

Regulations governing emergency response planning can be broken down into four general categories:

- Preparation
- Plans
- Reports and other communications
- Drills and evaluations

Figure 6.6 shows a matrix-type summary of the major federal laws and their requirements for emergency planning and response. Such a matrix is very helpful in determining what the requirements are and how they apply to a facility. It could be further tailored to cover only the requirements that apply to a specific site or operation.

Prevention and Preparation

Some regulations require that a facility conduct a risk assessment and/or other preparatory activities. RCRA calls it a preparedness and prevention plan. A facility subject to RCRA must determine how structures, processes, and operations can be changed in order to minimize the possibility of an emergency involving hazardous waste. The facility also has to determine the communications and alarm systems that will be used in the event of such an emergency. CWA includes prevention in its requirements for the Spill Prevention, Containment, and Countermeasure (SPCC) Plan. The 1990 amendments to the CAA added an accident prevention plan for extremely hazardous substances.

Plans

At the very least, a facility is required to develop a plan describing how it will respond to an incident that threatens human health and/or the environment. Generally, the plan includes notification, evacuation, protection of employees, and control of the incident. This emergency response plan usually must be in writing. For example, OSHA requires a minimum of three plans: emergency response, emergency action, and fire prevention. The CAA requires that the state implementation plan have an emergency air pollution episode plan.

Communications

There are two aspects to emergency communications: the actual equipment used to communicate information about the incident and the types of communications or information sharing required. RCRA has specific requirements for the types of emergency communication equipment (alarm systems, phone or radio communications) that must be present. Under EPCRA, facilities must provide information about their operations and substances used or stored on site when the Local Emergency Planning Committee (LEPC) or State Emergency Response Commission (SERC) requests it. If the facility uses or stores extremely hazardous substances (EHS) in reportable quantities, it must appoint a representative to the LEPC. Several laws require that a copy of the emergency response plan be made available to employees and representatives of government agencies during working hours. OSHA requires that facilities provide material safety data sheets (MSDS) for all hazardous substances present on the site.

Reports

Reports are another important communications aspect of the emergency response program. Most laws insist on prompt notification of the proper agencies immediately after an incident occurs. These reporting requirements can be complex, particularly in view of the fact that many laws have their own lists of hazardous substances and reportable quantities. CERCLA requires that releases of a reportable quantity of what it defines as a hazardous substance must be reported immediately to the National Response Center (NRC). EPCRA requires facilities that store and/or release reportable quantities of substances on its EHS list to report that information to the LEPC and the SERC.

Written followup reports are often a requirement. HMTA has identified six specific

	RCRA	OSHA	DOT/HMTA	EPCRA	CERCLA
PREVENTION AND PLANNING	Preparedness & prevention plan Contingency Plan (CP), in writing ☐ Emergency Coordinator ☐ Evacuation ☐ Access ☐ Equipment ☐ Communications	Emergency Response Plan ☐ For entire site ☐ For employees who respond to uncontrolled releases of hazardous substances, including hazardous waste Emergency Action Plan ☐ Evacuation for employees in case of incidental chemical releases ☐ How to report an incident Fire Prevention Plan	Incident prevention and response	Local emergency planning committee (LEPC) prepares emergency response plan for community. State emergency planning commission (SERC) oversees	National Contingency Plan (NCP) Facility plan for response and cleanup of oil or hazardous substance must meet NCP standards.
REPORTS	Incidents in transit Transporter must ☐ Notify National Response Center (NRC) at once. ☐ Submit written report within 15 days to DOT. ☐ Coordinate with DOT. Hazardous waste emergency on site ☐ Immediately-NRC ☐ Follow-up, in writing to EPA RA within 15 days ☐ UST Releases		Report six specific hazardous material incidents, at once to DOT/NRC, written follow-up at once, to NRC. Spill of RQ into navigable waters	Releases of extremely hazardous substance (EHS) over reportable quantity (RQ) EHS stored on site in quantities ≥ RQ	Releases of RQ or 1 pound of hazardous substance, to NRC immediately
INFORMATION	Maintain copy of CP at site. Provide copy to local emergency response organization. Establish alarm and communication systems for emergency notification.	MSDSs to employees and emergency response organizations	Emergency response information available during transportation and at facilities where hazardous materials are loaded or stored.	As requested by LEPC and SERC. Designate representative to LEPC. Coordinate internal plans or make them available to LEPC.	
TRAINING, DRILLS, AND EVALUATION	Emergency response must be documented, records retained. Initial and annual review Evacuation drill	Initial and annual refresher training for employees involved in emergency response. Requirements vary with roles. All employees trained in Emergency Action Plan: initially and with every change to plan. Training in MSDS information			

Fig. 6.6. Emergency prevention, planning, and response matrix.

hazardous material incidents that must be reported immediately and again in writing. RCRA gives managers 15 days after a hazardous waste emergency to submit a written report to EPA.

Training, Drills, Audits, and Evaluations

An emergency plan is relatively useless unless the employees affected by it are trained in its use. RCRA, OSHA, HMTA, CWA, and the Energy Reorganization Act require annual and refresher training. In addition, the facilities must keep records of the training, and must make them available to the appropriate agency when they are requested. Some laws go so far as to require practice drills. Nuclear power plants must conduct on- and off-site training, and go through annual graded emergency response exercises. The plan and the response executed according to the plan

CWA	CAA	TSCA	NUREG 054	USCG
Spill Prevention Control and Countermeasure (SPCC) plan. Shows how facility will ☐ prevent ☐ respond ☐ follow-up to oil spills in harmful quantities. Must be in writing.	State Implementation Plan (SIP) must include an Emergency Air Pollution Episode plan. Accident Prevention Program for EHSs States may require prevention and emergency response plans.		Emergency response plan, including ☐ Emergency Planning Zones ☐ Prevention, mitigation, and limitation of core damage and consequences of release Subject to annual review	
Release of RQ of oil or hazardous substance to NRC, immediately	Announce uncontrolled releases of pollutants over certain set levels. Releases ≥ RQ to NRC	Emergency incidents of environmental contamination: ☐ At once to EPA ☐ Written follow-up within 10 days	Notify state and local officials ☐ Change in conditions ☐ Protective action recommendations Notify community within 15 minutes, 100% notification within 15 miles	All spills into navigable waters of oil, petroleum products, or hazardous substances, ≥ RQ, at once, to U.S. Coast Guard or to NRC.
Keep copy of SPCC at site available to EPA RA during normal working hours. Submit SPCC amendments to EPA RA and state water pollution control agency.				
Train ☐ SPCC responders. ☐ Employees who operate maintain equipment.			Annual training ☐ On-site ☐ Off-site Annual graded emergency response exercises	

then are evaluated so that the plan can be improved.

Sources of Assistance

Seeing all of the requirements together can be overwhelming. Fortunately, there are agencies, associations, and programs that can assist in the preparation of a comprehensive emergency prevention and response plan.

The federal government and the agencies responsible for the laws that govern emergency response planning provide 800-number hotlines and manuals that describe various aspects of emergency prevention, planning, and response.

The volunteer or professional emergency responders in the community have valuable practical experience that can be put to work in developing the facility emergency response plan. Working with them also establishes a forum for communications and understanding with the community.

The Chemical Manufacturers Association (CMA) Community Awareness and Emergency Response (CAER) program provides comprehensive guidelines for the development and implementation of an emergency response plan. The CAER program has been expanded to include all aspects of the chemical industry in an initiative called Responsible Care.

Other services of the CMA include CHEMTREC, a 24-hour emergency response service for people who respond to emergencies involving chemicals; CHEMNET, a mutual aid agreement between chemical producers and emergency response contractors; and workshops and videotape training programs for first responders and other emergency response personnel.

Additional sources of assistance and information include other professional associations, such as the American Institute of Chemical Engineers, and publications, seminars, workshops, and videotapes offered by educational organizations.

A bibliography; a list of laws, regulations, and standards; and a compilation of suggested reading material follow.

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LAWS, REGULATIONS, AND STANDARDS

Laws and Regulations

CAA (Clean Air Act)
  40CFR 51 SIP Emergency air pollution episode plan
  CAA Reauthorization Section 304, Prevention of sudden, accidental releases
CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act)
  40CFR 300-306 Section 103(a) Spill reporting requirements
  40CFR 355 Emergency planning

- CWA (Clean Water Act)
  - 40CFR 112.3-7 Spill prevention, control, and countermeasure plan (SPCC) requirements, modifications, preparation, and implementation
- Energy Reorganization Act (was Atomic Energy Act)
  - 10CFR 50.47, also Appendix E NRC (Nuclear Regulatory Commission) Standards for on-site and off-site emergency plans
- HMTA (Hazardous Materials Transportation Act)
  - 49CFR Parts 171-177 DOT requirements for providing information and advice on meeting emergencies; FEMA requirements for evaluation of training programs for incident prevention and response
- OSHA (Occupational Safety and Health Act)
  - 29CFR 1910.1200 Hazard communication standard
  - 29CFR 1910-210 and Appendices, Hazardous waste operations and emergency response
  - 29CFR 1910.35-38 Requirements for evacuation route and exit posting, emergency lighting, accessibility of exits, and emergency action plan
  - 29CFR 1910.156 Fire brigades
  - 29CFR 1910.157-164 Fire extinguishing and detection systems
  - 29CFR 1910.165 Employee alarm systems
- RCRA (Resource Conservation and Recovery Act)
  - 40CFR 263.30,31 Transporter responsibilities in hazardous waste transportation incidents
  - 40CFR 264.30-37 and 40CFR 265.30-37 Preparedness and prevention
  - 40CFR 264.50-56 and 40CFR 265.50-56 Contingency Plan
- SARA Title III (Superfund Amendment and Reauthorization Act, Emergency Planning and Community Right-to-Know)
  - 40CFR 355.3, Section 302(c), Emergency planning notification
    - Section 303(d), Appointment of emergency coordinator, provision of information; Section 304, Emergency release notification requirements
- U.S. Coast Guard
  - 33CFR 126.9 Reporting requirements for discharge of petroleum products or dangerous liquid commodities into navigable waters of USA
  - 33CFR 153.023 Reporting requirements for discharge of reportable quantity (RQ) of oil or hazardous substance into navigable waters

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7

Wood and Wood Products

Raymond A. Young*

Wood has been utilized by humans since antiquity. Trees provided a source of many products required by early humans such as food, medicine, fuel, and tools. For example, the bark of the willow tree, when chewed, was used as a painkiller in early Greece and was the precursor of the present-day aspirin. Wood served as the primary fuel in the United States until about the turn of the century, and even today over one-half of the wood now harvested in the world is used for heating fuel.

Throughout history different types of wood have served many purposes. The tough, strong, and durable white oak, for example, was a well-proven raw material for ships, bridges, cooperage, barn timbers, farm implements, railroad ties, fence posts, flooring, paneling, and other products. In contrast, woods such as black walnut and cherry became primarily cabinet woods. Hickory was manufactured into tough, hard, resilient tool handles. Black locust was used for barn timbers and treenails. What the early artisan learned by trial and error became the basis for intelligent decisions concerning which species was best suited to a given purpose, as well as what characteristics should be looked for in selecting trees for different applications. It was known that wood from trees grown in certain locations was stronger, more durable, and more easily worked with tools than wood from the same species grown in other locations. Modern wood quality research has substantiated that location and growth conditions significantly affect wood properties.[1]

In the United States more than 100 kinds of wood are available to the prospective user, but it is very unlikely that all are available in any one locality. About 60 native woods are of major commercial importance. Another 30 wood types are commonly imported in the form of logs, cants, lumber, and veneer for industrial uses, the building trades, and crafts.[2,3]

The importance of wood as a raw material supplying fiber, energy, and chemicals is similar in magnitude to its use as a solid material. Lumber, plywood, and reconstituted boards consume about one-half of the timber

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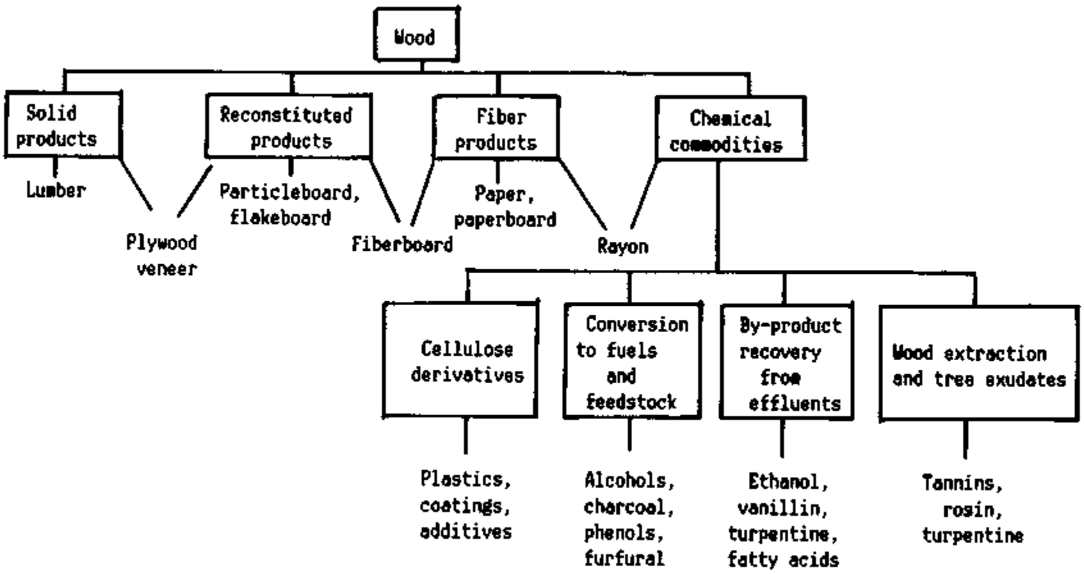


Fig. 7.1. Summary of uses for wood. (*From* Introduction to Forest Science, *2nd ed., R. A. Young and R. L. Giese, Eds., copyright © 1990 John Wiley & Sons, New York; with permission of John Wiley & Sons Publisher.)*

harvest; usage for fiber, chemicals, and fuels accounts for the remaining half. Fiber production consumes about 25 percent of the total timber use. In 1990 over 55 million metric tons of pulp fiber for papermaking were derived from the forest. Although the relative value of wood as a source of energy and chemicals has varied considerably through the decades, wood continues to be an important source of specialty chemicals and renewable energy, and may be even more important in the future. The many uses for wood are summarized in Fig. 7.1. In this chapter we discuss the chemical nature of wood and provide a description of the technology for conversion of wood to pulp fibers for papermaking, to fuels for energy, and to chemicals for industry and consumers.

WOOD STRUCTURE

The wood from the many different species of trees is divided into two major categories according to the botanical classification of the trees as seed plants. The hardwoods are derived from the angiosperms (encased seeds), which are generally the deciduous broad-leaved trees; the softwoods are from the gymnosperms (naked seeds), generally characterized as cone-bearing trees with persistent needlelike foliage. The majority of the trees in the latter classification fall into the division Coniferophyta and thus are often referred to as conifers. It is important to note that the terms "hardwood" and "softwood" have no direct relation to the hardness or softness of the wood. In fact, hardwood trees such as cottonwood, aspen, and balsa have softer wood than the western white pines and true firs; and certain softwoods, such as longleaf pine and Douglas fir, produce wood that is much harder than that of basswood or yellow poplar.

Wood can be considered as a biological composite of hollow tubes of cellulose fibers held together by a lignin matrix gluing material. Liquids are transported up and down the trees through the tubular plumbing system. About 90 percent of the wood tissue of softwood trees consists of fiber tracheid cells for liquid conduction and support. The hardwood trees evolved after the softwoods and have specialized water conduction cells called vessels.

Each vessel consists of numerous drum-shaped vessel members with open ends, stacked one above the other to form a continuous vessel pipeline from root tips to the leaves. The vessels in oaks and some other broad-leaved trees are large enough to be seen with the unaided eye, that is, as round pores at the end surface and as needlelike grooves at the lateral surface (Fig. 7.2).[4]

In some woods such as oak, the vessels in the earlywood (produced early in the growing season) are much wider than those in latewood and form the distinct growth rings of these ring-porous woods (Fig. 7.3a). In the diffuse-porous maple, birch, and many other genera, the vessels are of the same size throughout the growth ring, the boundary of which is marked only by extremely thin cells (Fig. 7.3b). Because coniferous woods lack vessels, they sometimes are designated non-porous, in contrast to the porous broad-leaved trees, particularly those with relatively wide pores. Coniferous wood has growth rings because the earlywood tracheids have wider cavities and thinner cells than do the latewood tracheids; the earlywood–latewood contrast is especially sharp in southern pines.

On tree cross sections, rays of parenchyma cells resemble spokes of a wheel as they extend from the bark into the wood, in the radial direction of the circular growth rings and perpendicular to the tangent of the rings or to the tangential direction (Fig. 7.2). Radial and tangential are both transverse directions, that is, horizontal to the trunk of the standing tree.

Fibers and vessels die at an age of a few weeks, after attaining their final shape and chemical composition. Parenchyma cells live much longer, some remaining alive until sapwood becomes heartwood. One of the tasks of parenchyma cells is to convert sugars into storage starch to serve as food reserves for the tree, and to reconvert starch to sugars

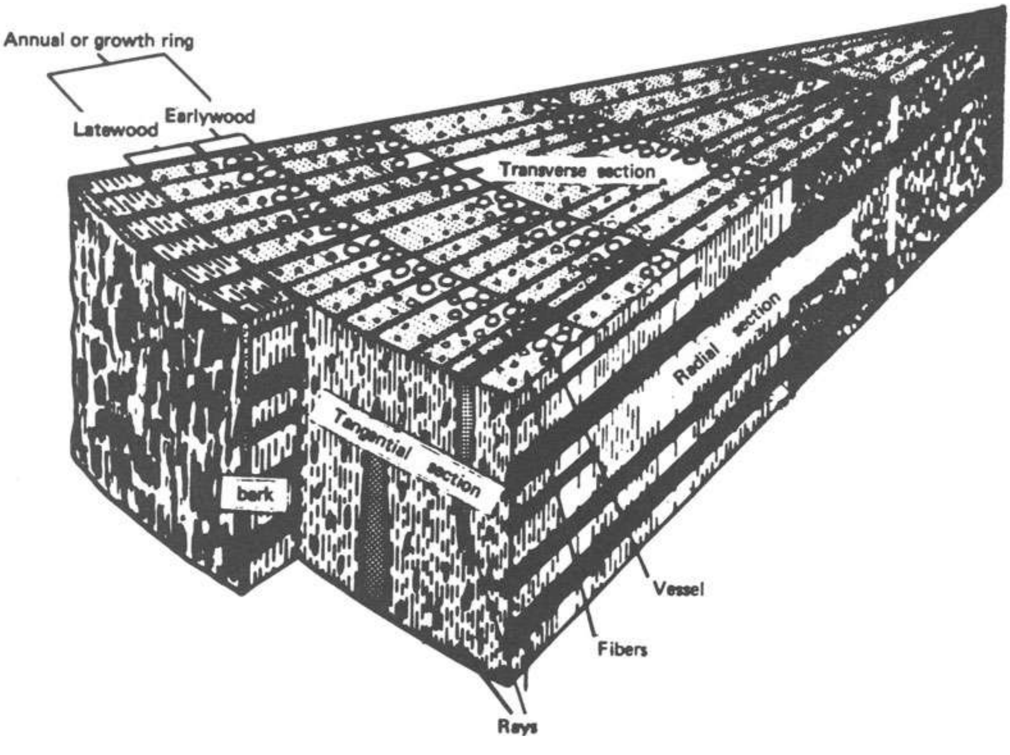


Fig. 7.2. Diagrammatic wedge section of a five-year-old oak trunk. The term "transverse section" is synonymous with end surface and cross section. Both radial section and tangential section are lateral surfaces. (*Courtesy of U.S.D.A. Forest Products Laboratory.*)

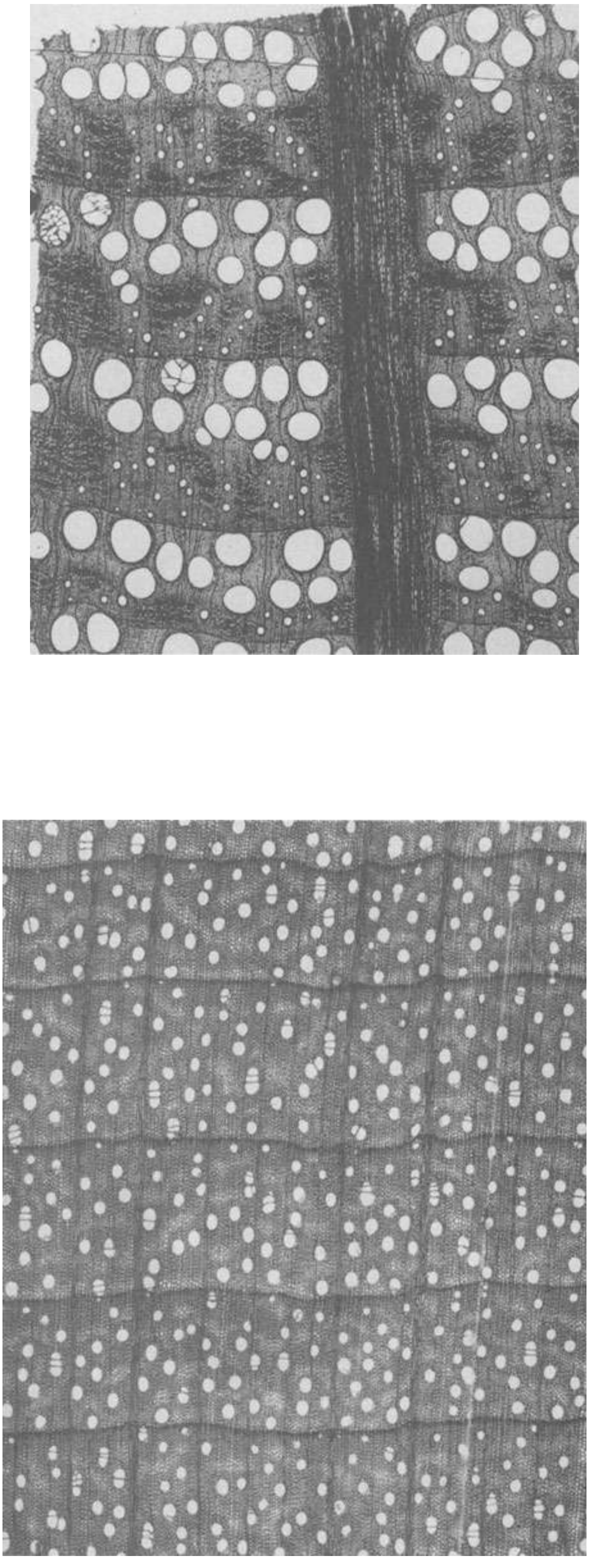


Fig. 7.3. Photomicrograph of hardwood cross sections depicting (a) ring-porous and (b) diffuse porous wood. (*Courtesy of U.S.D.A. Forest Products Laboratory.*)

when they are needed for growth. The starch and sugar content of sapwood is one reason why most wood-damaging organisms prefer dead sapwood over heartwood, and why sapwood is never quite as durable as heartwood, except in living trees whose sapwood cells fight attacking organisms.

Practically all cavities of wood cells are interconnected, as mentioned above for the vessel members of hardwoods. Tiny openings in the cell walls of overlapping ends of tracheids provide vertical passageways for water rising from cell to cell in conifers. Thin walls of ray cells are perforated for the radial transport of sugars, and tangential connections provide for growing cells. Hence, wood is permeable in all three of its cardinal directions. The longitudinal orientation of most cells, however, causes liquids and gases to flow and diffuse many times faster in the longitudinal or fiber direction than in the two transverse directions. This explains why stacked firewood dries predominantly at the exposed ends. The radial orientation of rays allow liquids and gases to move radially up to twice as rapidly as tangentially.[4]

As a porous material, wood contains air-filled or water-filled cell cavities surrounded by cell walls (Fig. 7.3). The cell wall substance is remarkably uniform; it differs very little even between conifers and broad-leaves trees and has a constant density of around 1.5 g/cm^3. The density of wood thus depends on the proportion of the cell wall volume to the volume of the bulk wood.

Wood density is *the* indicator of nearly all wood properties and of wood quality. Relatively dense species are strong, as one might expect from their large cell wall mass. Wood species also vary in features not related to density, such as color, percentage and arrangement of cell types, and minor chemical constituents. Therefore, even woods of the same density are likely to differ, with the properties varying more than the densities.

The widespread use of wood is due to its many advantages, including its very high strength-to-mass ratio, good toughness, low cost and availability, workability, attractive appearance, and good thermal and electrical insulating properties. However, there also are a number of disadvantages of wood, which have limited its usage for many applications; these include its lack of plasticity and fusibility, shrinkage and swelling properties, deterioration due to fungi and insects, and variability. However, most of its negative properties can be corrected by proper treatment and modification, as described later in this chapter.

CHEMICAL COMPOSITION AND FIBER STRUCTURE

Wood is composed of three major polymeric materials: cellulose, hemicelluloses, and lignin. Cellulose is the common name used for the glucan present in wood, which constitutes about 42 percent of wood's dry weight. Cellulose is the primary component of the walls of cells making up wood fibers and is the main structural material of wood and other plants. Paper, paperboard, and other wood fiber products thus also are composed mostly of cellulose. The chemical structure of the cellulose macromolecule is shown in Fig. 7.4. In the plant the degree of polymerization (DP) of cellulose is approximately 14,000.[5]

Closely associated with cellulose in the wood structure and paper products are other polysaccharides called hemicelluloses, which often have been labeled as the matrix material

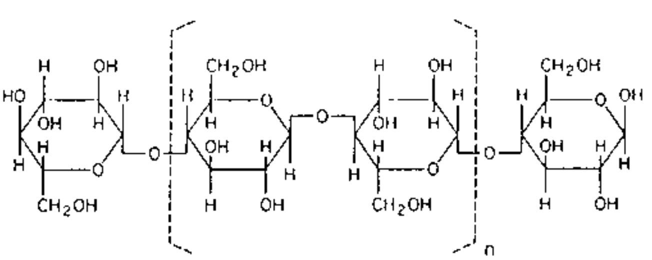


Fig. 7.4. The chemical structure of cellulose with the cellulose repeat unit in brackets.

of wood. In hardwoods the primary hemicellulose is a xylan (polymer of xylose), whereas in softwoods the primary hemicellulose is a glucomannan, although both of these polysaccharides occur to some extent in both types of wood. The DP of the hemicelluloses is much less than that of cellulose, in the range of 100 to 200.

Table 7.1 compares the chemical composition of extractive-free hardwoods and softwoods. As cellulose and the hemicelluloses are both polysaccharides, it is obvious that the polysaccharide of wood is by far the dominant component, making up approximately 70 percent of both hardwoods and softwoods. Additional polysaccharides may occur as extraneous components of wood, which are not part of the cell wall; for example, the heartwood of species of larch can contain up to 25 percent (dry weight) of arabinogalactan, a water-soluble polysaccharide that occurs only in trace quantities in other wood species.[5]

The third major component of wood shown in Table 7.1 is lignin. Although lignin also is a polymer, it has a different chemical structure from that of the polysaccharides. The monomeric units in lignin are phenolic-type compounds, but the exact chemical structure of lignin still is not known after 100 years of intensive research. The spaces between fibers in wood are almost pure lignin and are termed the middle lamella. Lignin is considered the gluing or encrusting substance of wood and adds mechanical strength or stiffness to the tree and to wood. Higher plants commonly are referred to as lignocellulosic because of the typical joint occurrence in them of lignin and cellulose.

TABLE 7.1 Chemical Composition and Fiber Length of Extractive-Free Wood

Component	*Hardwood (Red Maple) (percent)*	*Softwood (Balsam Fir) (percent)*
Cellulose	44	42
Hemicelluloses		
Xylan	25	9
Glucomannan	4	18
Lignin	25	29
Pectin, starch	2	2
Average fiber length (mm)	0.8–1.5	2.5–6.0

In the tree the cellulose polymers are laid down uniformly, the chains paralleling one another, and the long-chain molecules associate strongly through hydrogen bonds that develop between hydroxyl groups. These bonds create very strong associations between the cellulose macromolecules, producing very uniform crystalline structures known as micelles or microcrystallites (see Fig. 7.5).

The micelles also are associated in the tree to give long threadlike structures termed microfibrils (Fig. 7.5). However, the structure of the microfibrils is not completely uniform in terms of the alignment of the cellulose macromolecules, and the regions of nonuniformity between the micelles in the microfibrils are called amorphous regions. Thus the cellulose microfibril has a crystalline–amorphous character. Water molecules enter the amorphous regions and swell the microfibrils; ultimately this is the mechanism by which fibers and wood swell in moist or wet environments.

The final fiber cell wall structure is essentially layers of the microfibrils or macrofibrils aligned in several different directions, as shown in Fig. 7.6. The microfibrils that make up the wood fiber are visible under the scanning electron microscope, which has a greater magnification than the light microscope.

The entity holding the fibers together, the middle lamella, is almost pure lignin (90%), as mentioned earlier. For the cellulose fibers to be separated, the middle lamella lignin must be chemically removed, a process that also removes most of the hemicelluloses, or must be mechanically degraded to free the fibers for papermaking. A paper sheet then can be formed from the separated cellulose fibers by depositing them from a water slurry onto a wire screen. The water drains away and the fibers collapse, leaving a fiber mat that derives its main strength from reassociation of the fibers through many hydrogen bonds—the same type of bond that gives mechanical integrity to the fibers.[5]

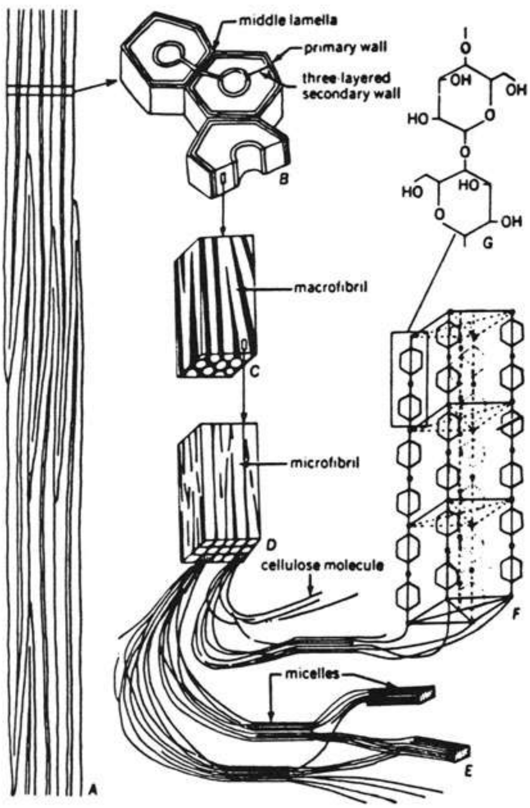


Fig. 7.5. Detailed structure of cell walls. (A) Strand of fiber cells. (B) Cross section of fiber cells showing gross layering: a layer of primary wall and three layers of secondary wall. (C) Fragment from the middle layer of a secondary wall showing macrofibrils (white) of cellulose and interfibrillar spaces (black), which are filled with noncellulosic materials. (D) Fragment of a macrofibril showing microfibrils (white), which may be seen in electron micrographs (Fig. 7.6). The spaces among microfibrils (black) are filled with noncellulosic materials. (E) Structure of microfibrils: chainlike molecules of cellulose, which in some part parts of the microfibrils are orderly in arrangement. These parts are the micelles. (F) Fragment of a micelle showing parts of chainlike cellulose molecules arranged in a space lattice. (G) Two glucose residues connected by an oxygen atom—a fragment of a cellulose molecule. (*From K. Esau,* Anatomy of Seed Plants, *Second Edition, 1977, copyright © by John Wiley & Sons, 1977,* reprinted by permission of the copyright owner.)

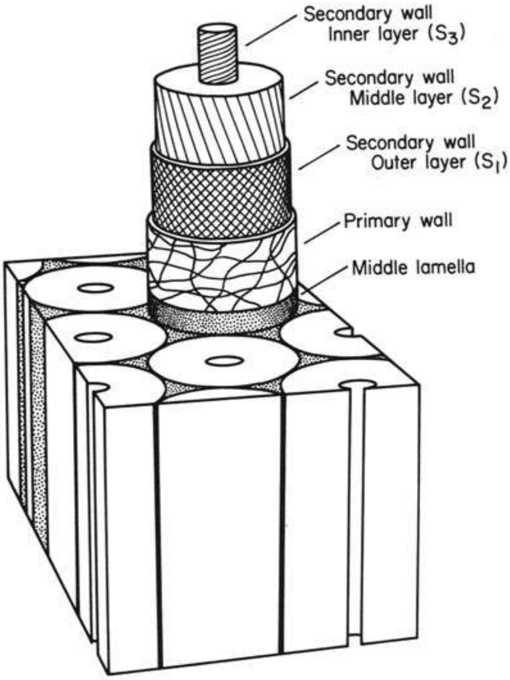


Fig. 7.6. A section of wood made up of fibers and middle lamella. The structure of a fiber is given, showing the micro-fibrillar orientations in the different layers of the fiber cell wall. (*From* Introduction to Forest Science, *2nd ed., R. A. Young and R. L. Giese, Eds. Copyright © 1990 by John Wiley & Sons, Inc., New York, and reproduced by permission of the copyright owner.*)

The long fibers from softwoods (Table 7.1) usually are preferred in papermaking for products that must resist tearing, such as grocery bags, whereas the shorter hardwood fibers give improved opacity, or covering power, and printability to the final paper sheet. The type of pulping process also affects the pulp properties, as described in a later section.

PULP AND PAPER

The concept of making paper from the fibers from lignocellulosic materials—an integrated system of fiber separation (pulping) and re-forming of the fibers into a mat (papermaking)—is attributed to T'sai Lun, a court official in southeast China in A.D. 105. The first fibers were obtained from old hemp rags and ramie fishnets, but shortly thereafter, the inner bark fibers from paper mulberry trees also were utilized for papermaking. Bamboo was used as a source of fiber several centuries later. The rags were macerated into a pulp in water with a mortar and pestle; then, after dilution in a vat, the pulp was formed into a wet mat on a bamboo frame equipped with a cloth screen to drain the free water. The mat was dried in the sun. The invention was based on the need for a writing material to replace the expensive silk and inconvenient bamboo strips. The invention was a closely guarded secret for many centuries but eventually filtered west, reaching Europe in 1151 and the United States (Pennsylvania) in 1690.[5]

The importance of the pulp and paper industry to the American economy is exemplified by the growth rate in the use of paper and paper products. New uses continually are being found for paper, and these developments together with a rising standard of living have resulted in a constant increase in the per capita consumption of paper. The industry has shown constant growth since about the middle of the nineteenth century, when processes were invented for production of fiber from wood, replacing reliance on cotton rags as a source of fiber (Fig. 7.7). The relative paper consumption by grade is shown in Fig. 7.8, and differences in the economies of developed and less developed countries are demonstrated in Fig. 7.9 by the wide disparity in per capita consumption of paper and paperboard.

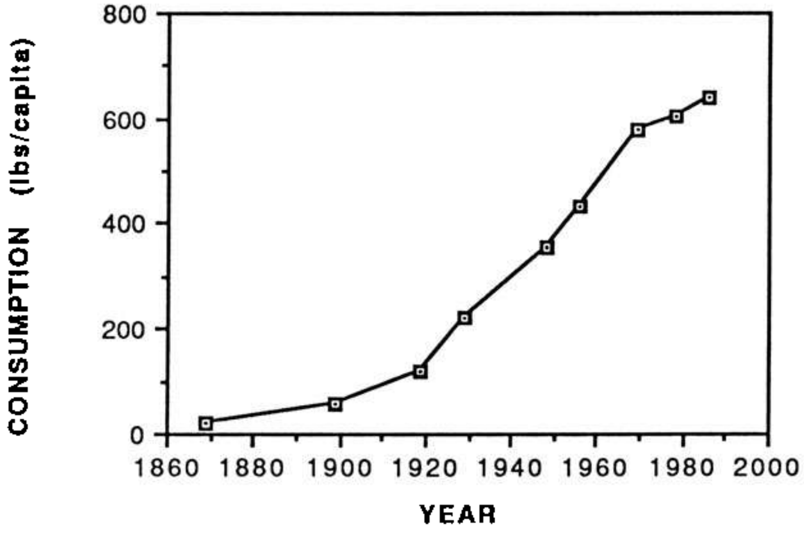


Fig. 7.7. Consumption of paper in the United States since the year 1860.

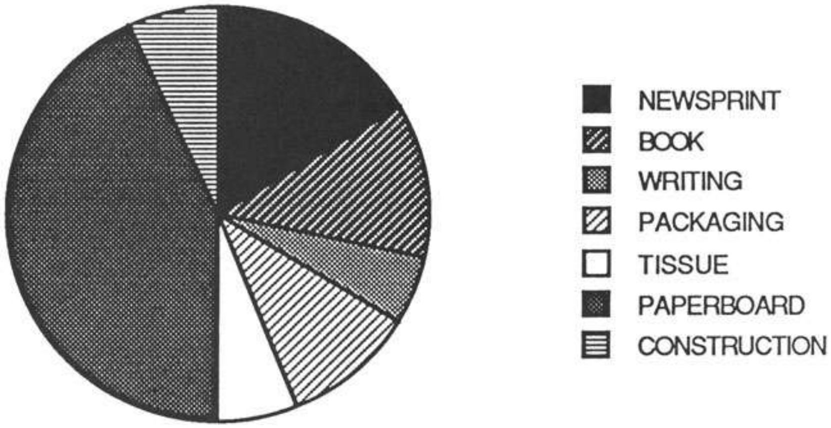


Fig. 7.8. Relative consumption of paper by grade.

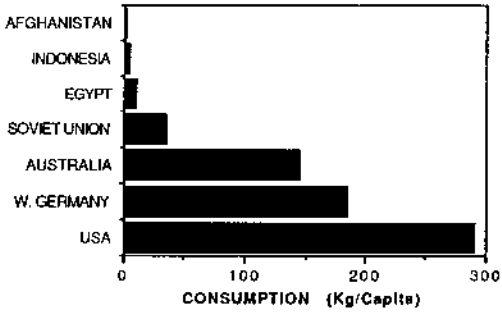


Fig. 7.9. Comparison of paper consumption in developed and developing countries.

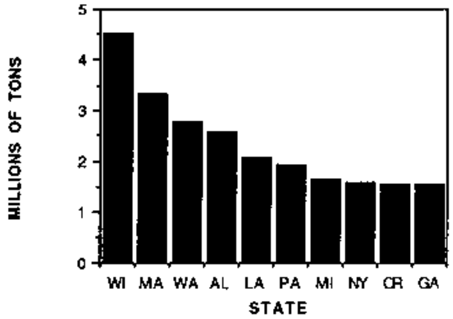


Fig. 7.10. Paper production in the ten leading states.

In 1988, the United States produced a total of 69,477,000 tons of paper and paperboard in hundreds of separate mill locations. This paper and board was made from 55,530,000 tons of pulp, produced primarily from wood in over 200 pulp mills, and 15,000,000 tons of recycled waste paper.[6]

Figure 7.10 shows the leading states for paper production in 1988. Only a small amount of paper is made from rags or other fiber sources (agricultural residues); so most wood pulp is produced from those areas of the country that are heavily forested. With the exception of Maine and Wisconsin, pulp production is concentrated in the southern and northwestern sections of the United States. Georgia and Washington are the top pulp-producing states. Although a high percentage of pulp is converted into paper or board at the same plant site, a significant portion (classified as "market pulp") is sold in bales to mills in other sections of the country for subsequent manufacture into paper. Thus, New York and Michigan are relatively important in papermaking, but they rank quite low as pulp producers. However, both New York and Michigan are large users of waste paper that is reprocessed into usable fiber. With the current emphasis upon recycling, it is probable that the use of waste paper will be greatly accelerated in the near future.

Raw materials for the pulp and paper industry can be classified as fibrous and nonfibrous. Wood accounts for over 95 percent of the fibrous raw material (other than waste paper) in the United States. Cotton and linen rags, cotton linters, cereal straws, esparto, hemp, jute, flax, bagasse, and bamboo also are used and in some countries are the major source of papermaking fiber.

Wood is converted into pulp by mechanical, chemical, or semichemical processes. Sulfite and kraft (sulfate) are the common chemical processes, and neutral sulfite is the principal semichemical process (NSSC). Coniferous wood species (softwoods) are the most desirable, but the deciduous, broad-leaved species (hardwoods) have gained rapidly in their usage and constitute about 25 percent of pulpwood. Table 7.2 summarizes the conditions utilized with the various pulping processes, and Fig. 7.11 shows the relative production of pulp by the major processes.[5]

Nonfibrous raw materials include the chemicals used for the preparation of pulping liquors and bleaching solutions and the various additions to the fiber during the papermaking process. For pulping and bleaching, these raw materials include sulfur, lime, limestone, caustic soda, salt cake, soda ash, hydrogen peroxide, chlorine, sodium chlorate, and magnesium hydroxide. For papermaking, they include rosin, starch, alum, kaolin clay, titanium dioxide, dyestuffs, and numerous other specialty chemicals.

Wood Preparation

The bark of trees contains relatively little fiber and much strongly colored nonfibrous material; what fiber there is, is of poor quality. The nonfibrous material usually will appear as dark-colored dirt specks in the finished

TABLE 7.2 Wood Pulping by Process and Yield

		Treatment		
Process	*Acronym*	*Chemical*	*Mechanical*	*Pulp Yield (percent)*
Mechanical Processes				
Stone groundwood	SGW	None	Grinder	93–95
Pressure groundwood	PGW	None	Grinder	93–95
Refiner mechanical	RMP	None	Disk refiner (pressure)	93–95
Thermomechanical	TMP	Steam	Disk refiner (pressure)	80–90
Chemithermomechanical	CTMP	Sodium sulfite or sodium hydroxide[a]	Disk refiner (pressure)	80–90 80–90
Chemimechanical[b]	CMP	Sodium sulfite or sodium hydroxide	Disk refiner	80–90
Semichemical Processes				
Neutral sulfite	NSSC	Sodium sulfite + sodium carbonate	Disk refiner	70–85
Green liquor	GLSC	Sodium hydroxide + sodium carbonate	Disk refiner	70–85
Nonsulfur	—	Sodium carbonate + sodium hydroxide	Disk refiner	70–85
Chemical Processes				
Kraft	—	Sodium hydroxide + sodium sulfide	None	45–55
Sulfite	—	Calcium bisulfite in sulfurous acid[c,d]	None	40–50
Magnefite	—	Magnesium bisulfite in sulfurous acid[e]	None	45–55
Soda	—	Sodium hydroxide	None	40–50
Soda-oxygen	—	Sodium hydroxide + oxygen	None	45–55
Soda-anthraquinone	SAq	Sodium hydroxide + anthraquinone	None	45–55
Dissolving Processes				
Prehydrolysis kraft	—	Steaming and kraft (two-step process)	None	35
Acid sulfite	—	Acid sulfite (Ca, Na)	None	35

Source: Data taken from references 1 through 5. [a]Sodium sulfite or sodium hydroxide, 2 to 7% of wood. [b]Also chemical treatment after fiberizing. [c]Also sodium, magnesium, ammonia. [d]pH 2. [e]pH 5.

paper. Therefore, for all but low-grade pulps, bark should be removed as well as possible, and this removal must be very thorough in the case of groundwood and sulfite pulps if the finished paper is to appear clean.

Debarking usually is done in a drum barker, where the bark is removed by the rubbing action of logs against each other in a large rotating drum. Hydraulic barkers using high-pressure water jets are excellent for large logs and are common on the West Coast. Mechanical knife barkers are becoming more common and are used extensively in smaller operations because of their relatively low capital cost. Also they have found widespread use in sawmills to debark logs prior to sawing so that the wood wastes can be used to produce pulp.

Wood cut in the spring of the year during the active growing season is very easy to peel. Much of the spruce and fir cut in the North is still hand-peeled during this season and usually represents the optimum in bark removal.

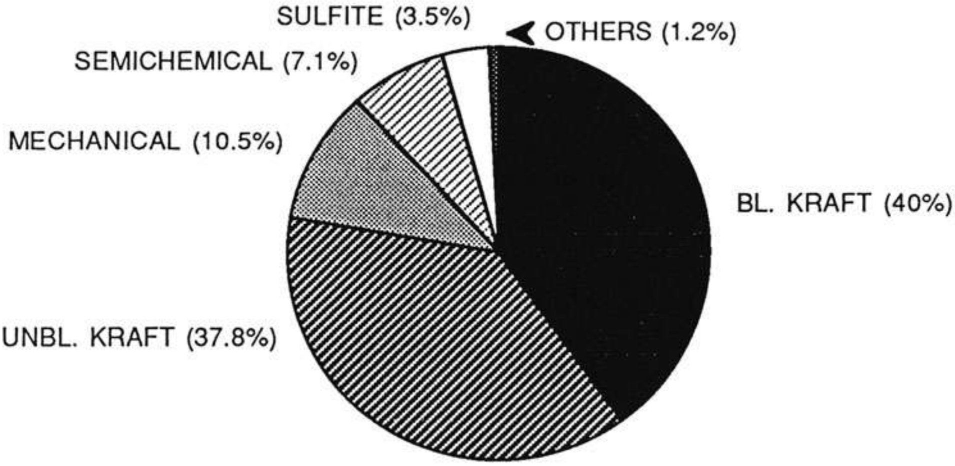


Fig. 7.11. Relative wood pulp production by grade.

The standard log length used in the Northeast is 48 inches, whereas 63 inches is common in the South. Wood generally is measured by log volume, a standard cord being considered to contain 128 cubic feet. Large timber on the West Coast generally is measured in board feet of solid volume. Measurement and purchase of wood on a weight basis are practiced, and are desirable because weight is directly related to fiber content.[1]

The growth in the use of wood residues has been substantial. By barking the sawlogs, the slabs, edgings, and other trimmings that formerly were burned now can be used to make pulp. Almost 28 percent of the wood used by the pulp industry is classified as waste wood. Several mills have been built that use no logs whatsoever but depend on residuals from satellite sawmill operations. Special sawmilling equipment has been developed to produce sawdust of a proper size so that it too can be used.

Wood used in producing groundwood or mechanical pulp requires no further preparation after debarking, but that used in the other chemical processes first must be chipped into small pieces averaging one-half to one inch in length and about one-eighth to one-quarter inch in thickness. Chipping is accomplished with a machine consisting of a rotating disc with knives mounted radially in slots in the face of the disc. Modern chippers have up to 12 knives; the ends of the logs are fed against the disc at about a 45° angle.

Mechanical Pulping

Mechanical pulping, as the name implies, involves mainly grinding and abrading action on wood to produce a mechanical pulp—the primary component of newsprint. Modern mechanical pulping includes stone groundwood pulping (SGW), in which bolts of wood are pressed against a revolving grindstone, and refiner mechanical pulping (RMP), in which chips are passed between single- or double-rotating plates of a vertical-disc attrition mill. Recent developments in stone grinding include application of pressure to the grinder (PGW) and control of temperature.

At one time, natural sandstone was used for the grindstone, but modern stones are either silicon carbide or aluminum oxide grits in a vitrified clay binder. Thus the characteristics of the stone can be varied to produce pulps "tailor-made" to fit their desired end use. Groundwood pulps for roofing or flooring felts must be extremely coarse and free-draining, so they require a stone with large grits, whereas newsprint pulps are very fine and require the use of small grits.

Pulp characteristics also can be varied by changing the stone surface pattern, the stone speed, the pressure of the logs against the stone, and the temperature of the ground-pulp slurry. Generally a coarser and more freely draining pulp is obtained with a coarse surface pattern and high speed, pressure, and temperature. The type and the condition of the wood also are factors, but groundwood pulps usually are made from the coniferous or long-fibered species because the deciduous or short-fibered species give very weak pulps.

Basic changes in mechanical pulping technology include pretreating chips with chemicals, steam, or both. These developments started 30 years ago when chips were pretreated with caustic soda, in a process called chemimechanical pulping (CMP). Presteaming and pressure refining of chips gives a thermomechanical pulp (TMP). The chips are steamed at 40 psi for 2 to 4 minutes and sent to a refiner modified to operate under pressurized conditions. When chemical pretreatment and pressure steaming are combined, the pulp is referred to as chemithermomechanical pulp (CTMP). Sulfite solutions commonly are used to produce CTMP, but there are many variations of these processes. These treatments are employed to improve pulp quality. The steam and chemicals aid fiberizing by giving a less-damaged fiber, which makes the final paper stronger. The pulps are sufficiently improved over stone groundwood that they can be used to partially substitute for chemical pulps. Newsprint consisting of 100 percent TMP or CTMP is produced commercially.

Groundwood or mechanical pulp is low in strength compared to the chemical pulps. It is composed of a mixture of individual fibers, broken fibers, fines, and bundles of fibers. Papers made from groundwood also lose strength and turn yellow with time. Thus, groundwood pulps are used only in relatively impermanent papers such as for newsprint, catalogs, magazines, and paperboard. Groundwood papers have excellent printing qualities because of high bulk, smoothness, resiliency, and good ink absorption. Newsprint contains about 80 percent groundwood, and the other publication paper grades contain about 30 to 70 percent, with the remainder a chemical pulp to provide greater strength. Groundwood is the cheapest pulp made and also utilizes the entire wood, giving close to a 100 percent yield.

Chemical Pulping

The objective of chemical pulping is to solubilize and remove the lignin portion of wood so that very little mechanical treatment is necessary to fiberize the wood. Many variations are used throughout the world, the simplest classification of pulping methods depending on whether they are acidic or alkaline. Each has its own specific advantages and disadvantages, but the kraft (alkaline) process accounts for over 90 percent of all chemical pulp produced in the United States. All present commercial processes use aqueous systems under heat and pressure although several organosolv systems are at the demonstration-plant stage.

The lignin-removal and fiber-separation mechanisms involved in chemical pulping are alkaline hydrolysis (lignin bond cleavage) and formation of soluble sulfur-containing lignin (thiolignins) in kraft pulping. The chemical mechanisms in sulfite pulping also involve lignin bond hydrolysis and formation of soluble sulfur-containing lignin derivatives, termed lignosulfonates.[5] Polysaccharide reactions are secondary to fiber separation in chemical pulping although polysaccharide retention, solution, or modification profoundly affects pulp yield and properties. Neutral sodium sulfite reactions in neutral sulfite semichemical (NSSC) pulping also are based on sulfonation for partial dissolution of lignin and a partial modification of the fiber bond to permit a clean separation of the fibers by mechanical action in disk refiner mills. The pulping chemicals are applied in water solutions (white liquor) at various concentrations and ratios of liquids to solids under different conditions of temperature and pressure to achieve the desired degree of delignification.

Kraft Process. The kraft (sulfate) process uses a mixture of sodium hydroxide and sodium sulfide as the active chemical. Although

TABLE 7.3 Typical Kraft Pulping Conditions

Pressure	100–110 psig
Temperature	170–175°C
Time	2–3 hrs
Alkali charge	15–25% of weight of wood (calculated as Na_2O but consisting of approximately $5NaOH + 2Na_2S$)

Liquor to wood ratio is 4 to 1 (by weight).

the designation sulfate process is misleading, it sometimes is used because sodium sulfate is the makeup chemical in the process. The word "kraft" now is mainly used to describe this process, derived from the Swedish or German word for strength, as this process produces the strongest pulp. Historically, sodium hydroxide alone (soda process) first was used as the alkaline pulping agent, but all these mills have converted to the kraft process because the other pulp is weak and inferior to kraft pulp.

The pulping (cooking) process traditionally was performed on a batch basis in a large pressure vessel called a digester. Conditions vary depending upon the type of wood being pulped and the quality of end product desired. Typical conditions for kraft cooking are listed in Table 7.3.

Digesters are cylindrical in shape with a dome at the top and a cone at the bottom. Ranging in size up to 40 feet high and 20 feet in diameter, the largest will hold about 7000 cubic feet of wood chips (about 35 tons) for each charge. The chips are admitted through a large valve at the top, and at the end of the cook they are blown from the bottom through a valve to a large blow tank. During the cook the liquor is heated by circulation through a steam heat exchanger, which also avoids the dilution of the cooling liquor that would occur from heating by direct injection of steam.

The development of the continuous digester (Fig. 7.12) significantly facilitated the use of kraft pulping. Chips are admitted continuously at the top through a special high-pressure feeder, and the cooked pulp is withdrawn continuously from the bottom through a special blow unit. Recent installations range in size up to 150 feet high and are capable of

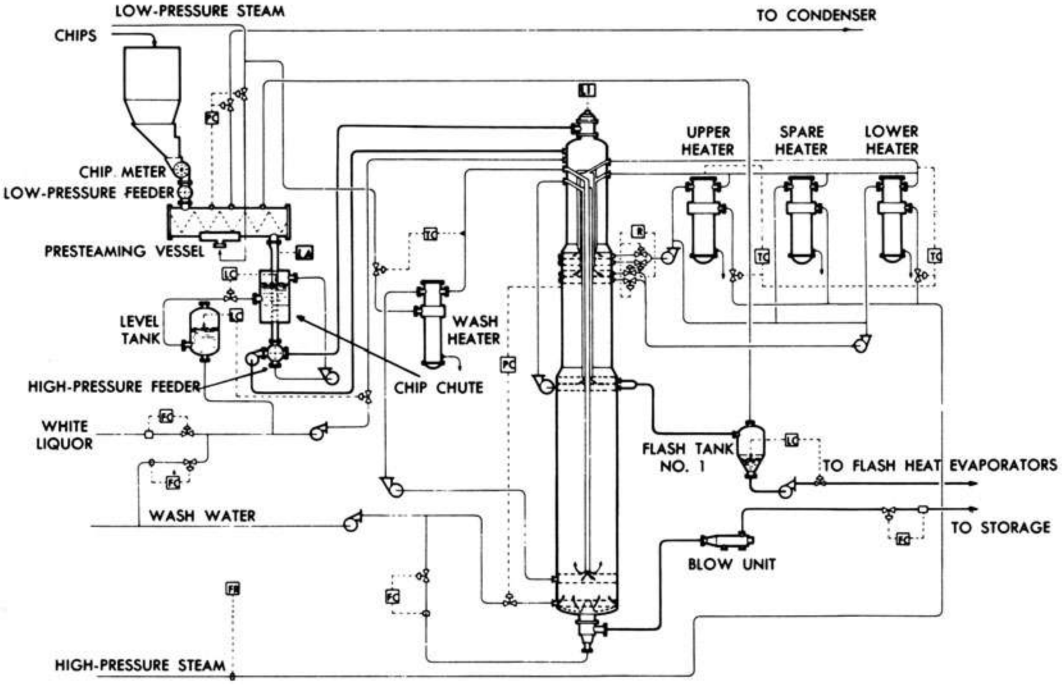


Fig. 7.12. Typical Kaymr continuous cooking system for kraft pulp. (*Courtesy Kamyr, Inc.*)

producing about 1000 tons of pulp per day in one unit. Cooking liquors and conditions are approximately the same as for the batch digesters. These units offer both good economics in the production of pulp and a quality advantage compared to the batch digester. However, because the capital investment for these units is somewhat higher, both systems are installed for new mills.

Because of the high alkali charge, the chemicals must be recovered and reused. This process also alleviates pollution problems because the yield of pulp is only about 45 percent of the original wood weight, and the organic residues must be eliminated. After being cooked in the digester, the pulp is washed in a countercurrent rotary vacuum washer system using three or four stages. The pulp then is ready for bleaching or for use in papers such as grocery bags where the brown color is not objectionable.

The separated liquor, which is very dark, is known as "black liquor." It is concentrated in multi-effect evaporators to 60 to 65 percent solids. At this concentration the quantity of dissolved organic compounds from the wood (lignin and carbohydrate degradation products) is sufficient to allow the liquor to be burned in the recovery furnace.

By controlling the amount of excess air admitted to the furnace and the temperatures, the organics in the liquor can be burned. The inorganics collect on the bottom of the furnace as a molten smelt of Na_2CO_3 and Na_2S. Sodium sulfate is added to the liquor as makeup and is reduced to Na_2S by carbon. After dissolving in water, this mixture (called "green liquor") is reacted with slaked lime:

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$$

The Na_2S does not react with the lime, so the resultant mixture of NaOH and Na_2S (called "white liquor") can be reused to pulp more wood. The $CaCO_3$ sludge is filtered off, burned in a lime kiln, and reused. Thus, the chemical system is a closed one, as shown in Fig. 7.13, and this minimizes costs and pollution.

The kraft process has had a serious problem with air pollution due to the production of

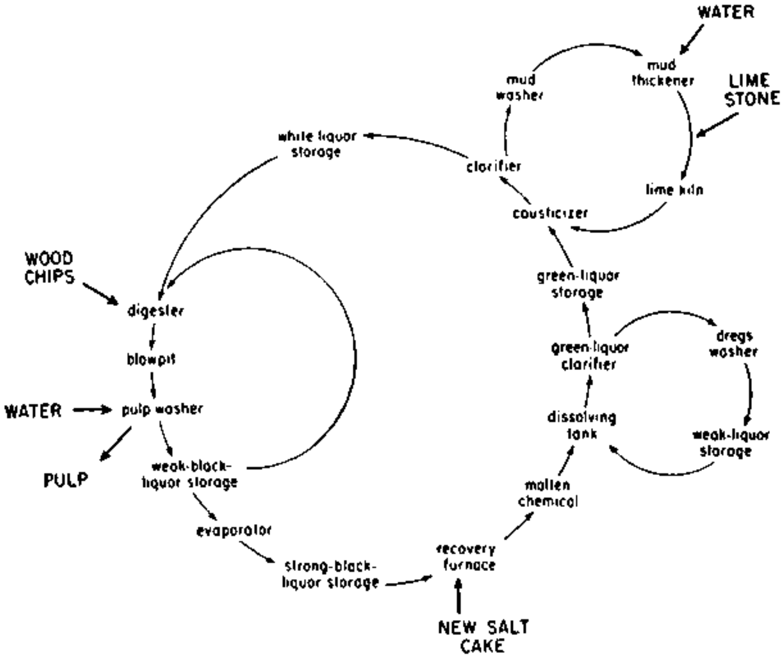


Fig. 7.13. Diagram showing cyclic nature of kraft recovery process. (*From* Pulp and Paper, *3rd ed., Casey, J. P., Ed. Wiley-Interscience Pub., New York. Copyright © 1980 by John Wiley & Sons, Inc. and reproduced by permission of the copyright owner.)*

hydrogen sulfide, mercaptans, and other vile-smelling sulfur compounds. In recent years, the use of various techniques such as black-liquor oxidation, improved evaporators and furnaces, and control of emissions has greatly improved this situation. However, older mills are being forced to expend large amounts of money to bring their operations up to the environmental standards.

Practically any kind of wood can be pulped by the kraft process; and because it produces the strongest pulps with good economies, it has grown to be the dominant process in the world. Although the odor problem is very severe, it does not appear that this process will be supplanted in the near future; instead, it will be improved and modified. When pulping resin-rich woods such as southern pine, the kraft process yields turpentine and tall oil as valuable by-products. The steam generated in the recovery furnace is almost enough to make the pulp mill energy self-sufficient.

A recent discovery that small amounts of anthraquinone (0.05–0.25% on wood) added to alkali liquors can enhance delignification and produce kraft quality pulp has been of great interest. Although the price of anthraquinone (AQ) is high and the chemical is not recovered, only small quantities are required, and the benefits outweigh the costs sufficiently that a number of mills around the world now routinely add AQ to the kraft pulpwood digester.

Sulfite Process. The sulfite process uses a cooking liquor of sulfurous acid and a salt of the acid. Although calcium was the most widely used base at one time, it has been supplanted by sodium, magnesium, and ammonia. Lignin will react with the bisulfite ion (HSO_3^-) under acidic conditions to form lignosulfonates that are soluble in water. For many years this was the preferred process because it produced pulps of light color that could easily be bleached, it used cheap chemicals in fairly limited amounts so that no recovery was necessary, and it was a relatively simple process to operate.

Although the production of sulfite pulp has remained relatively constant for the last 30 years, the rapid growth of kraft pulping has reduced sulfite's share to less than 10 percent of the chemical pulp produced. There are several reasons for this, but the primary ones are the inability to cook resinous woods such as pine, problems in producing strong pulps from hardwoods, and of the greatest importance, the lack of a cheap and simple recovery system to reduce water pollution problems. However, this process produces pulps with special qualities such as high alpha-cellulose grades for rayon, so it will continue to be used.

Initially calcium was the preferred base because it was cheap and convenient to use. However, no recovery system is available for this base, so most calcium-base mills either have ceased operation or have converted to sodium, magnesium, or ammonia, for which recovery systems are available.

Regardless of the base used, the initial step is the burning of sulfur to produce sulfur dioxide (SO_2). The air supply to the burner must be carefully controlled, as too much air will enhance the formation of sulfur trioxide (SO_3) and subsequent production of sulfuric acid (H_2SO_4), which is very undesirable. The gas also must be cooled quickly from 1000°C, leaving the burner at below 400°C, to minimize formation of SO_3. After cooling to 20 to 30°C, the SO_2 gas must be absorbed in water and reacted with the proper base to form the cooking liquor.

For calcium-base liquor, the gas is passed through towers packed with limestone with water flowing down through the tower. Because of the limited solubility of calcium bisulfite [$Ca(HSO_3)_2$], the pH of the liquor is very low (about 2), and free sulfurous acid is present. This usually is called the acid sulfite process. As mentioned before, calcium-base mills have essentially disappeared in the United States.

The so-called soluble bases now are used, with each having certain advantages. Because solutions of sodium, magnesium, and ammonium bisulfite are all soluble at pH 4.5, the current practice is to pulp at the higher pH, which is usually called bisulfite pulping. Extremely long cooking times (7–10 hours) are necessary with acid sulfite, whereas 4 to 5 hours is sufficient with bisulfite.

Sodium base is the easiest to prepare (Na_2CO_3 or NaOH usually is used as the makeup chemical) and gives the highest-quality pulp; however, recovery processes, though available, are complicated and expensive. Magnesium base [from $Mg(OH)_2$] is somewhat more difficult to handle, but recovery systems are available, and the majority of the sulfite pulp now is produced from this base. Ammonium base (from NH_4OH) was used in the past; the ammonia cannot be recovered, but the liquor can be evaporated and burned without leaving any solid residue, thus reducing water pollution. As long as aqueous ammonia remains low in price, this process will be attractive because the SO_2 can be recovered from the waste gases by passing them through a wet scrubber flooded with fresh ammonium hydroxide. The various sulfite-based processes are summarized in Fig. 7.14.

Batch digesters usually are used in the sulfite process. Cooking temperatures are lower (140–150°C), and times are longer than in the kraft process, with pulp yields about the same as in the kraft process. Spruce and fir are the preferred species for cooking by the sulfite process because they produce relatively strong, light-colored pulps. About 20 percent of newsprint consists of this type of pulp that has not been bleached. Thus the sulfite industry is concentrated in Canada, the northern United States, and the Pacific Coast, where the supplies of spruce and fir are greatest and the largest quantities of newsprint are produced.

A large amount of research has been done on developing products from the waste sulfite liquor, and some success has been achieved. Vanillin, alcohol, and torula yeast can be

	Acid Sulphite	Bisulfite	Neutral Sulfite Semichemical
pH	1.5	4 - 5	8 - 9
Chemicals	H_2SO_3, $NaHSO_3$	$NaHSO_3$	Na_2SO_3, Na_2CO_3
Base	Ca, Na, Mg, NH_4	Na, Mg, NH_4	Na, NH_4
Rate of Cooking (Given temp.)	——— Decreasing ———→		
Temperature	140°C	170°C	170 - 180°C
Brightness	— Slight increase →		— Decrease →
Strength Characteristics (Given yield)	——— Increasing ———→		
Species	Nonresinous	Hardwood & Softwood	Hardwood
Equipment Corrosion	——— Decreasing ———→		

Fig. 7.14. Summary of sulfite pulping processes.

produced as by-products, and the lignosulfonates are used as viscosity modifiers in drilling muds and for similar purposes. However, the majority of waste liquor is burned to recover the cooking chemicals and the heat values.

Semichemical Pulping. Various combinations of chemical and mechanical treatments have been used to produce pulps with specific properties. Mild chemical treatments to give partial delignification and softening are followed by mechanical means to complete fiber separation.

The neutral sulfite semichemical (NSSC) process is one in which wood chips, usually from hardwoods, are cooked with Na_2SO_3 liquor buffered with either $NaHCO_3$, Na_2CO_3, or NaOH to maintain a slightly alkaline pH during the cook. Unbleached pulp from hardwoods cooked to a yield of about 75 percent is widely used for the corrugating medium. Although bleachable pulps can be produced by this process, they require large quantities of bleaching chemicals, and the waste liquors are difficult to recover. Currently many NSSC mills are located adjacent to kraft mills, and the liquors can be treated in the same furnace. Thus the waste liquor from the NSSC mill becomes the makeup chemical for the kraft mill, solving the waste problem. NSSC hardwood pulp is the premier pulp for the corrugating medium and cannot be matched by any other process.

Chemimechanical pulps usually are produced by soaking the chips in solutions of NaOH or Na_2SO_3, and then refining in disc refiners to produce a groundwood-type pulp. Chemical consumption is very low, and yields are usually 85 to 95 percent.

Solvent Pulping. The concept of using solvents to dissolve lignin was first explored by Peter Klason in 1893. In the 1930s, Kleinert developed and patented the first solvent (organosolv) pulping process based on 50 percent aqueous ethanol.[7] Until recently there was little incentive to pursue alternatives to the kraft process because energy and chemicals were reasonably cheap, there were few environmental regulations, and there was little interest in by-products. However, new, strict environmental regulations, rising energy and chemical costs, and the very large capital investments needed to construct new kraft mills have stimulated research and investment in alternate solvent pulping processes.

With organosolv pulping, wood chips are contacted with an aqueous solvent mixture and cooked (digested) for a period of time at elevated temperatures. Digestion pressures range from atmospheric to 500 psig. Cooking initially releases acetic and formic acids from ester functionalities in the wood, and these acids further promote hydrolysis of lignin and hemicelluloses to low molecular weight species. Catalysts such as mineral acids (HCl), organic acids (acetic, formic), sulfonic acids, and Lewis acids and bases ($AlCl_3$, $Fe_2(SiO_4)_3$, $Mg(SO_4)$, $CaCl_2$) can be employed to promote delignification. Cellulose pulp is filtered from the liquor, and the solvent is recovered, usually by distillation. Lignin becomes insoluble at this point and precipitates from the liquor, leaving an aqueous solution of primarily hemicellulosic sugars. Conditions for a variety of organosolv processes are compared in Table 7.4.[8]

Two processes that have reached the demonstration-plant scale are the Alcell and the MD-Organosolv processes, both of which are basic modifications on the original process patented by Kleinert.[7] In the Alcell process preheated chips (80°C) are packed in the digester using steam, and the steaming is continued to displace air from the chips. Preheated solvent that has been previously used as a wash liquor for two earlier batches is pumped in and rapidly brought up to pulping temperatures of 190 to 200°C, corresponding to an operational pressure of 500 psi. The liquor is continuously circulated in the digester during the pulping period. At the end of this period, the liquor in the digester is displaced by wash liquor that was used in the second washing stage of the previous batch. The displaced liquor from the digester flows to the lignin and sugar recovery system. The third-stage wash liquor is displaced by fresh liquor and flows into an intermediate

TABLE 7.4 Solvent Pulping Process Characteristics

Process Name Developer	*Solvent Used*	*Additional Reactants*	*Digestion Temperature*	*Digestion Time*	*Reference*
Acetic Acid (Herdle, Young)	90% acetic acid[a]	0.2% H_2SO_4	150°C	4 hr	(9)
Acetosolv (Nimz)	95% acetic acid	0.1% HCl	110°C	3–5 hr	
Ester (Young)	50–75% acetic acid[a]	Ethyl acetate[d]	170°C	1 hr	(10)
Formic Acid (Jordan)	80% formic acid	Unspecified organic catalyst	105°C	45 min	(11)
Peroxoic Acid (Poppins, Sundquist)	80–100% formic acid and hydrogen peroxide	None	70–80°C	60 min	
Hydrotropic Pulping (Springer)	2.0 M xylene-sulfonic acid[a]	None	100°C	60 min	(12)
Battelle-Geneva Process (Sachetto)	Aqueous phenol[b]	Acid catalyst	100°C	30–60 min	(13)
Sulfolane (Clemont)	50% sulfolane	None	175°C	2 hr	(14)
Acetone (DeHaas and Lang)	Aqueous acetone[b]	NH_3/Na_2S	160–190°C	1–2 hr	(15)
Glycol (Burkart, Quigley)	20–100% glycol	Mineral, salicylic, sulfonic acids	100–205°C	1–3 hr	
Phenol (Sweers)	20–50% phenol	HCl. sulfonic acids	80–205°C	1–4 hr	
Cresol (Sakakibara)	20–80% cresol	Cuprous oxide, acetic acid, AQ	160–190°C	1–4 hr	
Amine (Wallis)	25–90% mono- or triethanol amine	None, AQ	165–200°C	1–2 hr	
Kleinert Process	20–75% ethanol[a,c] usually 50%	Uncatalyzed or metal salt catalysts	160–195°C	30–60 min	(7, 16, 17)
Alcell (Pye)	50% aq. ethanol	Uncatalyzed	195°C	1–2 hr	
AEM (Paszner)	Aqueous methanol[b]	Alkali earth salt catalysts	195–210°C	25–45 min	(18)
MD-Organosolv (Edel)	Aqueous methanol	NaOH	170–195°C	45 min	(19)
ASAM (Patt)	30–50% aq. methanol	NaOH, Na_2SO_3, and AQ (all)	180°C	2–3 hr	

[a]Other compound is water. [b]Concentration not reported. [c]*n*-Butanol also has been employed. [d]A three-component (ethyl acetate/acetic acid/water) pulping process.

storage tank for use in the second stage. The second-stage wash liquor is drained into another storage tank for use in the digester.

At this point, the digester contains soaked, delignified chips and alcohol–water vapor at pulping temperature and pressure. It is now depressurized, and the departing vapor is condensed for reuse as fresh pulping liquor. Finally, the alcohol remaining in the digester is driven off by steaming. The pulp is diluted with water and pumped out of the digester for cleaning and bleaching treatments. The first-stage spent liquor entering the by-product recovery area is first flashed and then diluted with process water to precipitate the dissolved lignin. After settling, the solid lignin is separated by centrifugation, washed, and dried. The filtrate enters a distillation tower, where alcohols and some acetic acid and furfural are recovered. Finally, the remaining aqueous liquor is further evaporated to a sugar syrup.[20]

Currently a demonstration plant is producing 15 metric tons of organosolv pulp a day in New Brunswick, Ontario. A comparison of the strength properties of Alcell and kraft pulps is given in Table 7.5. The process as described above is only suitable for hardwoods.[21]

The principles of the MD-Organosolv process, developed in Germany, are illustrated in Fig. 7.15. The process consists of first impregnating softwood chips with 50 percent aqueous methanol before they enter the

TABLE 7.5 Comparison of Properties of Allcell and Kraft Hardwood Pulps*

Property	*Alcell Pulp*	*Commercial Kraft Pulp*
Tensile (km)	7.47	7.40
Tear ($mN \cdot m^2/g$)	7.20	6.75
Burst ($kPa \cdot m^2/g$)	5.08	5.18
Brightness (ISO)	88.7	89.6

*Pulps 50% maple, 35% birch, 15% poplar; beaten to 400 Canadian Standard Freeness.

Source: McCready, M. (Ed.), *Paper Age* (Mar. 1991).

first-stage continuous reactor. The first pulping stage is operated under 40-bar pressure at 195°C and removes approximately 20 percent of the lignin and a major part of the hemicelluloses from the chips. The chips then are transported hydraulically to the second-stage digester where alkali is charged at 15 to 20 percent based on wood, and the methanol concentration is reduced to about 30 percent. The second stage is operated at 170°C, and the combined residence time in both reactors is only 45 minutes. The strength properties of the pulps produced are only slightly lower than those of corresponding kraft pulps. The recovery of organics and NaOH from the second-stage liquor is performed in a novel manner. After methanol evaporation, the liquor enters an electrolytic cell that not only separates NaOH but also precipitates lignin in a filterable form. The 5 ton/day demonstration plant will be scaled up to an 85 ton/day installation to supplement kraft pulp demands.[20]

Screening and Cleaning of Wood Pulp

The desired pulp fibers are usually between 1 and 3 mm in length with a diameter about one-hundredth as large. Any bundles of fibers or other impurities would show up as defects in the finished paper and must be screened out. Wood knots usually are difficult to pulp and must be removed.

Screening is usually a two-stage process with the coarse material being removed by screens with relatively large perforations (1/4 to 3/8 in.). Additional fine screening is done with screens using very small (0.008 to 0.014 in.) slots to ensure removal of oversized impurities. Screen size openings will depend on the species of wood being processed and the desired quality of the end product. Because of the tendency of the fibers to agglomerate when suspended in water, it is customary to screen at very low solids (consistencies) of about 0.5 percent fiber and 99.5 percent water.

To meet the ever increasing demands for cleaner pulps, centrifugal cyclone cleaners have come into almost universal use. The screened pulp is pumped through these units at low consistencies and high velocities. The fiber slurry enters the cone tangentially at the top, and a free vortex is formed with the velocity of the flow greatly increased as the diameter of the conical section is reduced. Heavier particles of sand, scale, or other dirt are forced to the outside of the cleaner and are discharged from the bottom tip through a small orifice. Because of the velocity gradients existing in the cone, the longer fibers (75–95%) are carried into the ascending center column and are discharged through the larger accept nozzle at the top. In a properly designed and operated unit, a shape separation also is made so that round particles, even though of the same specific gravity as the good fibers, will be discharged as rejects through the bottom orifice. In this way, small pieces of bark also are removed. To reduce the quantity of rejects to an acceptable level, they in turn are processed through a second, a third, or even a fourth stage of cleaners, thus holding the final loss of pulp to about 1/4 to 1 percent of the feed, depending upon quality demands and the dirt level of the incoming pulp.

Bleaching of Wood Pulp

The color of unbleached pulp ranges from cream or tan for the sulfite process to dark brown for the kraft process. Although about 75 to 90 percent of the lignin has been removed by the pulping process, the remainder, along with other colored degradation products, must be removed by bleaching.

Although it is possible to improve the brightness (whiteness) of the pulp in one stage,

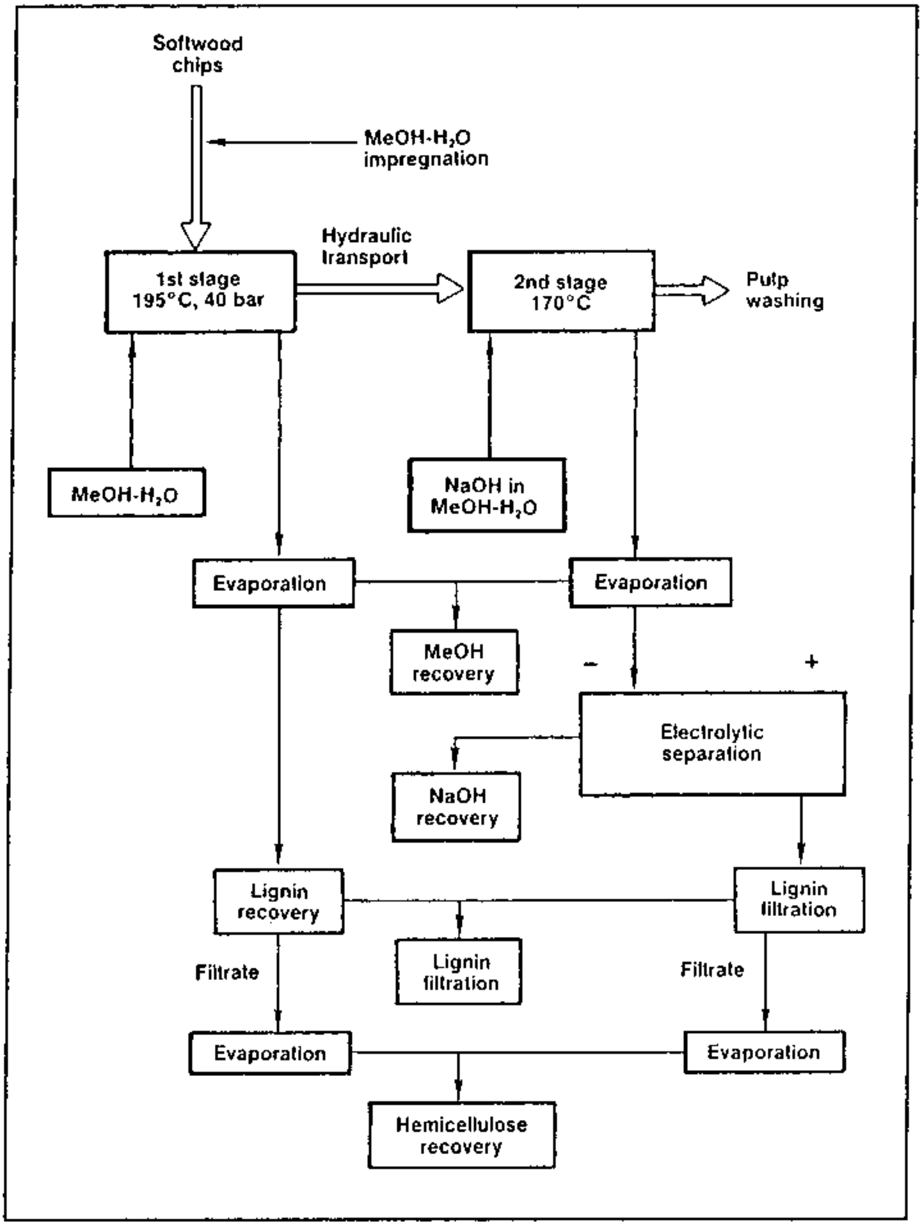


Fig. 7.15. lowsheet of MD-Organosolv pulping system. (*From Aziz, A., and K. V. Sarkanen,* Tappi **72**, *No. 3, 169–175 (1989); with permission of Tappi, Atlanta, GA.*)

the economical achievement of high brightness requires the use of several stages. Current practice uses combinations of chlorination with elemental chlorine (C), alkaline extraction with sodium hydroxide (E), and various oxidative stages using sodium or calcium hypochlorite (H), chlorine dioxide (D), or hydrogen peroxide (P). The pulp is washed between each stage to remove solubilized impurities. Many combinations are possible, and each mill selects the sequence that fits its requirements the best. The sequences most commonly utilized are:

CEH	CED
CEHD	CEDED
CEHDP	CEHDED

TABLE 7.6 Typical Conditions for Bleaching Kraft Pulp

Stage	*% Chemical on Pulp*	*Time (min)*	*Temperature (°F)*
Chlorination	5–6	30	70
Extraction	2½–3	60	140
Hypochlorite	1–2	90	105
Chlorine dioxide	½–1	240	160

The greater the number of stages, the higher the quality of the final pulp but at increased cost. Sulfite pulps are much easier to bleach and usually use only the three- or four-stage sequences, whereas kraft pulps require additional stages. Typical conditions for bleaching a kraft pulp are given in Table 7.6.

Chlorine and caustic are purchased, but chlorine dioxide must be generated at the site by using sodium chlorate as the basic chemical. Effluents from bleach plants are a source of great concern in regard to pollution. Large quantities of water are discharged (typically 10,000–20,000 gal/ton of pulp) that are high in color, especially the water coming from the chlorination and extraction stages.

New developments involve the replacement of the chlorination and extraction stages with a single stage involving gaseous oxygen and sodium hydroxide. The pulp is dewatered to about 15 to 25 percent solids, treated with about 4 to 6 percent NaOH, and passed through a reactor in a fluffed condition using oxygen gas at about 150 psi. The pulp consumes about 1 to 2 percent oxygen in about 15 minutes and leaves in a semibleached condition. After washing, the use of conventional chlorine dioxide stages will produce the desired level of whiteness. The advantage of this process is that the effluent contains no chlorides and can be used as process water in the pulp mill. Any sodium and organics in the effluent then will enter the kraft recovery cycle and serve as makeup, thus reducing the pollution load.

These bleaching sequences are designed to remove lignin, yielding a highly purified fiber consisting only of carbohydrate material. For producing high-yield pulps such as groundwood, where all of the lignin is retained in the pulp, it is not possible to use these systems. However, extremely high brightness is not required in this case; thus, some improvement is attained by using one stage with either peroxide or hydrosulfite (dithionite). No yield loss is encountered as the action of both of these is merely to decolorize the pulp rather than to remove any impurities. Usually about 0.5 percent of either of these chemicals will give a noticeable increase in brightness, and they are widely used to upgrade the quality of groundwood.

Biotechnology—Biopulping and Biobleaching

The pulping of wood is at present based on either mechanical or chemical methods or combinations thereof, as previously described in this chapter. The interfiber lignin bond is broken down by the mechanical and chemical treatments to free the cellulose fibers for papermaking. In the forest, white rot fungi perform a similar task on wood left behind. The enzymes of the fungi do the work of lignin degradation.

It should be possible to isolate these specific enzymes from the fungus for use in biological pulping or biopulping. Indeed, researchers at several laboratories are attempting to isolate lignin-degrading enzymes (lignases) from the white rot fungus *Phanerochaete chrysoporium.* They are quick to point out, however, that there probably is a lignase complex, in which several enzymes work together to degrade lignin. Once specific enzymes are isolated, work can commence on producing the enzymes in greater quantities through genetic engineering. Another drawback is the slow rate of reaction.

The initial applications of lignases would be to degrade the lignin partially before mechanical treatment so that the process would require less energy, and the pulp would have more strength after this biomechanical pulping. Biobleaching also would be possible for brightening or whitening pulp fibers, in lieu of the toxic chlorine compounds utilized at present by the industry. A particularly exciting application would be to use these types of enzymes for removal of lignin pollutants from waste effluents. Biotechnology should lead to safer and cleaner methods for pulping and bleaching.

Recycling

Worldwide, approximately 32 percent of wastepaper (73 million tons) is recycled. However, the rate of recycling varies considerably between countries, as shown in Fig. 7.16. The United States is a major exporter of wastepaper—over 4 million metric tons in 1990. The majority of the wastepaper exported goes to "fiber-poor" countries that have much less virgin fiber than does the United States and therefore recycle much greater quantities of paper.[5]

A variety of problems are associated with paper recycling, such as collection, distribution, and wild cyclic swings in the market. However, with landfill sites now at a premium and paper representing about 40 percent of municipal solid waste, it makes good sense in the long run to promote paper recycling, which reduces landfill needs and the consumption of virgin timber. The U.S. paper industry has set the goal of a 40 percent wastepaper collection rate by the year 1995. This means that large volumes of wastepaper will be available for reuse in the future.

There are a wide range of different grades of wastepaper available, depending on the source and the extent of separation. As the name implies, wastepaper designated as "direct pulp substitutes" is utilized with little treatment before reslushing in a hydrapulper. The direct pulp substitutes are the highest grade of wastepaper.

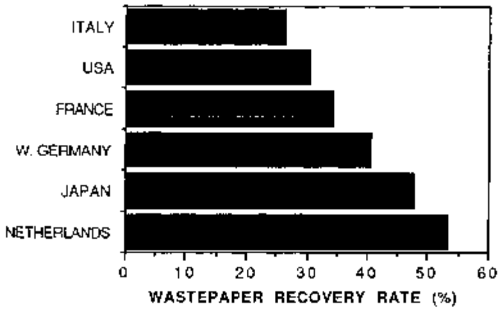


Fig. 7.16. Comparison of paper recycling in selected countries.

The majority of recycled paper (about 75%) is used with no attempt to remove inks, dyes, or pigments from the paper. The resultant pulp is of rather poor color and quality, and is used primarily as filler stock in paperboard. The bulk grades are the largest-volume wastepaper source.

Deinked grades of wastepaper require special techniques and equipment to remove inks, coatings, adhesives, and so on. The deinking process is complicated and time-consuming; depending on the quality of deinked pulp required, the process may involve a number of combinations of washing, flotation, dispersion, screening, and use of cyclone cleaners. The newer noncontact inks present special removal problems, as do wet-strength agents, adhesives, and the so-called stickies. Stickies are made from hot-melt adhesives (vinyl acetate polymers and copolymers), pressure-sensitive adhesives (styrene-butadiene), and lattices (natural and synthetic rubber). Tackifiers and waxes also are usually included in these adhesive formulations. A variety of additives are used to help remove stickies and other contaminants from wastepaper, including solvents, nonionic and cationic surfactants, zirconium compounds (to reduce tackiness), and talc. Of course, all of the additional steps and additives add to the expense of recycling. There is also the problem of waste disposal from the deinking process, which must be properly handled. Table 7.7 shows the projected consumption of wastepaper according to paper grade for 1995.[22]

Stock Preparation

Stock preparation in a paper mill includes all intermediate operations between preparation of the pulp and the final papermaking process. It can be subdivided into (1) preparation of the "furnish" and (2) "beating" or "refining." Furnish is the name for the water slurry of

TABLE 7.7 Projected Consumption of Wastepaper in Paper and Paperboard Manufacture for 1995

	Total Production	*Wastepaper (%)*
Production	93,250	29.9
Paper	47.450	17.1
Newsprint	7,400	36.5
Printing and writing	28,800	7.0
Packaging	4,850	5.2
Tissue	6,400	49.4
Paperboard	44,200	43.0
Unbleached kraft	22,000	20.0
Bleached kraft	48,000	0
Semichemical	6,400	40.6
Recycled	11,000	109.1
Construction paper and board	1,600	50.0

fiber and other chemicals that goes to the paper machine. Beating or refining refers to the mechanical treatment given to the furnish to develop the strength properties of the pulp and impart the proper characteristics to the finished paper.

Cellulosic fibers are unique in that, when suspended in water, they will bond to each other very strongly as the water is removed by filtration and drying, with no need for an additional adhesive. This is so because of the large number of hydrogen bonds which form between the surfaces of fibers that are in close contact as the water is removed. This bonding is reversible and accounts for the well-known fact that paper loses most of its strength when wet. If paper is suspended in water and agitated, it will separate into the individual fibers, a behavior that allows the easy reuse of wastepaper or the processing-waste from the paper mill.

In order to enhance the bonding capability of the fibers, it is necessary to mechanically beat or refine them in equipment such as beaters, jordans, or disc refiners. This treatment of the pulp slurry at about 3 to 6 percent consistency is done by passing the pulp between the two rotating surfaces of the refiner. These surfaces contain metal bars and operate at very close clearances. As the fibers pass between the bars, they are made more flexible, and a larger surface for bonding is developed by the mechanical action.

This refining brings about fundamental changes in the pulp fibers and increases the degree of interfiber bonding in the final sheet of paper. Thus the final properties of the paper can be significantly changed by varying the degree and type of refining. As additional refining is performed, properties such as tensile strength, fold, and density are increased while tear resistance, opacity, thickness, and dimensional stability are decreased. Thus, the proper refining conditions must be selected to bring out the desired properties without detracting too much from other properties.

The furnish of a paper machine varies widely, depending on the grade of paper being made. Newsprint usually consists of about 80 percent groundwood and 20 percent chemical fiber (sulfite or semibleached kraft). Bag papers and linerboard are usually 100 percent unbleached softwood kraft. Printing papers are made from bleached pulps and contain both hardwoods and softwoods. By selecting the proper pulps and refining conditions, a wide variety of paper qualities can be achieved.

The paper industry is a large user of chemicals because relatively small quantities of additives can materially change the properties of paper. The use of 1 to 2 percent rosin size and 2 to 3 percent alum [$Al_2(SO_4)_3$] will greatly increase the resistance of paper to penetration by water or ink. Pigments such as kaolin clay, calcium carbonate, and titanium dioxide are added in amounts up to 15 percent to increase opacity and give a better printing surface. Organic dyes and colored pigments are added to produce the highly colored papers used for business and printing papers. Other additives such as wet-strength resins, retention aids, and starch can be used to give particular properties that are needed. Thus, in order to produce the wide variety of grades of paper now available, the papermaker selects the proper pulps, refining conditions, and additives, and then combines the pulp and additives before sending them on to the paper machine for the final step in the process.

Papermaking Process

Some paper mills are not integrated with pulp mills, and it is necessary for these mills to use dried, baled pulp manufactured at a separate location. Many mills making limited quantities of highly specialized papers fall into this category, as it allows maximum flexibility in selecting the optimum pulps for a particular paper grade. However, the papermaking process is the same regardless of the source of pulp.

After the furnish has been prepared with the proper refining treatment and additives, it is stored in the machine chest and then fed continuously into the paper machine system. A refiner or jordan is placed in this line to give the paper machine operators the opportunity to make small adjustments in the quality of the furnish as needed to give the desired paper properties. Screens and centrifugal cleaners also are included to ensure a high-quality paper.

The papermaking process is essentially a system whereby the pulp is diluted to a very low consistency (about 0.5%) and continuously formed into a sheet of paper at high speeds, and then the water is removed by filtration, pressing, and drying. The basic units of the fourdrinier paper machine are diagrammed in Fig. 7.17, a picture is shown in Fig. 7.18.

The section of the paper machine where the paper is formed is referred to as the "wet end." The fourdrinier machine is characterized by a headbox that allows the diluted stock to flow through an orifice (slice) onto the flat moving wire. This is actually an endless wire belt that returns on the underside of the machine, thus allowing the process to proceed continuously. Because a low headbox consistency (about 0.5%) is necessary for good formation, the volumes of water handled are very large (about 10,000 gal/min for a machine producing 300 tons/day). Much of the water is removed through the wire by the action of the table rolls and foils that support the wires in the forming area immediately following the headbox. At this point the stock consistency has been raised to about 2 percent,

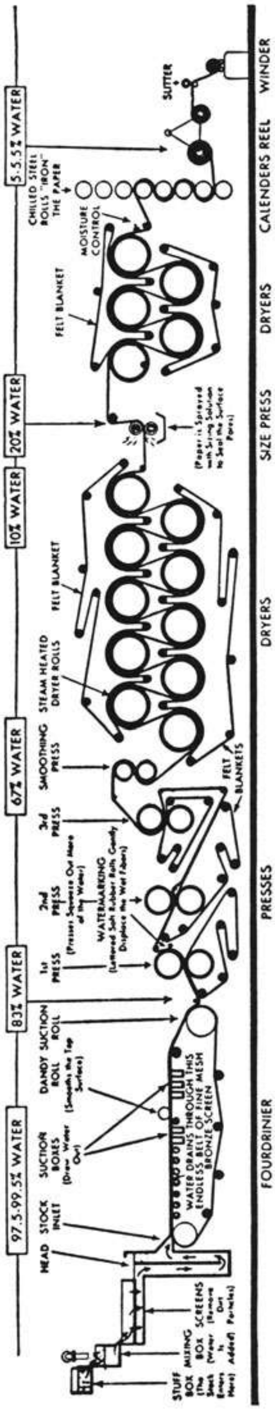


Fig. 7.17. Diagram of a fourdrinier paper machine. *(Courtesy Hammermill Paper Co.)*

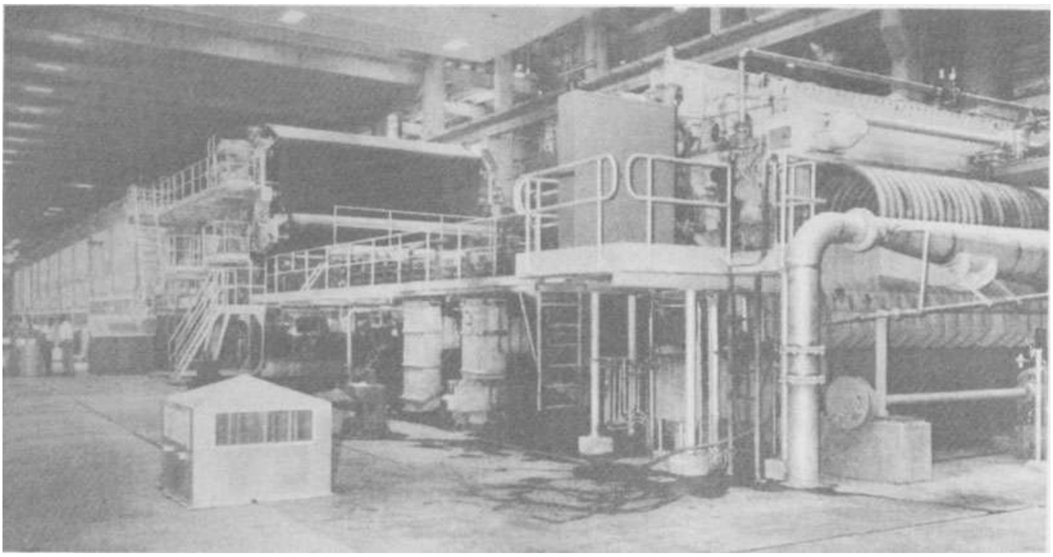


Fig. 7.18. Modern high-speed paper machine. (*Courtesy Beloit Corp.*)

and the stock no longer drains freely. By passing it over suction boxes operating at fairly high vacuum (6–8 in. Hg), the consistency is raised to about 15 to 20 percent. A dandy roll (covered with woven wire) rotating on top of the wet paper is used to improve the formation and can impact a watermark if it contains the proper pattern. The suction roll after the suction boxes has several functions: it removes additional water; it serves as the driving roll for the wire, and it serves as the point at which the paper separates from the wire and passes into the press section while the wire returns to pick up additional pulp at the headbox.

Modern fourdrinier machines are available up to a width of 360 inches and can operate at speeds up to 3000 ft/min. Newsprint machines are usually the widest and fastest, whereas those making heavier grades such as linerboard run somewhat more slowly. In the United States, there are several machines capable of producing over 1000 tons/day of linerboard. More specialized grades such as bond and printing papers are usually produced at a lower speed on narrower machines, and 150 to 250 tons/day would be considered a high output. Many specialized grades such as filter paper and tracing paper are produced on very small, slow machines producing only a few tons per day. Machines making tissue paper for sanitary purposes use modifications of the standard fourdrinier to produce tissue at speeds of up to 5000 ft/min. Because of the light weight of this paper, it is necessary to make many modifications in the equipment shown in Fig. 7.17.

Many new methods of forming a sheet of paper are being developed. The most common concept is to introduce the pulp slurry between two converging wires and remove the water from both sides. This is termed "twin-wire" forming, and many variations are now in operation. This technique has many advantages and may eventually replace the fourdrinier.

A second method of forming paper uses the cylinder machine. Actually these machines are used primarily to form the multi-ply board used in packaging such as cereal boxes. The cylinder wet end consists of one or more (up to eight) cylinder vats, each of which forms a separate wet web of fibers. Each vat contains a woven wire-covered cylinder rotating in the diluted pulp slurry. The liquid head on the outside of the cylinder is greater than that on

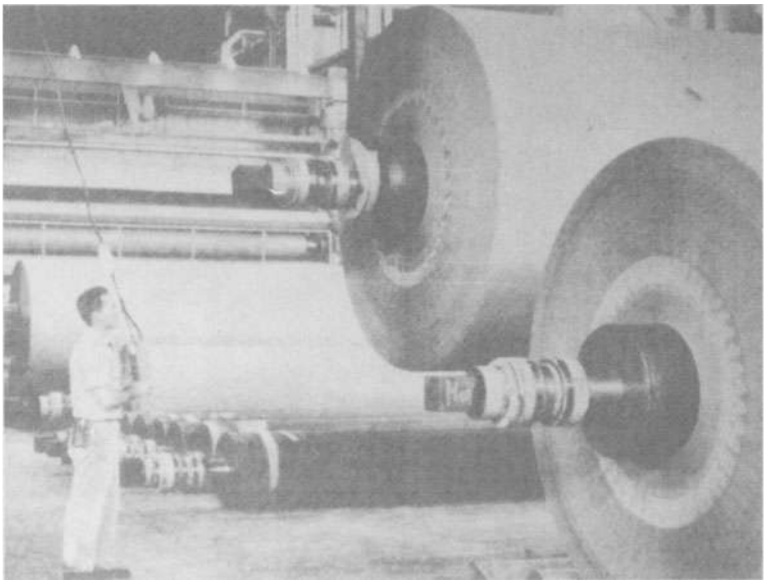


Fig. 7.19. Dry end of large fourdrinier paper machine. (*Courtesy St. Regis Paper Co.*)

the inside, resulting in a flow of water through the wire and out of the vat. The pulp mat that is formed on the face of the cylinder is removed by an endless woolen felt that moves in contact with the cylinder by means of a rubber roll riding on top of the felt. With machines having more than one cylinder, the same felt moves from one cylinder to the next, and the wet sheets from each cylinder are laminated to each other on the bottom side of the felt. Thus, very heavy papers or boards can be fabricated by multivat machines. Because each vat can be supplied with a different type of pulp, it is possible to make boards with a white surface of high-quality pulp and a center of low-cost pulp from waste newspaper or other cheap grades. Because of hydrodynamic problems, cylinder-machine speeds are limited to about 250 ft/min and widths of about 150 inches. However, because of the heavyweight board produced and the widespread use of cheap waste paper for most of the furnish, the cylinder machine is widely used. New forming units looking like miniature fourdrinier units (Ultra-former, Inverformer) have been developed and are rapidly replacing the old-fashioned cylinder vat because their speed is not so limited.

From the wet end of the machine, the wet sheet is conveyed by woolen felts through a series of roll-type presses for further water removal, increasing the consistency to about 35 percent. The sheet then is threaded through the dryer section, consisting of a long series of steam-heated cast iron cylinders that reduce the moisture content to approximately 5 percent, which is about the equilibrium moisture content for cellulosic fibers at 40 to 50 percent relative humidity. Tissue machines use one large dryer (called a Yankee dryer), ranging from 8 to 18 feet in diameter. Because of the light weight of the tissue paper, it can be dried at high speeds on a single dryer.

After drying, the paper is compacted and smoothed by passing through a calender stack consisting of a vertical row of highly polished cast iron rolls. Then the paper is wound into rolls on the reel, as shown in Fig. 7.19.

Finishing and Converting

The objectives in the final stage of the total papermaking system are to improve the paper surface, to reduce rolls and sheets in size, to modify paper for special properties, such as coat or emboss, to convert to finished products, such as bags and corrugated boxes, and to package for shipping.

Corrugated boxboard is made by gluing sheets of linerboard to each side of a fluted sheet of the corrugating medium. Papers for packing may be laminated to polyethylene film or aluminum foil, or coated with waxes and hot-melt resins. The printing and bag- and box-making industries depend on the production of many mills that produce the several hundred grades of paper used in the United States, and each user may require special paper characteristics to match its process.

The quality of many papers is improved by a surface treatment. A size press about two-thirds of the way along the dryer section can apply a solution of starch to improve surface bonding. Also, paper generally is coated to improve printing properties. A surface coating of a pigment (usually kaolin or china clay, calcium carbonate, or titanium dioxide) and an adhesive (such as starch, casein, and others) is applied to the partially dried web by brush, blade, spray, or other method, and dried during the papermaking (on-machine) operation or in a separate operation. The paper surface is brought to a high finish by passage through the calenders referred to above or through supercalenders. Supercalenders are stacks of alternate steel and densified fiber rolls that create a rubbing action on the sheet, imparting an extra-high gloss to the sheet surface.

Environmental Protection

The manufacture of pulp and paper is a chemical-process industry and produces air emissions, effluents, and solid and toxic wastes that are potential hazards. The paper industry uses large volumes of water as a fiber carrier and as a solvent. An increasing volume of water is being recycled, but makeup water still is required to cover losses. A bleached-pulp and paper mill may use 100 cubic meters (26,400 gallons) of fresh water per metric ton of product and 50,000 cubic meters (13.2 million gallons) daily for a plant producing 500 metric tons of products. In addition to this aqueous effluent that the mill must clean up, it must contend with polluted air and solid and toxic wastes. The nature of these emanations, their sources, and their treatments are summarized in Table 7.8. In this connection the paper industry generally has been in good compliance with governmental environmental regulations although at considerable nonreimbursed capital expense, which amounts to about 10 percent of the cost of the mill.

Using a revolving cylinder or other equipment (save-alls), in the 1930s mills recovered

TABLE 7.8 Summary of Pollution from Pulp and Paper Mill Operations

Type of Pollutant	*Mill Operation*	*Treatment*
Effluents		
Suspended solids (SS): fiber fragments, inerts, clay	Papermaking	Primary—clarification
Pulping residuals	Pulping	Secondary—biological treatment and clarification
Air emissions		
Total reduced sulfur (TRS)	Kraft liquor recovery	Oxidation, precipitation, scrubbing, incineration
Sulfur dioxide	Sulfite pulping	
Particulates	Steam generation	Precipitation, scrubbing
Solid wastes	Effluent treatment	Landfill, utilization, incineration
Toxic wastes: chlorinated compounds	Bleaching	Lime pretreatment, oxidation, biological

for reuse fibers and clay from the paper machine water (white water) system. In the 1970s, procedures for removal of the fibers and clay from the paper mill effluent were incorporated through settling or clarification or primary effluent treatment. About the same time, secondary effluent treatment (biochemical treatment) of the pulp mill effluent was necessary to remove pulping residuals. The purpose of this treatment is to reduce the biological oxygen demand (BOD) of the effluent, which, if untreated, reduces the oxygen content of the stream to a level incapable of supporting aquatic life. The most common method uses microorganisms that react with the wood sugars and other oxygen-consuming compounds in the spent liquors; this is called the activated-sludge method. The products of primary and secondary treatments are sludges, the handling of which is discussed later under solid wastes.

Two objectionable air emissions have characterized pulp mills for years: the sulfur dioxide of the sulfite pulping mill and the malodorous reduced sulfur compounds (TRS) (mercaptans and hydrogen sulfide) of the kraft mill. Still another less noxious air emission is the particulate matter from steam boilers. Coal-burning boilers also emit sulfur dioxide, as is well known. The treatments for the particulate emissions are shown in Table 7.8.

Solid wastes represent the ultimate in mill residues and include the accumulated refuse of the mill and the sludges from primary and secondary effluent treatment. There is difficulty in removing water from the secondary sludge; the primary and secondary sludges often are mixed to aid in water removal, which is important if the sludge is to be incinerated for disposal. The sludges from pulp and paper mills are handled mostly as landfill, and sometimes, if not toxic, they are spread for agricultural purposes.

Most mill solids are slightly toxic, predominantly from chlorination compounds in the wash waters from bleaching. This toxicity can be reduced with lime pretreatment and biological treatment. Toxicity has been the main concern of governmental regulating bodies in recent years.

BOARD AND STRUCTURAL MATERIALS

Board, sheets, panels, and other structural materials are manufactured from wood fibers and various other vegetable fibers, from wood particles, and from paper. The industries making these products are not generally classified as chemical industries; nevertheless, they are closely related to the chemical industry. Fiberboard manufacture is similar to paper-making; particleboards and paper laminates involve the use of synthetic resins and, therefore, chemical technology.

Fiberboard

Fiberboard is the name for rigid or semirigid sheet materials of widely varying densities and thicknesses manufactured from wood or other vegetable fibers. The board is formed by the felting of the fibers from a water slurry or an air suspension to produce a mat. Bonding agents may be incorporated to increase the strength, and other materials may be added to give special properties, such as resistance to moisture, fire, or decay.

Fiberboards are manufactured primarily for panels, insulation, and cover materials in buildings and other structures where flat sheets of moderate strength and/or insulating capacity are required. They also are used as components in doors, cupboards, cabinets, furniture, and millwork.

Classification of fiberboards is best done on the basis of density, as there is a great deal of overlap when classifying by use only. Table 7.9 shows the density classification of fiberboards as well as some of their major uses. Fiberboard factories equalize the mat of loose fibers between screens and rollers, whereas hardboard is press-bonded between hot plates to make it dense and strong. The dividing line between the two types of panels lies at a density of 0.5 g/cm^3. Both are manufactured for many specific uses, and they vary accordingly.

The production of fiberboards goes back to 1898 when the first plant was built in Great Britain. However, large-scale production, mainly of insulation board, developed in the

TABLE 7.9 Classification and Uses of Fiberboards*

Fiberboards	*Density Classification*		*Major Uses*
	g/cm³	*lb/cu ft*	
Noncompressed (insulation board) semirigid insulation	0.02–0.15	1.25– 9.5	Heat insulation as blankets and batts; industrial cushioning
Rigid insulation board (includes wallboard and softboard)	0.15–0.40	9.5 –25.0	Heat and sound insulation as sheathing, interior panelling, base for plaster or siding, thick laminated sheets for structural decking, cores for doors and partitions, acoustical ceilings
Compressed Intermediate or medium density fiberboard (includes laminated paperboards and homogeneous boards)	0.40–0.80	25–50	Structural use and heat insulation as sheathing base for plaster and siding, interior panelling, containers, underflooring
Hardboard	0.80–1.20	50–75	Panelling, counter tops, components in doors, cabinets, cupboards, furniture, containers, and millwork, concrete forms, flooring
Densified hardboard (superhardboard)	1.20–1.45	75–90	Electrical instrument panels, templets, jigs, die stock

*From information in Fiberboard and Particleboard," Food and Agriculture Organization of the United Nations, Rome, 1958.

United States between the two world wars. The United States is still the largest-producing country and accounts for about one-third of the world output. There has been a much more rapid increase in the production of compressed fiberboards (hardboards) than noncompressed fiberboards (insulation board) during recent years. In 1950 consumption of hardboard was, by weight, roughly 50 percent of insulation board; by 1976 the percentages were almost exactly reversed. Although the total use of insulation board has increased over the past 25 years by 73 percent, per capita consumption has remained constant or even declined, but for hardboard it has doubled. These figures indicate the faster growth rate of the hardboard industry, brought about because favorable prices have stimulated substitution of hardboard for plywood and lumber in construction and furniture. About 85 percent of all insulation board is used in construction, but because it is a nonstructural material, it is not readily substituted for either plywood or hardboard.[23]

Wood is the principal raw material for the manufacture of fiberboards. The species used are numerous, including both softwoods and hardwoods, and vary from region to region. The wood may come from the harvesting of commercial timber, from species not commonly used for lumber or pulp, or from cull timber, logging and forest management residues, and industrial wood residues. Other fiber raw materials for fiberboard manufacture are bagasse (sugar cane residue after sugar extraction) and waste paper. Only minor amounts of other plant fibers are used.

Wood handling and preparation for fiberboard manufacture is much the same as described for pulp and paper. Wood is debarked and chipped with the same type of equipment. If the chips are to be extracted first for rosin or tannin, then cylinder or drum-type chippers may be used instead of disc chippers.

Fibers for fiberboard are coarser and less refined chemically than those used for paper. Processes are used that bring about fiber separation with a minimum loss of chemical components and a maximum yield. The pulping processes used are generally the following: mechanical, thermomechanical, semichemical, and explosion methods. The pulping processes are essentially the same as that described for making paper pulp.

A unique explosion process for defibering wood was developed by W. H. Mason. Wood chips, about $\frac{3}{4}$ inch long, prepared in conventional chippers and screened, are subjected to high pressure, in a cylinder, commonly called a gun, about 2 × 6 feet in size, and ejected through a quick-opening valve. The elevated temperature softens the chips, and, upon ejection, they explode into a fluffy mass of fibers and fiber bundles. The process involves thermal plasticization of the lignin, partial hydrolysis, and disintegration by the sudden expansion of the steam within the chip.

About 260 lb of wood chips are fed into the cylinder and steamed to 600 psi for 30 to 60 seconds. Then the pressure is quickly raised to 1000 psi (about 285°C) and held only about 5 seconds before sudden release of the charge into a cyclone. The time of treatment at this high pressure and temperature is critical and depends upon the species of wood, chip size, moisture content, and quality of product desired. The steam is condensed in the cyclone, and the exploded fiber falls into a stock chest where it is mixed with water and pumped through washers, refiners, and screens.

The high temperature to which the chips have been subjected causes appreciable hydrolysis of the hemicelluloses, resulting in a somewhat lower yield of pulp than is obtained by mechanical or thermomechanical pulping. The hydrolysis results in a final board product with an enriched lignin content, about 38 percent compared to about 26 percent in the original softwood. The lignin content of the pulp can be varied by controlling the steaming process.

Board Formation. Pulp prepared by any of the above processes may be used for making insulation board. Mechanical (groundwood) pulp was the first type of pulp used in large-scale production of insulation boards, and is still being used in many plants. Pulps from other sources, such as disc mills, may be admixed with it. Groundwood pulp is not considered satisfactory for hardboard, and most hardboard is made from pulp prepared by the explosion process or by defibering with disc refiners.

Board making is basically similar to papermaking and involves refining, screening, mixing of additives, sheet forming, and drying operations. Pressing also is required for hardboards. The pulp is refined and screened prior to sheet formation.

Sizing agents in amounts up to one percent of the fiber are added to the pulp in mixing chests. Paraffin wax emulsion is commonly used for all types of boards. For insulation boards, rosin, cumarone resin, and asphalt also are used. Often a mixture of rosin and paraffin emulsion is used, with 10 to 25 percent rosin in the mixture. For hardboards, paraffin wax is the most common sizing agent although tall oil derivatives and phenol-formaldehyde resins also are used. The sizing agent is precipitated on the fibers by alum, with careful control of pH; the latter may be between 4.0 and 6.5, according to the conditions.

The strength properties of a fiberboard depend mainly upon the felting characteristics of the individual fibers and to a lesser degree upon their interfiber bonding. The felting or forming process usually is done from a water suspension of the fiber at a consistency of around one percent. This is the wet-felting process. An air-felting or dry-forming process is used in a few U.S. plants for hardboard manufacture.

The wet-felting process generally is carried out in a manner similar to papermaking, that is, in a continuous operation on a fourdrinier machine or on a cylinder machine. The machines move more slowly than in the case of papermaking (5–45 ft/min on the fourdrinier), and a coarser mesh wire is employed. In the cylinder-machine method, a single large vacuum cylinder, 8 to 14 feet in diameter, or two cylinders counter-rotating and forming a two-ply sheet are most commonly used. Further water removal is effected by section boxes and press rolls. The wet sheet is cut to length and conveyed on rollers from the press sections to a tunnel-type dryer. Then the dried sheets are cut into desired sizes.

A third type of wet-felting is a discontinuous method, known as the deckle-box method. The deckle box consists of a bottomless frame that can be raised or lowered onto a wire screen. A measured quantity of stock sufficient to form one sheet is pumped into the deckle box, and vacuum is applied to the lower side of the screen. After most of the water has drained off, pressure is applied from the top to express more water and compact the sheet, reducing its thickness. The deckleframe then is raised and the sheet conveyed to the dryers.

For the recent air-felting process, defibering usually is done in disc mills with control of the moisture content to give the minimum amount possible, consistent with good defibering conditions. Additional moisture may be removed by preheating the air that conveys the fiber from the refiners to the cyclone. The fiber may be further dried in a tunnel or other type of dryer. Fines are removed by either air classification or screens after the dryer. Wax for sizing is introduced either with the chips or added as a spray before or after passing the disc mills (about 2.5% of the weight of the fiber). Sometimes 0.5 to 5 percent of phenolic resin is added, depending upon the quality of board desired. The fiber-blend is fed to a moving screen by a metering unit through a combined air and mechanical action. The fibers felt as they fall on the screen, and the fiber mat thus formed is precompressed between belts and/or rollers. If the board is to be wet-pressed, water is added by spraying.

After the felting or sheet-forming operation, the subsequent operations differ for insulation board and hardboard (see Fig. 7.20). For insulation board, the sheets are dried without further compression, whereas for hardboard, the sheets are either pressed and dried simultaneously (wet-pressing) or are first dried and then pressed (dry-pressing). Air-felted sheets are pressed directly after forming.

Drying and Pressing. The wet-felted sheets for insulation board or for dry-pressed hardboard, containing 50 to 80 percent water, may be dried by any of three methods: (1) tunnel kilns using racks or carts to support the sheets, (2) steam-platen dryers, and (3) continuous roller dryers of single or multideck arrangement. Most widely used is the continuous roller-type multideck dryer, which has an average length of 150 to 300 feet but may be more than 600 feet long. An average dryer will have eight decks and be 12 feet wide.

The pressing conditions greatly affect the board properties. The conditions of time, temperature, pressure, and moisture content will depend upon the fiber in the board and the product desired. In wet pressing, a typical cycle has three phases and lasts from 6 to 15 minutes. The first is a short high-pressure stage (up to 710 psi) to remove most of the free water and bring the board to the desired

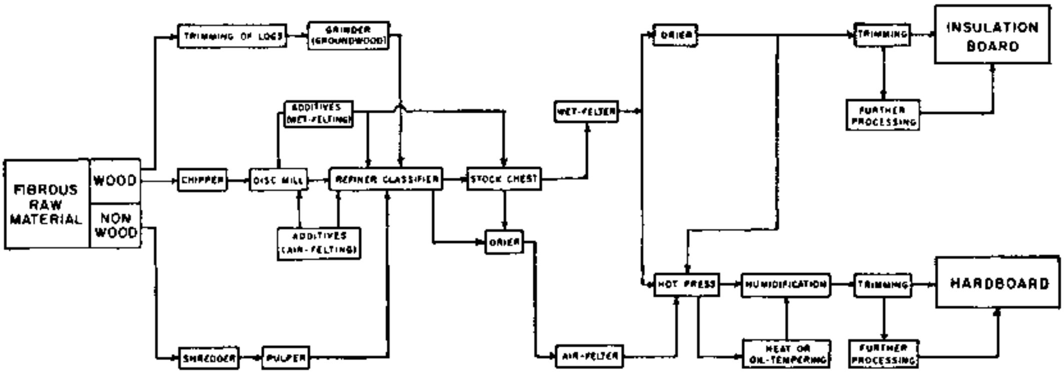


Fig. 7.20. Schematic outline for insulation board and hardboard manufacture. (*From "Fiberboard and Particleboard," Food and Agricultural Organization of the United Nations, Rome, 1958.*)

thickness; the second step serves to remove water vapor and requires most of the time; the third stage is a final short period at high pressure to effect a final "cure" or bonding by plastic flow of the lignin. To secure this fiber-to-fiber bond, a temperature of 185°C must be attained, and temperatures up to 210°C may be used to increase the production rate. In the dry-pressing process the cycles are shorter (1.5–3.5 min), and the temperatures and pressures usually are higher.

Conditioning. After the hardboard has been hot-pressed or has been heat-treated or oil-tempered, the moisture content is well below what will be attained at equilibrium with the atmosphere in normal use. Such very dry boards will change dimensions upon picking up moisture and may warp. It is important, therefore, to humidify the boards under controlled conditions before packaging. The desired equilibrium moisture content (EMC) reached will vary from 5 to 12 percent, depending upon the nature of the board and the general humidity conditions in the region of use.

Most humidifying is done in the chambers or tunnels, kept at 80 to 85 percent R.H. and 38 to 50°C. A lesser-used system of conditioning utilizes water spraying and dipping followed by standing to allow uniform absorption.

Special Treatments. Hardboards often are given a special treatment to improve their strength and resistance to moisture. The heat treatment method has come into wide use; the boards, which are kept apart to permit hot air circulation, are heated in chambers by either batch, continuous, or progressive systems. Typical heating conditions are 5 hours at 155 to 160°C. The heating increases the strength (except impact), sometimes as much as 25 percent, and the water resistance is improved. This operation may replace sizing wholly or in part. Some exothermic reaction takes place in the board, and the heat developed must be removed by the hot circulating air to prevent burning. Probably some chemical condensations occur in the wood fiber, producing an internal resin system, and there is the possibility of some crosslinking of large molecules.

Some hardboard is oil-tempered. A drying oil, such as linseed, tung, perilla, soya, or tall oil, or an alkyd resin, is impregnated into the board, by passing the hot-pressed board through a hot oil bath. About 4 to 8 percent of the oil is absorbed. The board then is heated in a kiln with circulating air at 160 to 170°C for 6 to 9 hours. This treatment hardens the oil as well as bringing about chemical reactions in the fiber, and results in greater strength and moisture resistance.

Various additives may be incorporated into insulation boards and hardboards, or they may be surface-treated to bring about resistance to decay, insects, and fire. Pentachlorophenol and copper pentachlorophenate are commonly used for preservative treatments. The sodium salt of pentachlorophenol is added before sizing and is precipitated onto the fiber along with the size by the alum. Special fire-retarding-paint coatings sometimes are used to give resistance to the spread of flame.

Particleboards

Although wood particleboard was patented in the United States as early as 1905, commercial development of the product usually is credited to either Germany or Czechoslovakia in 1941. Production was restricted by a shortage of gluing resins during most of World War II, but in 1945 the first U.S. plant began operation. Particleboard did not really begin to gain market acceptance until the 1960s. From 1964 to 1979 consumption increased at an average annual rate of 9.5 percent. In terms of total consumption of wood-based panels, however, particleboard held only about 15 percent of the market in 1984.[23]

Particleboards are composed of discrete particles of wood bonded together by a synthetic resin adhesive, most commonly urea-formaldehyde or phenol-formaldehyde. The material is consolidated and the resin cured under heat and pressure. The strength of the product depends mainly upon the adhesive and not upon fiber felting as in the case of fiberboards, although the size and shape of the particles influence strength properties. They may be fine slivers, coarse slivers, planar shavings, shreds, or flakes, and they are divided into two main groups: (1) hammer-mill-produced particles (slivers and splinters from solid wood residues, featherlike wisps to block-shaped pieces from planar shavings) and (2) cutter-type particles, sometimes termed "engineered" particles (flakes and shreds). The various steps in particleboard manufacture are illustrated in Fig. 7.21.

Hammer-milled particles usually vary appreciably in size. Dry raw material produces greater amounts of fines than green wood. Cutting machines (either cylinder-type or rotating-disc-type) give more uniform particles, with the length dimension in the direction of the grain of the wood. The thickness, size, and shape of particles influence the strength of the board. Boards made from sawdust have the lowest strength properties, hammer-milled particles give boards of intermediate strength, and solid wood, cut to flakes, gives boards of highest strength. The latter often are referred to as waferboards.

In another relatively new type of particleboard, the manufacturers align long strands of wood at the surface for increased strength in the direction of panel length. This oriented-strand board (OSB) and waferboard replaced a great deal of plywood sheathing in the early 1980s.

Particleboards may be made in a wide range of densities. Low-density or insulating types are a comparatively recent development in Central Europe, whereas the high-density-hardboard types are a U.S. development. Most particleboard production is in the middle-density range.

Particleboards most commonly are used as core stock for veneer in furniture and in doors, as interior panels for walls and ceilings, as subflooring, as sheathing and siding, and as components in interior millwork. The dense types are used in the same way as fiberboard hardboard, described above. Both dense particleboards and hardboards, after receiving a surface coating, may be printed with decorative designs.

Particleboard production has increased rapidly, both in the United States and worldwide, in recent years. Until recently the most significant limitation on the market for particleboard was the availability of inexpensive plywood. Now plywood is no longer inexpensive relative to particleboard, and the cost factor would seem to favor continued growth of the particleboard industry. However, the advent of waferboard and oriented-strand board has slowed this growth. These new entrants into the structural-panel market were first manufactured on a large scale in Canada, and much of the Canadian output was initially exported to the United States. Within the last decade, however, U.S. production capacity has increased from 9.8 million to 241 million square meters, and there is no indication that this rapid rate of growth will slow in the near future. It appears that waferboard and OSB and several new variants will become the major growth markets among

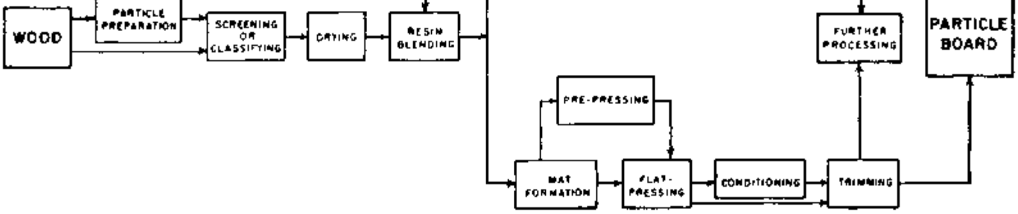


Fig. 7.21. Schematic outline for particleboard manufacture. (*From "Fiberboard and Particleboard," Food and Agricultural Organization of the United Nations, Rome, 1958.*)

structural panels, and probably will compete most directly with the more expensive softwood plywood.

Paper-Base Laminates

Paper-base laminates are panels or other laminated assemblies composed of many plies of resin-treated paper molded together under high temperatures and pressure to produce rigid structures that no longer have the characteristics of paper. These products are widely used in the electrical and machine industries for insulators, gears, pulleys, and a multitude of machine parts. They possess high impact strength and toughness, good electrical insulation, and high dimensional stability, and are not subject to corrosion; they also have a dampening effect on sound, eliminating rattling and drumming in steel cars and machinery. Furthermore, they easily can be manipulated into complex shapes and can be drilled, turned, and sawed. With these properties, these products are of great industrial value. They also are used in making trays, light flooring panels, table and counter tops, and many other products employing panels.

Paper-base laminates fall into four major classes: (1) mechanical or structural, (2) electrical, (3) punching, and (4) decorative. Phenolic resins are especially suitable and mostly are used where mechanical strength and resistance to heat, water, and electricity are required. For punching-grade laminates, phenolic resins are specially modified with plasticizers or drying oils to yield laminates having good plasticity and elasticity. For electrical grades the phenolics generally are catalyzed with ammonia, amines, or less conductive catalysts in place of the stronger alkaline catalysts otherwise used.

For decorative laminates, urea and melamine resins are the principal resins used. The melamines are used where translucent, light-colored products with good heat and water resistance are required. Polyesters and some melamines are used for low-pressure laminating, enabling the continuous production of counter and table tops by passing the assembly through a set of rolls and then through a heating chamber.

There are two broad general methods for introducing resins into papers for making paper-base laminates: (1) the beater addition process and (2) impregnation of the paper sheet. In the beater addition process the resin is added to the pulp in the beater and then precipitated on the fiber by alum or an acid. The resin adheres to the pulp fibers, which then are formed into a sheet. This type of paper–plastic combination commonly is called resin-filled paper. These resin-filled papers may be made into flat or shaped preforms. The former are flat sheets; the latter are vacuum-felted to a shape closely conforming to that of the final molded product. Shaped preforms are used for deep forms requiring high strength contours. Little flow is required on molding; hence the paper sheet does not break, and good strength properties are obtained. The use of stretchable cross-creped paper for postformable laminates is a new development.

The more common method of application of the resin is by impregnation of the wet or dry paper sheet (web) with a solution of resin. Such papers are called resin-impregnated papers. Water-soluble and alcohol-soluble types of phenolic resins both are used for paper-base laminates. The former tend to give more brittle but more dimensionally stable products than the latter. Phenolic resins are applied mostly by impregnation of the wet or dry paper sheet, producing resin-impregnated papers, although some progress has been made in the slush stock addition procedures to produce phenolic resin-filled papers.

In the wet-web process for impregnating paper for laminates, the wet sheet of paper on the paper machine is carried through a resin bath while the sheet is supported by a wire. The sheet contains up to 65 percent water, and the amount of resin taken up depends upon the moisture content of the paper, solids content of the resin solution, viscosity of the resin solution, temperature of the bath, machine speed, and pressure of the squeeze-rolls. Only water-soluble or water-dispersible resins can be used in the wet-web process.

Generally, however, phenolic impregnations of paper for laminates and other purposes demanding a high resin content are done with dry paper on off-machine equipment. The dry paper sheet is passed continuously through a resin solution, generally an alcoholic solution, and then moves under and between two metering rolls, after which the paper is dried to remove solvent and to complete the condensation of the thermosetting phenolic resin.

The addition of phenolic resins in the form of emulsions to the slush stock by the beater-addition process also has received considerable study. Papers containing 45 to 55 percent resin, and even as high as 65 percent, have been prepared. The resin is precipitated by adding alum to the beater. Papers prepared in this way are highly plastic and are suitable for low-pressure molding. The phenolic resins can also be used in combination with elastomers, such as GR-S types, neoprene, hycar, and vinyl polymers, to produce laminates of high impact strength and greater elongation under tension.

Lignin also is commercially used as a resin for paper laminates. Its low cost and availability as a by-product in pulp manufacture make it attractive. One of the most successful products is made with lignin recovered from the spent liquor of the soda pulping process. The lignin may be added to the pulp suspension in solution and precipitated directly among the fibers, or added in a preprecipitated form.

Properties of paper-base laminates depend upon both the resin and the paper. In general, the final product has the characteristics of the resin used, provided that over 30 percent is resin. The paper acts as a structural reinforcer, greatly enhancing toughness and tensile, flexural, and impact strength.

Electrical properties of the laminate depend upon both the paper and the resin although the amount of resin absorbed is the most important factor affecting electrical insulating properties. Papers of low power factor, good dielectric strength, and high dielectric constant are necessary for electrical grades of laminates. Other desired paper properties for good paper-base laminates are uniformity, cleanliness (freedom from slime, dirt, and fiber bundles), low finish, neutral pH, freedom from chemicals (bleach residues, etc.), low and uniform moisture content (under 4%), and uniform absorbency. High absorbency is desired when high electrical resistance and minimum water absorption are required, as greater amounts of resin are taken up by high-absorbency papers than by those with a low absorbency. For high-impact-strength punching grades of laminates, a low-absorbency paper is necessary to reduce the amount of resin absorbed.

Polymer-Modified Papers

In addition to paper-base laminates, polymers are combined in many ways with paper to develop new properties or to modify or enhance certain properties. Paper commonly is combined with polymers, such as synthetic resins, elastomers, and plastics in general, to produce products that may be classified as follows: (1) wet-strength paper, (2) special-purpose papers containing large amounts of resins or elastomers (chemical-resistant papers, sandpaper backings, gaskets, imitation leather, shoe parts, wood overlay and honeycomb core papers, air and oil filters, battery separators, etc.), (3) plastic-coated papers, and (4) paper-base laminates. The use of plastics in combination with paper has grown enormously during the past three decades. Large quantities of urea and melamine resins as well as polyethylene are used for coating and heating paper and paperboard.

Many other polymers are used in treating and coating papers, including polyesters, styrene, polyvinyl chloride, their copolymers, and others. Polymer-modified papers thus are very important in the present economy.

Overlaid lumber is a composite of lumber and phenolic resin-treated kraft paper. Similar paper overlays are applied to veneer, plywood, fiberboard, and particleboard. Paper honeycomb cores also are made from phenolic resin-treated kraft paper, which is formed into a honeycomb of different geometrical designs, such as figure eight or hexagonal, in special machines. Simpler types are made from resin-impregnated corrugated sheets, which can be assembled in several ways. This material permits construction of sandwich panels of light weight and high strength. Kraft papers for wood overlays or for honeycomb cores are treated with phenolic resin in the same ways as described above for paper-base laminates.

Paper overlays have three basic uses: masking, decoration, and structures. Masking overlays are used to cover minor defects and provide a more uniform paintable surface. Such overlays contain 20 to 25 percent phenolic resin based on the weight of the paper. For structural purposes, one or more sheets of paper may be used in the laminate. High-density and medium-density types are produced for plywood. The high-density type contains not less than 40 percent of a thermosetting resin, phenolic, or melamine; it has a hard smooth surface not requiring further finishing and may be used for exterior service. The curing of the resin is completed at the same time that the paper is bonded to the wood material in a hot press or, in the case of plywood, at the same time that the veneer is assembled into plywood. The overlay sheet swells and shrinks much less than wood and thus exerts a resistance to the dimensional changes of the wood and may reduce lateral swelling by as much as 40 percent. Overlay papers also upgrade the appearance of low-grade lumber, increase strength properties, improve finishability, and increase resistance to weathering.

Decorative surfaces are obtained by applying a top sheet of white paper on which there is a printed design. This is covered with a clear coating of melamine or vinyl resin. Or, a thin transparent (when cured) paper impregnated with melamine resin may be applied to a decorative veneer, providing a permanent protective finish.

For honeycomb cores, either water- or alcohol-soluble phenolic resins may be used. Many types of facings may be glued to the honeycomb cores: veneers, plywood, hardboards, asbestos board, aluminum, stainless steel, and paper-plastic laminates. Thin sheet material may be used because of the almost continuous support of the core.

The honeycomb sandwich possesses great strength in relation to its weight. It may carry loads as much as 25 tons/ft^2. Its strength and weight vary with the weight of the paper, quantity of resin impregnated, and honeycomb design.

Honeycomb sandwich construction has many uses, such as in airplanes, cargo containers, truck and trailer bodies, railway passenger cars, cabins, barns, airplane hangars, house floors, walls, roofs, doors, and a variety of other products. Besides combining strength with lightness, honeycomb sandwich material has high rigidity, good insulation properties, resistance to fungi and pests, and durability to temperature extremes.

Modified Wood and Wood Composites

Wood has a number of disadvantageous properties as described earlier in this chapter. It is biodegradable, flammable, dimensionally unstable to water, and degradable by ultraviolet light, acids, and bases. There has been a considerable amount of research expended over the years to correct these defective properties for both solid wood and reconstituted wood products.

A wood product of improved dimensional stability can be produced through heat treatment of wood at temperatures varying from 150°C to 320°C. For good temperature control and to avoid strength loss the heat treatment preferably is performed under the surface of molten metal or a fused salt for exclusion of oxygen. The modified wood product is referred to as staybwood.

Treatment of wood with polyethylene glycol (PEG) is the most commonly used method to impart dimensional stability to wood. PEG in a water solution can be used to permeate the lumens and penetrate the cell wall. A 30 to 50 percent solution of PEG in water generally is used on green wood; no pressure is required. Treatment times are adjusted so that a uniform uptake of 25 to 30 percent of PEG is achieved, based on the dry weight of the wood; temperatures range from

21°C to 60°C. The wood may require weeks of soaking, depending on species, density, and thickness. After treatment, the wood is dried in a well-ventilated space, preferably heated.

The PEG is not "fixed" or cured in the wood, and it leaches out if the wood contacts water. For this reason, PEG-treated wood usually is finished with a penetrating oil or polyurethane varnish. PEG is used primarily to treat cross sections of trees for plaques, clock faces, and tabletops. It also is used to stabilize bowls and other turnings, carvings, and rifle stocks, and to treat archaeological water-logged wood.

Resin impregnation can be used to add bulking agents to the cell wall. These resins have a low degree of polymerization, or the monomers are polymerized after impregnation. The best fiber-penetrating thermosetting resins are highly water-soluble, phenol-formaldehyde, resin-forming systems with low initial molecular weights. Green or dry veneers usually are treated by soaking or pressure treatment with a water-soluble resin in a 30 percent aqueous solution. Following impregnation, the wood is dried slowly and then heated at about 150°C for 20 minutes to set the resin. Laminates of treated wood are constructed by gluing the individual sheets together. This product, called Impreg, contains 25 to 35 percent resin and has a density about 20 percent higher than the original wood and an anti-shrink efficiently (ASE) of about 65 percent. As with PEG, the water-soluble resin penetrates the cell wall and keeps the wood in a swollen state. Unlike PEG, the phenol-formaldehyde resin is cured by heating to form a high-molecular-weight, water-insoluble resin in the cell wall. Thus, Impreg can be used in contact with water. Its compressive strength is higher than that of untreated wood, but it has much less toughness. It shows considerable resistance to decay and termite and marine-borer attack. Treating with phenolic resins imparts high acid resistance, greatly increases the temperature to which wood can be heated without appreciable change in properties, and increases electrical resistance. The largest industrial application of Impreg is in die molds for automobile body parts and other uses. Despite its high cost, the dimensional stability and plasticity of Impreg make it commercially viable.

Compreg is a highly dense product obtained by applying pressure to dry, resin-treated veneers during heat cure. It offers most of the advantages of Impreg. Its mechanical properties are appreciably better than those of the original uncompressed wood because of a two- to three-fold increase in density (1350 kg/m^3). The strength properties of Compreg are increased in proportion to the degree of compression. Only its toughness is lower than that of untreated wood, although greater than that of Impreg. Because of the plasticizing action of the resin-forming materials, treated wood can be compressed under considerably lower pressures than dry, untreated wood. For example, when subjected to a pressure of only 1.7 MPa (244 psi) at 149°C, treated spruce, cottonwood, and aspen wood, dried to a moisture content of about 6 percent but not cured, are compressed to about half the original thickness and a specific gravity of about 1.0.

In a 24-hour water-soaking test, Compreg has an ASE value of 95 percent. The rate of water pickup is so slow that complete swelling equilibrium of a 13-mm specimen is not reached after one year at room temperature. The product is brown and can be buffed to a high polish. Compreg is produced commercially in small quantities and is used for knife handles, gears, certain musical instruments, and decorative articles.

Composites of wood with vinyl polymers have been developed. Because the vinyl polymers are clear, colorless, thermoplastic materials, they do not significantly discolor the wood; thus its natural beauty is retained, whereas the phenolic resins darken the wood. However, the hygroscopic characteristics of the wood substance are unaffected because little, if any, resin penetrates the cell walls; the ASE is only about 10 to 15 percent. The high resin content (70–100%) greatly reduces the normally high void volume of wood, however. Thus, the elimination of this important pathway for vapor diffusion slows down the response of the wood substance to changes in relative humidity, and its moisture resistance is greatly improved compared to the original wood. The hardness of the wood-plastic composite also is greatly improved.

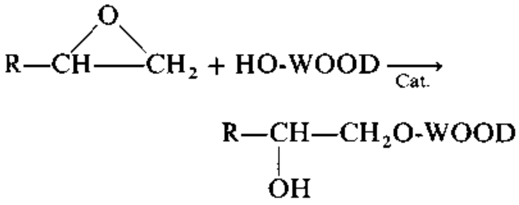
A variety of vinyl monomers, such as methyl methacrylate and styrene, may be used. Complete filling of the cell lumens and other voids (the "full-cell process") is easily accomplished by first subjecting the wood to a partial vacuum (about 0.3 in. of Hg) and then covering it with the monomer and soaking it for 2 to 6 hours, depending upon the species of wood and its dimensions. Some penetration of the monomer into the cell walls also may be obtained by using a diffusion process, such as a solvent-exchange method.

Polymerization of the vinyl monomer in the wood may be done with either radiation or free radical catalysts. The polymerization of the vinyl monomers in both processes depends upon the same mechanism, that is, initiation by free radicals. In the radiation process, the gamma rays passing through the monomer and the woody tissue create a large number of excited and ionized molecules, many of which break into fragments, namely, organic free radials (R·). These act as the initiator for the polymerization of an unsaturated monomer. Alternatively, the free radicals may be formed by thermal decomposition of compounds involving a weak bond. Commercially, the catalyst 2,2'-azobisisobutyronitrile now is most widely used, as it forms free radicals at a lower temperature than benzoyl peroxide.[24]

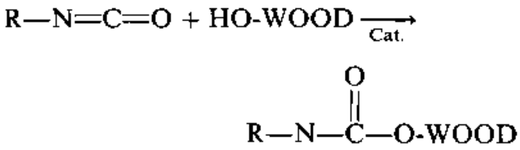
If the end use of the wood–polymer composite requires an abrasive (sanding) or cutting process that brings about high temperatures, the thermoplastic polymer will melt, causing machining difficulties. To prevent such melting, a crosslinking substance such as diethylene glycol dimethacrylate is added to the monomer before impregnation into the wood (about 5% of the volume of the monomer). Wood–plastic materials are used in parquet flooring, certain sporting equipment, musical instruments, and decorative articles.

Wood also can be modified by chemical reaction directly with the hydroxyl groups present in the polymer constituents in the cell wall of the wood. This treatment confers bulk to the cell wall with the help of a permanently bonded chemical. Many reactive chemicals have been used to modify wood chemically. For best results, the chemicals should be capable of reacting with the wood hydroxyl groups under neutral or mildly alkaline conditions at temperatures below 120°C. The chemical system should be simple and must be capable of swelling the wood structure to facilitate penetration. The complete molecule must react quickly with wood components, yielding stable chemical bonds; the treated wood still must possess the desirable properties of untreated wood. Anhydrides, epoxides, and isocyanates best conform to these conditions, conferring ASE values of 60 to 75 percent at chemical weight gains of 20 to 30 percent. Reactions of the chemicals with wood, as shown below, are fast and complete, and stable chemical bonds are formed. The systems swell the wood and penetrate well.[25]

Epoxides:

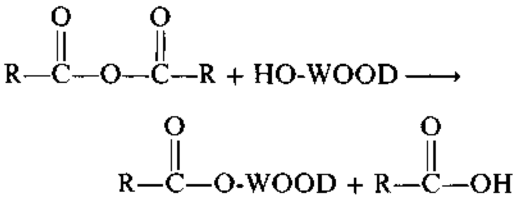


Isocyanates:



$$R{-}N{=}C{=}O + \text{HO-WOOD} \xrightarrow[\text{Cat.}]{} R{-}N{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\text{O-WOOD}$$

Anhydrides:



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R + \text{HO-WOOD} \longrightarrow R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\text{O-WOOD} + R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$$

In the epoxide reaction, a new hydroxyl group originating from the epoxide is formed; and from this new hydroxyl, a polymer can begin to form. Given the ionic nature of the reaction and the availability of alkoxyl ions in the wood components, the chain length probably is short because of chain transfer.

The optimum reaction conditions for reaction with epoxides are a 95/5 (v/v) mix of epoxide with triethylamine at 120°C and 150 psi nitrogen. Depending on the isocyanate used, reaction conditions of 120°C and 150 psi with no catalyst and 5 percent triethylamine or 5 to 35 percent dimethylformamide are optimum.

Of several anhydrides studied, acetic anhydride reacted the most readily. Reactions were carried out by refluxing the wood in a xylene/acetic anhydride solution or with acetic anhydride vapors alone at 120°C. With this system, for each mole of acetate bonded onto the wood a mole of acetic acid is generated as a by-product. Although this by-product generation is a disadvantage of the process, the chemical system does penetrate and react quickly with wood, without a catalyst. It is not so sensitive to moisture as are the epoxide and isocyanate systems.

Recently a very facile dip acetylation procedure has been developed for wood chips and fibers. The wood is dried at 105°C and then dipped in acetic anhydride for one minute and drained. Then the sample is placed in a preheated (120°C) reactor for different lengths of time, depending on the degree of substitution of acetyl groups desired in the sample.[26] The swelling of aspen flakeboard made from such chemically modified flakes is dramatically reduced. For example, while unmodified flakeboard swelled by over 60 percent after immersion in water for 5 days, the modified material swelled by only about 8 to 22 percent, depending on the extent of chemical modification.

Molded and Formed Wood. Historically wood has been bent and shaped first by steaming, which plasticizes the wood polymers. The new shape then is set in place by cooling and drying in the desired conformation. However, the curvature possible by this method is limited, and the process is time-consuming. Some chair backs and solid hickory and ash skis still are steam-bent.

Anhydrous ammonia also is known to cause temporary platicization of wood. The ammonia swells and plasicizes both the lignin and the cellulose, and the crystalline structure of the cellulose is converted to a different form in the process. To shape the wood, it is immersed in liquid ammonia or treated with gaseous ammonia under pressure until the cell walls have been penetrated and the wood becomes pliable and flexible. In this condition it is easily shaped and formed by hand or mechanically. The ammonia readily vaporizes and evaporates from the wood, so that the wood regains its normal stiffness but retains the new form into which it has been shaped. With this process the wood can be distorted into quite complex shapes without springing back to its original form. Treating plants have been developed on a pilot-plant scale, but the process has not been widely adopted.

There has been a concerted research effort in recent years to develop molded wood-based material. The Japanese have emphasized chemical modification approaches and have made considerable progress toward the development of a thermoplastic wood-based material.[27] Their most promising results are based on esterification of wood meals with subsequent thermomolding. As the size of the aliphatic group was increased, the melting temperature of the modified wood under pressure was decreased. It also was found that a very small degree of additional grafting of polystyrene to the esterified wood resulted in a dramatic improvement in the thermoplasticity of the product. Matsuda[28] developed a very facile method for production of moldable wood by simply heating the wood meal with an acid anhydride for 3 hours to temperatures greater than 60°C. The wood meal was readily moldable at high temperatures (180°C) under pressure (570 kg/cm^2) for 10 minutes. The moldability of the esterified wood decreased in the following order: succinic anhydride > maleic anhydride > phthalic anhydride.

Although it is possible to make wood thermoplastic through chemical modification, the handling of the finely divided wood (wood meal) becomes a problem when more complex shapes or deep draws are desired. Therefore, a totally new approach for the creation of molded products based on wood was developed by Hunter Brooks, formerly of the Triad Corp., Detroit, Michigan. The raw material is a dry attrition-milled wood fiber (80%), a polyester staple fiber 1 to 2 inches long (10%), and a phenolic resin (10%). The materials are formed into a nonwoven web on a Rando-webber machine. The longer polyester fibers are incorporated so that the web can be needle-punched to form a nonwoven fabric with good mechanical integrity. The phenolic resin is applied to the web either as a dry powder or as an aqueous solution. This fiber composite then is easily compression-molded into any of a variety of shapes. For deep-draw compression molding, patterns may be cut into the nonwoven web to allow the fiber mat to drop deep into the mold. Any type of fibrous material, synthetic or natural lignocellulosic, can be utilized in the web; so the process offers considerable flexibility for production of a wide variety of products engineered to specific applications. The processing equipment developed by Hunter Brooks has been donated to the USDA Forest Products Laboratory, where an active research program in cooperation with the University of Wisconsin is under way to perfect the process for industrial applications.[29]

A major application of these types of molded products would be for interior uses in automobiles, such as head liners, door panels, and dashboards. Although this is a low-cost, low-performance application, it represents a very large-volume market. Indeed, wood is already utilized in applications of this type, but as a finely ground flour that serves as a filler (up to 40%) in extrusion-molded polyolefin products. The use of recycled fiber in this process and the one described above offers the potential of even greater cost reductions, combined with alleviation of solid waste disposable problems.

PRESERVATIVE TREATMENT OF WOOD

Wood, as a natural plant tissue, is subject to attack by fungi, insects, and marine borers. Some species of wood are more resistant to decay than others (e.g., the heartwood of cedars, cypress, and redwood) because of the presence of natural toxic substances among the extractable components. Most woods, however, are rapidly attacked when used in contact with soil or water, or when exposed to high relative humidities without adequate air circulation. Wood for such service conditions requires chemical treatment with toxic chemicals, collectively termed wood preservatives. The service life of wood may be increased 5- to 15-fold, depending upon the conditions of preservative treatment and the nature of the service.

The preservative treatment of wood is the second largest chemical wood-processing industry; pulp and paper manufacture is the most important. Since 1950, the average annual volume of wood treated has been 250 to 300 million cubic feet. The more important types of wood products treated are shown in Fig. 7.22.

Preservative Chemicals

Owing to their toxic nature, all of the commercial wood preservatives presently used in the United States are effective in preventing attack by microorganisms. However, because of concern that these chemicals will have a deleterious effect on the environment, alternative methods based on nontoxic procedures also are being investigated. These nonconventional approaches are based on chemical modification, and are described briefly at the end of this section.

Toxic chemicals used for the preservation of wood may be classified as follows:

- *Organic liquids of low volatility and limited water solubility*:
  Coal-tar creosote
  Creosote–coal tar solutions
  Creosote–petroleum solutions
  Other creosotes
- *Chemicals dissolved in organic solvents, usually hydrocarbons*:
  Chlorinated phenols (principally pentachlorophenol)
  Copper naphthenate
  Solubilized copper 8-quinolinolate

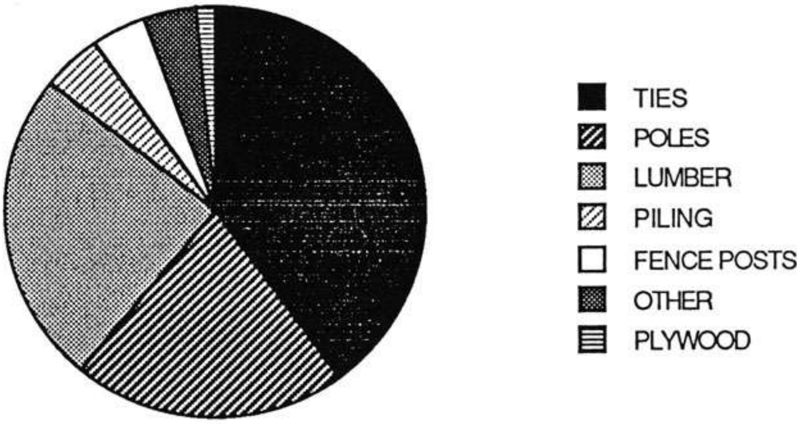


Fig. 7.22. Relative distribution of wood products treated with preservatives.

- *Water-soluble inorganic salts*:
  Acid copper chromate
  Ammoniacal copper arsenite
  Chromated copper arsenate
  Chromated zinc chloride
  Fluor chrome arsenate phenol

Creosote from coal tar is the most widely used wood preservative for several reasons: (1) it is highly toxic to wood-destroying organisms; (2) it has a high degree of permanence due to its relative insolubility in water and its low volatility; (3) it is easily applied, with deep penetration easily obtained; and (4) it is relatively cheap and widely available. For general outdoor service in structural timbers, poles, posts, piling, and mine props, and for marine uses, coal-tar creosote is the best and most important preservative. Because of its odor, dark color, and the fact that creosote-treated wood usually cannot be painted, creosote is unsuitable for finished lumber and for interior use.

Coal-tar creosote is a mixture of aromatic hydrocarbons containing appreciable amounts of tar acids and bases (up to about 5% of each), and has a boiling range between 200 and 355°C. The important hydrocarbons present include fluorene, anthracene, phenanthrene, and some naphthalene. The tar acids are mainly phenols, creosols, xylenols, and naphthols; the tar bases consist of pyridines, quinolines, and acridines.

Often coal tar or petroleum oil is mixed with coal-tar creosote, in amounts up to 50 percent, as a means of lowering preservative costs. Because coal tar and petroleum have a low toxicity, their mixtures with creosote are less toxic than is creosote alone.

A number of phenols, especially chlorinated phenols and certain metal-organic compounds, such as copper naphthenate and phenyl mercury oleate, are effective preservatives. Pentachlorophenol and copper naphthenate are most commonly used, and are carried into the wood in 1 to 5 percent solutions in petroleum oil. Pentachlorophenol is colorless, and can be applied in clear volatile mineral oils to millwork and window sash requiring a clean, nonswelling, and paintable treatment.

Inorganic salts are employed in preservative treatment where the wood will not be in contact with the ground or water, such as for indoor use or where the treated wood requires painting. They are also satisfactory for outdoor use in relatively dry regions.

Preservation Process

The methods for applying preservatives to wood are classified as follows:

- *Nonpressure processes*:
  Surface (superficial) applications by brushing, spraying, or dipping
  Soaking, steeping, and diffusion processes
  Thermal process
  Vacuum processes
  Miscellaneous processes

- *Pressure processes*:
  Full-cell process (Bethell)
  Empty-cell processes (Rueping and Lowry)

Brush and spray treatments usually give only limited protection because the penetration or depth of capillary absorption is slight. Dip treatments give slightly better protection. Organic chemicals dissolved in clear petroleum solvents often are applied to window sash and similar products by a dip treatment of 1 to 3 minutes.

Cold soaking of seasoned wood in low-viscosity preservative oil for several hours or days and the steeping of green or seasoned wood in waterborne preservatives for several days are methods sometimes employed for posts, lumber, and timbers on a limited basis. The diffusion process employs water-borne preservatives that will diffuse out of the treating solution into the water in green or wet wood.

The most effective of the nonpressure processes is the thermal method of applying coal-tar creosote or other oil-soluble preservatives, such as pentachlorophenol solution. The wood is heated in the preservative liquid in an open tank for several hours, after which it is quickly submerged in cold preservative in which it is allowed to remain for several hours. This is accomplished either by transferring the wood at the proper time from the hot tank to the cold tank, or by draining the hot preservative and quickly refilling the tank with cooler preservative. During the hot treatment, the air in the wood expands, and some is expelled. Heating also lowers the viscosity of the preservative so that there is better penetration. When the cooling takes place, the remaining air in the wood contracts, creating a partial vacuum that draws the preservative into the wood. For coal-tar creosote, the hot bath is at 210 to 235°F, and the cold bath at about 100°F. This temperature is required to keep the preservative fluid.

The hot- and cold-bath process is widely used for treating poles and, to a lesser extent, for fence posts, lumber, and timbers. This process gives the most effective results of the common nonpressure processes, which most nearly approach those obtained by the pressure processes.

The vacuum processes involve putting the wood under a vacuum to draw out part of the air. The wood may be subjected to a vacuum alone or to steaming and a vacuum before being submerged in a cold preservative. These methods are used to a limited extent in the treatment of lumber, timber, and millwork.

Commercial treatment of wood is most commonly done by one of the pressure processes, as they give deeper penetrations and more positive results than any of the nonpressure methods. The wood, on steel cars, is run into a long horizontal cylinder, which is closed and filled with preservative. Pressure is applied, forcing the preservative into the wood.

There are two types of pressure treatment, the full-cell and the empty-cell. The full-cell process seeks to fill the cell lumens of the wood with the preservative liquid, giving retention of a maximum quantity of preservative. The empty-cell process seeks deep penetration with a relatively low net retention of preservative by forcing out the bulk liquid in the wood cells, leaving the internal capillary structure coated with preservative.

In the full-cell process, the wood in the cylinder first is subjected to a vacuum of not less than 22 in. Hg for 15 to 60 minutes, to remove as much air as possible from the wood. The cylinder then is filled with hot treating liquid without admitting air. The maximum temperature for creosote and its solutions is 210°F, and for water-borne preservatives it is 120 to 150°F, depending upon the preservative. Then the liquid is placed under a pressure of 125 to 200 psi, and the temperature and pressure are maintained for the desired length of time, usually several hours. After the liquid is drawn from the cylinder, a short vacuum is applied to free the charge of surface-dripping preservative.

In the empty-cell process, the preservative liquid is forced under pressure into the wood, containing either its normal air content (Lowry process) or an excess of air, by first subjecting the wood to air pressure before applying the preservative under pressure (Rueping process). In the former case, the preservative is put in the cylinder containing the wood at atmospheric pressure, and, in the latter case, under air pressure of 25 to 100 psi. After the wood has been subjected to the hot preservative (about 190–200°F) under pressure (100–200 psi in the Lowry process and 150–200 psi in the Rueping process) and the pressure has been released, the back pressure of the compressed air in the wood forces out the free liquid from the wood. As much as 20 to 60 percent of the injected preservative may be recovered, yet good depth of penetration of the preservative is achieved.

Preservative Retention

Retention of preservative generally is specified in terms of the weight of preservative per cubic foot of wood, based on the total weight of preservative retained and the total volume of wood treated in a charge. Penetration and retention vary widely between different species of wood, as well as with woods of the same species grown in different areas. In most species, heartwood is much more difficult to penetrate than sapwood. Also, within each annual growth ring there is variability in penetration, the latewood generally being more easily treated than the earlywood.

The American Wood-Preservers' Association Standards specify methods of analysis to determine penetration and retention. They also specify minimum retention amounts for different preservatives according to the commodity, the species, the pretreatment of the wood, such as kiln drying, and the end use of the commodity. Heavier retention is required for products in contact with the ground (poles, timbers, etc.) or with marine waters (piles, timbers, etc.). Unprotected wood in contact with the ground is subject to severe attack by fungi and insects, and, in contact with seawater, it is quickly destroyed by marine borers. For wood products to be used in contact with the ground or marine waters, creosote is the major preservative employed because it can be readily impregnated to give high retention and good protection, and it is not leached out by water.

Nonconventional Wood Preservation

Chemical modification as a possible preservative treatment for wood is based on the theory that enzymes (cellulose) must directly contact the substrate (cellulose), and this substrate must have a specific configuration. If the cellulosic substrate is chemically changed, this highly selective reaction cannot take place. Chemical modification also can change the hydrophilic nature of wood. In some cases water, a necessity for decay organisms, is excluded from biological sites. The chemicals used for modification need not be toxic to the organism because their action renders the substrate unrecognizable as a food source to support microbial growth. For wood preservation, this means that it is possible to treat wood in such a manner that attack by wood-destroying fungi will be prevented, and the material will be safe for humans to handle. For applications of wood in which human contact is essential, nontoxic preservatives may well be specified or required in the future. An added benefit to wood of most chemical modification treatments is that the resulting bulking action gives the treated wood very good dimensional stability. The chemical modification of wood involves a chemical reaction between the hydroxyl groups in wood and a simple single chemical reagent, with or without a catalyst, to form a covalent bond between the two, as previously described for dimensional stability treatments.[30] The wood component may be cellulose, hemicellulose, or lignin.

The treated wood must continue to possess the desirable properties of untreated wood: the strength must remain high, there must be little or no color change (unless a color change is desirable), and it must be a good electrical insulator, safe to handle, gluable, paintable, and so on. These chemicals, once reacted, are effective in preventing attack by microorganisms, but they are not toxic to the decay organisms. The important factor in preventing attack is to attain a treatment level that inhibits the growth of the organisms. A recent review on this subject shows that treatments with acetic anhydride, dimethyl sulfate, acrylonitrile, butylene oxide, phenyl isocyanate, and β-propiolactone all give good rot resistance at a 17 to 25 weight percent gain (WPG).[30] The decay resistance of acetylated wood is proportional to the WPG, and the degree of dimensional stability also is proportional to the WPG; so the exclusion of cell wall or biological water may be a very important factor in the decay resistance mechanism.[31]

In preliminary tests, alkylene oxide–treated southern pine was found to be resistant to termite attack and attack from the marine borers *Teredo* (shipworm) and *Limnoria*.

In conclusion, chemical modification of wood results in a treatment that is nontoxic, effective, and nonleachable. The high chemical treatment level required for effectiveness, however, results in a rather expensive treatment. Dimensional stability also is obtained at these high (17–25 WPG) substitution levels; so, for those products where both rot resistance and dimensional stability are important, the present state of the technology is close to a viable industrial process. The use of toxic chemicals that are permanently bound to the wood components by this treatment may be an environmentally acceptable preservation method.

FIRE-RETARDANT TREATMENT OF WOOD

The Romans first treated wood for fire retardancy in the first century A.D. They used solutions of alum and vinegar to protect their boats against fire. In 1820, Gay-Lussac advocated the use of ammonium phosphates and borax for treating cellulosic material. Many of the promising inorganic chemicals used today were identified between 1800 and 1870. Since then, the development of fire retardants for wood has accelerated. Commercially treated wood became available after the U.S. Navy (1895) specified its use in ship construction, and New York City (1899) required its use in buildings over 12 stories tall. Production reached over 65 million board feet in 1943, but by 1964 only 32 million board feet was treated annually.[32]

However, starting in 1979 changes were made in some building codes that allowed structural changes if fire retardant (FR) treated wood was used in place of untreated plywood for roof sheathing. The structural changes resulted in sufficient savings such that FR-treated wood was utilized more extensively. Also the use of FR-treated plywood was mandated at other specific sites such as prisons.

Fire-retardant treatments for wood can be grouped into two general classes: (1) those impregnated into the wood or incorporated into wood composite products and (2) those applied as paint or surface coatings. Chemical impregnation has the greater use, primarily for new materials, whereas coatings have been limited primarily to materials in existing constructions. There are advantages and disadvantages to each class. Coatings are applied easily, and they are economical. Chemical impregnation usually involves full-cell pressure treatment and can be costly. A coating is subject to abrasion or wear that can destroy the effectiveness of the fire retardant. Chemical impregnations deposit the fire retardant within the wood, so that if the surface is abraded, chemicals are still present. On-site application of surface coatings requires strict control of the amount applied to ensure correct loading levels for a particular flame-spread rating. Both coating and impregnation systems are based on the same chemical compounds although the formulations for each vary. Among the most commonly used chemicals for impregnation treatments are diammonium phosphate, ammonium sulfate, borax, boric acid, zinc chloride, and most recently the leach-resistant amino-resin systems. These compounds have different characteristics with respect to fire resistance. Ammonium phosphate, for example, is effective in checking both flaming and glowing; borax is good in checking flaming but is not a satisfactory glow retardant. Boric acid is excellent in stopping glow but not so effective in retarding flaming. Because of these different characteristics, mixtures of chemicals usually are employed in treating formulations.

Fire-Retardant Formulations

Many chemicals have been evaluated for their effectiveness as fire retardants. Today most fire retardants for wood are based on phosphorus, nitrogen, boron, aluminum trihydrate, and a few other compounds. Phosphorus and nitrogen frequently are used together because they behave synergistically; amino-resins are an example of such a combination.

Most fire-retardant formulations are not resistant to leaching by water. Therefore, there have been increased efforts to develop leach-resistant chemicals that can be impregnated into wood products for use in exterior or high-humidity applications. Some of the proposed leach-resistant systems include chemical combinations that form insoluble complexes, amino-resin systems, and monomers that polymerize in the wood. A common amino-resin system for exterior use is dicyandiamide phosphoric acid formaldehyde. Guanylurea phosphate-boric acid also is a commonly used organic phosphate salt for modern commercial fire-resistant wood.

The American Wood-Preservers' Association Standards specified the four types of fire-retardant formulations given below (A, B, C, D). Many newer formulations have been developed by commercial enterprises and are proprietary.

Type A

Chromated zinc chloride—a mixture of sodium dichromate and zinc chloride having the composition: hexavalent chromium as CrO_3, 20% and zinc as ZnO, 80%.

Type B	
Chromated zinc chloride (as above)	80%
Ammonium sulfate	10%
Boric acid	10%
Type C	
Diammonium phosphate	10%
Ammonium sulfate	60%
Sodium tetraborate, anhydrous	10%
Boric acid	20%
Type D	
Zinc chloride	35%
Ammonium sulfate	35%
Boric acid	25%
Sodium dichromate	5%

Minimum and maximum limits of variation in the percentage of each component in the above formulations are specified in the standards.

The impregnation methods are similar to those employed for the preservative treatment of wood by water-borne salts using pressure processes. The maximum temperature of the solution must not exceed 140°F for formulation Types A, B, and D, and must not be over 160°F for Type C. After treatment, the wood must be dried to remove the water solvent to a moisture content of 19 percent or less. For most uses, the wood is kiln-dried to a moisture content of under 10 percent.

For effective fire protection larger amounts of chemicals must be deposited in the wood than the amounts necessary when water-borne chemicals are used for decay prevention. Whereas for the water-soluble toxic salts retentions from 0.22 to 1.00 lb/ft^3 of wood are specified according to commodity standards in order to give good protection against decay and insects, as much as 5 to 6 lb of some fire retardants may be required for a high degree of effectiveness against fire. Usually, however, smaller amounts will give a good degree of protection. For example, formulation Type B when impregnated in amounts of 1.5 to 3 lb/ft^3 of wood provides combined protection against fire, decay, and insects. Because the amino-resin systems are leach-resistant, high application levels are not necessary in practice.

Fire retardancy of wood involves a complex series of simultaneous chemical reactions, the products of which take part in subsequent reactions. Most fire retardants used for wood increase the dehydration reactions that occur during thermal degradation so that more char and fewer combustible volatiles are produced. The mechanism by which this happens depends on the particular fire retardant and the thermal-physical environment. The effectiveness of a fire-retardant treatment depends upon the performance rating of the treated material when tested in accordance with ASTM E84 (no greater flame spread than 25).

CONVERSION OF WOOD TO ENERGY, FUELS, AND CHEMICALS

Wood has been a source of energy and chemicals for hundreds of years and continues to be an important raw material for specific chemicals. The use of wood as a primary source of industrial chemicals decreased dramatically in the 1940s when oil became the preferred raw material. The term "silvichemicals" sometimes is used to refer to wood-derived chemicals analogous to petrochemicals.

The use of wood for energy, fuels, and chemicals can be conveniently divided into four major categories: direct combustion, saccharification-fermentation (SF), thermal decomposition, and thermochemical liquefaction. These methods are discussed in more detail in the following sections.[5]

Direct Combustion

The concept of using wood as a source of energy through direct combustion dates back to the very beginning of human existence. As soon as early people learned to use fire, wood became the major source of energy. It is important to note that fuel is still the major use of wood on a worldwide basis, amounting to an estimated $1.2 \times 10^9\,m^3$/year compared to $0.8 \times 10^9\,m^3$/year for lumber and other solid wood products, $0.34 \times 10^9\,m^3$/year for pulp, and $0.2 \times 10^9\,m^3$/year for other uses. Thus, on a global basis, nearly 50 percent of the wood harvest is used directly for fuel. In many nonindustrialized countries, fuel amounts to 80 to 90 percent of total wood consumption, compared with an average of 7 percent for industrialized regions.

The average stored energy content of wood is 8600 Btu/lb. Variations in heat values for wood as a function of species occur within a relatively narrow range of 8000 to 10,000 Btu/lb. Bark values are slightly higher than wood values, about 10,000 Btu/lb.

The greater the oxygen content of a carbon compound or carbonaceous substance is, the lower the heat of combustion. Lignin, with an elemental analysis of $C_{10}H_{11}O_2$ compared to $C_6H_{10}O_5$ for cellulose, has a lower degree of oxidation and a higher heat of combustion than cellulose. The fossil fuels which have very low or no oxygen content have much higher energy contents, for example, 12,000 to 13,500 Btu/lb for coal, 18,000 to 19,900 Btu/lb for oil, and 18,550 Btu/lb for natural gas.

Wood and other biomass materials are hygroscopic and retain substantial amounts of moisture (15–60%). Hence, some of the thermal energy of the wood is lost in vaporizing this water to steam during combustion. In addition, wood has a lower density than coals, so that a greater volume of material must be gathered and transported to provide the same heating value as that of coal. Wood has a negligible sulfur content, less than 0.1 percent compared to much larger amounts in coal (avg. 2%) and petroleum. Sulfur from coal and petroleum creates serious environmental problems by causing acid rain. Also, ash from coal presents a disposal problem and creates unhealthy fly ash, whereas the ash content of wood is less than 0.5 percent. The only environmental hazard produced from burning wood as a fuel is the production of particulates.

Most wood and wood-derived materials (spent pulping liquors) that are used for energy are consumed by the forest products industry itself. The source of this fuel is almost entirely in the wood processing and manufacturing operations, termed "manufacturing residuals" or "mill residues." Forest residues from logging operations and the noncommercial trees in the forest also are utilized for fuels.

Wood wastes supply the forest products industry with roughly 40 to 50 percent of the energy requirements in the form of spent liquors and wood and bark residues. The spent pulping liquor contains 40 to 50 percent of the wood as dissolved lignin and a large variety of other organic compounds. The spent liquor is used almost totally, after evaporation to about 65 percent solids, to produce steam and to recover the inorganic chemicals used in the pulping operation. The Tomlinson furnace is used almost universally and is the most efficient system for combined energy and chemical recovery yet devised.

The mixed wood and bark residues burned directly are collectively termed "hog fuel." Over the past decade, there has been a trend to channel more and more of the cleaner, drier, and larger-sized mill residues into raw materials for products. The coarse wood residues (slabs, trim, edgings, etc.) are chipped and sent to pulp mills. Also, considerable sawdust now is being pulped instead of being burned for fuel. Some of the residues, including shavings, also are used for particleboard. This means that hog fuel contains the less desirable, dirtier, and wetter forms of waste.

Combustion Technology. The hog fuel boiler represents the conventional technology of using wood for energy to produce process steam. Modern wood-fuel boilers have traveling grates and use mechanical draft fans. Many are of gigantic size, handling as much as 500,000 lb of wood per hour. Spreader stokes distribute the fuel evenly over the large grate areas to ensure efficient combustion. The ash can be removed continuously with traveling grates. Modern instrumentation meters air flow, controls fuel-to-air ratios, and meters combustion efficiency and stack emissions. With these developments, the energy recovery and environmental acceptability of wood-burning systems have been improved in the forest products industry.

The deterioration of hog fuel quality referred to above makes it more difficult to obtain efficient combustion, high reliability, and low stack emissions simultaneously. To overcome this difficulty, the fuel can be processed before combustion to remove dirt and moisture and produce clean-burning, efficient fuel. This can be done by drying, screening, grinding, washing, and pelletizing or densification of the hog fuel in order to remove noncombustible dirt and moisture, reduce the size of large and slow-burning material, and agglomerate small and fine material. Size uniformity is important for ease in transportation, storage, and fuel feeding. Dirt and moisture reduction reduces transportation costs, promotes efficient combustion, and minimizes air emissions. Another approach for using low-quality hog fuel is the development of improved combustors. Examples are: (1) the fluidized-bed combustors, which obtain excellent wood combustion at relatively high efficiencies with low quality, nonuniform fuels; and (2) the pyrolytic burner, which has very low stack emissions with relatively high thermal efficiencies and wood combustion rates.

Present day wood-fired boiler systems are complicated and cost considerably more than a comparable petroleum-fired installation. As much as 25 percent of the capital cost is in the fuel-handling equipment, and another 20 percent is in the air pollution control system. Because of the high capital costs and the lower thermal efficiencies of burning wood compared to oil (68% vs. 82%), the success of the wood-fired systems depends on the low cost of the wood fuel supplies.

The North American forest products industry has been successful in developing useful technologies for recovering energy from wood residues as process heat or steam, which are cost-effective. New technologies promise even greater economic benefits.

Cogeneration Technology. Cogeneration is the concurrent generation of electricity and the use of exhaust heat, usually in the form of process steam, for manufacturing operations. This is done by burning fuel (in this case, wood) to make high-pressure steam, 600 to 1200 lb/in.^{2}, passing this steam through a back-pressure or extraction turbine to drive a generator, and then using the steam exhausted from the turbine at lower pressures, 50 to 300 lb/in.^{2}, for process heat. This technology gets full use of the energy contained in the fuel. Wood at 55 percent moisture will generate power at about 60 percent efficiency.

The forest products industry is a major user of cogeneration technology, as it requires large quantities of process steam as well as electricity. It produces about 50 percent of its electricity needs in this way. The pulp and paper industry alone is the largest producer of energy by cogeneration of any U.S. industry. Electricity self-sufficiency is likely to increase to 80 to 90 percent for forest industries in the future through cogeneration. However, there is a minimum plant size for economical power generation. Steam usage should be more than 70,000 to 120,000 lb/hr, equivalent to 3 to 5 MW of back pressure, for a plant economically to employ cogeneration systems.

Saccharification–Fermentation

The saccharification–fermentation (SF) method for derivation of fuels and chemicals from wood is based on the breakdown or hydrolysis of the polysaccharides in wood to the constituent monomeric sugars. The six-carbon or hexose sugars (glucose, galactose, and mannose) then are fermentable to ethyl alcohol (ethanol or grain alcohol, C_2H_5OH) by yeast fermentation in the same way that ethanol is produced from grains or fruits. Obviously the concept is not a new one; the polysaccharide character of wood has been known for over 100 years. The limitations on the use of wood for ethanol production primarily have been the difficulties in separating and hydrolyzing the crystalline cellulose component in wood. Both acids and enzymes can be used to hydrolyze the cellulose to glucose, but only acids have been utilized commercially for wood hydrolysis to sugars, and only in foreign countries.[33]

In contrast to the Western economy, the Soviet Union continued expansion of wood hydrolysis facilities, and about 40 such plants are presently in operation. All the Russian plants are based on dilute sulfuric acid in percolation towers. In the West interest in producing alcohols from wood was revitalized by the dramatic increase in the price of petroleum in the 1970s and the push to decrease oil imports by substituting gasohol, which is one part alcohol in nine parts gasoline, for 100 percent gasoline at gas pumps. Both ethanol and methanol can be used in gasohol blends.

Because of the high oil prices, the country of Brazil (most of whose sugars are produced from sugarcane) took the dramatic step of shifting to a much greater use of fuel alcohol. One wood hydrolysis plant was constructed, but it was uneconomical to operate and was shut down. However, Brazilian experience has demonstrated that fermentation ethanol (95 percent ethanol and 5 percent water) is a perfectly satisfactory motor fuel. At least 500,000 Brazilian automobiles operate on undried alcohol continuously, and most of the rest of their fleet operates on this fuel on weekends when only alcohol is available at the gas stations.[33] A number of methods can be used for production of ethanol from wood, as described below.

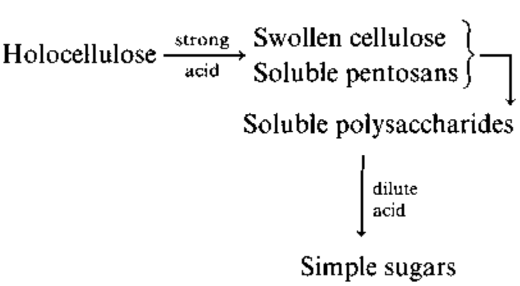
Cellulose, the major component of wood, gives about a 90 percent yield of pure glucose under laboratory conditions of hydrolysis, according to the following equation:

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{acid}} nC_6H_{12}O_6$$

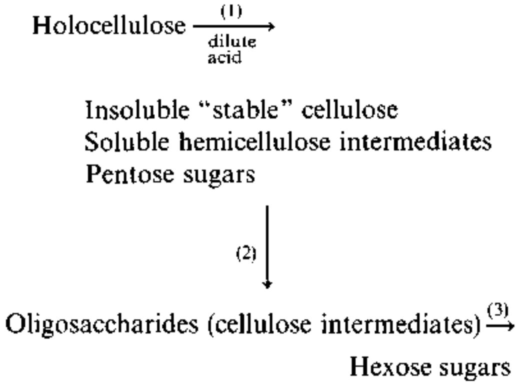
where n is in the range of 10,000 to 15,000. The hemicellulose fraction gives a mixture of sugars—xylose, arabinose, mannose, galactose, and glucose. Glucose, galactose, and mannose are yeast-fermentable sugars, whereas the pentoses (xylose and arabinose) are non-yeast-fermentable. The potential total reducing sugar yield from wood averages 65 to 70 percent, whereas the fermentable sugar yield is about 50 percent for the hardwoods and 58 percent for the softwoods. The lower quantity of fermentable sugar from the hardwoods is due to their higher content of pentosans, compared to the coniferous woods.

Hemicelluloses hydrolyze much more easily and rapidly than cellulose. Temperatures and acid concentrations that hydrolyze the cellulose to glucose in a matter of a few hours readily convert much of the hemicellulose into simple sugars in minutes or even seconds. Under industrial conditions of hydrolysis, the sugars formed undergo decomposition, with the pentoses decomposing more rapidly than the hexoses. Thus, the conditions of hydrolysis cause variations in the ratio and yields of the various sugars due to (1) their different rates of formation by hydrolysis and (2) their different rates of decomposition.

The polysaccharides of wood (holocellulose) may be hydrolyzed by two general methods: (1) by strong acids, such as 70 to 72 percent sulfuric acid or 40 to 45 percent hydrochloric acid; or (2) by dilute acids, such as 0.5 to 2.0 percent sulfuric acid. The hydrolysis by strong acids is constant, proceeds as a first-order reaction, and is independent of the degree of polymerization. The reaction may be represented as follows:



In dilute-acid hydrolysis, the reactions are heterogeneous and more complex than this because no swelling and solubilizing of the cellulose occurs. Cleavage of the insoluble cellulose results directly in low-molecular-weight oligosaccharides (intermediate products), which are rapidly converted to simple sugars, as indicated below:



Reaction (1) is rapid and occurs under mild conditions, hydrolyzing mainly the hemicelluloses. Reaction (2) is slow, proceeds as a first-order reaction, and is the limiting reaction in this process. Reaction (3) is rapid.

Based on the above methods, two classes of industrial processes have been developed, namely, the Bergius-Rheinau process, based on the use of concentrated hydrochloric acid at ordinary temperatures, and the Scholler-Tornesch process, in which very dilute sulfuric acid is used at temperatures of 170 to 180°C (338–356°F). The latter method in an improved form is known as the Madison process, based on work done at the United States Forest Products Laboratory in Madison, Wisconsin. A number of modifications have been developed, including four in Japan.

Bergius-Rheinau Process. Hydrochloric acid of about 40 to 45 percent (by weight) is produced by reinforcing recovered, weaker acid with hydrogen chloride from salt-sulfuric acid reactors, or by burning chlorine with illuminating gas.

Wood chips are air-dried, then charged into a tile-lined reactor, and extracted countercurrently by the acid. The fresh strong acid enters that part of the battery of diffusers or reactors which contains the most nearly exhausted wood, and is pumped through the following containers until it is nearly saturated with the carbohydrates dissolved from the wood. Part of this solution is mixed, under slight cooling, with fresh wood, and the mixture is charged into the head container of the battery. After the container is filled and a few hours are allowed for reaction time, an amount of solution is forced from this container, through the pressure of the incoming acid, that corresponds to the yield from one charge.

The drawn-off solution contains hydrochloric acid and carbohydrates in about equal parts, at a concentration of about 25 percent (by weight) each. It then is concentrated in stoneware tubes under vacuum. The distillate, containing about 80 percent hydrochloric acid with minor proportions of acetic acid and furfural, is reused after fortification. The concentrated sugar solution is dried to a powder in a spray-dryer, where it also loses most of the remaining acid.

The dry, somewhat acid, powder contains the carbohydrates in the form of intermediate polymers (oligosaccharides), which are water-soluble and must undergo further hydrolysis to yield simple sugars, either for fermentation or for crystallization. This is done by dissolving the oligosaccharides, diluting the solution to approximately 20 percent sugar concentration, and heating it for 2 hours in the presence of 2 percent acid at 125°C. Part of the glucose can be crystallized from the neutralized and reconcentrated solution, while the mother liquors are fermented to alcohol or used for growing yeast. A diagrammatic flow chart for the Bergius process is shown in Fig. 7.23.

When hardwoods are to be used, it is necessary to remove a part of the hemicellulose first by prehydrolysis. This has been done on a large scale with straw, a substance chemically similar to hardwood, by heating it in an 8-to-1 liquid-to-solid ratio, with 0.5 percent sulfuric acid for 2 to 3 hours at 130°C (266°F). Without prehydrolysis, hardwoods and straws form slimy materials, probably because of their high hemicellulose content, which prevent the flow of the hydrolyzing acid.

In the Bergius-Rheinau process the concentrated hydrochloric acid employed requires dried wood, and recovery of the acid is essential. The process gives high yields of sugars (to 65%) at high concentrations. The intermediate sugars first obtained, however, call for an extra processing step to reduce them to monomers, before fermentation or crystallization.

Two Japanese processes have been developed using concentrated (above 62%) sulfuric acid. In the Nihon-Mokuzai-Kagaku process, the acid is neutralized by lime, and the gypsum may be used for making gypsum board and for other purposes. In the Hokkaido process, the acid is recovered by dialysis. Two other Japanese developments are the Udic-Rheinau process, using 41 percent hydrochloric acid, and the Noguchi-Chisso process, using anhydrous hydrochloric acid. All four of these Japanese processes operate at atmospheric pressure and at temperatures below 100°C. All involve a prehydrolysis step to remove the hemicellulose because the main product is crystalline glucose.

Madison Process. In the Madison process, dilute sulfuric acid with an average concentration of 0.5 percent is pressed through wood in the form of sawdust and shavings. Regular flow of the acid and of the resulting sugar solution is one of the two principal requirements; the other is a lignin residue that can be discharged from the pressure vessels without manual labor. Both depend upon careful charging of the wood, which should not contain too many very fine particles, and upon maintaining a pressure differential of not more than 5 to 6 lb/in.^{2} between the top and the bottom of the digester.

The digesters or percolators are pressure hydrolyzing vessels, commonly employing a pressure of 150 lb/in.^{2}, and having a capacity of 2000 ft^3 each. In the original Scholler plants in Germany, the digesters were lined with lead and acid-proof brick; in the Madison process

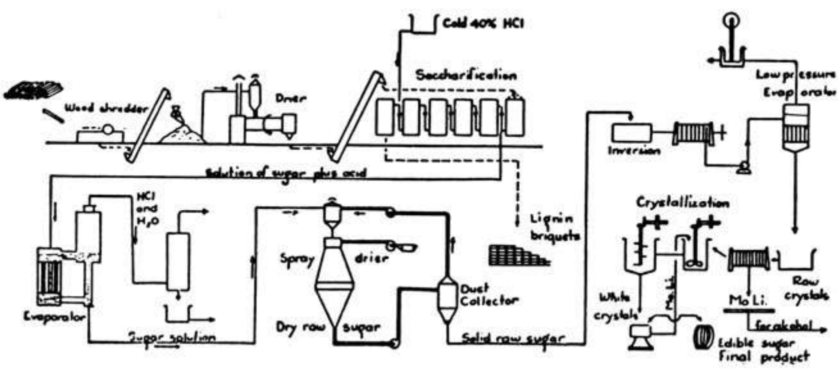


Fig. 7.23. Diagrammatic flow sheet for the Bergius wood hydrolysis process.

a lining of "Everdur" metal was found to give sufficient protection.

The wood, about 15 tons, is pressed down with steam and then is heated by direct steam, after which the acid is introduced. The practice in Germany was to bring the dilute acid into the digester in several batches, with rest periods of about 30 minutes, heating the wood to temperatures of 130°C (266°F) at first, then to 180°C (356°F), while keeping the temperature of the entering acid 10 to 20°C lower. A total of about 14 hours was required to exhaust the wood, yielding about 50 lb of carbohydrates for 100 lb of dry wood substance. In the Madison process, continuous flow of the acid, and, correspondingly, of the sugar solution, is provided—in other words, continuous percolation. The cycle is thereby reduced to 6 hours, and the yields are increased somewhat. The lignin is blown out of the digester by opening the specially constructed bottom valves while the vessel is still under pressure.

The sugar solutions usually contain about 5 percent sulfuric acid. The solutions, still under pressure (150 lb/in.^{2}), are flash-evaporated to 35 lb/in.^{2}, neutralized with lime at that pressure, and filtered. Calcium sulfate is much less soluble at the elevated temperature corresponding to the pressure than it is at 100°C. This is a fortunate circumstance, for it must be removed to an extent sufficient to avoid difficulties caused by the formation of incrustations in the subsequent alcohol distillation. The filtered solution is cooled by further flash evaporation and heat-exchanged with water to the fermentation temperature.

Sugar yields from coniferous woods (softwoods) are about 50 percent at an average concentration of 5 percent. When fermented, the average ethyl alcohol yield per ton of drywoods is 50 to 60 gallons and sometimes higher.

The dilute sulfuric acid employed in the Madison process gives lower yield (49–55%) of sugars than the Bergius-Rheinau process, and only very dilute solutions are obtained directly. Recovery of heat is easier in the Madison process, and the acid need not be recovered.

The dilute-acid hydrolysis method presently is preferred for production on a commercial scale although the yield of glucose is only about 50 percent based on the cellulose. Nearly quantitative yields can be obtained by strong-acid hydrolysis, but are offset by higher capital costs for corrosion-resistant equipment and higher operating costs for acid recovery plus acid losses. More recent efforts to hydrolyze cellulosics with dilute acid have involved innovative reactor schemes. Rugg and Brenner described equipment for a screw-fed, continuous, single-stage hydrolyzer, and Thompson and Grethlein investigated a plug-flow reactor.[33] Both processes take advantage of the improved kinetics of cellulose hydrolysis relative to glucose decomposition at higher temperatures and shorter retention times to improve sugar yields. Both also have the advantage of being simple one-stage processes.

The U.S. Forest Products Laboratory (FPL) in cooperation with the Tennessee Valley Authority (TVA) has been studying a two-stage dilute acid hydrolysis process based in part on studies of Cederquist in Sweden during the 1950s. The first stage (prehydrolysis) selectively removes the hemicellulosic sugars with dilute sulfuric acid at about 170°C prior to hydrolysis of the lignocellulosic residue to glucose in the higher-temperature (230°C) second stage. The two-stage dilute acid process has a number of important advantages: (a) the carbohydrates are fractionated into hemicellulosic sugars and glucose, so that the separate utilization of each fraction is facilitated; (b) glucose is isolated in moderately good yield (~50%); (c) the glucose solution from the second stage is moderately concentrated (~10–12%); and (d) the consumption of acid and steam is relatively low.

Despite recent efforts such as these to produce glucose from agricultural residues and wood, little attention has been given to improving the kinetic modeling of cellulose saccharification with dilute acid. Kinetic modeling plays an important role in the design, development, and operation of processes to hydrolyze cellulosics to fermentable sugar.

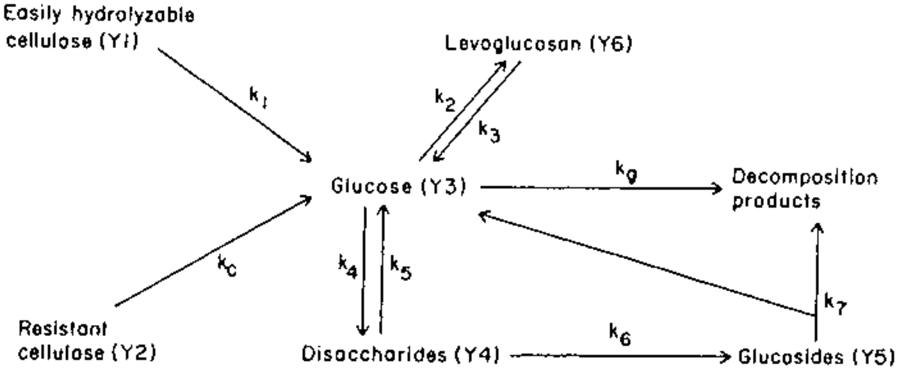


Fig. 7.24. Model for dilute acid hydrolysis of cellulosics. (*From Connor, A. H., et al.,* in Cellulose: Structure, Modification and Hydrolysis, *R. A. Young and R. M. Rowell, Eds., copyright © John Wiley & Sons, New York, 1986; with permission of the publisher.*)

A new model for the dilute acid hydrolysis of cellulose was developed at FPL in connection with studies of the two-stage dilute sulfuric acid hydrolysis process (Fig. 7.24).[34] The model incorporates the effect of the neutralizing capacity of the substrate, the presence of readily hydrolyzable cellulose, and the reversion reactions of glucose in acid solution. Although general in nature, the model was developed specifically for application to the dilute, sulfuric acid hydrolysis of prehydrolyzed wood. A computer program simulating the new model can be used to predict yields of free glucose, reducing sugars, reversion material, remaining cellulose, and glucose loss due to dehydration as a function of acid concentration, temperature, and reaction time.

Enzymatic Hydrolysis. Saccharification of wood polysaccharides to sugars can be accomplished by enzymatic techniques instead of acid hydrolysis. The U.S. Army Natick Laboratories developed a method for conversion of cellulose to glucose with a cellulose enzyme from an active strain of the fungus *Trichoderma viride.* However, extensive pretreatment of wood is necessary before sufficient enzymatic hydrolysis will take place.

Enzymatic methods show the biggest promise for conversion of waste paper from municipal waste into glucose for ethanol production. Because paper is composed primarily of wood cellulose fibers, the enzyme inhibition due to lack of accessibility with whole wood is partially alleviated. As mentioned previously, waste paper can represent up to 50 percent of typical municipal waste. Currently the separated paper from the waste is burned for its fuel value.

The Gulf Oil Company developed a method called simultaneous saccharification and fermentation (SSF) for enzymatic conversion of waste paper to ethanol.[35] In this process the cellulose is enzymatically hydrolyzed and the glucose yeast-fermented in one operation. This modification, along with improved enzyme production and performance, has made the enzymatic technique more economically viable for conversion of waste paper to ethanol. The process was donated to the University of Arkansas for further development.

Fermentation of Sulfite Waste Liquor. The sulfurous acid used in the sulfite pulping liquor causes hydrolysis of the more easily hydrolyzable components of wood, especially the pentosans in the hemicellulose. About 35 percent of the potentially fermentable sugars in the wood are hydrolyzed. However, most of them are decomposed during the long pulping procedure so that only one-fourth to one-third of the sugars, including the more resistant hexoses, remain in the waste sulfite liquor. If these sugars are fermented by yeast, about 12.5 gallons of 95 percent alcohol per ton of wood may be produced.

A large number of plants in Europe and a few in North America have been constructed to utilize the sugar hydrolyzate in sulfite waste liquors. The procedure as carried out in one American operation is as follows:

The liquor is recovered from the digester by discharging it in such a manner that as much sugar as possible is removed with a minimum of dilution by washing. Free sulfur dioxide is removed and recovered by blowing steam through the solution, which decreases the acidity from a pH of 2.2 to a pH of about 3.9. The liquors are cooled by a vacuum flash and neutralized by lime to a pH of about 4.2. A small amount of inorganic nitrogen is added for yeast growth, and about one percent by volume of yeast is added continuously. Fermentation is carried out in a series of tanks, the solution flowing from one to the other with agitation to keep the yeast in suspension. The yeast is recovered by centrifuging and mixed with the new sugar solution entering the fermenter. About 30 hours is required for fermentation. The alcohol content of the fermented liquor is about one percent by volume. The ethyl alcohol is recovered in stainless steel stills. Methanol and other alcohols are obtained in small amounts as by-products.

Thermal Decomposition

When wood is heated in the absence of air or with only limited amounts of air, thermal degradation takes place. This begins at about 100°C and increases with rising temperature. At about 270°C exothermic reactions set in, causing a rise in temperature (usually held at 400–500°C) bringing about complete carbonization. The products are charcoal, condensable liquids, and noncondensable gases.[36] The condensable liquids separate into aqueous (pyroligneous acid) and oil and tar fractions (Fig. 7.25). The charcoal, the gases (low Btu gas), and the oil fractions all may be used as fuels.

A number of terms are used for the thermal decomposition of wood and generally refer to similar processing methods: *carbonization, pyrolysis, gasification, wood distillation, destructive distillation*, and *dry distillation*. All result in the thermal breakdown of the wood polymers to smaller molecules in quantities dependent on reaction conditions. The hydrogen content of the gas increases with increasing temperature of pyrolysis. The wood gas has a fuel value of 300 Btu/ft^3.

The yields of the different materials obtained by pyrolysis vary with the species of woods used and the type of equipment and system employed. Manipulation of three variables, mainly the temperature, heating rate, and gas residence time, can greatly alter the relative proportions of the gas, liquid, and char produced. For example, the oil and tar yields can be varied between 1 and 40 percent and the char between 40 and 10 percent or less. Low temperatures favor liquids and char, low heating rates favor gas and char, and short gas residence favors liquids. Conversely, high temperatures favor gas, high heating rates favor liquids, and long gas residence times favor gas. Thus, the various product fractions can be preferentially manipulated by proper combinations of these variables.

During World War II in Germany, automobiles were fueled by the gases produced from thermal decomposition of wood; and research is ongoing today on the more efficient gasification of wood. Destructive distillation has been used throughout most recorded history to obtain turpentine from pinewood, as discussed later in the chapter.

Low Btu Gas and Oil. There has been considerable research activity to produce low Btu gas and oil from wood for energy. The Georgia Institute of Technology and the Tech-Air Corporation have intensively studied pyrolysis of biomass materials and have built several pilot plants. Their pyrolytic process (GT/T-A) has been applied to forestry residues. Their plant differs from the older wood-distillation plants, such as the Badger-Stafford retorts used in the 1930s, in several respects, such as the use of smaller-sized equipment to process 7 dry tons/hr compared to 3 to 4 tons/hr, the use of wood dried to 7% moisture

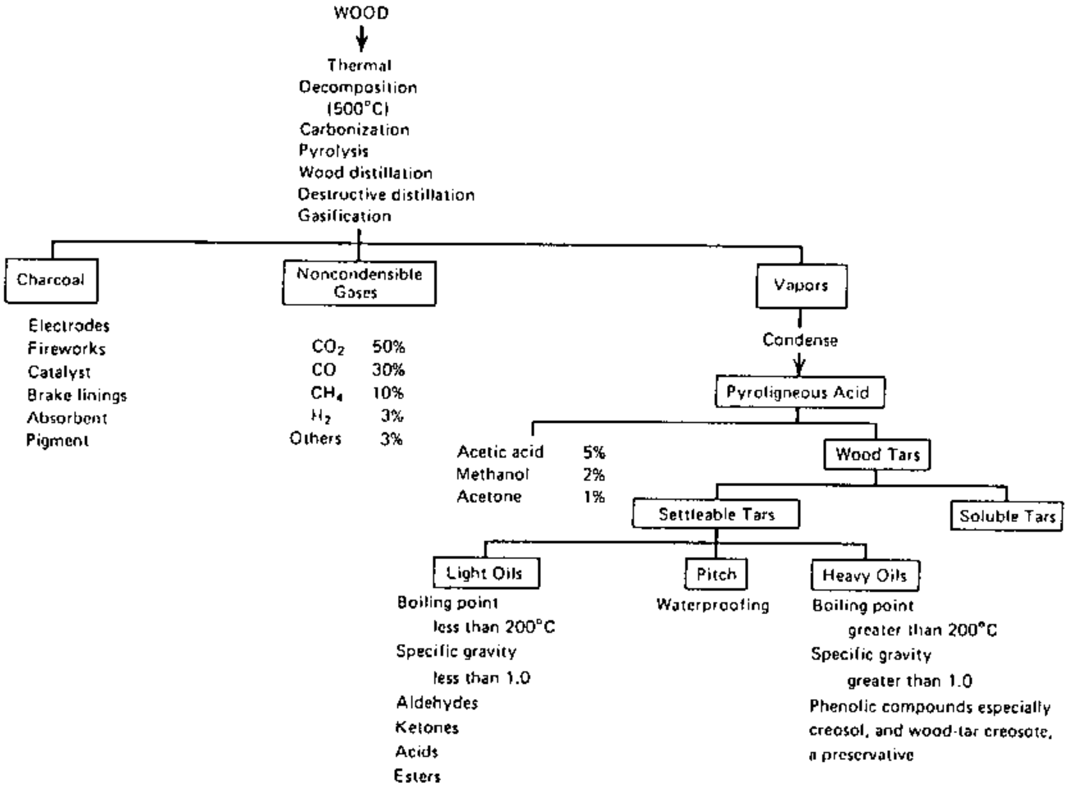


Fig. 7.25. Products obtained from the thermal decomposition of wood. (*From* Introduction to Forest Science, *2nd ed., R. A. Young and R. L. Giese, Eds., copyright © 1982 John Wiley & Sons, New York; with permission of the publisher.*)

instead of to less than 0.5%, and the use of a small quantity of air inside this retort (approx. 0.25 lb/lb feed) to sustain the reaction instead of using gases in order to heat it to 1000°F. The on-line time of the rated capacity for the GT/T-A system is claimed to be better than 90 percent, as compared to 67 percent for the Badger-Stafford units.

For the GT/T-A system the wood material is hogged so that the maximum size is not more than about one inch in any dimension. Sawdust may be used directly. The relatively uniform material is conveyed to a dryer where it is dried to about 7 percent water content. The dryer is heated by a portion of the wood gas from the reactor, and should this not be sufficient, the oil produced during pyrolysis can be used as a backup fuel.

The dried wood is fed into the top of the reactor though an air-lock and moves downward by gravity. A sensing device measures the bed height and controls the input of the wood. The temperature increases from 350 to 500°F at the top of the bed to 1000 to 1700°F in the pyrolysis zone. The gases move upward through the bed of descending wood and leave the top at 350 to 500°F. The reactor is operated at slightly under atmospheric pressure by an induced draft fan. The charcoal passes through an outfeed device at the bottom of the reactor into a sealed chamber, where it is cooled by a water spray and then conveyed to a storage bin. The rate of charcoal discharge controls the rate of passage of material though the unit.

The gases from the reactor pass into a scrubber where they are sprayed with cooled pyrolytic oil, which removes particulates and cools the gas stream to 180 to 200°F, causing condensation of the condensable organic substances into an oil mixture. The oil is filtered, the filter cake returned to the reactor, and the filtered oil pumped to a tank, cooled, and then recirculated through the scrubber. Excess oil is pumped to a storage tank.

The gases from the scrubber-condenser contain the noncondensable gases, low-boiling organic vapors, and water vapor. A portion of the gases is used to heat the wood dryer, and the remainder are available as a fuel for other purposes, but it is desirable that they be used near the pyrolysis plant.

Operating conditions can be controlled to vary the distribution of the energy among the products: gas, oil, and charcoal. Thus, high yields of charcoal can be obtained with correspondingly reduced yields of oil and gas and vice versa, or the unit may be operated as a gasifier with only a 3.8 percent yield of charcoal. The off-gases in the latter case can be burned directly in a gas-fired boiler, or the condensable oils can be removed first and used separately as fuel. The total energy recovery in the form of wood gas, oil, and charcoal is about 95 percent of the energy in the dry wood used in the process.

Gasification. Gasification is the thermal degradation of wood or other carbonaceous material in the presence of controlled amounts of oxidizing agents, such as air or pure oxygen. It is carried out at higher temperatures than those used in the pyrolysis process, up to around 1000°C. Hence, the reaction rates are very fast, making equipment design critical. The thermal efficiency for conversion of wood to gases is 60 to 80 percent, which compares favorably with that of coal. Wood gasification offers several advantages over coal: (1) much lower oxygen requirements, (2) practically no steam requirements, (3) lower costs for changing H_2/CO ratios, which are already higher in wood gas, and (4) no or very little desulfurization costs. Coal has an advantage in that larger plants can be built for coal gasification than is normally the case for wood, because of its procurement advantages.

As noted above, the GT/T-A pyrolysis system also can be used as a gasifier by increasing the amount of air to the reactor and screening the charcoal and recycling the coarser particles to the incoming feed material. In this way, most of the wood is converted to gas and oil. If all the off-gases from the converter are conducted directly into a boiler as a hot gaseous fuel, then the GT/T-A process is essentially a gasifier. This requires that the gases be utilized as a fuel close to the pyrolysis plant. The use of air in the reactor results in the presence of nitrogen in the gas, causing a reduction in fuel value from 360 to 420 Btu/ft^3 (without air) to 140 to 200 Btu/ft^3 (with air).

Several gasifiers have been designed to handle municipal refuse, wood wastes, and other biomass materials. Basically, gasifiers fall into two types: (1) those that use air and (2) those using oxygen. An example of the air system is the Moore-Canada gasifier. The wood residues are carried on a moving bed through stages of drying, reduction, and char oxidation, and the ash is discharged in granular form. The maximum temperature in the reaction zone is about 1222°C. The hydrogen content of the crude gas is increased from 8 to 10 percent up to 18 to 22 percent by adding steam to the air intake.

The Union Carbide Company Purox gasifier is an example of the oxygen system. This unit also uses a moving-bed reactor. Pure oxygen is the oxidizing agent used to convert the char into CO and CO_2. Molten ash leaves the bottom at about 1670°C.

If air is used, the crude gases contain about 46 percent nitrogen, which must be removed by cryogenic means; but if oxygen is used, it first must be separated from air, with oxygen and nitrogen separated by a cryogenic system. (Chapter 13). The crude gases also contain an oil and tar fraction, about 2 percent of the wood (dry basis). Gasifiers designed for wood operate at atmospheric pressure in contrast to coal gasifiers, which operate at pressures up to 400 psi.

The composition of the wood gas varies according to the technology used. If the limited oxygen required is supplied by air, a typical gas might contain 10 to 18 percent H_2, 22 to 30 percent CO, 6 to 9 percent CO_2, 45 to 50 percent N_2, and 3 to 5 percent hydrocarbons and have a heating value of about 1700 kcal/m^3 (180 Btu/ft^3). If pure oxygen is supplied to the process, the gas might contain 24 to 26 percent H_2, 40 percent CO, 10 percent hydrocarbons, and 23 to 25 percent CO_2 and have a heating value of 2900 kcal/m^3 (350 Btu/ft^3). The gas may be used directly as a fuel in a variety of ways; for example, supplying boiler energy in an industrial plant at the rate of 2.5×10^8 kcal/hr from about 136 kg/day of dry wood.

The technology of gasification is under active development in both equipment and process design to reduce capital costs, and in the chemistry of the process to improve yields and obtain more favorable gas ratios. The latter includes the use of catalysts to enhance the process and to promote the formation of specific products, such as methane or ethylene for increased thermal efficiency or for feedstocks for chemical synthesis.

Methanol. As is the case with ethanol, the concept of producing methanol from wood is now new. Methanol obtained from the destructive distillation of wood represented the only commercial source until the 1920s. The yield of methanol from wood by this method is low, only about 1 to 2 percent or 20 liters/metric ton (6 gal/ton) for hardwoods and about one-half that for softwoods. With the introduction of natural gas technology, the industry gradually switched to a synthetic methanol formed from a synthesis gas (syngas) produced from reformed natural gas. Two volumes of H_2 and one volume of CO are reacted in a catalytic converter at pressures of 1500 to 4000 psi to produce methanol. Presently, 99 percent of the methanol produced in the United States is derived from natural gas or petroleum.

Methanol also may be produced from wood gas; so wood could be a future raw material for making methanol, especially for use as an additive to gasoline for internal combustion engines. Thus reforming the gasification products obtained at high temperatures is a second method for the production of methanol from wood. This is in contrast to the older method (destructive distillation), which directly yields small quantities of methanol at lower temperatures as mentioned above.

If wood gas is produced in a gasifier using air as the oxidizing agent, the nitrogen (about 40%), as well as the CO_2 must be removed. The CO_2 is removed by passing the gas through hot potassium carbonate followed by scrubbing with monoethanolamine. The nitrogen, hydrocarbons, residual CO_2, and water are removed by freezing them out in a cryogenic system. By means of an iron catalyst, a "shift conversion" of a portion of the CO is carried out with steam in order to reach the required two parts of H_2 to one part of CO, as follows:

$$CO + H_2O \xrightarrow{\text{catal.}} H_2 + CO_2$$

$$\Delta H = -590 \text{ Btu/lb CO}$$

The pressurized gas then is led to the methanol reactor. Two different catalyst systems may be used: (1) a zinc–chromium catalyst requiring gas pressures of 2000 to 4000 psi or (2) a copper catalyst system at 1000 to 2000 psi. About 95 percent of the gas is converted to methanol by this exothermic reaction:

$$2H_2 + CO \xrightarrow{\text{catal.}} CH_3OH$$

$$\Delta H = -1200 \text{ Btu/lb CO}$$

The yield of methanol with present technology is about 390 liters/ton of oven dry wood. Conversion of wood to methanol is less efficient than producing methanol from natural gas or coal—about 38 percent compared to about 60 percent, based on the heat value of methanol as a percent of the total energy input into the plant.

The raw materials cost is the most significant operating cost. The production cost for methanol from wood is estimated to be almost twice that produced from natural gas. Improving the efficiency of the gasifier reactor to increase the quantities of CO and H_2 produced from wood would enhance the process.

Charcoal and Other Chemicals. Production of charcoal and tars by destructive distillation is the oldest of all chemical wood-processing methods. Charcoal probably was first discovered when the black material left over from a previous fire burned with intense heat and little smoke and flame. For centuries, charcoal has been used in braziers for heating purposes. Destructive distillation of hardwoods has been carried out with charcoal the product sought and volatiles as by-products; with softwoods (pines), volatiles were the principal products (naval stores), with charcoal considered a by-product.

In the United States, charcoal production began in early colonial days. During this period, principal uses of charcoal were as a fuel in blast furnaces for the production of pig iron and as an ingredient of gunpowder. Charcoal needed by the iron industry had to have a high crushing strength, and thus was made from dense hardwoods such as maple, birch, oak, and hickory. A softer charcoal was preferred for making gunpowder and was produced from willow and basswood. The first successful blast furnace was built in Saugus, Massachusetts, in 1645. Other furnaces were started in close proximity to iron ore deposits. These early furnaces were small, usually producing only 1 to 3 metric tons of pig iron per day. In the late 1880s, wood charcoal lost its metallurgical market to coke, which was better suited to the demands of the larger furnaces then being built.

In 1812, the additional collection, by condensation, of the volatile substances from hardwood carbonization began; the products then were charcoal, crude pyroligneous acid, and noncondensable gases. The pyroligneous acid was refined to produce methanol, acetate of lime, which in turn was used to make either acetic acid or acetone and tar. The noncondensable gases in a normal wood distillation consisted of about 50 percent carbon dioxide, 30 percent carbon monoxide, 10 percent methane, 3 percent heavier hydrocarbons, and 3 percent hydrogen.[5] Table 7.10 gives the yields of products from an industrial operation. The tars and noncondensable gases usually were used as fuel. From the late 1800s until the 1920s, destructive distillation of hardwoods was an important source of industrial acetic acid, methanol, and acetone. This market was lost when these materials were made synthetically from petroleum. In 1920, there were approximately 100 plants recovering these products from hardwood distillation; the last of these plants ceased operation in 1969. The reader interested in details of the wood distillation processes is referred to the 1962 edition of *Riegel's Industrial Chemistry*, Chapter 15.

TABLE 7.10 Yield of Products from Destructive Distillation of One Ton of Dry Hardwood

Product	*Quantity*
Charcoal	270 kg (600 lb)
Noncondensable gas[a]	150 m^3 (5000 ft^3)
Soluble tar	83.6 liters (22 gal)
Pitch	29.7 kg (66 lb)
Creosote oil	12.5 liters (3.3 gal)
Methanol	11.8 liters (3.1 gal)
Acetone	2.7 liters (0.7 gal)
Allyl alcohol	0.2 liters (0.5 gal)
Ketones	0.8 liters (0.2 gal)
Methyl acetate	3.8 liters (1.0 gal)
Acetic acid	45.5 kg (101 lb)

Source: U.S.D.A. Forest Service Data.
[a] Composition in order of highest to lowest: CO_2, CO, CH_4, H_2, others.

In the early 1900s, charcoal from by-product recovery plants usually was used for cooking and heating in low-income areas and was known as a "poor man's fuel." Beginning in about 1950, there was an upturn in demand for charcoal for recreation use. In this era of suburban living, the use of charcoal briquettes for cookouts represents a significant market. The charcoal briquette now can be considered a luxury fuel, as it is too expensive for heating.

Basic techniques for producing charcoal have not changed over the years although the equipment has. Charcoal is produced when wood is burned under conditions in which the supply of oxygen is severely limited. "Carbonization" is a term that aptly describes the thermal decomposition of wood for this application. Decomposition of carbon compounds takes place as the temperature rises, leading to a solid residue that is richer in carbon than the original material. Wood has a carbon content of about 50 percent, whereas charcoal of a quality suitable for general market acceptance will be analyzed as follows: fixed carbon 74 to 81 percent, volatiles 18 to

23 percent, moisture 2 to 4 percent, and ash 1 to 4 percent. Charcoal with a volatile content over 24 percent will cause smoking and is undesirable for recreational uses.

Earthen "pit kilns" originally were used to produce charcoal. A circular mound-shaped pile of wood (15 to 45 cords) was built up with an open core 30 to 60 centimeters (1 to 2 feet) in diameter to serve as a flue. The entire surface of the pile, except for the top flue opening and several small openings around the bottom periphery, then was covered with dirt or sod sufficiently thick to exclude air. The mound was allowed to "coal" for 20 to 30 days to give the final product.

In the second half of the nineteenth century, brick or masonry "beehive" kilns came into widespread use. The capacity of many of these kilns was from 50 to 90 cords, and operation was essentially the same as for the pit kilns. Many other types of kilns have been used from time to time. Small portable sheet-metal kilns of 1 to 2 cords have been widely used, as have rectangular masonry block kilns of various designs. These were predominantly used by farmers and small woodlot owners.

Large-scale production of charcoal was done by distilling the wood in steel buggies in long horizontal ovens. The buggies rode in steel rails that carried the cars in line from predryers to the ovens and then to coolers. Charcoal was produced by this method in a matter of 24 hours. The latest types of charcoal-producing equipment are designed for continuous operation and make use of residues instead of roundwood. An example is the Herreshoff multiple hearth furnace, in which several hearths or burning chambers are stacked on top of one another, the number depending on capacity. Production in this type of furnace is from 1 to $2\frac{1}{2}$ metric tons of charcoal per hour.

Thermochemical Liquefaction

Although a reasonable amount of research effort has been expended on thermochemical liquefaction of wood, extensive commercialization of this process is not anticipated in the near future. The basis of the method is a high-pressure and high-temperature treatment of wood chips in the presence of hydrogen gas or syngas to produce an oil instead of a gas. The low-grade oil produced potentially could be substituted for some present petroleum uses.

An oil of a heating value of about 35,200 Btu/kg can be obtained by reaction of wood waste for one hour with syngas, a catalyst, a temperature of 750°F, and a pressure of 5000 psi. The feasibility of the process has been tested in a pilot plant in Albany, Oregon, based on laboratory work conducted at the U.S. Bureau of Mines. So far, it has been determined that a barrel of oil equivalent to No. 6 bunker fuel can be produced from about 405 kg of wood chips.[37]

A similar process was developed in Japan in the 1950s specifically to degrade lignin. Called the Noguchi process, it was thought to hold promise for production of phenols from lignin. By 1955, the Japanese investigators had discovered superior catalysts that converted a substantial portion of the lignin into a relatively few phenols. The Crown-Zellerbach Corporation (now defunct) subsequently obtained an option on the process and initiated its own trials. Despite several improvements researchers were able to make, the process did not prove profitable at the time. However, the company was routinely able to obtain a yield of 55 percent (and up to 65%) of distillable products. The major drawback was the inability to separate cleanly even the few different phenols remaining after the reactions.

NAVAL STORES

The U.S. naval stores industry began in the very early colonial days, when wooden vessels used tar and pitch from the crude gum or oleoresin collected from the wounds of living pine trees. The demand for tar and pitch from crude gum is now of minor importance.

The industry is centered in the southeastern United States and is confined to the longleaf and slash pine areas. There is also a small, but locally important, naval stores–producing area in the Landes region of southwestern France, based on the maritime pine.

There are three routes by which naval stores are produced. The oldest method is the tapping of living trees to cause a flow of oleoresin. The second method is removal of naval stores by solvent extraction. The latter process now has replaced steam distillation as a means of recovering turpentine. In the United States, the latest and now the most important route is kraft (sulphate) pulping of pine, during which turpentine and tall oil are recovered as by-products of kraft pulp manufacture. A fourth process, no longer used in the United States, is recovery of turpentine and pine oils by the destructive distillation of pine wood.[38]

Worldwide, about 60 percent of naval stores are produced by tapping living trees, whereas gum naval stores account for only 4 percent of U.S. production. The sulfate process is now the major U.S. process.

Turpentine is a volatile oil consisting primarily of terpene hydrocarbons, having the empirical formula $C_{10}H_{16}$. These 26 atoms can have many different arrangements, only six of which are present in appreciable amounts in commercial turpentines: alpha-pinene (b.p. 156°C), beta-pinene (b.p. 164°C), camphene (b.p. 159°C), Δ^3-carene (b.p. 170°C), dipentene (b.p. 176°C), and terpinoline (b.p. 188°C). The molecular configurations of some of these are shown in Fig. 7.26.

Gum and sulfate turpentines have similar compositions. Gum turpentine contains 60 to 65 percent α-pinene, 25 to 35 percent β-pinene, and 5 to 8 percent other terpenes, compared to 60 to 70 percent α-pinene, 20 to 25 percent

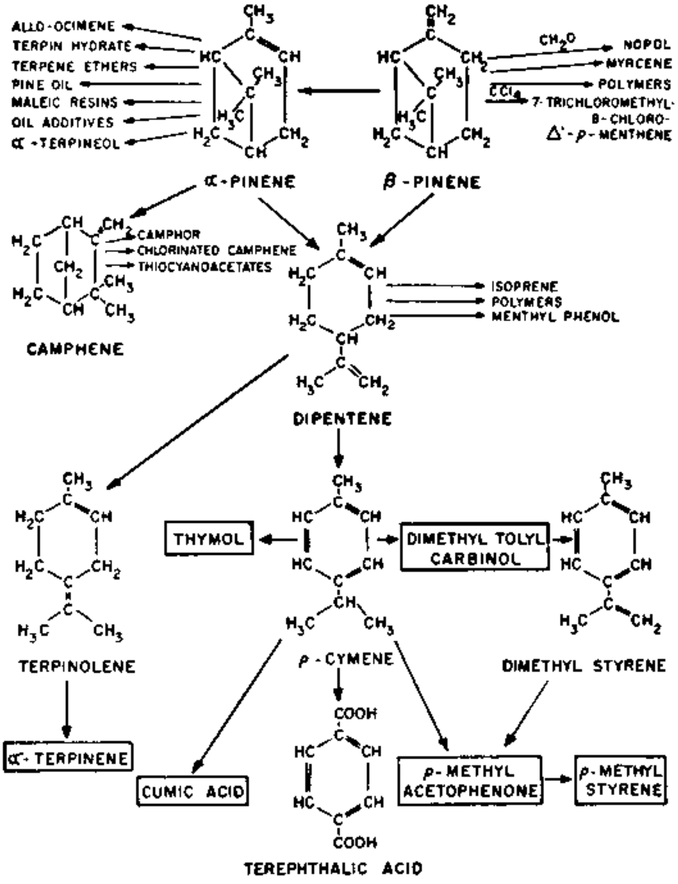


Fig. 7.26. Some reactions of alpha-pinene and beta-pinene. (From *Goldblatt, L. A., "Yearbook of Agriculture," U.S.D.A., 1950–51*).

β-pinene, and 6 to 12 percent other terpenes for sulfate turpentine. Wood turpentine, which has 75 to 80 percent α-pinene, has no or very little β-pinene (0–2%), and also contains 4 to 8 percent camphene and 15 to 20 percent other terpenes.

Rosin, the other major naval stores product, is a brittle solid that softens at 80°C. Chemically it is composed of about 90 percent resin acids and 10 percent neutral matter. The resin acids are mainly *l*-abietic acid and its isomers, $C_{20}H_{30}O_2$. These are tricyclic monocarboxylic acids and are diterpenes.

Rosin is graded and sold on the basis of color, the color grades ranging from pale yellow to dark red (almost black). The color is due almost entirely to iron contamination and oxidation products. Fresh oleoresin, as it exudes from the tree, will yield a rosin that is nearly colorless. Color-bodies are removed by selective solvents and selective absorption from a 10 to 15 percent gasoline solution passed through beds of diatomaceous earth. About 70 percent of the world's rosin is produced in the United States. Naval stores also include important fatty acids, as well as steroids and other products.

Gum Naval Stores

The crude gum or oleoresin is obtained from healthy trees by exposing the sapwood. The lower part of the tree is faced, that is, a section of bark is removed, giving a flat wood surface for the gutters, which are inserted into a slanting cut made by a special ax. The gutters conduct the gum to a container that can hold 1 to 2 quarts of gum. At the top of the exposed face, a new V-shaped strip of bark is removed about every two weeks.

The operations of inserting gutters, hanging cups, and cutting the first bark preferably are done in December or January, as early facing stimulates early season gum flow. The gum continues to flow until November, with the height of the season being from March to September. The collected gum is distilled from a copper still; turpentine and water pass over, and the rosin is left in the still. The remaining molten rosin, plus impurities, is passed through a series of strainers and cotton batting to remove dirt particles. Then the liquid rosin is run into tank cars, drums, or multiwall paper bags for shipment.

Increases in yield of naval stores are brought about by chemical treatment of the exposed wood, especially with paraquat herbicides (dipyridyl compounds). This treatment stimulates extensive oleoresin formation and diffusion into the wood, extending to the pith of the tree and several feet above the treatment level. As much as 40 percent oleoresin content in the wood has been produced. Such treatment could double naval stores production, for both gum and sulfate processes. It also has the potential of providing a new type of wood naval stores by solvent extraction prior to kraft pulping, or a combination of both methods.

Wood Naval Stores

"Wood" naval stores are produced by solvent extraction of resin-rich wood from old southern pine stumps and roots. The depletion of these stumps from the large trees of virgin forests, combined with high labor costs, has brought about a major decline in the production of wood naval stores by this process.

In modern practice, all the resin products are removed from the shredded wood by solvent extraction; the solvent retained by the extracted wood chips is recovered by steaming. Extraction is carried out with naphtha (b.p. 90–115°C fraction). Multiple extraction is carried out in a series of vertical extractors in a countercurrent manner, whereby fresh solvent is used for the final extraction of a charge.

The solution from the extractors is vacuum-distilled and the solvent recovered. The remaining terpene oils are fractionally redistilled under vacuum and recovered as turpentine, dipentene, and pine oil. The nonvolatile rosin is of dark color and is upgraded by clarification methods, such as selective absorption of its solution (bed-filtering).

Sulfate Naval Stores

Sulfate turpentine is obtained as a by-product during the kraft pulping of pine woods. Vapors periodically released from the top of the digesters are condensed, and the oily turpentine layer is separated and purified by fractional distillation and treatment with chemicals to remove traces of sulfur compounds. Sulfate turpentine is very similar to gum turpentine obtained from the oleoresin of the tree and contains 60 to 70 percent α-pinene, 20 to 25 percent β-pinene, and 6 to 12 percent other pinenes. Sulfate turpentine from western North America woods contains appreciable amounts of Δ^3-carene, which is used as a solvent. In the United States, about 80 percent of the annual production of turpentine is from the kraft pulping of southern pines (approximately 125 million liters).

The spent black liquor from the kraft pulping of pines contains the less volatile products of the wood resin in the form of sodium salts or soaps. The liquor first is concentrated in multiple-effect evaporators, and then the concentrate is sent to settling tanks. The soaps rise to the surface, are skimmed off, and then are acidified with sulfurous or sulfuric acid. The crude tall oil rises to the top and is mechanically separated. Crude tall oil from southern pines contains 40 to 60 percent resin acids and 40 to 55 percent fatty acids with 5 to 10 percent neutral substances. These components are separated by fractional distillation under vacuum.

One metric ton of crude tall oil yields about 350 kg of rosin, 300 kg of fatty acids, and 300 kg of head and pitch fractions. For each metric ton of pulp produced, northern pines yield about 50 kg of tall oil, and the southern pines yield about 125 kg. The U.S. capacity for fractional distillation of tall oil is nearly one million metric tons per year.

The rosin component of tall oil is mostly made up of resin acids, which are diterpene derivatives. The major compounds (figures indicate averages) are as follow:

1. Abietic type—abietic (32%), neoabietic (4%), palustric (10%), and dehydroabietic (30%) acids.
2. Pimaric type—pimaric (4%), isopimaric (10%), and sandara copimaric acids (small amounts).

The fatty acids from tall oil have the following components: oleic (50%), linoleic (35%), conjugated linoleic (8%), stearic (2%), palmitic (1%), and others (4%). From tall oil heads, a fraction is produced that is composed predominantly of saturated acids, containing 55 percent palmitic acid. Oleic acid is distilled in grades that are 99.5 percent pure.

The neutral or "unsaponifiable" materials present in tall oil include anhydrides, phenolics, diterpene aldehydes and alcohols, stilbenes, and steroids. In the neutral fraction of southern pine tall oil soap, 80 compounds have been identified. They include 25.1 percent sistosterol and a total of 32.4 percent steroids. The sistosterol content of crude tall oil is 2 to 3 percent and is the main component of the neutral fraction.

Uses of Naval Stores Products

Navel stores products have a wide range of uses from ordinary household commodities to complex industrial applications, as outlined below.[38]

Turpentine. Turpentine is used directly as a solvent, thinner, or additive for paints, varnishes, enamels, waxes, polishes, disinfectants, soaps, pharmaceuticals, wood stains, sealing wax, inks, and crayons, and as a general solvent. The chemistry of its monoterpenes offers many possibilities for conversion to other substances, as illustrated in Fig. 7.26. There is increasing use of turpentine to produce fine chemicals for flavors and fragrances. An important use of turpentine is in conversion by mineral acids to synthetic pine oil. It also is a raw material for making terpin hydrate, resins, camphene, insecticides, and other useful commodities. These uses are included in the following summary of its applications:

- Solvents for paints, etc. (11%).
- Synthetic pine oil (48%), used for mineral flotation, textile processing, solvents,

odorants, bactericides, and conversion to their chemicals such as terpin hydrate, etc.
- Polyterpene resins (600–1500 mol. wt.) (16%), used for adhesives, pressure-sensitive sizes (dry cleaning, paper, chewing gum).
- Camphene → toxophene insecticides (16%).
- Flavor and fragrance essential oils (9%).

Dipentene. Dipentene is present in the higher-boiling fractions of wood turpentine. It is used in paints and varnishes and as a penetrating and softening agent in rubber reclamation.

Pine Oil. Pine oil obtained from wood naval stores has similar uses to those of the synthetic pine oil made from turpentine, given above.

Rosin. Rosin is used mainly in some modified form. Because the abietic-type acids in rosin each contain a carboxyl group and double bonds, they are reactive and can be used to produce salts, soaps, esters, amines, amides, nitriles, and Diels-Alder adducts; and they can be isomerized, disproportionated, hydrogenated, dimerized, and polymerized. When destructively distilled, rosin produces a viscous liquid, termed rosin oil, used in lubricating greases.

The paper industry uses large amounts of the sodium salt of rosin as paper size, which accounts for the greatest single use of rosin. The synthetic rubber industry is the second most important user of rosin. In making styrene-butadiene rubber, disproportionated rosin soaps are used alone or in combination with fatty acid soaps as emulsifiers in the polymerization process. Disproportionation decreases the number of double bonds in the abietic acid of the rosin, making a more stable material.

The adhesives industry is the third most important market for rosin. Rosin, modified rosins, and rosin derivatives are used in several types of adhesives, including the pressure-sensitive, hot-melt, and elastomer-based latices, and solvent rubber cements.

Protective coatings are the fourth major user of rosin, either directly or in a modified or derivative form. Varnishes and alkyds are the most common types of protective coatings using rosin. Rosin is combined with a heat-reactive phenol-formaldehyde resin to produce a widely used varnish. Printing inks also use substantial amounts of rosin.

The above rosin uses are summarized as follows:

- Paper size (33%).
- Chemical intermediates and rubber (42%).
- Resins and ester gums (18%).
- Coatings (3.9%).
- Other uses (3.1%).

Fatty Acids. Of the total fatty acids produced annually in the United States, amounting to more than 450,000 tons, 35 percent come from tall oil. The solvent extraction of pine wood yields only one percent fatty acids and their esters. The yield is not increased, however, by paraquat (dipyridyl herbicides) treatment. Hence, the kraft-pulping industry will continue to be the major source of fatty acids from wood. The approximate distribution of uses of the fatty acids are:

- Intermediate chemicals (43%).
- Protective coatings (28%).
- Soaps and detergents (11%).
- Flotation (3%).
- Other uses (15%).

A future product from the neutral fraction of tall oil may be sistosterol. This chemical has potential use in the synthesis of cortisones and other steroids and hormones by fermentation processes.

ADDITIONAL CHEMICALS FROM WOOD

A variety of additional chemicals are derived directly from wood or as by-products from the pulp and paper industry.

Tannins and Other Extractives

The tissues of wood, bark, and the leaves of trees contain a great variety of chemical substances of considerable scientific interest and some of practical value. Turpentine, pine oil, and rosin from the resins of pines are the most important commercial extractives from American woods.

Tannin is a commercially important substance that can be extracted from the wood, bark, or leaves of certain trees and other plants. Tannins are complex dark-colored polyhydroxy phenolic compounds, related to catechol or pyrogallol, and vary in composition from species to species. They have the important property of combining with the proteins of animal skins to produce leather.

For many years, most of the leather in the United States was tanned with domestic tannins from hemlock and oak bark and from chestnut wood. Today only a small amount of tannin comes from these and other domestic sources. The most important source of vegetable tannin today is the wood of the quebracho tree, which grows mainly in Paraguay and Argentina. The tannin content of this tree and a few other sources of vegetable tannin are shown in Table 7.11.

The wood or bark for tannin production is reduced to chips and shreds by passing the material through hoggers or hammer mills. Then it is extracted with warm water in diffusion batteries. The dilute solutions are evaporated to the desired concentration. Loss of solubility of the tannin can be counteracted by treatment of the concentrate with sodium sulfite.

TABLE 7.11 Tannin Content of Some Plant Materials

Plant Material	*Percent Tannin*
Domestic sources	
Eastern hemlock bark	9–13
Western hemlock bark	10–20
Tanbark oak	15–16
Chestnut oak	10–14
Black oak	8–12
Chestnut wood	4–15
Sumac leaves	25–32
Foreign sources	
Quebracho heartwood	20–30
Mangrove bark	15–42
Wattle (*acacia* bark)	15–50
Myrobalan nuts	30–40
Sicilian suma leaves	25–30

Furfural

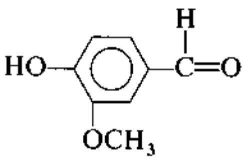
An additional, potentially important chemical derivable from wood as a result of hydrolytic (acid) treatment is furfural. Furfural is derived from the hemicellulose fraction of wood—specifically from the five-carbon or pentose sugars (primarily xylose). The pentose sugars are not yeast-fermentable by standard methods to ethanol but can be treated with acid, which causes dehydration and yields furfural.

$$\text{Hemicellulose} \xrightarrow{\text{Acid}} \text{Pentosans} \xrightarrow{\text{Acid}} \text{Furfural} \xrightarrow{\text{Reduce}} \text{Furfuryl alcohol}$$

Most furfural is produced from corncobs and oat and rice hulls, primarily by the Quaker Oats Company. The product is used in the chemical industry as a solvent and in wood rosin refining. A large amount of furfural is treated further to give furfuryl alcohol. The furfuryl alcohol is added to urea-formaldehyde resins in applications for adhesives and foundry core binders.

Vanillin

Vanillin is not a product of hydrolysis or of fermentation; in fact, it does not originate from the holocellulose, but rather than the lignin portion of the wood. The major organic material in sulfite waste liquor (spent liquor, after pulping wood by the sulfite process) is the lignin dissolved from the wood as lignosulfonic acid. Alkaline degradation of this lignin product produces vanillin, the same substance that occurs naturally in the vanilla bean:



Vanillin

With the Howard process, 5 to 10 percent vanillin is produced, based on the lignin in the waste sulfite liquor. Some vanillin is produced from sulfite waste liquor in both the United States and Canada.

Dimethyl Sulfide and DMSO

Dimethyl sulfide (DMS) is recovered from the waste black liquor from the kraft pulping process by flash drying of the liquor after the DMS content has been increased by additions of sulfur. DMS is an odorant for natural gas and a solvent. DMS is oxidized to give dimethylsulfoxide (DMSO), an important solvent and a medicinal of interest in the treatment of arthritis.

Medicinals

The bark of the cascara tree of the northwestern region of the United States yields cascara, a laxative used in medicine. Several hundred tons of bark are harvested annually. Recently, one of the most promising anticarcinogenic compounds to be discovered in the last 15 years was found in the bark and weed of the Pacific Yew tree from the Pacific Northwest of the United States. This compound, taxol, is now being evaluated on a large scale by the National Cancer Institute.

The red gum tree of the southern United States exudes a yellowish balsamic liquid or gum from wounds, which is known as storax. It is produced by removing a section of bark and incising the wood in much the same manner as that used for the production of naval stores gum described above. Storax is used in medicinal and pharmaceutical preparations, such as adhesives and salves, and as an incense, in perfuming powders and soaps, and for flavoring tobacco.

Biotechnology Chemicals

As with pulping and bleaching, biotechnology too could have a considerable impact on the production of chemicals from wood and other forms of plant biomass. The effects of biotechnology probably will be noticed first in areas of enzymatic hydrolysis of polysaccharides and fermentation technology.

It should be possible to improve the efficiency of the cellulose enzyme complex for hydrolyzing cellulose to glucose. The enzyme complex apparently contains decrystallizing and hydrolysis enzymes that work together to convert cellulose to glucose. Isolation of the specific enzymes and genetic engineering could provide a more efficient complex.

As discussed earlier in this chapter, enzymes are the basis for yeast conversion of hexose (six-carbon) sugars, such as glucose and mannose, to ethanol. These enzymes also could be genetically engineered to improve the efficiency of alcohol production; several biotechnology firms are exploring this possibility.

The yeast (*Saccharomyces cerevisiae*) enzymes are specific to six-carbon sugars, but wood and other forms of biomass also contain large quantities of pentose sugars, especially xylose in hardwoods. The pentoses are not fermentable to ethyl alcohol with conventional yeasts. However, researchers at the U.S.D.A. Forest Products Laboratory have discovered a xylose-fermenting yeast (*Candida tropicalis*). Thus it now is possible to convert all wood sugars to ethyl alcohol with a combination of yeasts. Isolation of the specific enzymes and genetic engineering of the enzymes could dramatically improve the efficiency of this conversion.

Many other chemicals can be obtained from both yeast and bacteria fermentation of sugars and pulp mill effluents. Potential fermentation products from wood hydrolysates include acetone, organic acids (acetic, butyric, lactic), glycerol, butanediol, and others.[39]

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8

Animal and Vegetable Fats, Oils and Waxes

Edmund W. Lusas and Khee Choon Rhee*

INTRODUCTION

Fats and oils predominantly are triesters (triacylglycerols, triglycerides) of glycerol and aliphatic fatty acids generally containing up to 24 carbon atoms. Waxes are esters of long-chain fatty acids, usually containing 24 to 28 carbon atoms, with long-chain primary alcohols (16 to 36 carbon atoms), or with alcohols of the steroid group.[1]

These compounds are members of a broader group of chemical substances called *lipids*, which has been classified by the National Research Council into: (1) *nonpolar lipids*—including esters of fatty acids (triacylglycerols and cholesteryl esters) that are virtually insoluble in water but soluble in most organic solvents, and enter metabolic pathways only after hydrolysis; and (2) *polar* or *amphipathic lipids*—including fatty acids, cholesterol, sphingolipids, and glycerophospholipids (mainly lecithins). The term *phospholipids* includes lecithins and sphingomyelins.[2] Other minor natural compounds, also extracted simultaneously by low-polarity organic solvents, include fat-soluble vitamins, colors, and flavors.

Fats and oils have a major role in human nutrition. They are concentrated dietary sources of energy, providing approximately 9 kcal/g when metabolized, compared to 4 kcal/g for carbohydrates and proteins, and account for about 36 percent of caloric intake per capita domestically.[1] Dietary lipids also can provide essential molecular structures that are synthesized by the body into compounds required for selective functioning of cell membranes and for regulation of life processes.

In the preparation of foods, fats and oils modify product texture, carry flavors, improve mouthfeel, provide a sensation of product richness, and induce satiety. They are used in many other commercial applications, including soaps and detergents, plastics and protective coatings, printing inks, and feeds for domesticated animals, and as carriers of pesticides for aerial spraying, for control of grain dust, and as feedstocks for chemical manufacturing processes.

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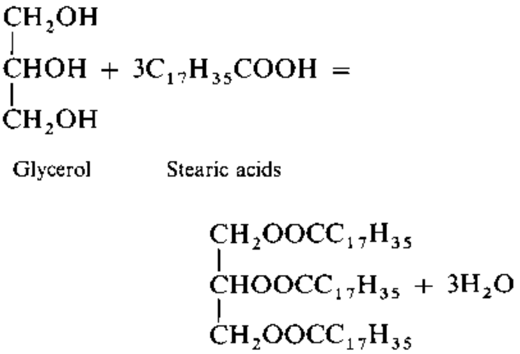
NOMENCLATURE, MOLECULAR STRUCTURES, AND POLYMORPHISM

General

The choice of the term "oil" or "fat" usually is based on the physical state of the material and tradition. Generally, oils are liquid at ambient temperatures, and fats are semisolid. Fats usually are of animal origin (beef tallow, pork lard and butter fat), while oils are extracted from fish or plant tissue or seeds. Nutritionists usually use the term "fat."

Over 95 percent of the weight of most extracted (*visible*) food fats are triacylglycerols formed by combination of glycerol (a trihydric alcohol) with three fatty acids, with loss of one molecule of water for each ester linkage:



$$\begin{array}{l} \mathrm{CH_2OH} \\ | \\ \mathrm{CHOH} \\ | \\ \mathrm{CH_2OH} \end{array} + 3\mathrm{C_{17}H_{35}COOH} = \begin{array}{l} \mathrm{CH_2OOCC_{17}H_{35}} \\ | \\ \mathrm{CHOOCC_{17}H_{35}} \\ | \\ \mathrm{CH_2OOCC_{17}H_{35}} \end{array} + 3\mathrm{H_2O}$$

Glycerol Stearic acids

Glycerol tristearate (tristearin)

Fatty Acids

The fatty acids are the building blocks of the triacylglycerols. Trace amounts of odd-number carbon fatty acids are found in most fats, and these compounds also have been synthesized for research purposes. Microorganisms frequently produce branched fatty acids. Heptadecenoic (17 carbon) acid is a major component of *Candida tropicalis* yeast fat. More than 90 percent of the fatty acids have an even number of carbon atoms, and are in aliphatic chains ranging from 4 to 24 carbons in length.

The names of common fatty acids under several conventions, carbon numbers, and selected properties are shown in Table 8.1. The common (trivial) names of some fatty acids are of long standing, and often indicate the initial source studied. As examples: butyric acid is a major component of butter flavor; the 6, 8, and 10 saturated fatty acids have been called the *goaty acids* because they impact characteristic flavors of goat and sheep milk and cheese; and the terms *olein* and *stearin* were applied in the early manufacture of oleomargarine and compounded shortenings to the liquid and solid fractions, respectively, of tallow separated by pressing.

Fatty acids sometimes are designated by the number of carbon atoms in the chain, followed by a colon and additional numbers indicating the number of double bonds. Thus, in the 18-carbon series, C18:0, C18:1, C18:2, and C18:3 represent stearic, oleic, linoleic, and linolenic acids, respectively. One or two letter abbreviations also are used, and these four acids sometimes are designated by St, O, L, and Ln, respectively.

Under the most common chemical convention, fatty acids are named on the basis of the number of carbon atoms, starting with the terminal carboxyl (COOH) carbon as number 1. The terminal letter *e* of the respective alkane hydrocarbon is replaced with *oic* to indicate an acid:

$$\mathrm{CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3}$$

Octane

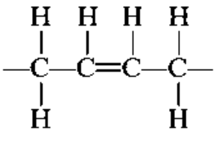
$$\overset{8}{\mathrm{CH_3}}\overset{7}{\mathrm{CH_2}}\overset{6}{\mathrm{CH_2}}\overset{5}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_2}}\overset{3}{\mathrm{CH_2}}\overset{2}{\mathrm{CH_2}}\overset{1}{\mathrm{COOH}}$$

Octanoic acid

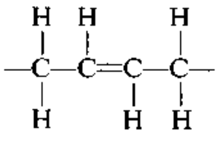
The suffix *dioic* is used if the acid contains two carboxyl groups.

When double bonds are present, the suffix *anoic* is changed to *enoic*, *dienoic*, or *trienoic* to indicate the number of bonds present, and the location of the first carbon in the double bond is indicated by a number preceding the systemic name. Under this convention, stearic, oleic, linoleic, and linolenic acids are called octadecanoic, 9-octadecenoic, 9,12-octadecadienoic, and 9,12,15-octadecatrienoic acids, respectively.

The geometric configuration of the double bonds is indicated by the latin prefixes *cis*- (both hydrogens on one side) and *trans*- (hydrogens across from each other). Linoleic acid, with *cis* configuration in both double bonds, is called *cis*-9,*cis*-12-octadecadienoic acid. Most fatty acids occur in nature in the *cis* form. Oleic acid is automatically assumed to be in the *cis* configuration, and the corresponding *trans* form is called elaidic acid.



cis



trans

The same system (with the carboxyl carbon designated as 1) also is used in naming fatty acids that are branched or include unusual structures, with numbers indicating the carbon to which the respective group or structure is attached.

Occasionally in the literature, the carboxyl unit is regarded as a group substituted for hydrogen. In this case, the number 1 location is moved one position away from the reactive end, and the suffix *carboxylic acid* is added:

$$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2COOH$$

1-Pentanecarboxylic acid
(hexanoic acid)
(caproic acid)

Locations of the last double bond are of special interest in long-chain polyunsaturated fatty acids. Their numbering sometimes begins from the noncarboxyl end, with the methyl carbon counted as 1 and the first unsaturated carbon designated as an *n* or omega (ω) number. Thus, linoleic acid (9,12-octadecadienoic) also may be designated as C18:2ω6. The polyunsaturated fatty acids consist mainly of two groups whose first double bonds occur either three or six carbons from the methyl end (n-3, ω-3 or n-6, ω-6, respectively). Distributions of individual fatty acids can vary by over 100 percent in the oil of a species. Table 8.2 summarizes general distribution for the major edible fats and oils, and Table 8.3 that for industrial fats and oils.

In recent years, research attention has turned to evaluating the potential of nontraditional fats/oils sources, including newly domesticated crops, forest oilseeds, bacteria, yeasts and molds, and algae. The reader should consult the references for types of fatty acids and their occurrence in these sources.[3,4]

Acylglycerols

Glycerol esterified with one, two, or three fatty acids is found in nature and can be made commercially. The designations monoacylglycerol, diacylglycerol, and triacylglycerol, respectively, now are encouraged in the scientific literature although the older terms mono-, di-, and triglycerides still are widely used in commerce. As the number of fatty esters on the glycerine decreases, the compound becomes more polar and functionally effective as a surfactant. Mono- and diacylglycerols are described in more detail in the section on emulsifiers.

The triacylglycerols are named in various ways. For example, unsaturated fatty acids sometimes are indicated as *U* and the saturated as *S*. If glycerol is completely esterified with stearic acid, the resulting monoacid triacylglycerol may be designated as SSS, or, more descriptively as StStSt, tristearin, tristearoylglycerol, or glycerol tristearate.

If more than one species of fatty acid is present, its relative location on the glycerol may be important to its functionality, enzyme susceptibility, and storage stability of the fat/oil. Several conventions have been developed to specify arrangements of fatty acids on the glycerol molecule (if known). To avoid confusion from inversion of the 1 and 3 carbon positions, hierarchies have been established to designate the number 1 carbon under the R/S system[5] and the *sn* (stereospecific numbering) system.[6] Three abbreviations are used under the *sn* system to indicate location of specific fatty acids in triacylglycerol molecules: *sn* immediately before the word glycerol, as in 1-stearoyl-2-oleoyl-3-myristoyl-*sn*-glycerol, indicates that the respective fatty

TABLE 8.1 Alternative Names and Selected Characteristics of Some Important Fatty Acids

Carbon Atoms	*Common Name*	*Letter Abbr.*	*Systematic Name*	*Melting Point, °C*	*Iodine Value*	*Common Sources*
Saturated Fatty Acids						
3	Propionic	—	Propanoic	−20.8	—	Bacterial fermentation
4	Butyric	—	Butanoic	−7.9	—	Milk fats
5	Valeric	—	Pentanoic	−33.8	—	Bacterial fermentation
5	Isovaleric		3-Methylbutanoic	−51.0	—	Dolphin and porpoise fats
6	Caproic	—	Hexanoic	−3.4	—	Milk fats, some seed oils
8	Caprylic	—	Octanoic	16.7	—	Milk fats, *Palmae* seed oils
10	Capric	—	Decanoic	31.6		Ship and goat milk, palm seed oils, sperm head oil
12	Lauric	—	Dodecanoic	44.2	—	Coconut-oil
14	Myristic	—	Tetradecanoic	54.4	—	Palm and coconut oils
16	Palmitic	—	Hexadecanoic	62.9	—	Palm oil
18	Stearic	St	Octadecanoic	69.6	—	Animal fats
19	Tuberculostearic	—	10-Methylstearic	11.0	—	Tubercle bacillus lipids
20	Arachidic	—	Eicosanoic	75.4	—	Some animal fats
22	Behenic	—	Docosanoic	80.0	—	Peanut and various other seed oils
24	Lignoceric	—	Tetracosanoic	84.2	—	Minor amounts in some seed oils
26	Cerotic	—	Hexacosanoic	87.8	—	Plant waxes
28	Montanic	—	Octacosanoic	90.9	—	Beeswax and other waxes
30	Mellisic	—	Triacontanoic	93.6	—	Beeswax and other waxes
Unsaturated Fatty Acids						
10	Caproleic	—	9-Decenoic		149.1	Milk fats
10	Stillingic	—	2,4-Decadienoic		—	*Stillingia* oil
12	Lauroleic	—	2-Dodecenoic	—	128.0	Butterfat

14	Myristoleic	—	9-Tetradecenoic	18.5	112.1	Some feed fats, milk fats
16	Palmitoleic	—	9-Hexadecenoic	—	99.8	Many fats and marine oils
16	Hiragonic	—	6,10,14-Hexadecatrienoic	—	—	Sardine oil
17	—	—	9-Heptadecenoic	14.0	—	*Candida tropicallis* yeast
18	Elaidic	—	9-Octadecenoic	43.7	—	Butterfat
18	Oleic	—	9-Octadecenoic	16.3	89.9	Almost all fats and oils
18	Petroselinic	—	6-Octadecenoic	30–33	—	Parsley seed oil
18	Vaccenic	—	11-Octadecenoic	44.0	—	Butterfat
18	Linoleic	Lo	9,12-Octadecadienoic	−6.5	181.0	Most vegetable oils
18	—	—	6,9,12-Octadecatrienoic	—	—	Evening primrose family
18	Eleostearic	—	9,11,13-Octadecatrienoic	—	—	Tung oil
18	Linolenic	Ln	9,12,15-Octadecatrienoic	−12.8	273.5	Linseed oil, soybean oil and canola oil
20	Gadoleic	—	9-Eicosenoic	23–24	81.8	Some fish oils
20	—	—	5,8,11-Eicosatrienoic	—	—	Brain phospholipids
20	—	—	8,11,14-Eicosatrienoic	—	—	Shark liver oil
22	Erucic	—	12-Docosenoic	33.5	75.0	Rapeseed oil
22	—	—	13,16-Docosadienoic	—	—	Rapeseed oil
Fatty Acids of More Unusual Structure						
18	Chaulmoogric	—	13,(2-Cyclopentenyl)tridecanoic	68.5	90.5	*Chaulmoogra* oil
18	Malvalic	—	8,9-Methylene-8-heptadecenoic	—	—	*Malvaceae* seeds, cottonseed
18	Ricinoleic	—	12-Hydroxy-9-octadecenoic	5.5	86.0	Castor oil
18	Vernolic	—	12,13-Epoxy-9-octadecenoic	30–31	—	Some *Compositae* seeds
19	Sterculic	—	9,10-Methylene-9-octadecenoic	—	—	*Sterculiaceae* seeds, cottonseed
20	Arachidonic	—	5,8,11,14-Eicosatetraenoic	−49.5	333.5	Lard
20	—	—	5,8,11,14,17-Eicosapentaenoic	—	—	Some fish oil
20	Lesquerolic	—	14-Hydroxy-11-eicosenoic	—	—	*Lesquerella* seed oil
22	—	—	4,7,10,13,16,19-Docosahexaenoic	—	—	Some fish oil

TABLE 8.2 Fatty Acid Composition of Some Edible Oils and Fats[a]

Source	*<14:0*	*14:0*	*16:0*	*16:1*	*18:0*	*18:1*	*18:2*	*18:3*	*20:0*	*20:1*	*22:0*	*22:1*	*24:0*	*24:1*
Almond oil	—	0.0	6.5	0.6	1.7	69.4	17.4	—	—	—	—	—	—	—
Avocado oil	—	—	11.0	3.4	0.7	71.5	12.0	1.5	—	—	—	—	—	—
Barley bran oil	—	0.5	10.8	0.2	1.0	17.8	55.3	4.4	—	—	—	—	—	—
Borage oil		—	11.3	—	3.7	16.3	38.1	23.0	0.2	3.9	—	2.4	—	1.4
Buffalo gourd seed oil	—	—	11.8	—	3.5	21.9	60.6	0.0	0.0	—	—	—	—	—
Butter fat	23.8	8.2	21.3	1.8	9.8	20.4	1.8	1.2	—	—	—	—	—	—
Canola oil[b]	-	—	4.8	0.5	1.6	53.8	22.1	11.1	1.1	1.5	0.3	0.1	0.1	—
Cherry pit oil	—	–	7.8	0.4	2.4	43.9	44.8	0.5	0.7	—	—	—	—	—
Cocoa butter	—	0.1	25.4	0.2	33.2	32.6	2.8	0.1	—	0.0	—	—	—	—
Coconut oil	58.7	16.8	8.2	—	2.8	5.8	1.8	—	—	—	—	—	—	—
Corn oil	0.0	0.0	10.9	—	1.8	24.2	58.0	0.7		—	-	—	—	—
Cottonseed oil	—	0.8	22.7	0.8	2.3	17.0	51.5	0.2	—	—	—	—	—	—
Evening primrose oil	—	-	8.5	—	2.5	8.5	72.5	11.0	—	—	—	—	—	-
Fish (manhaden) oil	—	9.6	20.5	12.6	3.3	11.0	0.7	1.6	0.3	—	-	0.8	–	—
Grapeseed oil	—	0.1	6.7	0.3	2.7	15.8	69.6	0.1	—	—	—	—	—	—
Illipe butter	—	—	23.7	—	19.3	43.3	13.7	—	—	—	—	—	—	—
Lard	0.5	1.3	23.8	2.7	13.5	41.2	10.2	1.0	—	1.0	—	—	—	—
Lupine oil	—	—	8.3	—	2.5	55.0	17.7	9.3	—	—	—	—	—	—
Macademia nut oil	—	0.6	8.5	21.7	3.7	56.0	1.7	—	—	1.4	—	—	—	—
Mango kernel oil	—	—	7.6	—	36.0	49.4	5.0	0.5	1.4	—	—	—	—	—
Mustard seed oil	—	0.1	1.9	0.3	0.1	17.7	9.1	0.5	0.6	3.91	1.8	55.1	0.2	1.9
Okra seed oil	—	0.2	33.7	0.6	3.3	17.9	42.2	0.2	0.1	—	0.2	—	—	—
Olive oil		0.0	11.0	0.8	2.2	72.5	7.9	0.6	—	—	—	-	—	—
Palm oil	0.1	1.0	43.5	0.3	4.3	36.6	9.1	0.2	—	0.1	—	—	—	—
Palm kernel oil	54.2	16.4	8.1		2.8	11.4	1.6	—	—	—	—	—	—	—
Peanut oil	—	0.1	9.5	0.1	2.2	44.8	32.0	—	—	1.3	—	—	1.8	—
Rapeseed oil[c]	—	—	1.7	—	0.9	12.3	12.7	7.6	1.2	5.8	0.9	59.4	0.5	1.6
Rice bran oil	—	0.7	16.9	0.2	1.6	39.1	33.4	1.6	—	—	—	—	—	—
Safflower oil	—	0.1	6.2	0.4	2.2	11.7	74.1	0.4	—	—	—	—	—	—
Safflower oil[d]	—	—	4.8	—	1.3	75.3	14.2	—	—	—	—	—	—	—
Sal seed oil	—	—	5.3	—	34.0	49.1	3.8	3.3	4.0	—	—	—	—	—
Sesame oil	—	—	8.9	0.2	4.8	39.3	41.3	0.3	—	0.2	—	—	—	—
Shea butter	1.7	0.1	4.4	0.1	38.8	43.5	4.9	0.3	—	0.0	—	—	—	—
Soybean oil	—	0.1	10.3	0.2	3.8	22.3	51.0	6.8	—	—	—	—	—	—
Sunflower oil[e]	—	—	5.4	0.2	3.5	80.6	8.4	0.2	0.3	—	—	—	—	—
Sunflower oil[f]	—	0.1	5.9	0.1	4.5	19.5	65.7	—	—	—	—	—	—	—
Tallow	0.9	3.7	24.9	4.2	18.9	36.0	3.1	0.6	—	0.3	—	—	—	—
Teaseed oil	0.1	0.1	17.5	0.5	3.1	49.9	22.2	0.7	–	1.0	—	–	—	—
Tomato seed oil	—	0.2	15.0	0.5	4.4	21.9	50.8	2.3	—	—	—	—	—	—
Walnut oil	—	—	7.0	0.1	2.0	22.2	0.4	52.9	10.4	—	—	—	—	—
Wild cucurbit oil	—	—	19.0	—	—	34.0	47.0	15.0	—	—	-	—	—	—

[a] These are average values from recent years' crops. [b] Low-erucic-acid variety rapeseed. [c] High-erucic-acid variety. [d] High-oleic variety. [e] Grown in colder climates. [f] High-oleic variety.

acids are in the 1, 2, and 3 positions; the term *rac* (racemic mixture), as in rac-StOM, indicates that the middle acid is in the glycerol 2 position, and the remaining fatty acids are equally divided between the sn-1 and sn-3 positions. The term *β*, as in *β*-StOM, indicates that the middle acid is in the glycerol 2 position, but distribution of the other two acids is unknown.[7]

Melting Points

Factors affecting melting points of different fat samples include the types of fatty acids

TABLE 8.3 Fatty Acid Composition of Some Industrial Oils and Fats[a]

Source	*<14:0*	*14:0*	*16:0*	*16:1*	*18:0*	*18:1*	*18:2*	*18:3*	*20:0*	*20:1*	*22:0*	*22:1*	*22:2*	*24:1*
Castor oil[b]	—	—	1.1	0.2	1.0	3.3	3.6	0.32	0.4	—	—	—	—	—
Chinese tallow	1.3	2.1	65.0	—	4.4	22.5	0.8	—	—	—	—	—	—	—
Crambe oil	—	—	2.0	0.4	0.4	16.9	8.6	6.4	0.5	3.2	2.0	57.2	—	1.4
Crepsis foetida oil[c]	—	0.1	4.8	—	2.9	4.3	27.8	—	—	0.3	—	—	—	—
Croton oil	2.5	5.4	6.2	0.2	3.2	15.8	49.4	3.0	2.9	8.9	0.2	0.6	—	—
Cuphea oil	—	76.4	7.8	2.4	—	0.7	5.9	6.9	0.1	—	—	—	—	—
Jojoba oil	—	—	1.0	—	—	9.0	—	—	—	70.7	—	16.3	—	3.0
Lesquerella seed oil	—	1.4	1.4	2.0	17.6	7.9	13.2	—	52.5	—	—	—	2.7	—
Linseed oil	—	—	5.3	—	4.1	20.2	12.7	53.3	—	—	—	—	—	—
Meadowfoam oil	—	—	—	—	—	—	—	—	—	64.5	—	18.5	13.5	—
Neatsfoot oil		0.7	16.9	—	2.7	64.4	2.3	0.7	0.1	—	—	—	—	—
Oitica oil[d]	—	—	7.0	—	5.0	6.0	—	—	—	—	—	—	—	—
Rapeseed[e]	—	0.1	2.6	0.3	0.9	11.2	12.8	8.6	—	7.5	—	48.1	—	—
Rubber seed oil	—	0.2	19.1	—	17.8	24.5	30.5	2.4	—	0.1	0.9	0.4	—	—
Stokes aster oil[f]	—	—	2.8	—	0.9	7.0	16.5	—	—	—	—	—	—	—
Tall oil	—	—	—	—	—	50.0	7.0	41.0	—	—	—	—	—	—
Tung oil	—	—	3.1	—	2.1	11.2	14.6	69.0	—	—	—	—	—	
Veronia seed oil[g]	—	—	2.7	—	1.3	2.0	8.8	0.4	—	—	—	—	—	—
Whale oil	—	3.3	8.1	26.9	1.1	33.3	—	—	—	10.9	—	2.2	—	—

[a]These are average values from recent years' crops. [b]Contains 89.2% ricinoleic and 1.4% dihydroxystearic acids. [c]Contains 59.8% crepenynic acid. [d]Contains 78.0% licanic acid and 4.0% hydroxy acids. [e]High-erucic-acid variety. [f]Contains 71.3% venolic acid. [g]Contains 78.5% vernolic acid and 5.8% hydroxy fatty acids.

present in the triacylglycerol and their location, chain length of the fatty acids, number and location of *cis* and *trans* double bonds on the fatty acid chains, and compatibility of the different triacylglycerols in the mixture and the type of crystal present.

Among the fatty acids, melting points increase with chain length. *Trans* fatty acids always have higher melting points than their *cis* counterparts for any chain length. Where only one double bond exists in a fatty acid, as in C18:1, the melting point is lower if it is located after an odd-number carbon than an even-number carbon, and also if the double bond is located near the middle of the chain as compared to a location at either end.[8] Compatibility of mixed fats from different sources also can be a factor. For example, the melting point of mixed triacylglycerols consisting primarily of 16 to 18 carbon fatty acids, whether of animal or vegetable origin, generally rises smoothly with increased content of higher melting fats. However, when triacylglycerols with 12 to 16 carbon fatty acid fats (from coconut, palm kernel, or palm oil) are added, concentration–related eutectic points and regions of noncompatibility (manifested as mixtures of solids in oil) may occur.[9,10]

Polymorphism and Crystal Types

The same sample of a pure or mixed fatty acid triacylglycerol may show as many as five different melting points, depending on its heating and cooling history. For example, tristearin has an amorphic (noncrystalline) solid form and three crystalline forms with melting points at 54.7°C, 63.2°C, and 73.5°C. If a small sample of fat is heated slowly (as in a capillary tube melting point determination), melting, resolidification, and remelting at increasingly higher temperatures may be observed. These changes result from the fat seeking the most compact crystal form and the most stable (lowest) thermodynamic energy state possible.

As fatty acids or triacylglycerols cool, Gibbs free energy ($G = H - TS$) decreases by reduction of both enthalpy (H) and entropy (S, the degree of disorder). At decreased S, the fatty acid chains assume polelike structures that are less co-repulsive and pack more tightly into crystal lattices. It is generally accepted that, to participate in a crystal structure, triacylglycerols assume an "h" configuration (also called a two-legged chair or tuning fork). This can be envisioned in our gravity-oriented macro world by assuming that each ester linkage acts as a hinge. If the glycerol number 2 carbon chain is held upright at the methyl end, the number 3 carbon chain falls directly beneath it, forming the back and one leg of the chair, and the number 1 carbon chain juts out at a right angle and curves downward to form the second leg.[11–13] In order to save space, half of the chairs are packed upside down to form a palisade-like structure. A stack of two such structures forms a bilayer whose outer surfaces consist of methyl groups, displaying low interattraction. This helps explain why triacylglycerol crystals are relatively flat, grow rapidly in length and less rapidly in width by adding parallel chair structures, but grow slowly in thickness by adding additional bilayers.

Within each layer, the chair backs and legs can be further envisioned to act like a vertical loose palisade of bumpy-surfaced posts. (Although the hydrocarbon chains have stiffened into pole shape, the carbon atoms are not positioned as beads on a tight string, but rather in sawtooth-like fashion with carbon–carbon bonds of 112°). The posts can slide behind each other to obtain a tighter packing with lowered free energy, and can be tilted in two directions to allow the sawtooth-configured carbon atoms on adjacent chains to slip by each other and pack more tightly. Also, the vertical units in one layer can all be tilted at an opposing angle to the units in the other layer.

On cooling, fats may assume various polymorphic forms. On slow cooling, or reheating of the vitreous form, they change to crystalline forms. The form showing the least amount of crystalline order for a triacylglycerol, as determined by X-ray diffraction and infrared spectroscopy, is called the *alpha* (α) form. The most compact crystalline form, with the lowest free energy and the highest melting point, is called the *beta* (β) form. One or more intermediate *beta prime* (β′) forms also may exist, and are indicated as β_3', β_2', and β_1' as the crystal progressively assumes tighter packing with lower free energy and increased melting points.[14]

When a monoacid triacylglycerol is cooled slowly and without mixing, it preferentially assumes the β crystal form. However, the required tight packing of crystals requires time for alignment, and may be thwarted by increased viscosity as the fat/oil mixture cools. However, if the heated oil is cooled rapidly, it may first be rushed into an amorphous (vitreous, glasslike) sub-α state. Upon exposure to heat, the fat then may pass directly to the β crystal form, or stepwise through the α and β′ forms until it reaches the β form.

The free energy relationships between the different crystal forms are depicted in Fig. 8.1. Although the β crystal form has the lowest free energy G, its formation also has the highest activation energy ΔG. Differential scanning calorimetry (DSC) often is used to follow free energy changes as fats melt and change between their polymorphic forms.

Formation of β crystals may intentionally be encouraged or kinetically hindered depending on the specific application. The α crystals are relatively unstable, and commercial interest is primarily placed on the differences between the β′ and β forms. Generally, β′ crystals are

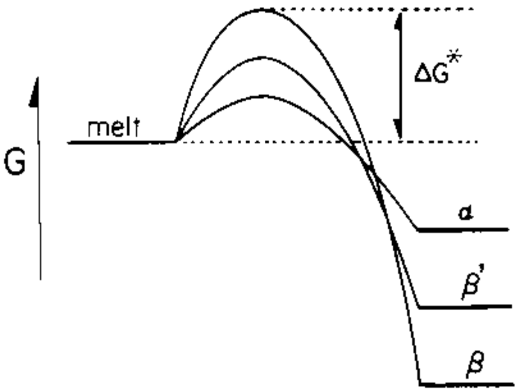


Fig. 8.1. Gibbs free energy relationships for establishment of α, β′, and β crystals. (*By permission of Marcel Dekker, Inc., New York.*)

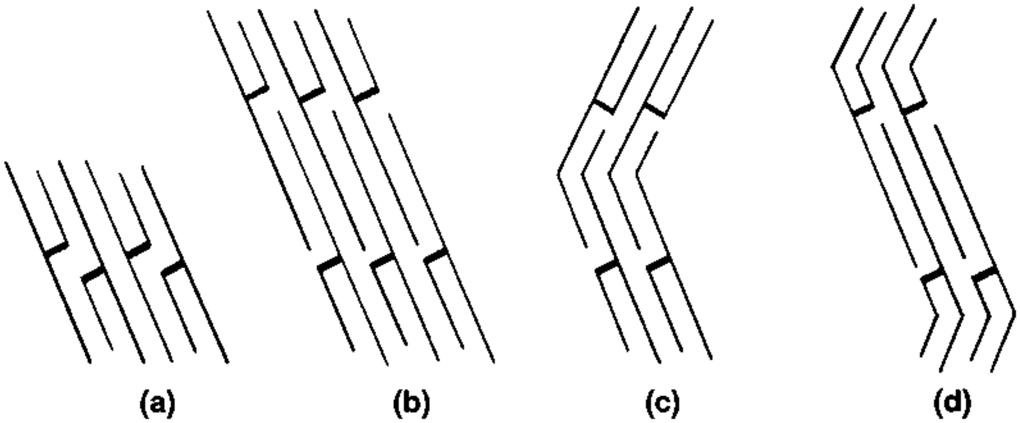


Fig. 8.2. Drawings of two- and three-chain triacylglycerol layers: (a) saturated monoacid SSS-type; (b) saturated symmetrical PSP-type where 2 chain differs from 1 and 3 chains in length; (c) symmetrical POP-type where 2 chain is unsaturated; and (d) symmetrical OPO-type where 1 and 3 chains are unsaturated. Crystals grow in bilayer units.

smaller (about 0.5–2.0 diameter microns in shortening, and 5–10 microns in margarine),[15] whereas β crystals can grow to as large as 20 to 30 microns. When the objective is to thermally fractionate fats by crystallization, production of the β form is encouraged by carefully controlling temperatures (to not shock the fat into a lower melting β' form), gentle stirring, and nuclei seeding. The smaller β' crystals have smoother mouthfeel, minimize oiling off of margarine, and entrap more air in creaming cake batters. Their production is intentionally encouraged by formulating mixtures of natural or preprocessed fats, by inclusion of emulsifiers to interfere with crystal growth, and by rapid agitation during plasticizing of the margarine or shortening.

An awareness of crystal packing characteristics and polymorphism helps one to understand incompatibility problems of different fats. As shown in Fig. 8.2, if the three fatty acids in the triacylglycerol are saturated and approximately of the same length, each of the layers in the fat bilayer will be approximately two fatty acid chains in height. If the fatty acid on the number 2 glycerol carbon is appreciably shorter than those on the 1 and 3 carbons, each of the layers will be three chains thick. If the triacylglycerol is symmetrical, with either the number 2 glycerol carbon or both the 1 and 3 carbons unsaturated, the layer will be three chains long, but with a zig-zag configuration to accommodate the *cis* configuration.

Crystal formation has specific demands, and individual crystals in mixed systems consist of only one species of triacylglycerol. However, surfactants and other molecules can act as impurities and interrupt crystal growth. Different triacylglycerols are considered *compatable* when they co-crystalize as separate crystals under the same conditions without formation of a eutectic.

Waxes

Waxes are fatty acid esters of alchols and are formed by the general reaction:

$$\underset{\text{Alcohol}}{CH_3(CH_2)_nCH_2OH} + \underset{\text{Fatty acid}}{CH_3(CH_2)_nCOOH} =$$

$$\underset{\text{Wax ester}}{CH_3(CH_2)_nCH_2COCH_2(CH_2)_nCH_3} + H_2O$$

A major role of waxes in nature is protection of plant tissues. Examples include coating upper surfaces of leaves to reduce dehydration by the sun and protecting seeds against moisture loss during storage. Minor quantities of waxes always are extracted from oilseeds by the commercial hexane process. Waxes extracted from seed hulls have been a problem in sunflower oil because their presence shortens

TABLE 8.4 Sources and Compositions of Natural Waxes

Type	*Melting Point °C*	*Main components*
Animal waxes		
Beeswax	64	Myricyl palmitate
Chinese	82–84	Isoheptacosyl isoheptacosanoate, ceryl lignocerate
Shellac	81–82	Ceryl lignocerate, ceryl cerotate
Spermaceti	—	Cetyl palmitate
Wool (anhydrous lanolin)	36–42	Cholesteryl estolidic esters, alcohol esters of iso- and anteiso acids
Mineral waxes		
Montan	86	Tricontanyl esters of C_{28-30} acids
Petroleum waxes		
Microcrystalline	71–88	Hydrocarbons (490–800 molecular weights)
Paraffin	54–57	Hydrocarbons (350–420 molecular weights)
Vegetable waxes		
Bayberry	43–48	Trimyristin, tristearin
Candelilla	70–80	C_{29-33} hydrocarbons, simple esters and lactones
Carnauba	80–85	Esters of C_{26-30} alcohols and C_{26-30} ω-hydroxy acids
Esparto	69–81	Hydrocarbons, esters of C_{26-32} acids and alcohols
Japan	51–62	Tripalmitin
Jojoba (a liquid wax)	11–12	Docosenyl eicosanoate
Ouricury	79–85	Myricyl cerotate and hydroxycerotate
Sugarcane	79–81	Myricyl palmitate stigmasteryl palmitate

the cold test of refrigerated oil. Sunflower oil may be dewaxed by first degumming or miscella-refining to remove the natural emulsifier lecithin, which limits growth of wax crystals, and then winterizing (chilling and filtering) the oil or its miscella.[16,17] With improvement of dehulling equipment, some sunflower seed processors have begun to remove the hulls before extraction. Domestic interest only now is turning to commercial extraction (*oil milling*) of rice bran, whose oil is believed to contain waxes that have commercial promise.

In some species, waxes serve the function of high-energy storage forms. Waxes are common in the oils of fish and other marine animals. The major lipids of commercial whale oil consist of approximately 65 percent waxes and 35 percent triacylglycerols. Essentially all of the oil in jojoba (*Simmondsia chiensis*) seed is in wax form. Whale and jojoba oils have been valued for stability in heavy-duty lubrication applications, and jojoba oil has been used in a variety of cosmetics.

Extraction processes for waxes vary in sophistication, from boiling and skimming crushed leaves and berries—as in the production of Candelilla wax (a substitute for hard carnauba wax) from *Euphorbia antisyphilitica* in the Big Bend areas of Texas and Mexico—to screwpressing seeds such as those of jojoba. Cold-pressed jojoba oil is preferred for cosmetics because of concern about other lipids that might be extracted in solvent processes, and prepressed jojoba meal sometimes is extracted by a secondary hexane process to recover oil for industrial uses. Waxes are susceptible to hydrolysis by nonspecific lipases, and also are at least partially digestible. They may be hydrogenated or sulfurized into solid forms. Compositions of significant commercial waxes from natural sources are given in Table 8.4

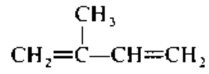
Terpenes, Carotenoids, Fat-Soluble Vitamins, and Steroids

Terpenes are condensation products of the five-carbon hydrocarbon *isoprene* (2-methyl-1,3-butadiene), and are extractable by nonpolar solvents. They are classified according to the number of isoprene units: two units, *mono-*

terpenes; three units, *sesquiterpenes*; four units, *diterpenes*; six units, *triterpenes*; eight units, *tetraterpenes*; and polyterpenes. Terpenes may be linear or cyclic. Taken together, this class of compounds includes the major essential oils, fat-soluble colors, fat-soluble vitamins, and steroids. A short-hand (sawtooth) form often is used to depict the longer chains.

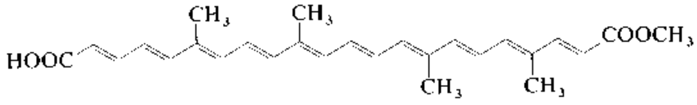
Examples of monoterenes include the linear aldehyde *citral* which is found in many essential oils, and the (*cis*) alcohol *geraniol*—a major component of oil of geranium. Cyclic mono-terpenes include *limonene*, *menthol*, *pinene*, *camphor*, and *carvone*—major components of lemon oil, mint oil, turpentine, camphor oil, and caraway oil, respectively. Sesquiterpenes include *farnesol*, a component of rose oil, and *bisabolene*, a component of Bisabol myrrh. The diterpenes include *phytol*, a component of chlorophyll, and vitamin A, which is one-half of the tetraterpene *β*-carotene. The triterenes include *squalene*, a precursor of cholesterol. Examples of tetraterpenes are the oil-soluble *carotenoid* plant pigments: xanthophylls, including the yellow pigments lutein in plant leaves and zeaxanthin in corn (*Zea mays*); capsanthin, the red pigment in red peppers (*Capsicum annum*); lycopene, the red coloring of tomatoes (*Lycopersicum esculentum*); and *β-carotene*, a yellow-orange pigment that is the precursor of Vitamin A. *Bixin*, from the seed pods of *Bixa orellana*, is the yellow-orange pigment in annatto food color; it is considered to be a form of carotene oxidized to remove both six-membered end rings. Polyterpenes include gutta, a natural water-repellant and electrical insulating material from *Palaquium gutta*, and natural rubbers with molecular weights of up to 1.2 million obtained from the latex of the *Hevea brasiliensis* tree and from rubber-filled cells in the branches and roots of the guayule shrub (*Parthenium argentatum*).

Important steroids derived from squalene include cholesterol, stigmasterol, sitosterol, and campesterol.

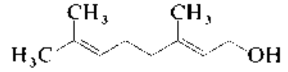


$CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2$

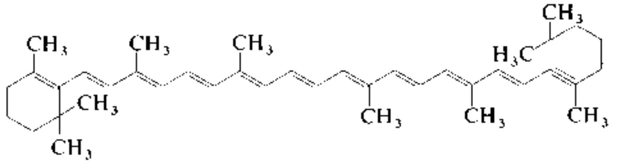
Isoprene



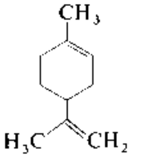
Bixin



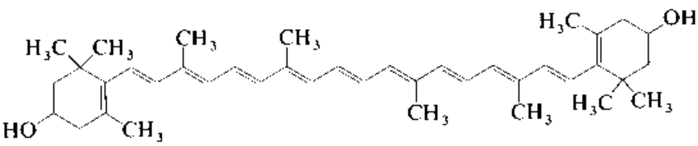
Geraniol



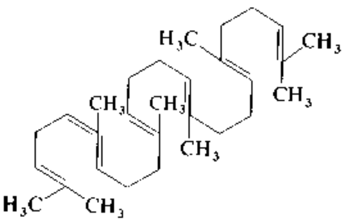
β-Carotene



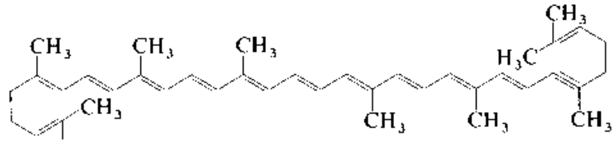
Limonene



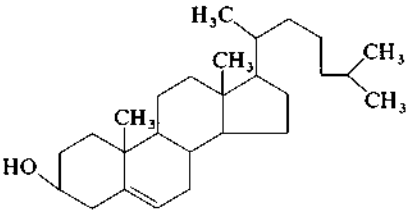
Zeaxanthin



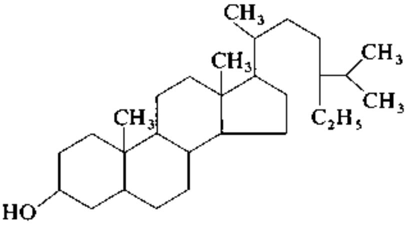
Squalene



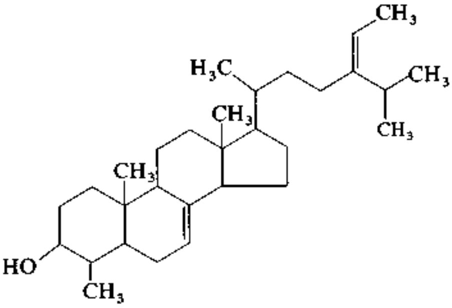
Lycopene



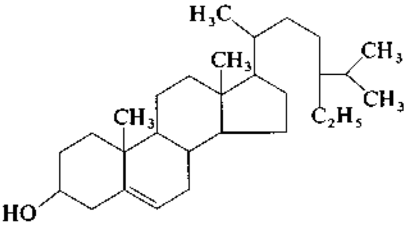
Cholesterol



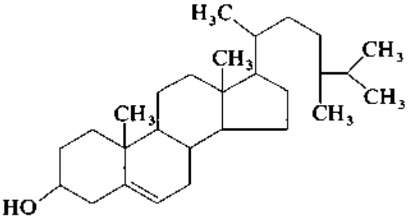
Stigmasterol



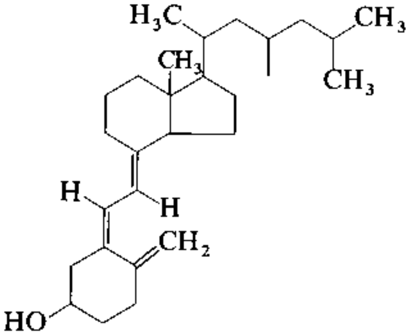
α_1-Sitosterol



β-Sitosterol

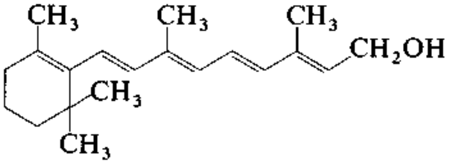


Campesterol

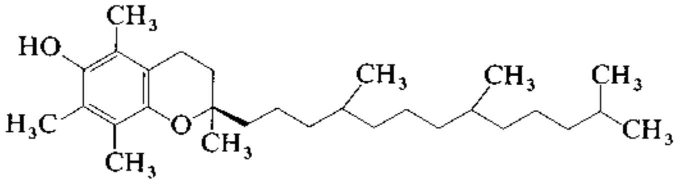


Vitamin D_3

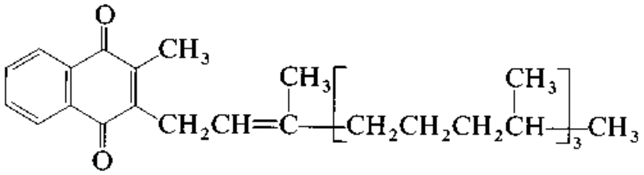
The fat-soluble vitamins include: vitamin A (*retinol*), a colorless compound considered to result from cleavage of β-carotene; vitamin D_3 (*cholecalciferol*), a steroid; and vitamins E and K (*α-tocopherol* and *menadione and its derivatives*, respectively), which consist of isoprene and phenolic-quinone components.



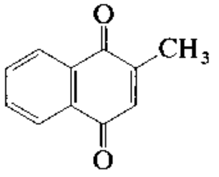
Vitamin A



Vitamin E



Vitamin K_1



Vitamin K_3

The carotenoids generally are highly susceptible to oxidation. Only selected members (xanthophylls, β-carotene, and bixin) are extracted for food coloring, and then they are used in products such as butter, margarine, and cheese, where exposure to oxygen and light is limited. The more stable pigments (lutein and xanthophylls) are extracted from alfalfa and marigold blossoms for use as poultry feed additives to increase yellow color in egg yolks and in the skins of broilers. Much of the world's β-carotene is produced synthetically, but crude (red) palm oil may be a significant future source.

Oils from livers of cod and other fish species were early sources of vitamin D_3; also, ergosterol was irradiated by ultraviolet light to produce vitamin D_2. Currently, most of the commercial vitamin D also is produced synthetically. Vitamin E has been obtained commercially from extracted wheat germ oil, and recovered from deodorizer condensates from oil refining plants. Palm oil refining residues also are indicated major sources in the future.

SOURCES AND UTILIZATION OF FATS AND OILS

Production

Over 50 percent of the world's production of vegetable oils enters international trade, 19 percent in seed form and 33 percent as extracted oil. Extensive records are kept, country by country, of production, imports, and exports. Global production and export data for 1987/88 are shown in Table 8.5. These figures include crops harvested in the last half of the first year in the Northern Hemisphere and during the first half of the succeeding year in the Southern Hemisphere.

By far, soybean is the world's largest source of visible fats/oils, accounting for approximately 21.5 percent of total production. It is followed by palm oil, rapeseed/canola oil, sunflower seed oil, and tallow and grease in tonnages produced. The United States is the world's leader in soybean growing, accounting for approximately 44 percent of the total tonnage produced. It is followed by Brazil, Argentina,

TABLE 8.5 Area, Yield, Oilseeds, Products, and Exports of World's Major Edible-Type Oils for 1987/88[1]

Oil/Fat Source	*Area*[a]	*Yield*[b]	*Oilseed*[c]	*Meal*[d]	*Oil*[e]	*Exports*[f]
Edible Fats						
Soybeans	53.48	1.82	103.66	67.55	15.24	3.84
Cottonseed	32.19	0.97	31.31	9.12	3.48	0.39
Peanut	18.38	1.13	20.86	4.98	3.10	0.31
Sunflower seed	14.95	1.31	20.92	7.75	7.28	2.18
Rapeseed/canola	15.55	1.30	23.44	9.05	7.75	1.83
Flaxseed/linseed	4.18	0.54	2.27	0.86	—	—
Copra/coconut	—	—	4.35	1.55	2.68	1.38
Palm oil	—	—	—	—	8.36	5.55
Palm kernel	—	—	2.69	1.43	1.20	0.74
Olive	—	—	—	—	1.90	0.46
Fish	—	—	—	6.79	—	—
Butter[g]	—	—	—	—	5.30	—
Total Edible	138.73	7.07	209.51	109.08	56.29	16.78
Industrial Fats						
Industrial linseed	—	—	—	—	0.62	0.22
Marine oils fish	—	—	—	—	1.54	0.76
Tallow and grease[h]	—	—	—	—	6.56	—
Total Industrial	—	—	—	—	8.72	0.98
Total Fats and Oils	138.73	7.07	209.51	109.08	65.01	17.76

[1] USDA FAS Circular Series FOP 11-90, Nov. 1990.

[a] In million hectares (2.47 acres). [b] In metric tons per hectare. [c] In million metric tons. [d] In million metric tons, converted to 44% (soybean) protein equivalent. [e] In million metric tons. [f] In million metric tons, transhipments for palm oil through Singapore excluded. [g] Converted to fat content basis. [h] Inedible and edible tallows and greases included.

and China. In 1987/88, 41 percent of United States produced soybean oil was exported, compared to 15 percent and 25 percent, respectively, for Brazil and approximately 22 percent and 90 percent, respectively, for Argentina. These two countries impose larger severance taxes on exports of raw crops to encourage exports of value-added products, thus keeping the processing jobs at home. Several countries, notably The Netherlands, Portugal, Taiwan, and Singapore, have established significant process-in-transit industries, importing whole soybeans and exporting the meal and oil.

The leading producers of other oilseeds are: for *rapeseed/canola*—China, the EC-12 (European Common Market), India, Canada, and Eastern European countries; for *sunflower seed*—Russia, Argentina, the EC-12, and Eastern European countries: for *ground nuts, peanuts*—India, China, and the United States; for *cottonseed*—China, Russia, India, the United States, and Pakistan; and for *palm oil*—Malaysia and Indonesia, with oil palm plantations and oil mills coming into production in many equatorial countries.

Many factors dictate which oilseed species will be grown and/or imported into a country. The local need for high-protein feed meals probably is the leading factor. As shown in Table 8.6, the oil content of row crop oilseeds varies from about 20 percent for soybeans to 45 percent for sunflower seed and 43 to 45 percent for rapeseed/canola. More feed coproducts always are produced than oils—by a ratio of as much as 4:1 in the case of soybeans. Soybean meal is the major feed protein source for production of poultry, currently the leading domestic and global meat source, and for the rapidly developing aquaculture industries. For example, Malaysia, which produces nearly two-thirds of the

TABLE 8.6 Gross Composition of Major Edible Oilseeds

Crop/Source	*Moisture*	*Protein*	*Fat*	*Fiber*	*Ash*	*Oil:Co-products Ratio*
Soybean	4.2	37.0	24.0	3.6	4.3	1:3
Cottonseed	4.7	32.6	36.3	2.0	4.6	1:2
Peanut	6.7	25.7	49.2	4.9	2.3	1:1
Sunflower	5.4	22.8	49.6	4.2	3.5	1:1
Safflower	5.6	16.2	38.5	2.5	5.5	1:2
Copra	3.0	6.9	64.5	5.3	1.9	2:1
Canola	7.5	21.8	44.9	4.5	4.7	1:1
Palm kernel	6.5	8.3	49.0	8.1	2.0	1:1
Sesame	4.7	17.7	49.7	4.6	4.5	1:1

world's exported palm oil, imports soybeans for crushing, retains the meal for local animal feeds industries, and exports the oil.

Cool weather and short growing seasons have essentially limited Canada, Northern Europe, and the European Russian republics to growing rapeseed/canola or sunflower seed. Insect problems were important factors in selecting crops before modern insecticides and integrated pest management systems became available. Devastation of the southeastern United States cotton crop by the boll weevil led to the introduction of peanut growing and to initial domestic acreages of soybeans as alternative crops. Also, subsidies to local farmers, by governments that have chosen self-sufficiency in food production in preference to free trade, have encouraged the growing of crops that otherwise would not be profitable in some climates.

The relative availability of fats/oils from by-products of other current agribusiness and commercial enterprises is an additional consideration in the types and amounts of oilseeds grown. As examples, cotton lint accounts for approximately 85 percent of total returns to the cotton farmer, with only 15 percent coming from the seed. The domestic supply of cottonseed for crushing is dictated by world demand and price of cotton and by whole-seed feed needs of the southern United States dairy industry. Availability of cottonseed for crushing is relatively unresponsive to the price of cottonseed oil. Although soybeans are the major supply of edible oil, their production is closely related to the demand for soybean meal, which typically accounts for 67 to 75 percent of the market value of this crop. Corn oil has become the second major oil in the United States last decade owing to the large quantities of corn germ made available by rapid growth of the domestic corn sweetener industry. Beef, pork, and poultry packing operations always produce fatty tissues for rendering into edible tallow, lard, and chicken fat, respectively. Generally, fats/oils from coproducts of other local processing industries must clear the market first, at whatever the going price, before growing or importing of significant quantities of high-oil-content crops such as rapeseed/canola, sunflower seed, and peanuts becomes economically attractive.

Consumption

Average per capita consumption of fats/oils is difficult to determine from gross disappearance figures because these materials also are used in animal feeds and industrial applications, but it generally is related to personal income. Consumption of oils is estimated at 10.4 kg/person for the world, and ranges from 27.2, 42.9, and 29.3 kg for the United States, Belgium, and West Germany, respectively, to 13.1, 4.7, and 5.9 kg, respectively, for Egypt, China, and India. Approximately 60 percent of the total fat consumed domestically is invisible in meat, poultry, fish, dairy products, and eggs, and the 40 percent visible fat is used primarily in the form of salad and cooking oils, shortenings, and margarine. The world needs about 1.5 to 2.0 million additional tons of fats/oils each year for its rapidly growing population.

From 1965 to 1985, the average domestic consumption of fat increased by 8.3 kg/capita, with 7.5 kg coming from visible sources. Approximately two-thirds of the visible fat available per capita in 1940 was from animal sources. The use of vegetable source fats has grown significantly, accounting for about two-thirds of the visible fats consumed in 1965, and 90 percent in 1985.[18]

Effects of Biotechnology

Compositions of oilseeds and their oils are being changed by classical plant breeding and biotechnology techniques. Examples include the development of canola, a low erucic acid–low glucosinolate seed by Canadian scientists in the 1960s and 1970s to replace traditional rapeseed, and sunflower and safflower seeds with high-oleic acid oils, which also are being grown. Other oilseeds in various stages of development include flaxseed and soybeans with reduced linolenic acid contents, soybeans with increased stearic acid content, and low-gossypol (glandless) cottonseed. Major investments have been made in oil palm biotechnology by PORIM—the Palm Oil Research Institute of Malaysia. Additionally, specialized enzyme systems are being developed for esterification/rearrangement of fatty acids on glycerol to produce fats similar to cocoa butter in composition.

EDIBLE FATS AND OILS EXTRACTION

Modern oilseed extraction plants are large, with capacities of up to 3000 to 4000 tons/day. Installations typically include facilities for unloading railroad cars, barges, or ships; storage of at least several weeks' supply of seed; solvent, meal, and crude oil storage tanks or facilities; processing facilities; and day facilities for personnel and supervisors. Additional space and facilities are required if refining and fats/oils processing facilities are done at the same location. A photo of an operating soybean extraction plant is shown in Fig. 8.3.

Oilseeds Solvent Extraction

Plant oils are derived mainly from: (1) dry, hull-covered, row crop seeds (soybeans, rapeseed/canola, cottonseed, peanuts, sunflower seed, and others); (2) the kernels of hard-shell nuts; and (3) pulpy flesh surrounding seeds (olive, palm, and avocado). Additionally, coconut flesh dried into copra, corn germ from dry or wet-milling processes, and bran from rice-polishing operations are rich in oil content and are handled somewhat like row crop oilseeds.

The oils of the ancient world were sesame and olive, probably because of their ease of extraction and high stability. Various societies have used plant oils for medicinal purposes. Later, they were used for lighting and then for food as extraction and refining techniques improved. Extraction technology has evolved from dispersing macerated or ground seed in hot water and skimming off the oil that rises to the surface (Cochin process), to pressing ground seeds (held in folded press cloths of human hair or other fibers) by lever or wedge presses, and later to mechanical and hydraulic batch presses. Some of these techniques are still used in remote areas of the world.

With growing demands for edible oils, industry adopted batch cage presses, and then continuous screw presses and solvent extractors. The latest technique, extraction with carbon dioxide in a high-pressure critical state, is being applied to high-value products such as essential oils, hops, and instant coffee. Usually, batch extractions are conducted because techniques for loading and unloading continuous extractors operating at 8000 to 12,000 psig have not been developed. More recently, however, batch extractions have evolved into "pulse-fed" continuous extractors operating at 8000 to 12,000 psig.

Oilseeds do not have fat cells like those of animals for storing fats. Instead, oil is stored in microscopic globules throughout the cells of dicotyledonous oilseeds, or in the seed germ or bran in monocotyledonous plants such as

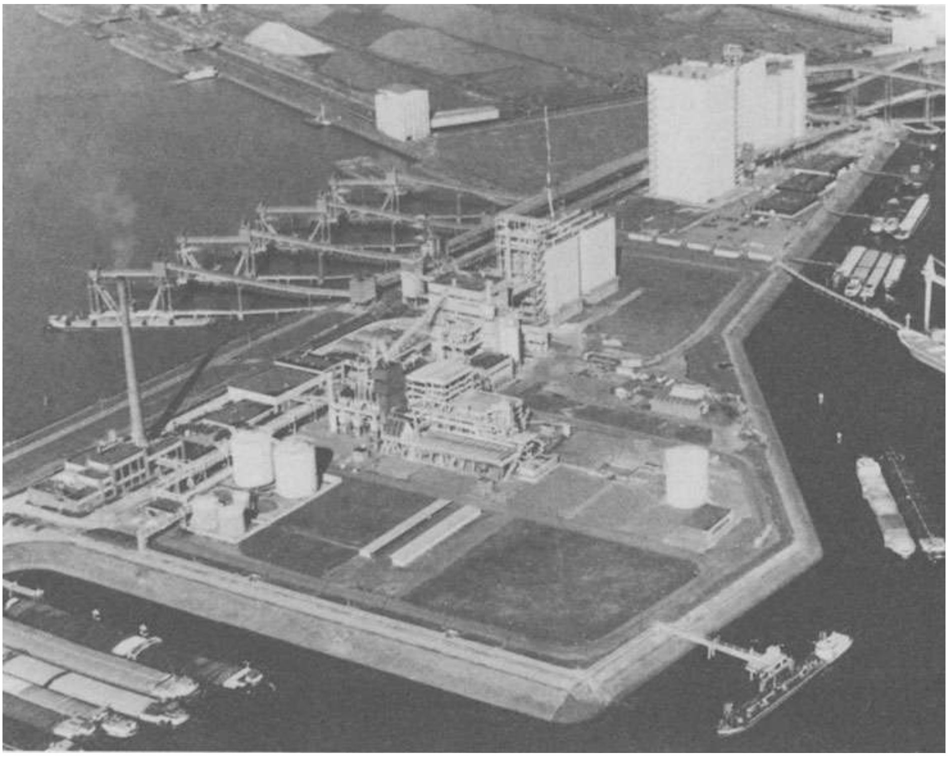


Fig. 8.3. Photograph of an operating soybean extraction plant. (*By permission of Archer Daniels Midland Company, Decatur, IL.*)

maize (corn) and rice, respectively. Oil yields and processing costs very much depend on the effectiveness of preextraction operations to disrupt cells and free the oil for recovery. Classical soy processing involves denaturing protein in cell walls to enhance rupturing and disrupting of the cell contents. A generalized flow sheet for direct solvent extraction of many row crop oilseeds is shown in Fig. 8.4. Operations differ among various oilseeds, mainly in techniques of dehulling.

At the beginning of the 1980s, processing concepts were based on the classification of oilseeds into two groups. *High*-oil-content seeds were those containing over 30 percent oil on a dehulled or as-processed basis, and included rapeseed/canola, oil-type sunflower seed, peanuts, safflower seed, and copra. Typically, these seeds were dehulled (shredded in the case of copra), heated, flaked, and *hard screw-pressed* leaving 5 to 8 percent residual oil in the meal. Processors desiring to recover additional oil would first prepress high-oil seeds to 15 to 18 percent oil content using lighter-duty screw presses, and then solvent-extract the press cake to less than one percent residual oil content; this process is called *prepress-solvent extraction.* Hard pressing was considered too inefficient for a *low*-oil-content seed such as soybeans unless nearby markets were available for the oil-bearing meal. Thus, soybeans primarily have been *direct-solvent-extracted* to less than one percent residual oil content. Cottonseed was processed originally by hard press and later by prepress-solvent extraction, and now is processed mainly by direct solvent extraction techniques.

The introduction of the expander, a high-shear extruder with cut-flight screw, revolutionized oilseed extraction practices in the latter half of the 1980s. By 1990, over 80 percent of the soybean and cottonseed tonnage processed domestically used this technique. The expander heats, homogenizes, and shapes

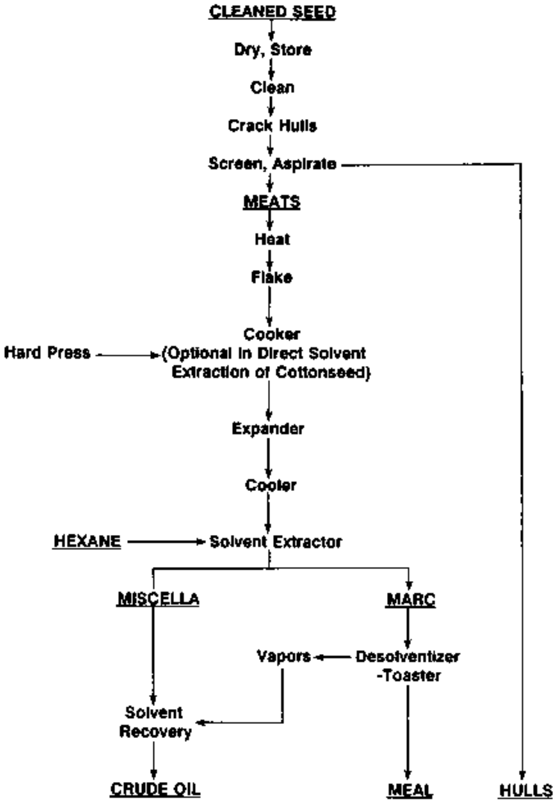


Fig. 8.4. General flow sheet for extraction of field crop oilseeds.

seeds into porous collets (pellets) that are more dense (weigh more per unit volume) but are more rapidly extracted than flakes, approximately doubling throughput of continuous solvent extractors. Collets also drain more completely, greatly reducing steam costs for desolventizing the extracted meal. The Anderson International Company of Cleveland, Ohio, has patented an expander with a drainage cage (Fig. 8.5) to reduce the oil content of high-oil seeds to less than 30 percent, thus enabling the production of intact collets for direct solvent extraction from completely dehulled seeds such as sunflower seed and peanuts.

Introduction of the expander has enabled extraction plants to handle additional seed species, with the purchase of only minimal dehulling equipment where needed. Prepress-solvent-extraction facilities are rapidly being replaced by expander-direct solvent extraction processes, leaving two basic extraction processes in the modern oilseed industry—expander-direct solvent extraction, and hard press for applications where seed supplies are limited or other considerations do not warrant the construction of solvent extraction plants

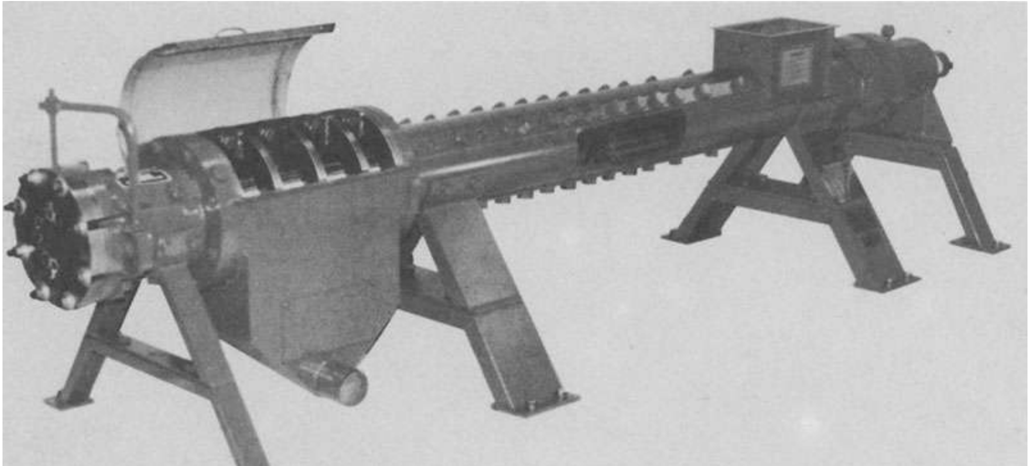


Fig. 8.5. Anderson International Corp. Hivex-Series Expander (TM) model An-88-H with oil drainage section for preparing extraction collects from high-oil-content seeds. (*By permission of Anderson International Corp., Cleveland, OH.*)

or the expenses of skilled personnel and additional safety precautions for their operation. Hydraulic cage presses still are used in processing industrial crops such as castor seed, and for edible oils in developing countries.

Referring to Fig. 8.4, freshly harvested seed should be cleaned of trash, which harbors moisture that may accelerate the formation of free fatty acids (FFAs), and dried before storage. The maximum moisture content for holding seed for long periods without spoilage varies with storage temperature and between species, and generally is in the 8 to 12 percent range. If the seed has not been adequately cleaned before storage, this must be done before extraction processing to prevent clogging and damage of equipment.

Hulls are removed in a two-step process, called *dehulling* or *decortication*, in which they are first cracked and then separated by screening and aspiration to produce a processing intermediate material sometimes called *meats*. The major objective of removing the hulls is reduction of the fiber content in meals for feeding poultry and monogastric animals such as swine. However, the protein content also is increased, and the volume of material handled in the extractor is reduced. Earlier operations required partial retention of hulls in the meats to improve handling in flaking and screw pressing operations, but hulls are no longer required with the advent of expanders equipped with oil drainage cages. It is common practice either to leave sufficient hulls with the meats to just surpass minimum protein guarantees of meals, or to adjust high protein meals to industry trading standards by adding back hulls. Currently, dehulled (low fiber) soybean meal trades at 48 percent protein, soybean meal at 44 percent, cottonseed meal at 41 percent, and dehulled sunflower seed meal at 42 percent protein.

The meats are heated, with the addition of steam to increase the moisture content if needed. Heaters (cookers), desolventizer-toasters (DTs) and coolers used in the oilseeds processing industry often are of the shallow circular pan, sweep arm, multi-stack design shown in a later figure. In earlier techniques, seed was heated to about 74°C (165°F) before flaking to about 0.3 mm (0.012 in.) thickness. However, now it is realized that phospholipase, an enzyme that makes the phospholipids nonhydratable and more difficult to remove in water degumming, is highly active at this temperature, and seeds preferably are heated to less than 57°C (135°F) or to over 85°C (185°F) to avoid the range of maximum phospholipase activity. The seed then passes to the expander for rapid heating to 105 to 121°C (220–250°F), homogenization, and reshaping.

Prolonged hot-moist holding of flakes was used benefically before development of the expander; for example, (1) in the ALCON™ process to reduce production of nonhydratable phospholipids, trypsin inhibitors, and urease in soybeans, and (2) "cooking" of cottonseed to bind ("fix") gossypol, thus reducing its free levels in meals intended for poultry and monogastric animals. Because of the relatively short residence time of seed in the expander, a second pass, a subsequent hot-hold period or additional heat treatment in the DT after extraction, is used to deactivate anti-nutrients and to bind gossypol. Even though the expander homogenizes the seed, prior flaking enhances oil recovery but can be done at 0.5 mm (0.020 in.) thickness instead of the typical 0.3 mm (0.012 in.). The flakes or collets are cooled to about 6°C (10°F) below the boiling point of the solvent before entering the extractor.

Hardly any batch-type oilseed extractors remain, and modern solvent extractors mainly are of two basic designs. In *shallow bed-type* extractors, a 0.5- to 1-meter-thick layer of collets or flakes is pulled across a linear screen (Fig. 8.6), or conveyed on a woven belt, and repeatedly percolated with solvent. *Deep bed* extractors mainly are constructed as carousels with pie-shaped cells (*baskets*), that are alternately filled (2–3 meters deep), extracted, and unloaded. In some designs, the baskets rotate between the loading, extraction, drainage, and unloading stations (Fig. 8.7); in others, the baskets are stationary with the various stations revolving (Fig. 8.8). Solvent flow always is countercurrent to the direction of

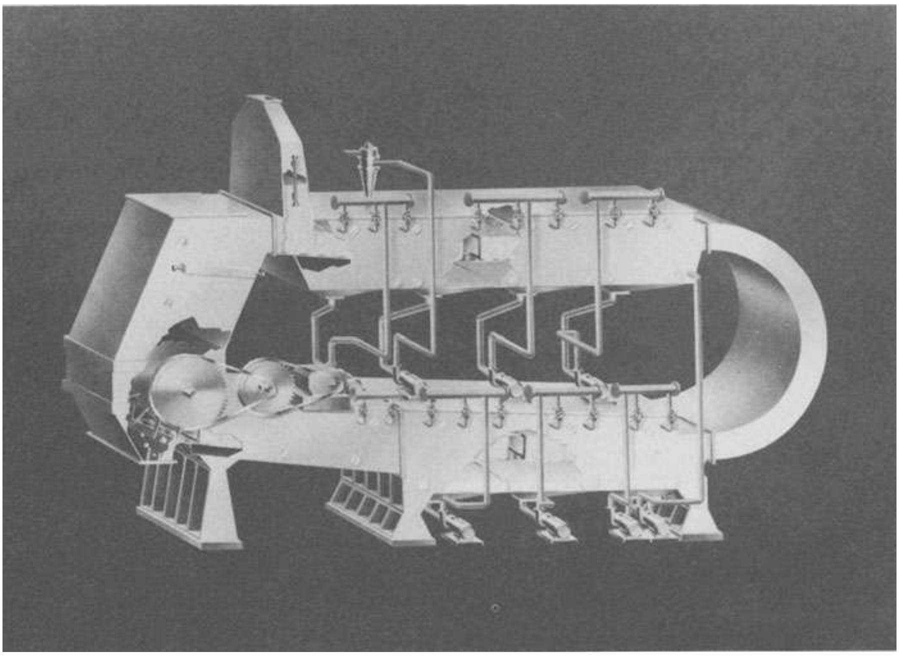


Fig. 8.6. Cutaway drawing of Crown Model III Extractor^{TM}. Collects or flakes enter through the top left of the machine and are pulled in clockwise direction by a chain-link mechanism across the top extraction section and then the bottom section while percolated with miscella traveling in a countercurrent direction. (*By permission of Crown Ironworks, Minneapolis, MN.*)

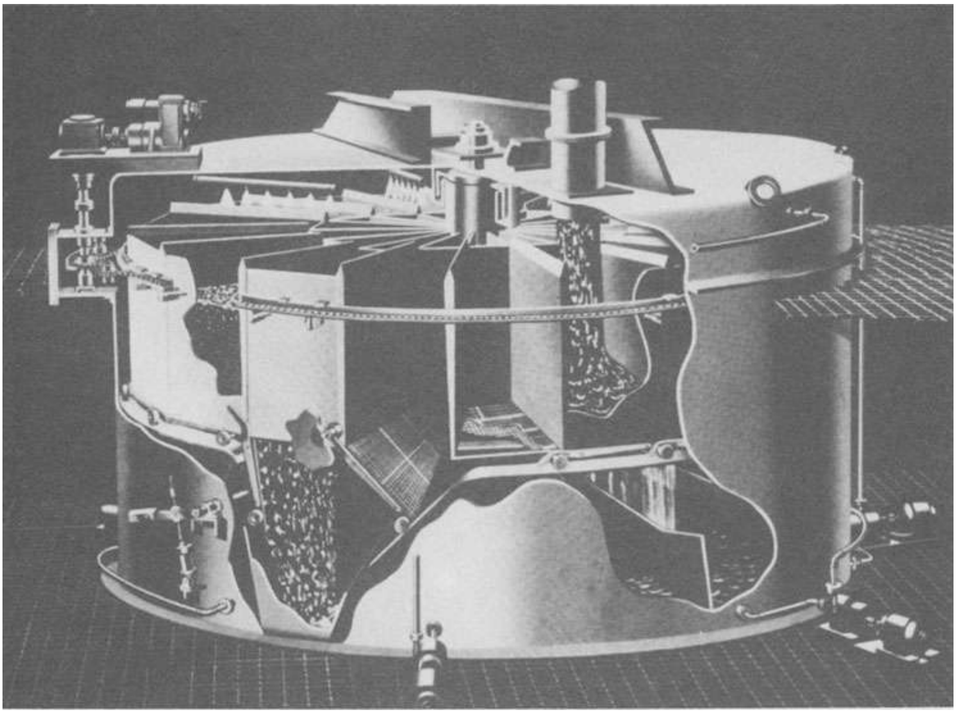


Fig. 8.7. Cutaway drawing of Rotocell Solvent Extractor^{TM}. A carousel with deep-bed baskets rotates by a series of collet/flake loading, solvent extraction, drainage, and unloading stations. (*By permission of Davy-Dravo, Inc., Pittsburgh, PA.*)

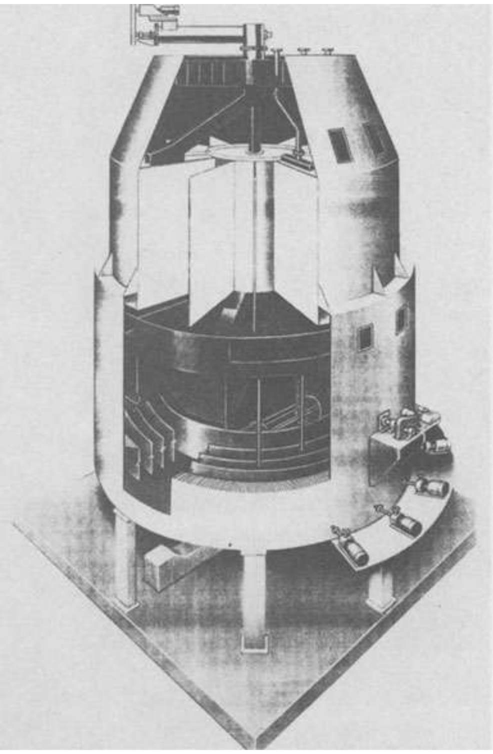


Fig. 8.8. Cutaway drawing of French Stationary Basket Extractor™. The deepbed baskets are stationary while the collet/flake loading, extraction, drainage, and unloading stations revolve. (*By permission of French Oil Machinery Co., Piqua, OH.*)

the material being extracted, with the most oil-rich solvent (*miscella*) contacting the fresh collets, and reclaimed or virgin solvent used for the final rinse of the extracted material (*marc*). Continuous solvent extractors are built in various sizes up to 3000 to 4000/tpd (tons per day).

Many solvents have been proposed or used for extracting oilseeds, but later have been found ineffective in extracting oil or have been disallowed because of health concerns about residues in food and feed products and exposure of employees. Essentially all commercial oil extraction now is done with hexane, a petroleum refinery fraction with a boiling point of 65 to 68°C (149–155°F) that consists of 48 to 98 percent *n*-hexane with the balance being short-chain homologs and branched compounds. Currently, ethyl and isopropyl alcohol are attracting the most attention as alternative extraction solvents.[19]

The extracted, drained marc contains approximately 20 percent hexane solvent holdup for soybean collets and 33 percent for flakes, and is vaporized in a DT. Some DTs have cooling sections, but separate dryer-coolers (*DCs*) often are used in large installations. Steam and sometimes hot solvent are sparged into the marc as heat sources for volatilizing the solvent; however, the condensed steam must then be removed by drying. The toasting operation destroys enzymes and anti-growth factors such as trypsin inhibitor in soybeans, reduces meal protein solubility and microbial digestibility, and improves *rumen by-pass* or *rumen escape* in feeding cattle and sheep. Figure 8.9 shows a cutaway drawing of a Crown/Schumacher design desolventizer-toaster-dryer-cooler (*DTDC*).

In processing most oilseeds, hexane is stripped from the miscella by distillation to produce a crude oil. However, gossypol and other pigments become extremely difficult to remove if left warm in cottonseed oil for more than a few days. It is common practice for cottonseed oil mills either to send their crude oil immediately to an alkali refinery or to have a miscella or alkali refinery on-site to arrest the fixing of color.[20]

In miscella refining, miscella leaving the extractor contains 30 to 35 percent oil and is raised to approximately 65 percent oil by evaporation. The FFAs in the concentrate then are reacted with alkali (sodium hydroxide solution) to produce soaps that are removed by centrifugation. Then the solvent is removed from the refined miscella by evaporation, and the soapstock is placed on the meal in the DT to recover its solvent. Hexane vapors from the miscella and the DT are condensed, and the solvent is recycled to the extractor for reuse. Noncondensable gases are passed through a mineral oil stripper to recover the last traces of hexane. A well-designed extraction plant should lose no more than about 0.5 gallon of solvent per short ton (2000 lb) of oilseed extracted.

Screw Pressing

The objective in screw pressing is to preheat (cook and dry) the seed tissue to the point

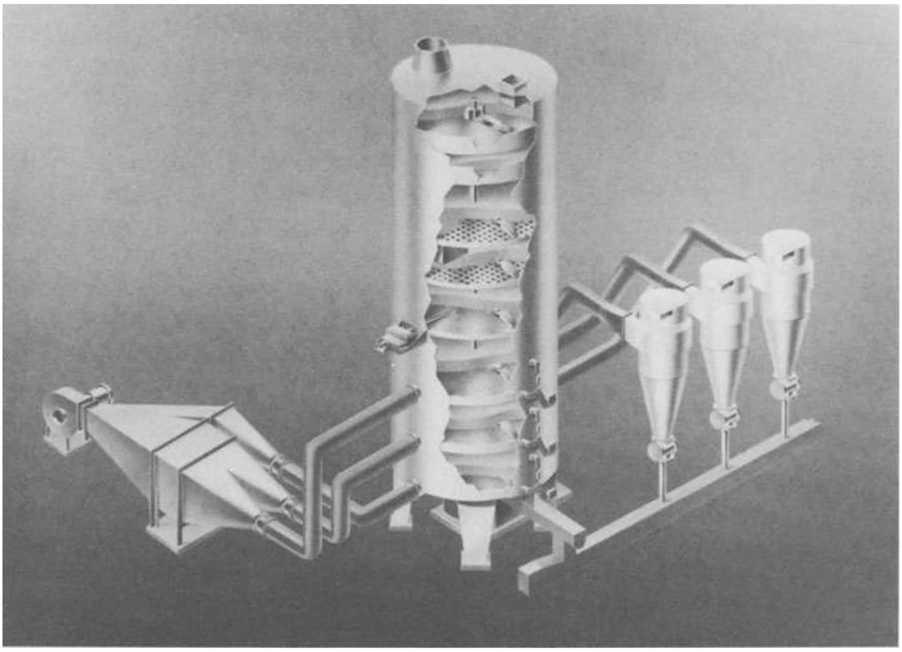


Fig. 8.9. Cutaway drawing of Crown/Schumacher desolventizer-toaster-dryer-cooler (DTDC). Note the stacked design of tray (ring) heaters-coolers with sweep arms, and steam-jacketed and perforated bottoms. Stack cookers generally have solid steam-jacketed bottoms for heating oilseeds. (*By permission of Crown Iron Works Company, Minneapolis, MN.*)

that the cell walls are brittle and rupture readily upon pressing. The seed generally is dehulled, tempered, flaked, and cooked to low moisture (2–4 percent) levels before hard pressing (Fig. 8.4). Concerns have been expressed about destruction of the essential amino acid lysine and reduction of nutritional quality and economic value of protein meals made by high-temperature, hard-press processes. Pressing typically is done in a two-stage continuous screw press or expeller, as shown in Fig. 8.10.

Extraction of Olive, Coconut, Palm and Palm Kernel Oils

Oil is extracted from the fruit of the olive tree, *Olea europea*, by milling to remove the pulpy flesh from the hard seed. The resulting paste then is: (1) pressed in hydraulic presses that use disk filters ("capachestas"); (2) diluted with water, homogenized, and allowed to settle by gravity; or (3) separated by using a continuous horizontal decanter (Fig. 8.11), sometimes followed by a vertical disc-type centrifuge for polishing (Fig. 8.12).[21]

Coconuts, *Cocos nucifera*, are hand-cut from the coconut palm with knives attached to long poles and dehusked, and the nut is cracked to drain away the coconut water. Then, the flesh is separated from the adhering shell and dried, raising the oil content from approximately 30 percent in the meat to 50 to 65 percent in the resulting copra. Considerable amounts of copra are prepared by hand and sun-dried to supplement family income in tropical countries. However, centralized coconut mechanical husking and dehulling facilities—which dry coconut meat using heat generated from burning the husks and offer the advantages of improved moisture control and reduced mold spoilage and aflatoxin problems—are growing in numbers. In the oil extraction process, copra is: (1) cleaned by shaker screens to remove trash; (2) size-reduced by hammer or attrition mills,

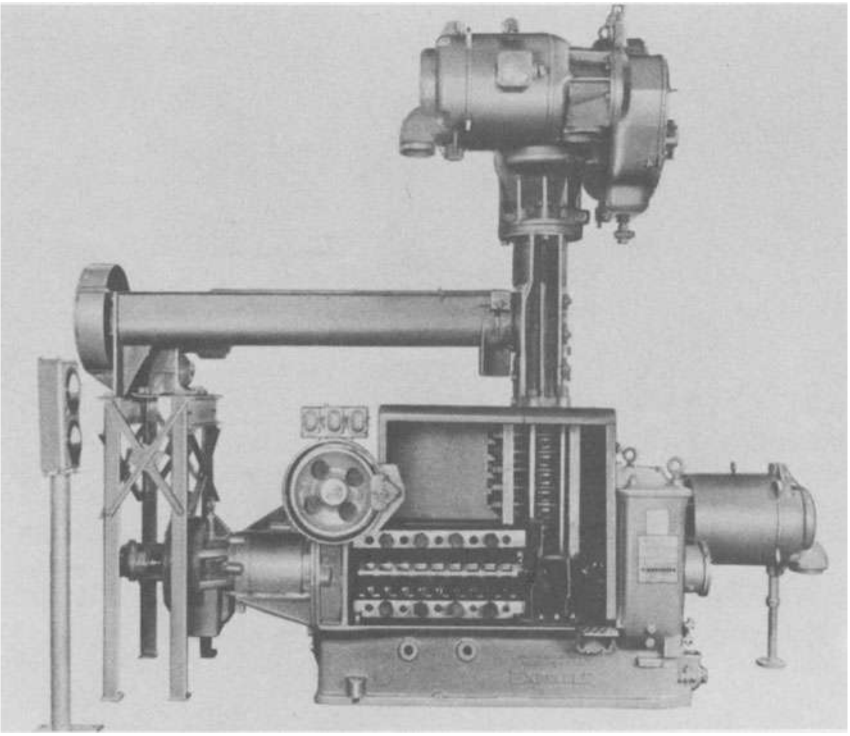


Fig. 8.10. Anderson Expeller^{TM} Press, model 55″ TMSD. Note elevated conditioner carrying product from left to right across top of press; vertical screw press section (right side); second (higher pressure) screw press section carrying product from right to left. Other brands of hard presses have both stages on one shaft. (*By permission of Anderson International Corp., Cleveland, OH*).

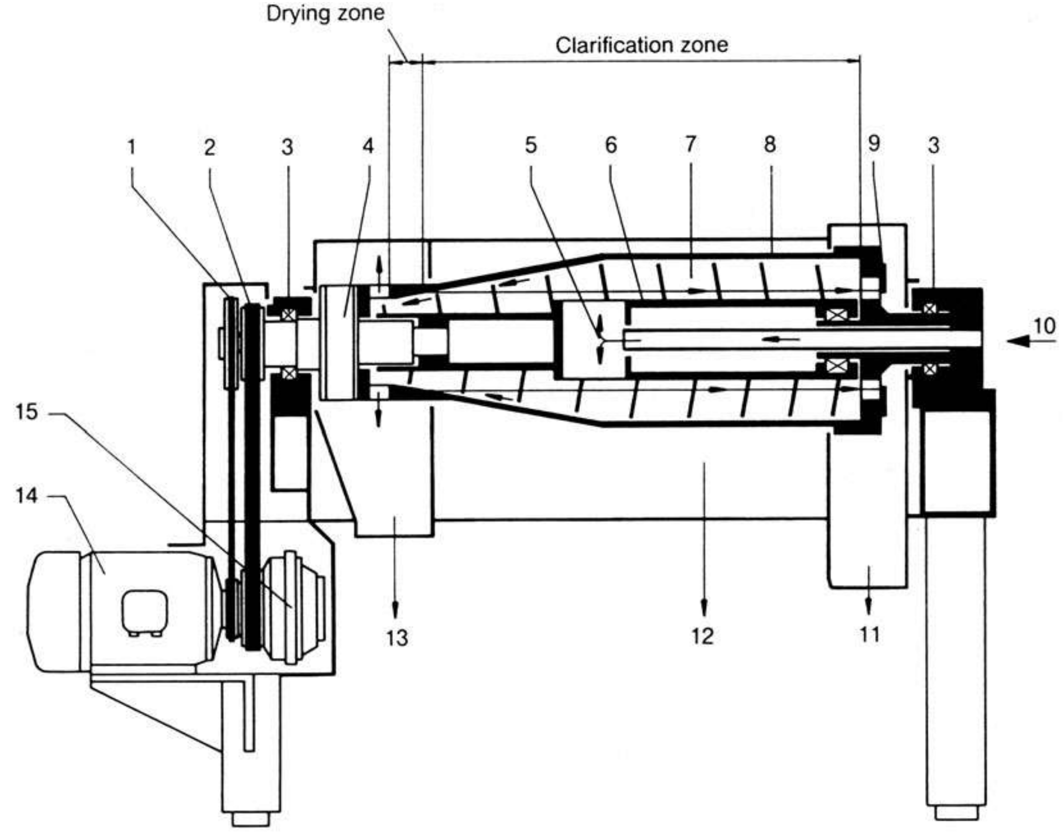
or fluted roller mills; (3) optionally flaked; (4) additionally dried if necessary; and (5) hard-pressed or prepress-solvent-extracted.

Two distinctly different types of oils are produced from the fruit of the Southeast Asia and African oil palm, *Elaeis guineensis*, and its hybrids with the South and Central American palm *E. oleifera*. Palm oil is otained from the fleshy part of the fruit, which resembles an oversized olive about the size of a small chicken egg. Palm kernel oil is derived from the kernel within the nut. Well over 98 percent of the fatty acids in palm oil belong to the C:16 and C:18 group, whereas approximately 64 percent of the fatty acids in palm kernel oil consist of the C:12 and C:14 lauric group.

A palm tree produces 10 to 15 fresh fruit bunches throughout the year, weighing 5 to 23 kg (10–50 lb) each. The bunches are cut from the tree with knives attached to long poles and are transported to the oil mill. There, they are sterilized by steam at about 40 psig for 50 to 75 minutes to deactivate lipase enzymes and loosen the fruits from the stalk. The fruits are knocked loose from the stalk in thresher drums, and passed through a digester to convert the fleshy pulp to mash. Then the mash is pressed by twin-screw expellers or hydraulically to yield red crude oil. The shells of the nuts are cracked, and the kernels are separated, dried, and bagged for later solvent extraction in a fashion similar to the processing of row crop oilseeds.

Extraction of Lards, Tallows and Fish Oils

Dry and wet rendering methods are used for extraction of animal fats and fish oils. In dry rendering of animal fats, the fatty tissue is



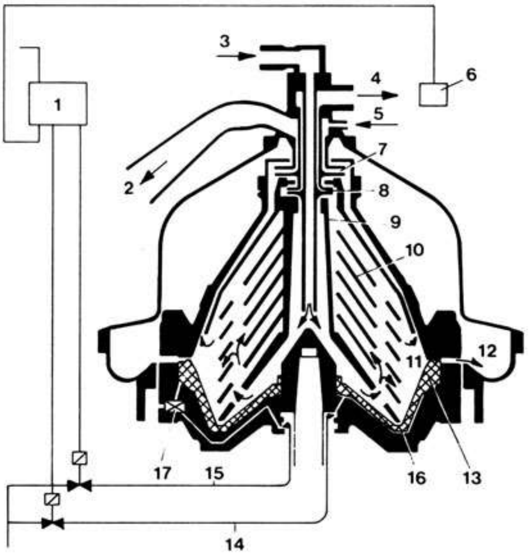
1 Conveyor screw drive
2 Bowl drive
3 Bowl bearings
4 Cyclo gear
5 Distributor
6 Conveyor screw
7 Centrifugation space
8 Bowl
9 Regulating plate
10 Feed
11 Discharge of the clarified liquid
12 Frame
13 Solids discharge
14 Drive motor
15 Clutch

Fig. 8.11. Schematic drawing of Westfalia Model CA 450 Continuous Clarifier Decanter. (*By permission of Centrico, Inc., Northvale, NJ.*)

ground and heated to drive off moisture, a process that makes the cell walls brittle by denaturing the protein. The resulting slurry of oil and cracklings is passed through a screw press to expel the oil, and the press cake then is ground into meat or meat by-product meal. Batch-type cookers of various types mainly are used, followed by continuous single-stage presses. Where batch-type cage presses still are used, the cake is formed in the shape of large wheels, sometimes called *greaves*.

In wet rendering of animal products, the flesh is ground and heated to denature the protein and release moisture and fat. Continuous decanters then are used to remove the liquid fraction, and the residue is frozen and sold as *partially defatted beef or pork tissue* for use in processed meats. The liquid portion is additionally heated to help break the emulsion, and the fat is separated from the aqueous phase by continuous centrifuges.

Much of the fish that is processed is cooked in batch or continuous cookers to coagulate the protein, and passed through a continuous screw press to remove the liquid portion. The liquid then is separated by continuous decanters



1 Timing unit
2 Heavy phase outlet
3 Feed
4 Light phase outlet
5 Flush water inlet
6 Pressure switch
7 Heavy phase centripetal pump
8 Light phase centripetal pump
9 Distributor
10 Disc set
11 Sediment holding space
12 Sediment ejection ports
13 Piston
14 Closing water
15 Opening water
16 Closing chamber
17 Bowl valve

Fig. 8.12. Schematic drawing of Westfalia Model RSA 150 Refining Separator with self-cleaning bowl. (*By permission of Centrico, Inc., Northvale, NJ.*)

into aqueous and oil fractions, and the latter then is passed through a continuous polishing centrifuge. The solid residue is dried and ground to produce fish meal.

Essential Oils

Essential oils are extracted in several ways: with fat, by distillation, and by batch solvent extraction. The oldest method, used today only for extremely valuable essential oils, is *enfleurage-défleurage*. This consists of layering blossoms of the material to be extracted between fat-coated glass plates and allowing the essential oil to perfuse into the fat. The blossoms are renewed daily. At the end of the season, the fat is scraped from the plates, melted, poured into containers, and sold as *pomade*, or is batch-extracted with cold ethanol and sold as *extraits*. Another technique consists of macerating the material and extracting with hot fat. The most common extraction process for essential oils is steam distillation of a mash of the leaves or seeds to be extracted. Selective solvent batch extraction also is used.

EDIBLE FATS AND OILS: REFINING, PROCESSING, AND COMPOUNDING

The objectives of refining and processing fats and oils include: (1) removal of free fatty acids, phospholipids (gums), color and off-flavor/odor compounds, and toxic substances to produce light-colored, bland products with long shelf lives; (2) obtaining a mixture of triacylglycerols with the desired solid content profiles over the range of product use; and (3) preparation and storage of semisolid products with desired textures.

Solid Fat Content

Crystallization characteristics of fats and oils were described in the section on polymorphism. The size, abundance, and stability of crystals are important in food processing/food service ingredients and consumer products. Clear salad oils are preferred, and are made by selecting low-melting-point oils that are *winterized* by chilling to crystalline the higher-melting triacylglycerols, which are then removed by filtration.

Margarines, shortenings, and coating fats are mixtures of fat crystals in oil, whose characteristics are described and controlled by Solid Fat Content (SFC) or Solid Fat Index (SFI) techniques. The results of the two analytical techniques are similar but not identical.

SFI curves of butter, stick and tub (soft) margarine, and general-purpose shortening oils are shown in Fig. 8.13. Note that stick margarine can be formulated to be softer (contain less solids) than butter when removed from the refrigerator, and to remain firmer at warm room temperatures. Tub margarines can be made soft and spreadable when taken directly from the refrigerator, with relatively small change in texture over a wide range of temperatures.

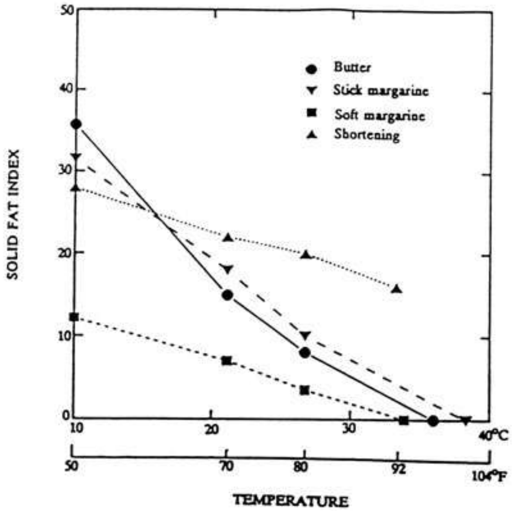


Fig. 8.13. Solid Fat Index curves of butter, stick and tub margarine fats, and a general-purpose shortening.

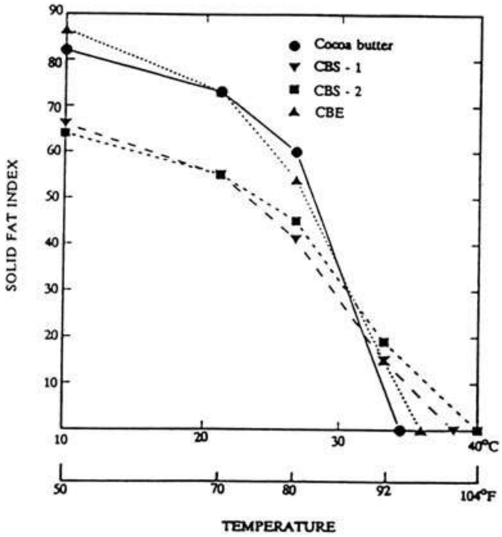


Fig. 8.14. Solid Fat Index curves of cocoa butter, cocoa butter equivalent (CBE, used as an extender), and higher-temperature-melting cocoa butter substitutes (CBSs).

Fats must melt completely just below body temperature (37°C) to avoid coating the roof of the mouth and giving the product a greasy feeling. This explains why the shortening depicted in Fig. 8.12 would taste very greasy, and why some stick margarines are slightly greasy. Another important concept in semisolid fat product technology is the *plastic range*, or the temperature span through which a product remains soft and workable but without being fluid; 17 to 25 SFI has often been used as the plastic range for shortenings.[22]

Figure 8.14 presents SFI curves of cocoa butter (from the kernel of *Theobroma cacao*), a cocoa butter equivalent (CBE) used as a cocoa butter extender, and two cocoa butter substitutes (CBS) or replacers. Cocoa butter, the main component of chocolate, has a pleasant mouthfeel because it completely melts from a solid product into a liquid in a short temperature span. Considerable energy uptake is required, and the melting of chocolate has an agreeable cooling effect in the mouth. CBEs are made by compositing triacylglycerols containing primarily C16 and C18 fatty acids. They are used as extenders, as enhancers to slightly raise the melting point of cocoa butter, and as replacements. CBEs are compatible with cocoa butter, and can extend marketing opportunities of confections to hot weather seasons and warmer climates. CBSs consist primarily of lauric acid–type fats (primarily C12 and C14 fatty acids from palm kernel and coconut oils). Although CBSs can simulate the characteristics of cocoa butter, these substances are not compatible and are used independently.

The production of semisolid oil and fat products with specific desired textures includes the selection of fat/oil mixtures with the desired SFI/SFC profiles and working the product into a stable crystal state. Thermodynamic principles dictate that fats eventually will undergo polymorphic changes to reach the most stable β state. However, changes can be appreciably delayed kinetically by: (1) selecting mixtures of triacylglycerols that co-crystallize as small crystals; (2) specifically including oils that are β'-formers (such as corn, cottonseed, fish, linseed, olive, palm, and peanut oils and tallow) in preference to β-formers (such as soybean, canola, sesame, and sunflower oils and lard)[23]; (3) including emulsifiers that interrupt the growth of crystals; (4) chilling-working the product into specific polymorphic states.

Regarding the last point, many melted shortenings normally would cool into mixtures

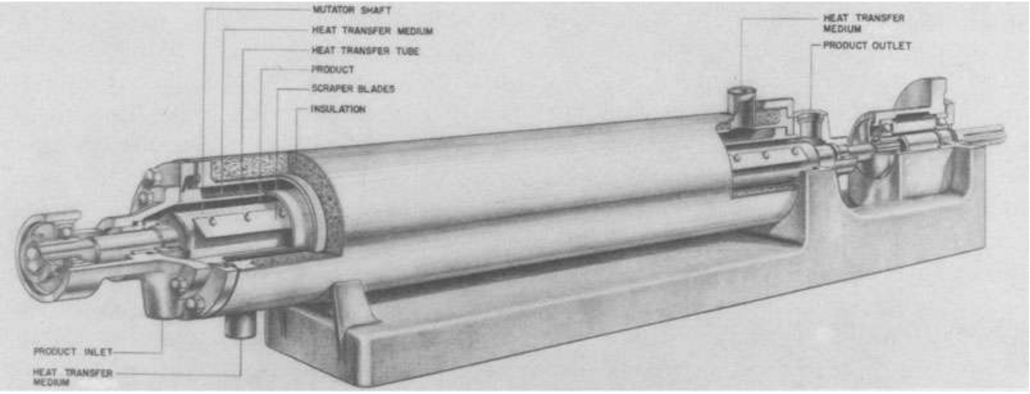


Fig. 8.15. Cut-away drawing of a Votator^{TM} scrape-surface heat exchange unit used for making plasticized shortening. (*By permission of Cherry-Burrell Process Equipment, A United Dominion Company, Louisville, KY.*)

of crystals in free oil, which are difficult to handle and have limited air-entrapment abilities in making cakes and pastries. Chilling the same stock to form small crystals and aeration with inert gases in scrape-surface heat exchangers called *Votators*^{TM} (Fig. 8.15) produce smooth-textured, semisoft products that are easy to handle.

Up to six polymorphic forms of cocoa butter crystals have been reported. It is common practice to work chocolate into very stable β' or small β crystal forms by slow agitation, careful control of temperatures, and tempering (holding) freshly cast products under specific conditions before release to the trade. *Bloom*, a grayish defect, occurs when chocolate or other types of coating fats have been allowed to partially melt, and some oils rise above the sugar and coloring matter in the product and recrystallize.

Degumming and Refining

Crude fats and oils are processed by the general scheme shown in Fig. 8.16, with modifications or exceptions for specific species. The phospholipids (lecithins) must be removed to avoid darkening of the oil during high-temperature deodorization and in deep-fat-frying applications. This removal typically is accomplished during the alkali refining process or in a separate water/acidic water

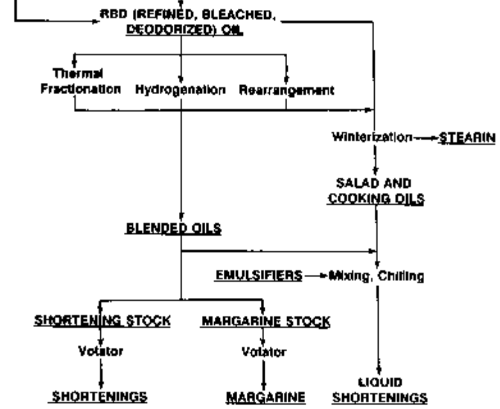


Fig. 8.16. Generalized flow sheet for refining and processing fats and oils.

degumming step before alkali refining. Crude soybean oil has an unusually high (2–3.5 percent) phospholipid content among oils, and often is degummed in a separate operation to no more than a 300 ppm level (as phosphorus) to avoid precipitation during shipping and storage. Levels of 10 ppm or less of phosphorus are achieved in the better-quality refined soybean oils. Degumming is achieved by mixing crude soybean oil with water to hydrate the phospholipids and enable their removal by centrifuge. Citric and other acids sometimes are added, in a step called *super degumming*, to help remove phospholipids that are not hydrated by water alone. The gums then may be purified into commercial lecithins, or placed back on the meal in the DT if a market is not available.[24]

Degummed soybean oils, or crude oils of other species, next are reacted (*neutralized*) with sodium hydroxide solution to form sodium salts of the fatty acids, which are removed as soapstock by a continuous centrifuge.[25] The soapstock also occludes remaining phospholipids, some color and flavor compounds, and several percentage points of neutral (salable) oil for each percentage of FFAs present. The soapstock can be put back on meal in the DT for drying if refining is done adjacent to an extraction plant, or acidified to again form fatty acids and sold to the oleochemicals industry. The oil then is water-washed and centrifuged one or two times to remove residual soaps.

Bleaching and Deodorization

Next, the refined oil is bleached (reacted with activated clays, diatomaceous earths, or recoverable silicas) to adsorb phospholipids, color pigments, soaps, peroxides, aldehydes, and other polar compounds, and is recovered by filtration. Spent bleaching earths in the filter cake contain pigments, occasional residual pesticides, aldehydes, and other compounds removed from the oil, and they often present disposal problems.[26]

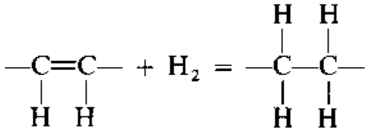
Deodorization consists of heating the oil to high temperatures under high vacuum with the addition of stripping steam to remove remaining odor-causing compounds, volatile pesticides, products of oxidative rancidity such as peroxides, aldehydes, tocopherol-like natural antioxidants, and residual amounts of free fatty acids.[27] The deodorizer condensate may be collected and processed to recover natural antioxidants. The final refined, bleached, and deodorized product is called *RBD oil*.

As an alternative, the degummed oil may be subjected to minor bleaching and then physically refined, using a high-temperature/high-vacuum process that strips away the compounds normally removed in the deodorizer plus the fatty acids.[28] The major advantage of physical refining is elimination of neutral oil losses that occur by occlusion in both miscella and alkali refining. Palm oil has low phospholipid content and generally is physically refined, but row crop oils need to be degummed before physical refining can be considered.

Hydrogenation, Rearrangement, and Thermal Fractionation

These three processes are mainly concerned with obtaining fats and oils with desired stability and solid content properties. In theory, they may be used alternatively or in any sequence; but, in practice, have been applied more to certain species of fats and oils than to others.

Hydrogenation is the process of adding hydrogen with the assistance of a catalyst (often nickel) to an unsaturated (double) bond of a triacylglycerol fatty acid:



$$-\underset{\mathrm{H}}{\underset{|}{\mathrm{C}}}=\underset{\mathrm{H}}{\underset{|}{\mathrm{C}}}- + \mathrm{H_2} = -\overset{\mathrm{H}}{\overset{|}{\underset{\mathrm{H}}{\underset{|}{\mathrm{C}}}}}-\overset{\mathrm{H}}{\overset{|}{\underset{\mathrm{H}}{\underset{|}{\mathrm{C}}}}}-$$

However, a polyunsaturated hydrocarbon chain can isomerize after hydrogenation to form either *cis*- or *trans*-isomers at the remaining unsaturated sites. Unsaturated oils in nature normally are in the *cis*-form, and concerns about potential roles of hydrogenation-produced *trans*-forms in circulatory and heart diseases have been voiced.[29] The ratios of *cis*:*trans* forms produced can be partially controlled by the catalyst and the temperature-pressure conditions selected for hydrogenation. With continued hydrogenation, polyunsaturated fats can be changed to fully saturated fats with high melting points. However, hydrogenation typically is used with discretion to achieve desired intermediate forms. "Brush" or light hydrogenation often is used to reduce the linolenic acid content and increase flavor stability of bottled soybean oil. Also, arrays of fats with different melting points are prepared as blending stocks for making shortenings, margarines, and specialty fats.[23]

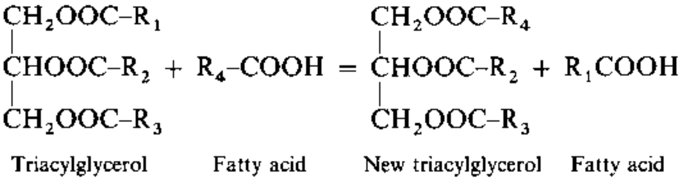
Hydrogenation is applied broadly to row crop oilseed oils.

cis-9, cis-12	trans-10, cis-12	trans-10 cis-12 trans-11 cis-11
	cis-9, trans-11	cis-9 trans-11 cis-10 trans-10
Linoleate	Conjugated dienes	Monoenes

Rearrangement, also called *interesterification*, is a means of changing the structure of a triacylglycerol. By controlling purity of the triacylglycerol stock, it is possible to rearrange the location of fatty acids on the glycerol, move (*transesterify*) fatty acids from one glycerol to another, or displace a fatty acid on a glycerol with a fatty acid introduced to the mixture.[30]

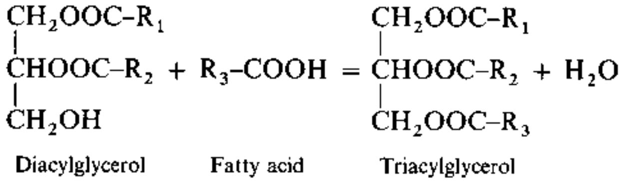
Fatty acids in natural fats are not randomized, but occur in specific distributions; however chemical interesterification randomizes both their distributions between triacylglycerols and locations on the glycerol molecule. For example, the natural distribution of saturated and mono- and polyunsaturated fatty acids in cocoa butter is: SSS—2.2 percent, SSU—84.6 percent, SUU—11.1 percent, and UUU—0.5 percent, with 1.6 percent unknown; whereas the distribution in randomized cocoa butter is: SSS—23.9 percent, SSU—43.8 percent, SUU—26.8 percent, and UUU—5.5 percent.[31] Depending on the fat, rearrangement can improve or damage the desirable SFC, plastic range, and melting characteristic. The functionality of lard often is improved by transesterification, but the highly desirable sharp melting characteristic of cocoa butter is destroyed by rearrangement. Rearrangement has been used very effectively to improve the functionality of lard.

Thermal fractionation is the process of chilling an oil to precipitate crystals of the higher-melting triacylglycerols, and removing these crystals with continuous filters.[32] *Dewaxing* is the process of chilling the oil and removing usually low levels of waxes by centrifugal force with the help of a wetting agent, or by filtration with the aid of filter aids. *Winterization* is the process of reducing the cold test of an oil by chilling followed by removal of the higher-melting triacylglycerols. *Dry fractionation* is the process of separating a fat or oil into two or more fractions by a



$$\begin{array}{l} CH_2OOC\text{-}R_1 \\ | \\ CHOOC\text{-}R_2 \\ | \\ CH_2OOC\text{-}R_3 \end{array} + R_4\text{-}COOH = \begin{array}{l} CH_2OOC\text{-}R_4 \\ | \\ CHOOC\text{-}R_2 \\ | \\ CH_2OOC\text{-}R_3 \end{array} + R_1COOH$$

Triacylglycerol Fatty acid New triacylglycerol Fatty acid



$$\begin{array}{l} CH_2OOC\text{-}R_1 \\ | \\ CHOOC\text{-}R_2 \\ | \\ CH_2OH \end{array} + R_3\text{-}COOH = \begin{array}{l} CH_2OOC\text{-}R_1 \\ | \\ CHOOC\text{-}R_2 \\ | \\ CH_2OOC\text{-}R_3 \end{array} + H_2O$$

Diacylglycerol Fatty acid Triacylglycerol combination of chilling, seeding with nuclei if necessary, and filtration. The liquid (oil) fraction is called *olein* and the solid fraction *stearin*. Dewaxing, winterization, and fractionation, in the presence of a solvent, are called *wet* or *miscella fractionation*.

Fat and Oil Products

Salad and *household cooking oils* typically are winterized before bottling. However, some premium-priced, cold-pressed, filtered low-fatty-acid oils are sold in health food outlets with the claim that they have received no chemical treatment.

Liquid shortenings consist of selected oils to which a crystal inhibitor (fatty acid, solid triacylglycerol, lecithin, glyceryl or sorbitan mono- or diester, or other compound) has been added; the product is chilled to retain the oil in the α-crystal form. Liquid shortenings are available in cloudy or clear form.

In making *shortenings*, oils and hardstocks made previously by hydrogenation are blended to obtain the desired plastic range, and are chilled and aerated using a Votator™ or other scrape-surface heat exchanger. In making *margarines*, water, milk solids, flavorings, and color are blended to obtain a mixture containing 80 percent fat and then are chilled by a scrape-surface or other type of heat exchanger. Time must be allowed during the process, or in a later tempering room, for the desired crystal forms to materialize before these products are shipped.

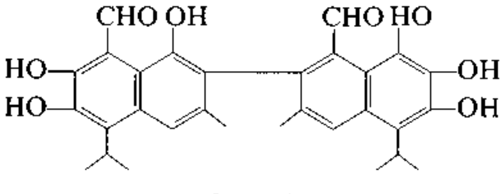
Notes on Selected Species

Soybeans (*Glycine max*). Soybeans originated in China, and were cultivated as early as 2836 B.C. The oil of this seed has presented numerous processing challenges because of its high phospholipid content and a tendency to "revert" to a beany flavor in the early days of processing technology. Recommendations for processing include exclusion of copper and iron in equipment and in lines, avoidance of light, and storage under a nitrogen blanket.

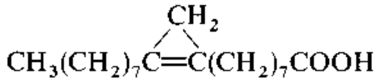
Cotton (*Gossypium arboreum* and *G. herbaceum*). Cotton was grown in the Indus River Valley (modern Pakistan) as early as 3000 B.C., "New World" cottons were grown in Peru (*G. hirsutum*) in 2500 B.C., and Sea Island cottons (*G. barbadense*) were grown in the Caribbean Islands. Most of the world's cotton today is *G. hirsutum*, with fuzzy seed that requires a delintering saw before dehulling and subsequent processing. Pima and Egyptian cottons (*G. barbadense-type*) have "naked" seed and can be processed directly. Cottonseed is among the first examples of a reclaimed by-product in our industrial world. Invention of the cotton gin by Eli Whitney in 1793 led to increased domestic production of cotton and also to seed disposal problems. The state of Mississippi passed the first anti-pollution law in the nation in 1857, prohibiting throwing cottonseed into rivers and requiring its orderly disposal from gins located less than one-half mile from a town.

Cottonseed contains the polyphenolic green-yellow pigment gossypol, 1,1′,6,6′,7,7′-hexahydroxy - 5,5′ - diisopropyl - 3,3′ - dimethyl(2, 2′-binapthalene)-8,8′-dicarboxaldehyde, in discrete bodies called *glands*. Processing challenges include removal of gossypol, or its 15 or more derivatives, from the oil to reduce color, and deactivating its toxic effects (through binding to the protein with moist heat) to enable feeding the meal to monogastric animals.

Cottonseed oil also contains the cyclopropenoic acids, C18:CE malvalic acid (8,9-methylene-8-heptadecenoic acid) and C19:CE sterculic acid (9,10-methylene-9-octadecenoic acid), which form the pink color in the Haphen test used to detect its adulteration of higher-priced olive oil.

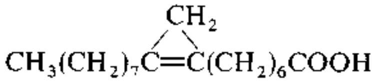


Gossypol



$$CH_3(CH_2)_7\overset{CH_2}{C{=}C}(CH_2)_7COOH$$

Sterculic acid



$$\mathrm{CH_3(CH_2)_7\overset{CH_2}{C{=}C}(CH_2)_6COOH}$$

Malvalic acid

Rapeseed/Canola. These belong to the turnip rutabaga, cabbage, Brussels sprouts, and mustard family of crops that can be grown at low temperatures and moderate humidity. Three species have been grown as oilseeds: *Brassica napus,* known in Europe as rape, oil rape, swede rape, and Argentine rape; *B. campestris,* known as rapeseed, oil turnip, turnip rape, and Polish rape; and *B. juncea,* known as leaf mustard, brown mustard, Oriental mustard, and Indian mustard.[33] *B. campestris* was grown in India as early as 2000 to 1500 B.C.

This crop is the classic example of an effective crop improvement program mobilized by one country in response to the impending loss of international markets. When it was reported in the early 1960s that the erucic acid in rapeseed oil can cause heart damage and other diseases, the Canadian government established a crash development program that led to release of the first low-erucic-acid rapeseed (*LEAR*) in 1969. Continuing efforts to develop varieties with even lower erucic acid led to the later release of "*double zero*" (low-erucic, low-glucosinolate) varieties, which were named *canola* in 1980. Because of reduced glucosinolate levels, considerably more of the meal could be used in animal feed than earlier. Canola oil, which contains less than 2 percent erucic acid compared to 20 to 40 percent in earlier rapeseeds, was granted GRAS (generally recognized as safe) status by the United States Food and Drug Administration in 1985.

However, introduction of canola did not solve all problems. An industrial market for erucic acid had developed earlier. High-erucic-acid rapeseed then was imported from Northern Europe for extraction, followed by efforts to develop industrial rapeseeds with increased erucic acid content as well as development of *crambe* (*Crambe abyssinica*) specifically for its erucic acid. At the current state of development, equipment corrosion and poisoning of hydrogenation catalysts by sulfur in canola oil still are problems. Also, oil from the new canola varieties favors formation of β-crystals, in contrast to β'-crystal formation in the earlier rapeseed varieties.

Sunflower (*Helianthus annus* var. *Marcocarpus*). This is a New World crop, known to have been grown in Arizona–New Mexico in 3000 B.C. and in the Mississippi–Missouri Basin at least since 900 B.C. The crop was taken to Europe by early explorers and was developed as a source of edible oil in Russia. The gray and white-striped seed is known as the *confectionary-type*. Its kernel is loose within the achene, and the seed usually is shelled and eaten. No major antinutritional factors are known to exist in the raw seed. *Oil-type* varieties predominantly are black-hulled, with seeds about one-third the weight of confectionary-types. The seed adheres tightly to the hull, and provides a challenge in dehulling. It has been repeatedly shown that, although the setting of seed by sunflower plants is not as sensitive to day length as that by soybeans, the oleic acid content is inversely related to the temperature of seed maturation. Thus, users desiring polyunsaturated oil with high linoleic acid content have specified northern-grown sunflower oil, whereas those desiring extended oil stability, as in production of fried foods, have preferred oil from seeds matured during the summer in the southern states. Sunflower varieties with high-oleic-acid content (85–92 percent) have been developed within the last decade, with intentions of using the oil as a feedstock in chemicals manufacturing processes. Also, high-oleic confectionary-type sunflower seed has been developed, enabling extension of the shelf-life of roasted seed.

Peanuts, Ground Nuts (*Arachis hypogae*). Also a New World crop, peanuts are known to have been grown in the Upper Plata Basin of Bolivia in 2000 B.C. They were taken to Europe by early explorers, and were returned to the southeastern United States from Africa by slave traders. Broad cultivation did not occur domestically until the early 1920s. Most of the peanuts grown in the world are processed into oil, but most domestic-grown peanuts are consumed as food, with over one-half of the crop production used in making peanut butter.

NONIONIC SURFACTANTS—EMULSIFIERS

Nonionic surfactants and emulsifiers are compounds whose molecules have both aqueous (polar) and alkane (nonpolar) compatible sectors. Their molecules have regions that are sufficiently similar to become part of either system, with the other sectors sufficiently dissimilar to interrupt continuation of that system. For example, when added to a crystallizing fat, some nonionic surfactants may orient themselves to become part of the crystal, and will prevent further replication thus limiting crystal size. Likewise, some will react wth gelatinized starch in aqueous systems and prevent its recrystallization (retrogradation). Further, surfactants may orient around discrete droplets to stabilize water in oil (W/O) or oil in water (O/W) emulsions. When this occurs, the compatible end becomes associated with the discrete droplet, leaving the other end turned outward to associate with the compatible continuous phase.

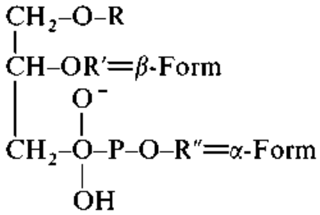
The major groups of commercial emulsion stabilizers include: (1) glycerol esters, favoring W/O emulsions; (2) esters of monoacylglycerols with hydroxycarboxylic acids (including lactic, succinic, malic, and tartaric); (3) sodium stearoyl-2-lactylate (SSL), favoring O/W emulsions; (4) fatty acid monoesters of ethylene glycol; (5) sorbitan fatty acid esters known as SPANS (W/O) and TWEENS (O/W); (6) phospholipids; (7) water-soluble gums, including gum arabic, tragacanth, xanthin, agar, pectin carrageenan, and methyl- and carboxymethylcellulose; and (8) proteins.

Glycerol has three exposed hydroxyl groups, resulting in a compound completely miscibile in water at all concentrations. Fatty acids have both hydrophilic (water-attracting) and lipophilic (oil-attracting) ends. As they are esterified to glycerol, a molecular structure that originally was primarily water-soluble becomes increasingly oil-soluble. Finally, when all three positions are esterified with nonhydroxy fatty acids, the molecule is nonpolar and soluble only in organic solvents.

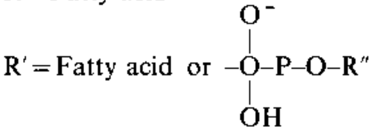
Limited amounts of monoacyglycerols and diacylglycerols are present in extracted crude oils. Additional quantities can be made by chemical or enzymatic hydrolysis, or by esterification of glycerol with one or more fatty acids. Also, phospholipids normally are present in extracted plant crude oils and have at least one chain with a water-soluble unattached end. At best, fatty acids, monoacylglycerols, and diacylglycerols are W/O emulsifiers. Additional types of surfactants can be made by esterifying fatty acids to compounds other than glycerol, including propylene glycol, surcrose, and sorbitol (resulting in SPANS™). TWEENs™, which are O/W emulsifiers, detergents, and solubilizers, are made by adding polyoxyethylene (POE) chains to SPANS.

The hydrophilicity of nonionic surfactants can be characterized numerically as their hydrophile–lipophile balance (HLB). An HLB value of 3 to 6 indicates that the compound is a likely W/O emulsifier; 7 to 9, a wetting agent; 8 to 13, an O/W emulsifier; 13 to 15, a detergent; and 15 to 18, a solubilizer (of oil or other nonpolar compounds into water).[34] HLB values of some common compounds are presented in Table 8.7.

A *phospholipid* is defined as any lipid containing phosphoric acid, and a *glycerophospholipid* is any derivative of glycerophosphoric acid that contains at least one O-acyl, O-alkyl-l-enyl, or O-l-alkyl group attached to the glycerol residue. The terms phosphatide and phosphoglyceride are no longer recommended. Under stereospecific nomenclature, the phosphate is assigned to the *sn*-3 position. By this convention, phosphatidylcholine (PtdCho), a major component of soya lecithin, is called 1,2-diacyl-*sn*-glycero-3-phosphocholine.[35] General structure formulas for the more common phospholipids in plant oils are shown below:



R = Fatty acid



$$R' = \text{Fatty acid or } -\overset{O^-}{\underset{OH}{O}}-P-O-R''$$

$R'' = H$	Phosphatidic acid
$R'' = C_6H_6(OH)_6$	Phosphatidylinositol
$R'' = CH_2CH_2NH_3^+$	Phosphatidylethanolamine
$R'' = CH_2CH_2N^+(CH_3)_3$	Phosphatidylcholine
$R'' = CH_2CH(NH_3^+)COOH$	Phosphatidylserine

Common phospholipids in plants

TABLE 8.7 HLB (Hydrophile–Lipophile Balance) Numbers for Some Surfactants

Name	*CAS Number*	*HLB Value*
Oleic acid	112-80-1	1.0
Acetylated monoglycerides (film formers)	—	1.5
Sorbitan trioleate (SPAN 85[1])	26266-58-6	1.8
Glycerol dioleate	25637-84-7	1.8
Sorbitan tristearate (SPAN 65[1])	26658-19-5	2.1
Glycerol monooleate	25496-72-4	3.4
Glycerol monostearate	31566-31-1	3.8
Sorbitan monooleate (SPAN 80[1])	1333-68-2	4.3
Sorbitan monostearate (SPAN 60[1])	1338-41-6	4.7
Soy lecithin	8020-84-6	8.0
Sodium stearoyllactylate (anionic type)	18200-72-1	8.3
POE sorbitan monooleate (TWEEN 81[1])	9005-65-6	10.0
POE sorbitan monostearate (TWEEN 60[1])	9005-67-8	14.9
POE sorbitan monooleate (TWEEN 80[1])	9005-65-6	15.0
POE stearic acid (monoester) (TWEEN 20[1])	9004-99-3	16.9

[1] Brand names by Atlas.

An HLB value of 8.0 is shown in Table 8.7 for lecithin, but manufacturers are able to supply lecithins with values of 2 to 12. The reader is cautioned that the terms "phosphatidylcholine" and "lecithin" sometimes are used interchangeably, especially in nutrition literature.

HEALTH AND CONSUMER INTERESTS

Non/Low-Caloric Fat Substitutes

Although various health groups recommend that no more than 30 percent of calories be consumed as fats and oils, the national average is approximately 37 percent. Research on military and astronaut rations has focused on increasing the caloric density of food to save both weight and cube (volume) without inducing nutritional problems. However, the most publicized research and development has been on ingredients that impart the desirable characteristics of fat at reduced calorie levels. Proposed replacements have been protein-based, carbohydrate-based, or synthetic (fatty acids and long-chain alcohols in structures that are resistant to hydrolysis by digestive enzymes).[36,37]

Protein-based substitutes are derived from egg and milk proteins that have been heated and blended in a process called microparticulation, which shears and shapes the heat-coagulated protein gels into small spheroidal particles that are below the perceptual threshold of the tongue, thus giving a rich and creamy sensation in the mouth. The only product granted GRAS status for use in frozen desserts by the FDA thus far is Simplesse^R, a product made by The NutraSweet Company, Skokie, IL. This is a hydrated protein, containing about 1.3 kcal/g, that is used to replace fat (9 kcal/g) in frozen desserts. Other potential applications include dairy products, salad dressings, mayonnaise, and margarine. Kraft General Foods, Glenview, IL, has petitioned for approval of Trailblazer^R, a product reported to be similar but made by a different process.

Carbohydrate-based replacements rely on a viscosity increase and smooth gel-like textures to simulate the properties of fats and oils. These substitutes include: gums, hydrophilic hydrocolloids that increase product viscosity and improve emulsion stability; polydextrose, a polymer of dextrose with small amounts of sorbitol and citric acid made by Pfizer Chemical Division, New York; and a variety of corn, tapioca and potato starch maltodextrins made by various starch processors. Neither the protein- nor the carbohydrate-based replacements can be used as frying or dry coating oils.

Synthetic compounds are fatlike materials that include fatty acids or long-chain alcohols esterified in structures that are not hydrolyzed by enzyme activity. None of these compounds has been approved yet by the FDA.

The best-known material under consideration is Olestra, a proposed generic name for sucrose polyester developed by the Procter & Gamble Company, Cincinnati, OH. This compound contains six to eight long-chain fatty acids, primarily C12 to C24, esterified to sucrose. It is made by converting RBD oil into methyl esters by reacting the triacylglycerol with methanol using sodium or potassium methoxide as the catalyst, and then combining the washed esters with sucrose using an alkaline catalyst. To best simulate their respective properties, Olestras preferably are made from fatty acids of the oils that are to be replaced, such as cottonseed or corn oil. Olestras are intended for entirely replacing fats and oils in deep-fat frying operations, coating snack foods, and other applications. It also is claimed that the problem of anal leakage (spotting of clothes by nonassimilated fats that pass intact through the digestive tract) has been solved by the development of Olestras that do not separate because their consistency is similar to that of the feces.

Other proposed synthetic compounds include esterified propoxylated glycerols (EPG), developed by ARCO Chemical Company, Newton Square, PA. The product is prepared by reacting glycerine with propylene oxide to form a polyether polyol that is esterified with one or more fatty acids. Frito-Lay, Inc., Dallas, TX, has developed DDM (dialkyl dihexadecymalonate), a fatty ester of malonic and alkylmalonic acids for high-temperature applications. Use of this product is reported to result in a 33 percent reduction in calories and a 60 percent reduction in fat content. The Best Foods Division of CPC International, Inc., Englewood Cliffs, NJ, is evaluating TATCA (trialkoxytricarballate), tricarballic acid esterified with fatty alcohols.

Nutrition and Health

Interest in the role of dietary fats in health has grown rapidly in the last four decades, focusing first on essential fatty acids and then on the role of fats and associated compounds in cardiovascular diseases. This is still a controversial and rapidly changing field, and the reader is urged to seek the latest information in the appropriate technical journals.

Currently, linoleic acid (C18:2*n*6) is considered a dietary essential fatty acid, as is arachidonic (C20:4*n*6)—but only when a linoleic acid deficiency exists. α-Linolenic acid (C18:3*n*3) generally is considered essential, but it still is undergoing review. Also, *n*-6 and *n*-3 polyunsaturated fatty acids have been shown to be precursors of eicosanoids (prostaglandins, thromboxanes, and leukotrienes), which are important in the regulation of many physiological processes. Eicosapentaenoic acid (EPA, C20:5*n*3) and docosahexaenoic acid (C22:6*n*3) are the major polyunsaturated fatty acids in fish, and consumption of fish rich in EPA is thought to modify blood platelet function and inflammatory responses. These types of interest have resulted in increased self-dosage with fish and other omega-3 oil sources by the general public. A linoleic acid intake to 1 to 2 percent of total dietary calories is considered sufficient to prevent biochemical and clinical evidence of deficiencies in human adults, and the American Academy of Pediatrics has recommended that infant formulas provide at least 2.7 percent of their energy as linoleic acid. The minimal daily intake of linoleic acid for adults is considered to be more than met by diets in the United States, and it is cautioned that large amounts of polyunsaturated fatty acids may increase the need for vitamin E, a fat-soluble, antioxidant nutrient. The NRC recommends that individual intakes of polyunsaturated fatty acids and of saturated fats each not exceed 10 percent of caloric intake.[2] However, because essential fatty acid deficiency has been observed exclusively in patients with medical problems of fat intake or absorption, a rationale may well exist for modified intakes supervised by physicians.

INDUSTRIAL FATS AND OILS

Fats and oils for industrial use typically are handled similarly to edible products, but usually with lower sanitation requirements.

Inedible Rendered Fats and Oils

Animal by-products, condemned carcasses and parts from packing plants, trimmings and bones from butcher shops, spent frying fats/oils, and fats collected from restaurant and food service kitchen grease traps are dry-rendered to produce inedible fats and oils.

Types of Industrial Fats and Oils Sought

Concentrated fatty acid sources offer the advantage of a reduced need for preconcentration of the feedstock in chemical processes. Safflower (*Carthamus tinctorius*) oil contains about 78 percent linoleic acid, and some high-oleic-acid type sunflower seed oils have been claimed to contain over 92 percent oleic acid.

Short-chain fatty acid sources mainly have been limited to coconut and palm kernel oils which contain C8, C10, and C12 fatty acids, but only at levels of 6 to 10 percent. *Cuphea* varieties, containing about 33 percent oil, are being evaluated as sources of short chain fatty acids, with reports of 18 percent C10 and 57 percent C12 in the oil of *C. carthagenesis*, 73 percent C8 and 24 percent C10 in *C. painteri* oil, 3 percent C8 and 87 percent C10 in *C. ignea* oil, and 85 percent C10 in *C. llavea*.[38]

Long-chain fatty acids generally are undesirable for food and feed use, but have been in demand for production of lubricants and polymers (Nylon 1313), and as plasticizers. Potential sources include: *Crambe abyssinica* oil containing over 60 percent C22; *Limnanthes alba* (Meadowfoam) oil with 95 percent C20 and C22; *Lunaria annua* oil wth 40 percent C22 and 20 percent C24; *Selenia grandis* oil with 58 percent C22; *Leavenworthia alabamica* oil with 50 percent C22; and *Marshallia caespitosa* oil with 44 percent C22.[38]

Hydroxy fatty acids are used for thickening greases and for improving the pliability of plastic covering materials. Domestic needs have been met primarily by imported castor oil. *Lesquerella* species are being explored for this purpose, with 70 percent 14-OH-C20 reported for *L. gracilis* oil, and 50 percent 12-OH-C18 diene for *L. densipila* oil.[38]

Epoxy fatty acids are used in the production of plastics and coatings. Significant quantities of soy oil are epoxidized yearly using a relatively expensive process. Potential new sources include: *Vernonia pauciflora* and *V. anthelmintica* oils, with 73 to 80 percent and 68 to 75 percent epoxy acid contents, respectively; *Euphorbia lagascae* with 60 to 70 percent epoxy acid content; and Stokes aster *Stokesia laevis* oil with 75 percent epoxy acid content.[38]

Conjugated Unsaturation Sources. Multiple bonds that are separated from each other by one single bond are said to be conjugated.

$$CH_3(CH_2)_n{-}CH{=}CH{-}CH{=}CH{-}(CH_2)_nCOOH$$

Conjugated double bonds

Fatty acids with conjugated unsaturation frequently are desired as chemical intermediates for industrial products. Tung oil is a source of conjugated unsaturation, which also is obtained by alkali isomerization of soybean and linseed fatty acids. Plant oils that have been reviewed as potential new sources of conjugated unsaturation include: *Valeriana officinalis* with 40 percent of its oil in 9, 11, 13 unsaturation; *Calendula oficinalis* oil with 55 percent 8, 10, 12 unsaturation; *Centranthus macrosiphon* oil with 65 percent 9, 11, 13 unsaturation; and *Impatiens edgeworthii* oil with 60 percent 9, 11, 13, 15 unsaturation.

Drying Oils. The value of drying oils depends on their ability to polymerize or dry upon application onto a surface to form tough, adherent, impervious, and abrasion-resistant films. These film-forming properties are closely related to the degree of unsaturation, and linsed, castor, fish, soybean, tung, oiticia, and tall oils are some of the important sources of domestic drying oils.

FATS AND OILS DEGRADATION AND ANTIOXIDANTS

The major types of fats and oils degradation are *lipolysis* (liberation of free fatty acids) and *oxidation* (formation of peroxides and aldehydes). Lipolysis can occur as the result of chemical (acid, base or water) or enzymatic (lipase) action. For example, free fatty acids develop more rapidly in oilseeds stored at increased moisture contents and temperatures because of increased enzymatic activity. Also, lipolysis in coconut oil can be induced by moisture and heat alone. Lipolytic spoilage and oxidative spoilage sometimes are called *hydrolytic rancidity* and *oxidative rancidity*, respectively. In some industries (such as dairy products) "rancidity" almost exclusively means lipolytic spoilage, whereas in the fats and oils industry "rancidity" often means oxidative spoilage.

Oxidation is thought to be induced by (singlet) oxygen at unsaturated bonds of fatty acids, and may be accelerated by the type of fatty acid, light, heat, oxygen concentration, extended surface areas exposed to air, and the presence of prooxidants (cobalt, copper, iron, manganese, and nickel), and by specific water activity (A_w) levels of 0.1 to 0.3 and 0.55 to 0.85. Fatty acids in triacylglycerols can undergo oxidation, but the reaction is more rapid if they have been freed by lipolysis. The process of oxidation consists of free radical creation, which then leads to the formation of hydroperoxides whose decomposition products catalyze a self-accelerating autoxidation process.

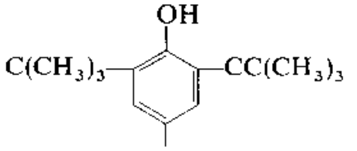
$$\begin{array}{l}
RH + \text{singlet oxygen} \rightarrow ROOH \\
ROOH + \text{catalysts} \rightarrow RO^{\cdot} + OH^{-} \\
RO^{\cdot} + RH \rightarrow ROH + R^{\cdot} \\
\\
R^{\cdot} + O_2 \rightarrow ROO^{\cdot} \\
ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot} \\
R^{\cdot} + O_2 + RH \rightarrow ROO^{\cdot} + R^{\cdot} \\
\\
R^{\cdot} + R^{\cdot} \rightarrow \text{Nonradical product} \\
ROO^{\cdot} + R^{\cdot} \rightarrow \text{Nonradical product} \\
ROO^{\cdot} + ROO^{\cdot} \rightarrow \text{Nonradical product}
\end{array}$$

The extent of prior oxidative activity in a fat sample may be estimated by the following: peroxide value (PV), thiobarbituric acid test (TBA) (which measures the presence of malonaldehyde), anisidine value—Totox, Kreis test, oxirane test, total and volatile carbonyl compounds, chromatographic analysis, ultraviolet spectroscopy, fluorescence, and especially organoleptic evaluation. However, the reader should be cautioned that the resulting peroxides are unstable and decompose. Thus, peroxide values are not cumulative and are not always indicative of the extent of earlier oxidation.

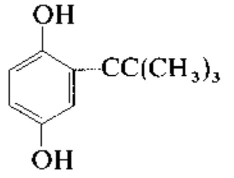
Predisposition (stability) to oxidation can be estimated for fats by the active oxygen method (AOM), and for fat-containing products by the Schall oven test and the oxygen bomb method and as a function of oxygen absorption.

Fats and fat-containing products may be stabilized against oxidation by the addition of antioxidants—compounds believed to inhibit an autoxidation chain reaction by acting as hydrogen donors or free radical acceptors. The major food grade synthetic antioxidants used include butylated hydroxytoluene (BHT), tertiary butylhydroquinine (TBHQ), propyl gallate (PG), and 2,4,5-trihydroxybutyrophenone (THBP), and generally they are allowed in food products at 0.01 percent of total fat weight each, with a total of 0.02 percent if a combination is used. Synergists used in combination with antioxidants include citric acid, isopropyl acid, phosphoric acid, ascorbic acid, ascorbyl palmitate, iso-ascorbic acid, tartaric acid, and lecithin, most of which act as chelators of prooxidative metals. Natural antioxidants include gum guaiac, tocotrienols (including vitamin E), and oil of rosemary (containing rosmaridiphenol). Antioxidants that no longer are used in food systems, or have not come into use, include the synthetics butylatedhydroxy anisole (BHA), 4-hydroxymethyl-2,6-ditertiarybutylphenol (an analog of BHT), and the natural compound nordihydroquaiaretic acid (NDGA) extracted from the desert plant *Larrea divaricata*.

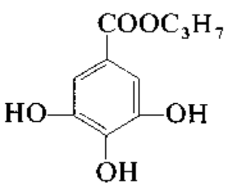
The crosslinking that occurs in drying oils also is an oxidation reaction. Polymerization of oils can occur rapidly in products such as fish meal that contain significant amounts of polyunsaturated triacylglycerols—even to the point of building up sufficient heat for a pile to spontaneously burst into flame. Thus, feed grade antioxidants such as ethoxyquin often are added before storage. Ethoxyquin also has been used for stabilizing feedstuffs against oxidation, thus sparing the natural tocopherols for their vitamin E activity in nutrition.



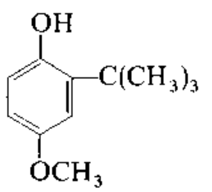
Butylated hydroxytoluene (BHT)



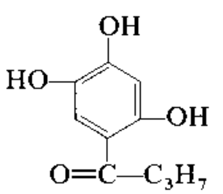
Tertiary butylhydroquinone (RBHQ)



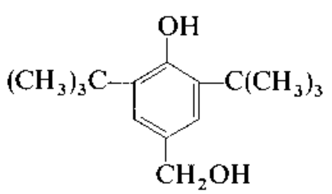
Propyl gallate (PG)



Butylated hydroxyanisol (BHA)



Trihydroxybutyrophenone (THBP)



Hydroxymethylditertiarybutylphenol

Synthetic and natural antioxidants are known to be heat- and steam-distillable, and preferably should be added to oil products after the maximum heat encountered in processing. It further is known that many natural phenolic compounds in cereal-oilseed products as well as reaction products of Maillard (nonenzymatic amino acid–reducing sugar) browning and natural wood smoke have antioxidant effects. Additional techniques for reducing oxidative activity include maintaining nitrogen blankets on oils stored in tanks, and preferentially distributing oils in opaque containers or brown bottles.

ANALYTICAL METHODS

Selected analytical methods, adopted by the American Oil Chemists' Society (AOCS) for characterizing composition, structure, physical properties, and stability of fats and oils, are summarized below.[39] Prescribed equipment must be used and conditions followed. Some of these techniques are limited to specific oil species, but adaptations are available for other species. Procedures for sample drawing and preparation also are specified.

Active Oxygen Method for Fat Stability—AOM (Cd 12–57): determines the time (in hours) for a sample of fat or oil to attain a predetermined peroxide value under conditions of the test. The method is used to estimate the comparative oxidative stability of fats and oils.

Bleaching Test for Soybean Oil (Cc 8e–63): determines the color of a sample of soybean oil after treatment with a specified bleaching earth. Specific methods exist for other oil species.

Cloud Point Test (Cc 6–25): determines the temperature at which a cloud first forms in a sample of melted fat in the first stage of crystallization.

Cold Test (Cc 11–53): measures the relative resistance of a sample to crystallize at an established temperature in terms of time. The test is often used as an index of stearin removal in winterization of salad oils.

Color Measurement by Lovibond—Wesson (Cc 13b–45): determines the color of clear oil samples by comparison with glasses of known color characteristics.

Fatty Acid Composition by Gas Chromatography (Ce 1–62): quantitatively determines saturated and unsaturated fatty acids with 8 to 24 carbon atoms in animal fats, vegetable oils, marine oils, and fatty acids after conversion to their methyl ester forms.

Fatty Acid Composition by GLC (Ce 1c–89): measures fatty acid composition and levels of *trans* unsaturation and *cis, cis* methylene-interrupted unsaturation of vegetable oils using capillary gas liquid chromatography.

Flash Point—Pensky-Martens Closed Cup for Fats and Oils (Cc 9b–55): determines the temperature at which a sample will flash when a test flame is applied. This technique is sometimes used to estimate levels of residual hexane as well as to assure safety of workers handling the oil.

Free Fatty Acids in Crude and Refined Fats and Oils (Ca 5a–40): determines FFAs, as oleic acid, by ethanolic sodium hydroxide titration.

Halphen Test for Detecting Cottonseed Oil (Cb 1–25): estimates the presence of cottonseed oil in vegetable or animal fats or oils as the result of a pink color formed between the reagent and cyclopropenoic fatty acids (sterculic and malvalic) normally present in cottonseed oil.

Hexane Residues in Fats and Oils (Ca 3b–87): determines, by gas chromatography, the "free" volatile hydrocarbons remaining in fats and oils after extraction with hydrocarbon solvents. The results are expressed in terms of hexane.

Insoluble Impurities in Fats and Oils (Ca 3a–46): determines dirt, meal, and foreign substances that are insoluble in kerosene and petroleum ether.

Iodine Value of Fats and Oils—Wijs (Cd 1–25): measures the unsaturation of fats and oils in terms of centigrams of iodine absorbed per gram of sample. The method is applicable to all normal fats that do not contain conjugated double bonds. It often is used to estimate the degree of hydrogenation of oils.

Lard, Foreign Fat—Boemer Number (Cb 5–40): estimates the presence of tallows and similar fats, based on differences in melting points of foreign glycerides and fatty acids as compared to pure pork fat.

Melting Point—Capillary Tube Method (Cc 1–25): determines the temperature at which a sample of fat in a closed capillary becomes completely clear and liquid.

Melting Point—Mettler Dropping Point (Cc 18–80): determines the temperature at which a sample becomes sufficiently fluid to flow in a specified apparatus.

Melting Point, Open Tube—Softening Point (Cc 3–25): determines the temperature at which a solidified fat, in an open capillary tube, softens sufficiently to slip and rise to the top of the heating bath. This method is applicable to fats such as coconut oil, stearin, hydrogenated fats, and hard tallows. The results sometimes are reported as "melting slip point," but the method is different from the AOCS Slip Point (Cc 4–25).

Melting Point—Wiley Method (Cc 2–38): determines the temperature at which a sample disc of solidified fat assumes a spherical shape while suspended in a heating bath with an alcohol–water density gradient.

Moisture—Distillation Method (Ca 2a–45): determines only moisture in triacylglycerols and emulsions by distillation with an immiscible solvent (toluene).

Moisture and Volatile Matter—Air Oven Method (Ca 2c–25): determines moisture and volatile matter by heating in a hot air oven. This method is applicable to animal and vegetable fats, but not to drying oils, coconut group fats, or oils with added monoacylglycerols.

Oil (Aa 4–38): determines oil content in a dried sample of oil-bearing material by extraction with petroleum ether. This method is specific for cottonseed, which first must be fumed with hydrochloric acid to prevent oil adsorption to the fiber. Additional methods exist for other oilseeds.

Peroxide Value, Fats and Oils (Cd 8–53): determines all substances, in terms of milliequivalent of peroxide per 1000 grams of sample, that oxidize potassium iodide (KI). These substances generally are assumed to be peroxides or products of fat oxidation.

Phosphorus in Oils (Ca 13–55): estimates the phospholipid content of crude, degummed, and refined vegetable oils in terms of phosphorus.

Refining Loss, Vegetable Oils, Crude (Ca 9a–52): determines the loss of free fatty acids and impurities when crude oils are refined under specified procedures.

Residual Lint (Aa 7–55): determines the lint content of cottonseed by fuming (digesting) with hydrochloric acid.

Saponification Value of Fats and Oils (Cd 3–25): determines the number of milligrams of (alcoholic) potassium hydroxide necessary to saponify a one-gram sample of a fat or an oil.

Smoke, Flash, and Fire Point—Cleveland Open Cup Method (Cc 9a–48): determines the temperatures at which fats and oils smoke, flash, or burn. Smoke point determinations sometimes are used to follow degradation of frying oils with use.

Solid Fat Content (SFC) of Fats and Oils by NMR (Cd 16–81): estimates the percent of solids in a semisolid fat on the basis of the pulsed nuclear magnetic resonance signal of hydrogen in the liquid fraction.

Solid Fat Index (SFI)—Dilatometric Method (Cd 10–57): estimates the percent of solids in a semisolid fat on the basis of changes in volume with temperature. This method utilizes glass dilatometers.

Triglycerides by GLC (Ce 5b–86): quantitatively determines triglycerides (triacylglycerols) in liquid vegetable oils in terms of molecular weight and degree of unsaturation as a function of their equivalent carbon number using high-pressure liquid chromatography.

Unsaponifiable Matter in Fats and Oils, Including Marine Oils (Ca 6b–53): determines substances dissolved in fats and oils that cannot be saponified (turned into sodium salts) by usual caustic treatment, including higher aliphatic alcohols, sterols, pigments, and hydrocarbons. This method is not suitable for marine oils or feed grade fats.

The following characterization methods also are used, but have not been included in AOCS *Official Methods*:

Anisidine Value: measures the extent of oxidative deterioration, which spectrophotometrically estimates aldehydes, and secondary oxidation products.

Schaal Test (Schaal Oven Method): an accelerated test for determining oxidative stability of a fat or a fat-containing food product. Results are reported as the time elapsed until a rancid odor is detected in a covered glass container held at an elevated temperature.

Totox Value: an estimate of the degree of oxidation of a fat or oil, calculated as: Totox = 2(Peroxide Value) + Anisidine Value.

TRADING OF FATS AND OILS

The Federal Grain Inspection Services certifies the quality of whole oilseeds for export trading. Fats and oils are traded domestically and in export markets, by mutual agreement of both parties, under trading rules established by various groups, including: National Oilseed Processors Association, Washington, DC—soybean oil, meal, and lecithin; National Cottonseed Products Association, Memphis, TN—cottonseed, oil, soapstock, tank bottoms, cottonseed cake and meal, cottonseed hulls, linters, and peanut oil; National Institute of Oilseed Products, Monterey, CA—coconut oil, palm oil, palm kernel oil, oleic safflower oil, high oleic sunflower oil, corn oil, LEAR rapeseed oil, raw soybean oil, cottonseed oil, peanut oil, sesame oil, teaseed oil, tung oil, *plus* palm kernels, babassu seed, flaxseed, castor seeds, ground nuts (peanuts), sesame seeds, safflower seed; and American Fats and Oils Association, Inc., Greatneck, NY—animal tallow and grease, vegetable oils, animal and poultry proteins, and fishmeal.

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9

Sugar and Other Sweeteners

Raymond D. Moroz* and Charles D. Broeg**

INTRODUCTION

Sugar and starch are among those organic "chemicals" found so abundantly in nature that no serious efforts have been made to synthesize them commercially from coal (or petroleum), air, and water. Both are available at such concentrations in some plants that sizable industries have resulted from growing those plants and extracting carbohydrates therefrom.

The primary use of sugar is in the manufacture of food or as a food in itself. When used for such purposes, most of it is highly refined or purified, but considerable quantities are consumed in some areas as a crude product, as in India where about 10 percent of the matured cane is consumed as unmilled sugar (gur and khandsari). Sugar is used to a limited extent in the production of other chemicals such as sucrose esters and in the form of by-product molasses as a substrate for fermentation processes. Currently, the juice of sugar-producing plants also is utilized for fermentation.[1]

Starch is extensively used in the textile and paper industries, but food is also a major outlet, especially if one considers flours that are primarily starch as a crude form of starch. However, a very important outlet for starch is its conversion to dextrose and glucose syrups for use in the food industry. Technological developments and governmental price-support programs for the domestic (U.S.) cane and beet sugar industries have greatly magnified the importance of starch as a source of sugars.[2] Those developments are based on the enzymatic conversion of glucose to fructose. The following discussion explores briefly the sources of various sugars and the processes by which they are converted into commercial products.

SUGAR

History

The ancestry of the sugar cane and its use as a food have been traced to the island of New Guinea. (However, a very interesting legend related by J. A. C. Hugill in Chapter 1 of *Sugar: Sucrie and Technology*[3] associates sugar cane with the origin of the human race.)

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Around 8000 B.C., the plant started on its migration from New Guinea to the many areas of southeastern Asia, Indonesia, the Philippines, Malay, Indochina, and eastern India, with humans probably as its main dispersal agent.[4] It was in Bengalese India that sugar cane first was cultivated as a field crop and that the juice was manufactured into various solid forms. A general knowledge of sugar was prevalent throughout India by 400 B.C. By the tenth century A.D., sugar cultivation and manufacturing had become important industries in Persia and Egypt. The early Islamic movement spread the knowledge of the sugar industry throughout the Mediterranean area. On the second voyage of Columbus to America, in 1493, sugar cane was introduced in Santo Domingo. It spread rapidly through the West Indies and Central America. Cortez brought the cane to Mexico, and Pizarro introduced it in Peru. By 1600, the sugar industry was the largest in tropical America.[5]

The modern sugar industry dates from the end of the eighteenth century when steam replaced animal energy and made possible the development of larger and more efficient production units. The vacuum pan appeared in 1813, bag filters in 1824, multiple-effect evaporators in 1846, filter presses in 1850, centrifugals in 1867, dryers in 1878, and packaging machines in 1891.[6]

Cultivation of the sugar beet plant and the manufacture of sugar from the beet developed in the industrial nations of Europe within the last two centuries. In 1747, a German chemist, Marggraf, established that sugar from beets was the same as sugar from cane. His pupil, Achard, in 1799, demonstrated that sugar can be commercially prepared from beets. During the Napoleonic wars, a short-lived beet sugar industry was established in France. It was slowly revived 20 years after Waterloo and spread to most European countries.[7] Today, sugar from beets accounts for about 35 percent of the world's supply.

Cane Sugar

Figure 9.1 is a generalized flow diagram for the manufacture of raw cane sugar.[8] The several steps are described in the sections that follow.

Agriculture. The sugar cane is a large perennial tropical grass belonging to the genus *Saccharum*. There are three basic species, *S. officinarum*, *S. robustum*, and *S. spontaneum*, and a large number of varieties. Sugar cane is propagated commercially by cuttings, each cutting consisting of portions of the cane plant having two or more buds. The buds sprout into shoots from which several other shoots arise below the soil level to form a clump of stalks or a "stool." From 12 to 20 months are required for crops maturity from new plantings and about 12 months for ratoon crops (i.e., cane stalks arising from stools that have been previously harvested). Most of the field operations have been mechanized, but planting is still done by hand in some cane-producing areas. Fields are replanted after two to five "cuttings" have been made from the original plantings. As cane grows, its foliage is largely limited to the upper one-third of the plant (the lower leaves die off from shading as the stalk grows taller). The cane stalk is round and from a few to more than 10 feet long when mature. It is covered with a hard rind that is light brown

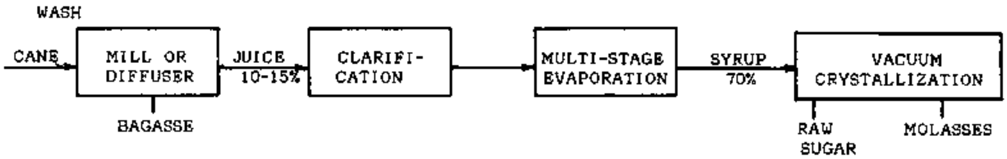


Fig. 9.1. Flow diagram showing principal steps in sugar cane manufacture. (*Adapted from Clarke, Margaret E., "Cane Sugar Process and Byproduct Streams," Iowa Biotechnology Consortium, Mar. 1991.*)

or green, yellowish green, or purple in color, depending on the variety. The stalk consists of a series of joints or internodes separated by nodes. The rind and the nodes are of a woody nature, whereas the internode is soft pith. The internode contains the greater part of the juice containing sucrose and the nodes contain "eyes" or buds that "sprout" when planted.[9]

Harvesting. The sugar cane is still cut by hand with machete-type knives in many producing areas. The canes are cut at ground level, and, at the same time, leaves and tops of the stalk are removed. In areas where labor is scarce or expensive, machine harvesting has come into widespread use. Some harvesters cut, chop, and load the cane into transporting vehicles in one operation at rates of 30 to 45 tons/hr. Other harvesters cut, bundle, and dump cane in rows for pickup by other machines. Transportation of field cane to the mill is accomplished by railcars, trucks, trailers, and carts.

Preparation of Cane for Milling. Mechanically harvested cane must be washed before milling in order to eliminate soil, rocks, and field trash. In some instances, "dry cleaning" precedes washing. Washing systems range from a simple spraying with warm water on the carrier or table to an elaborate system consisting of conveyors with water jets, stripping rolls, and baths for removal of stones.

Juice Extraction. The cane is first prepared for grinding by one or more of the following operations: (1) chopping it into smaller pieces with one or two sets of rotating knives (400–600 rpm; see Fig. 9.2); or (2) disintegrating the cane into finer sizes by a crusher and/or shredder (Fig. 9.3). The crusher usually is a two-roller mill of the Krajewski or Fulton type.

Recently, a new machine has been developed that combines the action of the chopper and the shredder into a single unit. It is commonly called a Unigrator or the "Ducasse Shredder."[10,11] The advantages gained have been a greater increase in juice extraction by the mills, an increase in the grinding rate, and, in some cases, a decrease in power consumption by the milling operation.

Radically new approaches to the preparation of sugar cane for the extraction of sugar have been under development for several years.[12] The basic concept consists of chopping cane stalks into short segments (8–12 in. long) and feeding these segments into a machine (Figs. 9.4 and 9.5) that separates the cane into three major fractions: (1) epidermis, (2) rind, and (3) pith. This approach to the preparation of cane for the extraction of sugar have several potential advantages: (1) reduced power requirements, (2) simplification of juice ex-

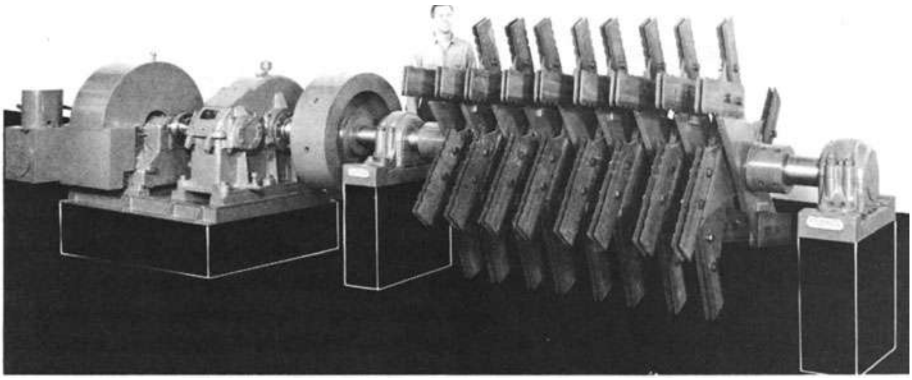


Fig. 9.2. Farrel Type K-4 cane knife to handle 4500 tons of cane per 24-hour day. (*Courtesy Farrel Co., Division of USM Corp.*)

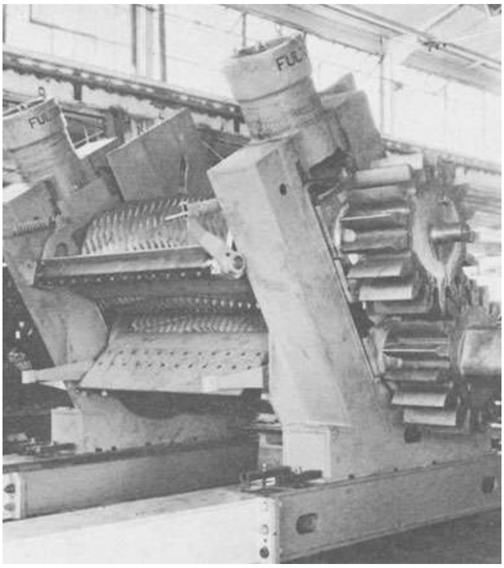


Fig. 9.3. Fulton crusher roll. (*Courtesy Fulton Iron Works Co., St. Louis, MO.*)

traction processes, and (3) the recovery of not less than three by-products having greater utility than bagasse.[12]

The crushed and shredded cane then passes through a series of three horizontal rollers (mill) arranged in a triangular pattern with the top roll rotating counterclockwise (Fig. 9.6) and the bottom two rollers clockwise. A series of three-roller mills, numbering 3 to 7, is called a tandem (Fig. 9.7). The pressure on the top roll is regulated by hydraulic rams and averages about 300 tons. Below each mill there is a juice pan into which expressed juice flows. The crusher and first mill extract 60 to 70 percent of the cane juice, and the remaining mills take out 22 to 24 percent.

When the fiber content of the bagasse reaches about 50 percent, extraction by conventional milling approaches zero. Because the juice that remains with the fiber contains the same proportion of sucrose as the original juice of the cane, the yield of sugar would be substantially lowered if extraction were terminated at that point. Consequently, a process called "compound imbibition" is used to reduce the sucrose in the fiber by repeated dilution and milling. In a five-mill tandem, water is added to the fourth mill, and the expressed juice from that mill is brought back to the second mill. The expressed juice from the third mill is recirculated to the first mill and the fifth mill to the third mill. In this way, the juice in the bagasse is always diluted ahead of each mill. The amount of imbibition applied at each mill is approximately equal to the amount of water applied to the fourth mill or to the penultimate mill in a differently numbered tandem.[13]

Before the expressed juice goes to clarification, it is screened through perforated metal screens with openings about 1 mm in diameter. Additional screening may be provided by stationary or vibrating metal cloths.

Diffusion. Diffusion is used to extract juice from the cells in the sugar cane. The diffusers used for this have capacities that range from 1000 to 6000 tons of cane per day. Normally they are used in conjunction with part of a milling tandem, the crusher and the first mill. Preparation of the cane prior to its entry into the diffuser is essential for good extraction. In the diffuser, the crushed cane is countercurrently washed with imbibition water at temperatures ranging from 50°C to 75°C. The last stage of a diffuser, the bagasse exit, receives water that gradually increases in sugar content as it proceeds to the first stage. Most of the sugar is extracted in the first four or five stages by simple displacement of sucrose from the open ruptured cane cells. In later stages, diffusion appears to take place in unruptured cane cells. One or two mills are used to express water from the bagasse after discharge from the diffuser. The crusher and one mill extract 70 percent of the juice from the cane, and the diffuser removes 30 percent of the expected yield. Sucrose extraction from a mill-diffusion system averages 97 percent compared to 90 to 91 percent with a straight milling system.[14]

Since 1962, a number of diffusers have been installed in cane mills throughout the world. Cane diffusers now are manufactured by a number of companies including Braunschweigische Maschinenbauanstalt, CF&I Engineers Inc., De Danske Sukker-

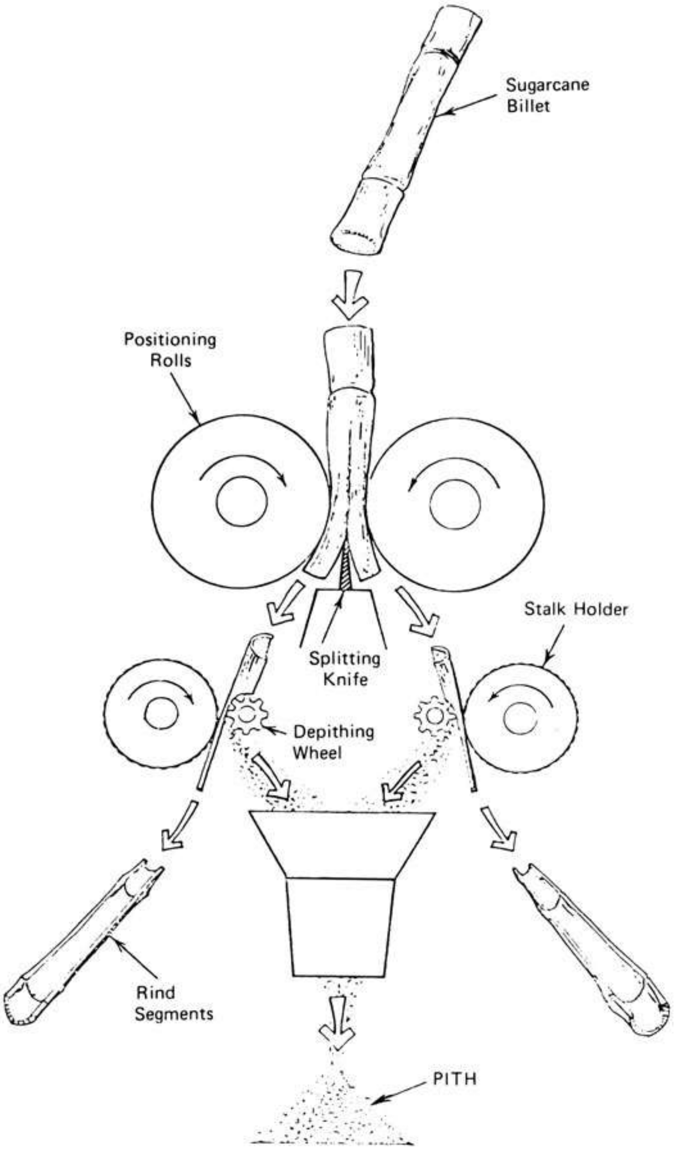


Fig. 9.4. Tilby separator process. (*Courtesy Ander-Cane, Inc., Naples, FL.*)

fabrikker, De Smet, S. A., Sucatlan Engineering, and Suchem Inc. of Puerto Rico (Figs. 9.8, 9.9).

Juice Purification. The juice from the milling station is an acidic, opaque, greenish liquid containing soluble and insoluble impurities such as soil, protein, fats, waxes, gums, fine bagasse, and coloring matter in addition to soluble salts. The process designed to remove as much of these impurities as possible employs lime and heat and is called clarification or defecation. In simple lime defecation, milk of lime is added to the cold juice in amounts (about one pound of calcium oxide per ton of cane) sufficient to bring the pH to the range of 7.5 to 8.5. The limed juice is pumped through heaters in which the juice is heated to temperatures between 90 and 115°C. There are many modifications to this basic

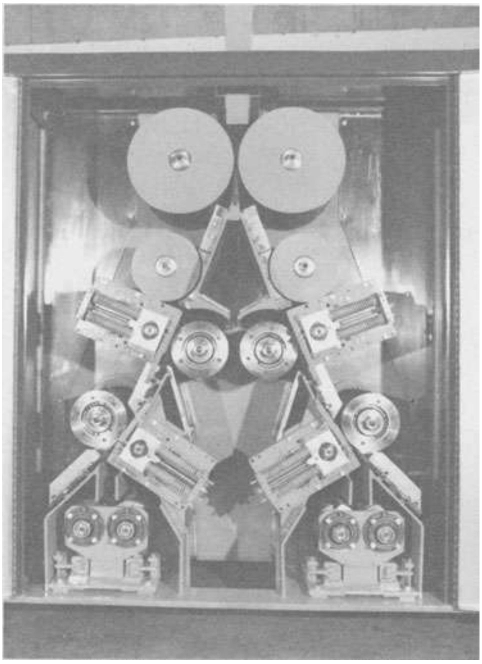
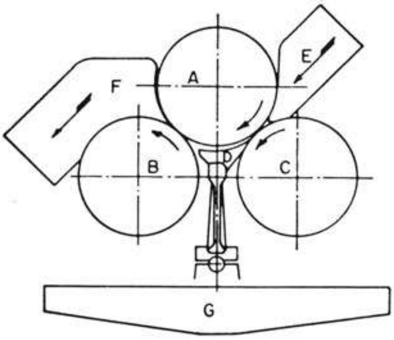


Fig. 9.5. Lignex sugar cane separator, full frontal working view. (*Courtesy Lignex Products Group, Hawker Siddeley Canada Ltd.*)



A - Top-roller.
B - Bagasse roller.
C - Feed roller.
D - Trash plate.
E - Feed of cane.
F - Discharge of crushed cane.
G - Juice-collecting trough.

Fig. 9.6. A cane mill with its three crushing rolls and with a typical turn-plate arrangement. A hydraulic piston maintains pressure on A, while B and C are fixed. The rolls are under pressure of 75–80 tons per foot of roll width.

process involving different sequences of lime and heat. For example, fractional liming with double heating involves liming the cold juice to pH 6.4, heating, liming to pH 7.6, and heating again before sending the juice to the clarifiers.

The combination of lime and heat forms a flocculent-type precipitate with various components in the juice, which consist mostly of insoluble lime salts, coagulated protein, and entrapped colloidal and suspended matter. The precipitate is removed by sedimentation or settling in continuous closed-tray clarifiers (i.e., Rapi-Dorr, Graver, BMA, and Bach Poly-Cell). The juice leaving the clarifier is a clear brownish liquid.

The flocculent precipitate, or "muds," which settles on the clarifier trays, contains about 5 percent solid matter. Sugar is recovered from the muds by means of rotary vacuum filters equipped with perforated metallic screen cloth (Fig. 9.10). The turbid filtrate is returned to the clarification system, and the press cake is discarded or sent to the fields as fertilizer.

Recent innovations in the filtration of muds include the use of tighter filter media. A clearer filtrate is obtained, which can be sent to the evaporators without reprocessing. The Eimcobelt rotary vacuum filter uses a tight filter cloth that is continuously removed from the drum and washed with hot water. Another approach is the direct filtration of muds with horizontal leaf filters (Fas Flo Filters). One process uses polyelectrolytes to increase the filterability of the muds through cloth filters (Rapid-Floc system).

Good clarification depends upon the formation of a stable flocculent precipitate that settles rapidly. Juices low in phosphates and other minerals, such as magnesium salts, tend to be refractory. Fine soil carried in from the field also may interfere with clarification.[15,16]

Evaporation. The clarified juice (about 85% water) is pumped to evaporators where it is concentrated to a clear heavy syrup containing about 65 percent solids. Evaporation is carried out in multiple-effect evaporators in order to achieve maximum steam economy.

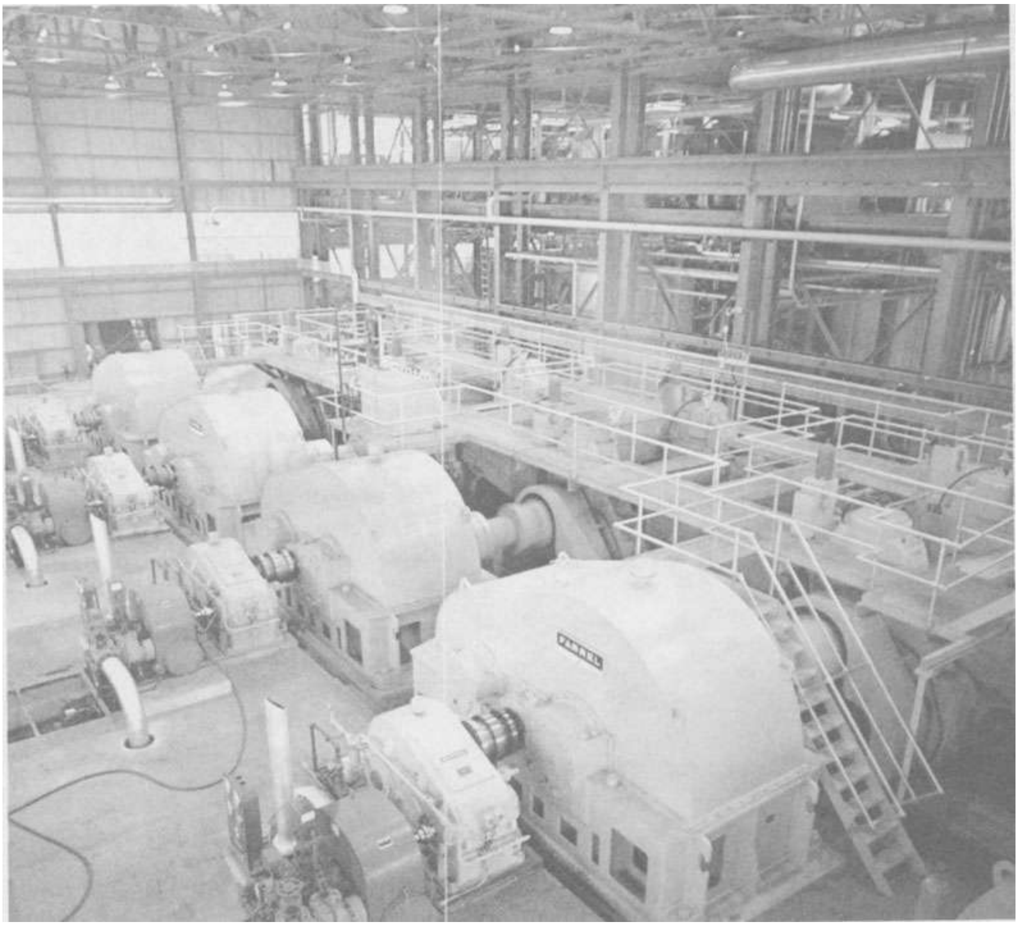


Fig. 9.7. Farrell four-unit milling train. (*Courtesy Farrel Co., Division of USM Corp.*)

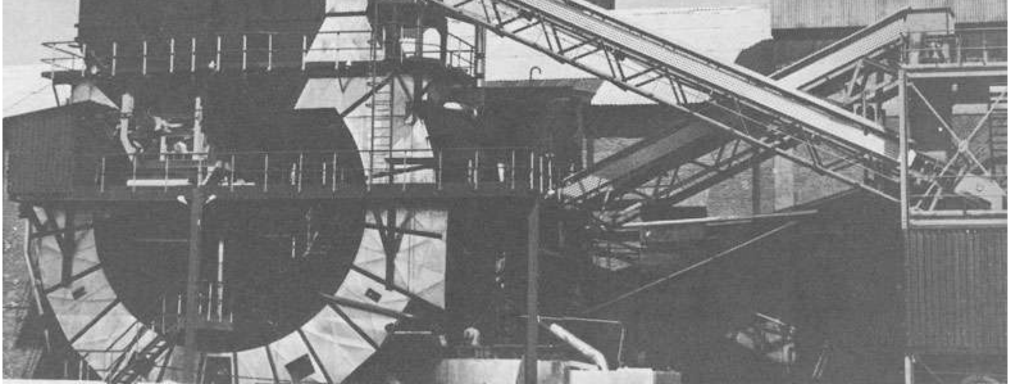


Fig. 9.8. Continuous ring type total masceration sugarcane diffuser. (*Courtesy Sucatlan Engineering, Paris.*)

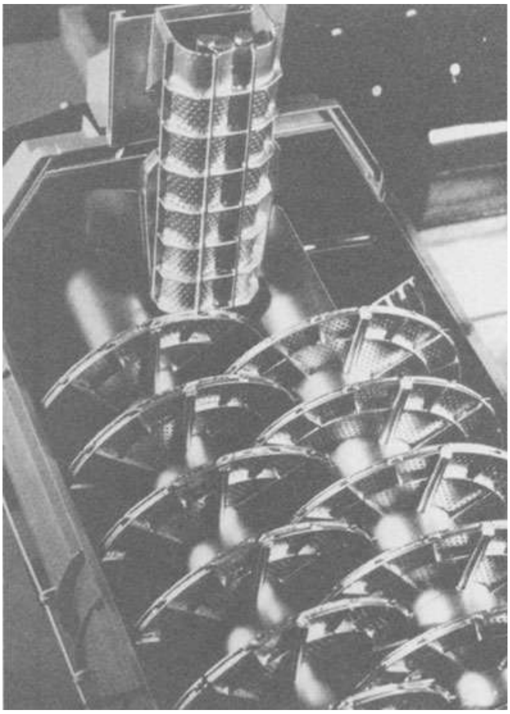


Fig. 9.9. Open top view of DDS double cylindrical tilted cane diffuser. (*Courtesy De Danske Sukkerfabrikker, Copenhagen.*)

Each effect is arranged in series and operated so that each succeeding one operates under a higher vacuum (lower pressure). This arrangement allows the juice to be drawn from one vessel to the next and permits it to boil at a low temperature. The concentrated juice (syrup) is removed from the last effect by a pump. Triple-, quadruple-, and quintuple-effect evaporators are used, but the quadruple-effect type is most common. In a four (quadruple)-effect evaporator, one pound of steam evaporates four pounds of water.

Crystallization. The syrup from the evaporator is pumped to a vacuum pan, in which it is evaporated to supersaturation in order to cause sugar to crystallize. The vacuum pan is a single-effect evaporator designed to handle viscous materials. It is a vertical cylinder with its bottom designed to allow easy removal of the crystallized mass. The heating elements used in vacuum pans either are short, large-diameter vertical tubes (calandria pans) or coil around the inner surface of the truncated cone of the pan (coil

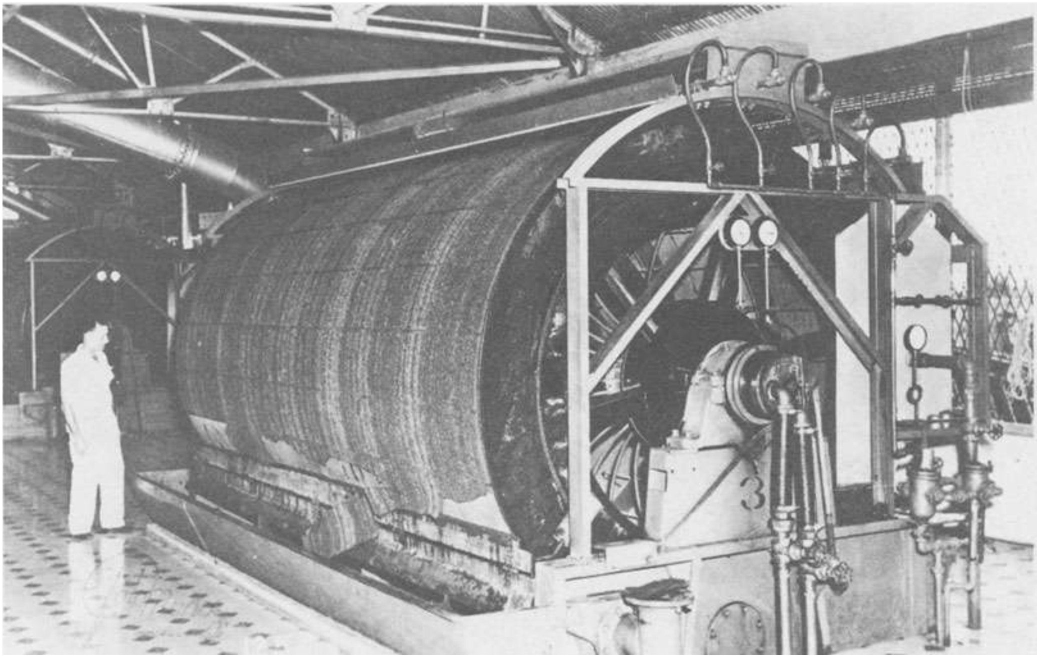


Fig. 9.10. Oliver Campbell vacuum mud filter applied to cane juice muds. (*Courtesy Dorr-Oliver, Inc. Stamford, Conn.*)

pans). A typical vacuum pan with a "catchall" or entrainment separator for separating syrup from vapors measures approximately 25 feet in height and 15 feet in diameter. The working capacity is about 1000 cubic feet of massecuite (mixture of crystals and syrup or mother liquor). The shape of the pan and the positioning of the heating elements within the pan are important design factors in maintaining good circulation of the massecuite. For example, floating calandrias (calandria not attached to shell of pan), horizontal pans, and pans having mechanical circulators[17] are used.

The move toward continuous processing has resulted in the development of continuous vacuum pans. One review[18] of continuous vacuum pan technology provides considerable information on this important area. According to the author, pan boiling is one of the last remaining batch operations in sugar processing and has attracted considerable attention in recent years. As a result, "low grade continuous pan boiling is now well established in the South Africa sugar industry." It is stated that the benefits of continuous pan boiling include considerable thermal economy and steadier operation of the entire pan floor. Batch pans still are required to produce the seed for feeding to continuous pans, but, it is expected that this batch operation eventually will be replaced by a continuous process. It also is reported[19] that "continuous vacuum pans are now used in many beet factories (Europe) and cane factories (U.S., S. Africa, Australia, Brazil and others). They are also used in refineries in the U.S. and other countries mentioned above. Continuous crystallizers are in most European beet factories and many cane factories and refineries."

One version of the continuous vacuum pan is a horizontal cylinder with compartments in its lower part (Fig. 9.11). The pan is provided with an additional evaporator called the concentrator, where the density of the syrup is raised to 78 to 80 degrees Brix.* Seed is added in the first compartment, and the resulting massecuite moves progressively through the compartments of the pan. Additional syrup is added to each compartment to control the fluidity of the massecuite. Approximately 20 percent of the syrup is introduced at the concentrator, and 80 percent of the syrup is fed to the various compartments through special feed headers. The rate of massecuite discharge is controlled by the level in the pan.[20]

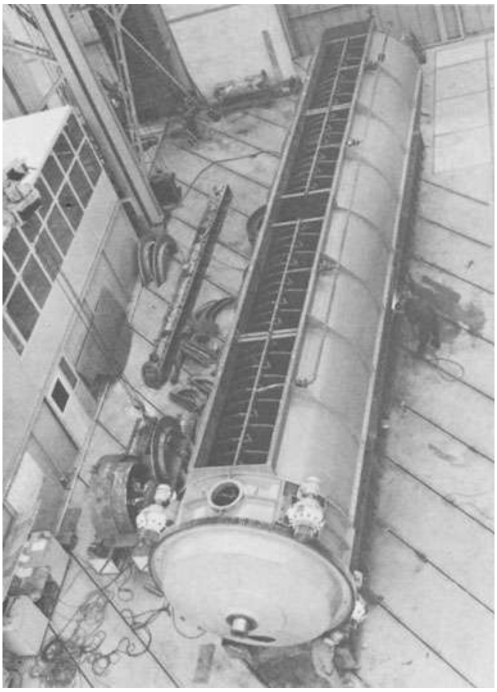


Fig. 9.11. Top view of open stork continuous crystallizer under construction. (*Courtesy Stork-Werkspoor Sugar, Hengelo, The Netherlands.*)

The crystallization of sucrose in vacuum pans is called "sugar boiling" and each boiling is termed a "strike." Because a single crystallization does not recover all of the sucrose from the syrup, mother liquor from a "strike" is recycled for recovery of additional sugar. There may be as few as two and as many as four reboilings to recover the maximum amount of sugar. A three-boiling system is the most popular. In order to distinguish among

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*The Brix scale is a density scale for sugar (sucrose) solutions. The degrees Brix are numerically equal to the percentage of sucrose in the solution. The term "Brix solids" refers to the solids as determined by the Brix hydrometer.

the boilings, a letter is assigned to each boiling and its products; that is, the first boiling (syrup massecuite) would be given the letter *A*, and its products after centrifugation would be *A* sugar and *A* molasses; the second and third boilings would be assigned the letters *B* and *C*, respectively.

The boiling systems are based on "apparent purity," the amount of sucrose remaining in solution, and usually are expressed as the ratio of the polarization value to the total solids as measured by the Brix hydrometer. In a three-boiling system, the purity of the *A* massecuite is set between 80 and 85 by blending syrup with *A* molasses, the purity of the *B* massecuite is set between 70 and 75 by blending with syrup and *A* molasses, and the *C* massecuite is set between 55 and 60 by blending with syrup and *B* molasses. Other variations are possible.[6]

The *A* and *B* massecuites, after being discharged from a vacuum pan, are sent to centrifugals for separation. The *A* and *B* sugars are combined and become commercial raw sugar, the principal product of a cane sugar factory.

The *C* massecuite is a low-purity, highly viscous material that is not immediately sent to the centrifugals because of the large amount of recoverable sucrose remaining in solution. Instead, it is placed in crystallizers, U-shaped or horizontal containers equipped with coils attached to a hollow rotating shaft through which water circulates. The massecuite remains in the crystallizer from one to four days to allow additional crystallization to take place. Centrifugation of the *C* massecuite yields a final molasses (blackstrap) and a *C* sugar that is used for seeding the *A* and *B* boilings.

Centrifugation. Massecuite from the vacuum pans is sent to centrifugal machines wherein the crystals are separated from the mother liquor. A centrifugal consists of a cylindrical perforated basket lined with a screen of perforated sheet metal. The basket, enclosed in a metal casing, is mounted on a vertical shaft that rotates the basket, imparting centrifugal force to the massecuite.

In a batch centrifugal, hot massecuite is fed into the basket through a short chute from the holding vessel. As the basket rotates, the massecuite forms a vertical layer on the screen lining. When the machine reaches operating speed (1000–1800 rpm), the syrup flows through the perforated lining and basket and is removed through an outlet at the bottom of the casing. The sugar on the lining is washed with a spray of water to decrease the amount of molasses adhering to the crystals. The basket continues rotating until the sugar is fairly dry, at which time the machine is switched off and brakes are applied. The sugar is discharged by a manually or automatically operated plough.

In continuous centrifugals, the machines do not stop but continue in motion while receiving fresh supplies of massecuite. The rate of feed must be carefully regulated to obtain optimum separation of molasses from crystals (Fig. 9.12).[21]

Packaging and Warehousing. The packaging of raw sugar in jute bags has decreased to a very low level in most areas of the world. In fact, all of the raw sugar produced in Louisiana, Florida, Hawaii, Australia, and Puerto Rico is shipped in bulk. Where raw sugar still is bagged, bag weights vary from 110 to 150 lb in the Philippines to 250 lb in the West Indies. Bulk raw is brought from the factories to seaport terminals by means of dump trucks, railroad cars, or barges. These terminals, with capacities of 75,000 tons or more, are warehouses that were originally intended for bagged sugar, but now are specially designed structures for bulk handling. Unloading and loading of ships is done by bucket cranes or by gantries with traveling cranes.[13]

SUGAR REFINING

The raw sugar produced as described in the preceding section (called "raw" in the industry) is light brown in color and contains about 98 percent sucrose. In order for it to be competitive in the marketplace, it is necessary to bring the level of sucrose purity to 99.9 percent and to make it white. This is

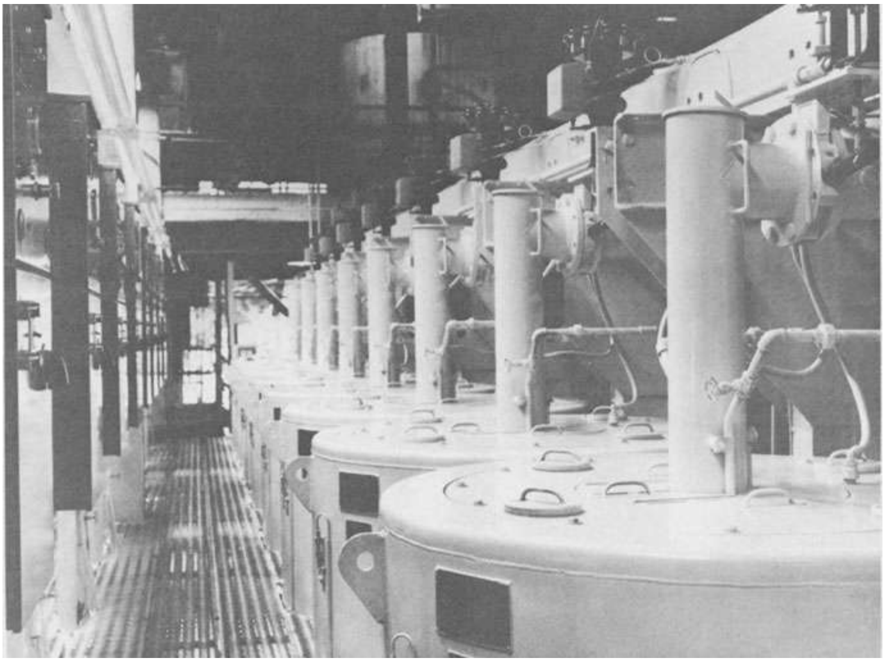


Fig. 9.12. Silver continuous centrifuge. (*Courtesy CF&I Engineers, Inc., Denver, CO.*)

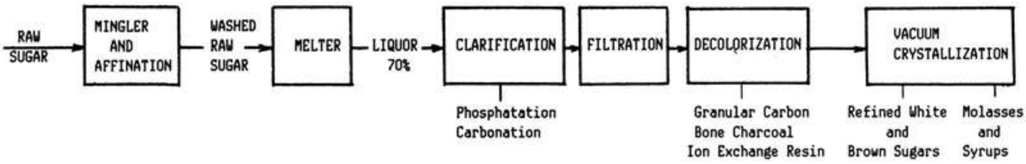


Fig. 9.13. Principal steps in manufacture of refined sugar. (*Adapted from Clarke, Margaret E., "Cane Sugar Process and Byproduct Streams," Iowa Biotechnology Consortium, March. 1991.*)

done in the refining process using the several steps depicted in Fig. 9.13.[8]

It may be helpful in establishing additional context for the previous section and for sugar refining to note that in 1970, there were four routes for the production of white sugar from sugarcane or raw cane sugar:[22] (1) traditional plantation white, obtained directly from sugar juice with settling clarification and sulfitation (SO_2 bleaching); (2) improved plantation white with carbonation and sulfitation; (3) refined white, from a white end refinery attached to a raw sugar factory, involving remelting (redissolving) raw sugar and refinery clarification and decolorizing processes; and (4) refined white, from a refinery not incorporated into a raw sugar factory.

Affination and Melting

The first step in the refining of raw sugar is called affination and consists of removing the film of molasses (in which a large portion of the impurities is contained) from the surface of the raw sugar crystal. The process involves the mixing of raw sugar with a saturated sugar syrup (72–75 degrees Brix) at about 120°F in a U-shaped trough called a mingler. (Saturated syrup is used to avoid dissolving the raw sugar.) The mingler has a rotating agitator to maintain maximum contact between the sugar and the syrup. The mixture is centrifuged to separate the crystals from the syrup, and the crystals are washed with hot water. The "washed" sugar is "melted" or dissolved in water to a density of 55 to 60 degrees Brix.

Potable water, steam condensate, and "sweet waters" are used for dissolution. The liquor from the melter is screened to remove nonsugar materials such as sand, stones, wood, cane fibers, and lint. Screening is done by vibrating screens (Tyler-Hummer), a cyclonic separator (Dorrclone), or centrifugal screens (DSM).[13,16]

Purification

A number of processes are available for purifying the liquor from the melter prior to its crystallization into granulated sugar. The two combinations most commonly used are:

1. Clarification–filtration–decolorization.
2. Clarification–filtration–decolorization–ion exchange.

Clarification. One of three types of chemical treatment is used as the first step in the purification process. These are liming, phosphatation, and carbonation.

Liming is the simplest of the chemical treatments. Process liquor is "limed" to a neutral pH using milk of lime and heated. A slurry of diatomaceous earth is added, and the treated liquor is pumped through a filter press, such as those discussed in the following section.

When phosphatation is used, the screened liquor is heated to 60 to 70°C and mixed with phosphoric acid (0.005–0.025% P_2O_5 on solids). The mixture is immediately limed to a pH of 7.0 to 8.0, aerated with compressed air, and sent to a clarifier (a rectangular tank equipped with heating coils). The liquor enters the clarifier at one end and is heated to 88°C while flowing to the outlet at the opposite end. The heated liquor releases air which rises, carrying the flocculent calcium phosphate precipitate to the surface. A blanket of this precipitate (scum) forms at the surface and is skimmed from the liquor surface by moving paddles. Clarifiers differ in shape and design; some of the best known are Williamson, Jacobs, Buckley-Dunton, and Sveen-Pederson.

In carbonation, process liquor heated to 60 to 80°C is limed to about pH 10 (0.03–0.8 percent CaO on solids), gassed with carbon dioxide, heated to 85°C, and regassed until the pH drops to between 8.4 and 9.0. Carbonation, because of the two-stage gassing, requires two clarifiers, primary and secondary. Washed flue gases are the source of carbon dioxide. The calcium carbonate precipitate that forms entraps colored matter, colloidals, and some inorganic compounds.[23]

A novel addition to phosphate clarification has been the Talofloc process for the cane refining industry and the Talodura process for the raw cane factory. The Talofloc process consists of the addition of two chemicals at specific points in the clarification station. First, a cationic surfactant called Talofloc is added to the unclarified melt liquor in concentrations ranging from 0.02 to 0.07 percent on solids. This step is followed by the addition of lime and phosphoric acid and the incorporation of air. Just before the liquor enters the clarifying chamber, a polyacrylamide flocculant (Taloflote) is added that induces the aggregation of the calcium phosphate precipitate, making a faster and more complete separation of the flow from the liquor. The Talofloc added prior to the chemical treatment causes at least a 50 percent increase in color removal when used in conjunction with Taloflote. The desugarization of the floc (scum) is best accomplished in a specially designed two-stage or three-stage counter-current flotation system with further addition of Taloflote. For plants that are expanding or replacing their old clarifiers with the Talofloc process, special clarifiers designed to operate at maximum efficiency with Taloflote and Talofloc are recommended. One such unit with a capacity of 40 tons/hr is described in the literature.[24]

Filtration. The liquor from a phosphatation or a carbonation clarifier contains small amounts of finely dispersed particulate matter that require filtration for removal. The filtration process is similar for both types of clarified liquor.

A precoat of a filter aid (diatomaceous earth or perlite) first is deposited on the filter surfaces of the press. (Additional filter aid is added to phosphate clarified liquors to improve press runs.) Liquor at 160 to 185°F is fed to the press at a pressure of about 60 psig until the flow rate drops below a predetermined level, ending the filtration cycle. The calcium carbonate particles in carbonated liquor act as a fairly good filter aid as long as the particles are developed to optimum size during carbonation. Large quantities of sugar polysaccharides (starch) in the melt liquor will restrict the growth of calcium carbonate, requiring the use of diatomaceous earth. A filter cycle may last from 2 to 12 hours depending upon the quality of the feed liquor.

Three types of filter presses generally are used, all of them leaf presses:

1. Horizontal body with vertical leaf filter, i.e., Sweetland, Vallez, Auto-Filters, and Industrial.
2. Vertical tank with vertical leaf filters; i.e., Niagara, Angola, and Pronto.
3. Vertical tank with horizontal plates; i.e., Sparkler and Fas-Flo.

The filter leaves are dressed with cloth made of cotton or synthetic fiber (nylon, dacron, etc.) or with a wire screen of 60 to 80 mesh size.

The sugar remaining in the filter cake is recovered by washing the cake in place (sweetening off) with hot water, or the cake is sluiced off the leaves with hot water and flushed to a holding tank for refiltration. The filtered sweet water generally is added back to the melter to dissolve washed raw sugar.[13,16]

Decolorization. Filtered clarified liquor is a clear, dark brown liquid having a solids content between 55 and 65 degrees Brix, a pH of 6.7 to 7.2, and temperatures between 65 and 85°C. If pulverized activated carbon is used as a decolorizing agent, it usually is added prior to filtration. Otherwise, the liquor is subjected to one or more decolorizing absorbents; for example, bone char, granular carbon, and ion exchange resins. Bone char removes colorants, colloidal matter, and some inorganic substances, whereas granular carbon is only a decolorizer. Ion exchange resins absorb color and change the composition of the ash.

Bone char and granular carbon are generally used in fixed beds or in cylindrical columns 20 to 25 feet high and about 10 feet in diameter. Some recent systems percolate liquor upward or downward through a stationary bed of adsorbent or by countercurrent flow of liquor and adsorbent (CAP or continuous adsorption process). (See below, Fig. 9.17.)

Liquor flow through bone char is about 1500 gal/hr over a period of 30 to 60 hours. For granular carbon, the flow rate is 3000 gal/hr for 20 to 30 days.

After the decolorizing cycle is completed, the adsorbent is sweetened off by displacing the liquor with water, and is washed. It is transferred to regenerating equipment consisting of dryers, kilns, and coolers. Bone char is regenerated at 540°C in a controlled amount of air. Granular carbon is revivified at 950°C in a limited oxygen and steam atmosphere. The kilns can be either the retort type on multiple hearths in columns (Herreshoff). After regeneration, the adsorbent is returned to the system for a new decoloring cycle.

Ion exchange resins are used in columns 8 to 10 feet high and 6 to 10 feet in diameter holding between 100 and 300 ft^3 of resin. The resin bed depth is only 2 to 4 feet. Flow rates are rapid (3000–4500 gal/hr), and the cycle is short (8–16 hours). Regeneration is accomplished in the column with a 10 to 15 percent salt solution at 140 to 160°F. The chloride form of a strong anionic resin decolorizes the liquor, and the sodium form of a strong cation resin softens the liquor. The sweet water from the various adsorbent columns are recovered by returning them to the melter.[13,25]

Crystallization

Decolorized liquor is a pale yellow liquid with a solids content of 55 to 65 degrees Brix. In some refineries, this liquor goes directly to a vacuum pan for crystallization, but most refineries (both cane and beet) preevaporate the liquor in a multiple-effect evaporator to a solids content of about 72 degrees Brix.

There are four stages in the process for crystallization of sucrose: (1) seeding or graining; (2) establishing the seed; (3) growth of crystals; and (4) concentration.

A sufficient quantity of evaporated liquor is drawn into the pan to cover the heating elements. Water is evaporated from the syrup until its supersaturation approaches 1.25. At this point, the steam pressure is lowered, and seed crystals are added. The seed is finely pulverized sugar dispersed in isopropyl alcohol or sugar liquor. This method is called shock seeding because addition of the seed induces an immediate formation of crystal nuclei throughout the supersaturated syrup. The nuclei are grown to a predetermined size or grain. Once the grain is established, the crystals are grown to size by maintaining supersaturation between 1.25 and 1.40 through control of steam pressure, vacuum, and the feed rate of the evaporated liquor. Adequate circulation during crystal growth is important.

When the volume of the massecuite reaches the maximum working capacity of the pan, the syrup feed is shut off, and evaporation is allowed to proceed until a thick massecuite is formed. When the massecuite concentration is considered "tight," the steam and the vacuum are shut off, and the massecuite is dropped into a holding tank equipped with agitators, where it is kept in motion until discharged into centrifuges.

Instrumentation is used extensively in sugar boiling to control the process of crystallization. Some of the principles used to provide control of vacuum pans for boiling a strike of sugar are:

1. Boiling point rise (BPR): thermometers are used to measure the temperature of the massecuite and its vapors (difference between these two temperatures is the observed BPR).
2. Electrical conductivity of the massecuite, based on the principle that conductivity is inversely proportional to the viscosity of the solution, which in turn has a similar relationship to the water content and thus the degree of supersaturation.
3. Fluidity of the massecuite: an ammeter is used to measure the current used by the motor of a mechanical circulator; changes in current indicate changes in the fluidity of the massecuite.
4. Soluble solids, measured by a refractometer.

Several systems employing instrumentation for automatic control of pan boilings by supersaturation have been used successfully (Fig. 9.14). However, controls are empirical in nature, and are based on the conversion of the various techniques and arts of a "sugar boiler" into mechanical operations that lend themselves to automation.

The boiling system of a refinery is straightforward: the first strike is boiled from evaporated liquor, the second strike is boiled from the runoff syrup of the first strike, continuing on to three or four strikes. The runoff of the last strike can be used in a variety of ways: (1) as syrup for affination, (2) as syrup for remelt, (3) or as syrup for producing a soft brown sugar; or (4) it can be reprocessed and reboiled.[13,17]

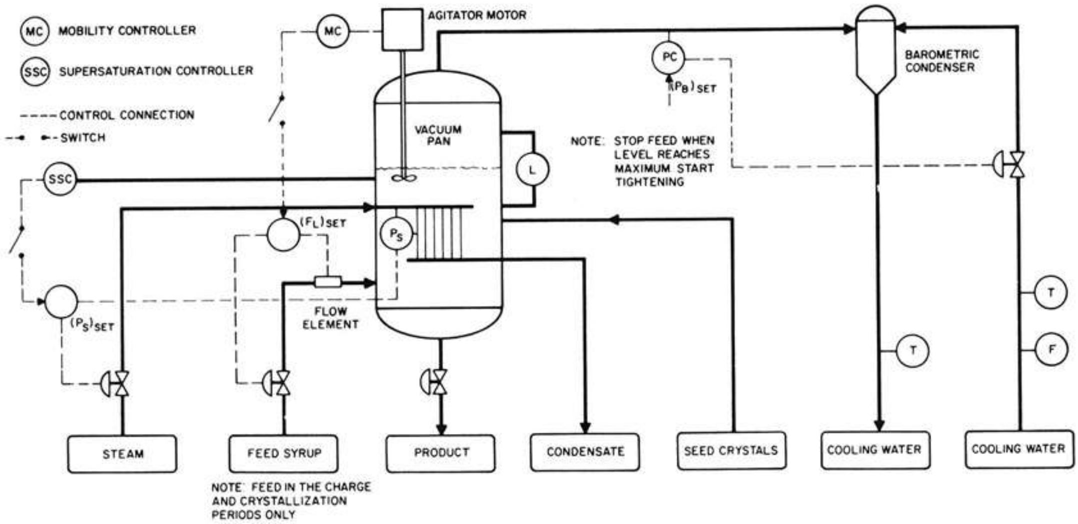
An innovative approach to the conversion of two-batch vacuum pans into a continuous crystallizing system was reported at the 1979 meeting of Sugar Industry Technologists.[26]

Remelt Sugars

The sugar contained in affination syrup must be recovered for economy. Recovery is accomplished by crystallizing the sugar in a vacuum pan. The resulting sugar is "raw" in composition and is returned to the refinery at the affination station. The residual syrup from the remelt station is known as refiners' blackstrap.

Centrifuging

Refined sugar crystals are recovered from the mother liquor by centrifuging the massecuite in equipment similar to that used for affining raw sugar. However, at this point, the crystals are washed with a greater quantity of hot



NOTE: STOP FEED WHEN LEVEL REACHES MAXIMUM START TIGHTENING

NOTE: FEED IN THE CHARGE AND CRYSTALLIZATION PERIODS ONLY

Fig. 9.14. Schematic drawing of vacuum pans and controls. (*Courtesy the Foxboro Co. Reproduced from* Sugar y Azucar, *Oct. 1970.*)

water. The washed crystals are discharged into a holding bin supplying a dryer.

Drying

Sugar from the centrifugals contains 1 to 2 percent moisture and is too wet to be placed in storage or packages. The wet sugar is fed to drying equipment called granulators, which usually are rotating drums, 15 to 35 feet long and 6 to 7 feet in diameter, inclined slightly so as to be discharged by gravity. Heated air is blown through the dryer concurrent with the flow of the sugar. Two types commonly used are the Roto-Louvre granulator and the Standard-Hershey granulator. The Roto-Louvre is a single rotating drum in which hot air from louvres in the wall dried a moving bed of sugar. The Hershey granulator consists of a rotary dryer followed by a second unit in which the sugar is cooled to 45 to 55°C after leaving the dryer at 52 to 55°C.

Packaging and Storing of Refined Granulated Sugar

In recent decades, there have been significant changes in the methods of handling refined sugar as it leaves the dryer. Bulk delivery of refined granulated sugar to customers has made it necessary for the refiner to store finished product in bulk rather than in bags. Granulated sugar remains free-flowing for a longer period of time if it is "conditioned," as conditioning reduces handling, packaging, and storage problems resulting from caking. Conditioning involves several factors, including control of the moisture content, the temperature, and the grain size, as well as good inventory management.[27]

As the sugar leaves the dryer, it can be cooled in one of several types of equipment, including the Holoflite screw conveyor, the thermal disc processor, and the Buttner turbo tray dryer; or it can proceed directly to large bins or silos, where it is cooled and conditioned in an atmosphere of controlled temperature and humidity. Circulation of dehumidified air through or above the sugar pile and mechanical movement from silo to silo also are practiced to prevent caking. The cooled, unconditioned refined sugar then is classified according to crystal size by a screening or sieving operation.

Shipment of conditioned bulk sugar is made in specially designed railcars (100,000–180,000 lb capacity) or in hopper trucks (40,000–60,000 lb capacity).

Conditioned sugar also is packaged in

multiwall paper bags of 2-, 5-, and 10-lb capacity. These sizes are overwrapped in 60-lb bales for shipment. Larger bags (100, 50, and 25 lb) also are packed.

Granulated sugar is available in several sizes according to the needs of customers. These range from very large to very small crystals.

Direct-Consumption Sugar

Some cane sugar mills produce white sugar by using sulfitation, carbonation, or, more recently, more complex processes such as Blanco Directo.

Sulfitation. The expressed juice from the mills is heated to 75°C, clarified with lime and sulfur dioxide, and in some cases filtered and then evaporated. After the syrup is treated with sulfur dioxide again, it goes through a three- or four-boiling system. The *A* and *B* sugars are mixed with a high-purity syrup, and then centrifuged, dried, and screened for size and distributed as white sugar.

Blanco Directo. Talo "Blanco Directo" is a trademark of Tate and Lyle Process Technology. This process and others (e.g., USP process of the Fabcon Co.) are used at sugarcane factories, in conjunction with raw or plantation white production, to produce a high grade white sugar suitable for use in food and beverages. This product is economically competitive with imported refined sugars. Although the term "Blanco Directo" is the trademark for one particular process, it appears to be used somewhat generically for many similar processes.

In using Blanco Directo or similar processes, instead of shipment of the raw sugar from a sugar factory to a refinery to be refined into white and brown sugar, the refined product is manufactured at the factory via the following steps:[28]

1. Phospho-flotation of juice or syrup to remove turbidity, ash, and color.
2. Addition of flocculation aids and ionic organic polymers to aid in color removal.
3. Flotation clarification of mud filtrate to remove nonsugars.
4. Sulfitation (but to a much lesser degree than in traditional plantation white) after initial partial liming of the juice.

According to Clarke.[72] "An important step in the process is clarification of the syrup coming from the evaporators, to reduce turbidity, color, and ash. Syrup clarification, such as the Talodura process, has in this decade (1980s) found widespread application in raw sugar production in the U.S., throughout the Far East, and Central and South America." Talodura consists of using a combination of sulfite clarification followed by subsequent clarification of the evaporated liquor with lime and phosphoric acid to which a flocculant is added. It has made improvements in the color of the mill white sugar, boiling-house recovery, and chemical costs per ton of sugar.[29]

Carbonation. In this process, the mixed juices from the mills are heated, clarified with lime, and evaporated to about 35 degrees Brix. This syrup is relimed and treated with carbon dioxide, filtered, recarbonated, reheated, and refiltered. After carbonation, the syrup is given a double sulfur dioxide treatment and filtered. The resulting syrup is subjected to a three- or four-boiling system with the *A* and *B* sugars used as the refined product.

Other Sugars

The cane and beet sugar industries manufacture several types of sugar in addition to granulated sugar. Among them are liquid sugars, brown or soft sugar, pulverized sugar, and special agglomerated sugars.

Liquid Sugars (Sugars Dissolved in Water). Liquid sugars are economically important largely because a number of food manufacturers use sugar in the form of a syrup, and also because of the efficiency and ease of handling of a liquid product. Liquid sugars are produced by one of two methods: (1) dissolution or melting of refined sugar in water; (2) further purification of in-process liquors by ion exchange treatment to remove minerals, and further decolorization using bone char and pulverized or granular carbon. Liquid sugar had other advantages over granulated in that it can be delivered as sucrose, as a mixture of sucrose and invert sugar, or as a blend of those sugars with various glucose syrups from starch hydrolysis and dextrose from the same source. Sucrose liquid sugars usually are distributed at a 67 percent sugar concentration, whereas invert sugar and mixtures of invert and sucrose are distributed at concentrations of 72 to 77 percent sugar. Invert sugar is an equimolecular mixture of dextrose and levulose resulting from the hydrolysis of sucrose.

Brown or Soft Sugars. These are specialty "dry" products ranging in color from light to dark brown. In addition to sucrose, soft sugars contain varying amounts of water, invert sugar, and nonsugars. These sugars have a characteristic flavor. In some cases, soft sugars are "boiled" from a low-purity process liquor to obtain the desired color, flavor, and composition. In other instances, refined granulated sugar is "painted" with refiner's syrup or molasses to produce a product of similar appearance and characteristics.

Pulverized Sugars. These sugars are manufactured by milling granulated sugar to the desired size. In most instances, pulverized sugars are mixed with small amounts of dried starch or tricalcium phosphate to prevent caking. A free-flowing agglomerated pulverized sugar without anticaking agents has been manufactured.[24]

Agglomerated Sugars. Several kinds of these sugars are manufactured. Because soft sugars are subject to severe caking, one sugar refiner has resolved the problem by converting soft sugar into an agglomerated free-flowing dry product. Several companies manufacture "dry fondant" by agglomerating mixtures of invert sugar and very fine (less than 40 microns) sucrose particles.

Amorphous Sugar. Amorphous sugar is a microcrystalline sugar agglomerated during crystallization, similar to dry fondants without having invert or reducing sugars added to it. Its polarization ranges from 99.1 to 99.2 with an invert content of from 0.01 percent to 0.15 percent, a color of 20 to 40 m.a.u., and a size in the 40 to 80 mesh range.[30]

BEET SUGAR

Agriculture

The sugar beet, *Beta vulgaris*, is a Temperate Zone plant grown largely in the Northern Hemisphere. A long growing season is required, and in the United States it is one of the first crops planted and the last harvested. The seed is planted in rows, and after the plants have emerged, they are "thinned" to permit better development of a smaller number of beets. Unlike sugarcane, which cannot be cultivated after the cane has reached a certain height, sugar beets require a considerable amount of cultivation. Both cultivating and harvesting operations have been largely mechanized in the United States.

After the plants have reached maturity in late fall (October and November), they are harvested by machines that remove the top growth of leaves, lift the roots from the ground, and deliver them to a holding bin or a truck. Because the harvesting season is much shorter than the processing season, beets are stored in piles at the factory or at outlying points near transportation. Frequently, storage piles are ventilated to lower the temperature of the beets, thus reducing sugar loss due to respiration during storage.[7,31]

In the Red River Valley area of Minnesota and North Dakota, storage sheds for sugar beets were constructed in the mid-1980s that measure 210 feet wide by 520 feet long and hold 50,000 tons of beets. The temperature in these storage facilities is controlled at not much above freezing to minimize degradation of the sucrose content.

Washing

Beets are transferred from storage into the factory in water flumes. These flumes lead directly into a rock-catcher, which allows rocks to settle out, and then on into a trash-catcher and a rotary washer.

Slicing

The washed beets are sliced into thin V-shaped cossettes by means of specially shaped knives set in frames mounted around the periphery of a rotating drum. Good removal of rocks and trash is essential to a reasonable life for the knives.

Diffusion

The cossettes are weighed and transferred continuously into a diffuser where water passes countercurrently to the movement of the cossettes, and where, by dialysis, sugar and some of the nonsugars of the beet are extracted.

Both continuous and batch diffusers are used, but batch processes largely are being displaced. Continuous diffusers come in a variety of forms and shapes, but all of them employ the same principle, that is, movement of juice countercurrently to the movement of the cossettes. In batch diffusers, the cossettes are held stationary, and the diffusion juice is moved from cell to cell. A few of the well-known types of continuous diffusers are the RT, BMA, DDS, DeSmet, Buckau-Wolf, and Olier.

The RT-type diffuser is a large revolving drum with an internal helix that separates the drum into moving compartments. As the drum revolves, the cossettes travel by the action of the moving helix from one end of the drum to the other end, while the juice moves in the opposite direction.

The BMA diffuser is a cylindrical tower with a conveyor mechanism attached to a central rotating shaft. Guide plates on the shaft direct the cossettes upward, while the juice exits through screens at the bottom.

The temperature of the juices during diffusion ranges up to 60 to 75°C. Antifoaming agents are used to control foam in continuous diffusers, and bactericides are added for microbiological control.[7]

Juice Purification

The diffusion juice is a dark turbid liquid containing 10 to 15 percent sucrose and 1 to 3 percent nonsugars, including proteins, nitrogenous bases, amino acids, amides, inorganic material, and pectinous matter. It also contains $\frac{1}{4}$ percent sodium and potassium. These impurities are removed by a series of processes using lime and carbon dioxide (carbonation), sulfur dioxide (sulfitation), and crystallization. In recent years, there has been an increasing use of ion exchange resins in these plants where refined granulated sugar is made.

Carbonation. In this process, the juice is heated to 80 to 90°C, limed, and then sent to a carbonator for gassing with carbon dioxide. The resulting mixture, containing insoluble lime salts, chiefly calcium carbonate, is pumped to subsiders (thickeners, clarifiers) to remove the insolubles by settling. From the subsider, the partially clarified filtrate is recarbonated, and the residual lime is precipitated. This treatment is followed by press filtration. The sludge from the subsiders is filtered on rotary-drum filters, and the sugar-laden filtrate is returned to the first carbonation step. The carbonation process can be either continuous or batch.

One continuous system for carbonation used in the United States is the Dorr process, introduced in the 1930s. In this process, heated juice is treated with milk of lime or lime saccharate in a cylindrical column (primary tank) where carbon dioxide gas is added. The contents of the secondary tank are continuously pumped into the bottom of the primary tank. The finished first-carbonated juice flows from an overflow line in the discharge of the recirculation pump to a subsider in which the insoluble matter is separated from the juice. The thickener is a cylindrical tank consisting of a number of shallow compartments with trays and rotating paddles that continuously remove the settled sludge. The filtrate is reheated (90–95°C) and sent to another carbonation tank. The effluent from the second carbonation tank is pressure-filtered on a leaf press such as those manufactured by U.S. Filter, Industrial Filter, Sweetland, Vallez, or Angola. (Membrane filters are beginning to replace presses.) The filtered liquor is treated with a small amount of sulfur dioxide in a tower, heated, and refiltered.

Pre-liming. The Dorr process is being supplanted in the United States and Canada by European technology that uses a pre-liming system. In pre-liming, diffusion juice is sent through a series of tanks where lime is added to various levels of alkalinity. The limed juice then is carbonated and generally follows a purification pattern not unlike that described for the Dorr process. The pre-liming system allows the process to handle a wider range of beet quality and leads to a more uniform product. According to one authority,[71] the DeDanske Sukkerfabrikker integrated juice purification system, which incorporates fractional cold liming, increases the yield of high-quality white sugar while effecting marked cost reductions.

Ion exchange resins are used in some plants to decolorize, deionize, and delime the juices.

Evaporation and Standard Liquor

The thin juice (about 15% solids) discharged from the filter presses after clarification is evaporated to thick juice (50–65% solids) in multiple-effect evaporators. If decolorizing adsorbents are used, they usually are added to the thick juice. Granular carbon and pulverized carbon have been used for this purpose. Thick juice treated with pulverized carbon usually must be double-filtered to remove all of the carbon.

Low raw sugars (sugars with purities below that of refined) are added to the thick juice in the melters to make standard liquor from which white sugar is crystallized. Standard liquor usually is filtered with diatomaceous earth before going to the vacuum pan.

Crystallization, Centrifuging, and Drying

Crystallization practices in U.S. beet sugar factories are similar to those in a cane sugar refinery and result in a white granulated sugar comparable in quality to refined cane sugar. However, some European factories may make "raw sugar" as a separate product. White-sugar centrifuge stations as well as drying operations are comparable to the same operations in a cane sugar refinery.

Sugar Recovery from Molasses

Molasses is the material that remains when no more sugar can be economically extracted in the crystallization process. Generally it is quite high in sugar content (60% dry basis) and represents considerable value. It is now possible, using recently developed ion exclusion chromatography, significantly to increase the recovery of these sugar values.

Historically, recovery of sucrose from molasses was accomplished by using the Steffan's process, in which sucrose is separated by means of a lime salt known as calcium saccharate. Another process, known as the barium process, precipitated sucrose in the form of barium saccharate. Descriptions of both of these processes can be found in the preceding edition of this book and elsewhere. Because they both are being replaced by ion exclusion, only that process is described here.

The ion exclusion process utilizes a bed of ion exchange resin operated in such a way as to simulate a countercurrent moving bed system. Its rationale and theory have been discussed in detail in at least one paper.[32] The ion exclusion process for desugarization of molasses provides for lower sucrose content in the final molasses—up to 90 percent of the sucrose in the molasses can be recovered—and has been put into every major beet sugar operation in the United States. Suppliers of the technology are Amalgamated Sugar, Finnish Sugar, and Illinois Water Treatment.

The resin used as a strong-acid cationic resin, crosslinked with divinylbenzene to form a polymer network, in the monovalent salt form. It is placed in a column alternately fed with molasses and water. The height-to-diameter ratio of the column is important (not less than 4 to 1 and preferably around 20 to 1), and flow rates of from 0.4 to 0.6 gal/ft^2/min have been suggested. The clarity and temperature (70–80°C) of the feed also are important. Sugar and nonsugar components of the molasses are separated chromatographically. Four fractions are obtained: the first fraction contains most of the inorganic substances, colorants, and organic nonsugars; the second fraction is similar to the first in composition of the feed but contains about 25 percent more water; the third fraction is a high-purity sucrose solution between 10 and 20 degrees Brix; the fourth fraction is an extremely dilute solution of sucrose and invert sugar (2–5 degrees Brix). The sucrose fraction either goes to pan crystallization or is further purified with activated carbon and ion exchange resins and sold as liquid sugar. The first or waste fraction is concentrated to 70 degrees Brix and marketed as "fodder molasses." The resin, after a number of cycles, has to be regenerated with salt because of the accumulation of calcium and magnesium ions. In some cases, the feed molasses first is softened prior to ion exclusion treatment.[33,34]

Sugarcane molasses can be subjected to the same basic ion exclusion process with some modification: (1) the molasses must be clarified to remove as much suspended matter as possible, and (2) prior softening is necessary to extend operating cycles. Because cane molasses contains substantial quantities of reducing sugar, the resulting fractions consist of nonsugars, a mixture similar in composition to feed, a mixture of sucrose and reducing sugars rich in sucrose, and a mixture of reducing sugars and sucrose.[35,36]

Sugar Recovery from Syrup

In 1962, a beet sugar company in the United States built a tank system for storing thick juice produced in excess of its crystallizing capacity. This storage system served two purposes: (1) it enabled the "beet end" of the factory to operate at full capacity even though the "sugar end" could not handle the output; and (2) it provided raw material for the sugar end to operate at full capacity when the beet end was in trouble (Fig. 9.15).

The system proved such a success that other beet factories adopted the practice. Furthermore, improvements made in the storage systems have made it possible to extend the operating time of the sugar end far beyond the termination of the slicing compaign (Fig. 9.16).[37]

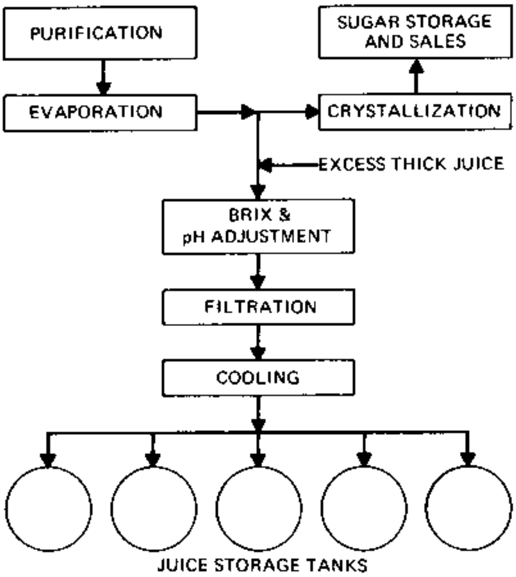


Fig. 9.15. Schematic flow diagram showing flow of thick juice to storage. (*Courtesy the Amalgamated Sugar Co., Ogden Utah.*)

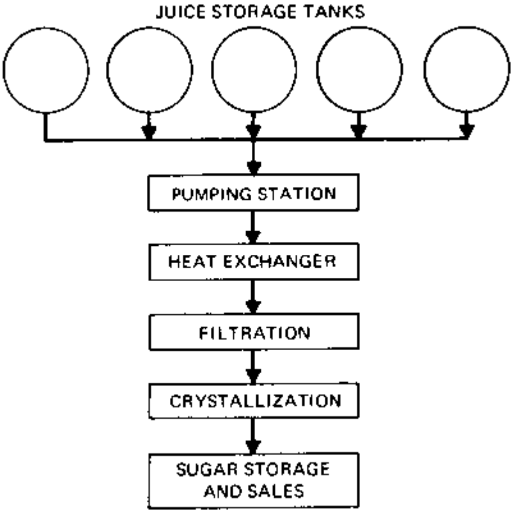


Fig. 9.16. Flow diagram showing flow of thick juice from storage through processing. (*Courtesy the Amalgamated Sugar Co., Ogden, Utah.*)

Storage and Packaging

In the past several years, both beet sugar factories and cane sugar refineries have gone extensively to bulk storage of finished products. Beet sugar bulk storage usually is more extensive because of the need to hold sugar to meet customer needs from one processing season to the next. The daily capacities of cane sugar refineries are such, however, that it would be uneconomical to store more than a few days' output.

Prior to bulk storage, refined beet sugar was stored in bags (mostly 100 lb). Such storage was acceptable as long as large customers purchased sugar in bags. However, a shift in the consumption of sugar from the home to food processors and the development of bulk transportation facilities made bulk storage a natural consequence. Thus, beet sugar is packed in the usual customer-size packages and 100-lb bags, and it is also shipped in bulk containers ranging in size from "tote bins" (2000 lb) to railcars holding several tons.

Cane and Beet Sugar Production

Cane sugar is primarily a product of tropical countries, whereas beet sugar is produced in temperate climates. However, both are produced in a few countries, among them the United States, China, Afghanistan, Spain, Iran, and Pakistan.[38] The total annual production of centrifugal or crystalline sugar is shown in Table 9.1, together with average annual production for representative periods over the years 1985–90.

Cane sugar production currently amounts to approximately 65 percent of the total world sugar production. The largest seven producers are EC-12, India, the former Soviet Union, Cuba, Brazil, China, and the United States, in that order.[39]

The United States in 1977–78 produced less than 6 million short tons and in 1989–90 6.6 million short tons, raw value, of sugar.[75,76] About half of this amount was cane sugar produced in Florida, Hawaii, Louisiana, Texas, and Puerto Rico. The remainder was beet sugar produced in all the states west of the Mississippi River except Arkansas, Missouri, Oklahoma, and Nevada, and, in addition, in the states of Michigan and Ohio.

Sugar Consumption and Usage

Per capita consumption of sugar varies widely from country to country. Although Europe, the Americas, and Oceania consume more than 70 kg per capita, the average for the world is only slightly more than 37 kg.

TABLE 9.1 Centrifugal[a] Sugar Production Raw Value[b] by Continent, 1986/86–1989/90 (in Units of One-Million Metric Tons)

	1985/86	*1986/87*	*1987/88*	*1988/89*	*1989/90*
North America	19.9	20.9	20.9	21.0	20.4
South America[c]	13.0	13.6	13.3	13.7	12.8
Europe (west)	16.3	16.7	15.8	16.4	17.2
Europe (east)	4.8	4.8	4.6	4.2	4.8
Africa	7.7	7.9	7.7	7.7	7.8
Oceania	3.8	4.0	4.0	4.1	4.3
U.S.S.R (Europe & Asia)	8.3	8.7	9.6	8.9	9.5
World Total	98.7	103.5	103.4	105.5	108.2

[a] Noncentrifugal sugars are usually consumed in the area of origin. Production from 1979 to 1980 ranged from 10.4 to 11.9 million metric tons (1979/80).

[b] Raw value is a term defined mathematically to reduce sugars of differing sucrose contents (from raw sugar containing varying amounts of sucrose to refined sugar containing approximately 100% sucrose) to an equivalent basis in pounds.

[c] Includes the Caribbean and Central America.

Source: U.S. Department of Agriculture.[75]

Sugar usage patterns, particularly in developed countries, have not changed markedly over the years except in the United States, where high fructose corn syrup (HFCS) replaced sugar in the manufacture of beverages (see Table 9.2). Nonfood uses continue to be a very small portion of the total.[73]

Although the nonfood uses of sugar are relatively small in comparison with its food use, because of its availability in large quantities at very high purities sugar always has been viewed as an attractive raw material for organic chemical synthesis. Research in this area has been aggressively pursued for more then 25 years,[40] and a great number of products have resulted from those efforts although few of them have been commercialized, either for economic reasons or because of the complexity of the chemical synthesis. Among the derivatives produced in the laboratory over the years are ethers, fatty and other esters, acetals, reduction products, halogen, sulfur, metal derivatives, and others.[41] Potential applications include products for use such as surfactants, surface coatings, food and feed additives, polymers, textile chemicals, pharmaceuticals, and pesticides.[42]

The reduction products sorbitol and mannitol have been manufactured from sugar and sugar products. Sugar's use for that purpose usually depends upon its being competitively priced with dextrose or glucose syrups, which are the most commonly used raw materials. A review of the potential applications of sucrose derivatives in other areas is contained in *Sucrochemistry*, ACS Symposium Series 41, 1977, American Chemical Society, Washington, DC.

Fatty acid esters of sucrose have been manufactured in the United States and some foreign countries on a commercial basis for many years.[40] Plants for a solventless process for manufacturing esters are in various stages of design and construction. An almost ironic laboratory development, casting chlorosucrose derivatives in the role of a noncaloric sweetener, has received widespread interest in recent years.[43,44]

TABLE 9.2 U.S. Sugar Deliveries to Industrial and Nonindustrial Users, Calendar Years, 1978–90 (Biennial)

	Calendar Year						
Type of Buyer	*1978*	*1980*	*1982*	*1984*	*1986*	*1988*	*1990*
	1000 short tons, refined						
Industrial users (food use):							
Bakery and cereal	1265	1284	1296	1404	1432	1541	1607
Confectionery products	895	895	939	1115	1051	1107	1277
Processed foods	672	516	1150	433	387	354	331
Dairy products	538	436	404	408	447	394	460
Beverage use	2558	2119	1583	908	266	237	228
Other	407	548	526	416	443	529	641
Total industrial use	6335	5798	5898	4684	4026	4162	4544
Nonindustrial Users:							
Institutions	104	96	85	108	84	89	106
Wholesale grocers	1963	1841	1951	1744	1867	2200	2121
Retail grocers	1168	1150	1086	1100	1066	940	1071
Others	124	205	92	101	58	86	75
Total nonindustrial use	3359	3292	3214	3053	3075	3315	3373
Nonfood use	158	117	106	127	138	121	107
Total use in U.S.A.	9852	9207	9218	7864	7239	7598	8024

SUGARS DERIVED FROM STARCH

Starch Hydrolysis

Undried starch, usually from wet milling, is pumped as a slurry to the conversion plant where it undergoes one or more hydrolytic processes to yield mixtures of various carbohydrates in the form of syrups or as crystalline dextrose. The kind and amount of the various carbohydrates obtained depend upon the type of hydrolysis system used (acid, acid–enzyme, or enzyme–enzyme), the extent to which the hydrolytic reaction is allowed to proceed, and the type of enzyme used. The fact that most starches consist of two different kinds of polymers (amylose and amylopectin) also has an effect on the nature of the products obtained.

The extent to which starch is converted into simpler carbohydrates is indicated by the dextrose equivalent (D.E.), a measure of the reducing sugar content calculated as dextrose and expressed as a percentage of the dry substances. Hydrolyzates having dextrose equivalents ranging from 5 to 100 are produced. Those having a very low dextrose equivalent frequently are referred to as dextrins. They are produced by minimal acid hydrolysis or roasting. Starch-hydrolyzate syrups commonly are produced as "low," "regular," "intermediate," "high," or "extra-high" conversion products, as more or less standard products.

Table 9.3 shows the composition of some of the various syrups. In addition to carbohydrates, the syrups contain minerals (largely sodium chloride) and nitrogenous substances. Maltodextrin is a dried dextrose having a D.E. below 20, while the dry dextrins with a D.E. above 20 are called corn solids.

Acid Hydrolysis. A starch slurry containing 35 to 45 percent solids is acidified with hydrochloric acid to about pH 1.8 to 1.9. The suspension is pumped into an autoclave (convertor) where live steam is gradually admitted to a pressure of 30 to 45 psi. The conversion time largely determines the D.E. of the hydrolyzate; e.g., 8 minutes may produce 42 D.E. syrup, and 10 minutes may produce 55 D.E.[45] Converted liquors are neutralized with sodium carbonate to a pH of 5 to 7, with coagulation of insoluble protein, fats, and colloidal matter. The scum is removed by centrifuge.

The dark-colored clarified liquor is pressure-filtered and then concentrated to 60 percent solids in multiple-effect evaporators. The concentrated liquor is decolorized with granular carbon in columns 12 feet in diameter and 30 feet high in a countercurrent manner; that is, liquor flows upward in the columns, while a portion of the carbon is removed from the bottom periodically (Fig. 9.17). It has been reported that carbon is used at a rate of 2.5 percent of dry solid processed, and that 5 percent of carbon is lost during revivification.[46] "Low ash" syrups usually are deionized with ion exchange resins. Finally, the processed liquor is evaporated to a final solids content of 75 to 85 percent in a single-effect evaporator.

TABLE 9.3 Carbohydrate Composition of Glucose Syrups (Saccharide as a % of Total Carbohydrates)

DE	*Mono*	*Di*	*Tri*	*Tetra*	*Penta*	*Hexa*	*Hepta*	*Higher*
15	3.7	4.4	4.4	4.5	4.3	3.3	3.0	72.4
35	13.4	11.3	10.0	9.1	7.8	6.5	5.5	36.4
45	21.0	14.9	12.2	10.1	8.4	6.5	5.6	21.3
55	30.8	18.1	13.2	9.5	7.2	5.1	4.2	11.9
65	42.5	20.9	12.7	7.5	5.1	3.6	2.2	5.5

Source: Corn Industries Research Foundation, "Corn Syrups and Sugars," Washington, DC, 1965.[70]

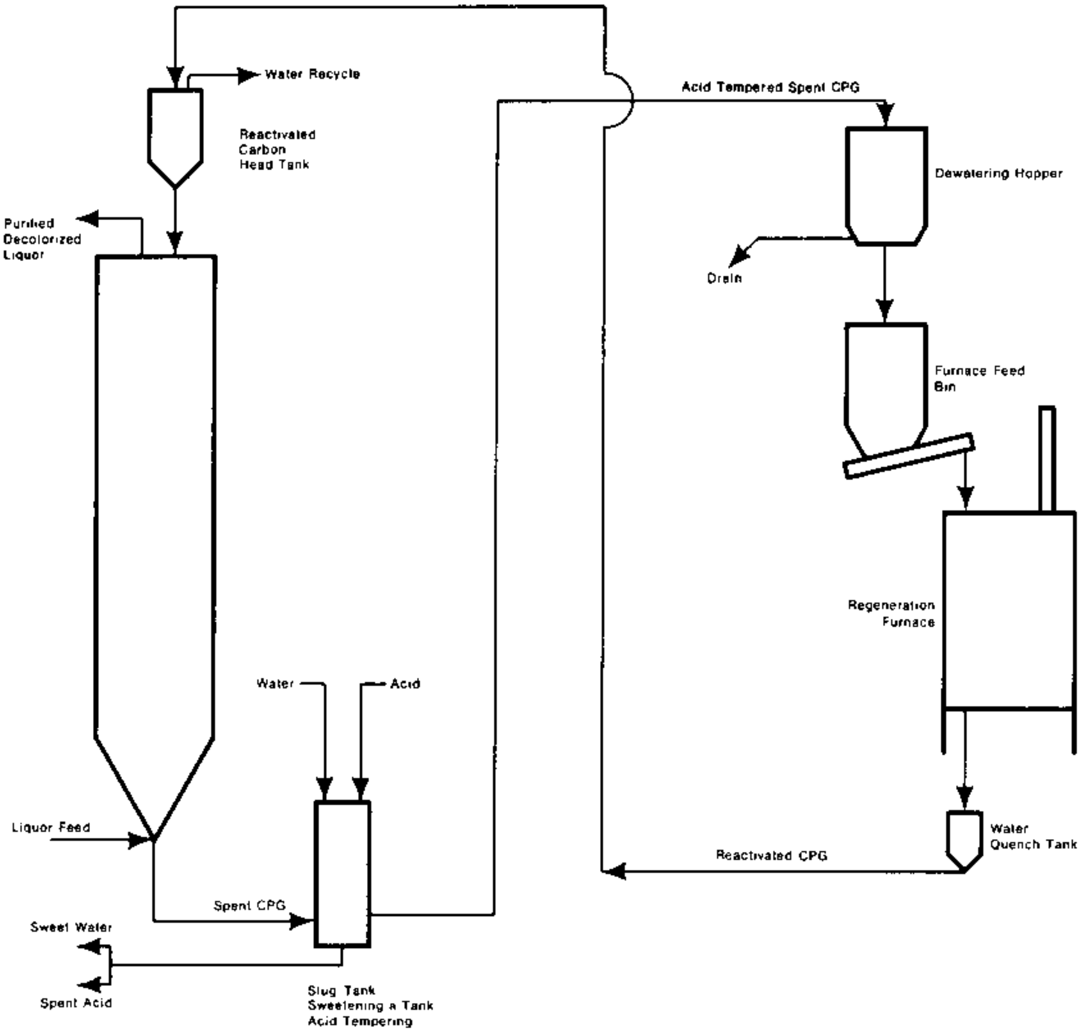


Fig. 9.17. Flow diagram of Pittsburgh moving bed system for glucose-dextrose. (*Courtesy Activated Carbon Div., Calgon Corp.*)

Acid–Enzyme Hydrolysis. Starch first is liquefied and hydrolyzed to specific dextrose equivalents with hydrochloric acid. After evaporation to 60 percent solids, a saccharifying enzyme (fungal amylases) is added to continue hydrolysis to the desired level. By choosing two or more types of enzymes (such as alpha-amylases, beta-amylases, or glucoamylases) and adjusting the initial acid hydrolysis, syrups with different ratios of dextrose, maltose, and higher saccharides can be obtained.[47]

Enzyme–Enzyme Hydrolysis. Enzyme–enzyme conversion employs an enzyme for starch liquefaction in place of acid. Subsequent hydrolysis is by enzymes as above. The choice of hydrolytic system depends upon economics and the kind of end product desired. Enzymes usually are inactivated by heating to 75 to 80°C.[47]

Conversion to Dextrose

The manufacture of dextrose requires conditions different from those used for the manufacture of syrups. When acid hydrolysis is used, the density of the starch slurry is lower

(15–20%). Hydrochloric acid is added to a concentration of 0.03 N, and higher steam pressures (40–50 psi) are used. The time of hydrolysis is extended to about 30 minutes or until the purity reaches 90 to 91 D.E. The hydrolyzate is neutralized to a pH of 4 to 5 with sodium carbonate. Other purification steps are similar to those employed in syrup manufacture.

The high-purity liquor is pumped to insulated crystallizers fitted with slowly moving agitators for crystallization of dextrose monohydrate. A heavy seed base (about 25%) from a previous batch is mingled with the syrup and cooled to about 38°C. The seeded liquor is held at this temperature for several days until about 60 percent has crystallized. The mixture then is centrifuged to separate crystals from the mother liquor. The wet sugar is dried in rotary dryers or recrystallized into anhydrous dextrose. The monohydrate also may be converted to anhydrous dextrose by drying the monohydrate in hot air. A second crop of crystals is taken from the mother liquor, and the runoff syrup from this step is final molasses or "hydrol."[48,49]

Dextrose also may be made by acid–enzyme and enzyme–enzyme systems. In the acid–enzyme process, acid hydrolysis is stopped near 18 D.E. The liquefied slurry is evaporated to 60 percent solids and treated with a fungal glucoamylase until the D.E. is about 90. With the enzyme–enzyme process, a 30 percent starch slurry is liquefied with a heat-stable bacterial amylase followed by treatment with fungal glycoamylase. The liquor is purified in the same manner as used for others.[47]

In addition to syrups, several solid products are manufactured, including several kinds of dried sugar. "Crude sugar" is a solidified liquor containing large amounts of dextrose and substantial quantities of nondextrose solids as well. A solid product of recent development, "noncrystalline" or "enzyme-converted" dextrose, is highly refined and contains about 92 percent dextrose.

High Fructose Syrup

The rapid development of enzyme technology has made available in commercial quantities a new sweetener derived from starch. This new product, which is generally known as high fructose corn syrup (HFCS) contains 30 percent fructose, 35 percent glucose, and 6 percent higher saccharides. The fructose fraction is obtained by the isomerization of glucose through the catalytic action of the enzyme glucose isomerase.

Glucose isomerase can be derived from a variety of microorganisms; *Bacillus coagulans*,[50] *Actinoplanes missourensis*,[51] and several organisms from the *Streptomyces* genus.[52] Because glucose isomerase is an intracellular enzyme, it commonly is used today in an immobilized form fixed on an inert carrier, geometrically shaped for use in vertical columns.

The basic feature of the isomerization process is a series of reactors containing the immobilized enzyme fixed in a packed bed. The feed material is of the highest practical purity possible because enzymatic activity and life are closely related to the purity of the glucose syrup. Glucose syrup of about 94 D.E. is filtered, treated with activated carbon to remove residual color, and deionized with ion exchange resin to lower the ash content, particularly the calcium ion. The dissolved oxygen is reduced by flash evaporation, which also concentrates the feed stock to 40 to 45 percent glucose and raises the temperature to 60 to 65°C. At this point, prior to entering the reactors, enzyme activators are added, particularly magnesium ions and, in some cases, hydrogen sulfite ions. Also the pH is adjusted to about 8. Isomerized liquor is removed from the process when the equivalent of 42 percent fructose on a dry basis is reached. The isomerized syrup is further treated with activated carbon and ion exchange resin and finally concentrated to 71 percent solids.[46,50,54]

In the late seventies, a "second generation" of HFCS became commercially available containing 55 percent fructose on a dry basis. The higher fructose content is achieved by subjecting the 42 percent fructose syrup to a chromatographic separation of fructose from glucose by means of strong cationic resins of low cross-linkage in the calcium form. The fructose is preferentially held by the resin and is later eluted with water.[46,55] Recently, a process has been described that uses a nonresin absorbent—a rigid, nonswelling inorganic product. The process employs a unique cycling device to remove from, or feed to, various parts of the chromatographic column liquids of different composition. The product stream has a fructose content of 95 percent on a dry basis.[56]

Fructose

Fructose, also known as levulose and fruit sugar, has been recognized as a naturally occurring sugar found in several fruits as well as honey for many years; but it has become commercially significant only in the past several years.[57] Fructose, as a laboratory chemical, has been prepared from inulin and invert sugar,[58] but its commercialization was based on its extraction from hydrolized sucrose solutions or invert sugar syrup (crystalline fructose).

Fructose has had wider usage in Europe, where it is manufactured by several companies. Those processes have been based on the hydrolysis of sucrose followed by chromatographic or ion exclusion separation, with subsequent crystallization of fructose after its separation from glucose and sucrose. The development of processes for isomerizing glucose into fructose, together with commercialization of chromatographic separation of mixtures of sugars, has led to the use of high fructose corn syrup as a raw material for the manufacture of pure fructose. The technology was reviewed by M. Seidman.[59]

The role of fructose as a food and in the food processing industry in the United States is not yet clear. Although its desirable physical and chemical characteristics are well documented,[57] its basic attractiveness appears to be related to its relative sweetness when compared with sucrose.[60] In theory, substitution of fructose for sucrose in foods (especially soft drinks) would permit a reduction in the caloric content of a food because of the greater relative sweetening power of fructose. However, experimental studies have demonstrated that fructose sweetness varies with the conditions under which it is used.[61] A theoretical basis explaining this variability in sweetness has been set forth by Shallenberger.[62]

BY-PRODUCTS

Molasses

Molasses, a residual mother liquor from which little or no additional sugars can be recovered economically, is a by-product common to the cane and beet sugar industries, as well as the dextrose industry. Each type of manufacturer has designated this liquid by-product with its own peculiar name: the molasses from cane sugar production is most commonly called blackstrap, that from beets is simply beet molasses, while that from starch hydrolysis is known in the United States as hydrol.

The molasses from each source differs considerably from the others, as shown in Table 9.4.

Blackstrap contains a significant quantity of both sucrose and reducing sugars. A substantial amount of reducing sugar is produced during the processing of cane juice into sugar and molasses. Beet molasses contains primarily sucrose and little or no reducing sugar because of highly alkaline processing conditions that destroy reducing sugars. Hydrol, of course, contains no sucrose. Higher saccharides result from incomplete

TABLE 9.4 Analysis of Molasses from Various Sources

Constituent	*Blackstrap*[63] *(Dry Basis)*	*Beet Molasses*[64] *(Dry Basis)*	*Hydrol*[21] *(Wet Basis)*
Sucrose	37.4	63.0	
Reducing sugars	32.7	0.7	55.0
Higher saccharides		1.5	
Ash	13.5	12.0	7.2
Nitrogen	0.4	2.0	0.07

TABLE 9.5 Cane and Beet Molasses Approximate Production, 1985–89 (Millions of Metric Tons)

Year	*Production*
1985/86	36.9
86/87	39.8
87/88	40.5
88/89	41.7
89/90	43.3

hydrolysis or from the polymerization of "sugar" units during processing.

The world production of blackstrap and beet molasses closely parallels sugar production. Total world production is shown in Table 9.5.

The major outlet for all molasses at the present time is in feed for cattle or other animals. Fermentation into rum, potable ethanol, citric acid, and vinegar continues to be a market for considerable quantities of molasses; and large quantities are used for growing yeasts. However, these uses have diminished in relation to feed use over the years. Beet molasses, because of its high content of nitrogeneous substances, is valued for the production of citric acid by fermentation.

When the price of petroleum is high, conversion of molasses and cane juice into absolute ethanol as partial or total substitution for gasoline in automotive vehicles becomes attractive. Brazil uses more than half of the available cane to produce ethanol, for use mainly as fuel for its cars.[65–67]

Bagasse and Beet Pulp

An important by-product from a cane sugar mill is bagasse, the fibrous portion of cane from which juice is extracted. When it is discharged from the milling train, bagasse contains solid matter (short fibers and the spongy tissue of the pith) and 50 percent by weight of water. Because the average fuel value of ash-free dry bagasse is 8300 Btu/lb, it is primarily used as fuel for the generation of steam in sugar factories. However, when an excess of bagasse is available or alternate fuels are plentiful and reasonably priced, the bagasse is utilized as a raw material for the pulp, paper, paperboard, and wallboard industries, especially in wood-poor areas of the world. Other successful uses of bagasse include its conversion into furfural and its use as a filler for explosives. Today, bagasse is receiving a great amount of attention as a source of sugar and fuel.[68]

Beet pulp is the structural portion of beet roots that remains after spent beets are discharged from a diffuser. As it is highly hydrated at that time, the wet pulp is dewatered in pulp presses. Then it is discharged into wet silos, and it may be sold as wet pulp for animal feed. However, more often it is dried or mixed with molasses and dried, in both of which cases it is used in the manufacture of animal feeds.

Other By-products

When grains such as corn, sorghum, and wheat are used as sources of starch, a number of important by-products are obtained, including steep water, corn oil, gluten, and hulls. Most of these products are used as ingredients in mixed feeds, but corn oil is used widely as a food product. By-products from the other commercial sources of starch are not so important as those from grains, but they usually find their way into feeds if they are salvaged.

TRADE IN SUGAR AND OTHER SWEETENERS

Many countries—especially the tropical, cane-sugar-producing ones—produce more sugar than is consumed locally. A number of beet-sugar-producing countries, particularly in Europe, became self-sufficient in the late 1970s. However, some European countries continue to import raw sugar to be refined. Altogether, 29.3 million metric tons, raw value, of centrifugal sugar were exported globally in 1989–90. Russia, EC-12 countries, the United States, Japan, China, South Korea, and Mexico are the largest importers, with Cuba, Australia, Thailand and Brazil among the largest exporters of raw sugar. The EC-12 countries are the world's largest exporter of refined white sugar, and the world's second largest sugar exporter, behind Cuba.

Trade in sugar throughout much of the world is influenced by agreements and special trading arrangements. For instance, the United States regulated sugar production, distribution, and importation by means of the Sugar Act of 1948 as amended,[69] but the act was allowed to expire in 1974. From 1981 to the present, the United States has had a price-support program, connected to farm legislation. In 1982, an import quote system went into effect to supplement the price-support program. In 1988, Australia filed a complaint against the United States, charging that the import restriction on sugar violated the General Agreement of Tariffs and Trade (GATT) rules. When the United States was found to be in violation on some of these rules, it implemented a change from an absolute quota to a tariff-rate quota.

The United States also has a program called the General System of Preferences (GSP) that exempts countries (mostly in the Caribbean area) from any duty.

The EC-12 countries import raw sugar within a special arrangement with ACP (Africa, Caribbean, and Pacific) countries.

Since 1986, the world community of nations has tried to expand world trade by formulating new rules and regulations on a wide variety of products within the General Agreement on Tariffs and Trade (GATT). Of all the products discussed, sugar became a major stumbling block, and the end result with sugar was a stalemate. Negotiations were concluded in December 1990.

Other sweeteners, such as dextrose, glucose syrups, honey, maple sugar and syrup, and edible molasses, have been available in the United States for many years. However, only dextrose and glucose syrup have been produced and distributed in substantial quantities in the United States (and many other countries, particularly western Europe) as alternative or supplemental sweeteners.

Per capita consumption of dextrose in the United States has been relatively constant at 4 to 5 lb for many years. The growth in the per capita consumption of starch-derived sweeteners prior to 1970 occurred in glucose syrup (a family of hydrolyzed syrups manufactured from starch), but that growth was limited to less than 2 lb per year. The increased use in the starch-derived sweeteners had no apparent effect on the consumption of cane and beet sugar, which had remained more or less constant at 97 to 99 lb per capita until the mid-1970s when HFCS began to replace sugar significantly in the beverage industry.[39] That change was due largely to the utilization of a new technology (immobilized enzymes), as well as governmental action to protect the domestic sweetener industry. The trend of the changes introduced by this product is shown in Fig. 9.18. HFCS consumption increased from less than one pound per capita in 1968 to more than 48 lb in 1990. For all intents and purposes HFCS is a replacement for invert sugar syrups. HFCS also displaces sucrose syrups in some applications. Those trends are apparent from Fig. 9.18, which shows steady increases in HFCS consumption during the same period. However, the declining consumption of sugar is due to several factors, only some of which are related to the availability of HFCS.

HFCS technology and products have spread to other countries, particularly Canada, Japan, and several countries in western Europe. The pace of commercial development in those other areas does not appear to be so rapid as that in the United States, where a combination of plentiful supplies of starch at reasonable prices and an existing industry based on starch hydrolysis appear to catalyze the development.

ENVIRONMENTAL CONCERNS

The sugar industry, in common with all other sectors of the chemical process industries, must be concerned with protecting the environment. This means that close attention must be paid to all gaseous and liquid effluents, with the aim of minimizing their production and ensuring that they at least meet all minimum standards before being discharged into the environment.

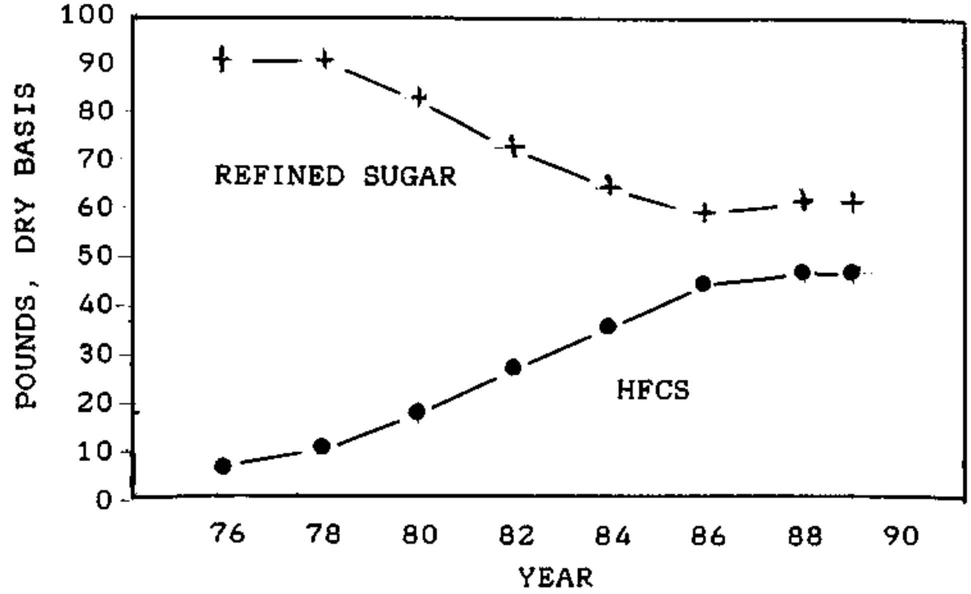


Fig. 9.18. Trends in distribution of sugars in the United States.

It is certain that present standards will not be relaxed, and that they can be expected to become even more restrictive as time goes on. It is therefore essential that older plants and operations be reviewed continually to determine what further steps can be taken to control emissions and reduce their volume. It is assumed that any changes made to existing operations, as well as all new designs, will include careful evaluation of their implications for waste management requirements. Chapters 2 and 3 treat the subjects of waste minimization and wastewater treatment at length and can be useful in planning waste management strategies.

Clarke[72] has written that: "A recent review of the U.S. beet sugar industry emphasizes the increasing severity of impending restrictions. Of particular concern are pesticide and heavy metal residues that can enter groundwater from any source. It is in these areas of water treatment, particularly for refineries and factories in urban areas, that such processes as reverse osmosis treatment may find application."

The following tables from Clarke's paper provide information on the by-products generated in the industry. Some of them are useful and can be sold, whereas others constitute waste streams and must be disposed of in acceptable ways.

Sugarcane Factory By-products

	% on cane
Molasses	2.6%–4% (85 Bx)
Bagasse	23%–35% (50% mois.)
Filter muds	2.5%–4.5% (75% mois.)
Flue gases	100%–130%
Furnace ash	0.3%–0.5%
Factory effluent waters:	0.05–0.1m^3/ton cane

Byproducts from U.S. Cane Sugar Refineries

Molasses		
Effluent water:		
	Type:	*BOD, mg/l*
	Vessel and filter wash	10–600
	Char wash water	800–2400
	Truck and rail car wash	15,000–18,000
Filter muds	calcium carbonate calcium phosphate	
Spent carbon, bone char, resin		

Clark also refers to several studies related to odor control problems and current and pending environmental controls in the Netherlands and Germany.

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10

Phosphorus and Phosphates

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INTRODUCTION

Phosphates, compounds of the element phosphorus, are produced from relatively abundant supplies of phosphate rock, containing apatite, $Ca_3(PO_4)\cdot CaF_2$, together with up to 40 percent of other minerals and impurities.

The major use of phosphate, referred to generally as P_2O_5, its anhydride, is as one of the three major plant foods, N, P, and K. The technology of the extraction of phosphate rock from its ore and its subsequent processing to fertilizer materials and industrial chemicals is a relatively mature art. Phosphate in the form of single superphosphate, a mixture of monocalcium monohydrate and gypsum, formed by the reaction of sulfuric acid with phosphate rock, has been used as a fertilizer since the mid-1800s. Phosphoric acid, derived by the treatment of phosphate rock with sulfuric acid so as to produce gypsum in a separable form, was produced in many locations by batch and countercurrent decantation methods in the 1920s.

This latter process is known as the "wet" process to distinguish it from the thermal or furnace process, in which elemental phosphorus is volatized and subsequently burned to P_2O_5 and hydrolyzed to H_3PO_4.

The "wet" processes, used for the bulk of today's phosphoric acid and fertilizer production, trace their origin to the early 1930s.[1]

This text has utilized portions of the chapter on phosphorus and phosphates from the eighth edition by J. H. McLellan, particularly the description of the furnace production of phosphorus and its derivative phosphates, which has remained relatively unchanged over the last decade.

Furnace processing, in contrast to the "wet" process, has been the method most often used for the production of higher-purity industrial and food-grade phosphates. Recently, however, solvent extraction technology has advanced to the level that food grade phosphates are being produced from relatively impure wet process phosphoric acid.

PHOSPHATE ROCK

Naturally occurring phosphate products having commercial value are classified as phosphate rock. The grade or phosphate content of these

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*Jacobs Engineering Group, Inc..

TABLE 10.1 Phosphate Rock Value (United States Marketable Production)

Year	*Total Value billion $*	*Unit Value $ per metric ton*
1980	1.148	21.34
1981	1.368	24.49
1982	1.204	26.44
1983	0.918	24.88
1984	1.182	24.03
1985	1.236	24.31
1986	0.897	22.25
1987	0.793	19.37
1988	0.888	19.56
1989	1.084	21.76

Source: Mineral Industry Surveys, U.S. Department of Interior, Bureau of Mines.

products traditionally has been reported as $Ca_3(PO_4)_2$, which may be called bone phosphate of lime (BPL), tricalcium phosphate (TCP), or triphosphate of lime (TPL). Factors equating the traditional rock analysis to the analytical terms commonly used in chemical and fertilizer technologies are: 100.00 percent BPL = 45.77 percent P_2O_5 = 19.96 percent P.

International trade of phosphate rock is based on dry metric tons, whereas U.S. domestic sales are on a short ton basis for either dry rock or wet rock. Chemical impurities such as CaO, MgO, Al_2O_3, Fe_2O_3, Na_2O, K_2O, F, Cl, and organic matter may be of importance, depending on the intended use of the phosphate rock.

Value

The value of phosphate rock, like that of many industrial minerals, is influenced by supply and demand, product specifications, and freight costs. Values of U.S. marketable production of phosphate rock from selected years are listed in Table 10.1.

Production

Phosphorus, in addition to nitrogen and potassium, is an essential ingredient of modern high analysis fertilizers. An ever-increasing global demand for food has resulted in increased fertilizer use and increased phosphate rock consumption. The data presented in Table 10.2 show a marked increase in world phosphate production, equivalent to an annual growth rate of 3.5 percent from 1970 to 1989.

Many countries use indigenous phsophate rock as a source of phosphorus and phosphates for industrial chemicals and fertilizers. Few countries, however, are self-sufficient, and supplemental sources of phosphate rock are essential.

Comparative statistics for the six leading exporters of phosphate rock are given in Table 10.3.

Resources

McKelvey[2] reported that the earth's crust contains an average of about 0.27 percent P_2O_5, most of which occurs as species of

TABLE 10.2 World Production of Phosphate Rock Production (Millions of Short Tons)

	1970	*1975*	*1980*	*1985*	*1989*
United States	38.7	48.8	58.8	54.6	54.2
Soviet Union	22.5	26.6	27.2	37.8	42.9
Morocco	12.6	14.9	20.8	22.9	19.8
China	1.3	3.7	11.8	7.7	18.7
Tunisia	3.3	3.8	5.1	5.0	7.3
Jordan	1.3	1.5	4.7	6.7	7.3
Other	14.1	19.3	14.4	28.7	29.6
Total World	93.8	118.6	142.8	163.4	179.8

Source: "Central Florida Phosphate Industry 1990 Status and Outlook," Zellars-Williams Company.

TABLE 10.3 Major Exporters of Phosphate Rock (Million Short Tons of Exported Phosphate Rock)

	1988	*1989*
Morocco	15.7	13.6
United States	10.2	9.2
Jordan	6.2	6.5
Soviet Union	3.5	3.5
Togo	3.2	3.7
Senegal	2.0	1.6

Source: "Central Florida Phosphate Industry 1990 Status and Outlook," Zellars-Williams Company.

apatite. Igneous rocks make up about 95 percent of the earth's crust but contain few apatite deposits of commercial value. Sedimentary rocks, which make up about 75 percent of the earth's surface, host the majority of commercially exploited phosphate deposits. Guano deposits formed from sea bird droppings and from bat droppings are of minor importance, as are guano-related deposits.

Naturally occurring phosphates exist as, or orginated as, accessory minerals in igneous rocks. Prolonged weathering gradually decomposes apatite so that its phosphate content becomes soluble. Eventually the soluble phosphate concentrates in the world's oceans where it is precipitated through chemical or biochemical reactions to form sedimentary marine phosphorites. Precambrian sedimentary phosphate deposits of commercial value exist in China; however, marine phosphorite deposition was more common in the Mesozoic and Cenozoic eras. deBelinko[3] has used paleogeographic reconstruction to summarize major periods of phosphate deposition and formation. The world's resources of phosphatic material amount to hundreds of billions of tons. According to Bernardi and Hall,[4] secondary enrichment through weathering, water action, and phosphatization is an important aspect in the formation of deposits.

Phosphatic resources normally are quantified in terms of in situ tons of phosphate material, without regard to economic and chemical criteria. Northolt, Sheldon, and Davidson[5] state that the identified phosphate resources in North America total over 35 billion metric tons. Phosphate ore reserves should be quantified in terms of phosphate rock recoverable at specified chemical and economic criteria. The definition of phosphate ore reserves normally requires an integrated program of geological exploration, laboratory testing, and application of criteria.

PHOSPHATE ORES

Phosphate ores occur in igneous deposits, sedimentary deposits, and guano-related deposits. According to Cathcart,[6] the percentages of phosphate rock produced from igneous, sedimentary, and guano-related deposits are 20, 75, and 5, respectively.

The types of igneous deposits in which commercially important concentrations of apatite have been found are nepheline-seyenite and carbonatites. The world's largest apatite deposit, located in Russia's Kola Peninsula, is associated with nepheline-seyenite. Carbonatite deposits that are mined for their phosphate content include Siilinjarvi in Finland, Araxa and Jacupiranga in Brazil, and Phalaborwa in South Africa. By-product recovery from carbonatite ores is common. At Siilinjarvi, by-product calcite is recovered for use as agricultural lime, whereas copper concentrate and baddeleyite (zirconium oxide) are by-products at Phalaborwa.

Sedimentary phosphate ores may be distinguished by their gangue minerals. Typically, phosphorite ores are characterized as having siliceous gangue or carbonate gangue. Soluble salts and organic material are also of concern. The Bone Valley formation in central Florida, which has been mined for one hundred years, contains phosphate ore with siliceous gangue comprised of quartz and clay minerals. The Hawthorn formation, also in central Florida, contains both siliceous gangue and carbonate gangue.

Examples of phosphorites containing carbonate gangue are Djebel Onk in Algeria and Akashat in Iraq. The usual carbonate minerals are calcite and dolomite. By-products from phosphorite ores are not common; however, uranium (U_3O_8) has been extracted commercially from phosphoric acid.

The common phosphate minerals are of the apatite group, with fluorapatite, hydroxyapatite, and chlorapatite in igneous rocks, and carbonate fluorapatite or francolite in sedimentary rocks. McClellan,[7] has quantified the chemical composition of the end members of the fluorapatite-francolite series as shown in Table 10.4. The empirical formulas for the end members are:

$$\text{Fluoroapatite} = Ca_{10}(PO_4)_6F_2$$

$$\text{Francolite} = Ca_{10-a-b}Na_aMg(PO_4)_{6-x}(CO_3)_xF_{0.4x}F_2$$

TABLE 10.4 Mineral Composition of the End-Members of the Fluorapatite–Francolite Series

Constituent	*Fluorapatite*	*Francolite*
% CaO	55.6	55.1
% P_2O_5	42.2	34.0
% CO_2	0	6.3
% F	3.77	5.04
% Na_2O	0	1.4
% MgO	0	0.7

Source: McClellan.[7]

TABLE 10.5 Typical Phosphate Rock Analysis, % Dry Basis[10]

	Central Florida 68 BPL	*Morocco K-20, 70–71 BPL*
H_2O	(1.3)	(1.3)
P_2O_5	31.2	32.0
SO_3	1.1	1.88
F	3.7	3.9
SiO_3	9.0	2.1
CO_2	3.8	6.0
Cl	0.01	0.02
CaO	46.7	51.2
Al_2O_3	1.1	0.3
Fe_2O_3	1.5	0.2
MgO	0.5	0.5
Na_2O	0.5	0.9
K_2O	0.11	0.07
C(org.)	0.28	0.22
Cd	5	18
U_3O_8	185	134

As the carbonate content of the ore increases, the substitution of carbonate in the francolite tends to increase. It is common for trace quantities of heavy metals, toxic elements such as cadmium, and radionuclides such as uranium to exist in phosphate rock owing to substitution in the crystal lattice (see Table 10.5). Usually the quantities of these elements are insufficient to be of concern.

Mining

Phosphate ores are extracted by underground methods from deep deposits and by surface mining methods from shallow deposits—the former being more costly and thus less common than the latter.

Tunisia has seven underground mines; six use room and pillar mining techniques, while the seventh extracts the ore by longwall mining. Room and pillar mining also is utilized at Warm Springs in Montana, Khouribga in Morocco, and San Juan de la Costa, Baja California. Shrinkage stopping is the mining method at Kola, Russia.

Many shallow phosphate deposits have unconsolidated ore and are covered by unconsolidated overburden. Large electric walking draglines are ideally suited for such deposits, as evidenced by their use at large-capacity phosphate mines in the United States, Morocco, Jordan, Senegal, and Togo. Some sedimentary deposits have overburden and ore ranging from partially to fully consolidated. For these deposits, ripping or drilling and blasting are required to fragment the overburden and ore so that they can be excavated. In addition to draglines, power shovels, backhoes, and wheeled loaders commonly are used for excavation.

Bucketwheel excavators and cutter head dredges have not yet found wide acceptance in phosphate mining. The Lee Creek phosphate mine in North Carolina has used both cutter head dredges and bucketwheel excavators to remove the upper portion of the overburden, with the remaining overburden and ore excavated by dragline. In Togo, a combination of bucketwheel excavator and dragline is used for stripping overburden and mining ore. The

Wingate Creek phosphate mine in central Florida uses two cutter head dredges; one for stripping overburden and the second for mining ore and pumping the slurried ore to the beneficiation plant.

Transportation of phosphate ore from the mine to the beneficiation plant is an important component of production. Typical modes of transportation are slurry pipeline, truck, railroad, and belt conveyor. Slurry pipelines 18 to 22 inches in diameter operating at less than 100 psi are used exclusively in central Florida, North Florida, and North Carolina. Conventional centrifugal slurry pumps are spaced at approximately 1000-yard intervals to extend the pipelines up to 10 miles or more. Phosphate mines in Tennessee use trucks to haul ore several miles from scattered mine areas to a centralized beneficiation plant. In Iraq, phosphate ore is shipped from the Akashat mine 150 km by railroad to the plant at Al Qaim. Phosphate ore from the Bou Craa mine in Morocco (formerly the Spanish Sahara) is transported 30 km by belt conveyor to the plant at La Youn.

Beneficiation

A vast majority of phosphate ores yield commercial phosphate rock only after the removal of impurities by beneficiation. Also known as mineral dressing and ore processing, beneficiation may involve a variety of operations such as size reduction, size separation, mineral separation, and thermal processing.

The usual first beneficiation operation is size reduction by crushing, grinding, or disaggregation from washing and scrubbing. This step liberates the mineral species so that they later can be separated. Size separation usually follows size reduction. Frequently carbonate and silicate gangue is more indurated than the phosphate mineral and can be rejected as oversize by wet or dry screening. Argillaceous material and some microcrystalline carbonates are smaller than the phosphate mineral grains and can be rejected as fines by either wet or dry classification. A few phosphate ores contain soluble chlorides, and some ores are beneficiated with seawater. The phosphate rock recovered from these ores must be washed or rinsed with fresh water to remove chlorides.

When the gangue minerals have the same particle size as the phosphate grains, process techniques such as froth flotation, magnetic separation, and heavy media separation are required to reject the impurities. Froth flotation is the proven method for rejecting silica and silicate gangue from sedimentary phosphate ore. A two-stage flotation process consisting of anionic flotation to recover a low-grade phosphate concentrate with fatty acid collectors and fuel oil, followed by cationic flotation with amine collectors to reject quartz and obtain a high-grade phosphate concentrate, is used in Florida and North Carolina. A typical flow diagram for beneficiating Florida phosphate ore is given in Fig. 10.1. Several Florida phosphate flotation plants installed column flotation cells during the period 1978 to 1984. These cells have met with varying degrees of success, but remain strong contenders for plant modifications or expansions.

Igneous phosphate ores having carbonate gangue also are successfully treated by froth flotation at Siilinjarvi, Jacupiranga, and Phalaborwa. Froth flotation has not yet been widely adopted for sedimentary phosphate ores containing carbonate gangue. Commercial plants where flotation systems have been installed to separate carbonates from phosphates are Kara Tau in Russia, Wangji in China, and Conda in Idaho. Houot gave a good review of phosphate flotation technology.[8]

Magnetite, an accessory mineral in some of the igneous ore deposits, is easily removed from phosphate rock by low-intensity magnetic separators. In Brazil, magnetic separation is required at Arafertil, Camig, and Fosfago. Heavy media separation has been proposed as a method of rejecting low-density carbonate gangue from phosphate pebble recovered from the southern extension of the central Florida district.[9]

Thermal drying to reduce the moisture to about 3 percent, or less, frequently is necessary to prepare phosphate rock for export sales. Rotary dryers, fluid bed dryers, and, to a lesser

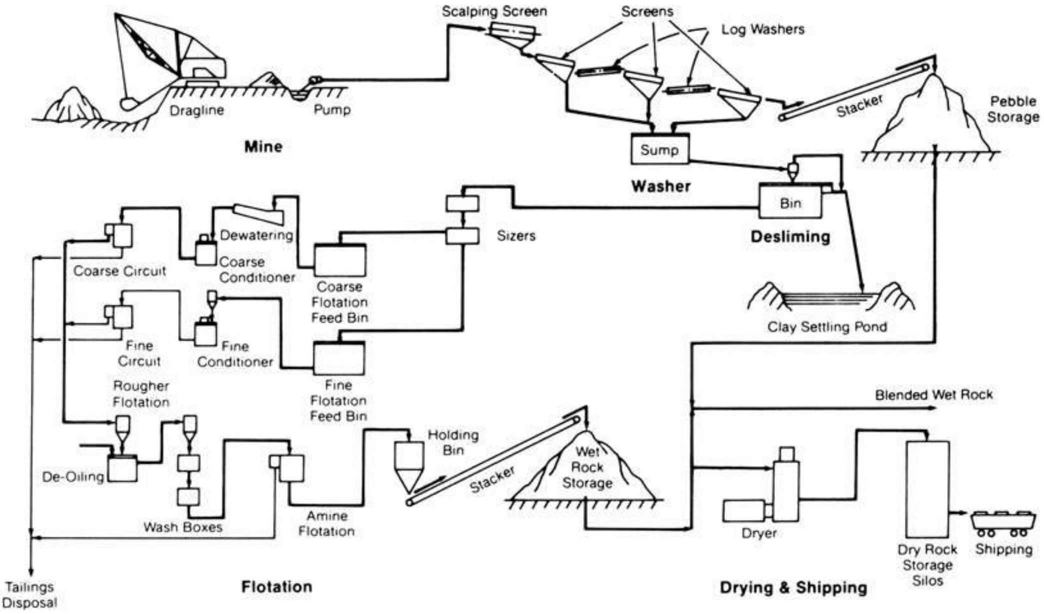

Fig. 10.1. Typical flow diagram, Florida phosphate rock concentration. (*Courtesy Jacobs Engineering Group, Inc.*)

extent, flash dryers are used for this purpose. Organic matter may be removed from phosphate rock by calcining at temperatures of about 1300 to 1500°F. Organic removal by calcination is practiced at Lee Creek, North Carolina and at Youssoufia, Morocco. Calcination of phosphate rock at about 1800°F decomposes calcium and magnesium carbonates and drives off carbon dioxide. The calcium and magnesium oxides may be removed by quenching and slaking of the calcine followed by size separation to reject the hydroxides. The removal of carbonates by calcination with subsequent quenching and slaking is accomplished at Al Qaim, Iraq and Djebel Onk, Algeria. Phosphate rock may be defluorinated by calcining at about 2400°F.

ELEMENTAL PHOSPHORUS AND PHOSPHORIC ACID

Phosphate rock is converted into usable chemicals by two methods. In one, the rock is charged to an electric furnace with silica and coke to produce elemental phosphorus. The phosphorus then is converted into phosphoric acid and other compounds. In the other, the phosphate rock is reacted with sulfuric acid in a medium of phosphoric acid and gypsum crystals to form dilute, impure phosphoric acid. The acid is separated and used to make fertilizers. This is known as the wet process method.

The furnace or thermal process is shown in Fig. 10.2. The approximate reaction is:

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow 6CaSiO_3 + P_4 + 10CO$$

The charge or furnace burden must have certain physical and chemical properties. The particles should be dry, durable masses in the 1/4 to 3/4 inch size range that will not break up or segregate in the furnace. Phosphatic shale is siliceous and is a suitable material, but usually it must be sintered or briquetted before use. Quartz gravel is a good source of supplementary silica, and metallurgical coke is the form of carbon used.

The energy required is about 12,000 kWh per ton of phosphorus produced. The most modern furnaces are quite large, with ratings in the range of 60,000 kVA.

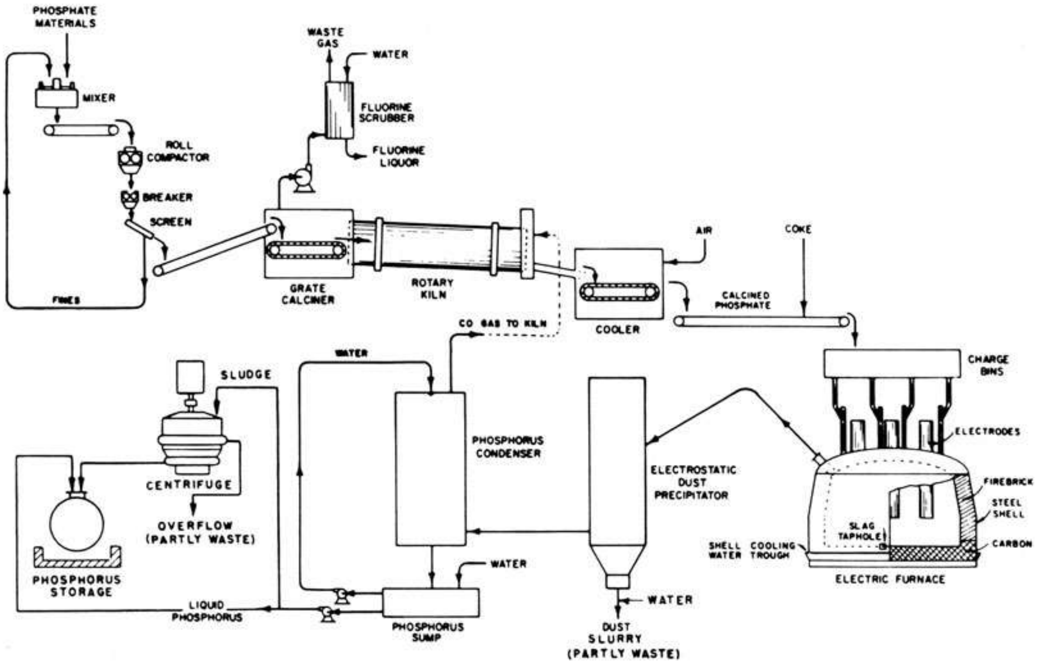

Fig. 10.2. Electric furnace process for production of elemental phosphorus. (*Courtesy Tennessee Valley Authority.*)

The furnace is a water-cooled circular steel shell lined with refractories. The bottom or hearth is made of thick blocks of carbon. Three large carbon electrodes are mounted through the roof of the furnace and are slowly lowered into the charge as the bottom ends are consumed. A three-phase electrical system is used, and the electrodes must be precisely positioned to balance the phases and maintain a high power factor.

The phosphorus leaves the furnace as a vapor. After passing through an electrostatic precipitator, it is condensed by direct contact with water. Then the liquid phosphorus is filtered or centrifuged to remove dust particles and is shipped in tank cars. CO discharged from the furnace is used as fuel in the feed preparation operations or is burned in a flare.

In 1990, there were about eight plants in operation, some with multiple furnaces. No new electric furnaces have been built in the United States since 1968; moreover, many units have been closed down in recent years. New emission standards, the high capital and operating costs, and competitive wet acid purification technology make it unlikely that new furnaces will be built in the near future. See the discussion of purified phosphoric acid later in this chapter.

Furnace Phosphoric Acid

Phosphoric acid of high purity is made by burning phosphorus with air and hydrating the resulting P_2O_5 with water, according to the reaction:

$$P_4 + 5O_2 + 6H_2O \rightarrow 4H_3PO_4$$

Equipment for this operation has been constructed from both carbon blocks and stainless steel. The water quantity is controlled to give product acid corresponding to 75 or 85 percent H_3PO_4. If food-grade acid is specified, some additional chemical treatment of the acid may be required. For example, slight traces of arsenic are removed by treatment with H_2S.

If even less water is used for hydration, a product known as polyphosphoric acid results. Ordinary phosphoric acid is a solution of the monomer, H_3PO_4, in water, and is called orthophosphoric acid. If a molecule of water is removed between two orthophosphoric molecules, the dimer, pyrophosphoric acid, $H_4P_2O_7$, is formed. Similarly, the trimer and higher polymers can be made. Superphosphoric acid is a mixture of orthophosphoric acid and polyphosphoric acid. Thermal phosphoric acid has become too expensive for use in the fertilizer industry.

Industrial Phosphates

A portion of the phosphorus currently produced in the United States is consumed to make compounds such as phosphorus pentoxide, phosphoric trichloride, and phosphorus pentasulfide, which find use for the preparation of drying agents, plasticizers, oil additives, fire retardants, and insecticides. Most of the phosphorus, however, is converted into orthophosphoric acid, some of which is used in soft drinks, candy, baked goods, and various other food products. Furnace-grade acid finds wide use in metal-treating methods.

The cheapest and most important salts of phosphoric acid are the sodium salts, made by reacting the acid with sodium carbonate or sodium hydroxide. Sodium phosphates may be classified in a general way as (1) orthophosphates, (2) crystalline condensed phosphates, and (3) glassy condensed phosphates.

Three sodium orthophosphates can be prepared, depending on whether one, two, or three hydrogen atoms are replaced by sodium. Monosodium phosphate is formed in the following reaction:

$$2H_3PO_4 + Na_2CO_3 \rightarrow 2NaH_2PO_4 + H_2O + CO_2$$

Sodium carbonate also is used to make disodium phosphate, Na_2HPO_4, but sodium hydroxide must be used to replace the third hydrogen in trisodium phosphate, Na_3PO_4. The orthophosphates have a wide range of uses in industry. Sodium phosphates are made abroad in large quantities from wet process phosphoric acid by stepwise neutralization. Impurities must be purged from the solution and the salts purified by recrystallization.

TABLE 10.6 Estimated World Consumption of STPP in Soaps, Detergents, and Cleaners 1974–87 (Thousand Tonnes Product)

	1974	*1980*	*1985*	*1987*
West Europe	1000	960	930	725
East Europe	270	340	380	395
North America	825	680	580	555
Africa	50	95	120	130
Latin America	210	275	320	350
Asia and Oceania	210	370	425	460
World	2565	2720	2755	2615

Courtesy British Sulphur Corporation.

Condensed phosphates are made by eliminating water from orthophosphates. The most important compound is sodium tripolyphosphate (STPP), made according to the following reaction:

$$2Na_2HPO_4 + NaH_2PO_4 \xrightarrow{-H_2O} Na_5P_3O_{10}$$

The most important use of sodium tripolyphosphate is as a builder of detergents. However, legislative restrictions on the use of phosphorus compounds in household detergents have caused a worldwide flattening of consumption. See Table 10.6.

Glassy condensed phosphates are represented by sodium hexametaphosphate, in which the O:P ratio is 3:1. There can be considerable variation in the Na_2O to P_2O_5 ratio.

The principal use of the condensed phosphates is to sequester metallic ions in water. They form water-soluble complexes with the metals and prevent metallic compounds from precipitating to cause discoloration, scale, and sludges.

Wet Process Phosphoric Acid

In the wet process, phosphate rock is reacted in a slurry of phosphoric acid and gypsum containing a controlled quantity of sulfuric acid. The simplified reaction is as follows:

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow CaSO_4 + 2H_3PO_4$$

Until 1969, virtually all wet process acid was made at strengths of 26 to 32 percent

P_2O_5, separating the calcium sulfate as gypsum containing two molecules of water.

Since 1969, a substantial number of commercial hemihydrate process plants have been built in various modes. In the hemihydrate process, reaction conditions are higher in temperature and phosphoric acid strength so that the stable solid phase is calcium sulfate with one half molecule of water.

The hemihydrate process may be a single-stage process in which the hemihydrate solids are the waste product, or the process can have a second step in which the hemihydrate is recrystallized to gypsum.

In the hemihydrate process, acid strengths of 38 percent P_2O_5 to about 44 percent P_2O_5 normally are produced although strengths up to 50 percent can be produced under somewhat more difficult circumstances requiring more filter area.

The neutralization reaction of the above equation is conducted in one or more strongly agitated reaction vessels, whether in a gypsum or in a hemihydrate mode. The system is highly exothermic and the slurry is cooled. Slurry temperatures are maintained at 80 to 85°C for dihydrate processing, 95 to 100°C for hemihydrate.

During the reaction of phosphate rock with sulfuric acid, fluorine is evolved and must be scrubbed from the vent gas.

Table 10.7 shows production of phosphoric acid in the recent past.

Dihydrate Process

The conventional dihydrate process, as operated over the last 60 years, was first demonstrated by the Dorr Company in the Cominco plant at Trail, British Columbia in 1931. The principles discovered at that time for making an acid strength of up to 32 percent P_2O_5 and a highly filterable gypsum crystal are still used. The salient features of the process included maintaining H_2SO_4 content in the digestion acid of about 2.0 to 3.0 percent. Reaction slurry was recycled at a rate of 10 to 15 to one relative to the volume of product slurry sent to the filter. The relatively higher recirculation of seed gypsum than had previously been practiced, together with control of the free sulfate, resulted in product acid well above the previous 22 percent P_2O_5 possible with batch and countercurrent decantation systems.

If the sulfate in the solution is allowed to exceed certain limits, depending on rock reactivity and particle size, the rock becomes coated with gypsum, and the reaction becomes uncontrollable. If the sulfate level is too low, the precipitated gypsum filters poorly and contains excessive quantitites of crystallized (solid solution) P_2O_5, leading to excessive P_2O_5 losses.

Over the years, the process has evolved to employ increased slurry recirculation and different reactor configurations. In addition, several different filter designs are available.

TABLE 10.7 Annual Production of Phosphoric Acid, TPY P_2O_5

	1980	*1985*	*1988*
West Europe	3,669,700	3,442,863	3,322,735
East Europe	3,466,000	4,850,800	6,305,597
Africa	2,043,700	2,762,629	4,661,621
N. Amercia	10,016,800	9,600,200	10,411,968
Mexico	260,400	310,000	474,000
S. America	303,100	695,375	762,806
Middle East	157,000	712,005	813,354
China	9,000	31,500	50,000
South and East Asia	1,414,300	1,637,542	1,637,380
Australia	180,000	133,438	107,650
	21,520,000	24,176,352	28,547,111

Courtesy British Sulphur Corporation.

TABLE 10.8 Phosphoric Acid Plants, Worldwide Dihydrate Process, 1990

Process	*Number of Lines 450 MTPD or Larger*
Prayon	25–30
Rhone Poulenc	15–20
Nissan H	9
Jacobs/Dorr-Oliver	8
Badger-Isothermal	4

The principal processes currently in use are shown in Table 10.8. Over 90 percent of the world's phosphoric acid is produced by the dihydrate method, but there is likely to be increased production by the hemihydrate method because of advantages in some situations. The dihydrate processes listed have been modified over the years so that many slightly different configurations of the same process may exist.

The unique feature of each process is the reactor system configuration. The reactor or reactors normally provide from 3 to 6 hours' detention for the gypsum slurry. This is about 1.0 to 2.0 m^3 of reactor volume per ton of P_2O_5/day, meaning relatively large vessels totaling 1500 m^3 to over 2000 m^3 in size for large plants. The individual reactor systems are described briefly below.

The objective of the reaction system is to produce a highly filterable gypsum crystal that washes well, and that also contains a minimum amount of insoluble P_2O_5. The filterability of the gypsum slurry depends on the reactor configuration and on the rock source. Highly filterable gypsum slurries are produced from Florida, Togo, and Senegal phosphates. These rocks may provide more than double the P_2O_5 from a given filter when compared to gypsum produced from other sources. However, because phosphate rock is costly to transport, the use of local, less treatable phosphates can be quite economical. Table 10.9 lists the approximate filtration design rates for these groups of commercially available phosphate rock.

TABLE 10.9 Filtration Design Rates for Phosphoric Acid Produced from Various Rock Sources

Rock Source	*Tons P_2O_5 Produced/Sq. Meter Active Area*
Togo Florida Senegal	7.5 to 9.0
Morocco Khouribga Western U.S.A. Kola (USSR) N. Carolina	4.5 to 7.0
Morocco Safi Algeria Tunisia	3.5 to 5.0

Advantages of the dihydrate process versus the various, newer hemihydrate configurations are as follows:

1. The water balance permits the use of wet rock slurry feeds. This eliminates the cost to dry the rock and a dust nuisance. This is the principal benefit that has deterred most Florida producers from using the hemi routes.
2. Dihydrate gypsum, in the case of most phosphates, filters at relatively higher P_2O_5 throughput rates than hemihydrate, comparing dihydrate filter performance at 28 percent P_2O_5 and hemihydrate at 42 percent P_2O_5.
3. Dihydrate plants are proven at huge outputs, in excess of 1500 MTPD P_2O_5, thus offering economies of scale.
4. A vast amount of operating data and experience exists on a wide variety of phosphate rocks for the dihydrate mode.
5. Capital costs for the dihydrate system can be less than for the two-stage hemi processes even when evaporation and rock grinding are considered, because of the larger reaction vessels and two stages of filtration in the hemi process.
6. The yield across the filter for the dihydrate process, generally about 96 percent of the P_2O_5 fed, is about 3 to 4 percent above the single-stage hemi processes.
7. Dihydrate process maintenance costs are substantially less than those for hemi processes due to less severe process

conditions. The on-stream factor is also higher for the average dihydrate facility.

Major Dihydrate Processes

Prayon Process. The Prayon process has evolved from the cascade system first used by the Dorr Company in the 1930s. Instead of round, steel vessels with rubber and brick lining, in the early 1960s Prayon developed a multicompartmented reinforced concrete vessel, rectangular in shape, lined with a membrane and carbon brick. The construction has proved to be exceedingly durable. A similar concrete construction has been used by Dorr/Jacobs and by Rhone Poulenc. A flowsheet for a current configuration Prayon process digestion system is shown in Fig. 10.3. The Prayon process uses vacuum cooling, a vacuum chamber through which reaction slurry is circulated to maintain a reactor temperature of 80 to 85°C. There are numerous installations of large Prayon plants in the United States although the center of process technology is Belgium.

Rhone Poulenc Process. Most of Rhone Poulenc's existing plants are of a single stirred vessel configuration. However, a two-vessel arrangement, the Diplo system, has been offered and retrofitted into a few of the previous single reactor plants.

The original Rhone Poulenc Single Tank system is an exceedingly simple plant. It is air-cooled by passing a flow of air over slurry splashers, and does not have a filter feed tank, the slurry simply overflowing the reactor to a vertical pipe on top of the filter feed pump.

The newer Diplo system is said to offer a better yield, higher P_2O_5 product acid strength, and a more filterable gypsum by providing a better concentration gradient for gypsum growth.

Most Rhone Poulenc installations are located in France and North Africa.

Nissan H Process. In this process, the rock attack is done under conditions favoring the formation of an unstable hemihydrate. The slurry then is cooled and seeded to recrystallize to gypsum at high sulfate levels, producing a gypsum low in co-precipitated P_2O_5. Yields in the 97 to 98 percent range are reported. The process, in operation since the 1960s, has been favored in many instances where the phosphogypsum can be used for wallboard

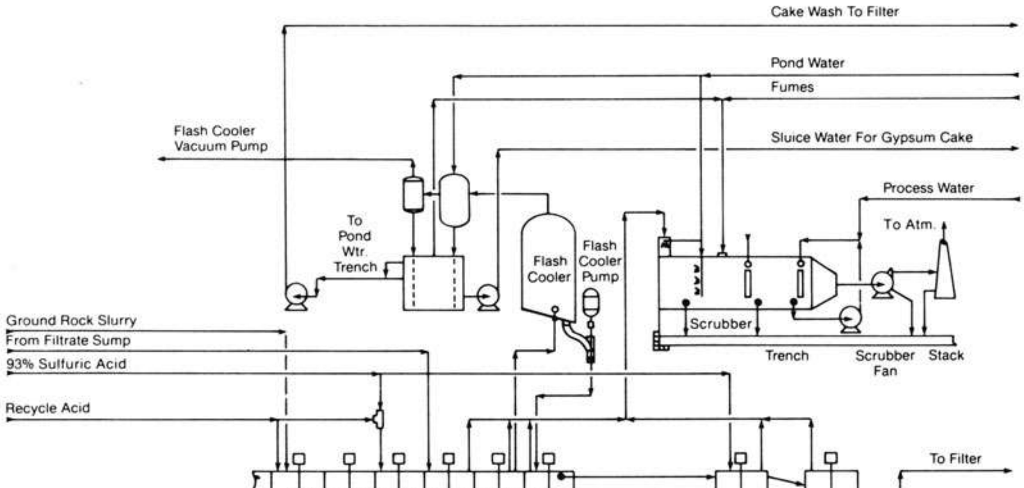

Fig. 10.3. Flow diagram of attack or reaction section of a wet process phosphoric acid plant. (*Prayon process courtesy Davy McKee Corp.*)

or other building materials. Major installations are located in Holland and Morocco.

Jacobs/Dorr-Oliver Process. Jacobs Engineering acquired the Dorrco process technology in 1974 and has carried on the annular reactor design begun by Dorr in the early 1960s. The reactor configuration is a compromise between a multicompartment system, as used in the earlier Dorr-Oliver cascade system and in the compartmented Prayon reactors, and the true single stirred vessel used by Rhone-Poulenc and Badger.

In the Jacobs system, the annulus of a large concrete tank is fitted with a series of agitators. There is baffling, but there are no walls between the agitators. High slurry recirculation rates are achieved by a combination of back-mixing and slurry pumping. Vacuum cooling normally is used.

Jacobs has installations mainly in the United States and India. One of the world's largest phosphoric acid reactors is shown in Fig. 10.4.[15] The process is offered in several configurations, high throughput, high yield, or coarse rock modes, and the reactor can be adapted to a hemihydrate mode making 42 percent P_2O_5 acid.

Badger—Isothermal Process. The Badger reactor is a draft tube mixer within a vacuum vessel. All reactants are added to this vessel, which is under vacuum, and cooling and rock digestion are achieved simultaneously. There are several relatively recent U.S. installations. While the system has low energy (power) consumption, the method is unproved on the more difficult-to-treat, high-organic, high-CO_2 phosphates.

Hemihydrate Processes for Phosphoric Acid

Methods for making higher-strength P_2O_5 acid have been known for a long time. The basic hemihydrate–dihydrate process shown in the Norsk Hydro flowsheet, Fig. 10.5,[14] is similar to the initial process attempted in 1931 at the Cominco plant at Trail, BC. The hemihydrate–dihydrate process failed there,

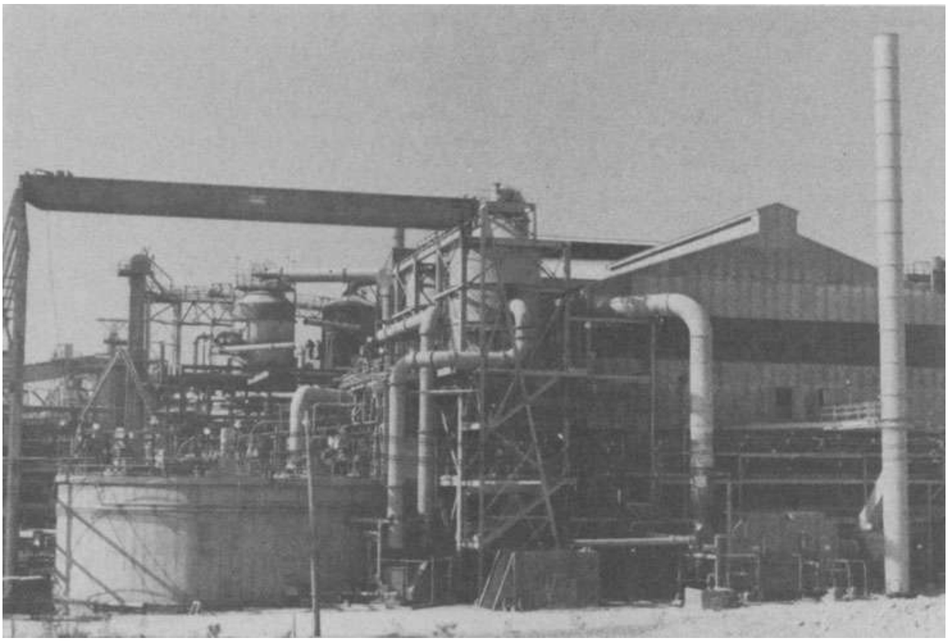

Fig. 10.4. Gardinier phosphoric acid plant, 1500 TPD, Jacobs process. (*Courtesy Jacobs Engineering Group, Inc.*)

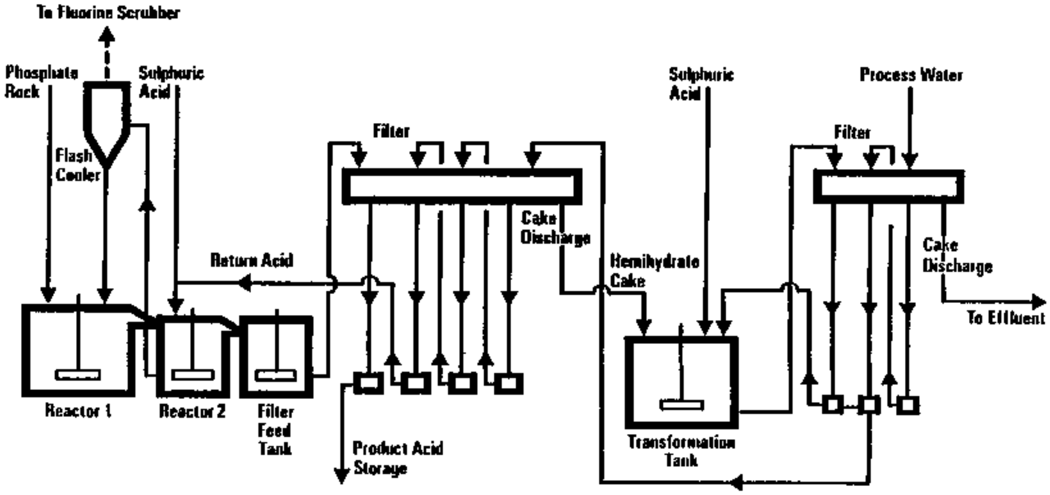

Fig. 10.5. Hemi–dihydrate process. (*Courtesy Norsk-Hydro, Ltd.*)

mostly because of inadequate filters, but the Dorr dihydrate process did emerge successfully (Table 10.10).

The first large hemi plant of more modern times was the Kemira hemi–dihydrate two-stage plant at Siilinjarvi, Finland, which started operation in 1969, using the Dorr HYS process. After about four years of operation at 250 MTPD P_2O_5, its rated design, the plant was expanded but operated in the dihydrate mode. In the hemihydrate mode, filtration and recrystallization problems had plagued the plant, which operated on Kola rock.

Hemihydrate processes are available for new facilities and also for the retrofitting of existing dihydrate plants. Several conversions to higher-strength acid have been made, where the steam saved in evaporation can replace fuel. Plants that make superphosphoric acid, or where sulfuric acid plant steam is not available, are likely targets for conversion.

The single-stage hemi process is smilar to the front end of the hemi–dihydrate process. However, in this case, the hemi is sent to waste without deliberate recrystallization after washing. Yields for the single-stage process are generally below the yields of the dihydrate process, whereas yields for the two-stage hemi–dihydrate process are very high.

TABLE 10.10 Range of P_2O_5 Yield through Filtration as % of P_2O_5 Fed

Phosphoric Acid Process	
Hemi–dihydrate	98–99
Conventional dihydrate	95–97
Single-stage hemi	91–94

Table 10.11 lists the major hemihydrate plants operating in 1990.

In the family of unconventional phosphoric acid processes is the Prayon-Central Glass process, which is a dihydrate–hemihydrate process in which the gypsum initially precipitated is recrystallized to hemihydrate by adding the bulk of the H_2SO_4 required for the digestion of the rock. This hemi, then, is in the most suitable phosphogypsum form (low impurities and low water content) for use as feed to the cement–sulfuric acid (Krupp-OSW) process and for gypsum plaster. Because of the capital costs for this combined cement-sulfuric acid process and operating difficulties, there have been only a few installations.

Advantages for the hemihydrate processes compared to the conventional dihydrate processes are:

1. Energy savings due to higher product acid strength.
2. Higher P_2O_5 recovery and lower H_2SO_4 consumption for the two-stage process.

TABLE 10.11 Major Hemihydrate Installations (1990)

Owner	*Location*	*Year in Oper.*	*Process*	*Product Acid Strength*	*Rock*	*Capacity MPTD P_2O_5*
Windmill	Holland	1970	N-H(H)	42	Togo/FL	700
Windmill	Holland	1985	N-H(C)(H)	42	Togo/FL	250
Albright & Wilson	UK	1978	N-H(NDH)	42	Mor.	600
SUPRA	Sweden	1988	N-H(C)(NDH)	42	Mor./FL	360
Chinhae	Korea	1990	N-H(C)(NDH)	45	FL	250
Belledune	Canada	1986	N-H(C)(H)	39	FL	500
Arcadian	(USA)	1980	N-H(C)(H)	40	Bou Cra	600
Occidental	Florida	1974	Oxy(H)	38	FL	300
Occidental	Florida	1980	Oxy(H)	38	FL	1400
Gresik	Indonesia	1984	Nissan C(HDH)	42	Jordan	550
Nam Hae	Korea	1988	Nissan C(C)(HDH)	42	FL/Jordan	1100
Yong Nam	Korea	1989	Nissan C(C)(HDH)	42	—	400
Copebras	Brazil	1987	Nissan C(C)(HDH)	—	Brazil	450
Coop Chem.	Japan	1987	Nissan C(HDH)	—	—	230
Zhanjang	China	1993	Oxy(H)	40	China	110
Yunnan	China	1992	N-H(HDH)	45	China	210

N-H = Norsk Hydro
(C) = Conversion
(H) = Hemihydrate, single stage
(HDH) = Hemihydrate–dihydrate

3. Lower capital cost for the single stage process, and possibly lower capital cost for the two-stage process where a highly filterable hemi can be produced.
4. Hemi–dihydrate recrystallized gypsum that is relatively pure, 0.2 to 0.4 percent total P_2O_5. This makes it more suitable for a cement additive or in wallboard, etc.
5. Less rock grinding required.

Energy Savings in Phosphoric Acid. As we have just noted, the hemi processes provide energy savings due to the reduced steam consumption for evaporation. This steam, even though low-pressure, 2.0 to 3.0 kg/cm^2, has significant value for the cogeneration of power. In some cases, the hemi process also saves rock grinding power. On the other hand, dihydrate processes have the ability to use wet rock slurries and to absorb, in the process, more contaminated water resulting from rainfall collected off the waste gypsum stacks. The latter advantage may be important to maintaining a zero water balance and eliminating costly effluent treatment. The use of wet grinding and slurry feeding eliminates the fuel and electricity consumed in drying the rock.

Another energy-saving option is the use of hot water for evaporation, instead of steam. This is an alternate, energy-wise, to the higher-strength hemi processes. Hot water normally is available from the heat of absorption of the sulfuric acid plant. Strengths of 40 to 42 percent P_2O_5 can readily be achieved. A few commercial installations exist in Europe. A more expensive alternative is offered in the HRS sulfuric acid process by Monsanto, which converts the absorption heat to low-pressure steam.

Unit Operations

In addition to the reaction step discussed above, there are a number of other unit operations used in producing wet process phosphoric acid.

Calcination. Phosphate rock normally is used as a dry rock or in slurry form. However, in some cases, particularly where the raw phosphate is high in carbonaceous matter or it is desirable to have a clean acid, the rock is calcined. Also, in a few cases, the phosphate rock is calcined, the product slaked, and free lime separated as a beneficiation step. Calcination is energy-intensive and produces a less reactive rock and in some cases a less filterable gypsum. Therefore, the use of calcination is diminishing, and in some cases has been replaced by a wet oxidation step to produce green acid. In separating calcium carbonate, flotation, where it is successful, is favored over calcination because of its lower cost.

Rock Grinding. Until 1973, most phosphate was ground dry in roller or ball mills. In that year, Agrico, at South Pierce, Florida, converted one of its dry mills to wet slurry grinding and proved that the plant water balance could manage the rock at a 65 to 68 percent solids slurry. Since that time, most U.S. installations have converted to wet grinding.

Relatively fine phosphates, such as Kola, North Florida, Senegal, and Togo, can be processed unground as dry concentrates or as dewatered beneficiated product with 12 to 15 percent moisture. In the hemi processes, somewhat coarser feed may be tolerated. For dihydrate, it is desirable to feed from $1\frac{1}{2}$ percent + 35 mesh (Tyler) to about 8 percent + 35.

Filtration. The separation of phosphogypsum or hemihydrate from its mother liquor has always been a difficult operation. The process has been subject to the formation of calcium sulfate, sodium fluosilicate, and other types of scale that clog the cloth and necessitate periodic filter washing. Filter cloth wear is severe, requiring cloth changes as often, in some cases, as two or three weeks apart.

Three types of filters have predominated over the past 20 years, the most widely used being the Bird-Prayon tilting pan filter shown in Fig. 10.6. The Ucego, a table filter with a peripheral side wall belt that leaves the filter to permit cake sluicing, has been popular worldwide since the late 1960s.

In the late 1970s and the 1980s, belt filters became more readily accepted. The belt filter

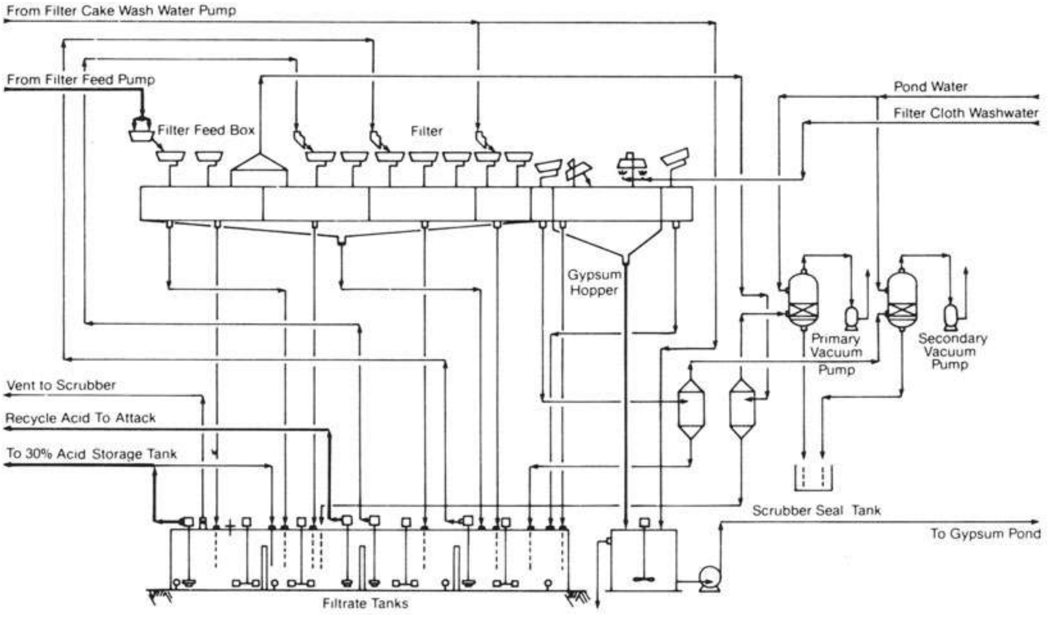

Fig. 10.6. Flow diagram of filtration section of a wet process phosphoric acid plant. (*Prayon process courtesy Davy McKee Corp.*)

has been used on phosphoric acid since the 1940s and 1950s, but in the past it was plagued by mechanical problems and materials failures. The filter, at least as offered by two vendors, has been improved substantially, but the units tend to have difficulties in containing splash and drips, and tend to dilute the product acid by water introduced as slide plate lubricant. Nevertheless, belt filters are in successful operation in many plants, particularly as supplemental filters to increase plant output.

The filtration step is a countercurrent washing using two or three washes. Usually the final wash is a contaminated pond water or a cooling loop water, thus providing for, in most cases, a zero effluent plant.

Sizes of the Bird-Prayon and Ucego filter can be very large, over 200 square meters of surface area, allowing rates up to 1600 to 2000 MTPD P_2O_5. Belt filters tend to be 100 square meters or less because of their length; however, they are relatively inexpensive because little alloy steel is used, and normally two belt filters would be less in first cost than one large tilting pan or table filter.

Evaporation. Most phosphoric acid is used at a strength of about 38 to 42 percent P_2O_5 for DAP and slurry process TSP. However, many fertilizer plants produce MGA, merchant grade acid, which, at 52 to 54 percent P_2O_5 is a world-traded commodity.

Evaporation normally is done under vacuum using forced circulation via an axial flow pump. Vacuum can be accomplished by steam ejectors, vacuum pumps, or with condenser water using an entraining condenser downleg. Heat exchangers normally have been shell and tube, with graphite tubes in the United States. French practice has been to use carbon block exchangers. Some newer shell and tube exchangers have been Sanicro 28 or Hastellov G3 or G30. A flowsheet is shown in Fig. 10.7.

Typical analyses of wet process phosphoric acid made from North Carolina calcined concentrate are shown in Table 10.12.

Superphosphoric Acid

Solution fertilizers have become very popular in the United States. The principal source of

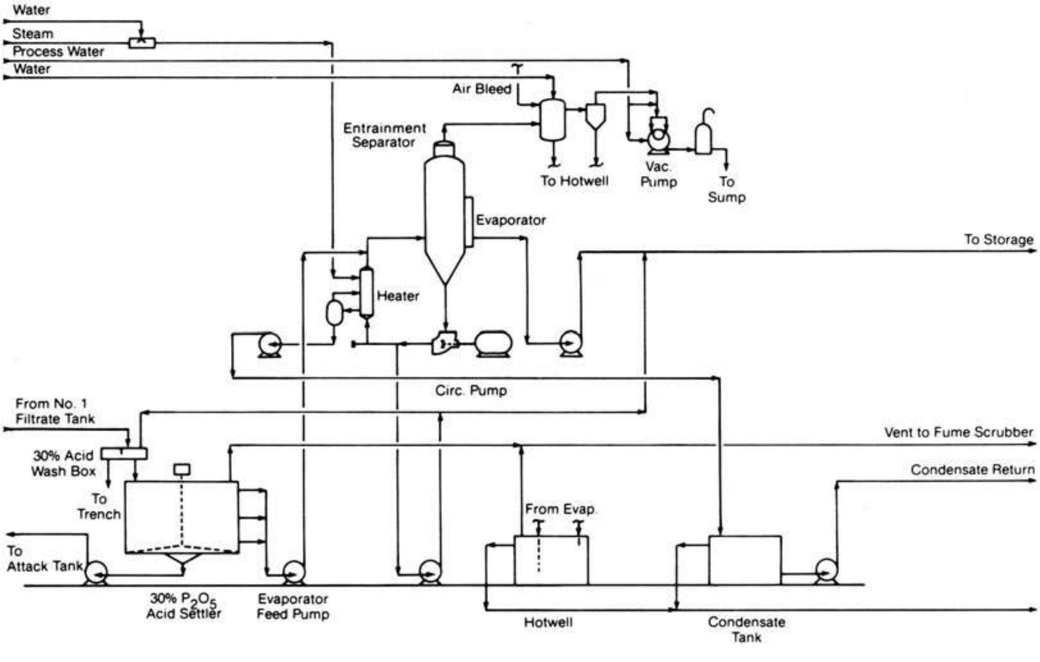

Fig. 10.7. Flow diagram of evaporation section of a wet process phosphoric acid plant. (*Courtesy Davy McKee Corp.*)

TABLE 10.12 Typical Analyses, Wet Process Phosphoric Acid Made from North Carolina Calcined Concentrate

	Weight Percentage	
Component	*Concentrated Acid*	*Superphosphoric Acid*
P_2O_5, total	53.0	69.5*
Solids	0.2	
Free water	22.0	
Fe_2O_3	1.5	2.0
Al_2O_3	0.7	1.0
F	0.6	0.3
MgO	1.1	1.3
SO_4	2.7	3.7
CaO	0.1	0.2
Sp.g, at 75°F	1.68	2.0

*About 36% of the total P_2O_5 is present as polyphosphates.
Courtesy Texasgulf, Inc.

P_2O_5 for these fertilizers is wet process superphosphoric acid containing about 70 percent P_2O_5, where 35 percent or more of the P_2O_5 is present in the polyphosphoric form. When this acid is ammoniated and diluted, the iron, aluminium, and magnesium compounds naturally present remain in solution, sequestered by the polyphosphates. Clear solutions result, and there is no clogging of the sprays used for applying the fertilizer. When ordinary phosphoric acid is neutralized with ammonia, heavy sludges form, and the resulting solution is difficult to store and apply.

Superphosphoric acid is made by the additional concentration of clarified phosphoric acid in vacuum evaporators of the falling-film or forced-circulation type. High-pressure steam or Dowtherm vapor is used for heating. Corrosion is a problem, so the equipment is made from high alloy stainless steels. The acid is shipped in special insulated tank cars to the solution fertilizer plants, which are located close to the farm areas they serve. Organic matter contributes to sludge problems in making solution fertilizers; therefore, calcination of the phosphate rock used for making the acid is advantageous. Organics also may be removed by oxidation with nitric acid or ammonium nitrate,[11] and several SPA producers have gone to such treatment to improve their product quality.

Additional details of the manufacture of superphosphoric acid, and of the triple superphosphate, are to be found in Chapter 11.

WET PROCESS ACID BY-PRODUCTS

Phosphogypsum

About 5 tons of gypsum on a dry basis are made for each ton of P_2O_5 produced in a wet process phosphoric plant. This material usually is disposed of as waste, by impounding it in old mine pits, stacking it in huge piles, or, in some cases, discharging it into very large rivers or river mouths. Phosphogypsum is sold to farmers in California for control of salt buildup in irrigated soils; a small quantity is sold to peanut farmers in the southeastern United States. However, there has been concern about the utilization of gypsum because of its low-level radioactivity in some instances. In addition, it contains fluosilicates and P_2O_5 so that utilization in building products, such as wallboard and blocks, has been limited to Europe and Japan, where natural gypsum is more costly than manufactured gypsum. In these cases, the phosphogypsum generally comes from a hemihydrate process producing a slightly purer form than natural gypsum.

Regeneration of SO_2 from gypsum has been done via the Krupp-OSW process, the most important facility formerly being the Fedmis plant in South Africa, which made about 300 TPD H_2SO_4 and a similar amount of cement. The remote location of this facility, where sulfur and cement were expensive, apparently was not enough to sustain operation, and the plant shut down in the late 1980s.

An SO_2 regeneration process, using grate calcination, under development by Davy-McKee and the Florida Institute of Phosphate Research,[12] has been pilot planted by Freeport McMoran at Uncle Sam, Louisiana. A relatively small continuous system producing

SO_2 at a rate comparable to about one ton per hour H_2SO_4 was operated for several months to produce by-product aggregate for testing as a road building material.

Much time and effort have been devoted to studying the utilization of phosphogypsum, but with only limited success. The U.S. EPA, which issued a decree in 1989 that phosphogypsum had to be put only in mined-out areas or in specific piles, has limited, at present, what can be done with the waste.

Fluorine Recovery

Phosphate rock contains about 3.5 percent fluorine, some of which is recovered as a by-product in manufacturing wet process phosphoric acid. During acidulation, the fluorine is released as hydrofluoric acid, HF, which reacts with the silica present as an impurity in the rock to form fluosilicic acid, H_2SiF_6. Some of the fluorine is lost with the gypsum as sodium or potassium fluosilicates, and some remains dissolved in the filter acid. When the acid is concentrated, much of the fluorine in the feed is boiled off, appearing as HF and silicon tetrafluoride, SiF_4, in the vapors.

Fluorine is recovered at the evaporator station by scrubbing the vapors leaving the flash chamber. The vapors pass through an entrainment separator to remove fine droplets of phosphoric acid and then into a spray tower where they are scrubbed with a weak solution of fluosilicic acid according to the reaction:

$$2HF + SiF_4 \rightarrow H_2SiF_6$$

Part of the circulating solution is continuously withdrawn as a 20 to 25 percent aqueous solution of H_2SiF_6. The solution is shipped in rubber-lined tank cars and is used for fluoridation of drinking water, the preparation of fluosilicates, and production of AlF_3. These salts find use in ceramics, pesticides, wood preservatives, concrete hardeners, and aluminium production.

Uranium Recovery

Uranium occurs in many phosphate rocks in the range of 0.005 to 0.03 percent U_3O_8. This is too low in grade for the rock to be economically processed for uranium alone. However, in the making of wet process acid, most of the uranium is put into solution and can be extracted from the filter-strength acid.

Typically, wet process phosphoric acid made from Florida rock contains about 1.0 lb of U_3O_8 per ton of P_2O_5. It is claimed that as much as 90 percent of this can be extracted. The uranium is present in solution in the acid in an oxidized state, U(VI).

Research done at the Oak Ridge National Laboratory resulted in a reduction stripping process based on using a mixture of di(2-ethylhexyl) phosphoric acid and trioctyl phosphine oxide (DEPA-TOPO) dissolved in kerosene as the extractant.

When the uranium price was about $40/lb, uranium recovery was attractive. However, with the use of nuclear power in a holding pattern, the price of uranium in the 1980s slipped below $20/lb. Only a few companies with long-term supply contracts were still in operation by 1990, and no new plants are likely until the uranium price rises substantially.

Animal Feed Supplements

Calcium phosphates for use in animal and poultry feeds are made from both furnace and wet process phosphoric acids. Dicalcium phosphate, $CaHPO_4$, containing 18.5 percent P, and monocalcium phosphate, $Ca(H_2PO_4)_2 \cdot H_2O$, containing 21.0 percent P, are made in large tonnages. Both grades are prepared by reacting phosphoric acid with pulverized limestone in a pug mixer. The limestone must be quite pure, and the phosphoric acid must have a low fluorine content. If 54 percent P_2O_5 wet process phosphoric acid is used, it is defluorinated first by adding diatomaceous earth and then sparging the acid with steam. An alternate method is to use wet process superphosphoric acid, which has a low fluorine content. The superphosphoric acid is hydrolyzed by diluting it with water and heating. The pug mixer product is a fine-granule, −12 mesh, which is dried and shipped in bulk to feed-mixing plants.

Purified Phosphoric Acid

High power costs and environmental problems have discouraged the installation of new phosphorus furnaces in the United States. Wet process phosphoric acid purification plants using solvent extraction are operating successfully in Europe, Japan, and the United States.

Wet process phosphoric acid made from calcined rock is preferred because organic matter in the acid is very troublesome. Acid at a concentration of 35 to 50 percent P_2O_5 is treated with various reagents and adsorbents and refiltered. Then the acid is fed to a column or a battery of mixer-settlers and extracted with a solvent such as butyl alcohol or tributyl phosphate. Generally, about three-fourths of the phosphoric acid transfers to the organic phase, leaving the impurities in the raffinate, which is sent to a fertilizer unit to recover its P_2O_5. The yield of cleaned acid can be increased by adding another mineral acid such as sulfuric acid or hydrochloric acid to the extraction step.

After washing, the phosphoric acid is stripped from the solvent with water, and the solvent is returned to the extraction section. The phosphoric acid now is quite dilute and still contains small amounts of impurities. The acid then is concentrated, and the impurities are removed by steam stripping and the addition of reagents and adsorbents followed

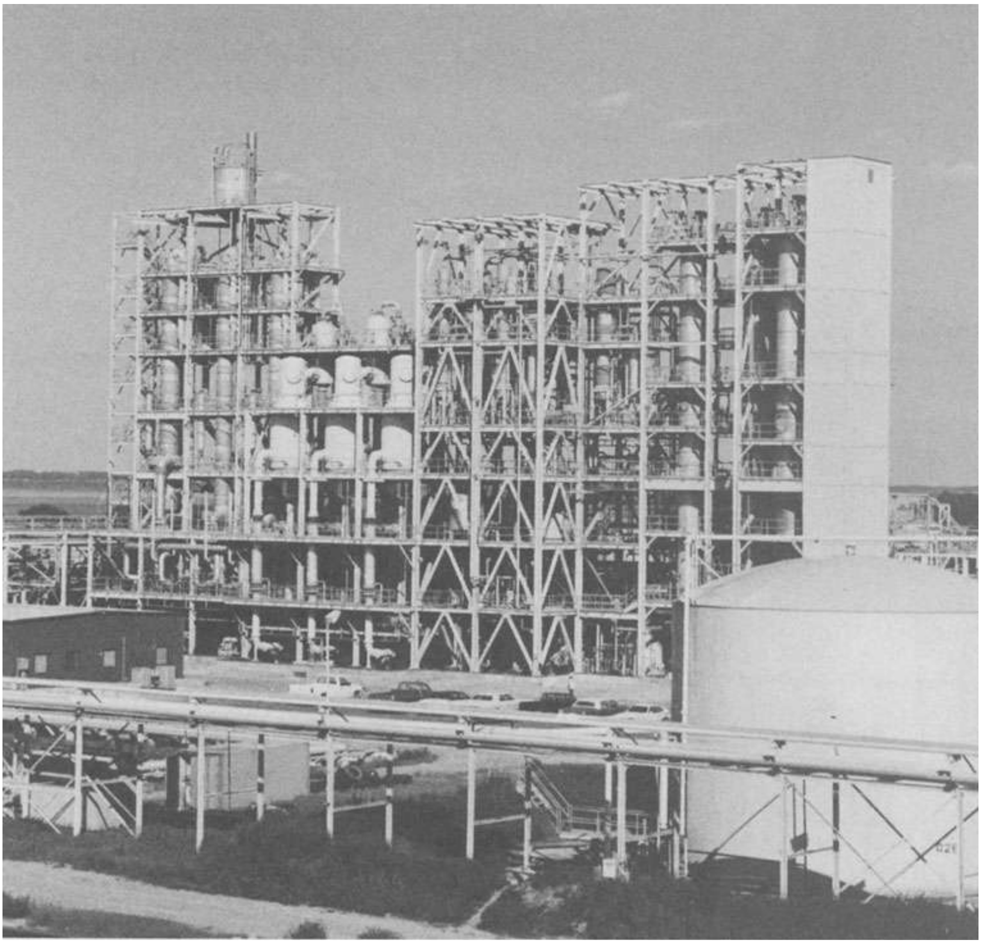

Fig. 10.8. Purified phosphoric acid plant for P.A. Partnership, Aurora, NC. (*Courtesy P.A. Partnership and Jacobs Engineering.*)

by filtration. The exact details of the process vary, depending upon the impurities present in the feed acid and the solvent used.

Purified wet phosphoric acid is suitable for both industrial and food-grade use. Two plants were in operation in the United States in 1991. One is pictured in Fig. 10.8. This facility, operated at Texasgulf's plant in North Carolina, is rated at 120,000 TPY P_2O_5. The second purified phosphoric acid plant is operated by Rhone Poulenc at Geismar, Louisiana. Of the North American capacity of approximately 900,000 TPY of high-purity P_2O_5 or equivalent P in 1991, about 78 percent still was furnace-derived.[13]

ENVIRONMENTAL ASPECTS

As implied earlier in this chapter, gypsum disposal is a problem that generally has defied an inexpensive solution. As a waste material, it is relatively benign, but P_2O_5, sulfate, fluorine, and other contaminants, including some heavy metals in small quantities, can leach from waste stacks into the nearby groundwater. In Florida, the underlying layers of limestone afford some protection, but the EPA will require future stacks be lined with a membrane to prevent seepage.

Although dumping of waste gypsum slurries into the ocean still is practiced in some locations outside the United States, and harmful effects are generally difficult to quantify, there is continuing pressure from environmental groups to cease dumping into rivers and the seas.

Gaseous emission from phosphoric acid plants can be handled with cool contaminated recycle cooling water to relatively low emission levels. However, to minimize cooling tower or cooling pond emission, fluorine recovery often is practiced on those streams that have a significant fluorine content.

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11

Fertilizers

George Hoffmeister*

INTRODUCTION

The growth and harvest of food and fiber crops is essential to the survival and well-being of humankind. As world population expands, or even "explodes," the challenge to increase crop production is a formidable one. The major means being employed to meet this challenge are: (1) increasing tilled acreage; (2) improvement of plant strains; (3) introduction of irrigation; (4) chemical and biological control of insects, plant diseases, and weeds; and, not the least of all, (5) introduction of or increase in fertilizer usage. It should be noted, however, that implementation of any of these methods for crop increase automatically dictates a corresponding increase in fertilizer usage. This has become especially clear during the so-called green revolution. During this period, which began in the late 1930s and extends to the present, tremendous advances in scientific crop breeding have made possible dramatic worldwide increases in the yields of corn, wheat, rice, and other staple crops, yet these increases have been sustainable only by suppling the improved varieties with increased nutrients, as fertilizer. Increasing crop acreage, introduction of irrigation, and effective use of pesticides likewise result in increased need for fertilizer in order to realize maximum yield benefits. Numerous estimates have been made in attempts to quantify the effect of fertilizers on U.S. and world food production. One of the more comprehensive indicates that approximately 37 percent of U.S. agricultural production is directly attributable to fertilizer usage.[1] However, even that statistic does not convey the full impact of fertilizer usage because without the use of fertilizer intensively farmed crop land soon would become depleted and nonproductive. For the "developing" countries of the world (as contrasted to "developed" countries) increasing the usage of fertilizer also holds great potential for reducing their dependence on imported food and for increasing human nutrition standards.

NUTRITION REQUIREMENTS OF CROPS

Twenty-one chemical elements are known to be essential to the normal development and

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*Retired from National Fertilizer and Environmental Research Center, TVA, Muscle Shoals, AL.

growth of plants. Their percentage in the dry matter of the plant varies somewhat with different species of plants and with different soil and climatic conditions under which plants are grown. However, the order of magnitude, expressed as the average percentage of each element present in the dry weight of the whole plant, is roughly as shown in Table 11.1.[2]

Oxygen, carbon, and hydrogen make up the greater part of the plant structure and comprise about 95 percent of the elemental content of the plant. The plant obtains these elements from the atmosphere and from water. The remaining 18 essential elements are supplied almost exclusively by soils and fertilizers. They comprise only about 4.9 percent of the elemental content of the plant, but are absolutely essential to healthy plant growth.

Of the 18 nutrient elements, nitrogen, phosphorus, and potassium are assimilated by plants in the greater amounts, and are the ones that most often become depleted in soils. Therefore, they are referred to universally as the "primary" plant nutrients. The overriding task of the fertilizer industry is to provide fertilizers that contain these three elements in chemical forms that, when applied to the soil, are soluble in the soil solution phase and assimilable by plant roots. Most often, this means chemical forms that are water-soluble. However, in the case of phosphorus, solubility in specially specified reagent solutions (citric acid, neutral ammonium citrate, or alkaline ammonium citrate) often is accepted as indicating "availability" to plants. In the case of nitrogen, slow solubility in water may be acceptable and may in fact, in some applications be more beneficial than easy solubility.

TABLE 11.1 Elemental Content of a Healthy Plant

Element	*Amount in Whole Plant % (Dry Weight)*
Structural Elements	
Oxygen	45
Carbon	44
Hydrogen	6
Primary Nutrients	
Nitrogen	2
Phosphorus	0.5
Potassium	1.0
Secondary Nutrients	
Calcium	0.6
Magnesium	0.3
Sulfur	0.4
Micronutrients	
Boron	0.005
Chlorine	0.015
Copper	0.0001
Iron	0.020
Manganese	0.050
Molybdenum	0.0001
Zinc	0.0100
TOTAL	99.9011

*Data from *Farm Chemicals Handbook*, p. 134, Meister Publishing Company, Willoughby, OH, 1970.

In the United States, and essentially in all other countries, there is close government monitoring of the chemical compostion of all marketed fertilizers to ensure that the nutrients claimed are present in acceptable forms and in the amounts claimed. Stiff penalties are assessed for failure to meet advertised compositions. In the United States, this control is under jurisdiction of the individual states, but differences in regulations from state to state are not great.[3] Methods of sampling and chemical analysis applied by the states to fertilizers in almost all cases are developed and/or approved by the Association of Official Analytical Chemists, a nonprofit, government-chartered, scientific organization.[4]

In Table 11.1, the elements calcium, magnesium, and sulfur are shown under their usual designation as "secondary" nutrients. These elements are required by plants in moderate amounts, but in most agricultural situations are not found to be deficient in the soil. There are exceptions, however. Areas of sulfur deficiency are well recognized in Australia, some U.S. locations, and elsewhere. Correction usually is made by application of fertilizers that are naturally high in sulfur content, such as normal superphosphate and ammonium sulfate, or by special application of gypsum or elemental sulfur. A very considerable amount of sulfur enters many soils dissolved in rainwater. The origin of this sulfur is stack gas from the burning of coal and gases from volcanic discharges. Several recent trends, however, suggest that sulfur deficiencies in the soil may increase in the future, and that sulfur fertilization thus may gain importance. One of these trends is an ongoing replacement of the sulfur-containing superphosphate and ammonium sulfate fertilizers with higher-analysis, more popular, nonsulfur fertilizers. The other trend is toward greater reduction of sulfur emissions from coal-fired power plants as a cure for "acid rain" and other environmental problems. The other two secondary nutrients, calcium and magnesium, are major chemical components of soil minerals and usually are available to plants in sufficient quantities without special supply as fertilizer. The application of lime (calcium carbonate or dolomite) to soils is a practice frequently used to regulate soil acidity, and such liming also furnishes additional calcium and magnesium.

The remaining essential plant nutrients listed in Table 11.1 are designated as "micronutrients," which reflects the fact that they are required by plants only in extremely small amounts. Nevertheless, they are essential, and deficiencies can seriously limit growth and yields.[5] Crops vary in their need for specific micronutrients. An example is boron, which is particularly required for cotton and alfalfa. There are numerous other examples. Also, there are many localized soils that are deficient in specific micronutrients. Some fertilizers, especially the older-type low-analysis superphosphates, contain significant amounts of micronutrient elements as natural impurities. However, modern scientific agriculture cannot rely on that source, especially in view of the trend toward higher-analysis fertilizers that generally contain little or no impurity usable as a micronutrient. The fertilizer industry thus includes a segment, relatively small in volume, devoted to furnishing micronutrients for fertilizer use. Often, the micronutrient compounds are incorporated in mixed fertilizers during their manufacture. As will be seen later, the now popular practice of "bulk blending" (dry mixing) fertilizer materials to "prescription" in the immediate farming locality lends itself well to the inclusion of specific amounts of specific micronutrients as required by local soils and crops.

OVERVIEW OF THE FERTILIZER INDUSTRY

For many centuries, even including ancient and medieval times, farmers have been deeply interested in improving crop yields through the addition of various mineral or organic substances to the soil. Up until the last two or three hundred years, however, the approach to the subject was highly empirical; only by accident or by trial and error was it found that applications to the soil of various organic wastes or naturally occurring mineral substances such as manure, ground bones, wood ashes, saltpeter, and gypsum dramatically improved plant growth. Still the results were not predictable; a treatment that benefited one field might have no effect—or even an adverse effect—on another.

As more and more chemical elements were identified, scientists became interested in determining the amounts and relative importance of various elements in plants. The German scientist Liebig clarified the value of elements derived from the soil in plant nutrition and stressed the necessity of replacing those elements to maintain soil fertility. He is usually credited with initiating the fertilizer industry. Liebig recognized the value of nitrogen but believed that all plants could get their nitrogen from the air, a concept that unfortunately is not true. He envisioned a fertilizer industry with nutrients such as phosphate, lime, magnesia, and potash prepared in chemical factories. In 1840, Liebig published a recommendation that pulverized animal bones be treated with sulfuric acid to make the phosphate more readily available to plants. This practice was accepted, and production of fertilizers by chemical processing thus began.[6]

Natural organic materials and various chemical by-products represented a large proportion of the total world fertilizer supply up until about the middle of the twentieth century; in the later years of the century, however, the dependence shifted almost entirely to synthesized or chemically processed materials. Only by this means has it been possible to keep up with increasing populations, increased farm acreage, and increased plant food needs of new and improved crop varieties. Today, the fertilizer industry utilizes many facets of highly sophisticated chemistry and engineering in the manufacture of fertilizers. The procuring and handling of raw materials and the distribution and marketing of products also involve the latest technology and many innovations. In addition, the agronomic aspects of fertilizer usage engage the efforts of many individuals and organizations. Both private companies and state and national governments operate laboratories to serve farmers with analysis of soils, prescription of fertilizers, and other services. In the United States, extensive research and development on improving fertilizer production and usage has been carried out by the U.S. Department of Agriculture and by the National Fertilizer Development Center of the U.S. Tennessee Valley Authority, as well as by numerous private companies.

The fertilizer industry is a large-volume one, usually classified among the "smokestack" industries. The magnitude of this industry is apparent from Fig. 11.1, which shows the yearly U.S. consumption of primary plant nutrients (N, P_2O_5, and K_2O) since 1965. For the most recent year shown (July 1, 1989, through June 30, 1990), U.S. total consumption of N, P_2O_5, and K_2O was 20.6 million short tons. The average nutrient content of all fertilizers for that period was 45.9 percent; so it is apparent that some 45 million tons of fertilizer was produced and handled by the industry during that year. In general, the industry includes a number of "basic producers," each of which typically concentrates on producing large amounts of single-nutrient or bi-nutrient fertilizer products, usually at locations near raw materials. Numerous other components of the industry concentrate on locating close to local farmers and distributing the basic products either in the form received from basic producers or after various secondary processing operations such as granulation, blending, or conversion to fluids.

Fig. 11.1. U.S. consumption of plant nutrients in fertilizers. (*Courtesy TVA.*)

NITROGEN FERTILIZERS

Nitrogen, one of the three primary nutrients required by growing plants, comprises 79 percent (by volume) of the earth's atmosphere. Above each acre of the earth, the atmosphere contains about 36,000 tons of nitrogen,[7] essentially all in elemental form. Ironically, however, only a very limited number of plant varieties, chiefly legumes, can utilize this nitrogen directly from the air. For most plants, including such important cereal crops as rice, wheat, and corn, the nitrogen uptake must be from "fixed nitrogen" (nitrogen in chemical compound form) dissolved in the soil solution. Lightning discharges, and perhaps other atmospheric phenomena, convert small amounts of atmospheric nitrogen to nitrogen oxides, which then enter the soil dissolved in rainwater. However, the resultant natural nitrogen content of soils is normally very low (less than 0.3%), and it becomes rapidly depleted if cropping is carried out without replenishment.[8]

Prior to about 1945, the use of chemical nitrogen fertilizers was considered of only minor importance, and was practiced on a relatively limited scale. The more widely accepted method of supplying nitrogen was through the application of manures (organic wastes) and the use of crop rotation. Crop rotation usually involved growth of a nitrogen-fixing legume crop, such as peas, clover, or alfalfa, which then, with its content of "fixed" nitrogen, was plowed into the soil to furnish nitrogen for a subsequent nonlegume crop, for example, corn. This method is an effective one and gives the added bonus of improving the physical condition of the soil through the introduction of organic matter. However, such crop rotation is relatively inefficient in regard to land usage and labor requirement. Modern, high-yield agriculture cannot, under most conditions, be sustained by such a system.

Miscellaneous Low-Volume Nitrogen Fertilizers

Natural Organics. Animal and human wastes have long been used as fertilizers, especially in Europe and Asia. Even some American Indians are said to have planted a dead fish in each corn hill to increase yields. Such materials contain small percentages of nitrogen and other plant nutrients that are assimilable by plants. Today, the use of raw sewage on crops persists in Asia and Europe, but volumewise is not of great significance. In the United States, the use of raw sewage is not considered acceptable, but some municipal sewage plants employ special sterilization and drying processes that yield acceptable fertilizers of low nitrogen content. The volume of such output is small, however. Other organic materials traditionally employed as fertilizers of usable nitrogen content include guano (deposits of accumulated bird droppings), fish meal, and packinghouse wastes including bone meal and dried blood. However, the cumulative importance of all such natural nitrogen sources in modern agriculture is minor. Less than one percent of the total fertilizer nitrogen now used comes from such sources. These products, for the most part, are not chemically altered prior to use. Processing is mainly physical in nature, to improve handling and distribution properties.

Mineral Nitrogen. The only nitrogen-containing mineral that is mined commercially for fertilizer use is saltpeter (sodium nitrate, $NaNO_3$). An impure form of sodium nitrate known as "coliche" is found in large, rocklike deposits in a relatively dry desert area of Chile, and these deposits have long been mined to provide natural sodium nitrate for the fertilizer market. The ore is blasted from open mines, sized, and leached with water in vats. Evaporation of the resultant solution yields the commercial crystalline fertilizer product known widely as "Chilean nitrate," "nitrate of soda," or among some farmers simply "sody." Its nitrogen content is 16 percent. This product first was imported and marketed in the United States in 1830; so it is one of the oldest fertilizers on the American market. Sodium nitrate now, however, is a relatively insignificant component of the world's nitrogen fertilizer market, having been supplanted by synthetic nitrogen compounds. In the year that ended

June 30, 1990, sodium nitrate use as fertilizer in the United States was equivalent to only 8400 short tons of nitrogen, out of a total usage of over 11 million tons of nitrogen in all fertilizers.[9]

By-product Ammonia. Coke, an essential ingredient in the smelting of iron ore and in some other metallurgical processes, is produced by the heating of coal in an essentially oxygen-free atmosphere. This heating volatilizes numerous hydrocarbon components of the coal and results in decomposition of some of these compounds. The nitrogen content of coals normally is about one percent, and approximately half of this is volatilized as ammonia gas in the coking process. Recovery of this ammonia has long been effected by passing the coke-oven effluent gas through scrubber-crystallizers containing sulfuric acid. The resultant crystalline by-product ammonium sulfate is an excellent fertilizer source of both nitrogen and the secondary plant nutrient sulfur. The nominal nitrogen content of the product is 20 percent, and the sulfur content is 24 percent. Prior to the introduction of synthetic ammonia production processes (1913–25), coke-oven ammonia was a major source of fertilizer nitrogen; however, its production was very small when compared to today's demand for fertilizer nitrogen. Today, ammonia production from coke ovens, although still carried out, is insignificant in volume compared with that from ammonia synthesis processes.

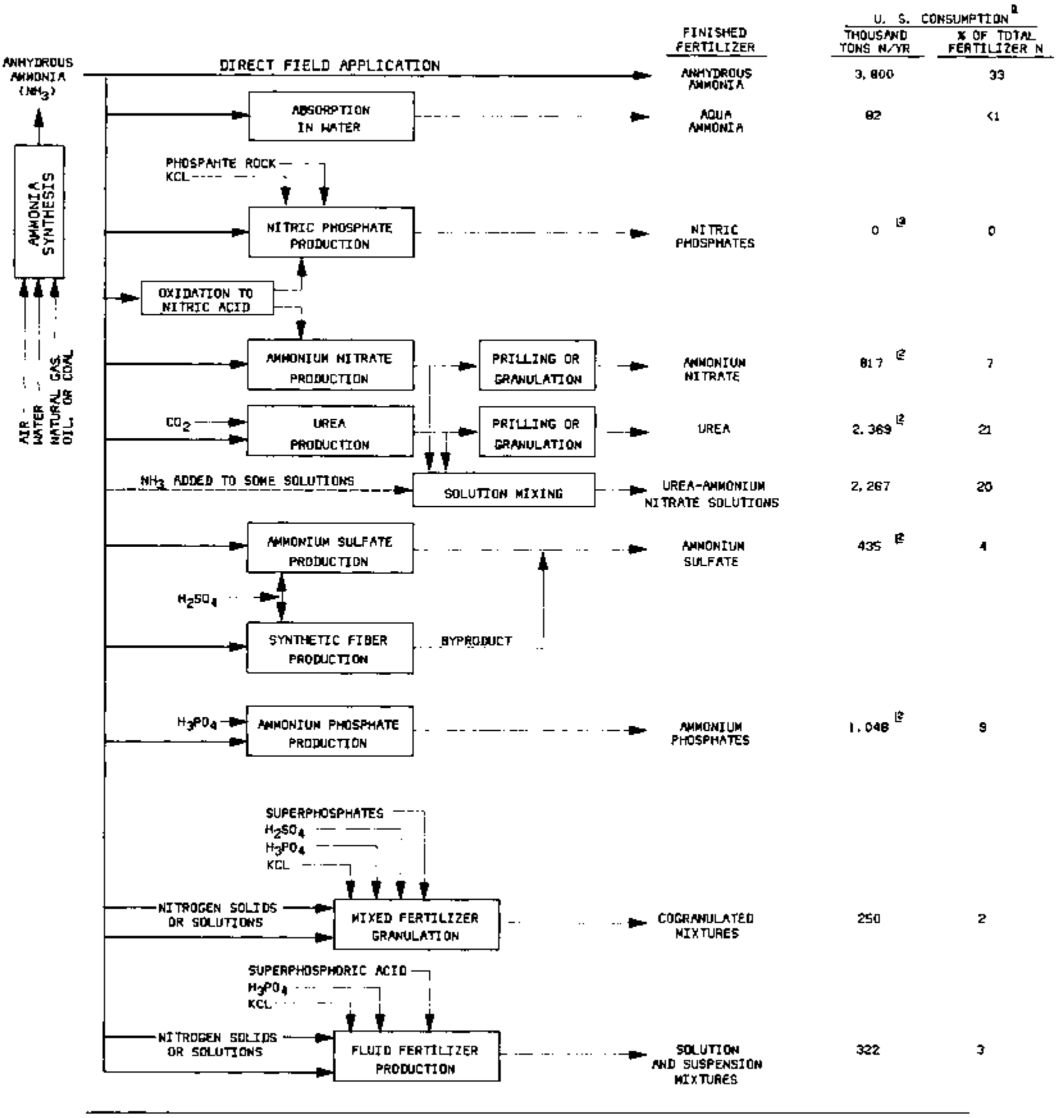
Nitrogen Fertilizers from Synthetic Ammonia

Over 95 percent of the 11 million tons of nitrogen supplied to U.S. farmers yearly in commercial fertilizers originates as synthetic ammonia made from air, water, and either a petroleum-based hydrocarbon or coal. The development of a practical ammonia synthesis process in the early years of the twentieth century was a profound scientific achievement of great social significance, in view of the subsequent dependence of the world on fertilizer for support of its growing population. Both the historical background and detailed technical descriptions of modern ammonia synthesis processes are covered in Chapter 28. These processes all are refinements of the original one conceived and developed by Fritz Haber and Carl Bosch in Germany during the period 1904–13. Basically, a gaseous mixture of nitrogen and hydrogen, in proper proportions to form ammonia, is compressed to very high pressure in the presence of an activated iron catalyst. Ammonia forms and is removed by cooling and condensation. The nitrogen feed is obtained from air by any of several routes that remove the oxygen. Likewise, there are several routes by which hydrogen feed is obtained, most of which involve decomposition of water by reaction with a carbon source such as natural gas, naphtha, or coke. The preparation and the purification of the synthesis gas and the synthesis itself are highly sophisticated modern processes that require great skill and know-how in design, construction, and operation of plants.

There are many processing routes by which synthetic ammonia subsequently finds its way into finished fertilizers. The major routes are outlined graphically in Fig. 11.2 and are discussed in some detail below. Figure 11.2 also shows the approximate percentage of total U.S. fertilizer nitrogen consumption currently furnished by each type of finished fertilizer.

Anhydrous Ammonia. Anhydrous ammonia, without further processing, is an excellent nitrogen fertilizer when properly injected in gaseous form below the surface of many soils. Such direct injection first came into farm use in the early 1940s and rapidly became accepted. The procedure today accounts for approximately one-third of total U.S. nitrogen fertilization (Fig. 11.2). This proportion of the nitrogen fertilizer market is greater than that claimed by any other finished fertilizer product. Anhydrous ammonia is also the major nitrogen fertilizer in Canada, Denmark, and Mexico, but in some other countries it is, for various reasons, a relatively minor nitrogen source.[10]

Anhydrous ammonia injection is popular for economic reasons. Ammonia is naturally



a BASED ON DATA FOR YEAR ENDED JUNE 30, 1990
b INCLUDES QUANTITIES APPLIED IN DRY BLENDS
c SIGNIFICANT QUANTITIES MADE AND USED IN SOME FOREIGN COUNTRIES

Fig. 11.2. Major routes of synthetic ammonia into finished fertilizers. (*Courtesy TVA.*)

the cheapest form of fixed nitrogen at the point of production, as no further processing is required. Also, the nitrogen content of anhydrous ammonia (88.2% N) is almost twice that of the next most concentrated nitrogen fertilizer (urea: 46% N); this high nitrogen content reduces shipping and handling weight proportionally.

From production to field application, ammonia is handled in liquefied form. Because ammonia is a gas at normal atmospheric pressure and temperatures, its maintenance in liquid form requires either pressurization or refrigeration. Although such handling requires specialized equipment and considerable safety precautions,[11] there are advantages and economies inherent in the handling of a fluid rather than a solid.

The vapour pressure of anhydrous ammonia as a function of temperature is shown in Fig.

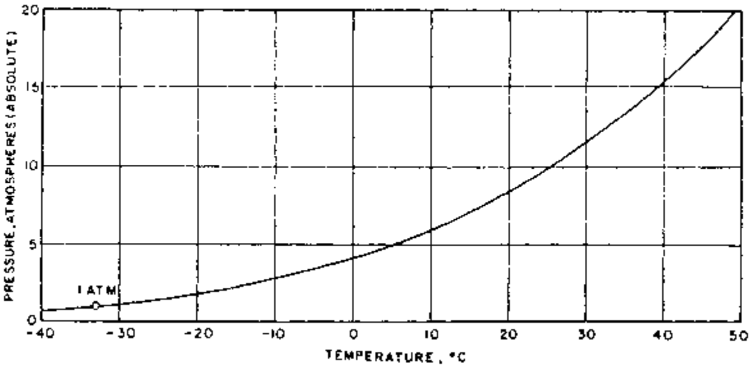


Fig. 11.3. Vapor pressure of anhydrous ammonia vs. temperature.

11.3. From this figure it can be seen that to maintain ammonia in liquid form at atmospheric pressure it is necessary to refrigerate it to at least −28°F (−33°C). In storage and handling without refrigeration, rather high pressures must be contained when atmospheric temperatures reach high levels. For example, a pressure of 265 psi, which, for safety reasons, has been set as the upper limit allowable for storage vessels at retail locations,[11] will maintain the liquid form only up to a temperature of 115°F. Safety pop-off valves are set to vent ammonia at higher pressures.

Facilities for handling liquid ammonia from points of production to points of use are highly developed in the United States. A considerable amount of ammonia is moved hundreds of miles through interstate pipelines. Major pipelines run from points of production in Texas, Oklahoma, and Louisiana oil fields all the way to the intensively farmed midwestern area of the United States. Storage at the points of production and at large terminals sometimes is in pressurized vessels (spheres), but more often it is at atmospheric pressure in large, insulated, refrigerated vessels. Refrigeration is effected simply by allowing vaporization of some of the contained ammonia, compressing the resulting vapor, and recondensing it in a water-cooled condenser. Barges with similar self-sustaining refrigeration systems commonly move large amounts of anhydrous ammonia on rivers and on the high seas. Also, specially designed railroad tank cars ranging in capacity from 24 to 73 tons are used widely for ammonia transport. These cars typically are nonrefrigerated, instead depending on pressure retention to maintain the liquid form. Large pressurized tank-trucks also are used. At retail depots in farming areas, storage normally is in pressure vessels, often with some compressor capability to recondense vapor and to facilitate transfers. Movement of ammonia to farm fields is via wheeled pressure tanks known as "nurse" tanks. Application equipment, usually tractor-drawn, is equipped with pressure tanks that are filled by transfer from nurse tanks.

Because anhydrous ammonia is gaseous at atmospheric conditions, for fertilizer use it must be injected below the surface of the soil to ensure absorption by the soil solution. Most applicators are equipped with a metering system and a series of soil-penetrating "knives"; the metered ammonia is piped through tubing down the trailing edge of each knife to a single opening at the deepest extremity. A penetration of 15 to 25 centimeters is typical.[10] Retention of ammonia in the soil is best when abundant soil moisture is present.

Aqua Ammonia. Ammonia in simple water solution is popular as a nitrogen fertilizer in some locations, but overall it claims less than one percent of the total nitrogen fertilizer market (Fig. 11.2). This product is made from anhydrous ammonia in units referred to as "converters." These units simply provide cooling as ammonia and water are combined in metered proportions. Aqua ammonia normally contains 20 percent nitrogen (23% NH_3). Its chief advantage over anhydrous ammonia is its low vapour pressure; this allows handling in nonpressure equipment, which simplifies design and reduces safety hazards. The chief disadvantage of aqua ammonia as a fertilizer is its relatively low nitrogen content, which limits its shipping range and increases field handling requirements. As with anhydrous ammonia, the preferred application method is knifing below the soil surface to limit volatilization loss; however, a relatively shallow injection depth of only 3 to 5 inches can be used.

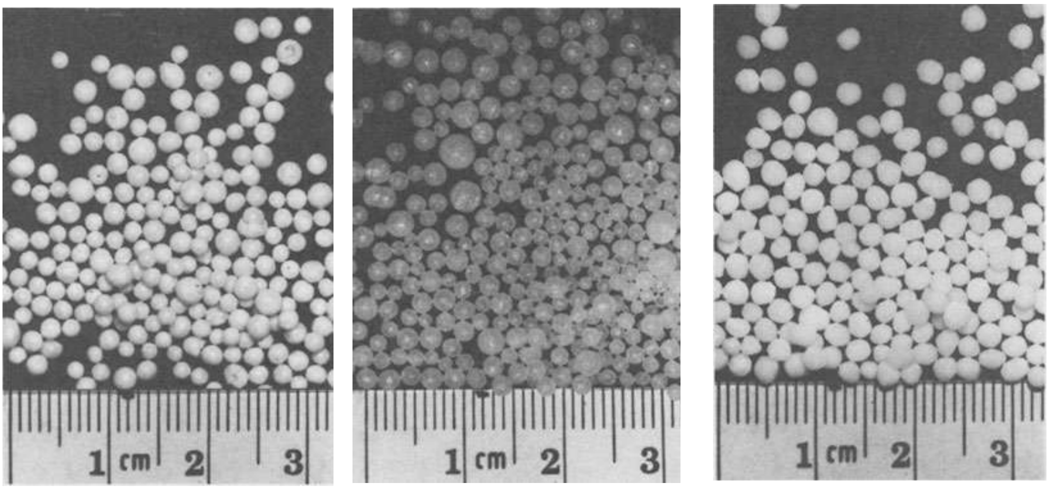
Ammonium Nitrate and Urea. Almost half of the total fertilizer nitrogen application in the United States is as ammonium nitrate or urea, in either solid or solution form. The breakdown for the year that ended June 30, 1990 (Fig. 11.2) is: ammonium nitrate solid 7 percent; urea solid, 21 percent; and urea–ammonium nitrate solutions, 20 percent. The history and the technology of ammonium nitrate and urea production from synthetic ammonia are covered in detail in Chapter 28. The production of nitric acid from synthetic ammonia, which is a prerequisite to the production of ammonium nitrate, also is covered completely in Chapter 28. The production plants for all these materials are, like synthetic ammonia plants, highly sophisticated, involving all facets of modern engineering.

The production processes for both ammonium nitrate and urea yield their products first in the form of saturated solutions. Typical ammonium nitrate solution concentration is 75 to 85 percent (26–30% N) at 105 to 170°F, and typical urea solution concentration is about 75 percent (34% N) at 200°F. To produce the solid forms of these products, the solutions first must be concentrated extremely low water contents (1–2% at 350–285°F) and then fed to prilling or granulation equipment. The resultant solid products (Fig. 11.4) are highly acceptable to farmers as high-nitrogen fertilizers and to "bulk blenders" as nitrogen sources in the formulation of dry-blend mixed fertilizers, as will be described later. The nitrogen content of solid ammonium nitrate is 34 percent, and that of urea is 46 percent.

The concentration and the solidification of ammonium nitrate and urea solutions to form solid fertilizers require considerable expenditure of energy and processing expense; so it is attractive to use the solutions in the formulation of liquid fertilizers, without processing them into solid form. However, neither ammonium nitrate nor urea alone is sufficiently soluble at ambient temperatures to be attractive for direct use as liquid fertilizer. With either compound alone, a solution with a salting-out temperature of 32°F would contain only about 18 percent nitrogen. Fortunately, however, the joint solubility of the two compounds in water is much more favorable than this; so the liquid nitrogen solutions marketed for fertilizer use almost invariably are joint solutions of ammonium nitrate and urea. Typical commercial solutions contain 28 to 32 percent nitrogen, with compositions and characteristics as shown in Table 11.2.

The high-volume use of these solutions is a result of their economy of production and the safety and convenience of their handling and application. The use of nonpressure equipment and surface application (in contrast to knifing) are normal. Nitrogen solutions of other compositions also are prepared commercially, but are used primarily as intermediates in the preparation of solid fertilizers. Such solutions usually consist of various combinations of water, ammonia, ammonium nitrate, and/or urea. Because of the content of free ammonia, most of these solutions require pressurized handling.

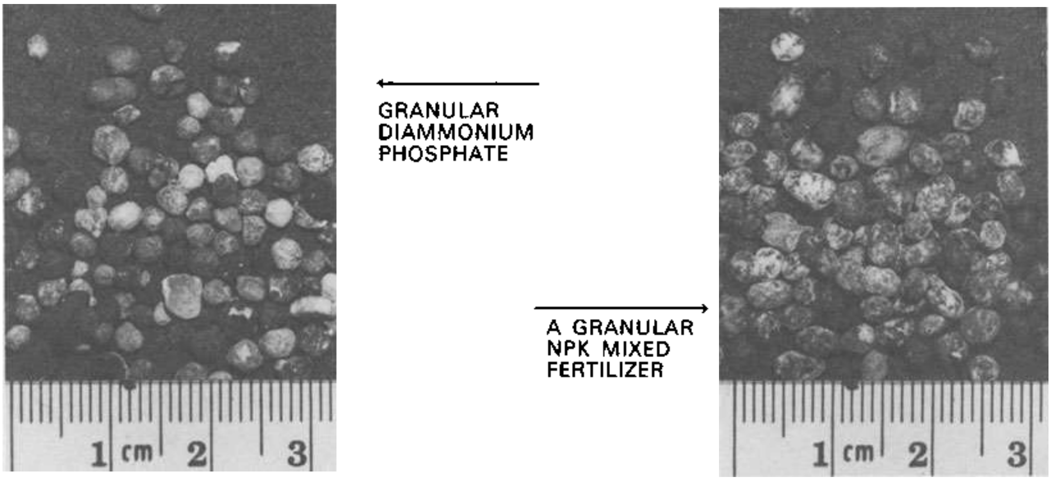
Ammonium Sulfate. Although an excellent nitrogen–sulfur fertilizer with good physical properties, ammonium sulfate is now outranked economically by ammonium nitrate and urea. Only about 4 percent of U.S. fertilizer nitrogen is furnished as ammonium sulfate. The chief reasons for the unpopularity of ammonium sulfate are its relatively low nitrogen content (21%) and its relatively low solubility in liquid fertilizers. At most U.S. locations, it is uneconomical to produce ammonium sulfate



PRILLED AMMONIUM NITRATE

PRILLED UREA

GRANULAR UREA



GRANULAR DIAMMONIUM PHOSPHATE

A GRANULAR NPK MIXED FERTILIZER

Fig. 11.4. Some major fertilizers in the prilled or granular form preferred by some farmers. (*Courtesy H. O. Hester.*)

TABLE 11.2 Physical and Chemical Characteristics of Urea–Ammonium Nitrate Nonpressure Nitrogen Solutions*

Grade, % N	*28*	*30*	*32*
Composition by weight			
Ammonium nitrate, %	40.1	42.2	43.3
Urea, %	30.0	32.7	35.4
Water, %	29.9	25.1	20.3
Specific gravity, 15.6°C (60°F)	1.283	1.303	1.32
Salt-out temperature, °C (°F)	−18 (1)	−10 (+14)	−2 (+28)

*Hignett, T. P. (Ed.), *Fertilizer Manual*, International Fertilizer Development Center, Muscle Shoals, AL (1978) from synthetic ammonia and virgin sulfuric acid. As a result, most of the ammonium sulfate available for fertilizer use is a by-product of other processes. Its production by scrubbing ammonia-containing coke-oven effluent gas with sulfuric acid already has been mentioned. A larger source now is by-product ammonium sulfate solution from the production of caprolactum and acrylonitrile, which are synthetic fiber intermediates. This by-product solution normally is fed to steam-heated evaporator-crystallizers to yield the solid ammonium sulfate. Additional production of by-product ammonium sulfate is obtained from "spent" sulfuric acid, by reaction with synthetic ammonia. In this case, the production of ammonium sulfate is a method of disposing of acid that already has been partially spent in other processes.

By-product ammonium sulfate produced by any of the above-mentioned methods is usually in the form of crystals that are 90 percent or more finer than 16 mesh, and thus are much smaller than the size preferred for present-day finished fertilizers. This small size is not undesirable if the material is to be used as feed to a fertilizer graulation plant, but it is undesirable for bulk-blending (dry mixing) or direct field application. It is possible to produce suitably large crystals, but only at the expense of greatly reducing crystalizer capacity. Both compaction and graulation processes have been employed with some success on a limited scale to convert the small-crystal material to larger-size product.[12,13]

Ammonia in Multi-nutrient Fertilizers. The ammonia-based fertilizers discussed thus far all contain only one of the three major plant nutrients, namely, nitrogen. Referring again to Fig. 11.2, one may see that ammonia is the source of fertilizer nitrogen also, either directly or via nitrogen solids or solutions, in multi-nutrient fertilizers. These are fertilizers that contain two or three of the major plant nutrients–nitrogen, phosphorus, and potassium. Ammonium phosphates, both mono- and di-, are phosphate fertilizer products that also carry nitrogen. (These will be discussed later, as major suppliers of phosphate.) As suppliers of nitrogen, the ammonium phosphates furnish only about 9 percent of all U.S. fertilizer nitrogen. Other multi-nutrient solid fertilizers, together with multi-nutrient fluid fertilizers, furnish an additional 5 percent of the total U.S. fertilizer nitrogen. (Production of these fertilizers also will be described later.) The source of their nitrogen is, in all cases, ammonia and/or ammonia-based solids or solutions. Nitric phosphates are suppliers of nitrogen through their content of nitric acid and ammonia. They are not presently produced, or used to any significant extent, in the United States, but are produced in Europe and some other locations. (Their production too will be discussed briefly later.)

PHOSPHATE FERTILIZERS

Phosphorus intake is essential to the metabolism of both plants and animals. In the case of plants, the entire uptake is from the soil solution via root absorption. Absorption occurs only when the phosphorus is present in the soil solution in the form of $H_2PO_4^{-}$, HPO_4^{--}, or PO_4^{---}, ions.[8] Native soils have an extremely low phosphorus content; in the United States, for example, the range is from 0.0 to 0.3 percent P_2O_5 equivalent.[8] Furthermore, a large proportion of the soil phosphorus is present in chemical forms that are not "available" (assimilable), or are only very slowly available, to crops. Cropping of native soils without phosphate fertilization soon depletes the supply of phosphorus and renders the soil barren. In times before fertilizers became readily available, it was not uncommon to "wear out" a farm by repeated cropping. Crop rotation, which was mentioned earlier as a useful method of converting atmospheric nitrogen to available soil nitrogen, is ineffective as a means of phosphorus fertilization. In fact, the nitrogen-converting legumes generally are voracious consumers of phosphate.

Modern, high-yield agriculture is dependent on regular fertilization with phosphorus compounds that either are immediately soluble in the soil solution or that become soluble at a rate sufficient to supply the crop. A factor to contend with in phosphate fertilization is soil "fixation" of phosphorus; that is, the characteristic of many soils to convert at least a portion of applied phosphate to chemical forms that are unavailable to plants. The fixation tendency varies with soil type, and generally is highest in soils of high clay content. The overall result of fixation is that considerably more phosphate must be applied as fertilizer than is removed with crops. Some estimates indicate that, nationwide, as much as 60 percent of applied phosphate may be lost to fixation.

Natural Organic Phosphate Fertilizers

In animal metabolism, phosphorus concentrates in the bones and, in the case of crustacea, in the shells. Manures and human wastes, previously mentioned as effective but low-volume sources of fertilizer nitrogen, are much less efficient sources of phosphorus than of nitrogen. The phosphorus content of such products is normally only 1.3 to 3 percent, which is only 25 to 50 percent as great as their nitrogen content. Bird droppings, including chicken manure and guano deposits, are somewhat higher in phosphorus content (7% P), but are available in only relatively insignificant amounts overall.

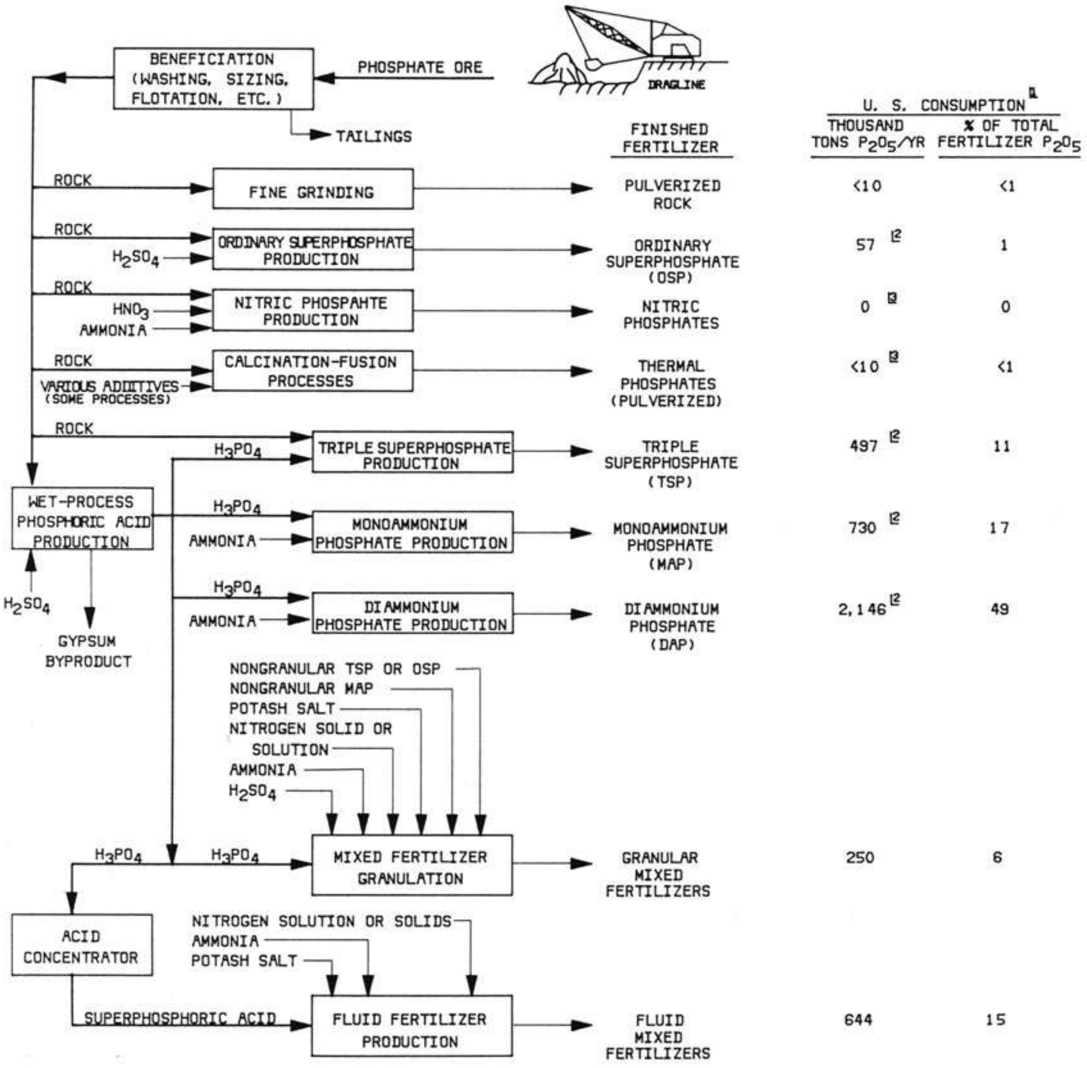
Raw animal bones normally contain 8 to 10 percent phosphorus (20–25% P_2O_5); thus they are a relatively rich source. The commerical grinding of bones for fertilizer use began in Europe in the early nineteenth century.[6] The practice persists today in the production of bone meal, but only in very low volume, chiefly to furnish slowly available nutrients for greenhouse and house plants. In about the year 1830, it was found that pretreatment of bone meal with dilute sulfuric acid greatly enhanced the "availability" of the phosphorus to plants, and the practice became common. The initiation of this practice now is regarded to have had considerable historic significance as the apparent beginning of the chemical fertilizer industry. The supply of bones being very limited, it soon was found (about 1840) that a similar acid treatment of mined phosphate ore rendered the phosphorus "available" as a fertilizer. Thus was born the still important "superphosphate" industry, and the supplanting of the very limited organic phosphorus sources by widely available mineral sources was begun. Today, organic sources of fertilizer phosphorus account for less than one percent of total worldwide consumption.

Fertilizers from Mineral Phosphates

Essentially all fertilizer phosphorus now is derived from mined ores. (The occurrence, mineral characteristics, mining, and beneficiation of major phosphate ores were described in some detail in Chapter 10.) Worldwide, about 85 percent of the mined phosphate eventually finds its way into fertilizer.[10] Estimates of the world reserves of ore vary widely, but even the most conservative estimates indicate a sufficiency for hundreds of years at expected consumption levels. Supply problems of the immediate future will relate chiefly to exhaustion of the better ores, with the result that ores of lower grades and higher impurity contents will have to be processed.

Major routes of mineral phosphate (phosphate rock) into finished fertilizers are outlined in Fig. 11.5 and are discussed below. It is obvious from the figure that although phosphate rock is used directly in several major fertilizer production processes (ordinary superphosphate, nitric phosphates), most important processes require that the rock phosphate first be converted to phosphoric acid (H_3PO_4). Phosphoric acid production, then, is a very significant component of the phosphate fertilizer industry. The processes used for the production of fertilizer-grade phosphoric acid are known collectively as "wet" processes, and involve, initially, dissolution of the rock in sulfuric acid. (The highly specialized technology of wet-process acid production was discussed in Chapter 10.)

Phosphate Rock for Direct Application. Application of finely pulverized raw phosphate



[a] BASED ON DATA FOR YEAR ENDING JUNE 30, 1990

[b] INCLUDES QUANTITIES APPLIED IN DRY BLENDS

[c] SIGNIFICANT QUANTITIES MADE AND USED IN SOME FOREIGN COUNTRIES

Fig. 11.5. Major routes of mineral phosphate into finished fertilizers. (*Courtesy TVA.*)

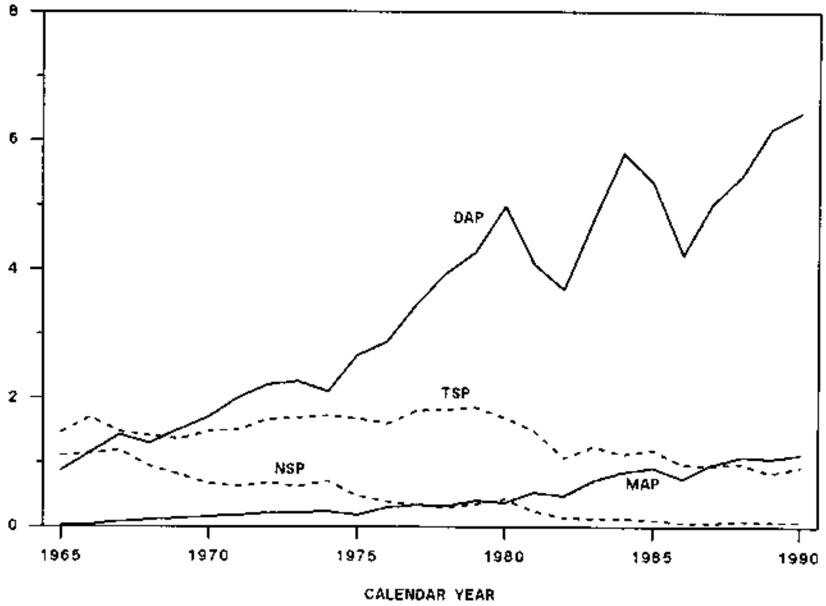
rock directly to the soil has been utilized almost from the beginning of fertilization practice. Although such direct use eliminates the need for most processing, there are major drawbacks. The ores are of low phosphorus content in comparison to most manufactured fertilizers, which increases shipping cost. Also, the very fine grinds that are required to encourage solubility are difficult to handle and to apply. The major drawback, however, is agronomic. The agronomic effectiveness of raw rock depends upon the chemical and mineralogical nature of the particular rock, the pH and other characteristics of the soil, and the crop produced. Researchers at TVA have characterized phosphate rocks from a large number of sources as to their reactivity.[14] Phosphate rock from North Carolina (U.S.A.) and Gafsa (Tunisia) are at the top, and are about equal in reactivity and suitability for direct application. Other phosphate rocks that are reasonably reactive and are marketed for this purpose include some types from Morocco, Israel, and a few other locations. In 1974, a world total of about 3.8 million metric tons of phosphate rock was used for direct application. In the United States, however, less than 10,000 tons of P_2O_5 per year currently is applied as direct application rock. This represents less than one percent of total P_2O_5 fertilization.

Ordinary Superphosphate (OSP). In 1842, Lawes in England followed up on the pioneering work of Liebig and received a patent on the use of sulfuric acid in reaction with raw phosphate material to produce "superphosphate" fertilizer. An industry grew slowly, and in 1862 about 150,000 tons of what later would be referred to as "ordinary" (OSP) or "normal" (NSP) superphosphate (16–18% P_2O_5) was produced in England. By 1870, there were 70 ordinary superphosphate plants in the United Kingdom and 7 in the Charleston, South Carolina, area of the United States.[15] In 1888, commercial shipment of phosphate rock from Florida was initiated, and a major mining industry followed in that state, which continues today. As late as 1955, OSP supplied over 60 percent of the world's phosphate fertilization and was the major phosphate fertilizer in the United States. Rock from Florida or South Carolina was shipped throughout the country to local OSP production facilities. These facilities usually included the capability of blending the OSP with nitrogen and potash materials and bagging the resultant mixtures.

In recent years, as indicated in Figure 11.6, U.S. production of OSP (shown as NSP), to a large extent, has given way to production of the higher-analysis "triple superphosphate" and ammonium phosphates. The U.S. production of OSP in the year that ended June 30, 1990 was equivalent to only 66,000 tons of P_2O_5 for direct application, plus perhaps an additional 40,000 tons for use in the manufacture of mixed fertilizers. This total production represents only about one percent of the U.S. fertilizer P_2O_5 usage. OSP retains greater importance than this in some countries. For example, OSP remains popular in Australia, at least in part because its sulfur content is particularly needed there.

OSP is the simplest, as well as the oldest, of manufactured phosphate fertilizers. Its manufacture consists of reacting pulverized phosphate rock with sulfuric acid in comparatively simple equipment, followed by sufficient aging (curing) to complete the reaction and improve the physical condition. The acid–rock reaction converts the water-insoluble apatite structure of the rock to soluble monocalcium phosphate. When produced from high-grade rock of 30 to 32 percent P_2O_5 content, OSP contains about 20 percent available P_2O_5; product made in earlier years from lower-grade rocks contained only 14 to 18 percent P_2O_5. OPS can be used for direct application, for bulk blending, or in the production of granular NPK fertilizers. If the product is to be used for direct application or bulk blending, it usually is granulated to improve handling properties.

The main equipment for manufacturing OSP consists of a mixer to bring together sulfuric acid and phosphate rock, followed by a den, and, if granulation is used, some suitable type of equipment for granulation with steam or water. Early plants used batch-type mixers for acid–rock mixing, but these mixers mostly have been replaced by continuous types. Several types of continuous mixers have been employed; of these, the lowest-cost, simplest, and apparently most satisfactory one is the TVA cone mixer, which has no moving parts (see Fig. 11.7). Mixing is accomplished by the swirling action of the acid. Short, single-shaft or double-shaft pug mills also are used for continuous mixing. The mixers discharge into a den, the purpose of which is to allow time for the acid–rock reaction to progress and the physical condition to reach a dry, friable state. The dens can be of either the batch or the continuous type. A slat-conveyor continuous den, commonly referred to as a Broadfield den, is used in many continuous systems.[16] A diagram of a typical OSP plant employing a cone mixer and a



(thousand short tons of P2O5)

Calendar	--Superphosphate--		------Multiple-Nutrient Materials------				
Year	Normal	Triple	DAP	MAP	Other*	Total	Total
1965	1,113	1,466	...	...	...	1,252	3,830
1966	1,138	1,696	...	...	...	1,615	4,450
1967	1,184	1,481	...	...	...	2,030	4,695
1968	938	1,419	...	...	...	1,839	4,196
1969	807	1,354	...	...	...	2,132	4,292
1970	670	1,474	...	...	...	2,452	4,596
1971	626	1,503	...	...	...	2,863	4,992
1972	677	1,659	...	...	...	3,147	5,482
1973	619	1,693	...	...	...	3,226	5,538
1974	698	1,719	2,100	...	626	2,950	5,367
1975	484	1,678	2,655	...	582	3,411	5,573
1976	383	1,595	2,876	...	677	3,847	5,824
1977	340	1,791	3,455	...	779	4,568	6,699
1978	291	1,820	3,936	...	807	5,065	7,176
1979	353	1,842	4,257	...	819	5,468	7,662
1980	425	1,693	4,972	...	854	6,191	8,309
1981	237	1,491	4,076	529	576	5,181	6,909
1982	139	1,065	3,681	484	237	4,402	5,606
1983	122	1,246	4,782	710	197	5,689	7,056
1984	127	1,124	5,804	844	134	6,781	8,032
1985	100	1,190	5,340	911	112	6,363	7,653
1986	65	972	4,222	741	109	5,071	6,108
1987	64	956	5,017	963	105	6,085	7,105
1988	86	976	5,450	1,084	82	6,615	7,677
1989	67	832	6,175	1,061	102	7,338	8,237
1990	66	929	6,427	1,119	90	7,636	8,631

*Includes MAP 1974-1980.

Fig. 11.6. Production of phosphate fertilizer materials in the United States. (*Source: ESDC, "Inorganic Fertilizer Materials and Related Products," Series M28B, monthly and annual reports.*)

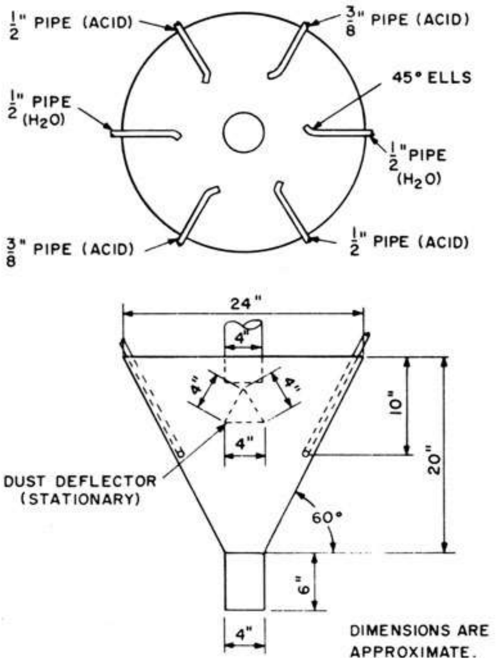


Fig. 11.7. Typical cone mixer for production of 25 to 30 tons/hr of normal superphosphate. (*Courtesy TVA.*)

continuous den (slat-conveyor) is shown in Fig. 11.8.

The reaction of phosphate rock with sulfuric acid to produce OSP can be approximated in chemical stoichiometric terms. However, in general practice the proportioning usually is based on a simpler relationship of about 0.6 lb of sulfuric acid (100% H_2SO_4 basis) per pound of phosphate rock (30–32% P_2O_5). The phosphate rock usually is pulverized to about 90 percent −100 mesh and 70 percent −200 mesh.

Gases that are released while the superphosphate is solidifying (setting) cause the mass in the den to become porous and friable so that it can be "cut" (disintegrated) and handled readily. OSP made from typical rock will "set" in 40 to 50 minutes in a continuous den, whereas the set time in a batch den is 1.5 to 2 hours. The superphosphate usually is held in storage piles (cured) for 4 to 6 weeks in order to obtain better handling properties and to allow the chemical reactions to continue. The usual grade of OSP made from Florida rock is 20 percent available P_2O_5. A

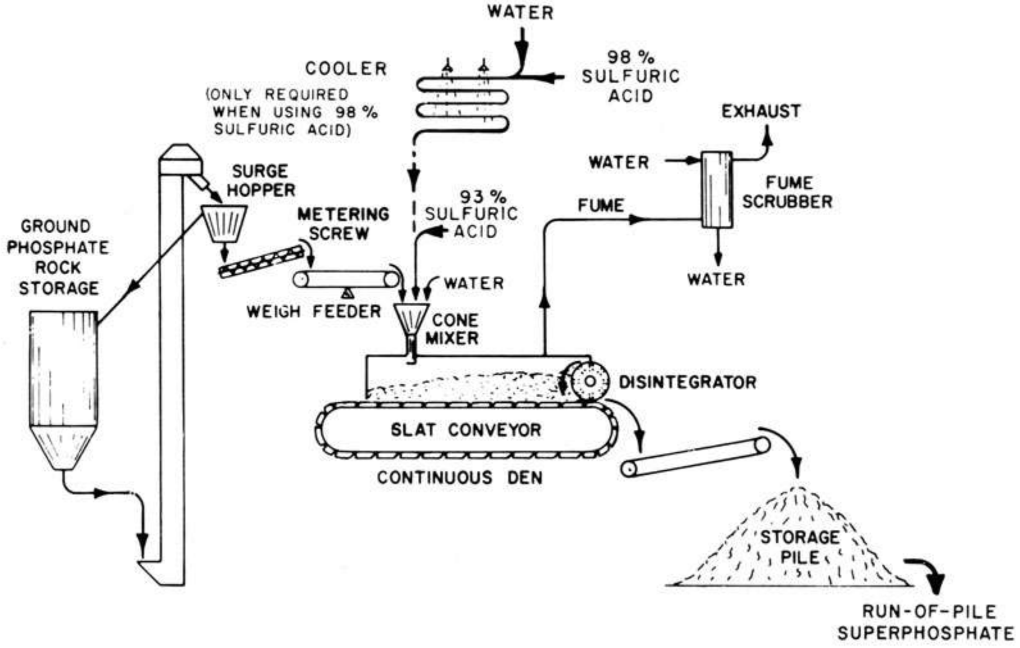


Fig. 11.8. Continuous process for the manufacture of normal superphosphate. (*Courtesy TVA.*)

typical analysis is shown below.

Analysis, % by Weight								
P_2O_5								
Total	*Available*	H_2O *Soluble*	*Free* *CaO*	*Acid*	SO_4	*F*	R_2O_3	*MgO*
20.2	19.8	18.0	28.1	3.7	29.7	1.6	1.6	0.15

Because of the low phosphate analysis of OSP (20% P_2O_5), economics favor shipping the rock (32% P_2O_5) to local plants and producing the superphosphate there. In present U.S. practice, a majority of the producers use the locally produced OSP in formulations for granular NPK fertilizers made in a TVA ammoniation-granulation process. The maximum amount of OSP possible is used in the NPK formulations, as it usually is the lowest-cost form of P_2O_5; however, because of the relatively low P_2O_5 content of OSP, not much can be used in high-analysis NPK formulations. OSP will readily absorb about 6 lb of ammonia per 20 lb of P_2O_5 during the ammoniation-granulation process. Production of granular OSP can be carried out by starting with either cured or ex-den OSP. The OSP is fed to a rotary drum or pan granulator along with a water spray and/or steam. The granulator is followed by a dryer and screening (sizing) system. Fines and crushed oversize material are fed back to the granulator.

Triple Superphosphate (TSP). Triple superphosphate is made by acidulation of phosphate rock with phosphoric acid, using equipment and processes similar to those for OSP. As in OSP production, the acid–rock reaction converts the water-insoluble apatite structure of the rock to water-soluble monocalcium phosphate. TSP, with its relatively high P_2O_5 content of 45 to 46 percent, did not appear on the scene in any appreciable quantity until wet-process phosphoric acid (see Chapter 10) was produced commercially. TVA carried out demonstration-scale production of triple superphosphate in the late 1930s by using electric-furnace phosphoric acid. Extensive agronomic testing and market development, through the use of large tonnages of this TSP by farmers and fertilizer manufacturers in TVA demonstration programs, led to the rapid acceptance, of TSP. Producers of phosphate rock in the United States and other countries moved into production of wet-process acid and TSP. Logistics favored production of the higher-analysis TSP (46% P_2O_5 vs. 32% P_2O_5 in phosphate rock) near the source of the phosphate rock, and shipment of the TSP to distribution facilities or blending plants near the markets. Today, the largest producers of TSP are located adjacent to phosphate mining operations in Florida, North Carolina, and the western United States. Since its introduction, TSP has steadily displaced OSP in the marketplace, as shown in Fig. 11.6. In the year that ended June 30, 1990, TSP provided 11 percent of U.S. phosphate fertilization, as compared to about one percent for OSP (Fig. 11.5).

The TVA-developed cone mixer has been used almost universally in the production of nongranular TSP. Because the "set time" for TSP is only 14 to 20 minutes, as compared to 40 to 50 minutes for OSP, a simple, cupped conveyor belt usually is used to hold the acidulate until the TSP solidifies; this is instead of the slat-type den used for OSP. With a belt about 5 feet wide and 100 feet long, the production rate usually is 40 to 50 tons/hr. A flow diagram for TSP production by the cone mixer–"wet-belt" system is shown in Fig. 11.9.

Proportioning for TSP typically is 2.4 to 2.5 lb of P_2O_5 from acid for each pound of P_2O_5 from rock. Nongranular TSP usually is cured 4 to 6 weeks prior to shipment or use at the site. Typical chemical analysis of TSP

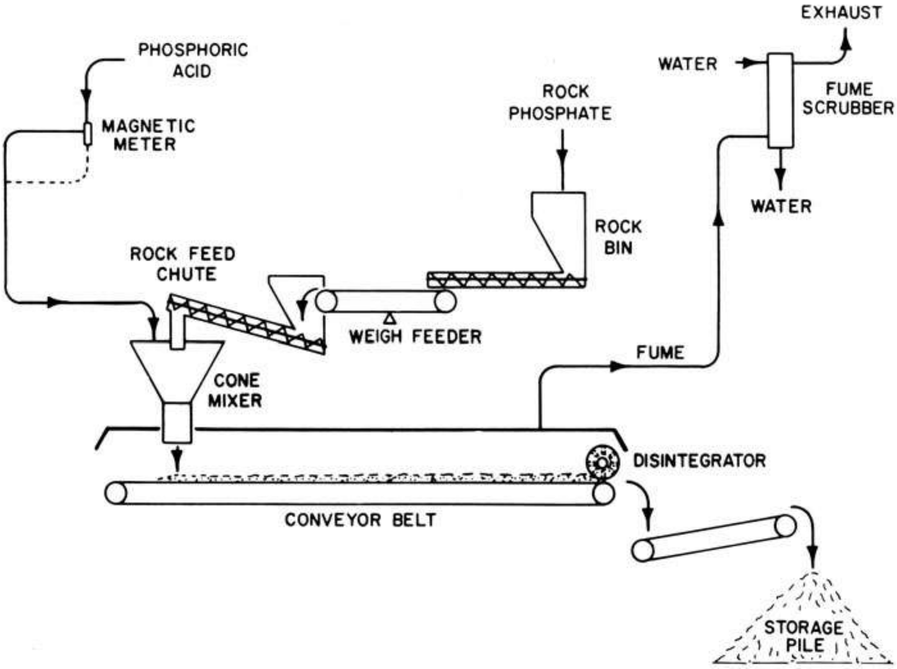


Fig. 11.9. Continuous system for manufacture of nongranular triple superphosphate. (*Courtesy TVA.*)

made with Florida rock is shown below:

Analysis, % by Weight

P_2O_5								
Total	*Available*	*H_2O Soluble*	*Free Acid*	*CaO*	*R_2O_3*	*MgO*	*F*	*H_2O*
46.9	46.3	42.0	3.4	19.3	3.1	0.5	2.7	4.5

The use of TSP in granular NPK fertilizer formulations, together with or in place of OSP, has allowed the production of higher-analysis grades of granular NPK fertilizers, such as 13-13-13 instead of 10-10-10. The TSP can readily be ammoniated to about 3.5 lb of ammonia per 20 lb of P_2O_5 during the granulation process.

TSP is produced in large quantities in granular form for use in direct application and for use in bulk blends. In some processes, cured or ex-den TSP, like OSP, is granulated in a rotary drum or pan granulator using steam and water to promote granulation.[10] A slurry-type granulation process, as outlined in Fig. 11.10, is used in the United States and some other countries. Pulverized phosphate rock is treated with wet-process phosphoric acid in a two-stage reaction system, and the slurry is sprayed into a pug mill or rotary drum, where it is layered on recycled undersize and crushed oversize at a ratio of 1 lb per 10 to 12 lb of recycle. Product granules (45% P_2O_5) are quite spherical and dense. The lower grade of the granular product, as compared to that of cured nongranular TSP, results from the need to decrease the acidulation ratio from the usual 2.45 lb of acid P_2O_5 per pound of rock P_2O_5 to about 2.25 in order to control the free-acid content and to minimize stickiness. For production rates higher than about 25 tons/hr, a rotary drum

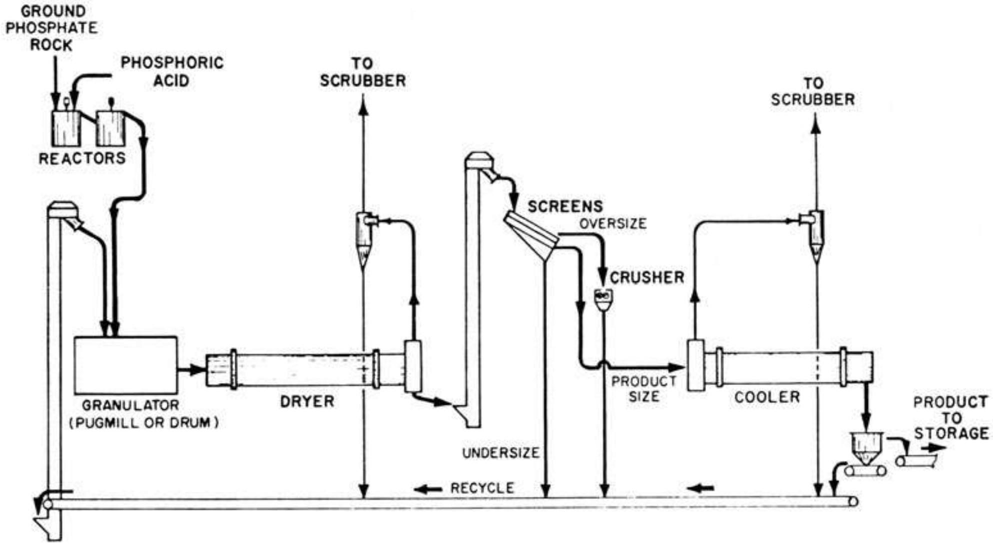


Fig. 11.10. Slurry process for production of granular triple superphosphate. (*Courtesy TVA.*)

usually is used instead of a pug mill. Most of the granular TSP produced in the United States is used in bulk blending, as is discussed later.

Nitric Phosphate. Fertilizers that are referred to as nitric phosphate or nitrophosphate are produced by acidulation of phosphate rock with nitric acid or with mixtures of nitric and sulfuric or phosphoric acids. As indicated in Fig. 11.5, there presently is no production, and little or no importation, of this type of fertilizer in the United States. The primary advantage of nitric phosphate processes is that no sulfur or less sulfur is required as compared with superphosphates or ammonium phosphates; this is particularly important during a shortage of sulfur, or in locations where sulfur must be shipped long distances. A variety of processes and equipment have been used in Europe since the late 1930s.[17] Also there are a number of plants in Central and South America and in Asia. In past years, there have been several U.S. ventures into production, but none has competed successfully with phosphoric acid-based processes. Production of nitric phosphates is complex. Simple substitution of nitric acid in a superphosphate-type acid–rock reaction is not feasible because (1) decomposition of the nitric acid would occur and cause noxious fumes and loss of nitrogen, and (2) the product would be extremely hygroscopic and unstable.

One process modification that overcomes these difficulties uses only nitric acid for acidulation; the extraction slurry is cooled to crystallize calcium nitrate, which then is removed by centrifugation. This process is referred to as the Odda process. The calcium nitrate by-product is either sold as a fertilizer or converted to coproduct ammonium nitrate. The extraction slurry, with its lowered calcium content, then is ammoniated and granulated. Various process modifications utilize a rotary drum, pug mill, or spray drum (Spherodizer) for granulation of the slurry. NPK nitric phosphate grades also have been produced by a prilling process in a few European plants. In earlier years, a main disadvantage of nitric phosphate processes was the low water solubility of phosphate in the products, as the main phosphatic constituent was dicalcium phosphate. The use of supplemental phosphoric acid, or "deep cooling" by refrigeration to remove a higher proportion of calcium nitrate in the Odda-type processes, now allows water solubility of 60 percent or higher. The remaining 40 percent of the phosphate, although water-insoluble, is almost completely citrate-soluble, and this is "available" as plant nutrient. Popular grades of nitric phosphates include 14-14-14, 22-11-11, 20-20-0, and 16-13-0.

Diammonium Phosphate (DAP). Ammonium phosphates did not come on the fertilizer scene in significant quantities until the early 1960s; however, they have rapidly become the leading form of phosphate fertilizer in the United States and in the world. Almost all new phosphate fertilizer complexes built in recent years, and those planned, are for the production of ammonium phosphate as the major product. In 1960, U.S. production of ammonium phosphates was equivalent to only 270,000 tons of P_2O_5. By 1974, production was up to 2.1 million tons of P_2O_5 per year, and by 1990 it has reached 6.4 million tons/year. Ammonium phosphates now provide two-thirds of total U.S. phosphate fertilization.

Prior to the late 1940s, diammonium phosphate $(NH_4)_2HPO_4$ was considered to be too unstable for use as a fertilizer. However, at about that time, exploratory work by TVA indicated otherwise. The first demonstration-scale diammonium phosphate made by TVA for fertilizer use was a monocrystal product made by ammoniation of pure electric-furnace acid in a vacuum crystallizer.[18] Demonstration programs showed this material to be stable and to be an excellent high-analysis fertilizer. Small amounts of similar product were produced by others using electric-furnace acid and by-product ammonia. However, general acceptance of diammonium phosphate by the fertilizer industry was not possible until procedures could be developed to produce it from wet-process phosphoric acid instead of the relatively expensive electric-furnace acid. This occurred in 1960–61 with the development and patenting of the "TVA process" for production of granular 18-46-0 grade DAP from wet-process acid.[19,20] This relatively simple process was rapidly adopted by the industry, and remains the basic process for production of this major phosphate fertilizer. Many granular DAP plants have production capacities of about 50 tons/hr, with some going as high as 70 to 100 tons/hr.

The flow diagram of a typical granular DAP production unit of the TVA type that has become standard in the industry is shown in Fig. 11.11. Wet-process phosphoric acid of

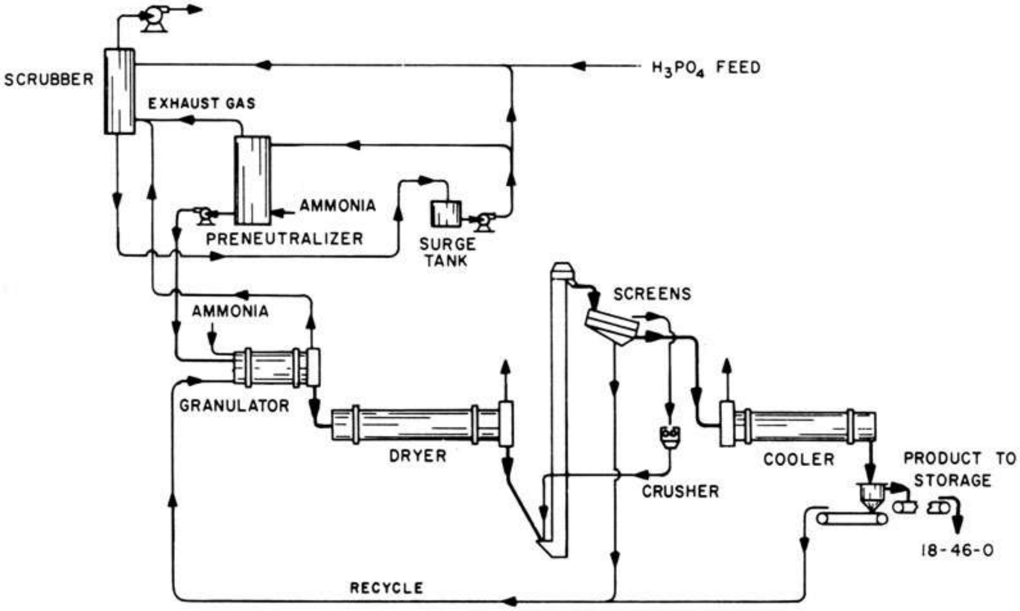


Fig. 11.11. TVA process for production of granular diammonium phosphate. (*Courtesy TVA.*)

about 40 percent P_2O_5 content (often a mixture of 54% P_2O_5 acid and acid from the scrubbing circuit of 28–30% P_2O_5 content) is fed to a preneutralizer vessel. Anhydrous ammonia is sparged into this preneutralizer through open-end pipes that project through the walls. A key feature of the process is that this neutralization of the acid is carried to a closely controlled $NH_3:H_3PO_4$ mole ratio of about 1.4. Ammoniation to this degree provides maximum solubility of ammonium phosphate, as is shown by the solubility curve of Fig. 11.12. The heat of the ammoniation reaction evaporates considerable water, with the result that the water content of the slurry is reduced to only 16 to 20 percent. The slurry still is fluid and pumpable, however, because of the high solubility at a 1.4 mole ratio.

The preneutralizer slurry is pumped at a controlled rate to a rotary-drum, TVA-type ammoniator-granulator; there it is distributed onto a rolling bed of recycled solids. The most commonly used metering system for the preneutralized slurry is a variable-speed centrifugal pump with automatic control from a magnetic flowmeter. Some plants have had success with a magnetic flowmeter and automatic control valve of a special ball type.

Ammonia is sparged beneath the bed in the rotary drum to ammoniate the slurry further to near the theoretical DAP ratio of 2.0; the usual finishing $NH_3:H_3PO_4$ mole ratio is 1.85 to 1.94. Metallic phosphate impurities such as iron, aluminium, and calcium phosphates account for most of the deviation from theoretical. This ammoniation in the granulator drastically decreases ammonium phosphate solubility (Fig. 11.12), and thus promotes solidification and granulation. Ammonia absorption is not 100 percent complete in either the preneutralizer or the granulator. However, the unabsorbed ammonia is recovered in a scrubbing circuit containing phosphoric acid of about 30 percent P_2O_5 content. Solid recycle to the granulator drum consists of undersize from screening of dried product plus some crushed, dry product and oversize. These combined materials are recycled at a rate of 5 to 7 lb per pound of product, and variation of this recycle rate is the primary method of controlling granulation efficiency.

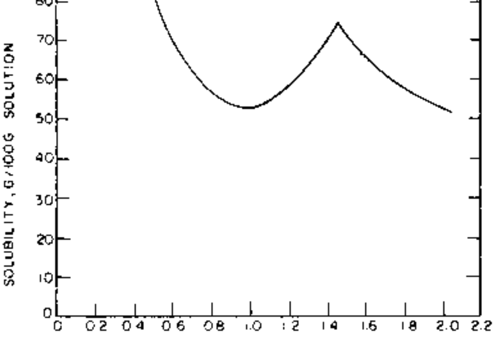


Fig. 11.12. Effect of $NH_3:H_3PO_4$ mole ratio on solubility in the system $NH_3–H_3PO_4–H_2O$.

Product discharged from the granulator is dried with moderate heat to a 180 to 190°F product temperature. Higher drying temperatures must be avoided because of a relatively low melting point for DAP. Most plants screen hot and cool only the product fraction because the material is not too sticky for recycle without cooling. Rotary coolers or fluidized-bed–type coolers are used. The product, with a moisture content of 1.5 to 2 percent, does not require a conditioner. It has excellent storage and handling properties in bags or in bulk. It has been shown that the iron and aluminium phosphate impurities in the product are present in a gel-like structure that favorably hardens the granules and increases their resistance to moisture.[21] The critical relative humidity of diammonium phosphate made from wet-process acid is about 70 percent; thus it is relatively nonhygroscopic.

Construction materials other than mild steel are required only for the acid lines, the preneutralizer, the slurry handling system, and the scrubbing circuits. Type 316L stainless steel or rubber- and brick-lined mild steel is used for the preneutralizer. Type 316L stainless is used also, for the slurry pumps and piping. Fiberglass-reinforced polyester plastic and high-density polyvinyl chloride sometimes are used for wet-process acid pipes and for scrubbers. Scrubbers also may be constructed of rubber-lined mild steel.

Monoammonium Phosphate (MAP). "Diammonium Phosphate," "DAP," and the grade designation "18-46-0" have become extremely familiar terms in the world fertilizer industry. However, substantial interest has developed also in fertilizer use of monoammonium phosphate, $NH_4H_2PO_4$. Agronomically, MAP is favored where soils are mainly alkaline, for example, in Canada and Pakistan. From an economic standpoint, the relatively high P_2O_5 contents of typical MAP grades (11-52-0 to 10-54-0) make them attractive where the primary interest is in producing and shipping phosphate; the MAPs provide a higher P_2O_5 payload than does DAP. In the year ending June 30, 1990, granular monoammonium phosphates applied to the soil directly or in dry blends accounted for 17 percent of total U.S. fertilizer P_2O_5 usage. Smaller, additional amounts of MAP were used also, in formulating some granular mixed fertilizers and fluid mixtures.

TVA developed two comparatively minor modifications of the granular DAP process to allow production of granular MAP.[22] In one method, the acid is ammoniated to an $NH_3:H_3PO_4$ mole ratio of only about 0.6 in the preneutralizer and then to about 1.0 in the granulator drum. The 0.6 ratio is, like the 1.4 used in DAP production, a high-solubility point in the ammonium phosphate system (Fig. 11.12); the subsequent ammoniation to 1.0 in the granulator decreases solubility and thus promotes granulation. In the other procedure, which has been preferred by the industry, acid in the preneutralizer is ammoniated to the high-solubility $NH_3:H_3PO_4$ ratio of about 1.4, as in DAP production; then, additional wet-process acid is distributed onto the bed in the granulator to adjust back to the low-solubility MAP mole ratio of about 1.0. With either modification, the remainder of the process is the same as for DAP, except that, because of the higher temperature stability of MAP, a higher drying temperature can be used to increase the production rate for MAP.

Starting about 1968, simple processes were developed for production of nongranular (sometimes called powdered) MAP. Chief developers were Fisons and Scottish Agricultural Industries (SAI) in the United Kingdom, Swift in the United States, and Nissan in Japan. These processes involve variations in the simple reaction of wet-process acid with ammonia followed by spray-type drying with air. Based on this work, a number of comparatively low-cost units for production of nongranular MAP have been built commercially, including plants in the United Kingdom, the Netherlands, Japan, Australia, Spain, United States, Brazil, and Iran. This intermediate usually is shipped to other plants, where it then is used in the production of NPK solid or fluid fertilizers. Thus far, however, the nongranular MAP has not attained the popularity that was predicted for it in the mid-1970s.

POTASSIUM SALTS*

The element potassium has been recognized to be beneficial to plant growth since J. R. Glauber in the Netherlands first proposed, in the middle of the seventeenth century, that saltpeter (KNO_3) was the "principle" of vegetation. This salt, derived from the leaching of corral soils, was thus the first chemical compound intentionally applied to crops to satisfy their nutrient needs. Justus von Leibig had established the essentiality of the element for plant growth in his pioneer work published in 1840. The potassium or potash chemical industry dates from the year 1861, following the discovery by German chemists of a process for recovery of KCl (muriate of potash) from rubbish salts, the residues remaining from the extraction of sodium chloride (NaCl). World consumption of K now exceeds 28 million metric tons of K_2O equivalent annually. About 93 percent of this is consumed in fertilizers, the balance going to process use in industry.

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*Sections on potassium were written by Dr. John A. Stewart, Libertyville, IL.

The functions of potassium in the plant are manifold. This element serves to activate or catalyze a host of enzyme actions, to facilitate the transport of nutrients and assimilates in the xylem and phloem, to maintain the structural integrity of the plant cell, to regulate turgor pressure, to mediate the fixation of nitrogen in leguminous plant species, and to protect plants to some degree from certain plant diseases. Plants affected by a deficiency of potassium usually are stunted and spindly, and exhibit a rather distinctive chlorosis and necrosis that is most prominent in the lower leaves (see Fig. 11.13). Crop yields may be severely reduced.

Potassium is a relatively abundant element in the earth's crust, ranking seventh in concentration. It is widely distributed geographically and is commonly found in association with sodium compounds. The feldspars, muscovite (white mica), granite, and gneiss are rich sources; but because they are siliceous and refractory, they are difficult and costly to convert to forms suitable for use as fertilizers. The common potassium minerals are listed in Table 11.3.

In the trade, potassium-containing compounds or salts that are applied primarily as a source of this nutrient or that find use in industry are referred to as potash. The name derives from an early production method in which potassium carbonate, leached from wood ashes, was crystallized by evaporating the leachate in large iron pots. The salt potassium chloride (muriate, muriate of potash, or KCl) is now the major source of the element (95%); other important salts are potassium sulfate (potassium sulphate, K_2SO_4, or sulphate of potash), potassium magnesium sulfates of varying K/Mg ratios, and potassium nitrate (KNO_3). The fertilizer industry expresses the potassium content of fertilizer salts in terms of the potassium oxide (K_2O) content, not as the K content. Muriate thus contains 60 percent+ of K_2O—which equates with 49.8 percent+ of potassium (K).

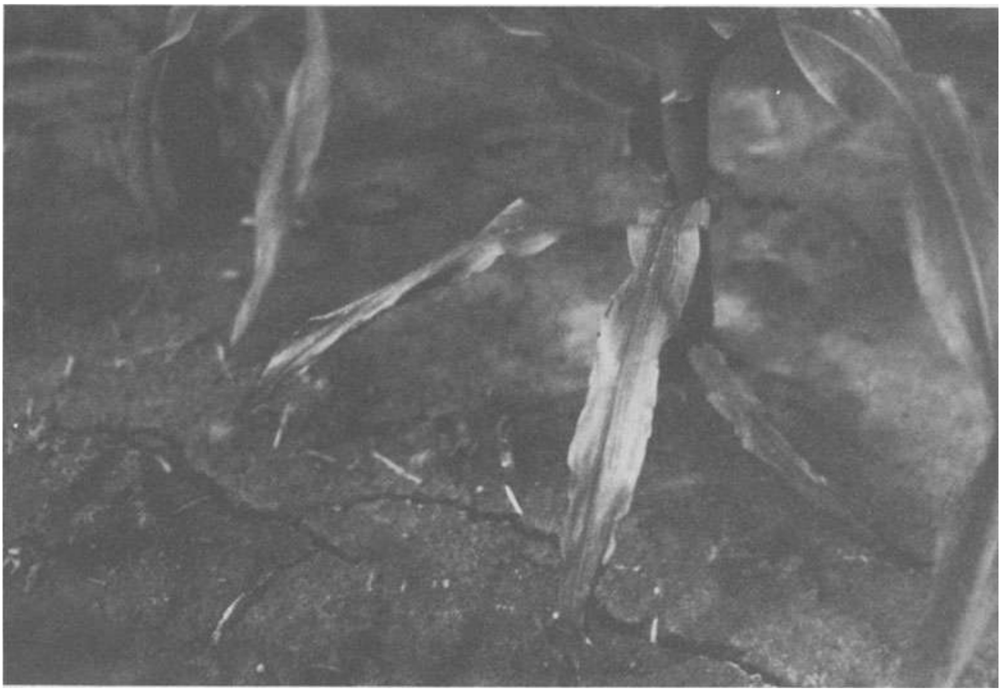
The potash industry is based on very large deposits of water-soluble potassium minerals resulting from the evaporation of shallow seas or natural brine lakes over a geological time span. These evaporites normally are located at depth in the earth's mantle. Ironically, the best deposits are found in areas quite remote from the more productive agricultural regions, which thus are the areas most in need of this element. Typically the deposits are to be found in horizontal tabular bodies or beds and may occur at depths up to 2100 meters or more. The beds may be only a few centimeters to a few meters thick, but commercial production is limited to strata that are at least one meter thick. As with hard-rock mining, the potash-bearing ores are extracted or harvested with continuous mining machines and brought to the surface through vertical shafts. Where the ores occur below a depth of about 1100 meters, or where the beds exhibit geological anomalies (e.g., folding), the potash is dissolved in a brine solution and pumped to the surface for recovery using solution mining techniques.

Potassium Minerals

The ore zone or stratum typically contains potassium or potassium–magnesium minerals along with halite (sodium chloride). Muriate of potash (M-O-P in the trade) is refined from sylvinite ore, a mechanical mixture of potassium chloride (KCl) and sodium chloride (NaCl). Because the latter salt is injurious to most crop plants, the KCl (sylvite) must be separated from the NaCl (halite).

For coarse-grained ores, physical methods employing froth flotation and/or heavy-media methods are employed to achieve separation. The heavy medium may consist of, for example, pulverized magnetite in a brine solution. The specific gravity of the medium is adjusted so that it falls between that of KCl (1.99 h/cm^3) and that of NaCl (2.17 g/cm^3).

When the crushed ore is placed in this medium, the K values are floated off, and the contaminating Na values sink and are drawn off and rejected from the bottom of the flotation vessel. Entrapped magnetite from both the product and waste streams is easily recovered magnetically and returned to the flotation vessel.



(A)

(B)

Fig. 11.13. Photographs of corn (A) and soybean (B), showing symptoms of potash deficiency.

TABLE 11.3 **Common K Minerals (Zandon)**

Mineral	*Formula*	*K Content*	*K_2O Content*
		$g\ kg^{-1}$	
Sylvite	KCl	524.4	631.7
Carnalite	$KCl \cdot MgCl_2 \cdot 6H_2O$	140.7	169.5
Kainite	$KCl \cdot MgSO_4 \cdot 3H_2O$	157.1	189.2
Langbeinite	$K_2SO_4 \cdot 2MgSO_4$	188.5	227.0
Leonite	$K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$	213.3	256.9
Schoenite	$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$	194.2	233.9
Polyhalite	$K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$	129.7	156.2

Source: Stewart, J. A., in *Potassium in Agriculture*, R. D. Munson (Ed.), p. 83, ASA-CSSA-SSSA, 1985.

In froth flotation the crushed ore, which has been scrubbed to remove contaminating clay particles, first is treated with an aliphatic amine acetate and a froth-promoting alcohol. The water-repellent amine acetate is attracted preferentially to the sylvite particles. In a subsequent step the ore or pulp is maintained in suspension, and the coated sylvite particles are attracted to and entrained on the rising air bubbles generated by the flotation agitator. They rise to the surface and are collected by hydraulic and mechanical means. The K-depleted pulp then is discarded. The sylvite or muriate is collected, centrifuged to remove the hydraulic medium, dried, screened into various particle size ranges, and sent to storage. Figure 11.14 shows a modern potash mine/refinery operation.

Potassium–Magnesium Minerals

Other important sources of K for fertilizer use are the double salts kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$) and langbeinite ($K_2SO \cdot 2MgSO_4$). The former is recovered from potash mines in Germany and Sicily; the latter is recovered and processed from mines in New Mexico (U.S.A.). These minerals supply important quantities of both magnesium and sulfur as well as potassium, and all are essential nutrients for plant growth. Kainite has a theoretical composition of 15.99 percent K (19.26% K_2O), 9.94 percent Mg, and 13.11 percent S, and langbeinite contains 18.85 percent K (22.7% K_2O), 11.71 percent Mg, and 23.18 percent S.

In the processing of langbeinite, the contaminating chlorides (NaCl, KCl) are removed by extracting the crushed ore with water. Centrifugation, drying, and screening follow to prepare the product in various size grades for the market. Where the mixed ore contains recoverable quantities of KCl as well as langbeinite, froth flotation and heavy-media methods may be employed to recover both K-containing salts.

Potassium Sulfate

Sulfate of potash (K_2SO_4 or SOP), unlike the earlier-discussed potash salts, does not occur as natural deposits. It can be recovered by fractional crystallization from the natural brines such as those of the Great Salt Lake in Utah, and Searles Lake in California. Here separation and recovery are achieved by solar evaporation in shallow ponds. These processes can be utilized only where a suitable brine source is available, and where solar evaporation rates are high.

A much more important source of K_2SO_4 is the product resulting from either a controlled decomposition reaction of a complex sulfate salt, reaction of the salt with KCl, or both. Thus kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$) may be reacted with water in a two-step reaction, first to form schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$), with the schoenite then reacted with KCl to form K_2SO_4.

Langbeinite likewise is reacted with KCl to form sulfate of potash, according to the

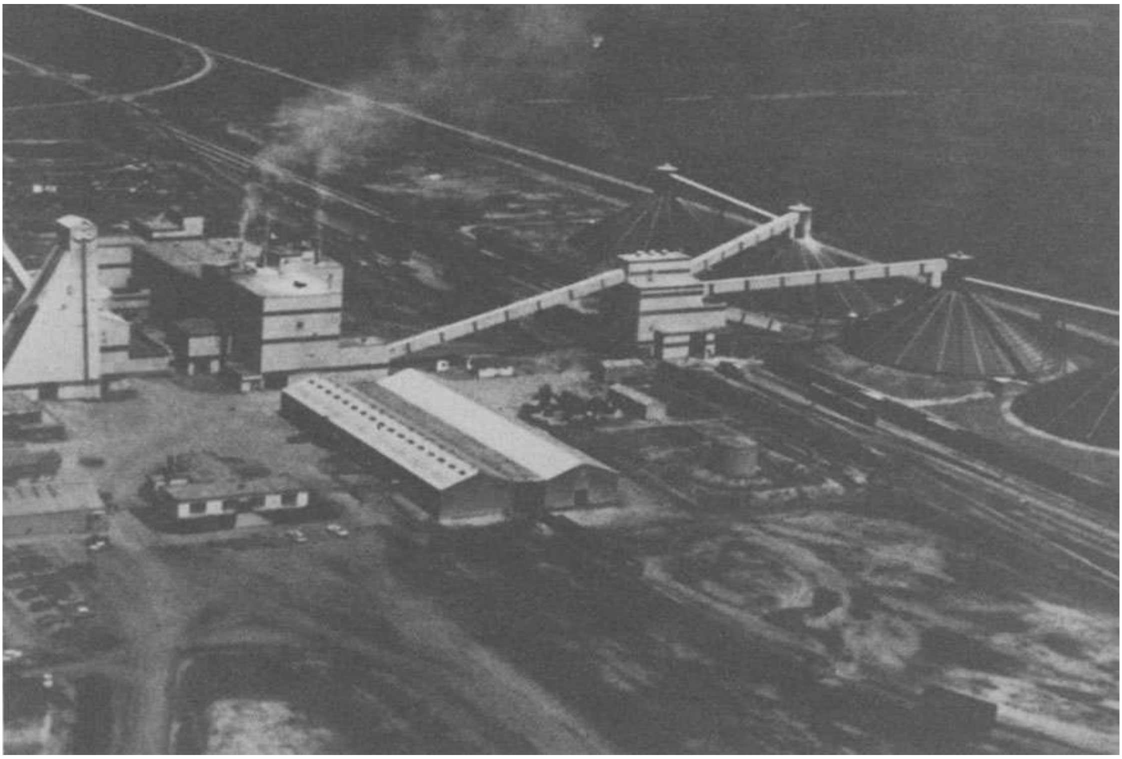


Fig. 11.14. Aerial view of IMC Fertilizers, Inc. potash mine/refinery at Esterhazy, Saskatchewan. Included in the photo are the head frame, cone storage buildings, and rail shipping facilities. The mine workings are 955 meters beneath the surface. (*Courtesy IMC Fertilizers, Inc.*)

following reaction:

$K_2SO_4 \cdot 2MgSO_4$	+	$4KCl$	→	$3K_2SO_4$	+	$2MgCl_2$(solution)
langbeinite		potassium chloride		potassium sulfate		magnesium chloride

Approximately 50 percent of world K_2SO_4 production is derived from the reaction of KCl with either kainite or langbeinite.

For those producers who do not have access to such suitable sulfate salts to serve as the sulfate donor, the so-called Mannheim process, in which sulfuric acid is reacted with KCl, may be utilized. The following reaction unfortunately generates the corrosive substance hydrochloric acid as a coproduct:

$2KCl$	+	H_2SO_4	→	K_2SO_4	+	$2HCl$
potassium chloride		sulphuric acid		potassium sulfate		hydrochloric acid

Potassium sulfate, though relatively costly to produce, is a preferred source of K for some vegetable and fruit crops and tobacco—crops that are sensitive to the chloride forms.

Potassium Nitrate

This salt is produced in small amounts commercially in the United States, Israel, and

Norway by the reaction of KCl with nitric acid. Though the salt is an attractive fertilizer material, containing the two essential nutrients nitrogen and potassium in plant-available form, it is expensive to produce and thus enjoys only a limited market. Small amounts of a crude potassium nitrate also are marketed from natural deposits of caliche ($NaNO_3$) in Chile.

Potassium Phosphates

The production of such salts would seem to be a desirable objective because plant needs for both potassium and phosphate would be satisfied. Phosphoric acid can be reacted with KCl to produce the products, but in practice this route is not economical because energy use is high, reagents of high purity must be employed, K losses in the process can be severe, and the corrosive HCl coproduct demands the use of expensive corrosion-resistant equipment. Further it might fairly be asked whether such highly refined products can be justified for application to the soil. Such products intended for general agricultural use were produced in the United States some years ago, but their production now has virtually ceased.

MIXED FERTILIZERS

Preceding sections of this chapter have described the production of nitrogen fertilizers, phosphate fertilizers, and potash fertilizers from basic raw materials. Application of any of these fertilizers singly to the soil, without further processing, is referred to as "direct application." In the year ending June 30, 1990, only about 60 percent of the total fertilizer applied in the United States was applied directly; the remaining 40 percent was applied in the form of "mixed" fertilizers, that is, fertilizers that contain more than one of the major plant nutrients N, P, and K.[9] A breakdown by plant nutrient is as follows:

	% of Nutrient Applied by Indicated Method	
	Direct Application	*In Mixtures*[1]
Nitrogen	80	20
Phosphate	8	92[2]
Potash	65	35
Total nutrients	61	39

[1]Includes bulk blends.

[2]Includes ammonium phosphates applied alone.

These statistics show that for the phosphate fertilizers, application as mixtures (assuming the ammonium phosphates to be mixtures) far exceeds direct application, whereas for nitrogen fertilizers direct application far exceeds application in mixtures. For potash fertilizers, about 35 percent is applied as mixtures and 65 percent by direct application. The reasons for these patterns are both agronomic and economic. Agronomically, large applications of nitrogen alone—for example, in the "side dressing" of corn—often are of considerable importance. For phosphate, there usually is no similar agronomic need for single-nutrient application; so application in mixtures, with the resultant elimination of multiple handling, is preferred. Another factor, this one economic, that favors the direct application of nitrogen is the relatively low cost of anhydrous ammonia and nitrogen solutions, products that can be directly applied but ones whose use in mixtures is very limited. About 75 percent of the directly applied nitrogen is in the form of anhydrous ammonia, aqua ammonia, or nitrogen solution. The major solid nitrogen products (urea, ammonium nitrate, and ammonium sulfate), like the phosphate products, are used for the most part in mixed fertilizers, that is, in mixtures that contain two or more of the major plant nutrients (NPK).

Mixed fertilizers can be divided, by physical characteristics and production methods, into the following categories, all of which will be discussed in some detail:

- Nongranular mixtures
- Compound granulars
- Bulk blends
- Fluid mixtures

Nongranular Mixtures

Until about 1950, essentially all the mixed fertilizers available to farmers were of the nongranular type. Production was by simple batch weighing and blending of available N, P, and K ingredients, usually in locations that were convenient with respect to rail or water receipt of raw materials and out-shipment of bagged mixtures to dealers in farm areas. The source of phosphate almost invariably was nongranular ordinary superphosphate (OSP) produced at the mixing location from in-shipped phosphate rock and locally produced sulfuric acid. In-shipment of elemental sulfur was required to produce the acid, usually by the now obsolescent "chamber" process. The major nitrogen ingredient used in the mixtures was fine-crystal by-product ammonium sulfate, and the potash source was nongranular potassium chloride. In most plants, the superphosphate was "ammoniated" by reaction with ammonia solution, either in a separate operation before mixing with the other ingredients or during the mixing operation. Such ammoniation was beneficial in reducing the corrosiveness (acidity) of the superphosphate and in improving its physical condition. The ammonia also provided nitrogen at relatively low cost, but the amount that could be absorbed by the superphosphate was limited. Organic materials often were included in the mixtures as nutrient sources, bulking agents, or physical conditioners. Materials used included fish meal, packinghouse wastes, dried blood, tobacco stems, cotton seed hulls, and others. Mineral materials such as kaolin clay, diatomaceous earth, and vermiculite sometimes were included as conditioners. Batch-type drum mixers of 1- to 3-ton capacity were used, with the ammonia solution piped directly into the mixer. Mixture grades were low by present-day standards, and storage and handling properties of these nongranular mixtures were generally poor. Caking problems, in particular, were considerable. Production of this type of fertilizer now persists in only a few locations. The quantity produced in the United States is very small.

Compound Granulars

TVA Continuous Ammoniator-Granulator Process. Following the close of World War II in 1945, farmer demands developed for much increased quantities of fertilizer and for products with better handling properties. Granulation, which provides an increase in particle size and the elimination of fines, was a promising avenue for the physical improvement that was pursued by researchers in both the United States and Europe. A milestone in this movement to granulation was the development, patenting, and demonstration by TVA, in 1954, of a continuous rotary-drum granulation process for mixed fertilizers.[23,24]

A flow diagram of a plant employing this process is shown in Fig. 11.15. The rotary drum granulator in this process is essentially the same as was pictured for the diammonium phosphate granulation process. In early versions of the process, feed to the drum consisted of (1) crushed oversize product and fines, (2) nongranular ordinary superphosphate, (3) nongranular potassium chloride, (4) ammonium sulfate crystals, (5) sulfuric acid, and (6) anhydrous ammonia or an ammonia-containing nitrogen solution. The acid and the ammonia or ammoniating solution were sparged under the rolling bed of solids in the drum with a sparger arrangement, as shown in Fig. 11.16. With the proper balance of liquid and solid feeds, granulation occurs as a result of the rolling action in the drum, and it is completed, with hardening, in a rotary drum dryer.

This process was rapidly and widely adopted by mixed-fertilizer producers throughout the United States. By the mid-1960s the number of U.S. plants employing the process had

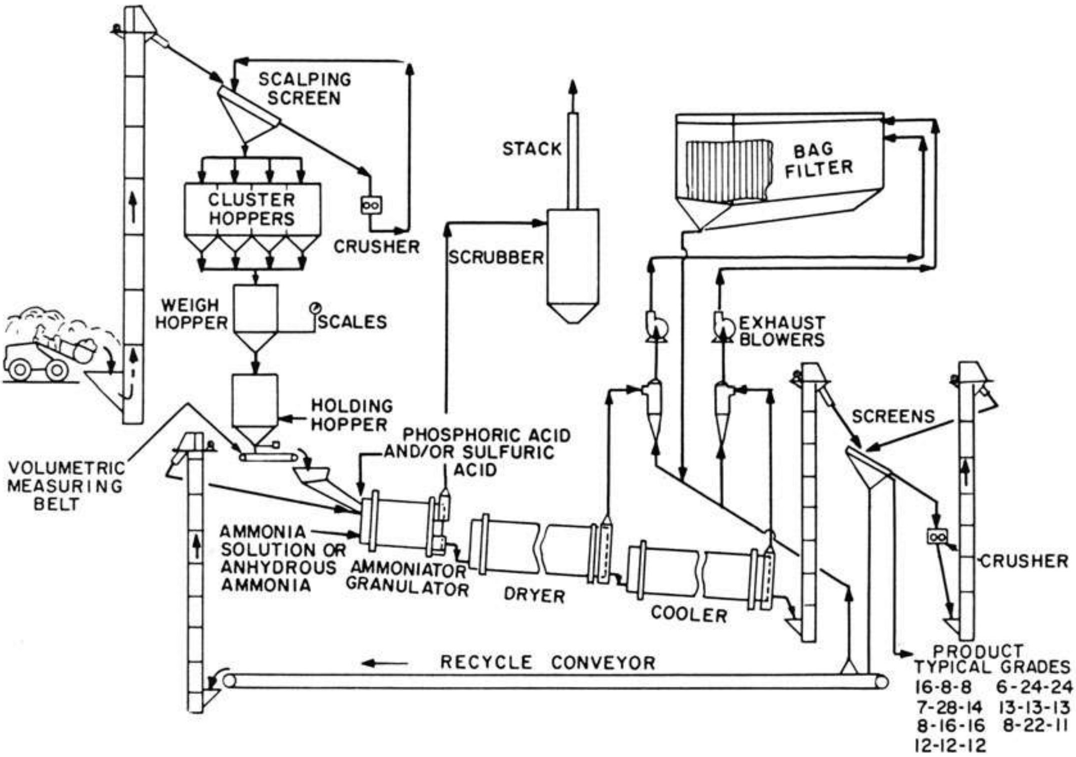
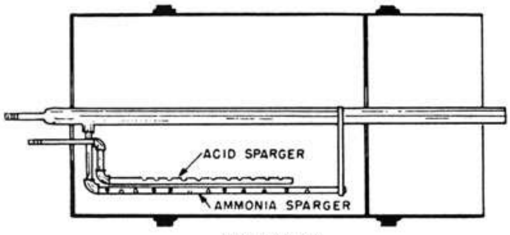
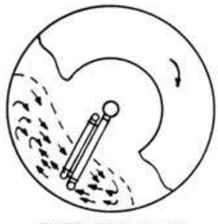


Fig. 11.15. TVA-type ammoniation–granulation plant for NPK mixed fertilizers. (Fertilizer Manual, *International Fertilizer Development Center, Muscle Shoals, AL, Courtesy TVA.*)



SIDE VIEW



FEED END VIEW

Fig. 11.16. Sparger location under rolling bed in TVA-type ammoniator–granulator. (Fertilizer Manual, *International Fertilizer Development Center, Muscle Shoals, AL, Courtesy TVA.*)

reached 200, with an average production rate of 100,000 tons/year per plant. The process was particularly attractive because: (1) the raw materials were essentially the same as materials that were already available at most batch-type nongranular plants, (2) higher proportions of relatively cheap anhydrous ammonia or nitrogen solution could be used, (3) continuous-type processing allowed higher production rates, and (4) product physical properties were much improved as a result of granulation. Today, the same basic process, but with numerous modifications, is used in most U.S. mixed-fertilizer granulation plants. However, the number of plants has dwindled to about 20, in favor of bulk blending and fluid fertilizers. One early modification to the process was the addition of phosphoric acid as a feed material, either along with or in place of sulfuric acid. Other feed materials used in some variations include triple superphosphate

(TSP), monoammonium phosphate, ammonium nitrate, and urea.

Use of a Preneutralizer (Slurry Granulation). A major improvement to the basic TVA granulation process was the incorporation in most plants of a preneutralizer vessel for prereaction of phosphoric acid with ammonia. This procedure, as applied to the production of granular diammonium phosphate (DAP), was described earlier and was pictured in Fig. 11.11. As in the DAP process, the preneutralizer used in the production of mixed fertilizers is operated at an NH_3:H_3PO_4 mole ratio of about 1.4 to give maximum ammonium phosphate solubility and thus maximum fluidity of the slurry pumped to the granulator. Subsequent further addition of ammonia in the granulator sharply decreases solubility, and thus promotes solidification and hardening of granules. As in ammonium phosphate production, the iron and aluminium impurities normally present in wet-process phosphoric acid contribute significantly to the hardening of granules during ammoniation.[21] Sulfuric acid, when used, is fed directly to the granulation drum, not to the preneutralizer. The use of the preneutralizer allows inclusion of higher proportions of acid in formulations. Also, better use is made of the heat of the ammonia–acid reaction for the evaporation of water, with resultant savings in dryer fuel.

Use of a Pipe Reactor (Melt Granulation). A more recent development that has been adopted in most U.S. granulation plants involves the substitution of a pipe reactor or a pipe-cross reactor for the preneutralizer vessel as the locale for the ammonia–acid reaction.[25–29] A simple pipe reactor differs from the pipe-cross reactor in that only one acid inlet port, usually for phosphoric acid, is provided.

The salient feature of the pipe reactor and pipe-cross reactor systems is that the heat of the ammonia–acid reaction is confined to the pipe and is efficiently utilized there to vaporize essentially all the moisture in the feed acid. The resultant steam exits the pipe discharge end, in the granulator, and is swept away in an air stream. The ammonium phosphate melt, which is of very low moisture content, also exits the pipe and is discharged onto the rolling bed of dry solids in the granulator. This melt serves as the binder for granule formation. The reaction temperature in the pipe reactor usually is held below 300°F to avoid a buildup of troublesome scale in the pipe. In view of this temperature limitation, there is little or no conversion of the phosphorus to polyphosphate forms. By allowing the pipe temperature to rise to 400°F or higher, polyphosphate can be formed without scaling, but this mode of operation seldom is used in mixed-fertilizer granulation. TVA has used such high pipe temperatures to produce 11-57-0 and 28-28-0 grade ammonium polyphosphate granules, in which 15 to 25 percent of the P_2O_5 is in polyphosphate form.[25] The physical properties of these products are exceptionally good, and the polyphosphate content makes them particularly suitable for dissolution to form fluid fertilizers. Because of the very low moisture content of the pipe reactor melts, even at the lower operating temperatures, the normally expensive drying of finished granular product usually is not needed; passage of the product through a cooler with an air sweep is sufficient for final drying. This results in a major fuel saving, which is a very significant economic advantage.

Pipe and pipe-cross reactors are being adopted by many plants; as of May 1990, about 15 were known to be in use in U.S. mixed-fertilizer granulation plants. Adaptability of the pipe reactor to DAP production is being explored, but is not yet firmly established.

Steam Granulation. A simple method for granulating dry mixtures of fertilizer materials was developed in Europe in the early 1950s and still is employed there to some extent. In this procedure, which is pictured in Fig. 11.17, the feed materials all are finely ground to ensure their incorporation in the granules. A dry mixture is made and then is moistened in a rotary drum or pan-type granulator with

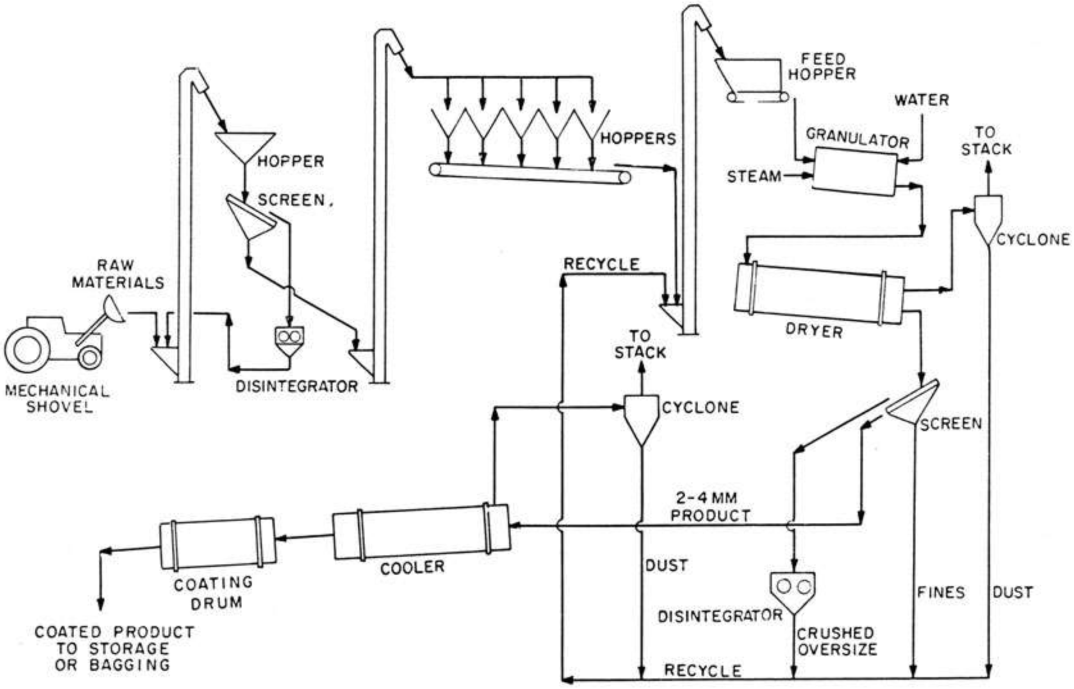


Fig. 11.17. Steam granulation process with feed of dry, pulverized fertilizer materials. (Fertilizer Manual, *International Fertilizer Development Center, Muscle Shoals, AL.* Courtesy TVA.)

either water spray, steam, or both. This added moisture forms a salt solution by partial dissolution of the mixture ingredients. The granules form because of the plasticity and rolling action in the granulator. Initially, these granules are very soft; but, with further rolling and drying in a subsequent drying operation, salt bridging imparts the required granule hardness. In contrast to the TVA ammoniation–granulation process, the steam granulation process usually causes no significant reaction between mixture ingredients. In Europe, this feature is of considerable significance when superphosphate is used as a feed material. Ammoniation of superphosphate, which occurs in the TVA ammoniation–granulation process, converts part of the water-soluble P_2O_5 content of the superphosphate to water-insoluble forms that are not accepted as marketable phosphate fertilizer in some European countries. This conversion, however, is mainly to citrate-soluble forms, which are accepted as effective, marketable phosphate forms in the United States.

Bulk Blends

History and Growth. In the "compound" (mixed) fertilizer granulation processes just described, the starting materials are N, P, and K materials in the form of (1) nongranular solids, (2) liquids, or (3) gas (ammonia). When N, P, and K materials are all available from basic producers in granular form, as they now are, granular mixed fertilizers of almost any nutrient proportion (grade) can be made by simple proportioning and dry blending of the granular N, P, and K materials; further granulation or other processing is not required. This is the basis of the presently popular "bulk blending" system of mixed fertilizer preparation and distribution.

As can be seen from Figure 11.18, this system, since 1960, has taken a considerable share of the U.S. mixed-fertilizer market away from the compound granulation plants. As of 1990, bulk blending was furnishing about 62 percent of the mixed fertilizer used in the United States, as compared to about 15

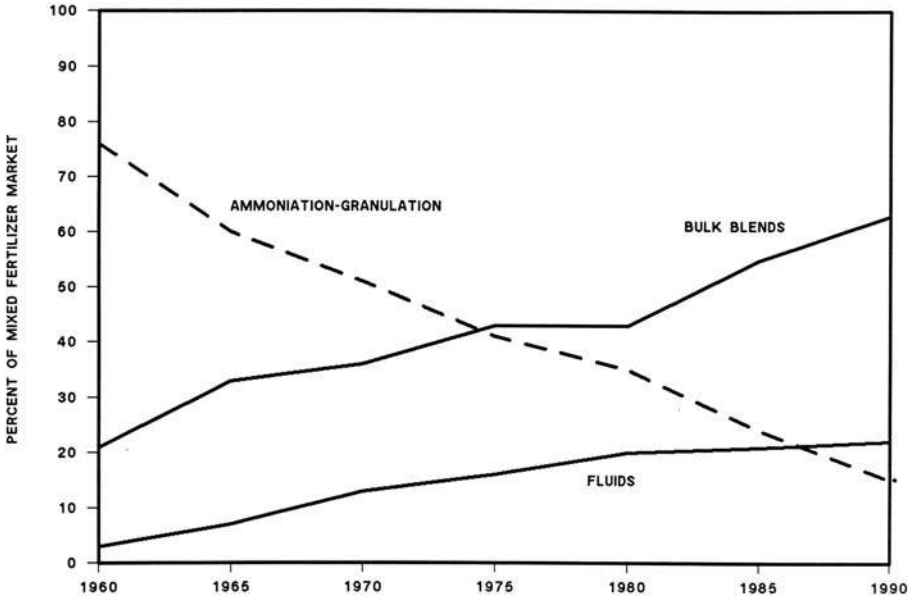


Fig. 11.18. Changing patterns in the mixed-fertilizer market. (*Courtesy TVA.*)

percent as compound granulars and 23 percent as fluid mixtures.

The simplicity of the bulk blending procedure is illustrated in Fig. 11.19. The operations consist of (1) in-shipment of granular fertilizer materials, (2) temporary storage, (3) proportioning, (4) blending, and (5) movement of finished blend to the field for spreading.

Key factors in the rapid growth of bulk blending have been: (1) convenience in providing the farmer a wide choice of plant-food ratios or grades on a "prescription" basis in relatively simple, small mixing plants located in the immediate farm area; (2) economy due to handling in bulk rather than bags; and (3) provision of spreading and other farmer services by the local blender.

In this streamlined production and marketing system, the bulk blender is the retail dealer. The blender's service area usually is limited to a 30-mile radius around his or her plant, thus enabling a close relationship with local

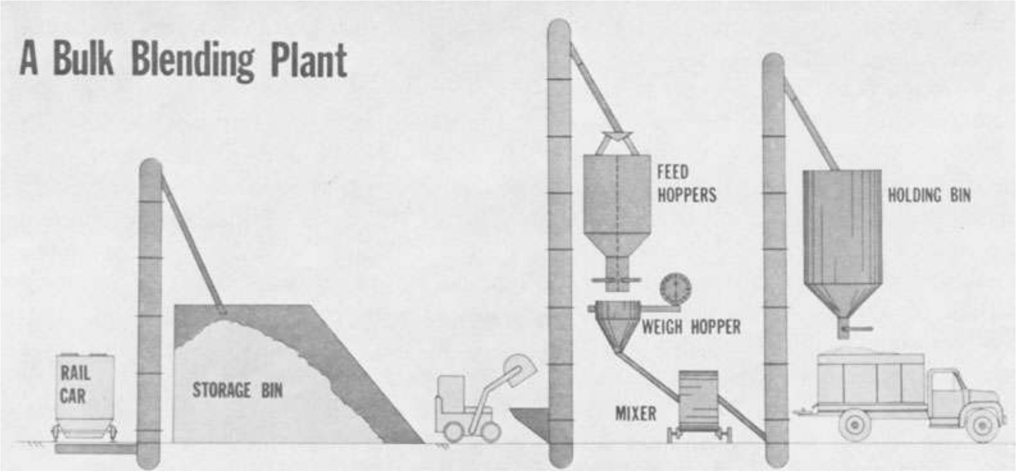


Fig. 11.19. Bulk blending—a simple concept. (*Courtesy TVA.*)

farmers. The blender usually transports the fertilizer to the farms and applies it, for a fee. In addition to preparing and applying blends, bulk blenders also market and apply single-nutrient direct-application fertilizers, frequently including anhydrous ammonia and nitrogen solutions.

Typical blending plants produce and market only 2000 to 6000 tons of blend per year, but there are over 5000 plants located throughout farming areas. There also are a few plants with a much larger annual production, designed to serve relatively large areas. The capital investment in blending plants is comparatively low, but most blenders have sizeable investments in application equipment. Blending plants operate on a quite seasonal basis, and often the operators have supplemental business enterprises.

Intermediates Used in Bulk Blending. The bulk blending system came into being only after suitable N, P, and K intermediates became available in granular form. In particular, the introduction of granular diammonium phosphate (DAP) of 18-46-0 grade in about 1960, as described in a previous section, was a major catalyst to bulk blending. Characteristics of that product that make it an ideal material for shipping and subsequent blending are: (1) a high plant food content of 64 percent, (2) high phosphorus content of 46 percent, (3) excellent storage and handling properties, (4) compatability with essentially all other fertilizer materials, and (5) economy of production near phosphate deposits. Most NPK bulk blends are prepared with DAP as the phosphate source. Granular triple superphosphate (TSP) is used for no-nitrogen (PK) grades, but for NPK blends TSP has the disadvantage of being incompatible (reactive) with urea.

In the preparation of bulk blends, it is of great importance to ensure that all ingredients of the blend are reasonably matched in particle size.[30] The use of unmatched materials results in poor mixing, segregation during handling, and uneven distribution on the field. Nitrogen materials used with the greatest success in bulk blends are (1) granular urea, (2) granular ammonium nitrate, and (3) large-crystal or granulated ammonium sulfate. Prilled ammonium nitrate also can be made of large-enough particle size for good blending, but prilled urea normally is of a smaller size than desirable. The chief potash material used in blends is granular-grade potassium chloride, which is sized specially by potash producers for use in blends. Although granular-size potash usually consists of irregular crusher fragments rather than well-rounded granules, studies have shown that this particle shape difference does not promote segregation or otherwise impair blend quality.[31] A somewhat smaller-size, coarse-grade potassium chloride sometimes is used in blends because it is cheaper, but segregation problems are invited. Potassium sulfate and potassium magnesium sulfate are made in granular form for the blending of specialized formulations.

The addition of micronutrients to bulk blends poses special problems because of the small quantities usually added. Although many micronutrients are available in granular form, intergranule spacing on the field can be excessive when the granular micronutrient constitutes only a very small proportion of the blend. Procedures have been devised and used for adding finely powdered micronutrients to blends together with a small amount of liquid binder.[32] The result is that each blend granule is coated with micronutrient, and the field distribution thus is better.

Operating experience and TVA studies have identified several combinations of materials that are incompatible in blends and should be avoided: (1) unammoniated superphosphates react with urea, and the result is wetting and caking; and (2) urea in contact with ammonium nitrate forms an extremely soluble hygroscopic mixture that liquifies in the presence of only minute amounts of moisture. Therefore, these two materials can never be used together in the same blend. Essentially all other combinations of available fertilizer materials are compatible in blends.

Equipment and Operating Technique. There are many different arrangements of equipment in the thousands of blending plants throughout the United States. The operations in such plants generally consist of: (1) receipt of the intermediate granular components in bulk by truck or railroad car, (2) storage of the intermediates separately in bins, (3) removal of the granular blend components from storage and weighing in desired proportions, (4) mixing to obtain uniformity, and (5) discharge of the mixed batch directly into a spreader truck or into a holding bin. The most popular type of mixer is the batch-type rotary drum.

Such mixing plants can be highly automated so that the output with a mixer of only one-ton capacity can be as much as 15 to 20 tons/hr. Mixers of several types are available with capacities up to 6 tons per batch.[33]

Problems in Bulk Blending. Bulk blending is a simple practice that can provide uniform mixtures in almost any desired proportions. However, unless proper materials are used and certain handling precautions are taken, segregation can occur, and nonuniform blends will result. In general, the blend-plant records of conformance to state analytical requirements have not been as good as those of compound granulation plants.[34] The factors involved and the precautions that are necessary have been described by TVA.[35] The main requirements are the use of granular materials with a well-matched range of particle size and the handling of the mixture after blending in ways that will minimize segregation. The mixing step is seldom a problem; it is quite easy to obtain a uniform blend by the use of proper materials and a few minutes of mixing. However, maintaining this uniformity during handling on the way to the farm and onto the soil requires precautions. Handling procedures that may cause segregation include coning (as occurs if the blend is allowed to drop from a discharge pipe onto a pile), vibration in hauling vehicles, and ballistic action imparted by some types of spreaders.

The problems of adding small quantities of micronutrient materials to bulk blends was mentioned earlier. This problem is being met by either using micronutrients in granular form or coating the blend particles with finely ground micronutrients and a liquid binder.[32]

Fluid Mixtures

Mention was made earlier of the significant quantity of nitrogen applied to farm lands in the form of urea–ammonium nitrate solution and aqua ammonia. Since the late 1950s, there also has been a growing practice of applying mixed fertilizers (NP and NPK) in fluid form. The growth curves in Fig. 11.18 show that by 1990 fluid mixtures had claimed about 23 percent of the mixed-fertilizer market. This growth paralleled the growth of bulk blending, at the expense of the compound-granular-type products. It is expected that, in the future, bulk blending and the production of fluids will continue their parallel growth patterns.

Numerous advantages have been cited[10] to explain the growth of fluid mixed fertilizers. Of these, the most significant is probably the ease and the precision with which fluids can be applied to the soil. When placement of the fertilizer is important, as in row fertilization, fluids often have an advantage. Also important is the adaptability of fluids to the homogeneous incorporation of micronutrients, herbicides, and insectiides. Another factor that encouraged the adoption of fluid mixtures was the prior existence of equipment and facilities for handling and applying nitrogen fluids; it was only logical for this practice to be expanded to include preparation and application of mixtures. There are some claims of agronomic superiority for fluid fertilizers over similarly applied solids, but such claims are debatable and are not widely accepted.

Solution Fertilizers. Fluid fertilizers in use today can be divided into two major categories: (1) solutions, in which the plant food content is entirely in solution; and (2) suspensions, in which the plant food content exceeds its solubility, and the excess is held in suspension, usually by addition of a suspending agent. The solution-type mixtures were the first to achieve commercial importance. Beginning about 1950, the practice of making solution mixtures was begun, with pure electric-furnace orthophosphoric acid (54% P_2O_5) as the source of phosphorus. Ammoniation of this acid yielded an 8-24-0 grade ammonium orthophosphate solution that could be shipped to mixing plants in farm areas and used as a base for blending with other fertilizer materials. Blending usually was with urea–ammonium nitrate solutions (28–32% N) and a pure grade (solution grade) potassium chloride.

With the system that employed these raw materials, numerous advantages of fluid mixtures were established, but a need to improve the economics of the procedure was obvious. Pure electric-furnace acid is much more expensive than wet-process acid, so ways were sought to use the cheaper but impure wet-process acids. Direct ammoniation of wet-process acid causes precipitation of numerous impurities as an intolerable, gelatinous sludge. Also, plant-food solubilities are undesirably limited in the orthophosphate system, so the concentration (grade) of the product made with electric-furnace orthophosphoric acid was limited to 8-24-0. A series of developments by TVA led the way to solving both of these problems.

The problem of limited plant-food solubility was much alleviated by TVA's introduction of superphosphoric acid in 1957.[36] Superphosphoric acids are acids of high P_2O_5 content (up to 80% P_2O_5) that contain significant proportions of polyphosphates (non-ortho, polymerized phosphates). The data in Fig. 11.20 show the favorable effects of polyphosphate on plant-food solubility in ammoniated phosphoric acids. The superphosphoric acid first produced by TVA was a pure electric-furnace product of 76 percent P_2O_5 content, of which about 50 percent was in polyphosphate form. With ammoniation of

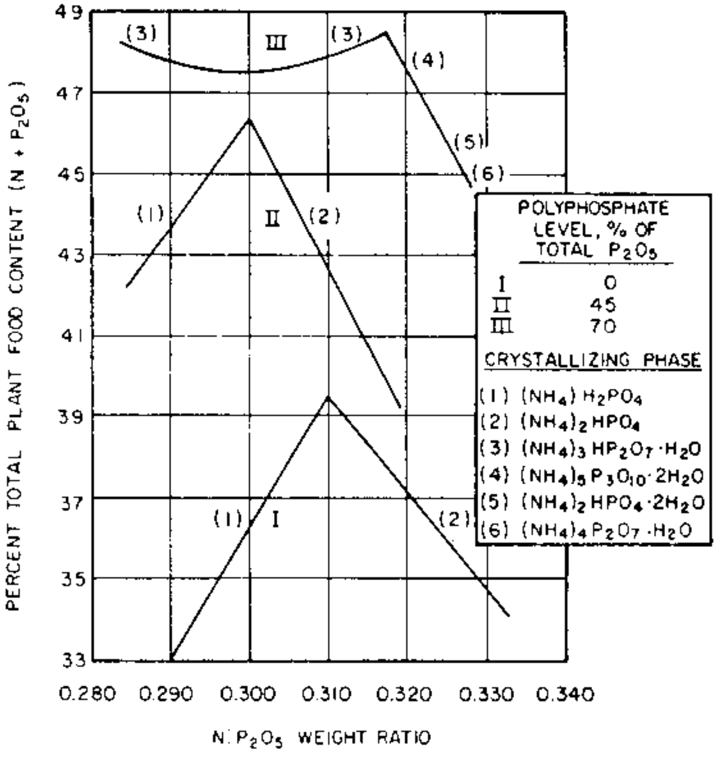


Fig. 11.20. Effect of polyphosphate level and $N:P_2O_5$ weight ratio on solubility of ammoniated phosphoric acids at 32°F. (*"Fluid Fertilizers,"* TVA Bulletin Y-185, *p. 76. Courtesy TVA.*)

this acid, it was possible to produce an 11-37-0 grade base solution instead of the 8-24-0 grade maximum made from ortho acid. Demonstration use of 11-37-0 base in a number of mixing plants showed that solution mixtures of relatively high concentration could be made. Also, it was found that the polyphosphate content enhanced the solubility of micronutrient additives by a sequestering action.

The unfavorable economics of the electric-furnace acid process, however, discouraged the commercial production of electric-furnace superphosphoric acid; so attention was directed toward concentration of the cheaper wet-process phosphoric acid to give wet-process superphosphoric acid. Satisfactory concentration methods were developed,[37] but the effects of acid impurities on handling properties of the concentrated acids limited the final P_2O_5 concentration and hence the polyphosphate content. The best handling properties were obtained with acids made from calcined rocks and with P_2O_5 concentration limited to 68 to 70 percent P_2O_5. In acid of this concentration, from 20 to 35 percent of the P_2O_5 is in the polyphosphate form, and the acid is referred to as low-conversion superphosphoric acid. Such acid today is the chief source of P_2O_5 for solution-type fertilizers.

The most popular scheme by which solution-type fertilizers are made from low-conversion wet-process superphosphoric acid is outlined in Fig. 11.21. The first step is ammoniation of the acid to produce ammonium polyphosphate base solution. By carrying out this ammoniation in a TVA-developed pipe reactor, a temperature of over 400°F is developed, which promotes an increase in polyphosphate content to 65 to 70 percent of total P_2O_5 in the ammoniated acid.[38,39] The grade of the resultant base is usually 10-34-0; an 11-37-0 grade can be made, but its storage properties are not as good, especially in cold weather. A sketch of a typical TVA pipe-reactor system for production of high-polyphosphate base solution from low-conversion wet-process superphosphoric acid is shown in Fig. 11.22.

More than 125 U.S. plants use this TVA pipe-reactor process to produce an estimated 2 million tons of 10-34-0 or 11-37-0 grade product per year. Other countries such as Belgium, France, and the Former Soviet Union (FSU) also use this process to produce ammonium polyphosphate solution. A considerable amount of the solution is used for direct application in the U.S. wheat belt and other areas in which potassium is not deficient. The rest is used in small mix plants to produce mixtures. The ammonium polyphosphate base solution is mixed with nitrogen solutions containing 28 to 32 percent N (urea–ammonium nitrate solutions) and sometimes also with potash to produce such clear liquid grades as 21-7-0, 7-21-7, and 8-8-8. As with bulk blending, the solution mixing operation usually is carried out in small mixing plants located in farm areas.

Suspension Fertilizers. Suspension fertilizers were developed chiefly as a means of breaking the grade barriers imposed on solution fertilizers by solubility limitations. The low solubility of potassium chloride was particularly troublesome, in that high-potash solution grades were not possible.

The feasibility of preparing and handling suspension-type fertilizers was demonstrated by TVA and others in 1959.[40,41] Two essential requirements for the preparation of a successful suspension were shown to be: (1) small particle size of the suspended solids, and (2) the addition of a gelling-type clay as a suspending agent along with sufficient high-shear agitation to properly disperse the clay. The most satisfactory gelling clay is attapulgite, obtained in south Georgia and north Florida.[42] Attapulgite is a hydrated magnesium aluminium silicate, which is composed of needle-shaped crystals so small that they can be seen only with use of high magnification. In the dry state, these crystals bond together in bundles as larger particles. These bundles must be disrupted and the individual crystals freed before they can assume the structural arrangement that is characteristic of a gel. When this disruption of the crystal bundles is carried out in the presence of an electrolyte, such as any of the common fertilizer salts present in fluid fertilizers, the individual

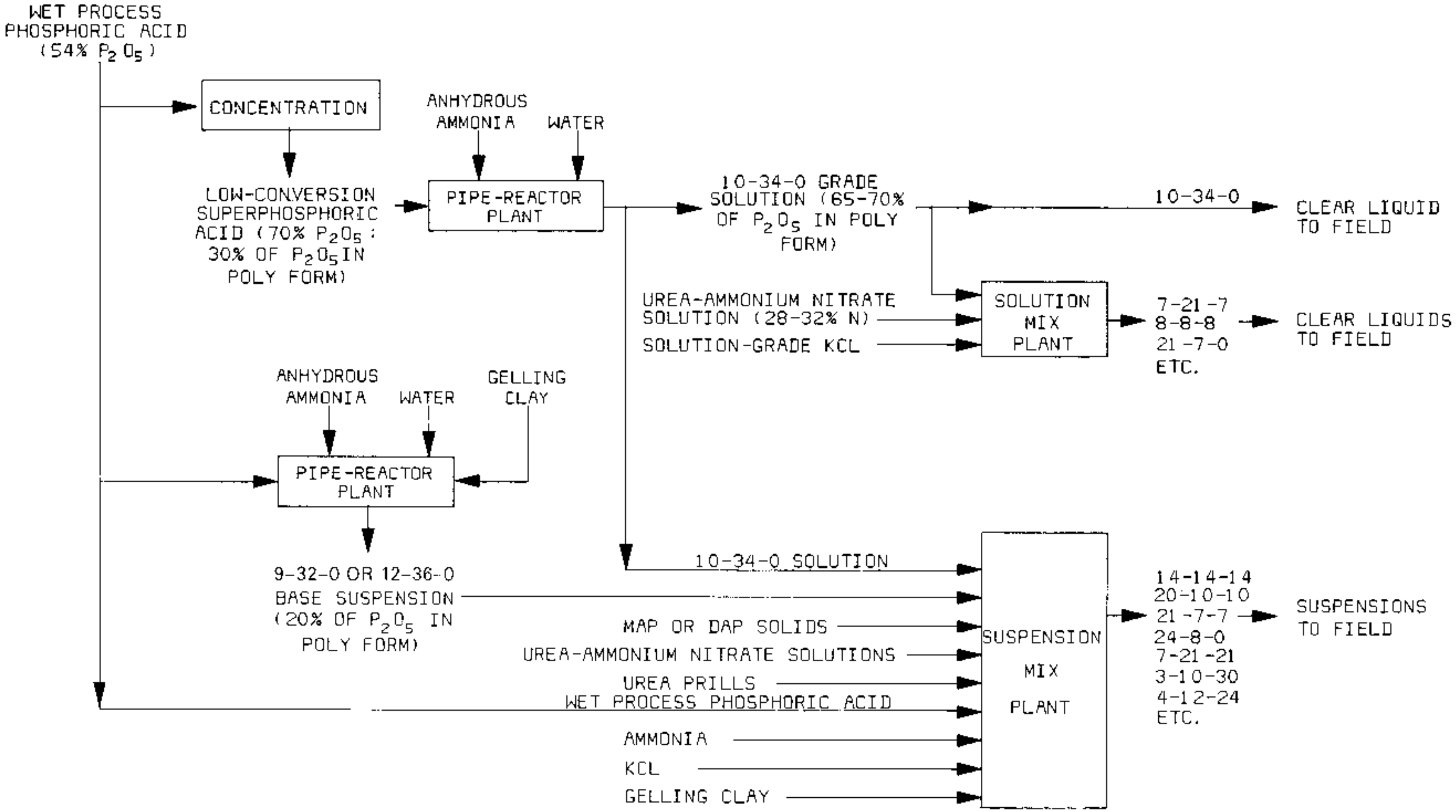


Fig. 11.21. Production methods for solution-type and suspension-type mixed fertilizers.

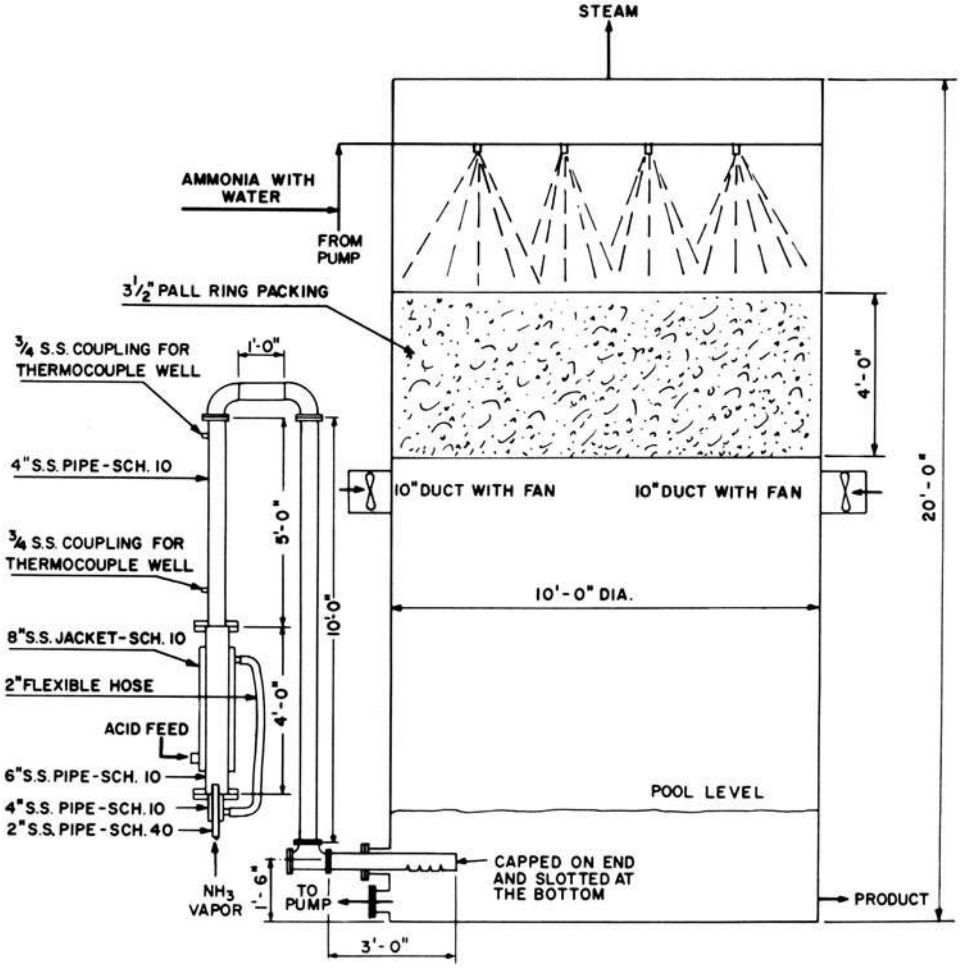


Fig. 11.22. TVA pipe reactor system for production of ammonium polyphosphate base solution from low-conversion superphosphoric acid. The product base solution is typically 10-34-0 with a 65–70% poly level. (*Courtesy TVA.*)

crystals immediately assume the regular structural orientation of a weak gel, and thus provide the desired suspending action.

Wetting of the clay by the fluid fertilizer causes some of the required disruption of crystal bundles and freeing of individual crystals, but not enough to provide good gelling without high-shear agitation. An addition of 2 to 3 percent of attapulgite is sufficient for most fertilizer suspensions. Instead of providing high-shear agitation for the entire batch of suspension, some operators carry out a pre-gelling operation in which high-shear agitation is applied only to the clay plus a limited amount of water or fertilizer solution. The pre-gelled mixture then is added to the major body of fertilizer with only mild mixing. Pre-gelled clay also is marketed as liquid clay and is transported in tank cars.

There is considerable variety in the types of fertilizer raw materials used commercially in preparation of suspension fertilizers. This is indicated in Fig. 11.21, where some of the more popular materials are listed. Likewise, production procedures and equipment vary considerably. Provision of a high-shear mixer is essential not only for gelling of the suspending clay but also for disintegration of

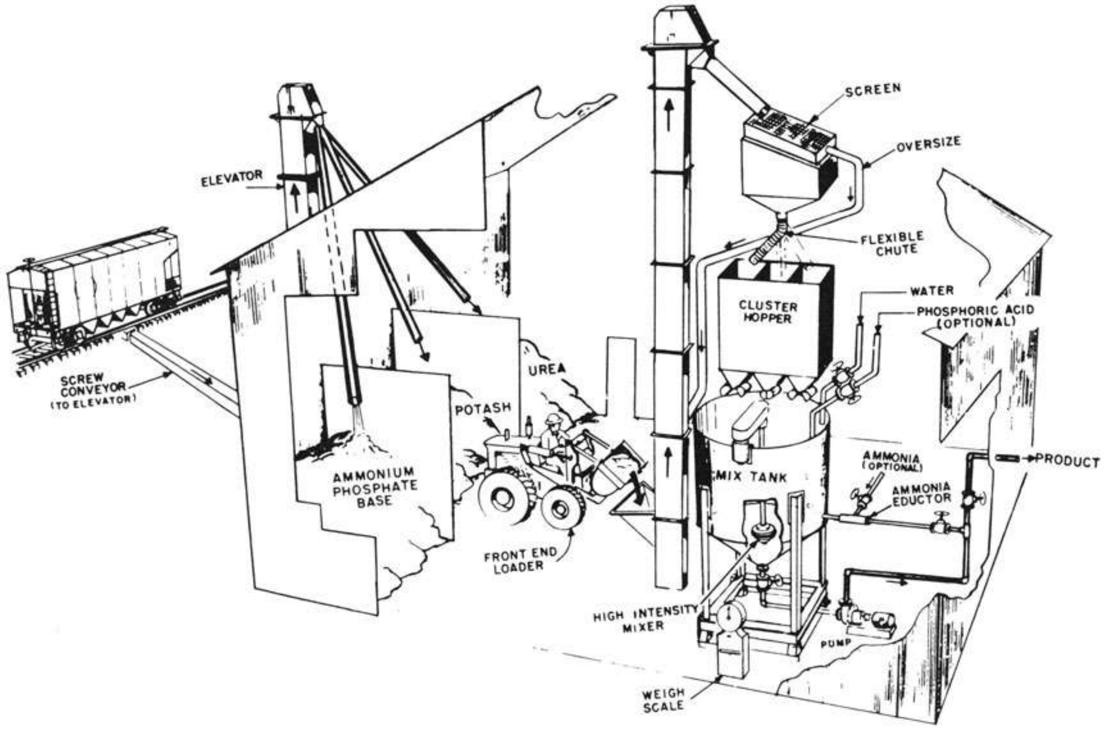


Fig. 11.23. Suspension fertilizer production using solid feeds (1–3% gelling clay also included in mix). (*Courtesy TVA.*)

any granular products such as diammonium phosphate or monoammonium phosphate that might be used in the suspension. A high-shear recirculation pump also is an aid to gelling of the clay.

Figure 11.23 shows the layout of a typical suspension mix plant in which all the major suspension ingredients are received as solids. This is presently a popular mode of operation. Raw material costs for such a plant often are less than for bulk blending because nongranular materials can be used. Piping for the optional addition of phosphoric acid and ammonia is shown. Such addition develops heat, which hastens the disintegration of some solids.

The storage and handling properties of suspensions can be enhanced by inclusion of some polyphosphate in the suspension. Low-temperature storage properties, in particular, are enhanced. One popular method of providing polyphosphate is to supply all or part of the P_2O_5 as 10-34-0 ammonium polyphosphate base solution, such as is used in solution fertilizers. A second method, shown as an option in Fig. 11.21, is the use of a pipe reactor to prepare 9-32-0 or 12-36-0 grade ammonium polyphosphate base suspension from relatively inexpensive wet-process orthophosphoric acid (54% P_2O_5), ammonia, and gelling clay. This process was introduced by TVA in 1982;[43] a flow diagram is shown in Fig. 11.24. About 20 percent of the P_2O_5 in the 9-32-0 or 12-36-0 product is in polyphosphate form. The clay content is 2 percent. When these base solutions are used for mixing with other suspension ingredients, their clay content often is sufficient to provide all the clay required in the final suspension. Commercial acceptance of 9-32-0 or 12-36-0 base suspension preparation has not yet occurred. At present, it apparently is most economical to furnish polyphosphate as 10-34-0 ammonium polyphosphate solution.

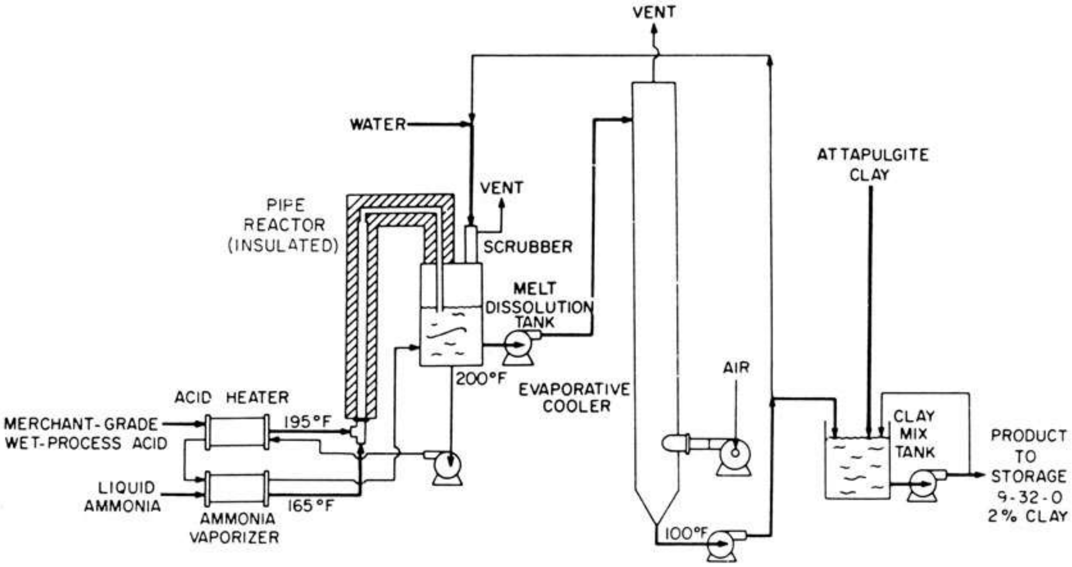


Fig. 11.24. TVA pipe-reactor process for production of 9-32-0 grade ammonium polyphosphate base suspension from wet-process orthophosphoric acid. (*"Fluid Fertilizers,"* TVA Bulletin Y-185, *p. 90. Courtesy TVA.*)

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12

Salt, Chlor-Alkali, and Related Heavy Chemicals

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SODIUM CHLORIDE

Common salt, sodium chloride, occurs in nature in almost unlimited quantities. It is a direct source of chlorine, caustic soda (sodium hydroxide), sodium chlorate, synthetic soda ash (sodium carbonate), sodium metal, and sodium sulfate. Indirectly, it is also the source of hydrochloric acid and a host of sodium salts. It has an imposing list of uses, placing it among the more important substances in the economic world. It is used to preserve meat, fish, and hides; it is a necessary component of the animal diet; it is used in refrigeration systems; and large quantities are used for ice control on highways in colder climates. Salt is used by the soap maker to separate soap from glycerine and lye, and by the dye manufacturer to precipitate dye products. In addition, salt is used extensively for the regeneration of water-softening resins (see Table 12.1).

Salt is mined as a solid in shaft mines with depths of 500 to 2000 feet, in Michigan, Ohio, New York, Kansas, Louisiana, and Texas. Run-of-the-mine salt contains 98 to 99 percent NaCl. Over 25 percent of the world's salt is produced in the United States.

More frequently, salt is obtained by solution mining. Typically, this is achieved by drilling a well into a salt formation, installing concentric piping into the well, pumping water in one pipe, and retrieving nearly saturated brine from the other pipe. The brine concentration is controlled by the rate of pumping and is kept slightly undersaturated to avoid salting up the brine lines at the wellhead. The brine is purified by chemical treatment, settling, and filtration. Such artificial brines permit a cheaper operating cost and are well adapted to the manufacture of synthetic soda ash, chlor-alkali products, and table salt.

Very extensive production of artificial brines is carried out along the U.S. Gulf Coast, principally in Texas and Louisiana, where huge domelike deposits of rock salt exist in readily accessible areas. Some of these domes are 4 miles in diameter and over 8 miles deep,[1] containing over 100 billion tons of salt each. In order to mine salt efficiently and safely and to utilize the subsequent cavern for storage,

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TABLE 12.1 1986 Uses of Salt (Millions of Short Tons) and 1992 Projected Demand[3]

	1986	*1992*
Chlor-alkali	19.0	10.0–20.5
Highway ice control	10.5	10.0–11.0
Food processing	1.2	1.0–1.5
Feed and mixes	1.3	1.4
Other chemicals	0.8	0.9
Industrial	1.8	1.9–2.0
Miscellaneous	8.7	9.0–9.5

tests are performed concerning the mechanical behavior of salt under the stresses of unequal and changing loads. Crude oil and processed hydrocarbons are conveniently stored in the caverns produced in these domes by solution mining of the salt. The hydrocarbons float on the brine within the cavern and are readily recovered by simply pumping brine back into the well. The Gulf Coast, with its salt and hydrocarbon deposits, deep water ports, and ready sources of energy, is ideally suited for the chemical manufacture of salt derivatives, especially chlorinated hydrocarbons.[2]

Artificial brines also are produced extensively from stratified salt deposits in Michigan, Ohio, New York, West Virginia, Ontario, and Western Canada. Much of the early chemical industry in North America was concentrated in these areas because of the availability of these brines and the need for salt in the production of soda ash, chlorine, and caustic. The stratified salt exists in layers 20 to 200 feet thick, associated with anhydrite ($CaSO_4$). The nature of these deposits is such that it leads to higher calcium levels in the brine when recovered by solution mining compared with the brine obtained from salt domes. In the vicinity of many of these stratified salt deposits, there also exist naturally occurring brines, which consist mainly of $CaCl_2$, with lesser amounts of $MgCl_2$, KCl, and NaCl, a few thousand parts per million of bromide and up to a few hundred parts per million of iodide. These natural brines are mined principally for their bromine content.

Salt also is derived from seawater in those places in the world, such as California, where solar evaporation is sufficient to concentrate the seawater in large basins until some of the salt deposits. The salt-based chemical industry in Asia and the West Coast of the United States derives its salt from solar evaporation, which accounts for about half the total world production (see Table 12.2).

TABLE 12.2 U.S. Salt Production in 1987 (Millions of Short Tons) and Unit Value of Shipments[3]

Evaporated salt	5	(\$93.00/ton)
Rock salt	12	(\$14.75/ton)
Brine	20	(\$4.50/ton)
Total	37	

Salt and other chemicals also are derived from naturally occurring brines, such as brine from Searles Lake in California, which typically contains 16.5 percent NaCl, 6.8 percent Na_2SO_4, 4.8 percent KCl, 4.8 percent Na_2CO_3, and 1.5 percent $Na_2B_4O_7$. Another source is the Great Salt Lake, with 27 percent salinity, of which 80 percent is NaCl.

At Searles Lake, the brine is concentrated in a multi-effect evaporator, from which NaCl is recovered. The process liquor is fractionated further to yield a KCl–borax concentrate and burkeite, a double salt of Na_2CO_3 and Na_2SO_4, which is processed still further to yield soda ash and salt cake (Na_2SO_4) as products.

The use of salt for ice control on highways is second only to the salt usage for caustic chlorine manufacture. In order to minimize damage to the environment, Germany has practiced the application of damp salt on highways. In this process, solid NaCl is dampened with $CaCl_2$ solution, which prevents the salt from being blown from the road and initiates the thawing process more quickly.

SODA ASH

Soda ash, sodium carbonate, is derived commercially from three sources, which are, in order of decreasing importance: (1) naturally occurring trona ore; (2) the Solvay ammonia-soda process; and (3) naturally occurring

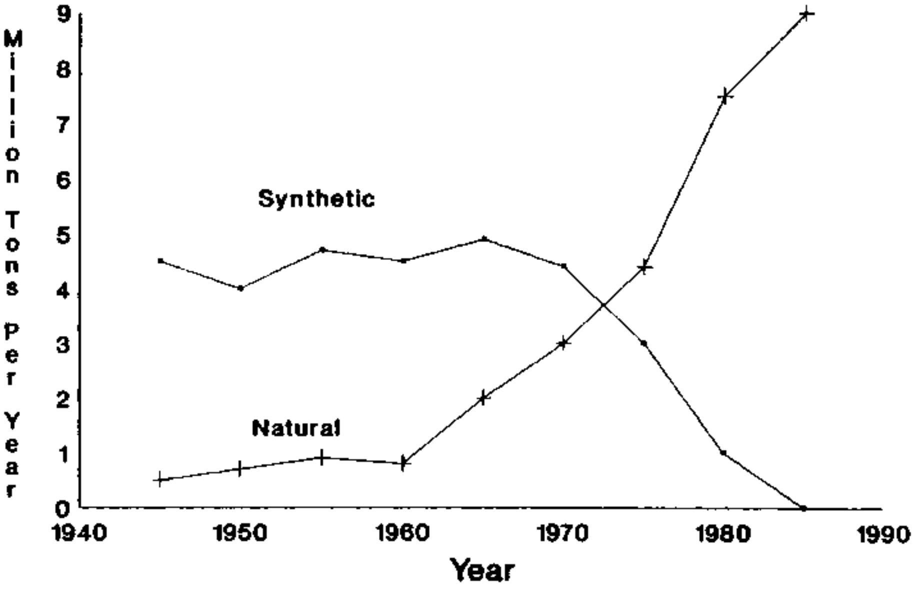


Fig. 12.1. U.S. production of synthetic vs. natural soda ash.[3]

alkaline brines. There has been a dramatic shift away from the synthetic or Solvay process ash in recent years, as is shown in Fig. 12.1.[3] No synthetic sodium carbonate has been produced in the United States since 1986. The Solvay process is still a major factor in ash production in Europe, but may decline there as well.

Like its predecessor, the Leblanc process, the Solvay process is on the decline for economic reasons. Increasing costs of production and environmental factors are the key issues in the many closings of synthetic ash plants in the last several years. However, a complete worldwide takeover by natural ash is doubtful because of two factors: (1) the limited amount of natural ash compared with the widespread availability of salt and limestone (the essential ingredients of the synthetic ash process); and (2) the locations of natural ash deposits relative to the locations of the ash consumers. Most of the U.S. natural ash is derived from the area of Green River, Wyoming. Significant amounts also are recovered from the alkaline brines of Searles Lake, California.

The synthetic ash process, or ammonia-soda process, was perfected by Ernest Solvay in 1865. The process is based on the precipitation of $NaHCO_3$ when an ammoniated solution of salt is carbonated with CO_2 from a coke-fired lime kiln. The $NaHCO_3$ is filtered, dried, and calcined to Na_2CO_3. The filtered ammonium chloride process liquor is made alkaline with slaked lime, and the ammonia is distilled out for recycle to the front end of the process. The resultant calcium chloride is a waste or by-product stream. The net overall chemical change in the process (shown schematically in Fig. 12.2) is represented by the following stoichiometry:

$$\begin{aligned}&CaCO_3\text{ (limestone)} + C\text{ (coke)} + O_2\text{ (air)}\\&\quad + 2NaCl\text{ (brine)} \rightarrow\\&\quad Na_2CO_3 + CO_2 + CaCl_2\text{ (brine)}\end{aligned}$$

The process requires a large amount of fuel to calcine both the limestone and sodium bicarbonate and to generate steam for ammonia recovery. For the reaction proper, no fuel is required. In fact, large volumes of cooling water are required to remove the heat generated by the absorption and reaction of ammonia and carbon dioxide. The process has an imperfection in that an undesirable solution of calcium chloride also is produced.

Prior to being fed to the process, the NaCl brine must be purified to remove calcium and

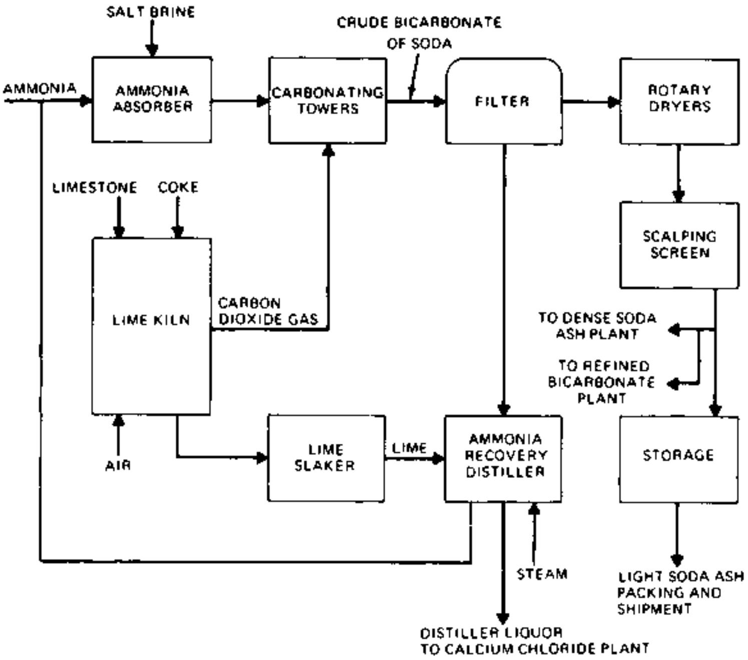


Fig. 12.2. Simplified diagrammatic flow sheet for the Solvay ammonia-soda process.

magnesium ions so that they will not be precipitated when the brine is carbonated, producing objectionable scale on equipment surfaces, as well as contaminating the product. A solution of soda ash and caustic is added to the brine to precipitate the calcium as $CaCO_3$ and the magnesium as $Mg(OH)_2$. These impurities are flocculated, removed in a settler, and discarded. The purified brine is fed to the ammonia absorber in the process.

Lime for recovering ammonia in the process and CO_2 for reacting with the ammoniated brine are produced by calcining the best available limestone with foundry coke in vertical shaft kilns. This type of equipment is preferred for producing the maximum yield of active lime and the maximum concentration of CO_2 in the kiln gas. The dry lime, drawn from the vertical kiln, is cooled by the entering air, which is thereby preheated. Likewise, for maximum fuel economy, the exiting gas preheats the incoming limestone and fuel. The gas composition should exceed 40 percent CO_2 with only factional percentages of CO and O_2.

The dry lime and hot water are fed to a rotating cylindrical slaker to produce milk of lime, which is pumped to the distillers for the recovery of ammonia.

The Solvay process recycles large quantities of NH_3, and it is necessary to minimize losses in scrubbing the various NH_3-containing gas streams. Thus, the incoming purified brine is used to wash the ammonia-bearing air, which is pulled through the bicarbonate cake on the vacuum filters. This is accomplished in a packed absorber. The brine then passes through a second packed section where it absorbs the NH_3 in the gases from the carbonating towers. The brine then flows to the main NH_3-absorber, which is also a packed tower. The brine is circulated through water-cooled heat exchangers to remove the heat of absorption. Ammonia, carbon dioxide, and small amounts of H_2S released in the distiller are absorbed in the packed tower. In addition, a small amount of makeup ammonia is added. A typical analysis of the cooled, ammoniated brine is:

Temperature	38°C
NH_3	90 g/l
CO_2	40 g/l
NaCl	260 g/l
H_2S	0.1 g/l

The total heat removed from the ammonia absorption is 1.25 million Btu per net ton of soda ash produced.

Next, the ammoniated brine is carbonated to a point just short of crystallization. Then the brine is given a final carbonation and cooled to produce the crude $NaHCO_3$ crystals. The equipment used in the carbonation step consists of groups of five identical towers having alternate rings and discs in the upper section to assure mixing of the falling liquor with the rising gas stream without plugging by the crystallizing solid phase. The lower section of each tower consists of a series of heat-exchanger bundles alternating with rings and discs.

The ammoniated brine is passed downward through one of the group of five columns, which has become fouled with sodium bicarbonate after operating as a crystallizing unit for several days. The 40 percent CO_2 gas from the kilns is pumped into the bottom of the column to provide agitation and heat in order to dissolve the crystalline scale and bring the liquor to a composition just short of crystallization. The liquor is adjusted to the desired temperature by passage through a heat exchanger in preparation for feeding to the crystallizing towers, and then it is fed into the top of each of the other four columns in the group.

A mixed gas of 60 to 75 percent CO_2 derived from mixing the 40 percent CO_2 from the kilns and the 90 percent CO_2 from the calcination of bicarbonate, is fed to the bottom of these crystallizing units. Absorption of CO_2 in the highly alkaline ammoniated brine results in crystallization of crude sodium bicarbonate. Because of the heat evolved in the absorption and neutralization of the carbonic acid gas and from crystallization of the sodium bicarbonate, the temperature of the liquor in the column rises from 38°C to a maximum of about 62 to 64°C. In normal operation, the temperature of the discharge slurry is maintained at about 27°C by automatic adjustment of the water flow through the cooling tubes. A tower such as that shown in Fig. 12.3 has a capacity for producing 50 tons/day of finished soda.

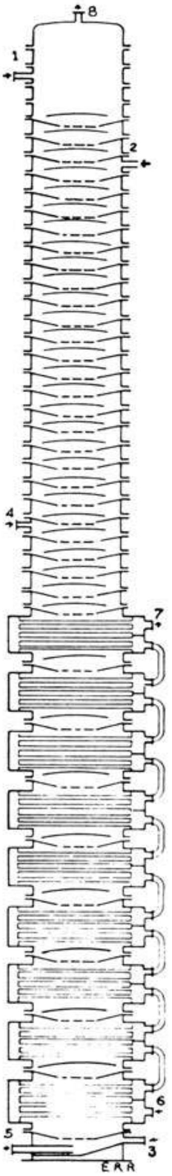


Fig. 12.3. A carbonating tower in the ammonia-soda process, 69 feet high and 6 feet in diameter. (1) Entry for ammoniated brine, used when the tower is being cleaned; (2) entry for the ammoniated brine for the regular bicarbonate precipitation; (3) and (4) carbon dioxide entries; (5) outlet for bicarbonate slurries; (6) cooling water inlet; (7) cooling water outlet; (8) escape for uncondensed gases. (*Modeled after Kirschner.*)

The heat removed from the carbonator is about 260,000 Btu/net ton of ash produced, whereas that removed from the crystallizing units is 1.25 million Btu/ton of product.

It is noteworthy that the presence of sulfide in the feed liquor to the towers serves to maintain a protective film of iron sulfide on the cast iron equipment, which minimizes the contamination of product crystals from iron corrosion products.

Slurry drawn from the crystallizing columns is filtered in rotary vacuum filters where the $NaHCO_3$ crystals are water-washed. The filtered liquor then flows to the distillation unit for recovery of ammonia. The crude bicarbonate filter cake contains 3 percent NH_4HCO_3, 12 to 15 percent H_2O, and 80 percent $NaHCO_3$.

Next, the liquor is pumped to the NH_3-still preheater. At this point, the sulfide solution required for corrosion protection is added. The preheated process stream enters a stripper where excess CO_2 is removed prior to treatment with lime and distillation removal of the NH_3. The hot liquor from the stripper flows to an agitated vessel, to which is added milk of lime to release NH_3:

$$Ca(OH)_2 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3 + 2H_2O$$

The lime-treated solution then is fed to the top of the bubble-cap distillation unit. Steam is injected at the bottom, stripping out the ammonia down to a residual level of only 0.001 percent.

The crude $NaHCO_3$ is calcinated in dryers constructed with rotating seals and gas-tight feed and discharge mechanisms, to ensure the production of CO_2 that is undiluted with air:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

The heat requirement is about 2 million Btu per ton of soda ash produced. Product from the dryers is cooled for shipment, or converted to other products. A typical analysis of good commercial light soda ash made by this process is:

Na_2CO_3	99.70%
NaCl	0.12%
H_2O	0.12%
Fe	15 ppm
Ca and Mg	75 ppm

TABLE 12.3 U.S. Consumption of Sodium Carbonate (Thousand Short Tons)[3]

Total exports	2224
Glass	3475
Chemicals	1300
Pulp and paper	200
Water and gas stack treatment	450
Soaps and detergents	650
Miscellaneous	515
Total	8814

The waste liquor from the process may be evaporated to produce by-product $CaCl_2$ and NaCl. However, the major portion is clarified and pumped into water courses whose natural flow is sufficient to provide the dilution needed for disposal.

Production of soda ash from trona ore mined in the Green River area of Wyoming is rapidly expanding. Two basic processes are used, involving dry mining of the ore from a depth of about 1500 feet. A third process based on solution mining of the ore has been developed. In the older dry-mining process, the ore is crushed and dissolved at the surface. Then the solution is purified by settling and filtration, followed by evaporative crystallization to form sesquicarbonate: $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$. The crystals are centrifuged off and calcined to ash in steam-tube dryers. In a more recent process the crushed ore is calcined immediately, then dissolved, purified, and evaporatively crystallized to sodium carbonate monohydrate, which is centrifuged and dried to product ash.

Relatively small quantities of soda ash are produced from alkaline brines at Searles Lake, California, by a process of fractional crystallization that also produces other sodium and potassium salts. Table 12.3 shows the current distribution of soda ash in the United States.

The 1990 contract price of soda ash at plants in Wyoming was about $93/ton.[6]

SODIUM BICARBONATE

Sodium bicarbonate is produced from a saturated solution of sodium carbonate by

TABLE 12.4 U.S. Consumption of Sodium Bicarbonate (1989) (Thousand Short Tons)[4]

Food	130–140
Animal feeds	85–90
Chemicals	40
Cleaning products	30
Pharmaceuticals/toiletries	20–25
Fire extinguishers	10
Other	35–40
Total	350–375

carbonation:

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$$

The precipitated bicarb crystals are centrifuged and then dried at low temperature to avoid reversion to carbonate.

Sodium bicarbonate also can be obtained by solution mining of natural sodium bicarbonate (nahcolite). In the mining procedure, pairs of well are sunk, warm water is pumped down one well, and dissolved sodium bicarbonate solution is pumped up from the other well. Solid sodium bicarbonate subsequently is crystallized from the solution.

The major use of sodium bicarbonate in North America is in foods as baking soda and as feed supplement for dairy cattle. Table 12.4 gives a breakdown of uses of $NaHCO_3$. The 1990 list price of $NaHCO_3$ was about 19 cents/lb.

SODIUM SULFATE

Production capacity for sodium sulfate, or salt cake, has remained fairly constant over the last decade, with the number of producing plants continuing to decline. Over half of the U.S. supply of Na_2SO_4 is produced from natural brines. Most of the remainder is by-product derived from the production of viscose rayon, sodium dichromate, and sulfonation process phenol. Salt cake produced in the manufacture of HCl from salt by the action of sulfuric acid (Mannheim process), or SO_2 and air (Hargreaves process), is on the decline.

TABLE 12.5 1986 Sodium Sulfate Production by Process[5]

Process	*Thousands of Tons*	*Percent*
Natural brine	396	48
Viscose rayon	136	17
Mannheim, Hargreaves	114	15
Dichromate, phenol, and other	172	21

Table 12.5 gives the 1986 U.S. production of salt cake. In addition, a small amount of Glauber's salt ($Na_2SO_4 \cdot 10H_2O$) still is produced for sale, but it has very little effect in the world of sodium sulfate.

The term "salt cake" now refers generally to sodium sulfate, but originally meant sulfate produced in the Mannheim furnace, which yields a product containing less than 99 percent Na_2SO_4, compared to the much purer anhydrous Na_2SO_4 derived from natural brines.

In the latter process (shown schematically in Fig. 12.4) the natural brine, containing about 10 percent Na_2SO_4, is saturated with NaCl by pumping it into a salt deposit. The concentrated brine then is pumped from the salt well through a refrigerated heat-exchanger, where it is cooled to around −10°C, and then into a crystallizer where quite pure crystals of Glauber's salt are formed. This solid hydrate of Na_2SO_4 then is melted and the water removed by evaporation using a submerged burner as the heat source. The wet Na_2SO_4 is dried further in a rotary kiln, producing anhydrous Na_2SO_4. Over 10 tons of natural brine and 1.6 million Btu of heat energy are required to produce one ton of product. The most significant production location is in Texas, where the sulfate-containing brine is conveniently located near deposits of both domed salt and natural gas.

A similar process is practiced at Searles Lake. There the brine first is carbonated and chilled to remove sodium carbonate and borax. Further chilling crystallizes Na_2SO_4 as the hydrate, Glauber's salt, and some remaining borax. The coarse crystals of Glauber's salt are separated from the fine

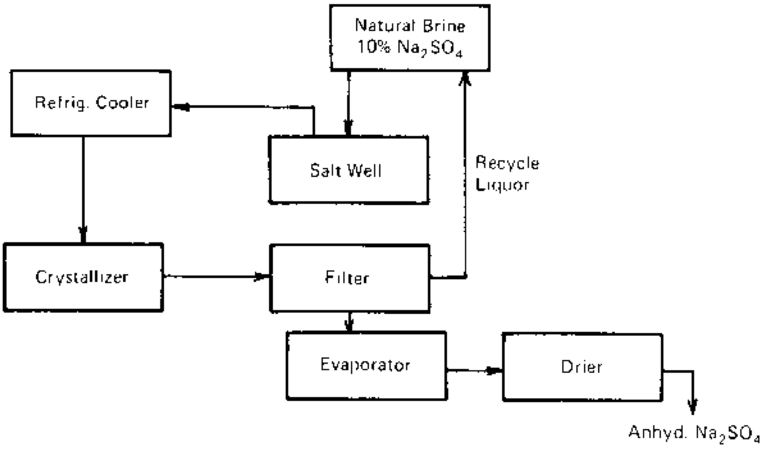


Fig. 12.4. Simplified flow sheet for the production of Na_2SO_4 from natural brine.

crystals of borax in a hydraulic classifier. The sulfate fraction then is filtered, washed, dried, and evaporated to produce anhydrous Na_2SO_4.

In another process at Searles Lake, the brine first is evaporated to produce NaCl and a double salt of Na_2CO_3 and Na_2SO_4. The two solids are separated in a hydraulic classifier, and the sulfate fraction is redissolved and recrystallized to Glauber's salt. Anhydrous Na_2SO_4 is recovered by mixing the Glauber's salt with sodium chloride brine. This dissolves the Glauber's salt and allows anhydrous Na_2SO_4 to precipitate because of its lowered solubility in the presence of sodium chloride.

In the Mannheim process, NaCl and 100 percent H_2SO_4 in amounts equivalent to complete conversion to Na_2SO_4 are fed to a circular muffle furnace made of cast iron. The furnace is equipped with a shaft, which penetrates from below and carries four arms, each of which is fitted with two cast iron plows. The shaft rotates at 0.5 rpm, slowly plowing the heated mixture to the circumference where the burned cake discharges through a chute. The furnace charge is heated to about 840°C, just below the fusion temperature of the salt cake. HCl is liberated, cooled, and absorbed in water to produce 32 percent HCl for sale. The salt cake is really a by-product of the operation.

A substantial amount of by-product Na_2SO_4 also is produced in a variety of processes involving the use of H_2SO_4 to react with a sodium salt, or to neutralize free caustic soda. Chief among these are the viscose rayon process and the manufacture of sodium dichromate. In the viscous process, Na_2SO_4 is formed by the reaction between H_2SO_4 and cellulose xanthate plus free caustic in the rayon fiber spinning bath. Spin-bath liquor is evaporated to crystallize Glauber's salt, which is centrifuged off, melted, and then evaporated to anhydrous Na_2SO_4. This is a significant source of sulfate, as 1.1 lb of Na_2SO_4 is produced per pound of rayon fiber spun.

In the manufacture of sodium dichromate, by-product Na_2SO_4 crystallizes directly as the anhydrous material when H_2SO_4 is added to a boiling solution of sodium chromate:

$$2Na_2CrO_4 + H_2SO_4 + H_2O \rightarrow Na_2Cr_2O_7 \cdot 2H_2O + Na_2SO_4$$

Decreased use of chrome by automobile and small-appliance manufacturers and mandated recycling of chromium wastes in the electroplating industry have led to a decline in Na_2SO_4 produced from this source.

Table 12.6[6] shows the U.S. distribution for consumption of Na_2SO_4. The price of salt cake is $65/ton and for the higher-quality detergent and rayon grade $90 to $100/ton.

In North America, Canada is a net exporter of sodium sulfate, the majority of the exported

TABLE 12.6 U.S. Distribution of Na_2SO_4[6]

Industry	*Thousands of Tons*	*Percent*
Kraft pulp	275	30
Detergents	460	50
Glass	65	7
Miscellaneous	114	13

product going to the United States. Canadian sodium sulfate production is about 450 metric tons/year, and about 85 percent of this is produced from natural brine in Western Canada.

In both Canada and the United States the major end use of sodium sulfate is in kraft pulping. In the kraft pulping process, sodium sulfate (salt cake) is added as makeup to the recycle black liquor just prior to entering the recovery furnace. In the recovery furnace the sodium sulfate is reduced to sodium sulfide. A decade ago, sulfur losses accounted for a sodium sulfate makeup of about 80 lb/ton of pulp. Since then, antipollution regulations have encouraged technical innovations to decrease sulfur losses in the pulping process to a level where a makeup of only 40 lb salt cake/ton of pulp is required. Also, in recent years the use of Na_2SO_4 in the manufacture of kraft paper has been giving way somewhat to the use of sodium sulfide, sodium hydrosulfide, and emulsified sulfur, which are more readily available as by-products of the petroleum industry, derived from the caustic scrubbing of sulfide-containing hydrocarbon gases. The sulfides often are preferred by the paper industry because the sulfate must be reduced to sulfide in the pulping process.

In dry detergents, sodium sulfate is used largely as a low-cost inert filler and diluent. In recent years detergents have become more concentrated, and sodium sulfate requirements have been reduced.

In glass manufacture, sodium sulfate is used in small amounts for its sulfur and sodium oxide values as a melting aid. In order to minimize the deleterious effects of volatilized sodium sulfate from glass manufacture, the amount of sodium sulfate consumed per ton of glass has been decreasing in recent years.

SODIUM SULFIDES

Sodium sulfide (Na_2S) and sodium hydrosulfide, sometimes referred to as sodium sulfhydrate (NaHS), share the same derivation: caustic soda and H_2S. Earlier processes based on reduction of salt cake with coal have largely been supplanted. In 1990 the U.S. installed capacity for NaHS was 134 tons/year. In addition, more than 100,000 tons/year of lower-purity lower-strength sodium hydrosulfide was recovered from small refineries, bromine operations, and other sources. The source of H_2S used in the manufacture of NaHS is essentially all by-product. Controlled caustic scrubbing of H_2S forms a solution of NaHS:

$$NaOH + H_2S \rightarrow NaHS + H_2O$$

The NaHS solution is filtered to remove the sulfides of heavy metals, such as Fe, Hg, Ni, Mn, and Cu. The clear filtrate may be sold as a 44 to 46 percent solution of NaHS or evaporated in stainless steel equipment to crystallize a solid hydrate containing 70 to 72 percent NaHS, which is sold as a flake product.

NaHS is easily converted to Na_2S by further reaction with caustic:

$$NaHS + NaOH \rightarrow Na_2S + H_2O$$

By using a NaHS solution of the proper concentration with a flake caustic, a hydrate product containing 60 to 62 percent Na_2S is obtained. This is sold directly as a flake product, or fused solid in drums. When high-quality H_2S and NaOH are used, the product Na_2S is suitable for use in dyes, photography, rayon, and leather manufacture.

Lower-quality sulfides are obtained by using H_2S produced as a by-product in the manufacture of CS_2 from methane (or other low molecular weight hydrocarbons) and sulfur:

$$CH_4 + 4S \rightarrow CS_2 + 2H_2S$$

The gas mixture from this catalytic reaction is cooled and scrubbed with caustic. The sulfides so produced contain small amounts of mercaptans (e.g., CH_3SH), which lend a very objectionable odor to the product.

TABLE 12.7 Uses for Na_2S and NaHS[6]

Industry	*% Total Market* Na_2S	*NaHS*
Pulp and paper	3	36
Dyestuffs and misc. chemicals	29	40
Rayon and film	3	6
Metals and minerals	3	—
Leather	62	18

Sulfides also are obtained as by-products in the manufacture of $BaCO_3$ from the barite ore, $BaSO_4$, by roasting with coal, water leaching, and treatment with soda ash:

$$BaSO_4 + 4C \rightarrow BaS + 4CO$$

$$BaS + Na_2CO_3 \rightarrow Na_2S + BaCO_3$$

Table 12.7 shows the distribution for consumption of Na_2S and NaHS by industry use. They both are used extensively in a variety of industries, and the use of NaHS in paper pulping is growing. The 1990 carload price for NaHS for 45 percent liquid (100% basis) was $500/ton. Tight caustic soda supplies have led to higher costs for an industry already faced with weak prices and overcapacity.

SODIUM THIOSULFATE

Eighty percent of sodium thiosulfate (hypo) ($Na_2S_2O_3$) is used in photography (Table 12.8) because of its ability to dissolve water-insoluble silver salts. However, because substantial market erosion has occurred concurrently with the growth in use of videotape, the market for sodium thiosulfate continues a steady decline from 40,000 tons/year 30 years ago to well under half that today.

TABLE 12.8 Sodium Thiosulfate Major Uses[6]

Industry	*Percent*
Photography	80
Oil recovery	7
Leather	5
Water treatment	5
Other	3

Most current production is derived as by-product from the manufacture of sulfur dyes and Na_2S:

$$Na_2S + SO_2 + H_2O \rightarrow Na_2SO_3 + H_2S$$

$$Na_2SO_3 + S \rightarrow Na_2S_2O_3$$

$$2Na_2S + Na_2CO_3 + 4SO_2 \rightarrow 3Na_2S_2O_3 + CO_2$$

In producing sulfur dyes, by-product leach liquor contains sodium thiosulfate, which is simply derived by evaporation and crystallization. Much of the thiosulfate is sold as the pentahydrate, $Na_2S_2O_3 \cdot 5H_2O$. Stainless steel equipment is used in processing thiosulfate.

Of less importance today is the older soda ash–sulfur process. Ash is dissolved in hot water, and the solution is pumped to SO_2 absorption towers. The resulting $NaHSO_3$ liquor is then heated with powdered sulfur in an agitated stainless steel digestion tank at elevated temperature. The product solution is filtered, evaporated, and crystallized to yield $Na_2S_2O_3 \cdot 5H_2O$ product, which is centrifuged, washed, dried, and packaged in airtight containers (to discourage efflorescence). In 1990 sodium thiosulphate pentahydrate sold for 32 cents/lb.[6]

SODIUM SULFITE

Sodium sulfite (Na_2SO_3) is produced by reacting sulfur dioxide with a solution of sodium carbonate or sodium hydroxide. Sodium sulfite also is recovered as a by-product of resorcinol production. About half of the sodium sulfite produced in North America is used by the pulp and paper industry (i.e., chemithermomechanical process). It also is used in photography, textile bleaching, and food preservation, and as a chemical intermediate. In 1990, 160,000 short tons of sodium sulfite were produced in the United States, excluding material produced and used captively by some paper mills. The 1990 selling price for sodium sulfite (anhydrous 95–100%) was about 24 cents/lb.

SODIUM BISULFITE

Most of the sodium bisulfite of commerce is really the anhydride, $Na_2S_2O_5$, sodium metabisulfite or sodium pyrosulfite. Sodium bisulfite is not stable and is generally transported in the metabisulfite form, which is a solid containing 98 percent $Na_2S_2O_5$, 1.5 percent Na_2SO_3, and 0.5 percent Na_2SO_4. Methods of manufacture of sodium metabisulfite are all variations of the same theme:

$$Na_2CO_3 + 2SO_2 \rightarrow Na_2S_2O_5 + CO_2$$

In one variation, SO_2 is sparged into a stainless steel absorber through which is passed a solution of Na_2CO_3. Formation of product crystals from the saturated solution is achieved by lowering the temperature. The crystals are centrifuged off and dried rapidly in a flash dryer in order to avoid air oxidation to sulfate. The markets for sodium metabisulfite include chemical intermediates, pharmaceuticals, food preservatives, and dye fixing. Additionally, sodium metabisulfite is used in photography, as an antichlor to remove excess chlorine from bleached kraft pulps, and for the manufacture of sodium hydrosulfite. North American sodium metabisulfite production in 1988 for merchant sales was about 50,000 tons, and the 1990 selling price for the anhydrous product was 28 to 32 cents/lb.

SODIUM HYPOSULFITE (HYDROSULFITE)

Not to be confused with "hypo" (the term used in photography to refer to thiosulfate), sodium hyposulfite (or hydrosulfite) ($Na_2S_2O_4$) also is referred to as sodium dithionite. $Na_2S_2O_4$ is a powerful reducing agent used principally for the reduction of vat dyes and brightening of mechanical wood pulps and clays (Table 12.9). There are numerous methods for production of sodium hyposulfite, all of which involve reduction of SO_2 or sodium bisulfite. Sulfur dioxide or $NaHSO_3$ is reduced by Zn, sodium amalgam, sodium formate, sodium borohydride, or cathodic reduction to produce $Na_2S_2O_4$.

TABLE 12.9 1990 U.S. Distribution of Merchant Sodium Hydrosulfite[4]

	Percent
Pulp bleaching	33
Textile dying	22
Clay bleaching	13
Exports	28
Other	4

There are two variations of the zinc method. In the first, a solution of sodium hydrogen sulfite is reduced with zinc dust in the presence of excess SO_2:

$$2NaHSO_3 + Zn + SO_2 \rightarrow Na_2S_2O_4 + ZnSO_3 + H_2O$$

Milk of lime is added to neutralize remaining sulfurous acid, and $CaSO_3$ and $ZnSO_3$ are removed by filtration. Common salt is added to the remaining solution to salt out $Na_2S_2O_4 \cdot 2H_2O$. The suspension of crystals is heated to 60°C to dehydrate the product, water is extracted with alcohol, and the product crystals are vacuum-dried. The crystals are stable only when completely dry.

The second method based on zinc consists of treating an aqueous suspension of zinc dust with SO_2 at 80°C:

$$Zn + 2SO_2 \rightarrow ZnS_2O_4$$

Treatment of this solution with soda ash precipitates a basic zinc carbonate, which is filtered off. The dry crystalline product $Na_2S_2O_4$ is obtained by salting out and drying, as in the first method. The zinc methods have become obsolete because of the environmental concerns associated with zinc discharge.

The amalgam process uses a dilute sodium amalgam (0.5% Na) derived from the cathode reaction of a mercury chlorine cell.[8] The amalgam is admixed with a solution of $NaHSO_3$ whose pH is controlled in the range of 5 to 7:

$$4NaHSO_3 + 2NaHg \rightarrow Na_2S_2O_4 + 2Na_2SO_3 + 2H_2O + Hg$$

The mercury is returned to the mercury cell to form more amalgam, and the $Na_2S_2O_3$ is allowed to react with aqueous SO_2 to form more $NaHSO_3$.

One common method for sodium hyposulfite production involves the use of sodium formate:

$$HCOONa + NaOH + 2SO_2 \rightarrow Na_2S_2O_4 + H_2O + CO_2$$

The above aqueous reaction requires the use of methanol under acidic conditions. In this process, the anhydrous sodium hydrosulfite is directly precipitated and is filtered off.

Sodium hyposulfite (5–7% $Na_2S_2O_4$) also is produced on-site at pulp and paper mills by reduction of SO_2 with sodium borohydride solution under alkaline conditions (Borol process):

$$\underset{\text{Borol solution}}{(NaBH_4 + 3.4NaOH)} + 5.6NaOH + 9SO_2$$
$$\rightarrow 4Na_2S_2O_4 + NaBO_2 + NaHSO_3 + 6H_2O$$

In a recent patent[9] an electrochemical process for producing hydrosulfite solutions was claimed. The cathode reaction is:

$$2HSO_3^- + 2H^+ + 2e^- \rightarrow S_2O_4^{2--} + 2H_2O$$

It is anticipated that such a process would be viable for on-site production of sodium hyposulfite.

In 1990 there were about 80,000 tons of merchant sodium hyposulfite produced. In addition, about 10,000 tons of sodium hyposulfite were produced on-site at pulp mills by reacting sodium borohydride and SO_2. The on-site process has the advantage of minimum hyposulfite degradation to thiosulfate, which is known to cause corrosion problems in pulp mills. The 1990 list produce for $Na_2S_2O_4$ was about 73 cents/lb, but discounting from the list price was prevalent.

SODIUM PHOSPHATES

In 1990 little over half of the 320,000 tons of phosphorus produced in the United States was utilized in the manufacture of the family of sodium phosphate products, chief among which is sodium tripolyphosphate, $Na_5P_3O_{10}$. Sodium tripolyphosphate (STPP) is approximately 57 percent P_2O_5 and 42 percent Na_2O. In 1990, 500 tons of STPP was produced and sold at about 30 cents/lb. It is made by the reaction between soda ash and phosphoric acid.[10] By far, the major source of phosphoric acid is furnace-grade acid, because of its high purity as compared with the less pure wet-process acid. A hot solution of Na_2CO_3 is reacted with 60 percent H_3PO_4, with a molar ratio of sodium to phosphorus of 1.67 maintained in order to achieve the desired stoichiometry. The solution is purged with steam to evolve all the CO_2, and then it is filtered, spray-dried, and granulated for shipment. By changing the ash-to-acid ratio, a variety of products can be produced.

This process forms the basis for an entire family of products, fundamental to which, in addition to the tripolyphosphate, is the production of the di- and trisodium salts. They may be produced in the same process by crystallizing out and recovering $Na_2HPO_4 \cdot 12H_2O$.

The major use of STPP is in home laundry, industrial, and institutional detergents, as indicated in Table 12.10.[6]

Phosphate bans in detergents continue to be legislated. The total demand for STPP in the last few years has declined at a rate of about 1.5 percent per year. The primary reason for this decline has been the penetration of the phosphate-free liquid detergents into the heavy-duty phosphate detergent powder market.

The mono-, di-, and pyrophosphates are used in foods, the latter two in baking powders. The monosodium salt is produced

TABLE 12.10 1990 STPP Uses[6]

Industry	*Percent*
Home laundry detergents	44
Industrial/institutional detergents	19
Dishwashing detergents	18
Food	4
Miscellaneous	2
Exports	13

from Na_2HPO_4 by further processing with H_3PO_4, evaporation, and crystallization. Prolonged heating of the monosodium derivative at 230°C produces the pyrophosphate, $Na_2H_2P_2O_7$. Further heating of the monosalt to the point of fusion produces hexametaphosphate, a glassy substance of uncertain stoichiometry, which is used in water treatment.

SODIUM SILICATE

The sodium silicate family is analogous to the phosphates in that a whole series of derivatives are produced in a reaction between Na_2CO_3 and silica by varying the ratio of soda ash to silica. The products often are referred to by the ratio of SiO_2 to Na_2O in a given composition. The U.S. production was almost 900,000 tons in 1990. Table 12.11 gives a typical use pattern for this heavy chemical group.

Sodium silicates are made in batches by fusing sand and soda ash in a furnace at about 1300°C, in whatever ratio is necessary to achieve the desired properties of the final compound. In general:

$$Na_2CO_3 + nSiO_2 \rightarrow Na_2O(SiO_2)_n + CO_2$$

$$2NaOH + nSiO_2 \rightarrow Na_2O(SiO_2)_n + H_2O$$

TABLE 12.11 1990 Uses for Sodium Silicates[6]

Industry	*Thousands of Tons*	*Percent*
Soaps and detergents	261	29
Catalysts and gels	252	28
Pigments	198	22
Boxboard adhesives	72	8
Paper and ore treatment	48	6
Other		7

The product is called water glass, because, when solid, it actually is a glass; but, unlike lime-soda glass (ordinary window glass), it is soluble in water. The process is carried out in large tank furnaces similar to window glass furnaces. The materials are introduced in batches at intervals, but the products may be drawn off continuously if desired. A mixture of salt cake and coal may replace a portion of the soda ash.

As the melt leaves the furnace, a stream of cold water shatters it into fragments. These are dissolved with superheated steam in tall, narrow steel cylinders with false bottoms,[11] and the product liquor is clarified.[12] Sodium silicates are sold as solutions that vary from the most viscous, 69°Be, to the thinner solutions, down to 22°Be, suitable for use in paints. The composition of typical commercial grades of sodium silicate solutions is shown in Table 12.12. A dry powder also is marketed (Table 12.13); it is made by forcing the thick liquor through a very fine opening into a chamber swept with a rapid current of cold air, which carries off the moisture.[13] Because the solid silicates are hygroscopic, they often are blended with Na_2SO_4 to prevent caking. Silicate solutions also are processed further with mineral acids to manufacture hydrated

TABLE 12.12 Composition of Typical Commercial Sodium Silicate Solutions[6]

Weight Ratio SiO_2:Na_2O	*% SiO_2*	*% Na_2O*	*Solids Content (%)*	*Specific Gravity (°Be)*	*Viscosity at 20°C (Centipoises)*	*Density (Pounds per Gal)*
3.22	28.7	8.9	38.0	41.2	290	11.7
3.00	30.9	10.3	41.2	44.6	412	12.0
2.84	31.9	11.2	43.1	47.0	690	12.3
2.58	32.1	12.5	34.6	NA	780	12.6
2.54	26.9	10.6	37.5	42.0	63	11.7
2.40	33.4	13.9	47.0	52.2	1700	13.0
2.00	29.4	14.7	44.1	50.0	335	12.7
1.80	24.1	13.4	37.5	54.6	60	13.4

TABLE 12.13 Commercially Available Alkaline Sodium Silicate Solids[6]

Name	*Chemical Formula*	*Molecular Ratio $Na_2O:SiO_2$*
Sodium metasilicate, anhydrous	$Na_2O \cdot SiO_2$	1.0
Sodium metasilicate, pentahydrate	$Na_2O \cdot SiO_2 \cdot 5H_2O$	1.0
Sodium sesquisilicate	$3Na_2O \cdot 2SiO_2$	1.5
Sodium orthosilicate, anhydrous	$2Na_2O \cdot SiO_2$	2.0
Sodium orthosilicate, hydrate	$2Na_2O \cdot SiO_2 \cdot 5H_2O$	2.0

silica, which yields silica gel upon being dried. Silica gel is used extensively in air-drying equipment and in the manufacture of catalysts.

There continues to be an overcapacity for sodium silicate manufacture in Canada and the United States. The sharply growing use of peroxide bleaching and waste paper deinking is boosting sodium silicate demand in the pulp and paper industry, particularly in Canada. The silicate sequesters iron and other metal ions that reduce the peroxide efficiency. It also keeps the pH buffered in the alkaline range required for peroxide bleaching of pulp. Sodium silicate also has become an important ingredient of the chemical formulation for the deinking of printed waste paper. In this process, in addition to being a buffering and sequestering agent, silicate is known to provide detergency and anti-redeposition properties during the flotation deinking process.

In 1990[6] 41°Be solution with a 3.22 to $3.25 SiO_2 : Na_2O$ weight ratio sold for about 10 cents/lb. The price for the similar-ratio solid product was about 22 cents/lb.

CHLOR-ALKALI (CHLORINE AND CAUSTIC SODA)

Ranking among the higher-volume chemicals produced in the world are chlorine and caustic (sodium hydroxide). In 1990 North America produced over 25 million tons of caustic and chlorine, and the value of these products was over $5 billion. Table 12.14 gives chlor-alkali production[4] in major regions of the world.

TABLE 12.14 Chlor-Alkali Production in Major Regions of the World[4]

	Thousands of Short Tons	
	Caustic	*Chlorine*
U.S.A.*	12,572	11,915
Canada*	1,334	1,326
Western Europe	11,623	10,810
Eastern Europe	6,580	5,442
Japan	3,537	3,193

*1989 Statistics; others 1987.

Historically, the electrolysis of brine accounts for approximately 96 percent of all chlorine production. About 2 percent of the total electrical power generated in the United States is used for chlor-alkali manufacture. Over a third of the total world chlor-alkali capacity exists in the United States in about 50 plants, by far the larger of which are concentrated in the Gulf Coast area of Louisiana and Texas.[14,15] This concentration derives from the combined availability in that region of salt, hydrocarbons (fuel and organic products based on chlorine and caustic), and deep-water ports for transportation. The intercoastal canal, the Mississippi and Ohio rivers, and their connecting waterways are also well suited for heavy barge traffic from the Gulf to much of the heartland.

Table 12.15 gives the distribution of U.S. chlorine by industry use. Table 12.16 similarly lists the market distribution for caustic.[6,16]

The heart of the chlor-alkali process is the electrolytic cell in which saturated, purified NaCl is electrolytically decomposed. There are basically three types of chlor-alkali cells currently in use, which are shown schematically

TABLE 12.15 Market Distribution of U.S. Chlorine[6,16]

Market	*Percent*
Ethylene chloride/vinyl chloride monomer	28
Pulp and paper	18
Inorganic chemicals	8
Chloromethanes	7
Chloroethanes	6
Propylene oxide and other organics	20
Water treatment	6
Miscellaneous	7

TABLE 12.16 Market Distribution of U.S. Caustic[6,16]

Market	*Percent*
Pulp and paper	22
Organic chemicals	20
Inorganic chemicals	11
Soaps and detergents	7
Petroleum	7
Water treatment	7
Textiles	5
Alumina	4
Other	9
Exports	8

in Fig. 12.5.[17-19] These cells are designed for continuous electrolysis of brine to produce chlorine gas, hydrogen gas, and aqueous caustic soda.

The diaphragm cell derives its name from the separator, or diaphragm, which is a mat of asbestos fiber vacuum-deposited directly on a woven-wire, mild steel member. The steel mesh serves doubly as a support for the diaphragm and as the cathode, or negative electrode, of the cell. The diaphragm separates the anode and cathode compartments of the cell to discourage direct mixing of the chlorine and caustic, and also to prevent chlorine and hydrogen from mixing, which can be a dangerous situation because they are capable of reacting violently with one another under certain conditions. A head of brine is maintained higher on the anode (the positive electrode, at which chlorine is produced) side of the diaphragm than the cell liquor level on the cathodic side. Thus brine slowly percolates through the diaphragm and into the cathode chamber of the cell, where water is decomposed to form hydrogen gas and hydroxide ion. The effluent cell liquor contains about 12 percent NaOH, 14 percent NaCl, and small amounts of chlorate, hypochlorite, sulfate, and carbonate—with the remainder being water. The usual caustic produced for sale is a 50 percent NaOH solution; so this cell effluent requires evaporation and separation of the salt.

The mercury cell differs from the diaphragm cell in that the cathode is a thin film of mercury, with no separator between it and the anode. Although chlorine is produced at the anode in both types of cell, the cathode reactions differ markedly. Instead of water decomposing at the cathode of the mercury cell, as it does in the diaphragm cell, sodium metal is deposited in the mercury to form a dilute (0.5%) amalgam. This amalgam flows out of the cell into a decomposer, in which water and the amalgam react directly to form a 50 percent NaOH solution of high purity, there being no evaporation required. The denuded mercury is returned to the cell.

Another difference between the two cell types is the brine flow. In the diaphragm cell about 50 percent of the NaCl is decomposed, and the remainder flows out of the cell in the weak caustic effluent. In the mercury cell, only a small fraction of the salt is decomposed per pass through the cell. The brine is immediately dechlorinated, resaturated with salt, and returned to the cell.

At first glance, it would appear that the mercury cell process is far superior to the diaphragm cell process. In many ways it is. However, the mercury cell requires much more electrical energy than does the diaphragm cell. In certain areas, especially where electrical energy is cheap and where small-capacity, easily run plants are required, the mercury cell is quite economical. Also, the mercury cell may be preferred if fuel costs are high, as that discourages the plant designer from installing evaporators—which require burning fuel just to make steam to run them. In large installations where it makes more sense to install a powerhouse at the site, the

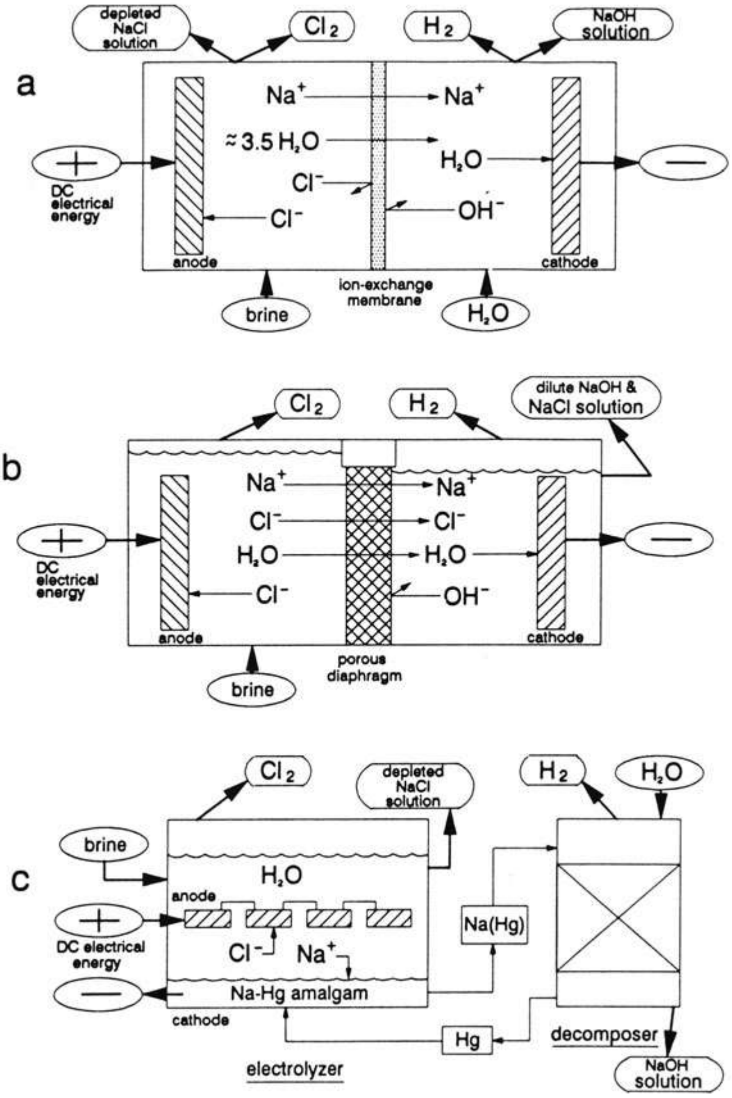


Fig. 12.5. Chlor-alkali electrolysis cells: (a) diaphragm cell; (b) membrane cell; (c) mercury cell. (*Courtesy the Dow Chemical Company.*)[17]

generation of power cogenerates lower-pressure steam, which may be used quite economically to drive a multiple-effect evaporator.

The membrane cell has some operating features reminiscent of both the diaphragm and the mercury cell. This new cell is somewhat like a diaphragm cell, in that it has a separator. However, the similarity ends there. The separator in the newer type cell is a perfluorinated ion-exchange membrane, through which essentially only hydrated sodium ions migrate under the influence of the electrical field.[20,21] Because there is no fluid flow through the membrane, the brine in the anode compartment becomes depleted in salt. As it does so, it is removed, dechlorinated, resaturated, and returned to the cell, just as in the case of the mercury cell. Also, very high-quality caustic is made in this cell, in concentrations ranging from 30 to 35 wt. % NaOH with less than 50 ppm NaCl. These solutions are more economically evaporated than is the diaphragm cell effluent, because

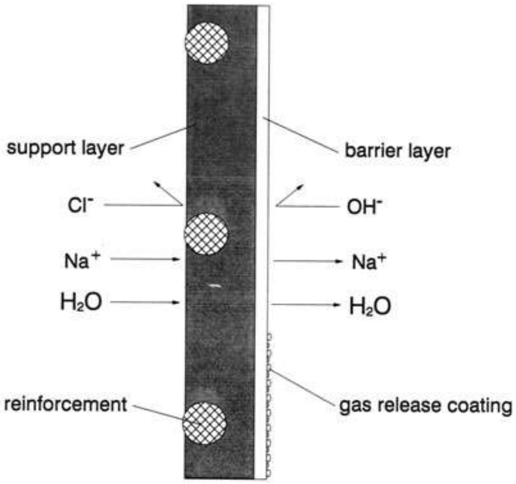
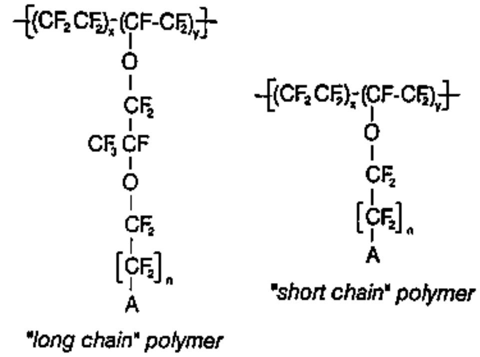


Fig. 12.6. Chlor-alkali membrane cross section.[17]



Note: ion exchange capacity determined by ratio of x and y,
$A = SO_2F$ or CO_2CH_3
$n = 1$ to 4

Fig. 12.7. Perfluorinated polymers for chlor-alkali membranes.

they are more concentrated and contain no salt, sodium sulfate, or sodium chlorate impurity to speak of.[22] This technology has emerged in the last 10 years and in time will largely displace other cells.

As mentioned earlier, the ion-exchange membrane allows the transport of primarily sodium ions and water from the anolyte to the catholyte compartments, whereas the diaphragm is designed to allow percolation of all the anolyte through the separator. The cation-conducting, ion-exchange membrane is designed to reject anions, as indicated in Fig. 12.6. The chlor-alkali membranes in use today consist of one or more perfluorinated, ion-exchange polymeric materials, as illustrated in Fig. 12.7. The short-chain polymers shown in Fig. 12.7 have been developed by the Dow, Asahi Glass, and Asahi Chemical companies.[17] Long-chain polymers are manufactured by Du Pont and sold under the trade name Nafion.*

A chlor-alkali membrane, designed to produce 30 to 35 percent NaOH, consists of at least two distinctly different polymer layers, as shown in Fig. 12.6. The anode side of the membrane is about a 0.1 mm film of sulfonic acid polymer, whereas the cathode side is about a 0.05 mm film of carboxylic acid polymer. A Teflon* fabric net is embedded in the polymer film to provide mechanical strength to the membrane. In some cases, the membrane surface is modified to facilitate gas bubble release.

A most significant advance in cell anode technology is being used to great advantage in all three cell types to conserve energy, reduce impurities, and lengthen cell life.[23,24] Prior to this development the cell anodes were made out of graphite. The new anodes are made out of titanium, which has excellent corrosion resistance in hot, chlorinated brine. However, the very oxide film that lends corrosion resistance is not an electrical conductor. By applying electroactive coatings, largely composed of mixed oxides of ruthenium and titanium, to the surface of the titanium, it remains conductive. These anodes give a vast improvement in performance over graphite for two reasons: (1) they do not wear away like graphite, which, as it becomes increasingly thinner, widens the electrode gap in the cell, requiring higher and higher voltages to operate the cell; (2) the electroactive coating is actually a catalyst that allows chlorine to be formed on the anode surface with essentially zero activation energy. Both properties contribute to much reduced power consumption in running the cells. In the case of the mercury cell, there is the added advantage that the dimensional stability of

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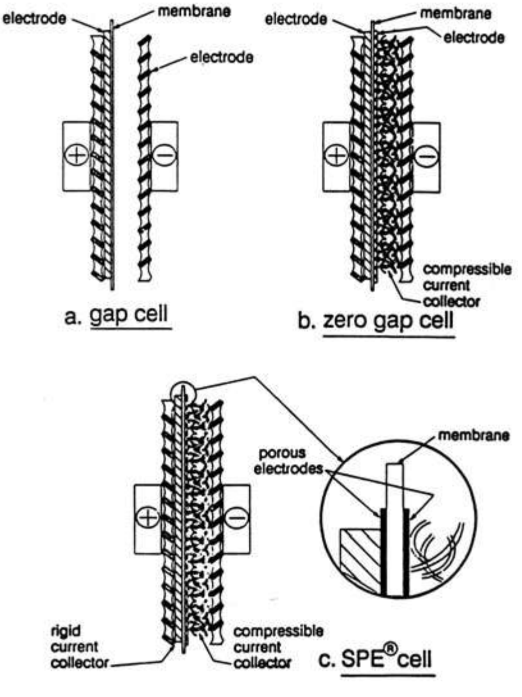
*Trademark of E. I. du Pont de Nemours & Company.

the new anode precludes the continual adjustment of electrode spacing, which is constantly necessary with graphite electrodes.

The ion-exchange membrane and dimensionally stable anode developments have impacted greatly on chlor-alkali operations, though the former is a very recent development. Their impact has been accelerated by both environmental and energy cost considerations. The cell capital cost is skyrocketing because of the expense of these new components; however, their usage does lower operating costs. In practice, a balance between capital costs and operating costs is sought to achieve an economic optimum for a given plant site.

Both membrane and diaphragm cells use punched plate, expanded mesh, or woven wire cathodes of nickel, nickel-plated steel, or stainless steel. In most modern membrane cells some type of activated or catalytic cathode is used. Usually the gap between the anode and cathode is minimized to reduce the electrical resistance of the cell.[17] Various cell configurations are shown in Fig. 12.8. A cell designed for zero gap operation usually has a compressible mesh to conduct the current. The SPE (Solid Polymer Electrode) concept shown in Fig. 12.8 is not commercial yet, but the concept is borrowed from fuel cell technology where the porous electrode is embedded into the membrane.



a. gap cell

b. zero gap cell

c. SPE®cell

Fig. 12.8. Chlor-alkali cell configurations: (a) gap cell; (b) zero gap cell; (c) SPE cell.

The chemistry at the anode is identical for all three cells:

$$2Cl^- \rightarrow 2e^- + Cl_2$$

The cathode reactions also are the same for the diaphragm and membrane cells:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

In the mercury cell, however, the cathode reaction is quite different, there being no hydrogen formed in the cell:

$$Na^+ + e^- \xrightarrow{(Hg)} Na \text{ (amalgam)}$$

The amalgam may be used as a chemical reductant (i.e., to reduce $NaHSO_3$ to the hydrosulfite[8] or to hydrodimerize acrylonitrile to adiponitrile[25]), or decomposed with water to make caustic, as is generally done.

Environmental pressures on mercury discharges have dealt a blow to the practice of mercury cell technology. As a result, there have been many plant closings. An excellent job has been done in achieving sustantial reductions of Hg losses, and this technology will continue to be practiced. However, most recent emphasis is on the diaphragm cell and ion-exchange membrane technology. As the latter matures, further inroads will be made against the mercury cell. This has already happened in Japan.

The theoretical decomposition potential, E°, of a cell (i.e., the voltage below which it is impossible to form any products at all) is strictly dependent on the nature of the electrode reactions. It is related to the Gibbs free energy of the net overall chemical change occurring in the cell: $G = nFE^\circ$, where n is the number of electrons involved in the electrode reaction, and F is the Faraday constant.[26] E° is the thermodynamic potential, to which the IR drops (voltage necessary to drive the current through the electrical resistances in the cell), and the overpotential (voltage associated with the kinetics of the reactions) must be added to get the actual cell voltage:

$$\text{Cell voltage} = \text{thermodynamic potential} + IR \text{ drop} + \text{Overvoltage}$$

Typical voltage components for a membrane cell are given in Table 12.17.

Using a modern diaphragm cell running at 1500 amps/m^2 as an example, the percentages of the total cell voltage attributable to these three components are: 65 percent thermodynamic, 25 percent IR, and 10 percent overvoltage. Cell design and development programs continue to search for better ways to reduce energy consumption. Rapidly rising power costs have made power consumption the primary criterion in evaluating cell performance.[27] Thus, higher cell capital becomes justifiable on the basis of performance. But as cell capital increases, it tends to force operation at increased current density in order to produce more pounds per cell per unit of time. In a practical sense, this translates to a compromise between cell cost and current density in order to minimize production cost. Figure 12.9 is a typical current–voltage curve for a diaphragm cell. The current density simply refers to total current divided by the nominal electrode area of either the anode or the cathode, often expressed as thousands of amperes (kA) per square meter. Figure 12.9 also shows the electrical energy consumption in kilowatt hours per 2000 lb of chlorine (kWh/T Cl_2).

TABLE 12.17 Typical Voltage Components for a Membrane Cell at 3.1 kA/m^2, 85°C, 34 Weight % NaOH, DSA Anode, 200 g/l NaCl Anolyte and Activated Cathode[16]

Component	*Voltage*	*% of Total*
Reversible potential of cell reactions	2.20	72
Membrane IR + concentration polarization	0.50	16
Electrode overpotentials	0.15	5
Solution IR	0.15	5
Structural IR	0.06	2
	3.06	100

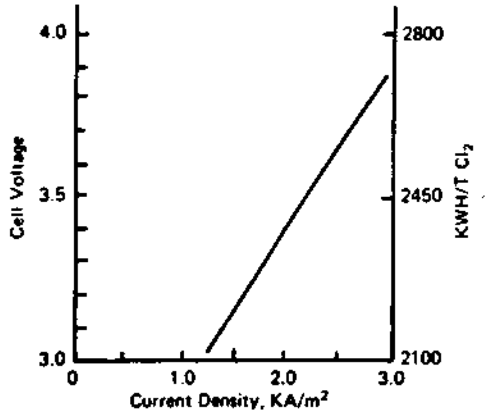


Fig. 12.9. Current–voltage curve for a typical diaphragm chlor-alkali plant.

The minimum energy requirement, unattainable in practice, is 1543 kWh/T Cl_2. This corresponds to 100 percent current efficiency (685.8 kAh/T Cl_2) and 100 percent voltage efficiency (i.e., no IR drops and zero overvoltage at both electrodes, so that the voltage is the thermodynamic potential, or 2.17 volts). The energy efficiency of a typical diaphragm cell is easily expressed as:

$$\frac{(2.17) \times (\%\ \text{Current efficiency})}{(\text{Cell voltage})}$$

For example, if a cell running at 80,000 amperes at a current density of 2.2 kA/m^2 and a current efficiency of 96 percent requires a cell voltage of 3.40, the overall energy efficiency is:

$$\frac{2.17 \times 96}{3.40} = 61.3\%$$

Figure 12.10 shows the dramatic improvements made in the electrical energy consumption of membrane cells since the mid-1970s.[17]

Much of the inefficiency results in heat generation; a cell will heat itself almost to boiling when fed brine at about 40°C. The self-heating tends to lower the cell voltage because the electrical resistance of the cell decreases with increasing temperature. As modern rectification equipment (transformers, controllers, and rectifiers) is very efficient, the

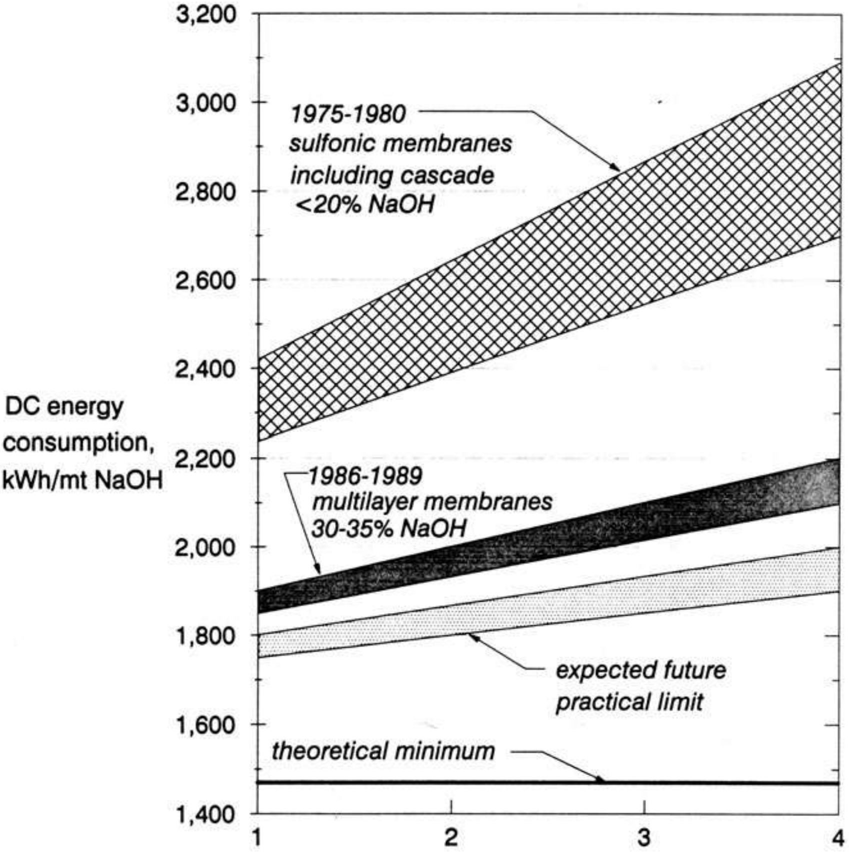


Fig. 12.10. Electrical energy consumption improvements in membrane cells.[17]

conversion of AC electricity into electrochemical products is essentially dependent on the cell efficiency. Typically, AC-kWh/lb product = 1.03 × (DC-kWh/lb product).

Figure 12.11 is a schematic of a commercial diaphragm cell, typically operated in the range of 75,000 to 150,000 amperes. Many such cells are connected in series, as shown in Figure 12.12, so that the current leaving at the anode of one cell enters the cathode of the next cell, with the anode terminal cell connected to the positive bus of the rectifier, and the cathode terminal cell connected to the negative bus of the rectifier. Bipolar and monopolar cell circuit layouts are shown in Fig. 12.13.[17]

With allowance for inefficiencies, each 30 kA increment of current that passes through the series circuit of cells produces 2000 lb of chlorine, 2100 lb of caustic, and 57 lb of hydrogen, per cell, in 24 hours of operation.

If a production plant is required to produce 900 tons of chlorine per day using rectification equipment capable of sustained operation at 90,000 amperes, the plant must operate a minimum of 300 cells. If the cell voltage is 3.4 volts at 90 kA, rectification equivalent to 1020 volts is required. In practice, the logistics of production requirements, plant reliability, and maintenance outages will dictate the size (i.e., number of cells and nominal amperage) of each circuit. In the example above, the plant would use a minimum of two circuits, with two nominal 90-kA, 600-volt rectifiers.

Figure 12.14 is a simplified flow sheet for a typical diaphragm cell chlor-alkali plant. The process begins with brine treating, in which

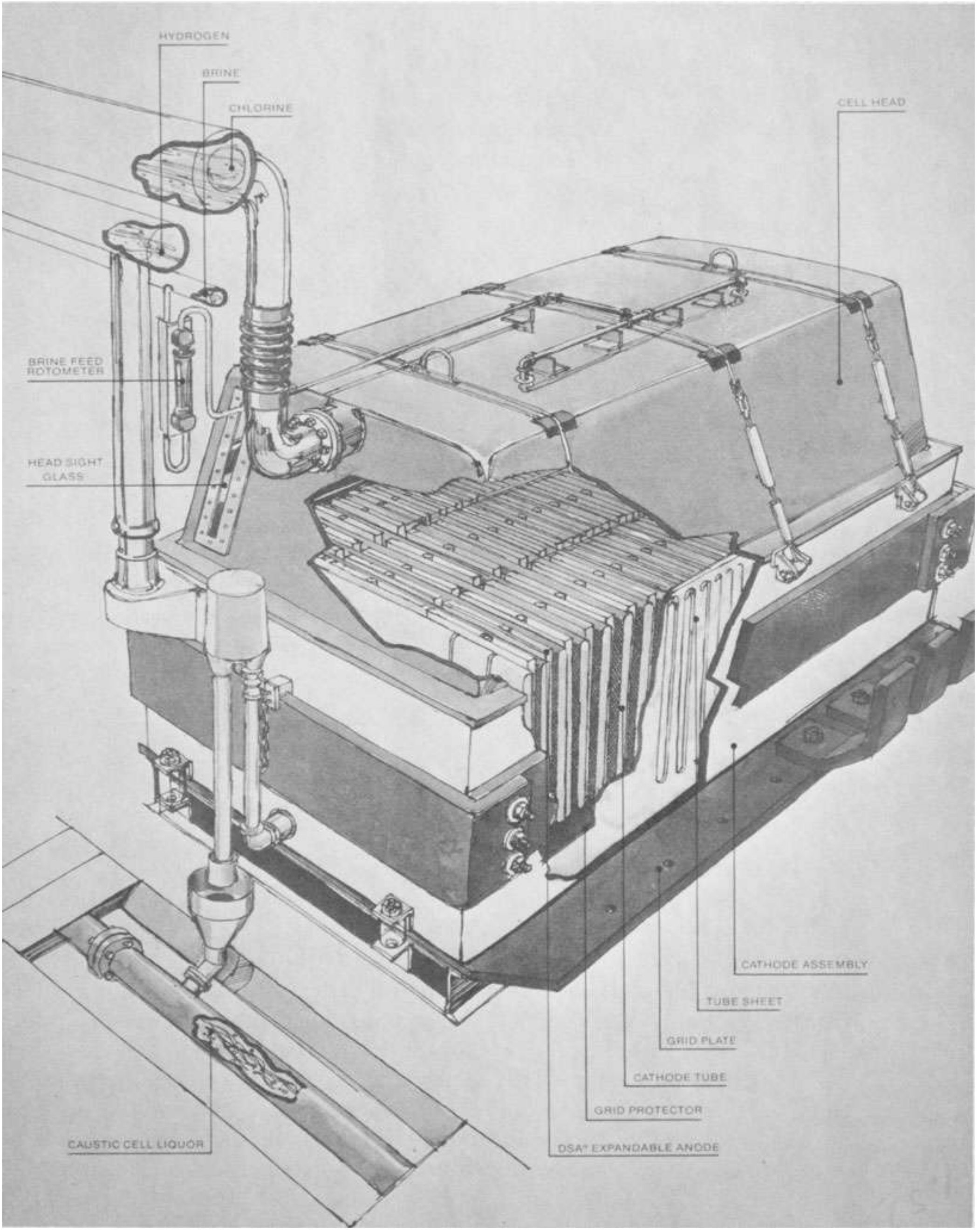


Fig. 12.11. Diamond Shamrock diaphragm cell. (*Courtesy Diamond Shamrock Corporation.*)

the well brine is saturated with return salt from the caustic evaporators, then treated with hypochlorite to destroy ammonia and amines, and also treated with carb-caustic liquor to remove calcium and magnesium impurities. Membrane cells require a secondary purification of the brine feed to provide parts per billion levels of Ca, Mg, and other heavy metals.

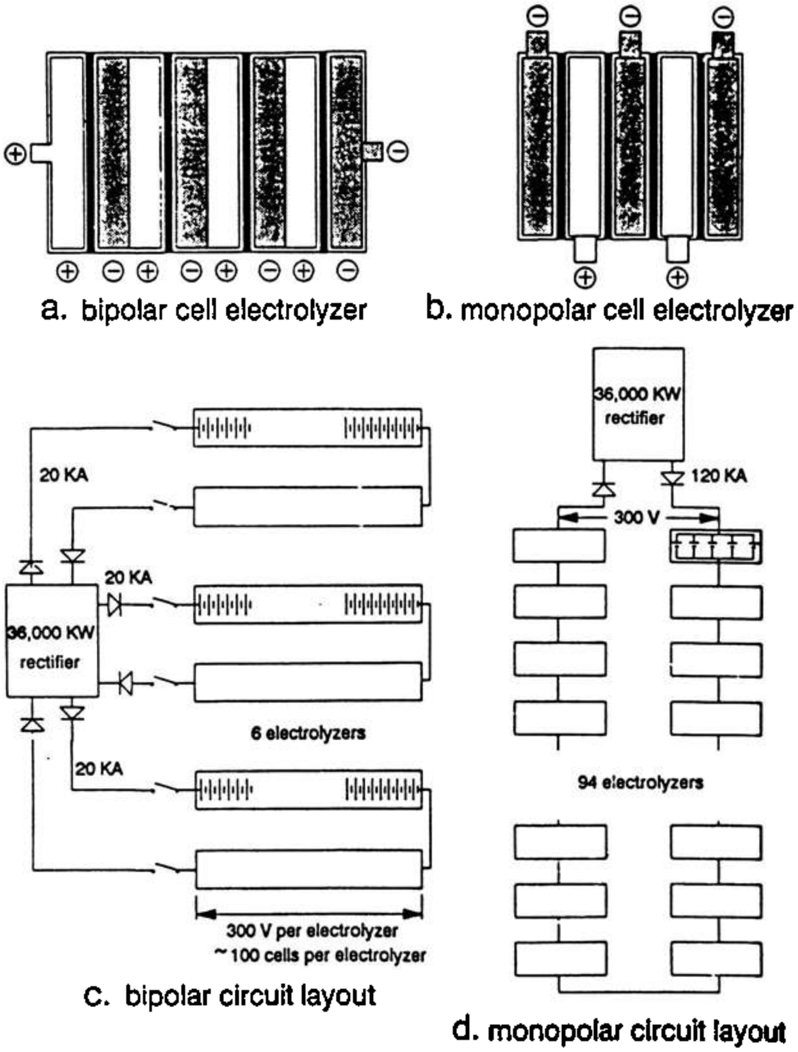
The removal of trace ammonia-nitrogen impurities is essential to avoid buildup of NCl_3 in the chlorine purification and lique-

Fig. 12.12. A series of Diamond Shamrock cells. (*Courtesy Diamond Shamrock Corporation.*)

faction stages. The NCl_3 is unstable in concentrations above a few thousand parts per million, and can decompose violently. The Ca and Mg impurities are removed to reduce plugging of the cell diaphragms, and to lengthen the time between diaphragm washing or diaphragm replacement. This was typically done every few months, but has now been extended to over a year, principally by replacement of the graphite anodes with the newer metal anodes. In the older cells, the slowly oxidizing graphite formed a sludge that tended to plug the diaphragm.

The hydrogen from the cells formerly was discarded (vented to the atmosphere) unless it was used in some of the larger plants to make NH_3 and other chemicals. It takes a large plant to produce a useful amount of H_2 because the cell produces only 0.028 lb H_2 per pound Cl_2. Also, the fuel value of H_2 is only a third that of methane. But since the energy crisis of the 1970s, the fuel value of the hydrogen has become sufficient to recover it for boiler fuel. This requires cooling to remove water, scrubbing to remove traces of chlorine, caustic, and salt, and then compressing sufficiently to satisfy the feed requirements of the burner. Of increasing importance is the burning of the hydrogen with the dilute chlorine stream known as tail gas from the liquid chlorine plant. Some chlorine producers sell their hydrogen to merchant hydrogen producers who further purify and liquefy the chlor-alkali electrolytic hydrogen for metallurgical use and rocket fuel.

The chlorine from the cell is saturated with water at the cell temperature, and contains lesser amounts of NCl_3, organic chlorides, and salt from brine entrainment. The gas is cooled to knock out the water, and this chlorinated water is returned to the brine plant. Then the cooled gas is dried by passage through towers of sulfuric acid. Strong (98%) acid is fed to one end of the drying train at



a. bipolar cell electrolyzer

b. monopolar cell electrolyzer

c. bipolar circuit layout

d. monopolar circuit layout

Fig. 12.13. Bipolar and monopolar cells and circuit layouts: (a) bipolar cell electrolyzer; (b) monopolar cell electrolyzer; (c) bipolar circuit layout; (d) monopolar circuit layout.[17]

a rate equivalent to the removal of weak (65%) acid from the opposite end. The waste acid often is used to neutralize alkaline wastes, and the reconcentration and recycling of this acid presents a challenge to a chlor-alkali manufacturer.

The moisture content of the chlorine at this stage usually is low enough to allow the use of steel in the remainder of the process. The gas is compressed, usually to whatever pressure is required by the user plant, or to sufficient pressure to liquefy it, the exact pressure depending upon the refrigeration capacity and the liquid chlorine storage requirements of a given plant. Figure 12.15 is the liquefaction curve for chlorine.[28]

In nothern climates, where ambient temperatures can fall below those required to liquefy chlorine at rather modest pressures, it is necessary to provide means for maintaining the temperatures in chlorine-gas distribution lines above the liquefaction point. This can be done by tracing or wrapping the lines with heating tape, using steam lines, and insulating the pipes. These precautions are especially important in organic process plants, which

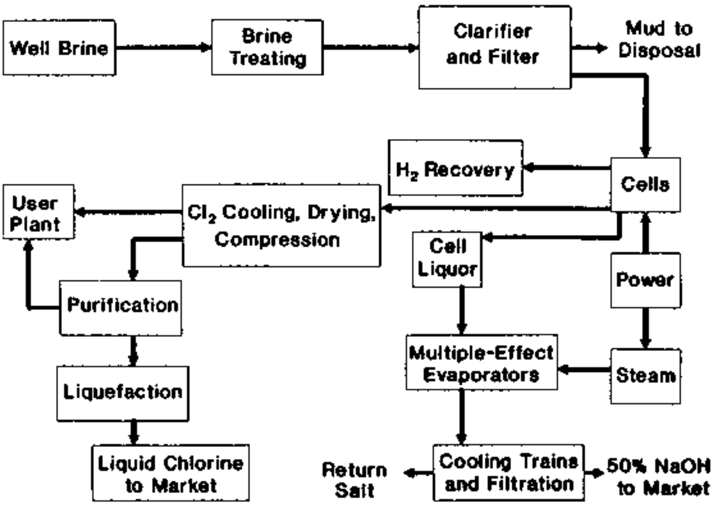


Fig. 12.14. Simplified flow sheet for chlor-alkali plant.

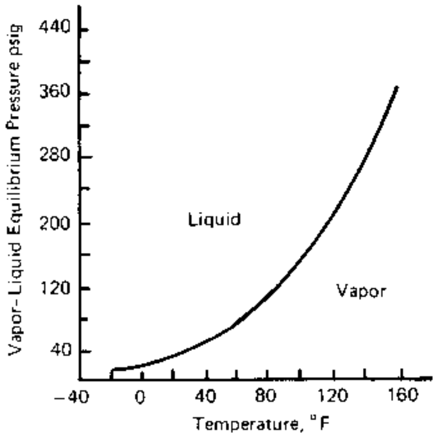


Fig. 12.15. Liquefaction curve for chlorine.

can run without incident while using gaseous chlorine but could explode if fed liquid chlorine.

Organic impurities and trace amounts of NCl_3 may be removed from gaseous chlorine in a simple extraction in which liquid chlorine is used as the extractant. The liquid bottoms flow from the extractor to a still in which chlorine is flashed off to recycle and the organic fraction (largely low molecular weight organic chlorides) is recovered for disposal by combustion to CO_2 and HCl, which is recovered for use.

There are many options in the liquefaction of chlorine, depending upon the storage requirements for the liquid and the system used to handle the tail gas. Low-pressure storage is recommended because of the reduced hazard in the event of a spill. However, this requires lower storage temperatures. Low temperatures also reduce the amount of chlorine in the tail gas from liquefaction. Yet lower temperature may not be necessary if a plant also deliberately produces bleach or HCl from the tail gas.

The components in the tail gas originate in the cells. At the anode, some water is oxidized to produce small amounts of oxygen. To this amount is added more oxygen from air, which may leak into the chlorine header from outside because the header is operated under a slight vacuum to prevent gas from escaping to the atmosphere. The cell gas typically contains about 97 percent Cl_2. Because the remaining 3 percent is noncondensable under the conditions in the liquid chlorine plant, it remains gaseous at the tail end of the liquefaction process, saturated with chlorine in an amount determined by the vapor pressure in that stage of the process. When air is deliberately added to the system to reduce the hydrogen content of tail gas to below 5 percent, the tail gas often increases in volume. With hydrogen above that level, there is a great risk of explosion. The hydrogen comes from the cathode compartment of the cell, which is operated under a slight pressure to avoid sucking air into the hydrogen collection system. Ordinarily, this leads to quite small amounts of hydrogen in the cell chlorine gas. But when diaphragm problems arise or pinholes develop in the membrane, the level can rise to undesirable values. In good plant practice, this is monitored continuously.

The cell liquor flowing from the cathode compartment of each cell is collected for evaporation to 50 percent product caustic. The diaphragm cell liquor contains 10 to 12 percent NaOH, 14 to 16 percent NaCl, 0.1 to 0.5 percent Na_2SO_4, 0.02 to 0.04 percent Na_2CO_3, and 0.01 to 0.2 percent $NaClO_3$. The evaporation is carried out in reverse feed nickel-lined multi-effect systems (i.e., feed liquor enters the opposite end of the train with respect to the primary steam entry). With rapidly rising fuel costs, it has become economically justifiable in the construction of new plants to install quadruple-effect evaporators. Previously triple-effect systems were installed. Most caustic evaporation still is done in triple-effect.

Because of the high salt content of the feed liquor originating from diaphragm cells, the evaporation system is really an evaporative-crystallizer. Salt is removed from each effect in the evaporaation train. Hydroclones, centrifuges, settlers, and filters are used extensively to remove the salt as efficiently as possible and return it to the brine plant with as little caustic loss as possible. In this regard, good plant practice strikes an economic balance between caustic loss and the addition of wash water to the system, which requires additional heat input.

The sulfate content of caustic evaporator feed can cause a problem during evaporation. When the caustic concentration reaches about the 32 percent level, the triple salt $NaCl \cdot Na_2SO_4 \cdot NaOH$ crystallizes out along with NaCl crystals. To avoid sulfate buildup in the system, which would lead to excessive caustic loss, the sulfate must be purged from the system. If it is recycled with the salt, its concentration will rise to unacceptable levels. Various schemes are used, but all plants purge sulfate at some point.

The hot 50 percent caustic from the evaporator train is cooled and filtered to remove salt down to the solubility limit. Typical analysis of diaphragm cell product caustic, on a 50 percent NaOH basis (actual caustic content varies from 48.5% to 50.5%) is: 1.0 percent NaCl, 0.15 percent Na_2CO_3, 0.025 percent Na_2SO_4, 0.15 percent $NaClO_3$, 5 ppm Fe, and a maximum of 30 ppm combined heavy metals (Sb, As, Bi, Cd, Cu, Pb, Hg, Ag, and Sn). Most often the billing weight of a shipment of caustic is based on its Na_2O content, equivalent to 76 percent Na_2O:

$$\frac{(\text{pounds solution}) \times (\%\ Na_2O)}{76} = \text{net pounds NaOH } (Na_2O \text{ basis})$$

Actually, pure NaOH contains 77.5 percent Na_2O. The value 76 percent is derived from tradition, based on the fact that many decades ago the purest form of commercially available caustic contained 76 percent Na_2O. In isolated cases, where the market is far removed from the source, the caustic is further concentrated and shipped hot as 73 percent NaOH. This saves on freight costs, but the solution must be kept hot because it freezes at about 160°F. Similarly, 50 percent caustic must be maintained above 60°F.

In selected markets, such as the rayon industry, low salt levels are required (typically 100 ppm). Mercury cell and membrane cell caustic are ideally suited for these markets. Diaphragm cell caustic is purified further in a few installations, but primarily to remove $NaClO_3$, which is corrosive to the equipment used to manufacture anhydrous caustic. Chlorate alone may be removed by reaction with a reducing agent, such as sugar, which is injected into the hot caustic feed to the anhydrous concentrator system. This has the disadvantage of increasing both the salt and the carbonate levels in the caustic.

To remove chlorate and other salts, the 50 percent diaphragm cell caustic may be extracted with liquid ammonia in a pressurized system.[29] The ammonia fraction then is processed through a stripper to remove and recycle the ammonia. The alkaline stripper bottoms are useful in neutralizing acidic waste streams. The purified caustic is evaporated further, and then fed to an anhydrous concentrator, typically an Inconel falling film evaporator, heated with molten salt. The anhydrous caustic, containing at least 97.5 percent NaOH, is marketed as one solid mass in drums, as flake caustic, or more desirably as beads or prills. The last are marketed in bulk or bags.

Since the binary system $H_2O-NaOH$ contains several hydrates that may be conveniently crystallized, another possibility exists for purifying caustic. Of special interest are the dihydrate, $NaOH \cdot 2H_2O$, which melts at about 55°F, and $NaOH \cdot 3.5H_2O$, which melts at 60°F. The impurities concentrate in the mother liquor; purified caustic then is produced by melting the crystals. The most recent attention to this method of purification has been in Japan.[30] These processes are more difficult than they appear, because of the high viscosity of concentrated caustic solutions near their freezing points and the resultant challenges of both adequately transferring heat and separating the crystals from the mother liquor. But with the advent of the membrane cell, there may be more development activity in this area.

In the handling and storage of 50 percent caustic, it is important to limit the amount of iron pickup. The iron spec is 5 ppm on a solution basis. Stainless steel offers little advantage over mild steel with respect to iron contamination. Furthermore, hot, salt-containing caustic leads to severe stress corrosion cracking of stainless steel. Carbon steel storage tanks often are lined with an epoxy-phenolic or neoprene latex coating. Iron pickup from transfer piping increases with increasing temperature and increasing linear velocity of pumping. Unnecessary recirculation or pumping through steel lines should be avoided.[31] Iron, copper, and nickel impurities are especially undesirable for the bleach manufacturer.[32]

About 75 percent of the caustic produced is concentrated. The remainder is used directly as alkaline cell liquor—as, for example, in the conversion of propylene to propylene oxide by the chlorhydrin process. Similarly, there is some chlorine produced by methods that do not produce caustic, as shown in Table 12.18. Fused chloride salt electrolysis produces chlorine in the manufacture of magnesium metal by the Dow process, and of sodium metal in the Downs cell. The only other process of note is the Kel-Chlor process.[33] This process converts by-product HCl to chlorine by oxidation with NO_2 through the intermediates NOCl and $HNSO_5$.

A small, but important, variation of NaCl electrolysis substitutes KCl as the feed. Both mercury cells and diaphragm cells are used, producing chlorine and KOH (caustic potash). The KOH is concentrated for sale as a 45 percent solution or in solid form, containing 88 to 92 percent KOH. A big use for KOH is in the manufacture of liquid soaps and detergents. The analogous sodium soaps and detergents are generally solids.

Table 12.19 gives the 1990 U.S. prices for chlorine and for caustic soda in its various forms.[6] These are typical values. For significant volumes, much movement of chlor-alkali goods is contracted below market price.

The entire chlor-alkali world must constantly perform a balancing act. The electrolysis of salt brine yields almost equal amounts of chlorine and caustic. It is rare that the growth or use-rates for the two products are equal. Furthermore, the chlor-alkali balance problem extends to related products such as soda ash,

TABLE 12.18 U.S. Chlorine Production by Process

Process	*Percent*
Diaphragm cells	75.4
Mercury cells	16.7
Membrane cells	4.9
Fused salt electrolysis	1.2
Other	1.8
Total	100.0

TABLE 12.19 1990 Value of Chlor-Alkali Products[6]

Product	*$/Ton (100% Basis)*
Liquid chlorine	125
50% caustic	300
50% caustic (rayon)	330
73% caustic	350
Solid caustic	560
Flake caustic	560
Bead caustic	560

lime, salt cake, and hydrochloric acid, even to the extent of influencing (and being influenced by) the current economics of chlorinated hydrocarbons.

For example, in the 1960s the demand for chlorine was so much greater than for caustic that concerted efforts had to be made to move caustic into new markets, such as the glass industry. Another effect of the same economic climate was a glut of HCl from the tremendous growth in vinyl chloride and a host of other chlorinated organic derivatives. Necessity being the mother of invention, this situation led to the development of the oxy-chlorination process for the production of vinyl chloride, resulting in no net production of HCl; to a route for producing methyl chloride using HCl and methanol; to the Kel-Chlor process for production of chlorine without caustic; and to the recycle of by-product HCl to chlorine by electrolysis.[34-36] There was a host of developmental activity in both the United States and Europe to convert caustic to soda ash and to improve the old Deacon process, which is a nonelectrolytic, catalytic conversion of HCl to chlorine.[37] In another case, a large consumer of sulfuric acid, the steel industry, was converted to the use of HCl for pickling steel. Huge amounts of caustic cell effluent were used to replace lime in a variety of applications.

By the mid-1970s, the picture was changing. Environmental pressures on fluorocarbon derivatives (derived from chlorinated compounds and creating by-product HCl), and on some of the chlorinated solvents, impacted negatively on chlorine growth. During the late 1980s, the pulp and paper industry started to come under intense environmental scrutiny due to the presence of total organic halides (AOX) in effluents from bleaching operations in kraft mills. As a result, it appears that the industry will voluntarily reduce chlorine usage by 50 to 70 percent in the early 1990s and use chlorine dioxide in its place. In order to reduce the AOX discharges from over 3.0 kg/ton of pulp manufactured to less than 1.5 kg/ton of pulp, the pulp and paper industry also will be pushed to use a more expensive oxygen delignification technology that would lead to further reductions in chlorine use in pulp bleaching applications. The result of this would be zero or negative growth for chlorine, a situation that has tremendous implications for caustic availability.

The swings in the chlor-alkali industry during the 1980s, coupled with environmental pressures on the use of mercury and asbestos in chlor-alkali cells, led to numerous plant closures. In 1989 there were 26 U.S. companies producing chlorine at 51 sites with an operating capacity of 12,275 short tons. Dow Chemical U.S.A. accounted for almost a third of U.S. capacity. The top four producers shown in Table 12.20 accounted for over 70 percent of the installed capacity.

In early 1992, Dow announced it would shut down all chlorine producing and using facilities at its Sarnia, Canada, plant by mid-1993. Essentially this would decrease North American chlorine capacity by about 1500 tons per day.

The U.S. chlorine supply–demand as projected by Dow analysts[39] at the end of 1990 is shown in Fig. 12.16. Dealing with multiple issues on the environmental front and the possibility of a recession, the chlor-

TABLE 12.20 Major North American Chlorine Producers[6]

Dow Chemical U.S.A.	30.7
Occidental Petroleum Corporation	24.4
PPG Industries, Inc.	11.6
Olin Corporation	7.2
22 other companies	26.1
	100.0

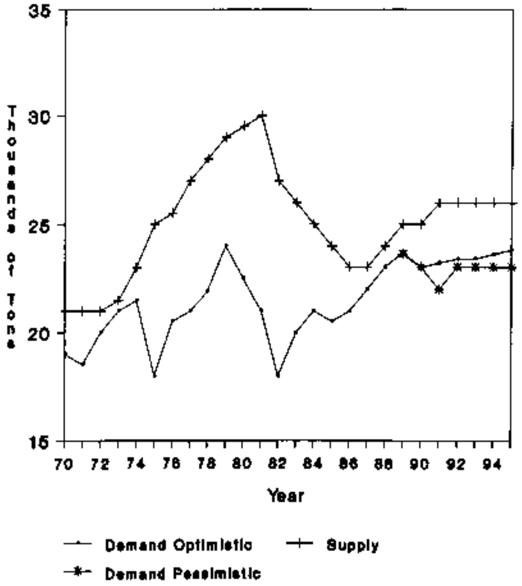


Fig. 12.16. U.S. chlorine supply and demand, based on many market variables. The more optimistic forecast assumed the pulp and paper segment would proceed only to a 50% reduction level, resulting in a 0.9% average annual growth rate for the 1988 to 1995 period. The second outlook assumed the recession forecast for the economy and a 70% reduction in demand from the pulp and paper segment, which would lead to no growth for chlorine. These two outlooks represent extreme cases. Dow analysis predicted that market growth figures would fall somewhere between the two. (*Courtesy the Dow Chemical Company.*)

alkali industry was faced with many challenges entering the 1990s.

The continued growth of vinyl chloride monomer, both domestically and globally, will ensure a sink for the bulk of the chlorine and adequate though tight caustic supplies for the pulp and paper industry. The tight caustic soda market will permit caustic producers to recover a larger portion of their chlor-alkali production costs from merchant caustic sales. The portion chargeable to chlorine will be lowered, and more ethylene dichloride capacity for VCM/PVC production will be installed.

Sodium carbonate will continue to make inroads into the caustic market. In some cases, even lime or magnesium hydroxide will be substituted for caustic. Consideration will be given to producing caustic without coproduced chlorine. The old lime soda process for the conversion of lime and soda ash into caustic will be practiced. There may even be a process to produce sodium hydroxide from sodium carbonate electrolysis, although there is currently no commercial production via this route.

HYDROCHLORIC ACID

The predominant source of HCl is as a by-product from the chlorination of hydrocarbons, including the incineration of chlorination organic wastes in thermal oxidizers. Hydrogen and chlorine can be burned together to produce HCl. Hydrochloric acid produced by the reaction of salt and sulfuric acid is not economically competitive in North America. By 1990, more than 93 percent of the HCl was being produced as a coproduct from the chlorination of hydrocarbons. HCl burners to convert chlorine plant tail gas to HCl accounted for 5 percent of total HCl production, and less than 2 percent of the HCl was produced by the salt and sulfuric acid process. It has been estimated that by 1990 over 6 million tons of HCl was being produced in North America. Accurate data for hydrochloric acid are difficult to obtain because of the large number of producing and consuming companies, the variety of grades, and the general reluctance of many producing companies to discuss HCl production and use. The production of HCl depends on demand for the primary product (vinyl chloride monomer, isocyanates, fluorocarbons, etc.). Current prices for HCl ranges from $300 to $340 per ton for the anhydrous product.

Hydrogen chloride is marketed both as anhydrous HCl and as hydrochloric acid, usually a 32 percent solution. The absorption of HCl in water customarily is achieved in a falling film absorber, followed by a packed tails tower that vents inerts to the atmosphere. The weak acid from the secondary absorber is fed to the primary absorber. The degree of absorption of the HCl is dependent on the concentration of inerts in the gas stream. The heat of absorption of HCl in water is about 700 Btu/lb of HCl, which requires that the primary absorber be water-cooled.

Acid made by burning hydrogen in chlorine tail gas is quite pure and requires no further treatment. By-product acid requires purification in packed scrubbers in which the scrubbing medium is the hydrocarbon, which is circulated in the scrubbing tower before being sent to the chlorinator. A refrigerated cooling system frequently is employed to maintain a low temperature in the circulating scrubber liquor in order to maximize absorption efficiency.

BROMINE AND BRINE CHEMICALS*

Although bromine once was recovered from seawater in the United States, and there still are seawater operations in France and Spain, the most important source of bromine is brines and bitterns (the mother liquor from a saltworks). Seawater contains only 65 ppm of bromine, so very large volumes of it must be processed to recover bromine. Major sources of commercial bromine are underground brines in Arkansas (which contain 3000 to 5000 ppm bromine), China, Russia, and the United Kingdom. Bitterns from mined potash in France and Germany, seawater bitterns in India, Italy, and Japan, and bitterns of potash production (which contain 12,000 ppm bromine) from Dead Sea brines in Israel are the other sources.[40] The United States now is the largest producer, with most U.S. production in the area around Magnolia, Arkansas. In 1990, U.S. bromine capacity was 575 million lb/year. Israel is the second largest producer, and its production is growing by far the fastest. The Former Soviet Union is third in production.

There are four major steps in bromine production: (1) oxidation of bromide to bromine with chlorine; (2) stripping of bromine from the aqueous solution; (3) separation of bromine from the vapor; and (4) purification of the bromine. The two major stripping vapors are steam and air. Steam is used when the concentration of bromine in brine is greater than 1000 ppm. The advantage of using steam is that bromine can be condensed directly from it. Air is used when seawater is the source of bromine because very large volumes of stripping gas are needed, and steam would be too expensive. When air is used, the bromine needs to be trapped in an alkaline or reducing solution to concentrate it.

In a newer steam-based process, vacuum is used, which, by matching the vapor pressure of the hot brine, causes bromine to be stripped out without the need for steam to heat the brine. Claimed benefits are increased plant capacity, reduced chlorine loss, less lime needed to treat the spent brine, lower plant maintenance costs, and decreased atmospheric emissions.[41,42]

Table 12.21[6] gives the market distribution for bromine, which in 1990 was selling for 43 to 46 cents/lb. The largest use of bromine is in the production of flame retardants. Additive-type flame retardants, such as decabromobiphenyl oxide, are physically blended into polymers; reactive types, such as tetrabromobisphenol A, chemically react during polymer formation. Brominated polymers are used in flame-retardant applications. Other large-volume bromine chemicals are methyl bromide, used as an agricultural fumigant, and ethylene dibromide, used in lead antiknock fluids outside the United States. Ethylene dibromide was once the largest-volume

TABLE 12.21 Market Distribution of Bromine[6]

Market	*Percent*
Flame retardants	27
Methyl bromide	25
Ethylene dibromide	20
Drilling fluids	10
Water treatment chemicals	
Other (i.e., photographic, rubber additives, etc.)	14
Exports	5

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*The material in this section was contributed by Philip F. Jackish, Ethyl Corp., Baton Rouge, LA, and John Pavlick, Dow Chemical U.S.A., Ludington, MI.

bromine chemical, but the phase-out of lead in gasoline and its banning as an agricultural fumigant have reduced its markets. Other bromine compounds find use as pesticides and as intermediates in various chemical processes.

A fairly new major use for bromine is in clear completion fluids used in crude oil production. These are concentrated solutions of $CaBr_2$ or $CaBr_2-ZnBr_2$, which have a high density. Several hundred pharmaceuticals contain bromine atoms. Other moderate-sized markets for bromine compounds are in photography, water treatment chemicals, extinguisher fluids, and dyes.

Miscellaneous bromine uses are in catalysts, fluxes, precious metal recovery, hair care products, food additives, flotation agents in ore treatment, solvents, refrigerants, quartz-halide light bulbs, some lasers, some photovoltaic batteries, and some electrically conductive polymers. Zinc-bromine storage batteries are being developed for use as load-leveling devices in electric utilities,[43] and this could became a significant market for bromine.

In Michigan, this debrominated brine (containing 10–20% $CaCl_2$ and 3–10% $MgCl_2$) is processed further to produce calcium chloride and magnesium hydroxide, as shown in Fig. 12.17.

Magnesium hydroxide is produced by precipitation of the magnesium ions with $Ca(OH)_2$ obtained from dolomitic limestone. The limestone is calcined in a rotary kiln to produce lime; and the lime is reacted with water to give $Ca(OH)_2$, which reacts with the Mg ions in the brine to give $Mg(OH)_2$. One-half of the $Mg(OH)_2$ comes from the dolomitic lime. The slurry of $Mg(OH)_2$ in $CaCl_2$ brine is thickened in settling tanks and filtered, and the $CaCl_2$ is washed out of the cake with water.

The major use of magnesium hydroxide is as the raw material for magnesium oxide

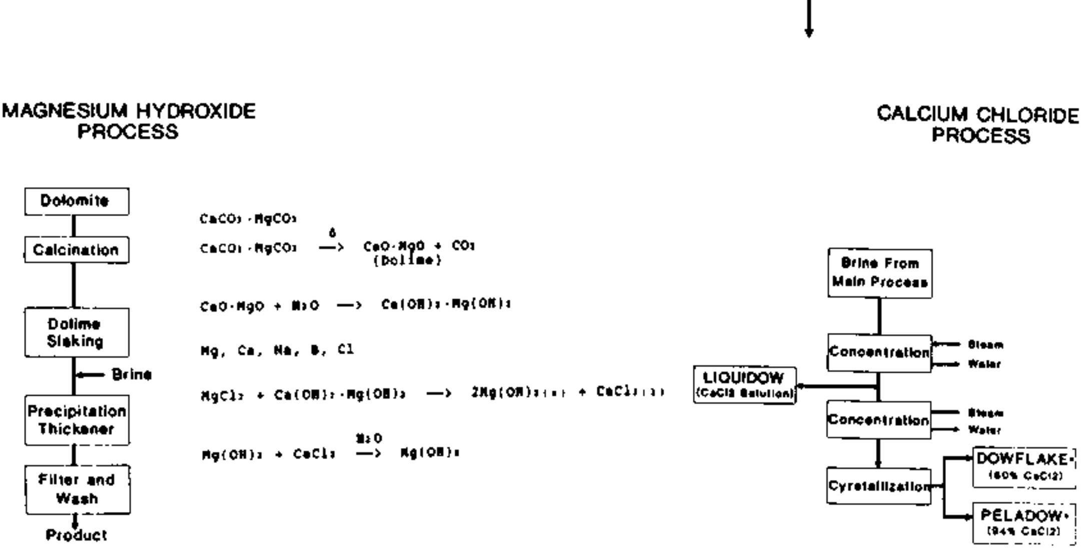

Fig. 12.17. Brine chemicals in Michigan. (*Courtesy Dow Chemical Company.*)

TABLE 12.22 Market Distribution of Calcium Chloride[6]

Market	*Percent*
Pavement deicing	35
Dust control/road stabilization	22
Industrial processing	21
Oil and gas well fluids	10
Concrete	5
Miscellaneous	4
Exports	3

production, which is used in refractory brick. The hydroxide is converted to the oxide by heat treatment in a rotary kiln or multiple hearth furnace. Other uses are in pulp and paper, Epsom salts, waste water treatment, flame retardants, and smoke supressants.

The effluent from the magnesium hydroxide process is a 25 percent calcium chloride brine. The water in the brine is boiled away with steam in triple-effect vacuum evaporators to make 32 to 45 percent $CaCl_2$. Alkali chlorides precipitate in the evaporators and are removed by settlers and centrifuges. Additional water is removed in evaporators and dryers to attain anhydrous calcium chloride at concentrations from 78 to 94 percent.

Calcium chloride is both hygroscopic and deliquescent. Thus, solid material will absorb moisture from the air or snow and ice until it dissolves, and the solution will continue to absorb moisture until an equilibrium is reached between the vapor pressure of the solution and that of the air. At 95 percent relative humidity, one pound of anhydrous calcium chloride will absorb 17.3 lb of water. The ability of calcium chloride to absorb moisture makes it useful in many construction, commercial, and industrial applications. Table 12.22 gives the market distribution of calcium chloride.[6] The 1990 calcium chloride price for 78 percent flakes was about $215/ton.

BLEACHES

Since the fledgling days of industrial chemical practice, the bleaching properties of chlorine have been in demand. It is noteworthy that the beginnings of the industry, some two hundred years ago, centered upon materials and methods of bleach manufacture. Much of modern chemical engineering practice has derived from the struggles and developments of this heritage, particularly in the closing years of the last century, when the electrolytic production of chlorine and caustic began to take hold. Rampant spread of the great killer diseases such as cholera and typhoid was shown to be easily eliminated by the treatment of wastewater and drinking water with small amounts of bleach. Textile manufacturers and the paper industry had established the value of bleach in their operations early on.

Prior to the development of the liquid chlorine industry, the only means of transporting chlorine was as bleach. Common practice in the early years was to absorb the chlorine in hydrated lime, $Ca(OH)_2$, to form chloride of lime, $CaOCl_2$. Easily transported as a solid, this chemical contains the equivalent of 35 percent Cl_2. When dissolved in water, it forms equal moles of $CaCl_2$ and $Ca(OCl)_2$:

$$2CaOCl_2 \text{ (dissolved)} \rightarrow CaCl_2 + Ca(OCl)_2$$

It is not the same as calcium hypochlorite, which contains over 99 percent available chlorine. (The term "available chlorine" refers to the oxidizing power of a bleach equivalent to that of free chlorine, as determined by the standard acidic-KI-thiosulfate titration.)

The most practical route to achieving a high available-chlorine content in a lime-based bleach involves chlorinating a slurry of lime in caustic,[8] followed by cooling to −10°F. Crystals are centrifuged off and added to a slurry of chlorinated lime containing $CaCl_2$ in an amount equivalent to the NaOCl content of the original crystals. Warming this solution produces crystals of $Ca(OCl)_2 \cdot 2H_2O$, containing around 3 percent lime as an impurity. This material, which is granulated, dried, and packaged for sale, has an available chlorine content over 70 percent.

Another approach uses chlorine monoxide and water to form a solution of HOCl, which is neutralized with a lime slurry, spray-dried, and granulated to yield a product containing 70 percent available chlorine.[32]

The lime-based products have the disadvantage of containing insoluble components, which has led to the necessity for settling and sludge disposal in some applications. These components are especially objectionable in laundry and dishwashing uses. A granular bleach based on LiOCl[30] is quite useful in these applications because it is completely soluble. It is prepared as a 35 percent solution of LiOCl by mixing solutions of LiCl and NaOCl, from which NaCl precipitates. The solution is evaporated, and the solid (containing LiOCl and NaCl) is dried and formulated with salt cake to a white, free-flowing, granular product that retains its bleaching power (35% available chlorine) reasonably well during storage.

In the bleaching of fibers for the manufacture of paper and textiles, sodium chlorite ($NaClO_2$) and/or chlorine dioxide (ClO_2) often is used because of the ability to achieve excellent whiteness without as much fiber degradation as occurs in chlorine or hypochlorite bleaching. For example, in the production of kraft paper, known for its strength, the product is brown when conventional bleach is used because bleaching to whiteness would destroy its strength. By using ClO_2, a high-strength, white product is obtained.

An additional benefit of bleaching with ClO_2 is that the waste lignin degradation products generally present fewer disposal problems than do waste products of chlorine-based bleaches.[44] Kraft pulp bleaching sequences that involved chlorine in the first stage (C), followed by caustic extraction (E), followed by two stages of hypochlorite bleaching (H), are being changed to vary the chlorine/chlorine dioxide ratio (D) in the first stage, followed by two stages of chlorine dioxide (i.e., CEHEH replaced by C_DEDED). Regulations are being contemplated regarding maximum discharge levels of chlorinated organics and dioxins. Sodium hypochlorite has been linked to the formation of harmful chloroform emissions from bleach plants. It is expected that chlorine dioxide use in bleaching will increase, both as a partial substitute for elemental chlorine and as a replacement for sodium hypochlorite. It has been shown that chlorine dioxide substitution in the first-stage bleaching sequence above the 50 percent level can reduce total organic halide (AOX) discharge by up to 50 percent and eliminate the formation of dioxins.[45] By the mid-1990s the use of oxygen and hydrogen peroxide in the lignin extraction stage (E-stage) is expected to be common, and it eventually could dampen ClO_2 demand. Also ozone bleaching may limit growth in ClO_2 bleaching.

The generation of ClO_2 from chlorate involves a complex reduction of the chlorine atom of chlorate from the +5 oxidation state to the +4 oxidation state in an acid medium. Chlorine dioxide is a very unstable molecule. It cannot be economically transported, but is easily produced in situ. Treatment of a solution of $NaClO_3$ and NaCl with acid (H_2SO_4 or HCl) produces ClO_2, which is immediately absorbed for use in bleaching. The ClO_2 generator must be operated with care to avoid ClO_2 concentrations above 10 percent, which can lead to explosion from self-decomposition. The molar ratio of ClO_2 to Cl_2 formed in the generator is 2:1. If this level of Cl_2 is objectionable, the gas mixture from the generator, which is mostly air (for safety), is passed through a tower through which chilled water is circulated. This dissolves the ClO_2, but only 25 percent of the Cl_2; so the remaining Cl_2 is scrubbed with alkali. This treatment raises the molar ratio to $8ClO_2:1Cl_2$.

Over the years a number of commercial chlorine dioxide generators have been developed. These generators can be classified according to the type of acid media (i.e., sulfuric acid or hydrochloric acid) and the type of reducing agent (i.e., sulfur dioxide, methanol, sodium chloride, or hydrochloric acid). In most processes, some elemental chlorine is liberated as a by-product. The generator using sulfuric acid produces sodium sulfate and/or waste sulfuric acid, which must be disposed. A new process (R-8 generator[46]) has been commercialized that is capable of eliminating by-product chlorine (i.e., so that there is no hypochlorite) and produces reduced quantities of by-product salt cake.

Although chlorine dioxide has replaced sodium hypochlorite use in kraft pulp bleaching, hypochlorite bleach is widely used as an ordinary household bleach because of its ease of manufacture, cost, and handling convenience. Sodium hypochlorite is produced mostly by reaction of liquid chlorine with 20 percent NaOH. Soda bleaches vary in their NaOCl content up to about 15 percent; and the higher the NaOCl content is, the higher the required excess of caustic to maintain stability. For this reason, household bleach contains 5.5 percent NaOCl. In the trade it is common to speak of the available chlorine level of soda bleach as the "trade percent." This is related to the NaOCl concentration, expressed in grams per liter, as:

$$(\text{Trade \% available } Cl_2) = (\text{GPL NaOCl}) \times 0.0953$$

$$(\text{Weight \% available } Cl_2) = (\text{Trade \%})/(\text{Specific gravity})$$

Household bleach has a weight % available Cl_2 of 5.2, and a trade % of 5.6, which is the percent of available chlorine per volume of solution. It is to be noted that not only is sodium hypochlorite an oxidant, but it yields oxygen on decomposition:

$$2NaOCl \rightarrow O_2 + 2NaCl$$

SODIUM CHLORATE

The rapidly growing use of ClO_2 in the pulp and paper industry has led to the rapid growth of sodium chlorate, $NaClO_3$, production in recent years. Sodium chlorate is rapidly produced in solution form by the electrolysis of NaCl brine in a cell that is very similar to a diaphragm chlor-alkali cell, except that it has no diaphragm. The overall reaction is as follows:

$$NaCl + 3H_2O \rightarrow NaClO_3 + 3H_2$$

In this process the chlorine and caustic produced in the cell react immediately, and the cell liquor is kept hot in an additional vessel that provides sufficient residence time for all the hypochlorite to disproportionate into chloride and chlorate:

$$3NaOCl \rightarrow NaClO_3 + 2NaCl$$

For optimum operation, the cell temperature is maintained at 65 to 75°C with a pH of 6.9. Current efficiencies of over 90 percent have been reported with a power consumption of 4500 to 5800 kWh/metric ton of sodium chlorate produced.

Various cell designs are offered by licensers of sodium chlorate technology, the anode design being the most significant variable in the chlorate cell. Coated titanium metal anodes and steel cathodes are used, and small amounts of dichromate are added to the cell liquor to passivate the steel so that corrosion is minimized. The cell liquor contains about 50 percent $NaClO_3$, which may be used as is, or evaporated to 75 percent to drop out salt, filtered, and cooled to crystallize out $NaClO_3$.

In 1990, the total North American sodium chlorate capacity was 1.1 million tons/year with 67 percent of this capacity in Canada because of its lower energy costs. Over 94 percent of the North American sodium chlorate is used for the manufacture of on-site ClO_2 for wood pulp bleaching, with the remainder being used for the manufacture of other chlorates and in perchlorates, chlorites, herbicides, and water treatment and mining. The 1990 price for bulk sodium chlorate was about $420/ton for the crystalline product. As a result of increasing demand for chlorine dioxide in pulp bleaching, a number of North American sodium chlorate producers have annomic plant expansions, particularly in Canada because of lower electric power costs. By 1995, once pulp mills reach their final chlorine dioxide substitution levels, sodium chlorate growth is expected to drop.

Akin to $NaClO_3$ is the similar manufacture of bromates, starting with NaBr, or KBr, cell feed. Bromates also are produced by bromination of the respective carbonates. The bromate business is extremely small by comparison to other oxidants, but bromates are important in the bread-making industry for maturing flour and in conditioning dough. They also are used in permanent wave lotions and in the manufacture of dyes. The bromates usually are sold as specialty chemicals. Both chlorates and bromates have substantial oxidizing power, and care must be taken in storage and handling of these solids. Contact with reducing agents and combustibles can be diastrous.

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13

Industrial Gases

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OVERVIEW

Industrial gases are considered to be those gases used in their pure form by industry in large quantities. They are used in industry as gases, liquids, or cryogenic liquids.

The gases we consider to be industrial gases have been in use for many years. For example, nitrous oxide was used as an anesthetic as early as 1799. By 1608, carbon dioxide had been identified as a specific substance acquired by several means. Some gases for industrial use are produced by means of cryogenics, which is the science and technology of dealing with the behavior of materials at extremely low temperatures.

In this chapter three types of gases are discussed: oxidizers, inert gases, and flammable gases. The gases that fall into the category of inert are nitrogen, argon, helium, and carbon dioxide. The oxidizers are oxygen and nitrous oxide. Acetylene, liquefied natural gas (LNG), and hydrogen are the flammable gases. These elements and compounds by no means encompass all gases considered to be industrial gases, but they represent the major gases used and produced in industry. (See Table 13.1.)

Nitrogen, oxygen, and argon produced for industry are primarily manufactured by the cryogenic air separation process, in which air is liquefied and separated into its major constituents (oxygen, nitrogen, argon) by the use of cryogenic technology. Table 13.2 gives the cryogenic boiling point temperatures and concentrations for some of the gases present in the atmosphere.

The cryogenic air separation process starts with air entering the plant through air filters, where it is compressed and cooled. The air is passed through heat exchangers for further cooling and for removal of water vapor and carbon dioxide by freezing. Alternatively, a molecular sieve can be used to remove the water and carbon dioxide by adsorption before separation of the air. When the air reaches a temperature of −170°C, it is sufficiently free of water and carbon dioxide and ready to be passed into the distillation column.[4]

Separation occurs by distillation. (See below, Fig. 13.5.) The distillation method used is

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[*] Air Products and Chemicals, Inc.

[**] The author wishes to acknowledge the assistance of Katanya Bolling in preparing this chapter.

TABLE 13.1 Properties of Industrial Gases

Gas Property		*Helium-4* *He*	*Para-Hydrogen* $p\text{-}H_2$	*Normal-Hydrogen* $n\text{-}H_2$	*Nitrogen* N_2	*Air*	*Argon* *Ar*	*Oxygen* O_2	*Methane* CH_4	*Acetylene* C_2H_2	*Carbon Dioxide* CO_2
(Basis)		(1)(2)	(1)(3)	(1)(3)(4)	(1)(5)	(6)	(1)(7)	(1)(8)(9)	(1)(3)	(10)(11)	(1)(8)(11)
Atomic/Molecular Weight		4.0026	2.0159	2.0159	28.0134	29.964	39.948	31.999	16.042	26.037	44.009
Normal Boiling Point	(°F)	−452.07	−423.19	−422.97	−320.42	−317.66 to −312.54 (B)	−302.56	−297.33	−258.75	−118.5 (C)	−109.33 (C)
Triple Point	(°F)	−455.75 (A)	−434.83	−434.55	−346.00	—	−308.83	−361.84	−296.45	−115.3	−69.90
	(PSIA)	0.730 (A)	1.021	1.045	1.818	—	9.994	0.02201	1.703	17.55	5.65
Critical Point	(°F)	−450.31	−400.31	−399.93	−232.44	−221.33 (B)	−188.05	−181.39	−116.59	96.5	87.8
	(PSIA)	32.99	187.51	187.51	493.00	545.01 (B)	711.52	731.42	666.88	905.4	1071.6
Gas Density											
@ NTP	(lb/CF)	0.01033	0.0052091	0.0052091	0.072456	0.074911	0.10336	0.082786	0.041553	0.067814	0.11438
@ STP	(lb/CF)	0.011150	0.0056113	0.0056113	0.078043	0.080721	0.11137	0.089209	0.044789	0.073184	0.12341
Vap. Density @ NBP	(lb/CF)	1.0543	0.083529	0.083529	0.2879	0.28057 (B)	0.3606	0.2795	0.1134		0.1462
Liq. Density @ NBP	(lb/CF)	7.8019	4.4190	4.4190	50.480	54.617	87.023	71.231	26.379	38.73 (D)	97.51 (D)
Specific Heat @ NTP	(BTU/lb-°F)	1.241	3.558	3.415	0.2487	0.2404	0.1247	0.2197	0.1134	0.3938	0.2025
Specific Heat Ratio @ NTP		1.6667	1.3834	1.4066	1.4019	1.3995	1.6693	1.3976	1.3077	1.240	1.2871
Latent Heat (D) @ NBP	(BTU/lb)	8.784	191.66	191.84	85.446	87.988 (B)	69.411	91.402	219.56	354.9 (B)	246.6 (B)

NTP = 14.696 PSIA and 70°F
STP = 14.696 PSIA and 32°F

Notes: (A) lower lambda point
(B) without CO_2
(C) sublimation temperature
(D) solid density
(E) latent heat of sublimation

Basis: (1)–NBS Computer Program MIPROPS, 32-Term Pure Component Equation Of State, APCI CAPP Ithermo 18.
(2)–NBS Technical Note 631, "Thermophysical Properties Of Helium-4 ...," Nov. 1972.
(3)–NBS Monograph 168, "Selected Properties Of Hydrogen (Engineering Design Data)," Feb. 1981.
(4)–NASA SP-3089, "Hydrogen Technological Survey—Thermophysical Properties," 1975.
(5)–NBS Technical Note 648, "Thermophysical Properties Of Nitrogen ...," Dec. 1973.
(6)–NBS Extended Corresponding States Equation Of State, APCI CAPP Ithermo 19, Dry Air Composition (Mole %): 78.088 N_2, 20.948 O_2, 0.929 Ar, 0.035 CO_2.
(7)–NBS Technical Note 27, "Thermodynamic Properties Of Argon ...," Mar. 1969.
(8)–NASA SP-3090, "ASRDI Oxygen Technology Survey, Vol. IX: Oxygen Systems Engineering Review," 1975.
(9)–NASA SP-3071, "ASRDI Oxygen Technology Survey, Vol. I: Thermophysical Properties," 1972.
(10)–Local Composition Peng-Robinson Equation Of State, APCI CAPP Ithermo 17.
(11)–Average of APCI, Linde, Matheson, and MSDS published thermophysical data.

TABLE 13.2 Cryogenic Gases: Boiling Point and Concentration in Air

	Normal Boiling Point (°F)	*Dry Air Concentration (by Vol.)*
Argon	−302.6	0.93%
Nitrogen	−320.5	78.1%
Oxygen	−297.3	20.94%
Helium	−452.1	0.0005%
Hydrogen	−422.99	0.00005%
Neon	−410.7	0.0018%
Krypton	−244.0	0.00011%
Xenon	−163.0	0.000008%

referred to as "double column," as it contains two separate distillation columns operated at two different pressures. The cooled air is fed to the bottom of the high-pressure column. Air is distilled in this column where the higher boiling temperature fluid oxygen stays at the bottom and the lower boiling temperature nitrogen boils to the top as a distillate product. The crude liquid oxygen from the high-pressure column is flashed into the low-pressure column as the two columns are thermally linked by a common reboiler/condenser. Vapor is withdrawn from the middle of the low-pressure column and is passed as feed to the crude argon column. The vapor in that column is condensed and taken off as liquid crude argon. Pure nitrogen vapor is extracted from the top of the low-pressure distillation column, and liquid oxygen is taken from the bottom of the column. Figure 13.1 shows an air separation plant with a molecular sieve front-end cleanup and liquid storage tanks.

There are other means by which the atmospheric industrial gases can be produced. In addition to cryogenic air separation, there are other, non-cryogenic-based processes,

Fig. 13.1. Air separation plant including cryogenic storage tanks and cold box. (*Courtesy Air Products and Chemicals, Inc.*)

including the membrane separation process and adsorption processes. The adsorption processes include pressure swing adsorption (PSA) and vacuum swing adsorption (VSA).

The membrane separation process is used to produce a number of gases for industrial use. The membrane may consist of a microporous substructure of cellulose acetate and a thin layer of dense cellulose acetate (active layer) on the upper surface, resembling a sponge covered by a plastic film. The membrane is cast into a supporting cloth for added mechanical strength. The active layer serves as the separating barrier and, because of its thinness, provides very high transport rates. The membrane selectively allows the smaller molecular-sized components to pass through the membrane substructure, thereby accomplishing the separation process.

The VSA system is a noncryogenic process that makes use of pressure that is less than atmospheric (vacuum) and adsorbents to separate nitrogen, and carbon dioxide from air. The PSA system is a similar process for producing a particular gas by passing a pressurized gas stream through a set of adsorbent beds. The impurities are selectively adsorbed using a molecular sieve to trap the undesired components. In the production of oxygen using the VSA process, the VSA system separates air at ambient temperature by passing it through a column of adsorbent. The adsorbent, which is an inorganic crystal material, selectively adsorbs nitrogen molecules on its surface, while the oxygen molecules pass on through the adsorbent column. The final oxygen product exits the adsorber column. The nitrogen adsorbed is released when the adsorber column is reactivated by use of differential pressure from a vacuum. Once the adsorber column is reactivated, the cycle is ready to be repeated.

In the PSA system, compressed air is passed through a column of chemical adsorbent, which is a carbon-based material that essentially traps the oxygen molecules and allows the nitrogen molecule to pass through to the use point. Figure 13.2 shows the process flow of a PSA system, which can produce 98 to 99.5 percent pure nitrogen without the need of downstream purification. These adsorption systems usually are located at the customer sites. See Fig. 13.3 for an example of an on-site PSA.

Most of the industrial gases are filled in high-pressure gas cylinders for small-volume users. These cylinders then are loaded onto flatbed trucks for delivery. For larger-volume gas transportation, long-length gas cylinders are permanently mounted on trailer frames. These high-pressure-cylinder vehicles commonly are referred to as tube trailers. The cylinders are constructed of alloy steels, and are designed, built, tested, and maintained in accordance with U.S. Department of Transportation (DOT) regulations. The typical small-volume cylinders are constructed to a DOT 3A or 3AA specification, and typically have rated service pressures from 2015 psig to 2640 psig and water volumes from 0.39 to 1.75 ft^3. The larger cylinders often have similar pressure ratings but water volumes of approximately 75 ft^3.

The containers used for transporting and storing the majority of cryogenic liquids are insulated cryogenic tankers, liquid cylinders, and stationary storage tanks. These containers are similar in design to a thermos bottle. There are an inner vessel, which contains the cryogenic product, and an outer vessel. The space between the two vessels is under a vacuum and usually contains a wrapped insulation material such as aluminized Mylar, or it may contain a powdered insulation such as expanded perlite. The liquid cylinders, usually 160 or 250 liters in capacity, are constructed to a DOT 4L specification and operate with pressures up to 235 psig. The cryogenic tank trucks may be constructed to a DOT MC-338 specification, and range in capacity from 3000 to 14,000 gallons, usually depending on the product. The operating pressures may range from 25 to 150 psig, and the vehicles often are equipped with cryogenic pumps used to deliver the product to higher-pressure storage tanks. The stationary storage tanks are designed and built to ASME standards, typically are constructed for pressures of 250 psig or less, and may range in capacity from 500 to 70,000 gallons.[2]

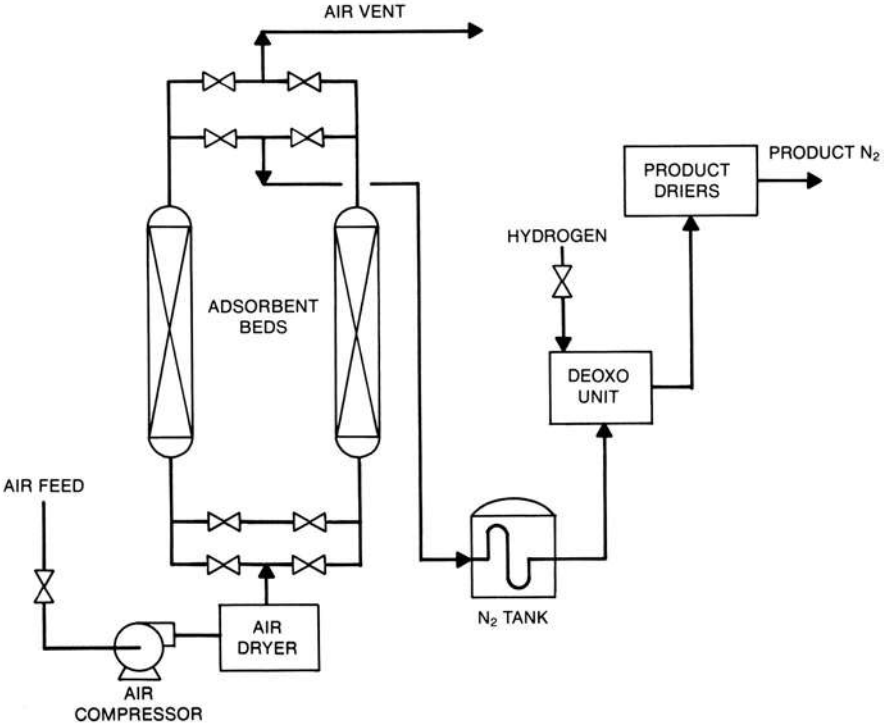

Fig. 13.2. Process diagram for nitrogen PSA (pressure swing absorption) system. (*Courtesy Air Products and Chemicals, Inc.*)

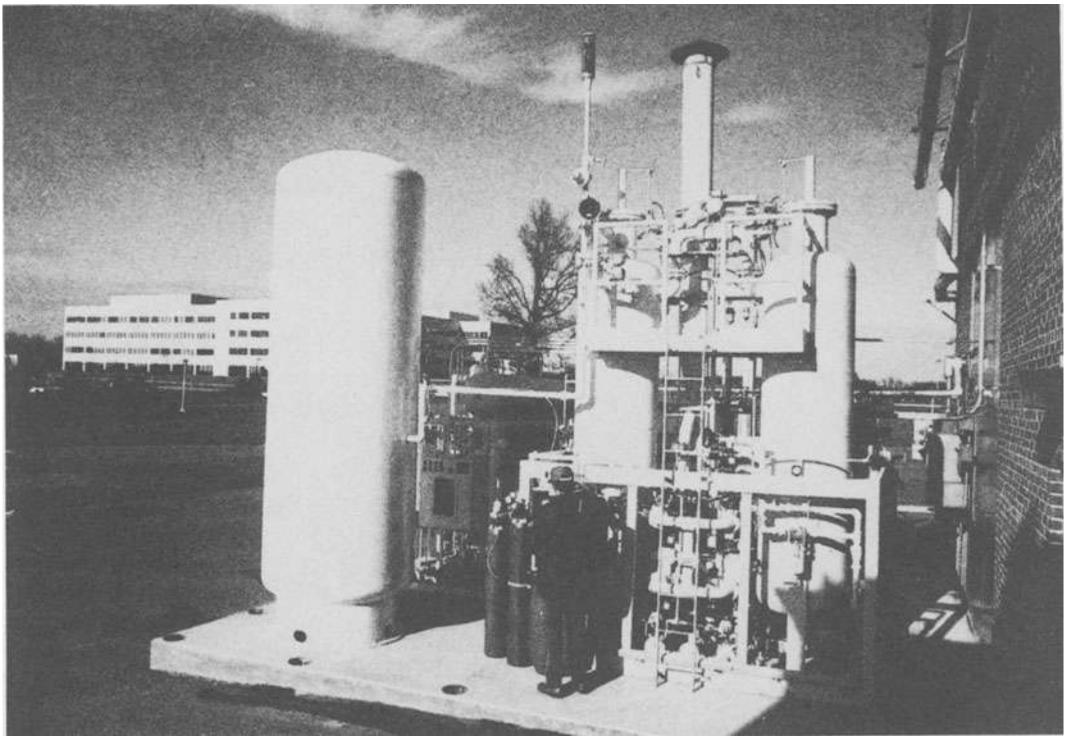

Fig. 13.3. An on-site nitrogen PSA supply system. (*Courtesy Air Products and Chemicals, Inc.*)

NITROGEN

Nitrogen makes up 78 percent of the earth's atmosphere. It is a colorless, tasteless, nontoxic, and inert gas. Nitrogen does not support combustion nor does it support respiration; but it reacts with the more active metals such as lithium and magnesium to form nitrides, and at high temperatures it will combine with hydrogen, oxygen, and other elements. As a cryogenic liquid, nitrogen is nonmagnetic, stable against mechanical shock, and free of toxic or irritant vapor.

Nitrogen usually is produced by cryogenic air separation, liquefaction of atmospheric air, and removal of the nitrogen by fractionation, as described earlier. Noncryogenic adsorption technology, including PSA and VSA systems, economically provides nitrogen for requirements between 4000 and 30,000 standard cubic feet per hour (scfh).

Nitrogen has many applications, both as a gas and as a liquid. As a gas, nitrogen is employed primarily as a fluid for inerting and pressurizing systems, used, for example, in the following ways: for the agitation of color film solutions in photographic processing and for blanketing of oxygen-sensitive liquids and volatile liquid chemicals; in the production of semiconductor electronic components and for dressing nonferrous metals; in the transportation industry, in pressurizing aircraft tires and emergency bottles to operate landing gear; and often to purge and pressurize pipelines, reactor vessels, or storage tanks throughout the petrochemical industry.

Gaseous and liquid nitrogen has applications in the foods industry in the areas of food processing and packaging. Liquid nitrogen is used for rapid freezing of expensive or highly perishable foods, such as shrimp and other meat products, as well as to refrigerate foods in long-distance hauling. A gaseous nitrogen atmosphere can help to retard the spoilage of some food products.

Liquid nitrogen is used in the cold-trapping of material such as carbon dioxide from gas streams, as a coolant for electronic equipment, for pulverizing plastics or rubber materials, and for simulating the conditions of outer space. It is used to freeze liquids in pipelines during repairs to the pipeline. Liquid nitrogen frequently is employed in medicine to preserve whole blood, livestock sperm, and other biological specimens.

Liquid nitrogen gas is transported in liquid cylinders, nonpressurized dewars, cryogenic tankers, and trailers. Gaseous nitrogen is transported in high-pressure gas cylinders and tube trailers. Both forms of nitrogen also are transported via pipeline when locations relative to sources permit.

OXYGEN

This substance, which occupies 21 percent of the earth's atmosphere, has a number of very important uses. Oxygen is a colorless, odorless, and tasteless gas that is essential to the support of life. All elements except the inert gases combine directly with oxygen to form oxides. Oxygen is nonflammable, but is an oxidizer that readily supports combustion.

A large percentage of the oxygen produced commercially is made by cryogenic air separation. However, this separation is not the only oxygen-producing system; oxygen also may be made by the most common decomposition reaction, electrolysis of water. This reaction produces not only oxygen but hydrogen as well, although it is not usually an economically viable alternative when compared to other technologies.

Oxygen's major applications stem from its life-supporting and combustion-supporting properties. It is used extensively in medical applications for therapeutic purposes, for resuscitation in asphyxia, and with other gases in anesthesia. Also it is used in high-altitude flying and deep sea diving, and it is an inhalant and a fuel oxidizer in the U.S. space program.

For industrial applications, oxygen is in large demand for use with acetylene, hydrogen, and other fuel gases for purposes such as metal cutting, welding, hardening, and dehydrating. Oxygen enhances the capability of steel and iron furnaces. Oxygen is used in the production of synthesis gas—hydrogen–carbon dioxide mixtures from coal, natural gas, or liquid fuels; the synthesis gases are used to make gasoline,

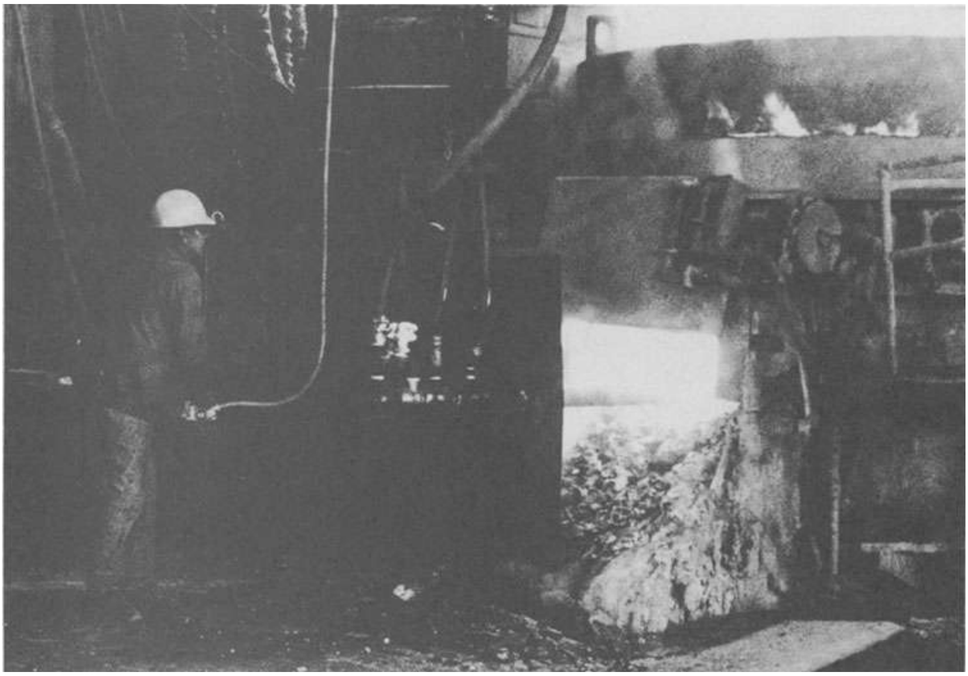

Fig. 13.4. Oxy-fuel burner firing into an arc furnace. (*Courtesy Air Products and Chemicals, Inc.*)

methanol, and ammonia. Oxygen may be used for the cracking of methane or natural gas by partial oxidation to produce acetylene, an important basic chemical.

One of the largest commercial applications for oxygen is the Basic Oxygen Furnace (BOF) for refining iron and making steel. Another common application is its use in oxy-fuel burners in the steel industry. It is used in electric arc furnaces, which melt scrap metals by passing an electric current through large graphite electrodes. Figure 13.4 shows such a burner.

Oxygen enrichment is a process whereby oxygen is added to an air stream to improve a plant's efficiency. Combustion results in the generation of heat and gaseous by-products, usually carbon monoxide, carbon dioxide, and water vapor. Oxygen enrichment is used in pulp mills to increase lime production from existing equipment and eliminate the need to purchase lime from other industries. It is used again in the pulp mills to reduce airborne sulfur emission to comply with federal environment regulations.

Gaseous oxygen is transported in high pressure gas cylinders, tube trailers, and portable cylinder modules. Liquid oxygen is transported as a cryogenic fluid in liquid cylinders and insulated cyogenic tankers. Customer on-site storage is usually accomplished in large insulated cryogenic tanks.

ARGON

A relatively scarce gas, argon is colorless, odorless, tasteless, and nontoxic. It forms no known chemical compound; thus it is extremely inert.

Representing only 0.93 percent of the earth's atmosphere, argon is utilized in a variety of applications. In the manufacture of lighting devices, it is used to fill lamp bulbs and to produce colors in display tubes for lighted signs. In the field of electronics, argon provides an inert atmosphere for the production of semiconductors. Some metal welding and cutting applications are required to have an inert gas shield, and argon gas often is used

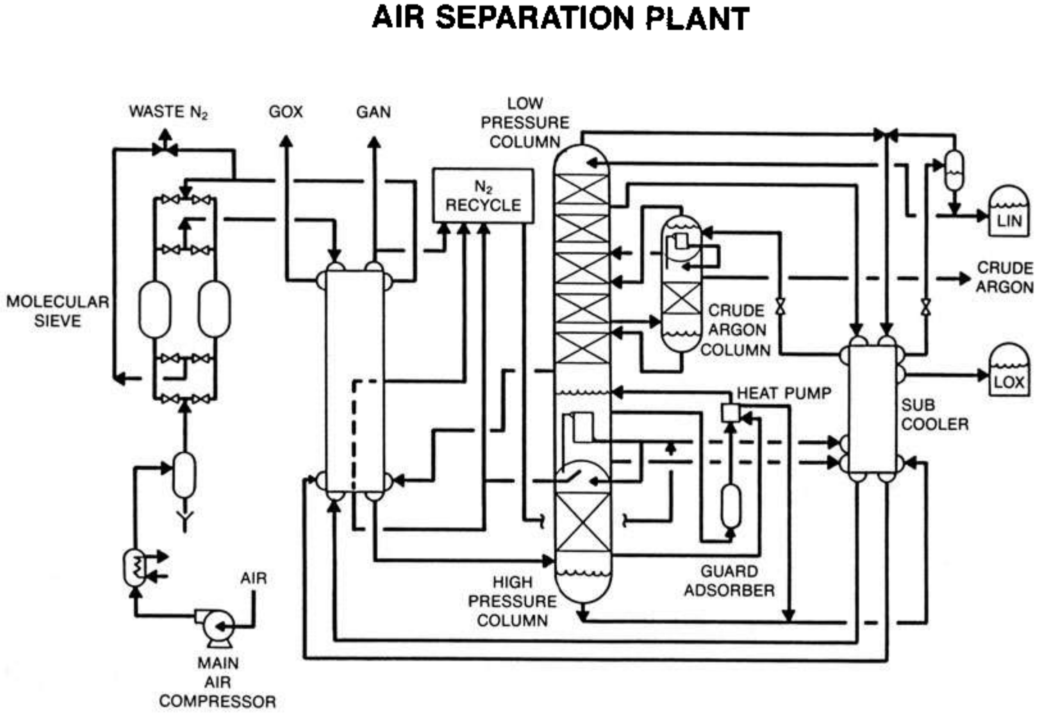

Fig. 13.5. Flow diagram for an air separation plant. (*Courtesy Air Products and Chemicals, Inc.*)

to fill this requirement. Also it is used as a blanket in the production of many reactive materials, including titanium and zirconium. It is often used to provide a protective shield for the growing of silicon and germanium crystals.

Argon is manufactured in oxygen–nitrogen plants by means of fractional distillation after the liquefaction of air as described above, in the cryogenic air separation process. In the distillation process where air is separated into oxygen and nitrogen, a stream of gas is withdrawn from the low-pressure column to enter the crude argon column. The argon content of the gas, initially 10 percent, is increased to 95 percent by subjecting the gas to several stages of distillation. This "crude" argon is further purified to yield the final pure argon product. Figure 13.5 shows a typical air separation process flow diagram.

For economic reasons argon often is shipped as a liquid. Liquid argon commonly is transported in liquid cylinders, cryogenic trailers, and portable tanks. Argon can be shipped in high-pressure gas cylinders and high-pressure cylinder trailers.

HYDROGEN

Hydrogen, the lightest element known, is extremely flammable and is found in 0.00005 percent concentration in air. The hydrogen molecule exists in two distinct forms: ortho and para, named according to their types of nuclear spins. Ortho-hydrogen molecules have a parallel spin, and para-hydrogen molecules have an anti-parallel spin. There is no difference in the chemical or transport properties of these forms, but there is a difference in thermodynamic properties. Para-hydrogen is the form preferred for rocket fuels. Hydrogen consists of about three parts ortho and one part para as a gas at room temperature, which is referred to as normal or equilibrium hydrogen. The concentration of the para form increases with decreasing temperature until, for the liquid, the para concentration is nearly 100 percent. If hydrogen should be cooled and liquefied rapidly, the relative three-to-one concentration of ortho to para would not immediately change.[2]

Conversion to the para form takes place at a relatively slow rate and is accompanied by the release of heat. For each pound of rapidly cooled liquid hydrogen that changes to the para form, enough heat is liberated to vaporize approximately 1.5 lb of liquid hydrogen. However, if a catalyst is used in the liquefaction cycle, para-hydrogen can be produced directly without loss from self-generated heat.

Hydrogen can be produced by steam methane reformation (the most widely used process) or by off-gas purification. Hydrogen can be produced at normal purity (95–98%) or at ultra-high purity (99.99%). The first step to obtain purity hydrogen in the steam reformer process when using a natural gas feedstock is to perform a pretreatment. There are small amounts of sulfur in natural gas that must be removed. The sulfur removal is done by preheating the natural gas to 700°F, and then sending it through a catalytic reactor. The catalyst inside the reactor absorbs the sulfur. The second step is steam methane reforming. In this procedure, natural gas and steam are sent through a set of reformer tubes which are packed with a reforming catalyst. The reaction is heated by a furnace inside the reformer. The methane and steam react, and the results are 45 percent hydrogen, 40 percent steam, 8 percent carbon monoxide, and 7 percent carbon dioxide. The third step to obtain normal purity hydrogen is gas shifting. Carbon monoxide, hydrogen, and steam are sent through a shift converter where the gas is heated between 400°F and 700°F. The carbon monoxide and steam react to yield hydrogen and carbon dioxide.

To produce pure hydrogen, the carbon dioxide must be removed. The gas passes through a carbon dioxide removal system, which contains a chemical solvent that goes through the gas and selectively absorbs the carbon dioxide. Heat then is added to the solvent to discharge the carbon dioxide. The regenerated solvent is returned to the system to continue the removal of carbon dioxide.

To obtain ultra-pure hydrogen, the pressure swing adsorption (PSA) system is considered. In this process, hydrogen, steam, and carbon dioxide are introduced to the system. At high pressure, the gas is passed through an adsorbent bed, and the adsorbent picks up the impurities and allows hydrogen to pass through the bed. In the regeneration process, the pressure is lowered to purge out impurities. Then the hydrogen is used to rinse the adsorbent and repressurize the vessel. The efficiency of the hydrogen purification system is optimized at an operating pressure that allows use of a catalyst tube in the reformer.

There are four other distinct processes by which hydrogen may be produced under the off-gas purification method: pressure swing adsorption (PSA), membrane separation, catalytic purification, and cryogenic separation. The cryogenic separation process uses cryogenic principles to condense and separate the impurities from hydrogen. Impure hydrogen is introduced to the cryogenic system or "cold box." The impurities are factored out, and pure hydrogen is obtained. Figure 13.6 shows a typical facility where liquid hydrogen is stored and produced.

Membrane separation makes use of two layers of membrane material; the first layer

Fig. 13.6. Liquid hydrogen plant. (*Courtesy Air Products and Chemicals, Inc.*)

is nonporous, and the second layer is porous. A gas mixture under increased pressure is subjected to the surface, which allows a smaller molecule such as hydrogen to permeate faster than a larger molecule such as carbon dioxide.

The catalytic purification process requires the use of many catalysts to convert impurities into compounds. Hydrogen, chlorides, oxygen, and carbon oxides are passed through several catalytic reactors. In the first reactor, the chlorides are absorbed. In the second reactor, oxygen and hydrogen react to obtain water/steam, which is easily separated. In the third reactor, the carbon oxides react with hydrogen to yield methane, which would be considered an acceptable impurity in this particular hydrogen product stream.

Some other sources for hydrogen are the dissociation of ammonia, steam reforming of light hydrocarbons, and by-product streams of chemical and petroleum processing. The "steam iron" process is another method used to make hydrogen. Passing steam over heated, spongy iron reduces the steam to hydrogen with additional formation of iron oxide. There are several varieties of this process. The water–gas reaction is a reaction of steam with incandescent coke or coal; it is a source of hydrogen with carbon monoxide as an additional product. In the catalytic version of this reaction, excess steam breaks down to form more hydrogen while oxidizing the carbon monoxide to form carbon dioxide. Hydrogen frequently is obtained as a by-product of cracking operations using petroleum liquids or vapors as feedstock. Also hydrogen may be produced through the electrolysis of water.

There are many applications for hydrogen. It is used to make fertilizers, as the active ingredient in detergents, and in the manufacture of polyurethanes. It finds application in the production of semiconductor devices, in the process of refining crude oil, in food processing for edible oils and shortening, and as fuel for the space shuttle. The hydrogenation of edible oils in soybeans, fish, cottonseed, and corn produces solids used in shortening and other foods. Many alcohols also are produced by the hydrogenation of the corresponding acids and aldehydes. It is possible to use hydrogen in low concentrations as a physiologically inert gas for a breathing atmosphere where multiple gases are involved.

In the metals industry, hydrogen is used for applications such as annealing metals. It is also used as a fuel in underwater oxy-hydrogen torches and with oxy-hydrogen welding and cutting systems. Hydrogen serves as a nonoxidizing shield alone or with other gases in furnace brazing and in welding aluminum, magnesium, and lead. The temperature in the oxy-hydrogen flames is about 4000°F, which is suitable for low-temperature welding and brazing. It also is used in underwater cutting. Oxy-hydrogen flames are used in the fabrication of quartz and glass. Atomic hydrogen welding is suitable for very thin stock and can be used with practically all nonferrous alloys. In the process, an arc with a temperature of about 11,000°F is maintained between two nonconsumable metal electrodes. Molecular hydrogen fed into the arc is transformed into atomic hydrogen, which sends heat from the arc to the weld zone. At the surface of the welding area, the atomic hydrogen recombines to molecular hydrogen, with the release of heat.

Liquid hydrogen is very important as a fuel for powering missiles and rockets. It is used in laboratory research on the properties of some materials at cryogenic temperatures, work often associated with studies of superconductivity. Liquid hydrogen can be used as a fuel, for either propulsion or heating.

Hydrogen gas is shipped in high-pressure gas cylinders and high-pressure cylinder trailers. Liquid hydrogen is shipped in insulated portable containers, and in cryogenic tankers. The normal liquid hydrogen supply system utilizes a cryogenic stationary storage tank rated at 150 psig, just below the critical pressure of hydrogen. A cryogenic pumping station, which has a liquid hydrogen storage tank, a high-pressure cryogenic pump capable of supplying liquid hydrogen at 3000 psig, and high-pressure gas storage tubes, often is used to supply large quantities at pressures above 150 psig.

HELIUM

Helium was discovered during an eclipse as an orange line in the spectrum of the sun's atmosphere. Physically, helium is colorless, odorless, and tasteless; and it is the second lightest element, second only to hydrogen. Helium is chemically inert and has only a 5 ppm concentration in the atmosphere.

One of helium's first uses was as a nonflammable replacement for hydrogen for inflation of lighter-than-air aircraft. Today liquid helium is vitally important in cryogenic research, as it is the only known substance to remain fluid at temperatures near absolute zero. It has a unique use as a refrigerant in cryogenics and is the only nuclear reactor coolant that does not become radioactive. Liquid helium is used extensively with superconducting magnets; in the medical field, it is used to cool the superconducting magnets for magnetic resonance imaging (MRI).

Helium has a variety of other uses in welding and lighting. It is used as an inert gas shield in arc welding, for filling cold weather fluorescent lamps, and to trace leaks in refrigeration and other closed systems. Also helium is used for specialized purging and pressurizing applications. Helium can be used in place of or together with nitrogen as the inert portion of the atmosphere in sealed environments such as space vehicles, deep-sea submergence vehicles, and diving suits. The use of helium in a plasma arc furnace, is becoming an increasingly popular method for melting precious metal ores and scrap.

Small amounts of helium are extracted from the atmosphere by fractionation methods, but not commercially because of the small amount of helium in the atmosphere. A number of natural gas wells contain helium, which can be recovered by a liquefaction and stripping process. Natural gas containing at least 0.2 percent helium has been found in the American Southwest, where the natural gas fields are the major U.S. source of helium. Those helium-rich fields are within 250 miles of Amarillo, Texas; other helium-bearing fields have been found in Saskatchewan, Canada, and in areas near the Black Sea. Helium cannot be synthesized; so conservation and cleanup recycle systems for "spent" gas are important means of preserving the earth's helium resources.

Gaseous helium is stored and transported in high-pressure gas cylinders, high-pressure gas trailers, and portable cylinder modules. Liquid helium is transported in liquid cylinders, portable tanks, and cryogenic tankers. Because of the extremely low temperature of liquid helium and the cost to produce it, special design considerations must be given to storage containers in order to maintain the helium in the liquid phase. Some containers are designed to include a sacrificial liquid nitrogen shield that intercepts heat before it is transferred into the liquid helium.

CARBON DIOXIDE—CO_2

The carbon dioxide market in the United States is served by both gaseous and liquid/solid carbon dioxide. The consumption of CO_2 gas is approximately 22 million tons per year with the enhanced oil recovery and urea production markets being the primary consumers. Liquid and solid consumption is about 5 million tons per year serving primarily the food and beverage processing industries. Carbon dioxide is used extensively in a variety of areas. It is used for pressurizing, and as a source of bubbles and the acidic taste in soft drinks. Carbon dioxide is used to fill a type of fire extinguisher that literally depends on the inertness of the compound. Carbon dioxide is also used in freezing specialty and quality foods.

More specifically, each physical phase of carbon dioxide has uses in many areas. Gaseous carbon dioxide is used for the pH control in water treatment and as a growth stimulant for plant life. Liquid carbon dioxide is used in one case as an expendable refrigerant for low-temperature testing of aviation, missiles, and electronic components. It is also used in controlling chemical reactions and for stimulation of oil and gas wells. Solid carbon dioxide, commonly called "dry ice," is used extensively as a refrigerant for dairy products, meat products, and other frozen foods while in transit. It is also used as a cooling agent in many industrial processes such as grinding heat-sensitive materials, cold-treating metals, shrink fitting machinery parts, in vacuum cold traps, in cryo-surgery, and specimen preservation and storage.

Carbon dioxide is usually nonreactive and nontoxic. At normal atmospheric pressure and temperature, it is colorless and odorless. Carbon dioxide will not burn, nor will it support combustion. Unrefined carbon dioxide gas is typically obtained from the combustion reaction of coal, coke, natural gas, and other carboniferous fuels. The gas obtained from the combustion process is liquefied and purified by several different processes to a purity of about 99.9 percent.

The major source of carbon dioxide is as a by-product of steam-methane reforming. The resulting reformer syngas may utilize one of the following three processes in the production of carbon dioxide. Carbon dioxide may be manufactured at 95 percent purity by the membrane separation process from a similar gas or from natural gas. In the recovery of high purity carbon dioxide from the syngas or natural gas, and before any separations can occur, a pretreatment step removes any contaminants and any condensate liquids that may be present. The feed gas then enters the membrane system at 300 to 1000 psig. The permeate gas is delivered at pressures between 50 to 150 psig and at a carbon dioxide purity of about 95 percent. The high pressure residual gas containing 10 to 30 percent carbon dioxide enters a conventional treatment process such as monoethanolamine or diethanolamine for a final cleanup. The carbon dioxide off-gas from the conventional treatment process is then elevated to the same pressure as that of the permeate gas from the membrane system. The combined streams may be further compressed to higher pressures, such as 2000 psig for applications in carbon dioxide flooding in enhanced oil recovery.

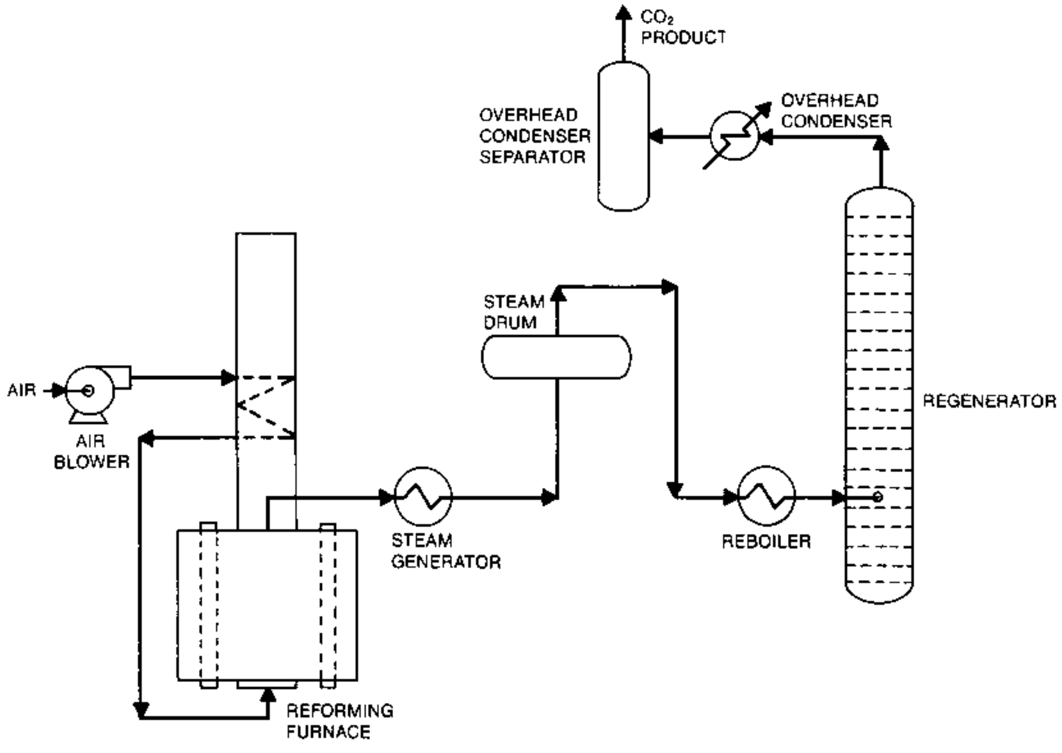

Fig. 13.7. Process diagram for CO_2 recovery using solvent absorption method. (*Courtesy Air Products and Chemicals, Inc.*)

A second process used in the production of carbon dioxide is pressure swing adsorption. The feed gas usually contains approximately 20 percent carbon dioxide, 70 percent hydrogen, and the remainder methane, carbon monoxide, nitrogen, and water. The feed gas is typically under a pressure of 125 psig to 400 psig at temperatures of 80 to 120 degrees Fahrenheit. The carbon dioxide and water are strongly adsorbed in the absorb beds and the residual gas stream is depressurized for further recovery. The absorber vessel is then evacuated through vacuum blowers where the carbon dioxide, which has been adsorbed by the bed, is relased at purities essentially 99 + % pure.

Recovery of pure carbon dioxide from reformer syngas has often been accomplished through absorption by liquid solvents. The solvents used are: monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA). See Fig. 13.7 for the process flow diagram. In this process, the syngas stream from the reformer is sent to the stripper column where the carbon dioxide is absorbed by the solvent. The residual gas stream components are discharged from the stripper column. The carbon dioxide in solvent is sent to the regeneration column where the carbon dioxide is regenerated and discharged for further purification by compression dehydration and refrigeration steps. The solvent is returned to the stripper column. The final product is essentially 99.9 percent pure.

Liquid carbon dioxide is transported in high pressure gas cylinders or liquid cylinders, and in foam insulated tank trucks. Solid carbon dioxide is packaged in various blocks wrapped in heavy paper or heavy insulated bags. Liquid carbon dioxide is normally stored in a foam insulated tank that has a refrigeration unit to maintain the tanks temperature and pressure.

LIQUEFIED NATURAL GAS

The advantages of liquefied natural gas (LNG) are evident in that over 600 standard cubic feet of natural gas occupy only one cubic foot of space in its liquid form at −260°F and atmospheric pressure. This significant volume reduction reduces the storage and transport volume, and allows shipment of natural gas in areas where pipelines were never feasible. The primary vehicle for transporting LNG is the cryogenic tanker. It also is transported in specially designed ships.

LNG is composed predominantly of methane, which may contain minor quantities of ethane, propane, nitrogen, helium, and other components normally found in natural gas.

In the past the liquefaction of natural gas used a classic cascade cycle. The process required 120,000 horsepower for liquefaction of over 150 million standard cubic feet per day. Provisions are made for some of these cycles to use seawater for cooling. Later, baseload LNG plants utilized mixed refrigerant cycles, such as Air Products and Chemicals, Inc.'s propane precooled mixed refrigerant system. Baseload plant capacities range from about 70 mmscf/day to about 350 mmscf/day of LNG. Baseload plants move LNG from remote sites by ship to populated areas. For example, Indonesia supplies LNG to Japan for electric power generation.[7]

At baseload LNG production plants, natural gas enters the plant at near 85°F and 600 psig. The gas is treated to remove carbon dioxide and any sulfur compounds, and it is cooled with high-level propane refrigerant to remove as much water as possible. Dehydration to a dew point of about −100°F is done by carrying out regeneration with dried outlet gas by way of a high-pressure steam heater and a regeneration gas compressor. The dry, treated gas is passed through a stationary bed of activated carbon for removal of mercury, and is cooled with two successively lower levels of propane refrigeration. A scrub column makes a rough fractionation to remove the heavier and medium carbon compounds. The gas at the bottom of the scrub column flows to a fractionation train, which consists of a deethanizer, a depropanizer, and a deubtanizer where relatively pure ethane and propane are produced. Excess ethane, propane, and butane from the

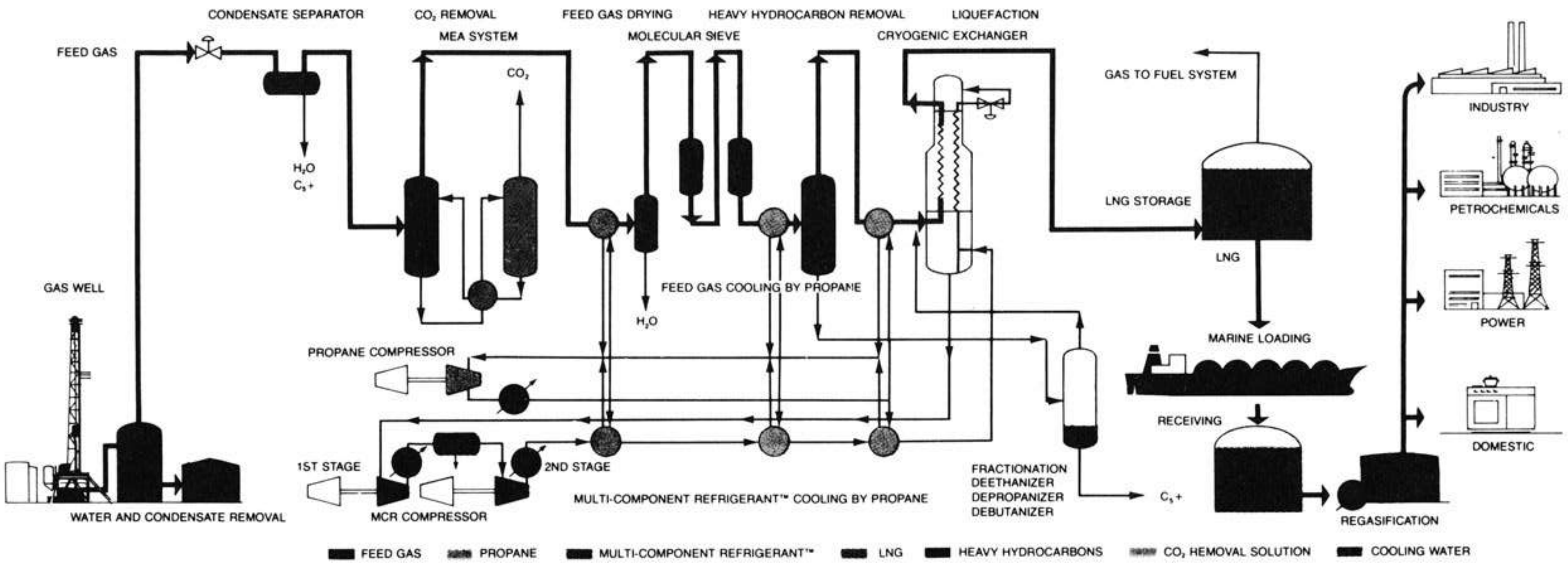

Fig. 13.8. Schematic of process flow for a baseload LNG plant. (*Courtesy Air Products and Chemicals, Inc.*)

fractionation process are reinjected into the main gas stream just prior to liquefaction. The overhead from the scrub column flows to the main heat exchanger for liquefaction to LNG. Figure 13.8 shows the process flow for a LNG plant.

For years LNG has been used for peak-shaving purposes, which is the storage of excess capacity of liquid natural gas to be revaporized for the coldest days of the year. In recent years LNG has been used in heating and vehicle propulsion. Also LNG is used to produce carbon black, which has applications in the manufacture of rubber products and printing ink. The burning of high-purity LNG (methane) is done to make carbon black for particular use in electronic devices.

ACETYLENE

Acetylene (C_2H_2) is a colorless and flammable gas. At 100 percent purity, acetylene is odorless, but at commercial purity it has a garliclike odor. Acetylene can be liquefied and solidified with ease, although in both cases it explodes with extreme violence when ignited.

Acetylene can be inhaled in rather high concentrations without chronic, harmful effects. In fact, it has been used as an anesthetic. However, it is a simple asphyxiant if present in concentrations high enough to deprive the lungs of oxygen and produce suffocation.[1]

A primary method for the manufacture of acetylene is to react calcium carbide, the principal raw material, with water to produce acetylene with calcium hydroxide as a by-product:

$$CaC_2 + H_2O \rightarrow C_2H_2 + Ca(OH)_2$$

Acetylene also is manufactured by thermal or arc cracking of hydrocarbons and by a process utilizing the partial combustion of methane with oxygen. The acetylene produced from calcium carbide is basically pure, with only water and air as impurities.

Eighty percent of the acetylene produced is used for chemical synthesis. Acetylene is an important raw material for a series of organic compounds such as acetaldehyde, acetic acid, acetic anhydride, acetone, and vinyl chloride. Those compounds are used to manufacture a large group of products, including plastics, synthetic rubber, dyestuffs, solvents, and pharmaceuticals, and in the manufacture of carbon black. The other 20 percent is used for oxy-acetylene welding, cutting, heat treating, lighting purposes, buoys and beacons.

In the primary method for producing acetylene, calcium carbide is fed into a generator containing water. The resulting wet acetylene gas at 120°F to 140°F is piped to a cooler condenser where it is cooled to 80°F to 90°F and the water vapor is condensed. This is the first step in the drying process. The gas then goes to a low-pressure dryer filled with calcium chloride. The calcium chloride absorbs the moisture from the acetylene gas, which then enters a compressor, where the pressure is increased to 200 to 375 psig. An oil separator filters out excess impurities and oil. The gas next goes to a high-pressure dryer, where all remaining water is removed. The gas is then pumped into cylinders for shipment. The by-product calcium hydroxide is sent to a storage tank, where water is decanted off the top, and is recovered.

The only method of distributing acetylene other than pipeline, is by means of portable steel tanks containing a porous solid filler saturated with acetone or other suitable solvent, in which the acetylene is dissolved under pressure. Acetylene alone is not handled at pressures higher than two atmospheres because of its tendency to decompose explosively dissolved in acetone it may be stored at pressures of 10 to 15 atmospheres.

NITROUS OXIDE

Nitrous oxide (N_2O), commonly known as laughing gas, is a colorless and practically odorless, tasteless, nontoxic gas. Nitrous oxide is an oxidizer that will support combustion, but it is a nonflammable gas. It is water-soluble; but when it is dissolved, its acidity does not change.

The primary commercial method for producing N_2O is by thermal decomposition of ammonium nitrate, with nitrous oxide and water in the primary reaction:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

The impurities formed are mostly high oxides of nitrogen and are highly toxic. After the water is removed in a condenser, the gas is washed in a solution of potassium dichromate to remove nitric oxide, in caustic to remove nitric acid, and finally in water.

Nitrous oxide is an inhalant type of anesthetic or analgesic gas. It serves as a propellant for various aerosol products, particularly with foods such as whipped cream; and it is used as an oxidizing agent in blowtorches and as a chemical reagent in the manufacture of various compounds, both organic and inorganic. It also serves as an ingredient in rocket fuel and high performance vehicle formulations, and it is used as part of the working fluid in hypersonic wind tunnels that have been investigated recently.

Nitrous oxide is filled and transported in its liquid phase in high-pressure gas cylinders or in liquid cylinders. It is transported as a liquefied compressed gas under high pressure in cylinders and at lower pressures and reduced temperatures in refrigerated cargo tanks and insulated portable tanks. Nitrous oxide is stored in a foam-insulated tank accompanied by a refrigeration unit, which is similar to the tank used for carbon dioxide.

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14

Sulfur and Sulfuric Acid

Robin W. Strickland, Ph.D.*

SULFUR

Sulfur is one of the few elements that is found in its elemental form in nature. Typical sulfur deposits occur in sedimentary limestone/gypsum formations, in limestone/anhydrite formations associated with salt domes, or in volcanic rock.[4] A yellow solid at normal temperatures, sulfur becomes progressively lighter in color at lower temperatures and is almost white at the temperature of liquid air. It melts at 114 to 119°C (depending on crystalline form) to a transparent light yellow liquid, becoming deep orange as the temperature is increased. The low viscosity of the liquid begins to rise sharply above 160°C, peaking at 93 Pa · s at 188°C, and then falling as the temperature continues to rise to its boiling point of 445°C. This and other anomalous properties of the liquid state are due to equilibria between the various molecular species of sulfur, which include small rings and chains.

Sulfur also is found as sulfide minerals in combination with iron or base metals (e.g., pyrites) and as sulfates in combination with alkali metals and alkaline earths (e.g., gypsum). Hydrogen sulfide with its "rotten egg" odor is the primary sour component of sour gas. Crude oil and coal contain a variety of complex sulfur-containing organic species. These sulfur compounds are removed from the liquid fuels by treatment with hydrogen to convert the sulfur to hydrogen sulfide, which is taken off in the gas stream. The recovery of sulfur values from sour fuels for environmental reasons is the largest source of sulfur today.

World sulfur production in 1989 was 40 million tons.[24] Over 99 percent of the sulfur that is marketed is sold as crude sulfur. The two primary grades are "bright," which is bright yellow and at least 99.5 percent (typically 99.9 + %) pure, and "dark," which can contain upwards of 0.25 percent carbonaceous material. Recovered sulfur generally is bright, whereas mined sulfur often is dark owing to traces of crude oil, which is associated with salt-dome sulfur deposits. Volcanic sulfur deposits yield bright sulfur, but it often is contaminated with toxic metal oxides. Sulfuric acid production accounts for 93 percent of the elemental sulfur

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*Freeport Research and Engineering (Affiliate of Freeport-McMoran).

used in the United States. Small quantities of several specialty sulfurs are produced for a wide variety of other applications, including fumigation, bleaching, pharmaceuticals, pyrotechnics, rubber making, and cutting oils.

For many years, the standard industry practice was to ship sulfur as a crushed bulk solid. The shipment of dry bulk sulfur, however, is prone to introduce contamination and to generate sulfur dust during handling.[9] The dust presents a potential environmental hazard and can result in dust explosions if proper preventive measures are not taken. In order to minimize these problems, the modern trend in handling solid sulfur is first to form it into slate, prills, pellets, or granules.[12,28] Canada is a major shipper of formed solid sulfur, and such sulfur is used by many industries in Europe and Asia. In the United States, over 95 percent of crude sulfur is shipped molten in specially designed railcars, tank barges, tank trucks, and ships. Liquid sulfur shipment and storage also is practiced in Europe. Molten sulfur generally is preferred by the sulfuric acid industry, primarily because there is no need for remelting prior to use.

Development of the Sulfur Industry

Early humans doubtless found elemental sulfur in volcanic craters, encrusting the edges of hot sulfur springs, and embedded in limestone formations. They discovered that it would burn and used it for medicinal purposes, as a bleach, as a fumigant, as a colorant, and as incense. Its use for these purposes is mentioned in ancient writings. The Romans produced incendiary weapons from sulfur. In the thirteenth century, the Chinese invented gunpowder using sulfur, nitrate, and charcoal.

The earliest commercial sulfur came from limestone deposits, of which those in Sicily and the Italian mainland developed world markets in the eighteenth and nineteenth centuries. Traditional mining methods were used to produce sulfur ore, which was burned slowly in a pile (Calcarone) to yield crude sulfur.[40] Steam smelting in autoclaves came into use about 1859. In 1890 Gill built a multichamber furnace to improve the process's production rate and efficiency. Italian monopoly of the sulfur markets continued until the early 1900s when the Frasch process brought previously unrecoverable sulfur deposits on the North American Gulf Coast into production.

Oil exploration efforts in Texas and Louisiana in the late 1800s uncovered sulfur deposits in limestone at depths of 200 to 300 meters. Mining was complicated by intervening layers of quicksand and the presence of hydrogen sulfide gas. Numerous conventional mining attempts at Sulphur, LA, proved disastrous. Finally, in December 1894, Hermann Frasch demonstrated the hot water process for mining underground sulfur deposits. With its favorable economics, the Frasch process completely displaced the Italian sulfur industry. Ready availability of low-cost sulfur opened the way for commercial sulfuric acid production by burning sulfur. This process largely supplanted the long-standing iron pyrite combustion process for sulfuric acid production by eliminating its extensive gas-cleaning operations.

In 1883 C. F. Claus patented a process for producing sulfur from hydrogen sulfide through partial combustion over an iron oxide catalyst. A number of improvements on the Claus process were made over the next 50 years, but it enjoyed limited success as a method for producing sulfur. Its primary driving force was, and remains, the need for a means to remove the sour component of sour gas for processing reasons and for environmental compatibility. Since the 1950s the demand for larger quantities of cleaner natural gas to meet increasingly more stringent environmental standards has caused a proliferation of the family of Claus processes. The processing of sour gases has increased to the extent that the production of recovered sulfur now exceeds that of mined sulfur.

Sulfur has been produced from sulfide ores (pyrites) by thermal decomposition in the absence of air, by roasting/smelting under reducing conditions, or by reaction of the ore with SO_2. Hydrometallurgical processes have produced sulfur from metal pyrites as a by-product. These processes do not contribute significant quantities of sulfur to the world markets. The reduction of sulfate ores (e.g., gypsum) to sulfur suffers from high energy costs. In general, the preferred product for these processes is sulfuric acid.

Sulfur Production Processes

At the present time the Frasch process is the most economical method for extracting sulfur from native deposits. Certain constraints on the geological formations required for the Frasch process limit its use to deposits along the Gulf of Mexico, in Poland, in the Former Soviet Union and in Iraq. Other sulfur deposits may yield to the Frasch process, but they have marginal economics. Figure 14.1 shows the structure needed for Frasch mining from salt domes. The sulfur-bearing limestone must have sufficient porosity to allow the sulfur to migrate upon melting. Both the caprock and the underlying anhydrite formation should be impervious to prevent loss of the hot water pumped into the mine. These salt-dome sulfur deposits typically are lens-shaped and are 1 to 75 meters thick with diameters of a few hundred meters up to several kilometers.

A sulfur well consists of a casing and three concentric pipes reaching into the sulfur-bearing strata. The outer 8- to 10-inch pipe carries 165°C water pumped into the formation to melt the sulfur. An inner cement-lined 3- to 6-inch pipe is used to transport the sulfur to the surface. Compressed air is passed through the 1-inch tube in the center to air-lift the sulfur. Without the air lift the molten sulfur would rise only partway in the middle pipe. The compressed air produces a low-density sulfur froth that rises to the surface.

The superheated water melts the sulfur in the vicinity of the well, forming a molten sulfur pool at the bottom of the well. As production continues, the formation fills with water. To continue production, bleedwells are drilled at the periphery of the formation to allow for discharge of the cooled minewater. In some mine fields, sufficient minewater is lost to the geological formation to provide for continued production. To limit minewater loss, mud

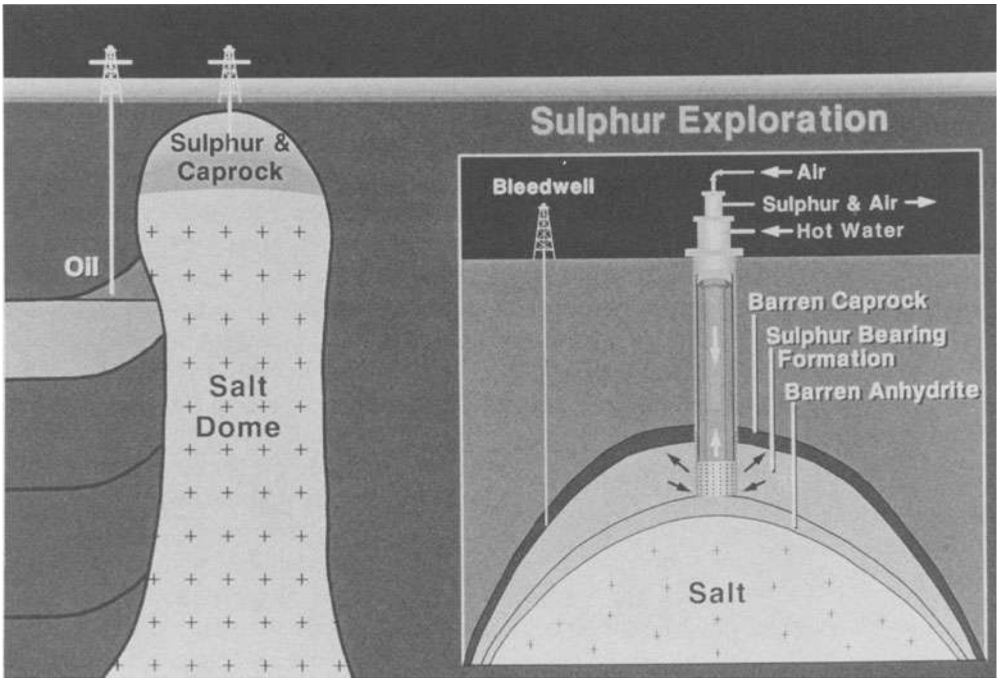


Fig. 14.1. Frasch process for mining sulfur from salt-dome formations. *(Courtesy Freeport Sulphur Co.)*

sometimes is pumped into the formation to seal major crevices.

Although most Frasch mines are located inland, since 1960 sulfur has been mined offshore in Louisiana by using drilling techniques developed for offshore oil production. Using saltwater to provide heated minewater has presented the Freeport Sulphur Company with some unique challenges in corrosion and scaling. Figure 14.2 shows an artist's depiction of Freeport's new 67-million-ton Main Pass 299 Frasch mine located 10 miles offshore in 200 feet of water near the mouth of the Mississippi River. The inset in Fig. 14.2 shows Freeport's Grand Isle sulfur mine 7 miles off the coast of Louisiana.

Sulfur produced from salt-dome structures can be quite pure, but it often contains up to 1 percent of bituminous residues, which render it dark and can make it unacceptable for sulfuric acid production. Some purification is obtained by filtering the dark sulfur through diatomaceous earth. The carbonaceous material can be formed into larger, filterable particles (Carsul) by treating the sulfur with heat or sulfuric acid. Freeport's submerged combustion distillation process was used from 1966 until 1979 to purify Frasch sulfur with up to 2 percent carbonaceous material.

Recovered Sulfur

Hydrogen sulfide is recovered from natural gas or refinery gases by absorption in a solvent or by regenerative chemical absorption.[7,13] In either case a concentrated hydrogen sulfide stream is produced that is treated further by the Claus process. A typical Claus plant has a feed stream of at least 45 percent H_2S, but with modifications can handle streams containing as little as 5 percent H_2S. For gas streams with low concentrations of hydrogen sulfide, direct conversion of the hydrogen sulfide to sulfur is accomplished in the solvent system (e.g., Stretford process).

The Claus process is based on the reaction of hydrogen sulfide with sulfur dioxide according to the highly exothermic reaction:

$$2H_2S + SO_2 \rightleftarrows 3S + 2H_2O$$

In practice the sulfur dioxide is produced in situ by partial oxidation of the hydrogen sulfide with air or oxygen in a furnace. In the split-flow arrangement, one-third of the H_2S stream is burned and then recombined with the remaining two-thirds before entering the Claus reactor. In the straight-through version, the entire H_2S stream is sent through the burner, and the extent of H_2S combustion is controlled by the air feed rate.

A flow diagram for a typical Claus process is shown in Fig. 14.3. The hydrogen sulfide is burned in a fuel-fired furnace (950–1250°C) with air to produce sulfur and a gas stream containing H_2S and SO_2. Process controls maintain the H_2S:SO_2 ratio near 2 in accordance with the stoichiometry. Heat is removed from the gas stream in a waste heat boiler to control the process gas temperature. The process gas is passed through one or more catalyst beds to convert the H_2S and SO_2 to sulfur, which is removed in condensers between each bed. High temperature shifts the equilibria toward the reactants, whereas low temperature causes sulfur condensation on the catalyst bed, leading to decreased catalyst activity. In practice the gas temperature is closely controlled for each Claus reactor, with higher temperatures at the first reactor where compounds such as COS and CS_2 are converted to S. Although efficiencies of 96 to 99 percent sulfur recovery have been demonstrated in Claus plants, it is common to have efficiencies in the 80 to 90 percent range. The conversion efficiency can be increased with multiple reactors in series. Oxygen enrichment can increase the throughput but does not improve the conversion.[22,34] Figure 14.4 shows a typical sulfur recovery plant based on the Claus process.

The tail gas from the Claus reactors may be further processed to remove any remaining sulfur compounds. This may be done by low-temperature Claus-type solid bed processes (e.g., the Sulfreen process), wet-Claus absorption/oxidation processes (e.g., Clauspol 1500 process), or hydrogenation of the off-gas to form H_2S for recycle (e.g., SCOT process). Residual sulfur compounds in the processed tail gas then are incinerated to SO_2. The residual SO_2 in the oxidized tail gas may be

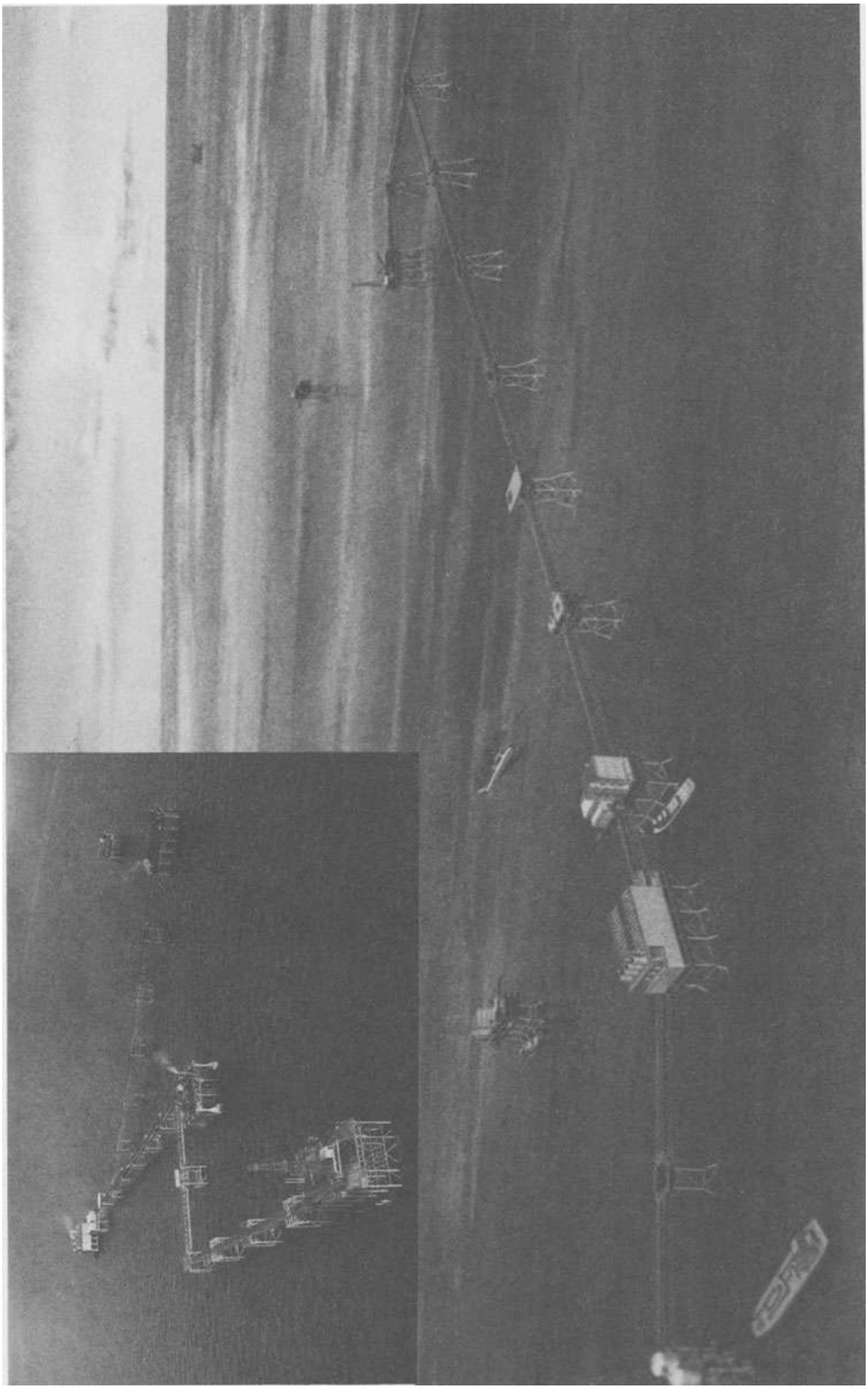


Fig. 14.2. Artist's rendition of Freeport Sulphur Co.'s new Main Pass 299 sulfur mine off the Louisiana coast. Inset shows Freeport's Grand isle sulfur mine. *(Courtesy Freeport Sulphur Co.)*

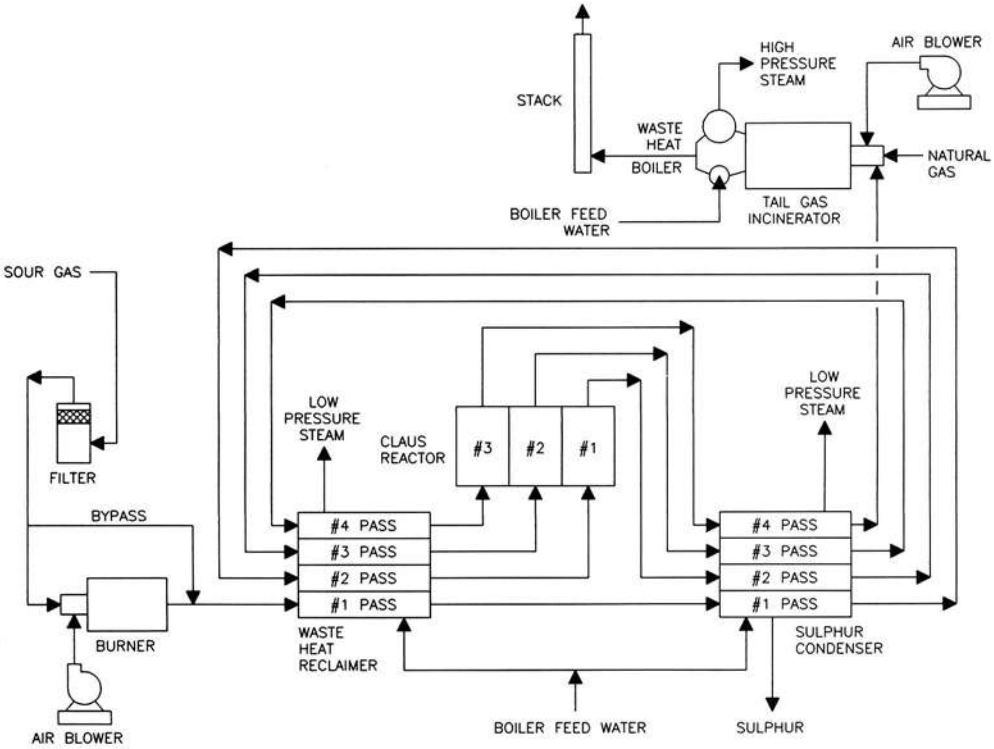


Fig. 14.3. Claus process flow diagram.

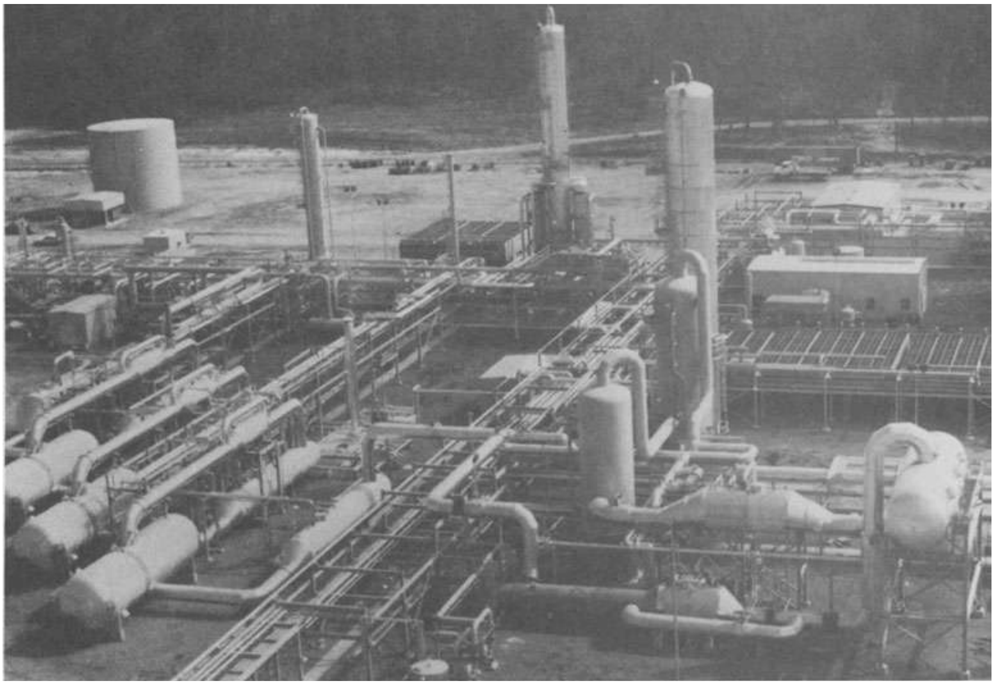


Fig. 14.4. Republic Refining Co. 440 metric ton/day Claus sulfur recovery unit (left) and SCOT tailgas cleanup unit (right). *(Courtesy Ortloff Engineers, Ltd.)*

scrubbed by any of several processes (e.g., Wellman-Lord process) before being vented to the environment. It is feasible to bring the SO_2 content of the final waste gas to as low as 200 to 500 ppmv by combinations of these processes. As of 1990, U.S. EPA regulations limited stack SO_2 emissions to 2000 ppmv. Individual states may apply more stringent regulations to achieve national ambient air quality standards for criteria pollutants including SO_2.

Production and Consumption of Sulfur

The 1989 world production of sulfur in all forms is given in Table 14.1 by region and for major producing countries. Recovered sulfur accounted for 63 percent of brimstone production in 1989. Most of the recovered sulfur was derived from sour gas wells in Canada, the Soviet Union, and the United States.[41] U.S. oil refineries recovered nearly 4 million tons of sulfur from the hydrotreating of sour crudes. Canadian tar-sands comprise the major source of other recovered sulfur production. Frasch and open pit mines in southeast Poland near the Russian border lead the world in native sulfur production. Most of the Russian native sulfur production comes from Frasch and open pit mines just across the Polish–Russian border. The U.S. Frasch sulfur production comes from West Texas and the Texas–Louisiana Gulf Coast. In 1989, China, the Soviet Union, and Spain accounted for 68 percent of pyritic sulfur production, virtually all of which was produced as sulfuric acid. Sulfur production listed as "Other Sulphur" in the table was primarily sulfur dioxide from the smelting of nonferrous metal sulfide ores.

The growing importance of recovered sulfur in world sulfur markets is mirrored in the U.S. market trends shown in Fig. 14.5.[33] Involuntary sulfur production from gas and oil began to climb in the early 1970s following environmental legislation to curb sulfur dioxide emissions. Large stockpiles of bright recovered sulfur began to appear in North America and especially in Western Canada. New Frasch sulfur mines in Poland, Texas, and Louisiana had begun production in the late 1960s, adding to the overall brimstone production and

TABLE 14.1 World Production of Sulfur in 1989 (Thousands of Metric Tons)

		Recovered Sulfur						
	Frasch/ Native	*Gas*	*Oil*	*Other*	*Total Brimstone*	*Pyrite Sulfur*	*Other Sulfur*	*Total*
West Europe	45	1,727	1,648	110	3,530	2,461	1,947	7,938
France	—	636	238	—	874	—	190	1 064
Germany FR	—	952	264	110	1 326	250	458	2,034
Spain	—	—	—	—	—	938	229	1,167
East Europe	7,765	2,775	488	305	11,333	2,690	2,957	16,980
Poland	4,865	—	35	—	4,900	—	180	5,080
U.S.S.R.	2,900	2,750	250	290	6,190	2,080	1,947	10,217
North America	3,888	7,693	4,068	591	16,240	179	1,919	18,338
Canada	—	5,156	160	526	5,842	179	699	6,720
U.S.	3,888	2,537	3,908	65	10,398	—	1,220	11,618
Latin America	1,528	500	339	—	2,367	72	741	3,180
Mexico	1,528	500	50	—	2,078	—	259	2,337
Asia	1,256	2,497	2,098	—	5,851	4,650	2,495	12,996
China PR	200	60	50	—	310	4,100	556	4,966
Iraq	1,050	250	50	—	1,350	—	8	1,358
Japan	—	—	1,176	—	1,176	161	1,423	2,760
Saudi Arabia	—	1,390	200	—	1,590	—	—	1,590
Oceania	—	—	70	—	70	29	216	315
Africa	—	3	40	—	43	580	405	1,080
World Total	14,482	15,195	8,751	1,006	39,434	10,661	10,680	60,715

Source: Freeport Sulphur Marketing Department estimates.

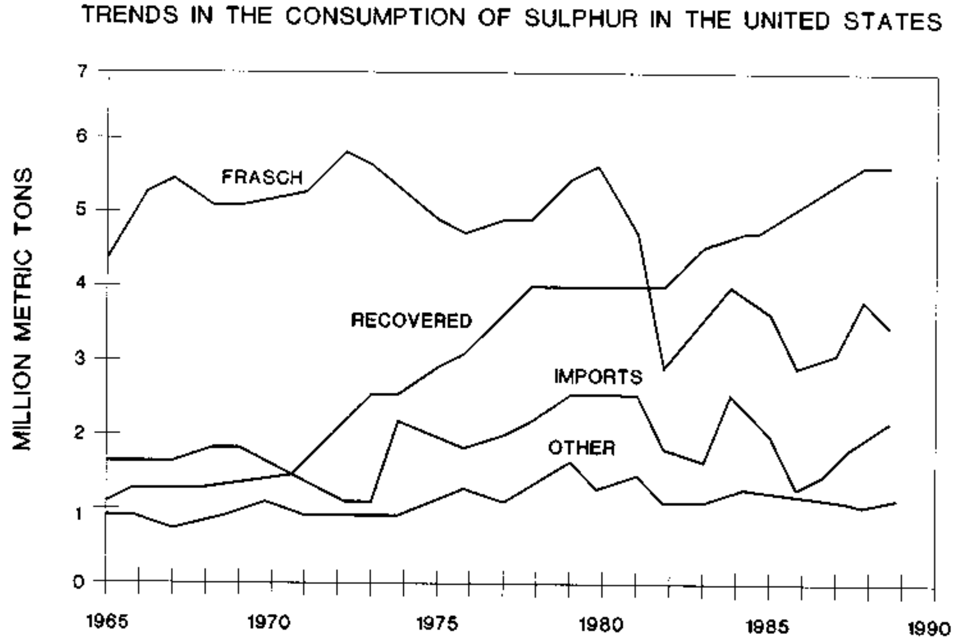


Fig. 14.5. Trends in U.S. sulfur consumption. (Morse 1990)[32]

causing a decrease in sulfur prices, as shown in Fig. 14.6. Low sulfur prices and higher energy costs in the early 1970s resulted in the closing of several high-cost Frasch mines, and the depletion of reserves caused the shutdown of other older Frasch mines. This reduction in Frasch sulfur production in the mid-1970s, coupled with increasing sulfur demand for fertilizers, led to sulfur price increases. These price increases were accelerated in 1979 after Canadian sulfur exports were interrupted by a blockage of Vancouver harbor, which resulted from a ship colliding with a bridge. Inflation and changes in the sulfur market

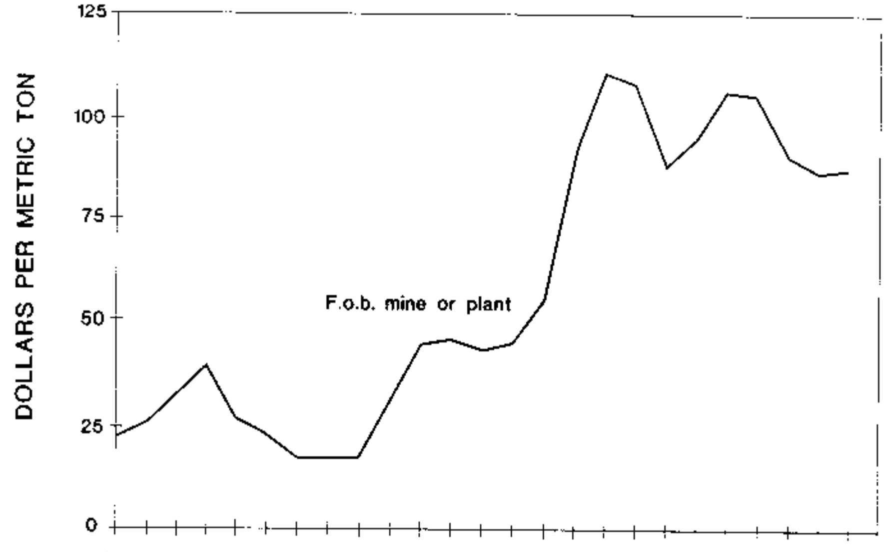


Fig. 14.6. U.S. sulfur price history. (Morse 1990)[32]

TABLE 14.2 Consumption of Sulfur in the United States (Thousands of Metric Tons)

Use	*1989*	*1984*	*1979*
Agricultural chemicals	277	480	272
Petroleum refining	142	278	103
Industrial organic chemicals	122	127	166
Industrial inorganic chemicals	188	285	192
Pulp and paper	8	29	124
Other	372	813	970
Nonacid consumption	1,109	2,012	1,827
Sulfuric acid			
Domestic sulfur	8,241	6,909	7,793
Imported sulfur	2,245	2,425	1,754
Acid consumption	10,486	9,334	9,547
Total U.S. consumption	11,595	11,346	11,374

Source: Mineral Industry Surveys, "Sulfur," U.S. Department of the Interior, Bureau of Mines.

prevented a return of sulfur prices to pre-1979 levels, although substantial liquidation of sulfur inventories in the early 1980s did cause a dip in prices. Sulfur stockpiles now have been largely depleted, and sulfur prices have stabilized in recent years.

More than 90 percent of the elemental sulfur consumed in the United States is converted to sulfuric acid. Table 14.2 shows the pattern of U.S. sulfur consumption during the 1980s.[33]

SULFURIC ACID

Sulfuric acid is the largest-volume industrial chemical manufactured in the world. Over 39 million tons of sulfuric acid were produced in the United States in 1990, of which 70 percent was used in fertilizer production.[33] Its use extends to nearly every major chemical sector, and its consumption is often cited as an indicator of the general state of a nation's economy.[35] This versatile acid is truly the "work horse" of the chemical industry.

Pure sulfuric acid is an oily, water-white, slightly viscous liquid with a melting point of 10.4°C and a boiling point of 279.6°C. It is infinitely miscible with water, forming sulfuric acid solutions characterized by their weight percent H_2SO_4. Oleum may be formed by dissolving SO_3 in sulfuric acid to attain fuming sulfuric acid, with concentrations nominally greater than 100 percent H_2SO_4. Historically, sulfuric acid concentrations were determined by measuring the solution density using hydrometers calibrated in degrees Baume (°Be). This practice is waning although some specifications and tables of properties still include this measurement.

Uses of Sulfuric Acid

The primary industrial uses of sulfuric acid are in phosphate fertilizer manufacture, petroleum refining, copper ore leaching, synthetic rubber and plastics, and pulp and paper mills.[25] It is used as a solvent, a dehydrating agent, a reagent in chemical reactions or processes, an acid, a catalyst, and an absorbent and in many other applications. In spite of its wide usage, sulfuric acid rarely is contained in the final product. Sulfuric acid ends up as gypsum in phosphate fertilizer manufacture, for example. In many other processes the sulfuric acid is converted to a waste product that requires disposal or reuse. Because disposal of waste sulfuric acid is becoming increasingly unacceptable environmentally, the recycle of sulfur values from waste sulfuric acid has become more widespread.

Nearly all sulfuric acid is manufactured by the contact process in which sulfur trioxide is absorbed into 93 to 98 percent H_2SO_4. The acid may be sold at various strengths, usually depending on the requirements of the consumer. It generally is marketed on a 100 percent basis, but normally is shipped as 93 percent H_2SO_4 (66°Be), as 98 percent acid, or as 20 to 22 percent fuming oleum. Table 14.3 shows common acid strengths and end uses. Concentrated acid may be stored in mild steel tanks, but dilute acid must be contained in lead-lined or plastic tanks. Bulk shipments of concentrated acid are made in steel tanks on ships, tank barges, or railcars. Reagent grade acid is commonly sold in 5-liter glass bottles.

Development of the Sulfuric Acid Industry

Sulfuric acid is formed in nature by the oxidation and chemical decomposition of naturally ocurring sulfur and sulfur-containing

TABLE 14.3 Acid Strengths and End Uses

Percent H_2SO_4	°*Be*	*Percent Oleum* (*% Free* SO_3)	*Specific Gravity*	*Uses*
35.67	30.8	—	1.27	Storage batteries, electric utilities.
62.18–69.65	50–55	—	—	Normal superphosphate and other fertilizers.
77.67	60.0	—	1.7059	Normal superphosphate and other fertilizers; isopropyl and *sec*-butyl alcohols.
80.00	61.3	—	1.7323	Copper leaching.
93.19	66.0	—	1.8354	Phosphoric acid, titanium dioxide, steel pickling, regenerating ion exchange resins.
98–99	—	—	—	Chlorine drying, alkylation, boric acid.
104.50	—	20	1.9056	Surfactants, nitrations.
106.75	—	30	1.9412	Hydrofluoric acid.
109.00	—	40	1.9737	Explosives.
111.24	—	50	1.9900	Reagent manufacture, organic.
113.50	—	60	1.9919	Sulfonations, blending with.
114.63	—	65	1.9842	Weaker acids.

Source: *Chemical Economics Handbook*, SRI International, Dec. 1990.

compounds. It is made by the action of bacteria (*Thiobacillus ferrooxidans*) on coal brasses or iron disulfide discarded on refuse dumps at coal and copper mines; it is produced in the atmosphere by the oxidation of sulfur dioxide emitted from the combustion of coal, oil, and other substances; and it also is formed by chemical decomposition resulting from geological changes.

Although there were vague references to "spirits" expelled from alum by Arabian alchemists in the tenth century and by Roman alchemists in the thirteenth century, the first distinct mention of sulfuric acid has been credited to Basil Valentine in the late 1400s.[21] He burned sulfur with saltpeter in glass retorts or bell jars with a little water, and he also calcined copperas (ferrous sulfate heptahydrate) with silica, with both processes yielding sulfuric acid, although he took them to be different substances. These processes for making sulfuric acid continued until 1746 when Dr. Roebuck constructed a lead chamber in England for sulfuric acid manufacture. This marked the beginning of the "chamber process" for sulfuric acid, which was to continue in use for the next two centuries.[19]

The first lead chamber was 1.8 meters square, and 8:1 mixtures of sulfur and saltpeter in iron carts were rolled into it and burned with intermittent admission of air.[42] As in the glass retorts, the sulfur trioxide that was formed combined with water to produce sulfuric acid, which condensed on the walls and collected in pans. Steam was introduced into the chambers in 1774, and continuous addition of air was begun in 1793. It then was recognized that the sulfurous acid from the burning of sulfur was oxidized by air and needed saltpeter only as a catalyst. In 1827 Gay-Lussac invented a tower for recovering the nitrogen oxides escaping from the chamber. The nitrogen oxides were condensed in sulfuric acid but could not be economically recovered from the acid until the invention of the Glover denitrating tower in 1859. The introduction of these two towers completed the chamber process except for various refinements to reduce costs. The process could produce acid with up to 77 percent H_2SO_4 but generally yielded strengths in a 65 to 68 percent range. Higher-strength acid was produced by boiling chamber acid to remove water. A platinum still for producing concentrated sulfuric acid from chamber acid was first built for the Harrison Works in Philadelphia in 1814.[16]

The developing markets for sulfuric acid in the late eighteenth century increased the demand for Sicilian sulfur.[23] By 1832, sulfur prices had risen to $80 a ton, and stocks rose; then in 1833 the market broke, with the sulfur price at $15 a ton. Sicilian government attempts to stabilize sulfur at $70 a ton failed, in part because of an 1833 discovery by a French chemist that sulfur dioxide could be obtained by roasting pyrites in a furnace. Process improvements in pyrite roasting by 1870 made pyrites competitive with sulfur as a raw material. By 1880, with the single exception of the United States, the sulfuric acid industries had gone to a pyrites basis. By 1909 virtually all U.S. sulfuric acid came from pyrites and as by-product acid from zinc and copper smelters. In the late 1890s, development of the Frasch process for sulfur mining lowered the price for sulfur. This change, coupled with new developments in sulfur burners, led sulfuric acid manufacturers back to sulfur as a raw material source. During World War I gypsum was burned with coal to produce SO_2 for sulfuric acid production. This process continued in Europe until the 1950s, with the last plant (in Great Britain) shut down in 1975. Today sulfuric acid production from pyrite roasting remains important in Spain, the Former Soviet Union, China, Japan, South Africa, Turkey, and some eastern European nations.[39] South Africa still has a gypsum sulfuric acid plant in operation.

The contact process for sulfuric acid dates from 1831, when a Briton patented a method for converting sulfur dioxide to sulfur trioxide by passing the gas through a heated tube filled with finely divided platinum.[21] The sulfur trioxide was adsorbed in chamber acid to produce concentrated and fuming sulfuric acids. Commercialization of the new process was delayed by lack of markets for the concentrated acid and poor understanding of the process parameters. About 1870, demand for fuming sulfuric acid spurred German development of the contact process. In 1901, BASF reported that the governing principles for the successful manufacture of contact acid were well understood. These included cleaning of the sulfur dioxide gas stream, use of excess oxygen, and temperature control of the catalyst bed. However, the reliance of the contact process on feed acid produced by the chamber process limited its development until about 1930. It became known that the acid in the final SO_3 absorption tower had to be kept in the range 98.5 to 99.0 percent H_2SO_4 to be effective. Accurate dilution techniques to allow recycle of the absorber acid were developed in the late 1920s. The contact process then could continuously produce diluted acid, and no longer required chamber acid. The development of poison-resistant vanadium catalysts for SO_2 conversion allowed the use of smelter gases in the contact process. With its lower capital and operating costs, the contact process then supplanted the chamber process for sulfuric acid production. By 1940 the United States had equal numbers of chamber and contact processes. Today no commercial chamber plants are operating in the United States.

Since the 1940s most developments in the contact process have focused on energy recovery and pollution abatement. The production of SO_2, its conversion to SO_3, and the dilution of H_2SO_4 are exothermic processes that are exploited to reduce energy costs at sulfuric acid plants. Sulfur emissions have been sharply reduced by using two SO_3 absorbers although one absorber is the economic choice. Tail gas scrubbing processes have been developed to further reduce sulfur emissions from sulfuric acid plants. As of 1990, U.S. EPA regulations limited sulfuric acid plant stack emissions to 2 kg SO_2 and 0.075 kg acid mist per metric ton of H_2SO_4 produced.

Manufacture of Sulfuric Acid by the Contact Process

The basic steps in the contact process are: (1) production of sulfur dioxide; (2) cooling and, for smelters, cleaning of the process gas; (3) conversion of the sulfur dioxide to sulfur trioxide; (4) cooling of the sulfur trioxide gas; and (5) absorption of the sulfur trioxide in sulfuric acid.[35] Figure 14.7 is a photograph of a contact process plant. A simplified diagram for a double absorption contact sulfuric acid process is shown in Fig. 14.8. Because sulfur dioxide is produced by several processes, it is convenient to separate the discussion of sulfur dioxide production from its conversion to sulfuric acid.

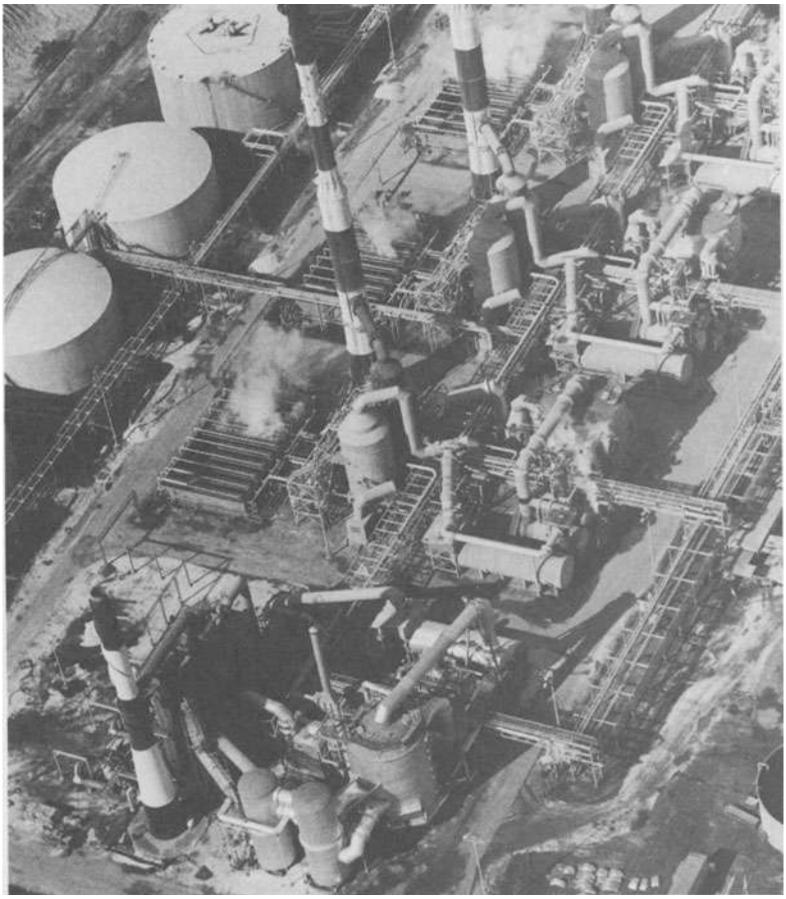


Fig. 14.7. Contact process sulfuric acid plant, showing a double absorption train (bottom) and three single absorption trains. *(Courtesy Agrico Chemical Co.)*

Sulfur Dioxide Production

Sulfur is converted to sulfur dioxide by burning molten sulfur with dried air in a sulfur burner to yield a 1000 to 1100°C gas stream containing 10 to 11 percent SO_2. The burner is mounted at one end of a sulfur furnace, and the gas passed through a waste heat boiler at the other end. The gas temperature is reduced to 420 to 440°C on leaving the boiler, which produces 40-bar steam. The gas stream usually is clean and requires no further treatment before entering the converter.

In the simple pressure-nozzle burner, the liquid sulfur is atomized by pumping it at 8 to 15 bar through the nozzle. In a two-component burner, the sulfur is atomized primarily by the combustion air stream. It operates at lower pressure and has a wider sulfur throughput range, 5 to 170 tons/day, than the simple burner. Lurgi's rotary burner can burn up to 400 tons/day of sulfur. Larger sulfuric acid plants use multiple sulfur burners. A process gas with 18 percent SO_2 can be achieved in Lurgi's two-stage sulfur combustion process. In the two-stage process, excess sulfur is burned in the first stage, consuming all of the oxygen. The low residual oxygen level limits the formation of nitrogen oxides, which otherwise would be very high at the combustion temperature of 1750°C. The combustion gas then is cooled to 620 to 650°C, and additional dried air is injected to burn the residual sulfur in an afterburner. A second waste heat boiler cools the process gas to 420 to 440°C before sending it to the converter.

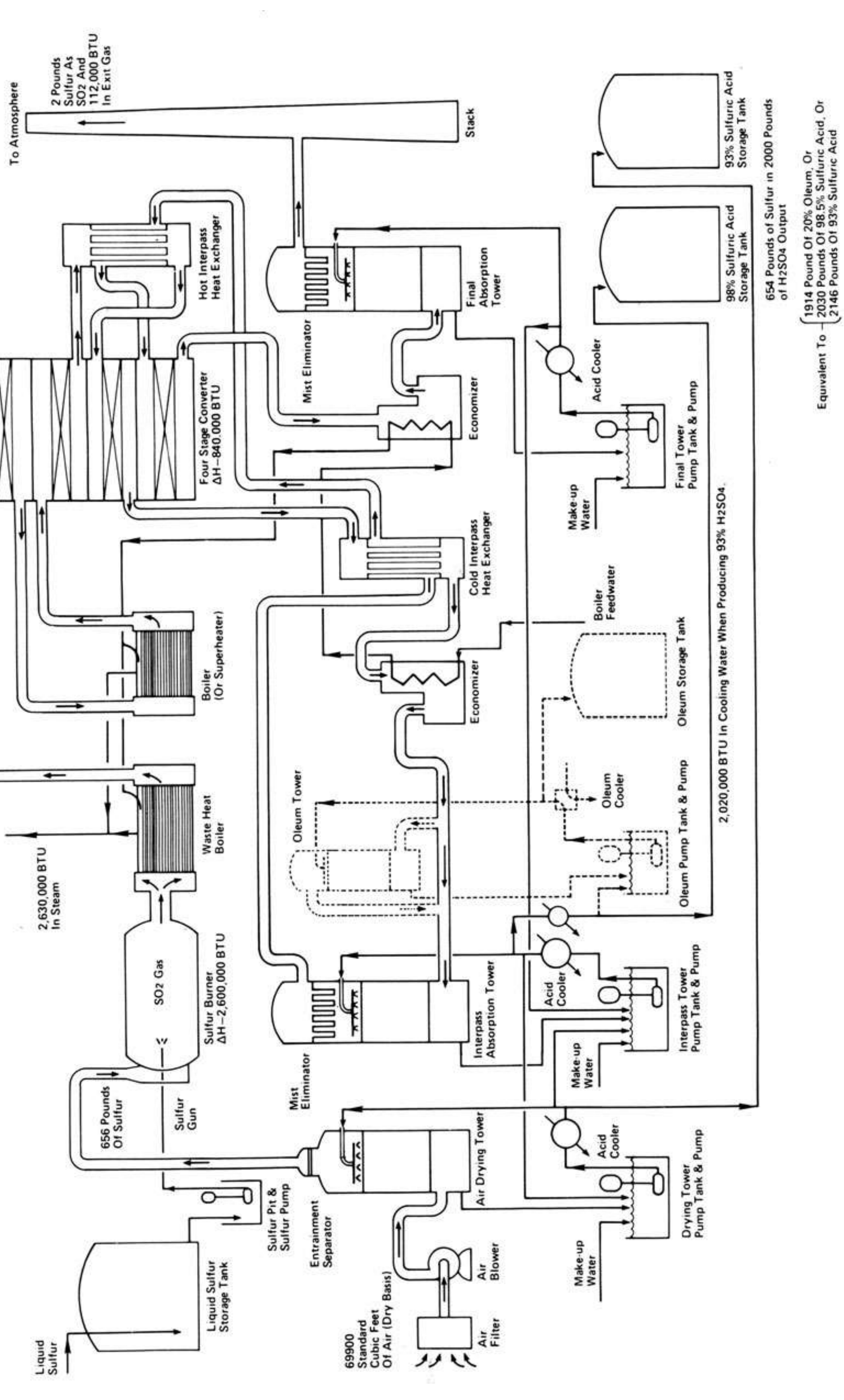


Fig. 14.8. Schematic flow diagram of a double absorption contact process for sulfuric acid manufacture.

Pyrites and other iron sulfides are roasted to produce an iron oxide cinder and an off-gas containing 7 to 14 percent SO_2, which is contaminated with varying amounts of arsenic, lead, zinc, and other metal oxides. The off-gas must be cleaned before it is sent to the converter. Various types of pyrite roasting equipment have been used in the past, including shaft furnaces, multiple hearth roasters, rotary kilns, and dust roasters. Fluid-bed roasters now are widely used for their superior process technology, throughput rates, and economics. The roasting process must be controlled between 850 and 940°C. At lower temperatures the reaction is incomplete, whereas at higher temperatures the iron oxides and sulfides form a eutectic melt that inhibits the reaction rate. Fluid-bed roasters surpass other types in temperature control and temperature uniformity throughout the bed. Fluid bed technology for SO_2 production was introduced in the early 1950s by Dorr Oliver in the United States and by BASF in the Federal Republic of Germany.

Copper, lead, zinc, and other sulfide ores may be processed by roasting or smelting.[38] Roasting or sintering of sulfide ore is essentially identical with pyrite roasting. Smelting generally occurs at higher temperatures. Older reverberatory furnace smelters produce off-gas with only 1 to 2 percent SO_2, too low for its economical recovery as acid. By using an oxygen-enriched air feed, the off-gas can be raised to 6 to 8 percent SO_2. Bath smelters (Mitsubishi, Noranda), where the ore concentrates are heated and reacted in the slag/matte melt, produce an off-gas with 10 to 20 percent SO_2.[38] Flash smelters (Inco, Outokumpu), which involve suspension and reaction of the concentrates in an oxidizing gas stream, operate at 1200 to 1300°C and produce a waste gas with 10 to 15 percent SO_2. Oxygen enrichment of the feed air can raise the SO_2 level in the off-gas to 30 to 80 percent. The Kivcet process smelts with pure oxygen and produces off-gas with 80 to 85 percent SO_2.[11] Figure 14.9 is a photo of a metallurgical gas sulfuric acid plant.

Off-gas from roasting and smelting operations may contain dust, SO_3, halogens, NO_x, arsenic and other toxic metal fumes, and mercury.[35,43] These components must be

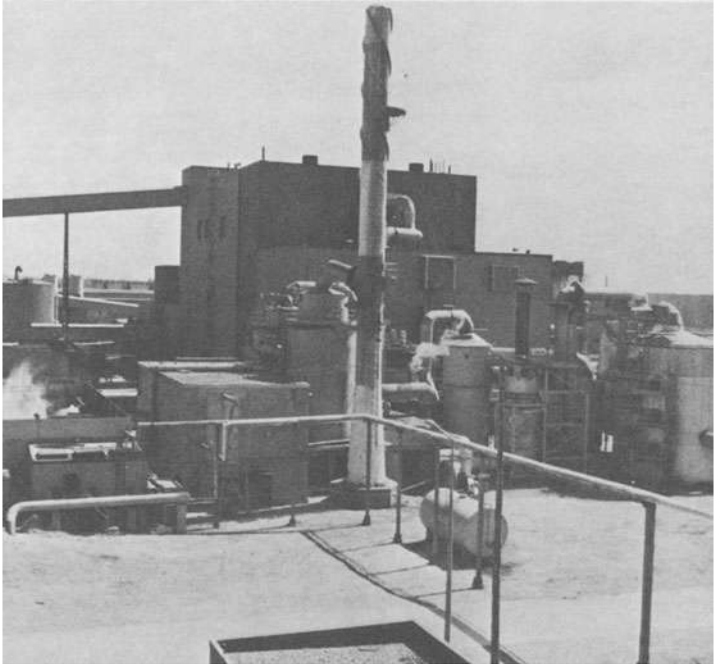


Fig. 14.9. Metallurgical gas sulfuric acid plant. *(Courtesy Texasgulf Inc.)*

removed from the gas stream before it is sent to the converter. Although SO_3 is produced in the converter, its presence in the cooled gases upstream of the converter will cause excessive corrosion by forming sulfuric acid mists.[14] The cleaning plant steps are: (1) hot-gas dedusting; (2) wet scrubbing; (3) gas cooling; (4) mist removal; and, if necessary, (5) mercury removal. The hot gases generally are passed first through a waste heat boiler to reduce the temperature to 250 to 400°C. Cyclones followed by hot-gas electrostatic precipitators (50–90 kV) remove nearly all (99 + %) of the dust. The gas is then contacted with weak (5–30%) H_2SO_4 in a spray tower or, preferably, a venturi scrubber, which removes metal vapors and additional solids, cools the gas to 50 to 80°C, and converts SO_3 to acid mist for later removal. The saturated gas next is cooled in a packed bed tower or shell and graphite tube heat exchanger to condense excess water. Silica packing may be used in the towers to remove fluorides as fluosilicic acid. Acid mist is removed in wet electrostatic precipitators fitted with lead tubes and star wires or, more recently, with FRP or PVC tubes specially treated to maintain a conductive liquid film surface (Lurgi)[8] and composite wires fabricated with barbs to promote corona discharge.[43] If present, mercury is removed in an additional tower by scrubbing with mercury chloride solution (Boliden),[6] hydrochloric acid solution, or 70 to 85 percent sulfuric acid.

Waste sulfuric acid sludges from petroleum refineries are disposed of by conversion to SO_2 for production of fresh sulfuric acid. The heavy organic components of the sludges can be decomposed thermally at 800 to 1300°C (Lurgi, Monsanto Enviro-Chem) or reductively at 200 to 600°C with coal in a rotary kiln (Chemico). Thermal decomposition is accomplished in a fuel-fired vertical or horizontal furnace. The acid sludge also can be injected into fluid-bed pyrite roasters as a means of disposing of the acid and reducing fossil fuel consumption. Dilute acid sludges must be concentrated to 60 to 75 percent H_2SO_4 for economical conversion. This is generally done by using waste heat from the decomposition process. The sulfur dioxide gas stream from these processes requires cleaning as described above for roasting and smelting plants.

Calcium sulfate may be decomposed to cement clinker and sulfur dioxide gas in a coke-fired rotary kiln at 900 to 1400°C (Müller-Kühne).[35] However, the unfavorable economics of this process relegate it to countries that do not have other sources of sulfur. Phosphogypsum (gypsum produced by the acidulation of phosphate rock) may be decomposed in this way as a means of recycling the sulfur values in the large waste phosphogypsum piles at fertilizer plants (OSW-Krupp). This process is hampered by the more extesive gas cleaning requirements for decomposing phosphogypsum as compared to natural gypsum. Interest in recycling phosphogypsum remains high, driven by environmental considerations. Recently a pilot plant was constructed in Louisiana to demonstrate FIPR/Davy McKee's circular grate process for recovering SO_2 from phosphogypsum. Environmental forces also are behind the recycling of ferrous sulfate from metals industry pickling liquors. This "green salt" is decomposed to sulfur dioxide and iron dioxide in pyrite roasters. Elemental sulfur, coal, or fuel oil may be used as supplementary fuels.

Refinery waste gases may be burned to eliminate hydrogen sulfide and other sulphur-containing contaminants. Streams containing small amounts of H_2S or constituents unsuitable for Claus plants may require combustion to SO_2 as the means of disposing of the toxic gas. The resulting effluent gas usually is low in SO_2 and contains water vapor and carbon dioxide. Flue gases from fossil fuel power plants also fall into this category. Recovery of the sulfur values from these dilute gases usually is driven by environmental considerations rather than economics. In the United States, power plant flue gas often is scrubbed with lime to convert the SO_2 to gypsum sludge for landfill disposal. Alternatively, the Bergbau-Forschung process recovers sulfur dioxide by dry adsorption on activated coke at 130°C. The SO_2 is released by heating the coke to 600 to 650°C. Sulfur dioxide can be absorbed in a sodium sulfite solution (Wellman-Lord) to produce sodium bisulfite. Pure moist sulfur dioxide can be recovered by heating the sodium bisulfite.

Conversion of SO_2 to H_2SO_4

The single absorption contact process for sulfuric acid is characterized by four main process steps: gas drying, catalytic conversion of SO_2 to SO_3, absorption of SO_3, and acid cooling. The maximum SO_2 conversion for a single absorption plant is about 97.5 to 98 percent. By adding another SO_3 absorber, the SO_2 conversion can be increased to 99.5 to 99.7 percent, resulting in lower SO_2 emissions. The so-called double absorption process is now the industry standard.

The gas drying step is not used in the wet catalysis process that was developed for waste gas streams from burning hydrogen sulfide. In the wet process, liquid acid is formed by condensation of H_2SO_4 vapor rather than by absorption of SO_3. However, the SO_2-laden process gas sent to the converter must be dry to protect the downstream process equipment against corrosion. The drying generally is done in a packed tower with recirculating concentrated (93–98%) sulfuric acid kept at 50 to 60°C by indirect cooling. The tower acid stream is heated by condensation of the water and by dilution of the acid. The tower temperature is used to control the moisture level of the gas sent to the converter. Acid from the drying tower is sent to storage tanks for shipment. When sulfur is burned, the combustion air to the sulfur burner is dried because the combustion of sulfur does not produce water. Off-gases from pyrite roasters and metallurgical smelters are dried as part of the gas cleaning process. For roaster gases with low SO_2 concentrations, a predryer may be added upstream of the main dryer.

Oxidation of SO_2 to SO_3 is accomplished in multi-stage fixed-bed catalytic converters equipped with interstage boilers or heat exchangers to remove the heat of reaction. Typically, four stages are compartmented within a single vertical converter, which may be brick-lined, steel, or cast iron. Newer converters are stainless steel, and some have five stages for higher conversion. Isothermal tubular converters are no longer suited to modern high-capacity plants. The extruded cylindrical catalyst pellets are usually 4 to 9 percent V_2O_5 with alkali metal sulfate promoters on a silica carrier (diatomaceous earth, silica gel, or zeolites). The reaction temperature is generally 410 to 440°C for these catalysts although several low-strike catalysts now operate at 360 to 400°C. Higher temperatures ($\sim$600°C) reduce the SO_2 conversion and lead to structural damage of the catalyst. High pressure drops across catalyst beds from catalyst dust formed during processing require periodic catalyst removal and screening to remove dust. Ring-shaped catalysts developed by Topsoe have lower dust pressure drops and now are in wide use. Other catalyst shapes used are ribbed rings and cylinders. The usual catalyst loading per one ton/day sulfuric acid capacity is 150 to 200 liters in a double absorption plant and 200 to 260 liters in a single absorption plant. Bayer developed and operates fluid-bed converters that utilize special 0.3 to 1 mm abrasion-resistant catalysts.

Absorption of SO_3

Sulfur trioxide from the converter is absorbed in 98 percent H_2SO_4 recirculated countercurrently through a packed tower maintained at 60 to 80°C by indirect cooling. The optimum concentration of the absorber acid is near the H_2O–H_2SO_4 azeotrope, 98.3 percent H_2SO_4, where the SO_3, H_2SO_4, and H_2O vapor pressures are at their lowest values. Absorption efficiencies in excess of 99.9 percent generally are obtained. On leaving the converter, the process gas is cooled first with feed gas in a gas–gas heat exchanger and then with a water feed preheater to 180 to 220°C before it enters the absorber. An impingement separator, or Teflon or glass fiber mist eliminator, is placed in the top of the absorber to remove acid mists. If oleum is produced at the plant, it is made in a separate oleum tower upstream of the absorber. A portion of the SO_3 stream to the absorber is diverted to the oleum tower where it is absorbed in 98 percent acid.

In double-absorption plants an additional absorber is placed between the second and third (or between the third and fourth) converter beds. By removing SO_3 from the gas stream at this intermediate point, higher SO_2 conversions are attained in the downstream converter beds, and the overall SO_2 conversion is increased. The cooled gas from the intermediate absorber is reheated by hot converter gas in gas–gas heat exchangers before returning to the converter. An oleum tower may be placed before the intermediate absorber.

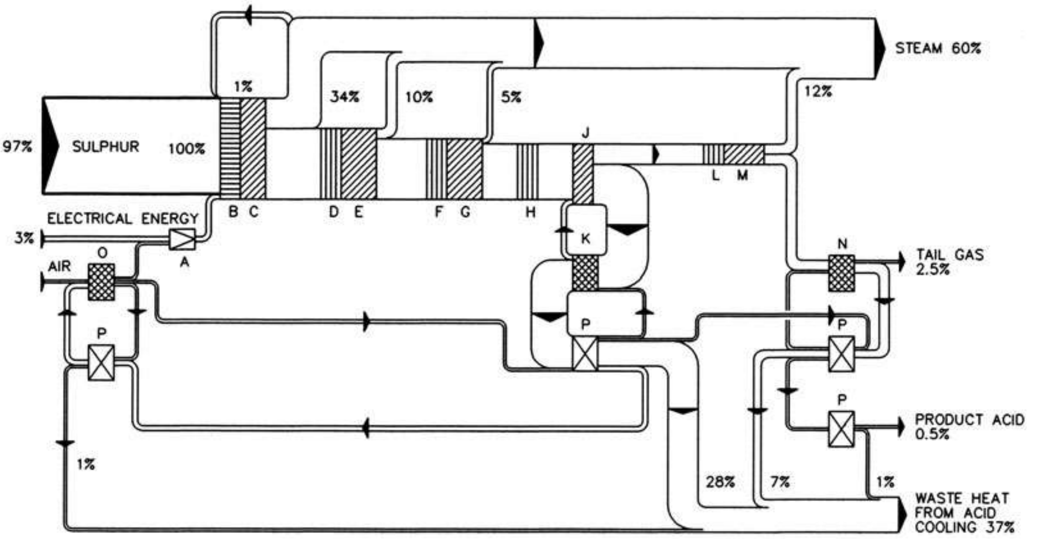
Absorption of SO_3 in concentrated sulfuric acid and the formation of H_2SO_4 from SO_3 and H_2O produce heat in the absorber, as does acid dilution from makeup water addition. Process control requires that the acid be cooled before it is recirculated to the dryer or absorber towers or sent to storage. Earlier acid coolers of parallel banks of stacked, irrigated, cast iron sections have been largely replaced by stainless steel shell and tube or plate exchangers, with or without anodic protection. Hastelloy, Sandvik SX, and Saramet alloys and Teflon also are used in acid piping and coolers.[15,17,27]

Tail gas emissions are controlled by improving the SO_2 conversion efficiency and by scrubbing the tail gas. In a double-absorption process plant, a five-bed converter has 0.3 percent unconverted SO_2, as compared to 0.5 percent for a four-bed converter. A Lurgi Peracidox scrubber may be used to remove up to 90 percent of the residual SO_2 in the tail gas from a double-absorption plant. Hydrogen peroxide or electrolytically produced peroxymonosulfuric acid is used to convert the SO_2 to H_2SO_4 in the Lurgi scrubber. Tail gas from single-absorption plants may be absorbed on activated carbon (Sulfacid) or scrubbed with ammonia or sodium sulfite (Wellman-Lord).

Metallurgical acid plants differ from sulfur-burning plants in that the cleaned SO_2 process gas must be heated before it is sent to the converter. Many of these plants have weak SO_2 streams that require large gas–gas heat exchangers for temperature control. Four plants in the Former Soviet Union processing 2 to 4 percent SO_2 use an unsteady-state oxidation process in which the cold (40–70°C) SO_2 gas is reacted on hot catalyst beds without intervening heat exchangers.[1,30] As the temperature front moves through the bed to the exit side, the flow is reversed. Cycle times are 30 to 120 minutes, and single-bed conversions of 80 to 90 percent are reported as compared to 55 to 60 percent for conventional processes at higher exit temperatures.

The thermal capacity of a 1000 ton/day sulfuric acid plant is about 63 MW. This heat liberation must be controlled in a manner that maintains optimum gas temperatures in the converter system and optimum acid temperatures in the dryer and absorber circuits. Tail gas emissions also are affected by the energy balance. Figure 14.10 shows an energy flow diagram for a contemporary sulfur-burning sulfuric acid plant. About 97 percent of the total energy input derives from burning sulfur, and 3 percent comes from electricity consumed to drive the gases through the plant. Most plants can recover 55 to 60 percent of the energy as high-pressure steam (40 bar, 400°C), but about 40 percent is lost as waste heat dissipated to the environment in the form of hot water from acid coolers.

During the late 1970s acid plants were optimized to generate more steam. Steam can be produced at pressures up to 80 bar from high-temperature sulfur burners such as the Lurgi two-stage combustion system. The high pressure steam is let down to low pressure steam through a turbo generator that cogenerates electricity. In double absorption plants, economizers were installed upstream or downstream of the heat exchanger servicing the intermediate absorber. Boiler feedwater is preheated to 90 to 95°C in this economizer to increase steam production. The energy recovery from acid plants was increased to 70 percent by installing low gas-temperature economizers, low pressure drop catalysts, and suction drying towers, by increasing the SO_2 feed gas concentration, and by preheating the boiler feedwater with hot acid. Further energy



A BLOWER; B SULPHUR FURNACE; C WASTE HEAT BOILER; D CATALYST BED 1; E STEAM SUPERHEATER; F CATALYST BED 2; G BOILER; H CATALYST BED 3; J INTERMEDIATE HEAT EXCHANGERS; K INTERMEDIATE ABSORBER; L CONVERTER BED 4; M ECONOMIZER; N FINAL ABSORBER; O AIR DRYER; P ACID COOLERS

Fig. 14.10. Sankey energy flow diagram for a 1000 ton/day sulfur-burning double absorption sulfuric acid plant (feed gas: 10% SO_2). *(Courtesy Lurgi GmbH, Frankfurt, Germany.)*

recovery requires higher operating temperatures for the absorbers and acid coolers. Venturi concurrent absorbers operating at acid temperatures of 130 to 140°C are installed in several plants. To recover acid heat directly as steam, it was necessary to increase the acid temperatures from 110 to 120°C to about 200°C.

In 1987 Monsanto Enviro-Chem demonstrated its new Heat Recovery System (HRS) at Namhae Chemical in South Korea.[36,37] The process is based on 310 stainless steel, which resists corrosion in 98.5 percent H_2SO_4 at temperatures up to 220°C. The intermediate absorber at Namhae takes 194°C gas from the converter third stage economizer and absorbs the SO_3 in 199°C, 99 percent acid. Recirculated acid from the absorber is cooled from 220°C in a 10-bar HRS boiler. The added energy recovery for this process is reported to increase the total energy recovery to 90 percent. Monsanto's proposed Monarch Process combines its HRW technology with the wet catalytic converter process (Lurgi) to increase heat recovery and shift it to high pressure stream production for electric power generation.[31]

Other Sources of Sulfuric Acid

Spent sulfuric acid usually is diluted in the process in which it is used: titanium dioxide pigment processing, plastics manufacture, and so on. The dilute acid may be used in processes requiring dilute acid or may be concentrated for reuse by a number of vacuum evaporation processes (Simonson-Mantius, Chemetics)[29] or by thin-film evaporation (DuPont, Bofors). In the submerged combustion distillation process, water is evaporated from the dilute acid by forcing hot flue gases from a fuel-fired burner below the acid surface (Chemico). Concentration of 75 percent acid to 95 to 98 percent H_2SO_4 by the Pauling-Plinke process is done by feeding the 75 percent acid to a stripping column fitted with a stirred cast iron pot mounted in a furnace. The acid concentration in the pot must be kept above 80 percent to minimize corrosion.

Chemetics has developed a process for treating spent alkylation sulfuric acid with nitric acid to produce a sulfuric acid that can be used to acidulate phosphate rock, the major use for sulfuric acid. The organic contaminants are converted to carbon particles that are removed with the gypsum on filtration of the phosphoric acid. Special alloys are used in the fabrication of the acid reactor.

Production and Consumption of Sulfuric Acid

The world production of sulfuric acid (1989) is presented in Table 14.4.[26] Nearly two-thirds of the world's new sulfuric acid production derives from brimstone burning. The balance of new acid production comes largely from pyrite combustion and nonferrous ore smelting. Recycled spent sulfuric acid is a significant fraction of acid production only in the United States and Oceania, primarily Australia. In the United States 52 percent of the spent acid comes from petroleum refineries, 38 percent from plastic and synthetic materials producers, and the balance from a wide variety of sources.

New sulfuric acid production and the number of sulfuric acid plants in the United States during the 1980s are given in Table 14.5 for major acid-producing states. The South accounts for about 75 percent of new sulfuric acid production, most of which is captive consumption for phosphate fertilizer production. With its massive phosphate rock deposits, Florida leads the nation in sulfuric acid production, to feed its phosphoric acid plants. Sulfur mines and recovered sulfur from oil and gas operations in Texas and Louisiana provide brimstone feed to sulfuric acid plants. Many of these plants are sited near major waterways to provide cheap transportation for raw materials and fertilizer products. Southwestern sulfuric acid plants usually are associated with smelters that ship the acid by rail to fertilizer plants.

Table 14.6 lists the sulfuric acid–consuming industries in the United States and shows the trends in their acid consumption rates through the 1980s. Agriculture accounted for 70 percent of U.S. consumption of sulfuric acid in 1989. Nearly all of the sulfuric acid

TABLE 14.4 World Production of New Sulfuric Acid for 1989 (Thousands of Metric Tons, 100% H_2SO_4)

		Sulfur Source		
	Brimstone	*Pyrite*	*Other*	*Total*
West Europe	12,269	6,943	5,655	24,867
France	3,500	—	580	4,080
Germany FR	1,590	800	1,300	3,690
Spain	10	2,550	700	3,260
East Europe	24,522	5,872	8,141	38,535
Poland	2,500	—	550	3,100
Former Soviet Union	18,720	4,250	5,350	28,320
North America	34,462	450	5,551	40,463
Canada	1,200	450	1,910	3,560
U.S.	33,262	—	3,641	36,903
Latin America	7,630	272	2,268	9,900
Brazil	3,050	202	450	3,702
Mexico	3,373	—	792	4,165
Asia	12,724	10,284	7,649	30,657
China PR	950	8,758	1,700	6,881
India	3,625	20	260	3,905
Japan	1,995	533	4,353	6,881
Oceania	1,380	—	600	1,980
Africa	10,054	1,534	1,240	12,828
Morocco	4,135	--	—	4,135
S. Africa	1,125	1,325	700	3,150
Tunisia	3,250	—	—	3,250
World Total	102,771	25,355	31,104	159,230

Source: Freeport Sulphur Marketing Department estimates.

TABLE 14.5 New Sulfuric Acid Production in the United States (Thousands of Metric Tons, 100% H_2SO_4)

	Number of Plants			*Sulfuric Acid Production*		
	1989	*1984*	*1979*	*1989*	*1984*	*1979*
Arizona	5	8	7	1,454	1,098	1,119
California	10	10	10	527	844	989
Florida	14	12	16	17,551	16,331	14,637
Idaho	2	2	3	(1)	(1)	1,257
Illinois	8	9	15	(1)	759	907
Louisiana	11	10	11	5,085	5,774	5,666
New Jersey	8	8	10	377	501	1,034
New Mexico	4	4	4	(1)	649	875
Oklahoma + Texas	15	17	17	1,772	1,842	3,107
Virginia	5	7	7	(1)	510	536
Unidentified	60	62	78	10,136	8,484	7,499
Total	142	149	178	36,903	36,794	37,627

Source: Hoffman, Current Industrial Reports, Series MA28B, U.S. Dept. of Commerce, Bureau of the Census, 1989;[26] *World Sulphur and Sulphuric Acid Atlas*, The British Sulphur Corp. Ltd.[39]
1. Data withheld to avoid disclosing figures for individual companies; data included in total.

consumed in agriculture was reacted with phosphate rock (principally $Ca_9(PO_4)_6 \cdot CaF_2$) to produce phosphoric acid. Granular phosphate fertilizers are produced by ammoniating phosphoric acid to yield mono- and diammonium phosphates; ammonium sulfate also is produced as a fertilizer. Petroleum refining is the largest nonfertilizer use for U.S. sulfuric acid. The acid competes with hydrogen fluoride as a catalyst in petroleum alkylation reactions

TABLE 14.6 Sulfuric Acid-Consuming Industries in the United States (Thousands of Metric Tons, 100% H_2SO_4)

Consuming Industries	*1898*	*1984*	*1979*
Agriculture	26,909	26,751	24,075
Phosphatic	26,436	26,373	23,192
Nitrogenous	285	261	546
Pesticides	99	70	148
Other agricultural	79	47	189
Other Industries	11,491	11,083	14,062
Petroleum refining	2,088	2,067	2,407
Synthetic rubber and plastics	1,172	959	647
Rayon and cellulose	159	155	252
Other chemicals	2,731	3,162	4,183
Copper ore processing	1,797	1,043	2,119
Uranium and other ore processing	257	357	416
Iron and steel	181	270	880
Other metals	157	163	125
Pulp and paper	978	814	760
Pigments and paint	423	332	628
Other	1,548	1,761	1,591
Total	38,400	37,834	38,083

Source: Morse, "End Uses of Sulfur and Sulfuric Acid," Mineral Industry Surveys, U.S. Department of the Interior, Bureau of Mines, 1990.[32]

for gasoline production. Sulfuric acid acts as a catalyst in synthetic rubber and plastics manufacture. Copper ore leaching is carried out by distributing the acid over leach piles of the ore and collecting the copper-rich leachate for processing. Sulfuric acid from nearby smelters is used in copper, uranium, and vanadium ore leaching.

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15

Petroleum and Its Products

H. L. Hoffman*

THE NATURE OF PETROLEUM

Petroleum is a mixture of hydrocarbons—chemical combinations of hydrogen and carbon. When burned completely, the hydrocarbons should yield only water (H_2O) and carbon dioxide (CO_2). When the burning is incomplete, carbon monoxide (CO) and various oxygenated hydrocarbons are formed. Since most burning uses air, nitrogen compounds also exist. In addition, there are other elements associated with the hydrocarbons in petroleum such as sulfur, nickel, and vanadium, just to name a few.

Petroleum is found normally at great depth underground or below seabeds. It can exist as a gas, liquid, solid, or a combination of these three states. Drilling is used to reach the gaseous and liquid deposits of petroleum. Then they are brought to the surface through pipe. The gas usually flows under its own pressure. The liquid may flow from its own pressure or be forced to the surface by submerged pumps. Solid or semisolid petroleum is brought to the surface in a number of ways: by digging with conventional mining techniques, by gasifying or liquefying with high temperature stream, or by burning a portion of the material in the ground so that the remainder can flow to the surface.

Natural gas is the gaseous form of petroleum. It is mostly the single-carbon molecule, methane (CH_4). When natural gas is associated with liquid petroleum underground, the methane will come to the surface in admixture with some heavier hydrocarbons. The gas is then said to be a wet gas. These heavier hydrocarbons are isolated and purified in natural gas processing plants. The operation yields ethane (petrochemical feed), propane (LPG), butane (refinery blending stock), and hydrocarbon liquids (natural gas condensate).

When the underground natural gas is associated with solid hydrocarbons such as tar or coal, the methane will have little other hydrocarbons. Then the gas is said to be a dry gas.

Crude oil is the common name given to the liquid form of petroleum. In some writings, one will see reference to "petroleum and natural gas," suggesting petroleum and crude oil are used as synonymous terms. Some crude

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oils have such great density that they are referred to as heavy oils and tars.

Tar sands are small particles of sandstone surrounded by an organic material called bitumen. The bitumen is so highly viscous and clings so tenaciously to the sandstone that it is easy to think of the mixture as a solid form of petroleum. Yet it is a mixture of high-density liquid on a supporting solid.

Oil shales are real petroleum solids. The curious thing about oil shales is that they do not contain petroleum crude oil. Instead, they contain an organic material called kerogen. The kerogen can be heated to yield a liquid substance called shale oil, which in turn can be refined into more conventional petroleum products.

Many products derived from petroleum are partly the consequence of the vast collection of hydrocarbons occurring in petroleum's natural state. A far more important factor is the ability of the hydrocarbon processing industries to transpose laboratory discoveries into large-scale commercial operations. Thus, the petroleum industry is an interesting study in applied organic chemistry and physical property manipulation.

Most of this discussion will concern the processing of petroleum crude oil, the most widely used form of petroleum resources. Natural gas processing will come in briefly at a few points. And since most of the world's petroleum is consumed as energy fuels, it is appropriate to begin with a brief review of the world's total energy situation.

Largest Energy Supplier

In Chapter 17, the point is made that coal offers a much more abundant primary source of energy than does petroleum. This is certainly true, but another fact remains: the world presently gets most of its energy from crude oil and natural gas. Petroleum is the major source of fuel used in transportation, manufacturing, and home heating.

Primary energy sources are defined as those coming from natural raw materials. Electricity is not included because it is a secondary energy source; that is, generated by consuming one or more of the other natural energy sources.

To put petroleum consumption into perspective, the primary energy sources considered here are: petroleum crude oil, natural gas, coal, hydropower (water to generate electricity), and nuclear energy. The quantities reported here will exclude energy from wood, peat, animal waste, and other sources—despite their importance to some localities. Documentation for these latter sources are sketchy, whereas the other energy sources are well documented.[1-4]

The common practice is to relate energy units to a common product—in this case, to petroleum liquid. For example, world consumption of crude oil and liquids (condensates) from natural gas in 1989 amounted to about 66 million barrels per day. If the amount of energy from other sources were converted to equivalent barrels of oil, the total world energy consumption in 1989 would be about 166 million daily barrels of oil equivalent. The relative distribution[1] of these sources is shown in Fig. 15.1. More energy (40%) comes from oil than from any other single source.

other single source.

Proven crude oil reserves determined for several earlier years[2] are shown in Table 15.1. Also included in this table are the annual production rates[3] and the ratio of the reserves to annual production.

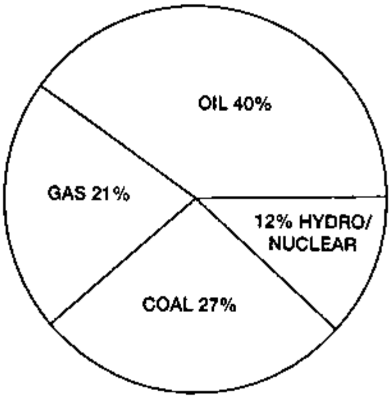


Fig. 15.1. Total world primary energy consumption in 1989 was equivalent to about 166 million daily barrels of oil.

TABLE 15.1 Proven Crude Oil Reserves Compared With Production Rates

	Billions of Barrels		
Year	*Proven Reserves, First of Year*[2]	*Annual Production*[3]	*Ratio, Reserves Divided by Production, Years*
1950	76	3.8	20
1955	154	5.6	27
1960	256	7.7	33
1965	342	11.0	31
1970	517	16.7	31
1975	569	19.3	29
1980	574	22.0	26
1985	696	19.6	36
1990*	933	21.8	43

*Author's estimate.

The ratio of reserves to production is a way of gauging natural reserves in terms of the years the proven reserves would sustain current production rates. Yet, if this measurement is taken literally, one might wonder how the petroleum industry grew and prospered during periods when there were less than 20 years of reserves. An explanation lies in the fact that the exploration and production segments of the petroleum industry seek and find oil sources to replace depleting ones. Note, for example, how the ratio jumped during the period between 1950 and 1955 as a result of the big oil reserves discovered in Middle Eastern countries.

Another interesting departure from past trends occurred in 1980, when oil consumption started to decline. The cause for the decline had its origins in 1974, when oil-exporting countries, especially countries in the Middle East, increased the price of their oil threefold. In 1980, the price of exported oil increased an additional twofold. These unusual price increases influenced the cost of other energy sources and set the stage for widespread energy conservation measures.

The oil price increases encouraged exploration for oil and other energy sources. At the same time, techniques were developed to recover more oil from existing reservoirs. Taken together, an increasing oil reserve and a slower energy growth rate placed the oil production rate in the early 1990s at a level that could be sustained by the then-known oil reserves for a longer time than in the recent past. But the continued use of oil as a major energy source will depend mostly on the ability to find more oil reserves.

Ultimate recoverable petroleum reserves have been estimated with wide variations, the consensus being between 1.5 to 2.5 trillion barrels (10^{12} bbl). Most estimators go to great lengths to explain the basis of their estimates. By comparison, proven reserves are in the neighborhood of 900 billion barrels. Proven reserves are generally taken to mean: "the oil remaining in the ground which geological and engineering information indicate with reasonable certainty to be recoverable in the future from known reservoirs under existing economic and operating conditions."[2]

Alternate feedstocks for refineries are being sought from coal, tar sands, and shale oil. Synthetic crude oil will be made from these raw materials so that conventional refining units can continue to be used to make consumer products.

In the meantime, top priority will be given to use crude oil to make liquid transportation fuels (because of their convenience) and petrochemical materials (because of their diversity of uses). It is a good bet that many of the gross conversion methods now applied to crude oil processing will be replaced in the future by more specific conversion. It is in this transition that knowledge of organic chemistry guides the development of new refining processes.

From Well to Refinery

A listing of crude oil production and consumption rates[1] for various countries and areas is shown in Table 15.2. Note that the countries in the Middle East produce much more oil than they consume, whereas the United States and countries in Western Europe consume much more than they produce. This situation points up the great importance of worldwide petroleum movement. The difference between production and

TABLE 15.2 Geographical Distribution of 1989 Production and Consumption[1] (millions of barrels daily)

Country/Area	*Produced*	*Consumed*
United States	9.2	17.3
Canada	2.0	1.8
Mexico	2.9	1.7
Central and S. America	4.2	3.6
Africa	6.1	2.0
W. Europe	4.2	12.9
USSR	12.1	8.8
Other E. Europe	0.3	1.8
Middle East	16.9	3.1
China	2.8	2.3
Japan	0.0	5.0
Far East and Oceania	3.7	5.6
World Total	64.4	65.9

Note: When consumption is more than production, the difference is made up from supplies held in storage.

consumption for any one period is balanced by oil being added to or removed from extensive storage areas around the world.

The growth of world refining capacity attempts to keep up with the growing demand for petroleum products. A measure of this growth[1] is shown in Fig. 15.2. The upper curve shows total refining capacity, while the lower curve shows the amount of crude oil run through the refineries.

One might wonder why refining capacity continued to surge ahead when crude throughput took a dip in the period from 1974 through 1976. For one thing, the amount of crude oil available for processing is subject to the whims of international trade. Since so much crude oil comes from some countries (notably, Middle Eastern countries) to be refined in other countries, international relations between countries strongly influence how much crude oil feedstock is available.

Another factor in refining growth is the time required to construct processing units. In highly industrialized countries such as the United States, Japan, and Western European countries there are mounting restrictions on new refinery sites. Thus, a decision to build a refinery and the actual completion of that refining capacity will take several year in order to fulfill local and governmental requirements. Then one to four years of actual construction activities are required before a new refinery will start processing feedstocks.

Refineries are located mostly in the countries consuming refined product. It is easier to transport crude oil to major refining centers than to transport separately the many individual products. The distribution of refining capacity[1] by areas for 1990 is depicted in Fig. 15.3.

The variety of ways crude oils are delivered to refineries is indicated by using U.S. refineries as an example. U.S. refineries get their feedstock via pipelines, tank trucks, barges, and oceangoing vessels.[4] The amount received by each of these routes is shown in Table 15.3. The large quantity coming by water explains why many refineries are located near oceans and why they own or lease such a large fleet of barges and oceangoing vessels.

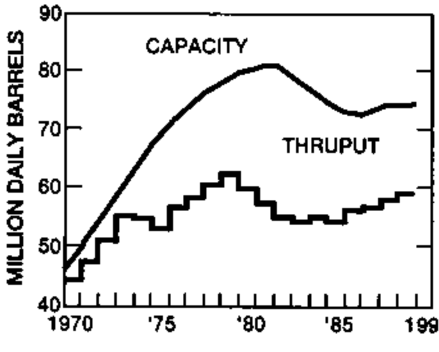


Fig. 15.2. World refining crude oil throughput is about 80% of the total available refining capacity.

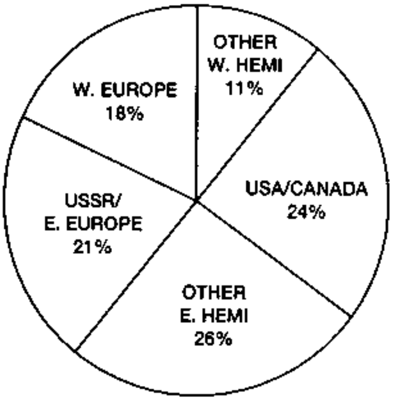


Fig. 15.3. Distribution of world refining capacity.

TABLE 15.3 Methods of Transportation for Crude Oil Received at U.S. Refineries, 1989[4]

Transportation Method	*Vol %*
Domestic crude oil	
Pipelines	40
Tankers and barges	14
Tank cars and trucks	2
Subtotal	56
Foreign crude oil	
Pipelines	15
Tankers and barges	29
Subtotal	44
Total receipts	100

PRODUCT NAMES

The distinction between refined products and petrochemicals is often a subtle one. In general, when the product is a fraction from crude oil that includes a fairly large group of hydrocarbons, the fraction is classified as a refined product. Examples of refined products are: gasoline, diesel fuel, heating oils, lubricants, waxes, asphalts, and petroleum coke.

By contrast, when the product from crude oil is limited to only one or two specific hydrocarbons of fairly high purity, the fraction is called a petrochemical. Examples of petrochemicals are: ethylene, propylene, benzene, toluene, and styrene—to name only a few.

There are many more identifiable petrochemical products than there are refined products. There are many specific hydrocarbons that can be derived from petroleum. However, these hydrocarbons lose individual identity when they are grouped into a refined product.

Refined Products

Most refined products at the consumer level are blends of several refinery streams. Product specifications determine which streams are suitable for a specific blend. Part of the difficulty of learning about refining lies in the industry's use of stream names that are different from the names of the consumer products.

Consider the listing in Table 15.4. The names in the last column should be familiar because they are used at the consumer level. Yet within a refinery, these products will be blended from portions of crude oil fractions having the names shown in the first column. To make matters worse, specifications and statistics for the industry are often reported under yet another set of names—those shown in the middle column of Table 15.4.

Gasoline at the consumer level, for example, may be called benzol or petrol, depending on the country where it is sold. In the early stages of crude oil processing, most gasoline components are called naphthas. Kerosine is

TABLE 15.4 Several Names for the Same Material

Crude oil cuts	*Refinery blends*	*Consumer products*
Gases	Still Gases	Fuel gas
	Propane/Butane	Liquefied petroleum gas (LPG)
Light/Heavy naphtha	Motor Fuel	Gasoline
	Aviation turbine, Jet-B	Jet fuel (naphtha type)
Kerosine	Aviation turbine, Jet-A	Jet fuel (kerosine type)
	No. 1 Fuel oil	Kerosine (range oil)
Light gas oil	Diesel	Auto and tractor diesel
	No. 2 fuel oil	Home heating oil
Heavy gas oil	No. 4 fuel oil	Commercial heating oil
	No. 5 fuel oil	Industrial heating oil
	Bright stock	Lubricants
Residuals	No. 6 fuel oil	Bunker C oil
	Heavy residual	Asphalt
	Coke	Coke

another example. It may be called coal oil to denote that it replaces stove oil (or range oil) once derived from coal. Kerosine's historical significance was first as an illuminating oil for lamps that once burned sperm oil taken from whales. But today, kerosine fractions go mostly into transportation fuels such as jet fuel and high quality No. 1 heating oil.

Product Specifications

Product application and customer acceptance set detailed specifications for various product properties. In the United States, the American Society for Testing and Materials (ASTM) and the American Petroleum Institute (API) are recognized for establishing specifications on both products and methods for testing. Other countries have similar referee organizations. For example, in the United Kingdom, it is the Institute of Petroleum (IP). In West Germany, it is Deutsches Institute suer Normung (DIN). In Japan, it is the Ministry of International Trade and Industry (MITI).

Boiling range is the major distinction among refined products, and many other properties are related directly to the products in these boiling ranges. A summary of ASTM specifications for fuel boiling ranges^5 is given in Table 15.5.

Boiling range also is used to identify individual refinery streams—as an example will show in a later section concerning crude oil distillation. The temperature that separates one fraction from an adjacent fraction will differ from refinery to refinery. Factors influencing the choice of cut point temperatures includes the following: type of crude oil feed, kind and size of downstream processes, and relative market demand among products.

Other specifications can involve either physical or chemical properties. Generally these specifications are stated as minimum or maximum quantities. Once a product qualifies to be in a certain group, it may receive a premium price by virtue of exceeding minimum specifications or by being below maximum specifications. Yet all too often, the only advantage for being better than specifications is an increase in the volume of sales in a competitive market.

The evolution of product specifications will, at times, appear sadly behind recent developments in more sophisticated analytical techniques. Certainly the ultimate specifications should be based on how well a product performs in use. Yet the industry has grown comfortable with certain comparisons, and these standards are retained for easier comparisons with earlier products. Thus, it is not uncommon to find petroleum products sold under an array of tests and specifications—some seemingly measuring similar properties.

It is behind the scenes that sophisticated analytical techniques prove their worth. These techniques are used to identify specific hydrocarbons responsible for one property or another. Then suitable refining processes are devised to accomplish a desired chemical reaction that will increase the production of specific types of hydrocarbons.

In the discussion on refining schemes, major specifications will be identified for each product category. It will be left to the reader to remember that a wide variety of other specifications also must be met.

Product Yields

As changes occur in relative demand for refined products, refiners turn their attention to ways that will alter internal refinery streams. The big problem here is that the increase in volume of one fraction of crude oil will deprive some other product of that same fraction. This point is often overlooked when the question arises: "How much of a specific product can a refinery make?" Such a question should always be followed by a second question: "What other products will be penalized?"

Envision, for example, what would happen if the refining industry were to make all the gasoline it possibly could with today's present technology. The result would be to rob many other petroleum products. A vehicle that needs gasoline for fuel also needs such products as industrial fuels to fabricate the

TABLE 15.5 Major Petroleum Products and Their Specified Boiling Range[5]

Product designation	*ASTM designation*	*Specified temp. for vol % distilled at 1 atm., °F* 10%	50%	90%
Liquefied petroleum gas (LPG)	D 1835			
Commercial propane		—[a]		—[b]
Commercial butane		—[a]		—[c]
Aviation gasoline (Avgas)	D 910	167 max	221 max	275 max[d]
Automotive gasoline	D 439			
Volatility class A		158 max	170–250	374 max[e]
Volatility class B		149 max	170–245	374 max[e]
Volatility class C		140 max	170–240	365 max[e]
Volatility class D		131 max	170–235	365 max[e]
Volatility class E		122 max	170–230	365 max[e]
Aviation turbine fuel	D 1655			
Jet A or A-1		400 max		—[f]
Jet B		—[g]	374 max	473 max
Diesel fuel oil	D 975			
Grade 1-D				550 max
Grade 2-D				540–640
Grade 4-D		—	not specified	—
Gas turbine fuel oil	D 2880			
No. 0-GT		—[h]	not specified	—
No. 1-GT				550 max
No. 2-GT				540–640
No. 3-GT		—	not specified	—
No. 4-GT		—	not specified	—
Fuel oil	D 396			
Grade No. 1		419 max		550 max
Grade No. 2		—[h]		540–640
Grade No. 4		—	not specified	—
Grade No. 5		—	not specified	—
Grade No. 6		—	not specified	—

[a] vapor pressure specified instead of front end distillation
[b] 95% point, −37°F max
[c] 95% point, 36°F max
[d] final point, 338°F max
[e] final point, all classes, 437°F max
[f] final point, 572°F max
[g] 20% point, 293°F max
[h] flash point specified instead of front end distillation

vehicle, lubricants for the engine's operation, asphalt for roads upon which the vehicle is to move, and petrochemical plastics and fibers for the vehicle's interior. Until adequate substitutes are found for these other petroleum products, it would be unwise to make only one product, even though sufficient technology may exist to offer this option.

This is not to say that substitutes will not be found, that these substitutes will not be better than petroleum products. In fact, many forecasts suggest that petroleum will ultimately be allocated only to transportation fuels and petrochemical feedstocks. It appeaars that these uses are the most suitable options for petroleum crude oil.

In the United States, the relative portions of refined products[4] made from crude oil are shown in Table 15.6. This distribution of products is the result of a long-standing trend to convert the heavier less valuable fractions into lighter more valuable fractions. The ways

TABLE 15.6 Product Yields from U.S. Refineries, 1989[4]

Product	*Vol % of Refinery Input*
Still gas	4.9
Liquefied gas	4.0
Gasoline	45.9
Jet fuel	10.1
Kerosine	0.5
Special naphtha	0.4
Petrochemical feed	2.5
Distillates	20.8
Lubricants	1.2
Waxes	0.1
Coke	3.9
Asphalt/road oil	3.1
Residuals	6.9
Miscellaneous	0.5
Total	104.8*

*Includes 4.8 vol % gain because most products are of less density than original feedstock.

this can be done will be discussed in the section on refinery schemes.

Petrochemicals

The portion of crude oil going to petrochemicals may appear small compared to fuels, but the variety of petrochemicals is huge. The listing in Table 15.7 will give some idea of the range of petrochemical applications. Many of these products are described in Chapter 22. A few will be included here as they come into competition with the manufacture of fuels.

Despite their variety, all commercially manufactured petrochemicals account for the consumption of only a small part of the total crude oil processed. In the United States, where petrochemicals have grown swiftly, the total petrochemical output at the beginning of 1990 was little more than 7 volume percent (vol %) of all petroleum feedstocks. An estimated 2 vol % went to energy of conversion, leaving 5 vol % represented as petrochemical products. Even so, this quantity has been sufficient for petrochemical-based materials to replace many products once made from such raw materials as coal, lumber, metal ores, and so forth.

REFINING SCHEMES

A refinery is a massive network of vessels, equipment, and pipes. The total scheme can be divided into a number of unit processes. In the discussion to follow, only major flow streams will be shown, and each unit will be depicted by a single block on a simplified flow diagram. Details will be discussed later.

TABLE 15.7 Petrochemical Applications

Absorbents
Activators
Adhesives
Adsorbents
Analgesics
Anesthetics
Antifreezes
Antiknocks
Beltings
Biocides
Bleaches
Catalysts
Chelating agents
Cleaners
Coatings
Containers
Corrosion inhib.
Cosmetics
Cushions
De-emulsifiers
Desiccants
Detergents
Drugs
Drying oils
Dyes
Elastomers
Emulsifiers
Explosives
Fertilizers
Fibers
Films
Finish removers
Fire-proofers
Flavors
Food supplements
Fumigants
Fungicides
Gaskets
Hair conditioners
Heat transfer fluids
Herbicides
Hoses
Humectants
Inks
Insecticides
Insulations
Lacquers
Laxatives
Odorants
Oxidation inhib.
Packagings
Paints
Paper sizings
Perfumes
Pesticides
Pharmaceuticals
Photographic chem.
Pipe
Plasticizers
Preservatives
Refrigerants
Resins
Rigid foams
Rust inhib.
Safety glass
Scavengers
Stabilizers
Soldering flux
Solvents
Surfactants
Sweeteners
Synthetic rubber
Textile sizings
Tire cord

Refined products establish the order in which each refining unit will be introduced. Only one or two key product specifications are used to explain the purpose of each unit. Nevertheless, the reader is reminded that the choice from among several types of units and the size of these units are complicated economic decisions. The trade-offs among product types, quantity, and quality will be mentioned to the extent that they influence the choice of one kind of process unit over another.

Feedstock Identification

Each refinery has its own range of preferred crude oil feedstock for which a desired distribution of products is obtained. The crude oil usually is identified by its source country, underground reservoir, or some distinguishing physical or chemical property. The three most frequently specified properties are density, chemical characterization, and sulfur content.

API gravity is a contrived measure of density.[6] The relation of API gravity to specific gravity is given by the following:

$$^{\circ}\mathrm{API} = \frac{141.5}{sp\ gr} - 131.5$$

where *sp gr* is the specific gravity, or the ratio of the weight of a given volume of oil to the weight of the same volume of water at a standard temperature, usually 60°F.

An oil with a density the same as that of water, or with a specific gravity of 1.0, would then be 10°API oil. Oils with higher than 10°API gravity are lighter than water. Since lighter crude oil fractions are usually more valuable, a crude oil with a higher °API gravity will bring a premium price in the market place.

Heavier crude oils are getting renewed attention as supplies of lighter crude oil dwindle. In 1967, the U.S. Bureau of Mines (now part of the U.S. Department of Energy) defined heavy crudes as those of 25°API or less. More recently, the American Petroleum Institute proposed to use 20°API or less as the distinction for heavy crude oils.

A characterization factor was introduced by Watson and Nelson[7] to use as an index of the chemical character of a crude oil or its fractions. The Watson characterization factor is defined as follows:

$$\text{Watson } K = (T_B)^{1/3}/sp\ gr$$

where T_B is the absolute boiling point in degrees Rankin, and *sp gr* is specific gravity compared to water at 60°F. For a wide boiling range material like crude oil, the boiling point is taken as an average of the five temperatures at which 10, 30, 50, 70, and 90 percent are vaporized.

A highly paraffinic crude oil might have a characterization factor as high as 13, whereas a highly naphthenic crude oil could be as low as about 10.5. Highly paraffinic crude oils can also contain heavy waxes which make it difficult for the oil to flow. Thus, another test for paraffin content is to measure how cold a crude oil can be before it fails to flow under specific test conditions. The higher the pour point temperature, the greater the paraffin content for a given boiling range.

Sour and *sweet* are terms referring to a crude oil's approximate sulfur content. In early days, these terms designated smell. A crude oil with a high sulfur content usually contains hydrogen sulfide—the gas associated with rotten eggs. Then the crude oil was called sour. Without this disagreeable odor, the crude oil was judged sweet. Today, the distinction between sour and sweet is based on total sulfur content. A sour crude oil is one with more than 0.5 wt % sulfur, whereas a sweet crude oil has 0.5 wt % or less sulfur. It has been estimated that 58 percent of U.S. crude oil reserves are sour. More important, an estimated 81 percent of world crude oil reserves are sour.[8]

ASTM distillation is a test prescribed by the American Society for Testing and Materials to measure the volume percent distilled at various temperatures.[5] The results are often reported the other way around: the temperatures at which given volume percents vaporize.[9] These data indicate the quantity of conventional boiling range products occurring naturally in the crude oil. Analytical tests on

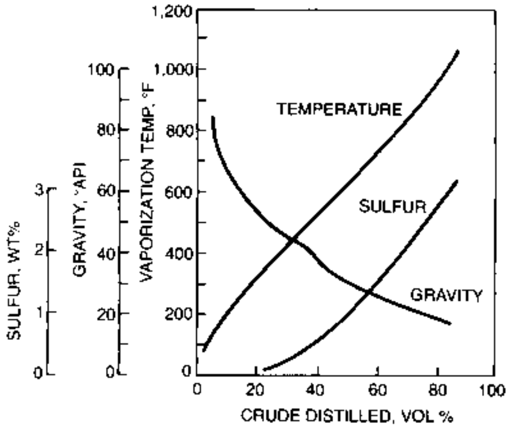


Fig. 15.4. Analysis of Light Arabian crude oil.

each fraction indicate the kind of processing that may be needed to make specification products. A plot of boiling point, sulfur content, and API gravity for fractions of Light Abrabian crude oil is shown in Fig. 15.4. This crude oil is among the ones most traded in the international crude oil market.

In effect, Fig. 15.4 shows that the material in the mid-volume range of Light Arabian crude oil has a boiling point of approximately 600°F, a liquid density of approximately 30°API and an approximate sulfur content of 1.0 wt %. These data are an average of eight samples of Light Arabian crude oil. More precise values would be obtained on a specific crude oil if the data were to be used in design work.

Since a refinery stream spans a fairly wide boiling range, the crude oil analysis data would be accumulated throughout that range to give fraction properties. The intent here is to show an example of the relation between volume distilled, boiling point, liquid density, and sulfur content.

Crude Oil Pretreatment

Crude oil comes from the ground admixed with a variety of substances: gases, water, and dirt (minerals). The technical literature devoted to petroleum refining often omits crude oil cleanup steps. It is likely presumed that the reader wishing to compare refining schemes will understand that the crude has already been through these cleanup steps. Yet cleanup is important if the crude oil is to be transported effectively and to be processed without causing fouling and corrosion. Cleanup takes place in two ways: field separation and crude desalting.

Field separation is the first attempt to remove the gases, water, and dirt that accompany crude oil coming from the ground. As the term implies, field separation is located in the field near the site of the oil wells. The field separator is often no more than a large vessel that gives a quieting zone to permit gravity separation of three phases: gases, crude oil, and water (with entrained dirt).

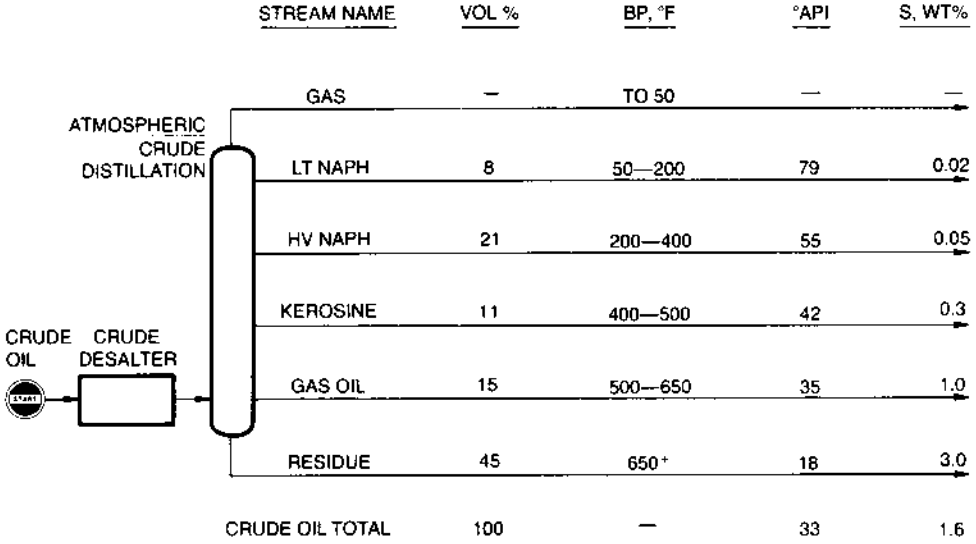
The crude oil is lighter than water but heavier than the gases. Therefore, crude oil appears within the field separator as a middle layer. The water is withdrawn from the bottom to be disposed of at the well site. The gases are withdrawn from the top to be piped to a natural gas processing plant or are pumped back into the oil well to maintain well pressure. The crude oil from the middle layer is pumped to a refinery or to storage awaiting transportation by other means.

Crude desalting is a water-washing operation performed at the refinery site to get additional crude oil cleanup.[10] The crude oil coming from field separators will continue to have some water and dirt entrained with it. Water washing removes much of the water-soluble minerals and entrained solids.

If these crude oil contaminants were not removed, they would cause operating problems during refinery processing. The solids (dirt and silt) would plug equipment. Some of the solids, being minerals, would dissociate at high temperature and corrode equipment. Still others would deactivate catalysts used in some refining processes.

Crude Oil Fractions

The importance of boiling range for petroleum products already has been discussed in connection with Table 15.5. The simplest form of refining would isolate crude oil into



STREAM NAME	VOL %	BP, °F	°API	S, WT%
GAS	–	TO 50	–	–
LT NAPH	8	50—200	79	0.02
HV NAPH	21	200—400	55	0.05
KEROSINE	11	400—500	42	0.3
GAS OIL	15	500—650	35	1.0
RESIDUE	45	650⁺	18	3.0
CRUDE OIL TOTAL	100	–	33	1.6

Fig. 15.5. Separating desalted crude oil into fractions.

fractions having boiling ranges that would coincide with the temperature ranges for consumer products. Some treating steps might be added to remove or alter undesirable components, and a very small quantity of various chemical additives would be included to enhance final properties.

Crude oil distillation separates the desalted crude oil into fractions of differing boiling ranges. Instead of trying to match final product boiling ranges at this point, the fractions are defined by the number and kind of downstream processes.

The desalting and distillation units are depicted in Fig. 15.5 to show the usual fractions coming from crude oil distillation units. The discussion in the following paragraphs shows the relationships between some finished products and downstream processing steps.

GASOLINE

The light and heavy naphtha fractions from crude oil distillation are ultimately combined to make gasoline. The two streams are isolated early in the refining scheme so that each can be refined separately for optimum blending in order to achieve required specifications—of which only volatility, sulfur content, and octane number will be discussed.

Volatility

A gasoline's boiling range is important during its aspiration into the combustion chamber of a gasoline-powered engine. Vapor pressure, a function of the fuel's boiling range, is also important. Boiling range and vapor pressure are lumped into one concept, volatility.[11]

Lighter components in the gasoline blend are established as a compromise between two extremes: enough light components are needed to give adequate vaporization of the fuel–air mixture for easy engine starting in cold weather, but too much of the light components can cause the fuel to vaporize within the fuel pump and result in vapor lock.

Environmental studies suggest that hydrocarbons in the atmosphere near large cities are the result of evaporation of lighter components from the gasoline in automobiles. This evaporation is reduced by designing automobile to use closed fuel systems and fuel-injected engines. Then the concentration of the lighter components in the fuel can be reduced and is not so critical as it is for fuel-aspirated engines.

Heavier components are a trade-off between fuel volume and combustion chamber deposits. They extend the yield of gasoline that can be made from a given volume of crude oil, but they also contribute to combustion chamber deposits and spark plug fouling. Thus, an upper limit is set on gasoline's boiling range to give a clean-burning fuel.

Sulfur Content

Sulfur compounds are corrosive and foul-smelling. When burned in an engine, these compounds result in sulfur dioxide exhaust. Should the engine be equipped with a catalytic muffler, as is the case for many modern automobile engines, the sulfur is exhausted from the muffler as sulfur trioxide, or sulfuric acid mist.

Caustic wash or some other enhanced solvent washing technique is usually sufficient to remove sulfur from light naphtha. The sulfur compounds in light naphtha are mercaptans and organic sulfides that are removed readily by these washing processes.

Heavy naphtha is harder to desulfurize. The sulfur compounds are in greater concentration and are of more complicated molecular structure. A more severe desulfurization method is needed to break these structures and release the sulfur. One such process is hydrotreating.

Hydrotreating is a catalytic process that converts sulfur-containing hydrocarbons into low-sulfur liquids and hydrogen sulfide.[12] The process is operated under a hydrogen-rich blanket at elevated temperature and pressure. A separate supply of hydrogen is needed to compensate for the amount of hydrogen required to occupy the vacant hydrocarbon site once held by the sulfur. Also, hydrogen is consumed to convert the sulfur to hydrogen sulfide gas.

Nitrogen and oxygen compounds are also dissociated by hydrotreating. The beauty of the process is that molecules are split at the points where these contaminants are attached. For nitrogen and oxygen compounds, the products of hydrotreating are ammonia and water, respectively. Thus, the contaminants will appear in the offgases and are easily removed by conventional gas treating processes.

Octane Number

Another condition to keep gasoline engines running smoothly is that the fuel–air mixture start burning at a precise time in the combustion cycle. An electrical spark starts the ignition. The remainder of the fuel–air mix should be consumed by a flame front moving out from the initial spark.

Under some conditions, a portion of the fuel–air mixture will ignite spontaneously instead of waiting for the flame front from the carefully timed spark. The extra pressure pulses resulting from spontaneous combustion are usually audible above the normal sounds of a running engine and give rise to the phenomenon called knock. Some special attributes of the knocking phenomenon are called pinging and rumble. All of these forms of knock are undesirable because they waste some of the available power of an otherwise smooth-running engine.

Octane number is a measure of a fuel's ability to avoid knocking. The octane number of a gasoline is determined in a special single cylinder engine where various combustion conditions can be controlled.[5] The test engine is adjusted to give trace knock from the fuel to be rated. Then various mixtures of iso-octane (2,2,4-trimethyl pentane) and normal heptane are used to find the ratio of the two reference fuels that will give the same intensity of knock as that from the unknown fuel. Defining iso-octane as 100 octane number and normal heptane as 0 octane number, the volumetric percentage of iso-octane in heptane that matches knock from the unknown fuel is reported as the octane number of the fuel. For example, 90 vol % iso-octane and 10 vol % normal heptane establishes a 90 octane number reference fuel.

Two kinds of octane number ratings are specified, although other methods are often used for engine and fuel development. Both methods use the same reference fuels and essentially the same test engine. Engine operating conditions are the difference. In one, called the *Research method*, the spark advance is fixed, the air inlet temperature is 125°F and engine speed is 600 rpm. The other, called the *Motor method*, uses variable spark timing, a higher mixture temperature (300°F), and a faster engine speed (900 rpm).

The more severe conditions of the Motor method have a greater influence on commercial blends than they do on the reference fuels. Thus, a Motor octane number of a commercial blend tends to be lower than the Research octane number. Recently, it has become the practice to label gasoline with an arithmetic avarage of both ratings, abbreviated $(R + M)/2$.

Catalytic reforming is the principal process for improving the octane number of a naphtha for gasoline blending.[13] The process gets its name from its ability to re-form or re-shape the molecular structure of a feedstock. The transformation that accounts for the improvement in octane number is the conversion of paraffins and naphthenes to aromatics. The aromatics have better octane numbers than their paraffin or naphthene homologs. The greater octane number increase for the heavier molecules explains why catalytic reforming is usually applied to the heavy naphtha fractions.

Catalysts for reforming typically contain platinum or a mixture of platinum and other metal promoters on a silica–alumina support. Only a small concentration of platinum is used, averaging about 0.4 wt %. The need to sustain catalyst activity and the expense of the platinum make it common practice to pretreat the reformer's feedstock to remove catalyst poisons.

Hydrotreating, already discussed, is an effective process to pretreat reforming feedstocks. The two processes go together well for another reason. The reformer is a net producer of hydrogen by virtue of its cyclization and dehydrogenation reactions. Thus, the reformer can supply the hydrogen needed by the hydrotreating reactions. A rough rule of thumb is that a catalytic reformer produces 800 to 1200 scf of hydrogen per barrel of feed, while the hydrotreater consumes about 100 to 200 scf/bbl for naphtha treating. The excess hydrogen is available for hydrotreating other fractions in separate hydrotreaters.

DISTILLATES

Jet fuel, kerosine (range oil), No. 1 fuel oil, No. 2 fuel oil, and diesel fuel are all popular distillate products coming from 400°F to 600°F fractions of crude oil. One grade of jet fuel uses the heavy naphtha fraction, but the kerosine fraction supplies the more popular heavier grade of jet fuel, with smaller amounts sold as burner fuel (range oil) or No. 1 heating oil.

Some heating oil (generally No. 2 heating oil) and diesel fuel are very similar and are sometimes substitutes for each other. The home heating oil is intended to be burned within a furnace for space heating. The diesel fuel is intended for compression-ignition engines.

Hydrotreating improves the properties of all these distillate products. The process not only reduces the sulfur content of the distillates to a low level but also hydrogenates unsaturated hydrocarbons so that they will not contribute to smoke and particulate emissions —whether the fuel is burned in a furnace or used in an engine.

RESIDUALS

Crude oil is seldom distilled at temperatures above about 650°F. At higher temperatures, coke will form and plug the lower section of the crude oil distillation tower. Therefore, the portion with a boiling point above 650°F is not vaporized—or at least not with the processing units introduced so far. This residual liquid is disposed of as industrial fuel oils, road oils, and so forth. The residual is sometimes called reduced crude because the lighter fractions have been removed.

PRODUCING MORE LIGHT PRODUCTS

The refining scheme evolved to this point is shown in Fig. 15.6. It is typical of a low-investment refinery designed to make

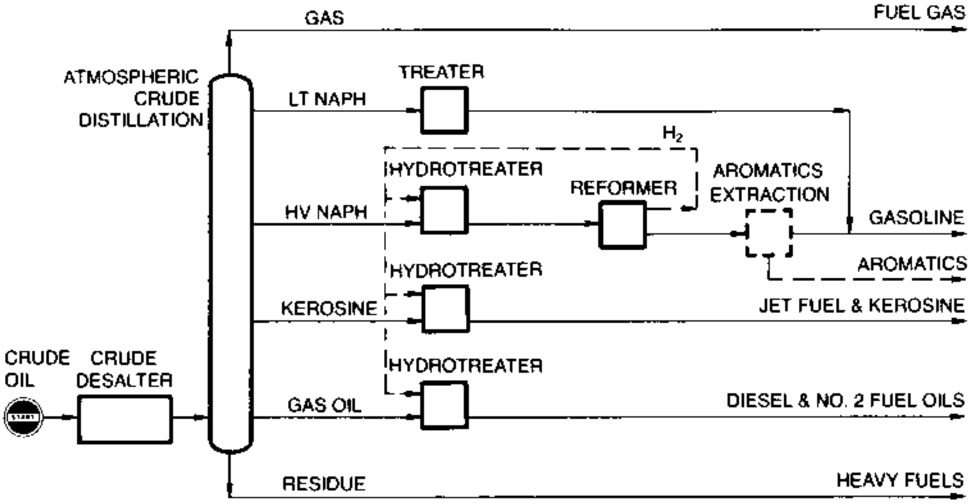


Fig. 15.6. Low-investment route to modern products.

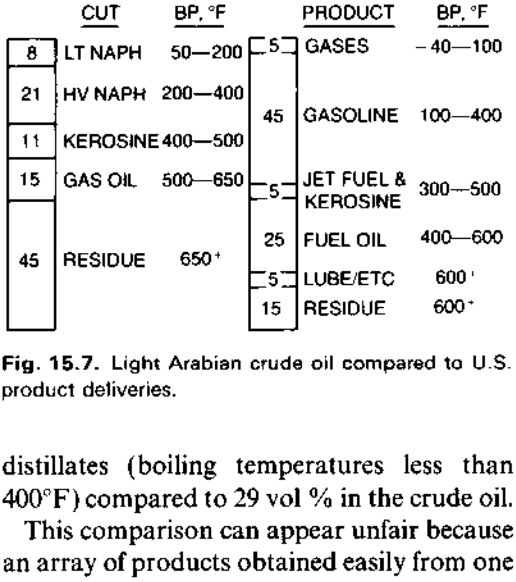


Fig. 15.7. Light Arabian crude oil compared to U.S. product deliveries.

products of modern quality. Yet the relative amounts of products are dictated by the boiling range of the crude oil feed. For Light Arabian crude oil reported earlier (see Fig. 15.4), all distillate fuel oils and lighter products (those boiling below 650°F) would comprise only about 55 vol % of the crude oil feed rate.

For industrialized areas where the principal demand is for transportation fuels or high-quality heating oils, a refining scheme of the type shown in Fig. 15.6 would need to dispose of almost half of the crude oil as low-quality, less desirable, residual products. Moreover, the price obtained for these residual products is not only much lower than revenues from lighter products but also lower than the cost of the original crude oil. Thus, there are economic incentives to convert much of the residual portions into lighter products of suitable properties.

Relative volumes of petroleum product deliveries in the United States and the portions existing in Light Arabian crude oil are compared by boiling ranges in Fig. 15.7. Note that 80 to 85 vol % of all U.S. petroleum products are lighter than the boiling temperature of 650°F compared to the 55 vol % existing in the crude oil. Furthermore, half of all U.S. products are gasoline and lighter distillates (boiling temperatures less than 400°F) compared to 29 vol % in the crude oil.

This comparison can appear unfair because an array of products obtained easily from one crude oil would be difficult to obtain from another crude oil feed. Total product deliveries in the United States come from a variety of different crude oils, processed in a variety of different refining schemes. But the comparison serves to emphasize a long-term trend in the refining industry—to convert heavy, less desirable fractions into lighter, more valuable products. The comparison also lays the foundation for the next group of processes to be discussed. The choice and the arrangement of processes hereafter are intended to depict a breadth of refining technology, rather than suggest a commercial scheme for handling the example crude oil.

Cracking

These processes cause hydrocarbon molecules to break apart into two or more smaller molecules. Thermal cracking uses high temperature (above 650°F) and long residence time to accomplish the molecular split. Catalytic cracking accomplishes the split much faster and at lower temperatures because of the presence of a cracking catalyst.

Catalytic cracking involves not only some of the biggest units, with their large catalyst reactor-separators and regenerator, but it is also among the more profitable operations with its effective conversion of heavy feeds to light products. Gasoline from catalytic cracking has a higher octane number than thermally cracked gasoline. Yields include less gas and coke than thermal cracking; that is, more useful liquid products are made. The distribution of products between gasoline and heating oils can be varied by different choices for catalysts and operating conditions.

The best feeds for catalytic crackers are determined by a number of factors. The feed should be heavy enough to justify conversion. This usually sets a lower boiling point of about 650°F. The feed should not be so heavy that it contains undue amounts of metal-bearing compounds or carbon-forming materials. Either of these substances is more prevalent in heavier fractions and can cause the catalyst to lose activity more quickly.

Visbreaking is basically a mild, once-through thermal-cracking process. It is used to get just sufficient cracking of resid so that fuel oil specifications can be made. Although some gasoline and light distillates are made, this is not the purpose of the visbreaker.

Coking is another matter. It is a severe form of thermal cracking in which coke formation is tolerated to get additional lighter liquids from the heavier, dirtier fractions of crude oil. Here, the metals that would otherwise foul a catalytic process are laid down with the coke. The coke settles out in large coke drums that are removed from service frequently (about one a day) to have the coke cut out with high-pressure water lances. To make the process continuous, multiple coke drums are used so that some drums can be onstream while others are being unloaded.

Hydrocracking achieves cracking with a rugged catalyst to withstand resid contaminants and with a hydrogen atmosphere to minimize coking. Hydrocracking combines hydrotreating and catalytic-cracking goals, but a hydrocracker is much more expensive than either of the other two. The pressure is so high (up to 3000 psi) that very thick walled vessels must be used for reactors (up to 9 inches thick). The products from a hydrocracker will be clean (desulfurized, denitrified, and demetalized) and will contain isomerized hydrocarbons in greater amount than in conventional catalytic cracking. A significant part of the expense of operating a hydrocracker is for the hydrogen that it consumes.

Vacuum Distillation

Among the greater variety of products made from crude oil, some of the products (lubricating oils for example) have boiling ranges that exceed 650°F—the general vicinity where cracking would occur in atmospheric distillation. Thus, by using a second distillation unit under vacuum, the heavier parts of the crude oil can continue to be divided into specific products. Furthermore, some of the fractions distilled from vacuum units are better than atmospheric residue for cracking because the metal-bearing compounds and carbon-forming materials are more highly concentrated in the vacuum residue.

Reconstituting Gases

Cracking processes to convert heavy liquids to lighter liquids also make gases. Another way to make more liquid products is to combine gaseous hydrocarbons. A few small molecules of a gas can be combined to make one bigger molecular with fairly specific properties. Here, a gas separation unit is added to the refinery scheme to isolate the individual types of gases. When catalytic cracking is also part of the refining scheme, there will be a greater supply of olefins—ethylene, propylene, and butylene. Two routes for reconstituting these gaseous olefins into gasoline blending stocks are described below.

Polymerization ties two or more olefins together to make polymer gasoline. The double bond in only one olefin is changed to a single bond during each link between two olefins. This means the product will still have a double bond. For gasoline, these polymer stocks are good for blending because olefins tend to have higher octane numbers than their paraffin homolog.

However, the olefinic nature of polymer gasoline can also be a drawback. During long storage in warmer climates, the olefins can continue to link up to form bigger molecules of gum and sludge. This effect, though, is seldom important when the gasoline goes through ordinary distribution systems.

Alkylation combines an olefin and isobutane when gasoline is desired. The product is mostly isomers. If the olefin were butylene, the product would contain a high concentration of 2,2,4-trimethyl pentane. The reader is reminded that this is the standard compound that defines 100 on the octane number scale. Alkylates are high-quality gasoline-blending compounds, having good stability as well as high octane numbers.

Ether processes combine an alcohol with an iso-olefin. This is a recent addition to the gasoline manufacturing scheme. These processes were prompted by newer regulations requiring gasoline blends to contain some oxygenated compounds. When the alcohol is methanol and the iso-olefin is isobutylene, the product is methyl tertiary butyl ether (MTBE). When the alcohol is ethanol, and product is ethyl tertiary butyl ether (ETBE). When the alcohol is methanol and the iso-olefin is isoamylene, the product is tertiary amyl methyl ether (TAME).

A MODERN REFINERY

A refining scheme incorporating the processes discussed so far is shown in Fig. 15.8. The variations are quite numerous, though. Types of crude oil available, local product demands, and competitive quality goals are just a few of the factors considered to decide a specific scheme.

Many other processes play an important role in the final scheme. A partial list of these other processes would have the following goals: dewaxing lubricating oils, deoiling waxes, deasphalting heavy fractions, manufacturing specific compounds for gasoline blending (alcohols, ethers, etc.), and isolating specific fractions for use as petrochemical feedstocks.

Petrochemicals

It has already been mentioned that petrochemicals account for only a little more than 7 vol % of all petroleum feedstocks. Earlier, Table 15.7 gave the vast array of the applications of these petrochemicals. Olefins and aromatics make up a big part of the total.

Ethylene is one of the most important olefins. It is usually made by cracking gases—ethane, propane, butane or a mixture of these as might exist in a refinery's offgases. When gas feedstock is scarce or expensive, naphthas and even whole crude oil have been used in specially designed ethylene crackers. The heavier feeds also give significant quantities of higher molecular weight olefins and aromatics.

Aromatics, as were pointed out, are in high concentration in the product from a catalytic reformer. When aromatics are needed for petrochemical manufacture, they are extracted from the reformer's product using solvents such as glycols or sulfolane, to name two popular ones.

The mixed aromatics are called BTX as an abbreviation for benzene, toluene, and xylene. The first two are isolated by distillation, and the isomers of the third are separated by partial crystallization. Benzene is the starting material for styrene, phenol, and a number of fibers and plastics. Toluene is used to make a number of chemicals, but most of it is blended into gasoline. Xylene use depends on the isomer, *para*-xylene going into polyester

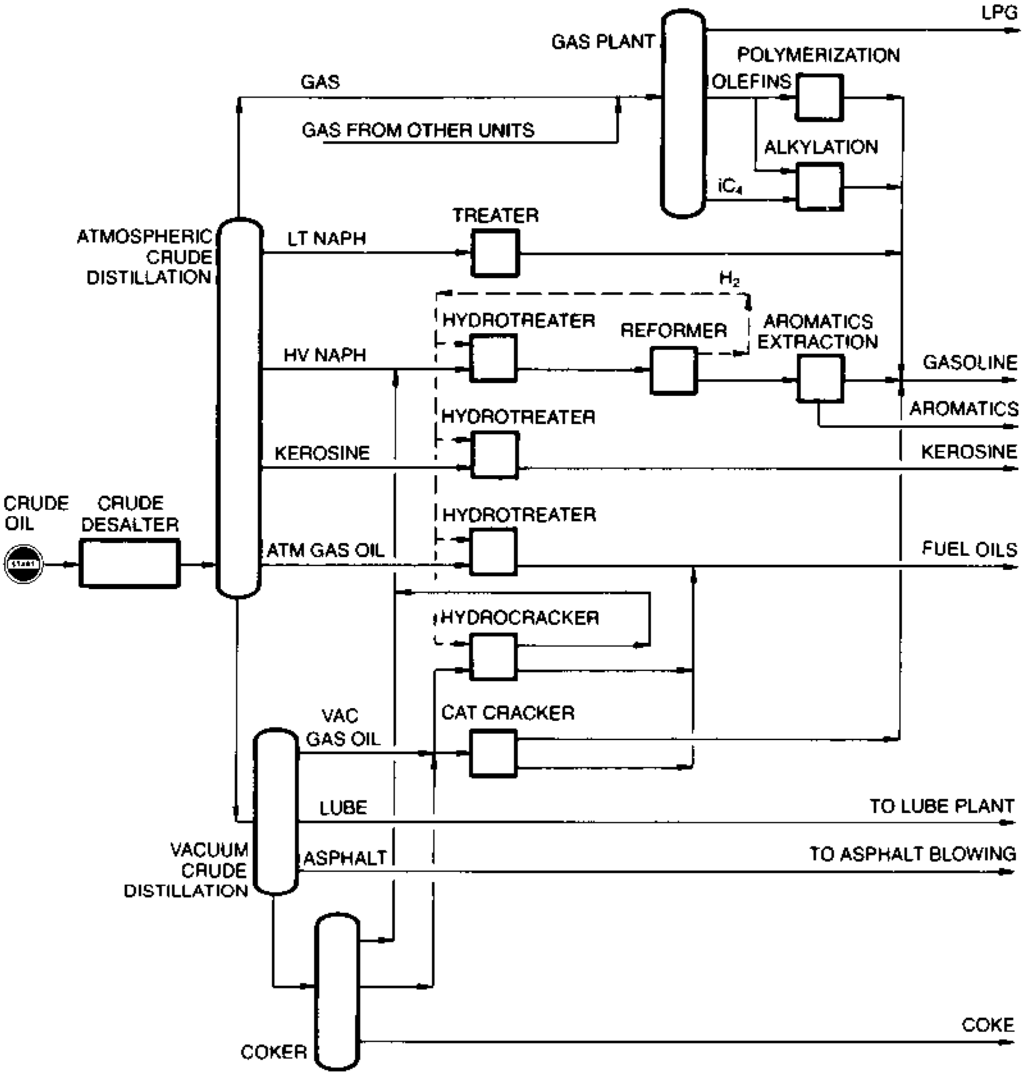


Fig. 15.8. High conversion refinery.

and *ortho*-xylene going into phthalic anhydride. Both are involved in a wide variety of consumer products.

PROCESS DETAILS

So far, refining units have been described as they relate to other units and to final product specifications. Now, typical flow diagrams[15] of some major processes will be presented to highlight individual features. In many cases, the specific design shown is an arbitrary choice from the work of several equally qualified designers.

Crude Desalting

Basically a water-washing process, the crude desalter must accomplish intimate mixing between the crude oil and water, then separate them sufficiently so that water will not enter subsequent crude-oil distillation heaters.

A typical flow diagram is shown in Fig. 15.9. The unrefined crude oil is heated to 100 to 300°F for suitable fluid properties. The

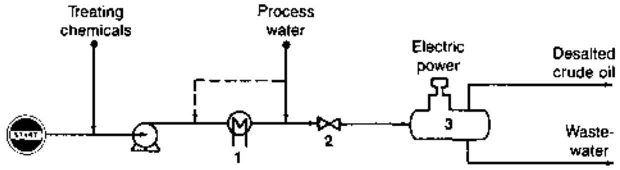


Fig. 15.9. Crude desalting. Includes: heater (1), mixing valve (2), and electrostatic water settler (3). (Hydrocarbon Processing, *69, no. 11, p. 86, Nov. 1990; copyright 1990 by Gulf Publishing Co. and used by permission of the copyright owner.*)

operating pressure is 40 psig or more. Elevated temperatures reduce oil viscosity for better mixing, and elevated pressure suppresses vaporization. The wash water can be added either before or after heating.

Mixing between the water and crude oil is assured by passing the mixture through a throttling valve or emulsifier orifice. Trace quantities of caustic, acid, or other chemicals are sometimes added to promote treating. Then the water-in-oil emulsion is introduced into a high voltage electrostatic field inside a gravity settler. The electrostatic field helps the water droplets to agglomerate for easier settling.

Salts, minerals, and other water-soluble impurities in the crude oil are carried off with the water discharged from the settler. Clean desalted crude oil flows from the top of the settler and is ready for subsequent refining.

Additional stages can be used in series to get additional reduction in salt content of the crude oil. Two stages are typical, but some installations use three stages. The increased investment cost for multiple stages is offset by reduced corrosion, plugging, and catalyst poisoning in downstream equipment by virtue of lower salt content.

Crude Distillation

Single or multiple distillation columns are used to separate crude oil into fractions determined by their boiling range. Common identification of these fractions was discussed in connection with Fig. 15.5, but should only be considered as a guide because a variety of refining schemes call for altering the type of separation made at this point.

A typical flow diagram of a two-stage crude oil distillation system is shown in Fig. 15.10. The crude oil is heated by exchange with various hot products coming from the system before it passes through a fired heater. The temperature of the crude oil entering the first column is 600 to 700°F, or high enough to vaporize the heavy gas oil and all lighter fractions.

Because light products must pass from the feed point up to their respective drawoff point, any intermediate stream will contain some of these lighter materials. Stream stripping (note the group of steam strippers beside the first column in Fig. 15.10) is a way to reintroduce these light materials back into the tower to continue their passage up through the column.

The bottom stream from the first fractionating column goes into a second column operated under vacuum. Steam jet ejectors are used to create the vacuum so that the absolute pressure can be as low as 30 to 40 mm Hg (about 0.7 psia). The vacuum permits hydrocarbons to be vaporized at temperatures much below their normal boiling points. Thus, fractions with normal boiling points above 650°F can be separated by vacuum distillation without causing thermal cracking.

Lately, a popular addition to a crude distillation system has been a preflash column ahead of the two stages shown in Fig. 15.10. The preflash tower strips out the lighter portions of a crude oil before the remainder enters the atmospheric column. It is the lighter portions that set the vapor loading in the atmospheric column, which, in turn, determines the diameter of the upper section of the column.

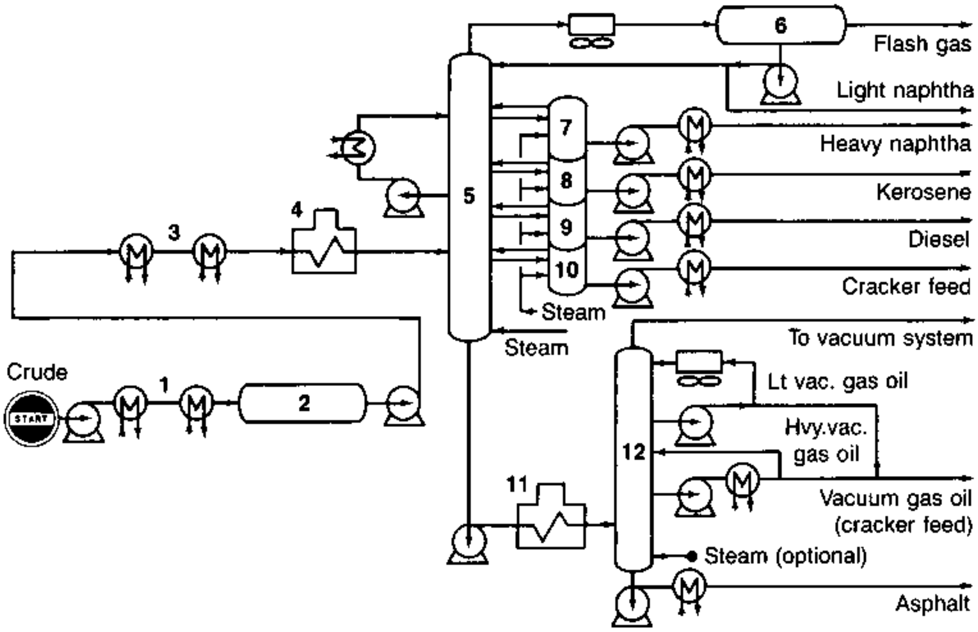


Fig. 15.10. Crude distillation—Foster Wheeler USA Corp. Includes: exchanger heaters (1, 3), desalter process (2), fired heater (4), main fractionator (5), overhead gas accumulator (6), sidestream strippers (7, 8, 9, 10), second fired heater (11), and vacuum fractionator (12). (Hydrocarbon Processing, *69, no. 11, p. 86, Nov. 1990; copyright 1990 by Gulf Publishing Co. and used by permission of the copyright owner.*)

Incidentally, total refining capacity of a facility is reported in terms of its crude-oil handling capacity. Thus, the size of the first distillation column, whether a preflash or an atmospheric distillation column, sets the reported size of the entire refinery. Ratings in barrels per stream day (bpsd) will be greater than barrels per calendar day (bpcd). Processing units must be shut down on occasion for maintenance, repairs, and equipment replacement. The ratio of operating days to total days (or bpcd divided by bpsd) is called an "onstream factor" or "operating factor." The ratio will be expressed as either a percent or a decimal. For example, if a refinery unit undergoes one shutdown period of one month during a three year duration, its operating factor is $(36 - 1)/36$, or 0.972, or 97.2 percent.

Outside the United States, refining capacity is given normally in metric tons per year. Precise conversion from one unit of measure to the other depends upon the specific gravity of the crude oil, but the approximate relation is one barrel per day equals 50 tons/year.

Hydrotreating

This is a catalytic hydrogenation process that reduces the concentration of sulfur, nitrogen, oxygen, metals, and other contaminants in a hydrocarbon feed. In more severe forms, hydrotreating saturates olefins and aromatics.

A typical flow diagram is shown in Fig. 15.11. The feed is pumped to operating pressure and mixed with a hydrogen-rich gas, either before or after being heated to the proper reactor inlet temperature. The heated mixture passes through a fixed bed of catalyst where exothermic hydrogenation reactions occur. The effluent from the reactor is then cooled and sent through two separation stages. In the first, the high pressure separator, unreacted hydrogen is taken overhead to be scrubbed for hydrogen sulfide removal; the cleaned hydrogen is then recycled. In the second, the lower-pressure separator takes off the remaining gases and light hydrocarbons from the liquid product. If the feed is

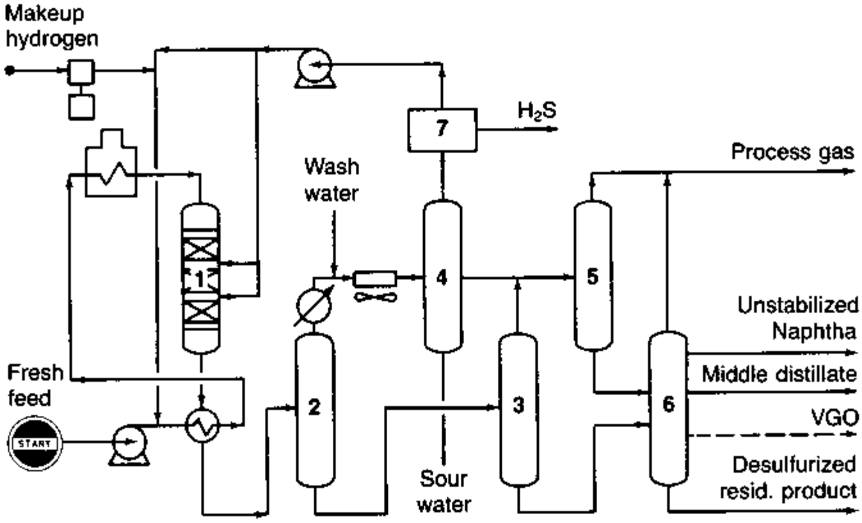


Fig. 15.11. Hydrotreating—Chevron Research and Technology Co. Includes: reactor (1), hot high pressure separator (2), hot low pressure separator (3), cold high pressure separator (4), cold low pressure separator (5), and product fractionator (6). (Hydrocarbon Processing, *69, no. 11, p. 114, Nov. 1990; copyright 1990 by Gulf Publishing Co. and used by permission of the copyright owner.*)

a wide-boiling range material from which several blending stocks are to be made, the hot low pressure separator is followed by a fractionation column to remove various liquid fractions.

The feed for hydrotreating can be a variety of different boiling range materials extending from light naphtha to vacuum residues. Generally, each fraction is treated separately to permit optimum conditions—the higher boiling materials requiring more severe treating conditions. For example, naphtha hydrotreating can be carried out at 200 to 500 psia and at 500 to 650°F, with a hydrogen consumption of 10 to 50 scf/bbl of feed. On the other hand, a residue hydrotreating process can operate at 1000 to 2000 psia and at 650 to 800°F, with a hydrogen consumption of 600 to 1200 scf/bbl.[14] Nevertheless, hydrotreating is such a desirable cleanup step that it can justify its own hydrogen manufacturing facilities, although the hydrogen-rich stream obtained as a by-product from catalytic reforming usually is sufficient for most operations.

Catalyst formulations constitute a significant difference among hydrotreating processes. Each catalyst is designed to be best suited to one type of feed or one type of treating goal.[16] When hydrotreating is done for sulfur removal, the process is called hydrodesulfurization, and the catalyst generally is cobalt and molybdenum oxides on alumina. A catalyst of nickel-molybdenum compounds on alumina can be used for denitrogenation and cracked-stock saturation.

Catalytic Reforming

Some confusion comes from the literature when the term "naphtha reforming" is used to designate processes to make synthesis gas—a mixture containing predominantly carbon monoxide and hydrogen. However, naphtha reforming has another meaning, which is the one intended here—production of an aromatic-rich liquid for use in gasoline blending.

A typical flow diagram is shown in Fig. 15.12. The feed is pumped to operating pressure and mixed with a hydrogen-rich gas before heating to reaction temperatures. Actually, hydrogen is a by-product of the dehydrogenation and cyclization reactions,

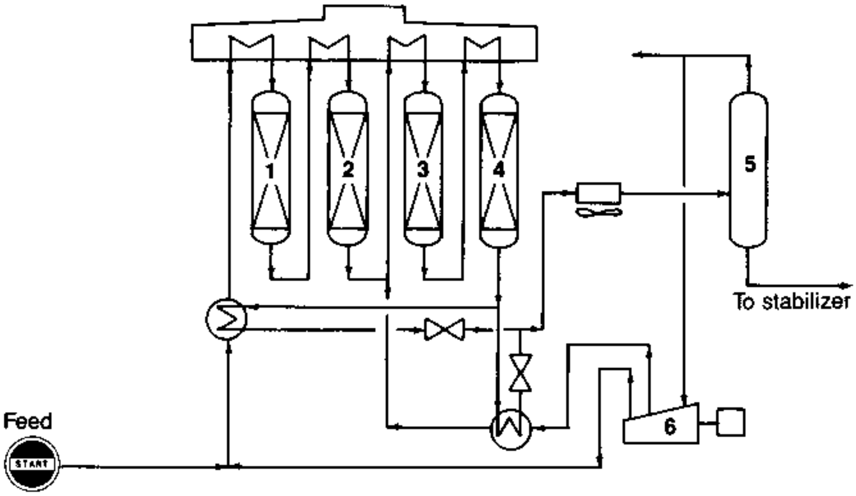


Fig. 15.12. Catalytic reforming—Engelhard Corp. Includes: multibed reactors (1, 2, 3, 4), common heater, hydrogen separator (5), and compressor (6). (*Hydrocarbon Processing, 69, no. 11, p. 120, Nov. 1990; copyright 1990 by Gulf Publishing Co. and used by permission of the copyright owner.*)

but by sustaining a hydrogen atmosphere, cracking and coke formation are minimized.

The feed for catalytic reforming is mostly in the boiling range of gasoline to start with. The intent is to convert the paraffin and naphthene portions to aromatics. As an example, a 180 to 310°F fraction of Light Arabian crude oil was reported to have 8 vol % aromatics before catalytic reforming, but was 68 vol % aromatics afterwards. The feed paraffin content (69 vol %) was reduced to less than half, and the feed naphthene content (23 vol %) was almost completely absent in the product.[13]

The extent of octane number change with changes in molecular configuration is shown in Table 15.8, where normal paraffins and naphthenes are compared with their aromatic homologs.

If the naphthenes are condensed (multi-rings or indanes) they tend to deactivate the reforming catalyst quickly. Control of the end point of the feed will exclude these deactivating compounds.

TABLE 15.8 Aromatics Have Higher Octane Numbers[6]

		Octane number, clear	
Hydrocarbon homologs		*Motor*	*Research*
C_7 hydrocarbons			
n-paraffin	C_7H_{16} (*n*-heptane)	0.0	0.0
naphthene	C_7H_{14} (cycloheptane)	40.2	38.8
	" (methylcyclohexane)	71.1	74.8
aromatic	C_7H_8 (toluene)	103.5	120.1
C_8 hydrocarbons			
n-paraffin	C_8H_{18} (*n*-octane)	−15[a]	−19[a]
naphthene	C_8H_{16} (cyclooctane)	58.2	71.0
	" (ethylcyclohexane)	40.8	45.6
aromatic	C_8H_{10} (ethylbenzene)	97.9	10.4
	" (*o*-xylene)	100.0	120[a]
	" (*m*-xylene)	115.0	117.5
	" (*p*-xylene)	109.6	116.4

[a] Blending value at 20 vol % in 60 octane number reference fuel.

TABLE 15.9 Favored Operating Conditions for Desired Reaction Rates[17]

Feed	*Reaction*	*Product*	*Desired rate*	*To get desired rate*	
				Press.	*Temp.*
Paraffins	Isomerization	Iso-paraffins	Inc.	Inc.	Inc.
	Dehydrocyclization	Naphthenes	Inc.	Dec.	Inc.
	Hydrocracking	Lower mol. wt.	Dec.	Dec.	Dec.
Naphthenes	Dehydrogenation	Aromatics	Inc.	Dec.	Inc.
	Isomerization	Iso-paraffins	Inc.	Inc.	Inc.
	Hydrocracking	Lower mol. wt.	Dec.	Dec.	Inc.
Aromatics	Hydrodealkylation	Lower mol. wt.	Dec.	Dec.	Dec.

Catalysts that promote reforming reactions can give side-reactions. Isomerization is acceptable, but hydrocracking gives unwanted saturates and gases. Therefore, higher operating pressures are used to suppress hydrocracking. This remedy has disadvantages. Higher pressures suppress reforming reactions too, although to a lesser extent. Generally, a compromise is made between desired reforming and undesired hydrocracking. The effects of operating conditions on competing reactions[17] are shown in Table 15.9.

In the late 1960s, it was discovered that the addition of certain promoters, such as rhenium, germanium, or tin, to the platinum-containing catalyst would reduce cracking and coke formation. The resulting catalysts, referred to as bimetallic catalysts, permit the process to enjoy the better reforming conditions of lower pressure without being unduly penalized by hydrocracking. Earlier pressures of 500 psig are now down to 150 psig.

Operating temperatures are important, too. The reactions are endothermic. Best yields would come from isothermal reaction zones, but they are difficult to achieve. Instead, the reaction beds are separated into a number of adiabatic zones operating at 500 to 1000°F with heaters between stages to supply the necessary heat of reaction and hold the overall train near a constant temperature. Three or four reactor zones are commonly used when it is desired to have a product with high octane numbers.

In making gasoline with high octane numbers but without the use of antiknock additives, high severity catalytic reforming is the prime route. The big disadvantage is a yield loss. Newer catalysts make the loss less dramatic, but the penalty remains,[18] as can be seen from Fig. 15.13.

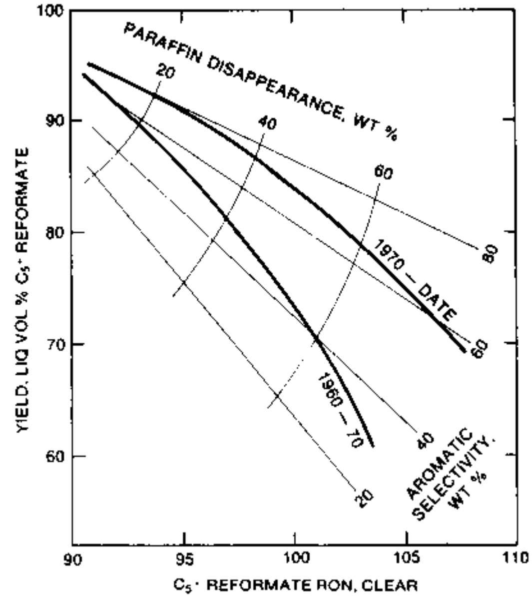


Fig. 15.13. Better octane numbers, less yield (Kuwait naphtha). (*McDonald, G. W. G.,* Hydrocarbon Processing, *56 (6), 147–150, June 1977; copyright 1977 by Gulf Publishing Co. and used by permission of the copyright owner.*)

Catalytic Cracking

A typical diagram of a fluid catalytic cracking is shown in Fig. 15.14. The unit is characterized by two huge vessels, one to react the feed with hot catalyst and the other to regenerate the

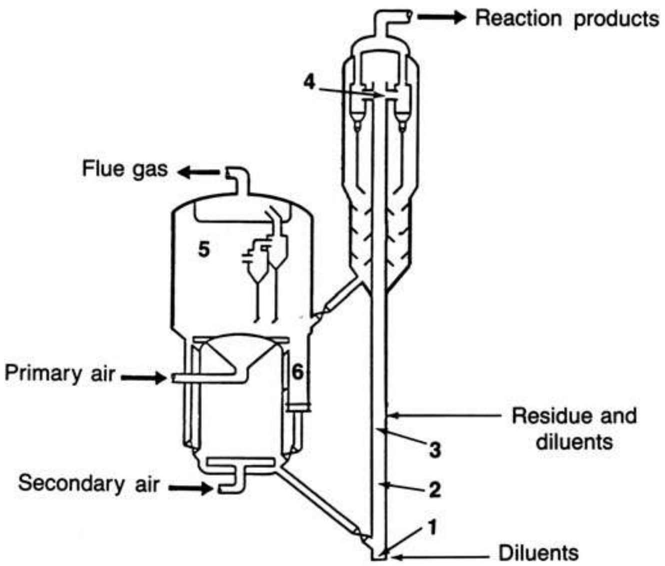


Fig. 15.14. Fluid catalytic cracking—UOP. Includes: light recycle gas diluent addition at base of reactor (1), preacceleration zone (2), feed addition distributor (3), catalyst separator (4), catalyst regenerator (5), and catalyst cooler (6). (Hydrocarbon Processing, *69, no. 11, p. 98, Nov. 1990; copyright 1990 by Gulf Publishing Co. and used by permission of the copyright owner.*)

spent catalyst by burning off carbon with air. The activity of molecular-sieve catalysts is so great that the contact time between feed and catalyst is reduced drastically. If not, the oil will overcrack to give unwanted gases and coke. The short contact time is accomplished by using a transfer line between the regenerator and reactor vessels. In fact, the major portion of the reaction occurs in this piece of pipe or riser, and the products are taken quickly overhead. The main reactor vessels then are used to hold cyclone separators to remove the catalyst from the vapor products and to give additional space for cracking the heavier portions of the feed.

There are several configurations of reactors and regenerators. In some designs, one vessel is stacked on top of the other. All are big structures (150–200 ft high).

Riser cracking, as the short-time contacting is called, has a number of advantages. It is easier to design and operate. It can be operated at higher temperatures to give more gasoline olefins. It minimizes the destruction of any aromatics formed during cracking. The net effect can be the production of gasoline having octane numbers two or three numbers higher than earlier designs would give.

Better regeneration of the spent catalyst is obtained by operating at higher temperatures (1300–1400°F).[19] The coke that is deposited on the catalyst is more completely burned away by higher-temperature air blowing. The newer catalysts are rugged enough to withstand the extra heat, and newer metallurgy gives the regenerator vessel the strength it needs at higher temperatures.

Heavier feedstocks can be put into catalytic crackers. The nickel, vanadium, and iron in these heavier fractions do not deactivate the catalysts as fast as they once did because passivators are available now to add to the catalysts.[20] The extra sulfur that comes with heavier feeds can be prevented from exhausting into the atmosphere during regeneration because of catalysts that hold onto the sulfur compounds until the catalysts get into the reactor.[21] Then the sulfur compounds are cracked to light gases and leave the unit with the cracked products. Ordinary gas treating methods are used to capture the hydrogen sulfide coming from the sulfur in the feedstock.

Coking

Coking is an extreme form of thermal cracking. The process converts residual materials that might not easily be converted by the more popular catalytic cracking process. Coking is also a less expensive process for getting more light stocks from residual fractions. In the coking process, the coke is considered a by-product that is tolerated in the interest of more complete conversion of residues to lighter liquids.

A typical flow diagram of a delayed coker is shown in Fig. 15.15. There are several possible configurations, but in this one the feed goes directly into the product fractionator to pick up heavier products to be recycled to the cracking operation. The term "delayed coker" signifies that the heat of cracking is added by the furnace, and the cracking occurs during the longer residence time in the following coke drums. Furnace outlet temperatures are in the range of 900 to 950°F while the coke drum pressures are in the range of 15 to 90 psig.

The coke accumulates in the coke drum, and the remaining products go overhead as vapors to be fractionated into various products. In this case, the products are gas, naphtha, light gas oil, heavy gas oil, and coke. When a coke drum is to be emptied, a large drilling structure mounted on top of the drum is used to make a center hole in the coke formation. The drill is equipped with high-pressure water jets (3000 psig or more) to cut the coke from the drum so that it can fall out a bottom hatch into a coke pit. From there, belt conveyors and bucket cranes move the coke to storage or to market.[22]

Fluid coking is a proprietary name given to a different type of coking process in which the coke is suspended as particles in fluids flowing from a reactor to a heater and back again. When part of the coke is gasified, the process is called *Flexicoking*. Both Fluid coking and Flexicoking are proprietary processes of Exxon Research and Engineering Co.

A flow diagram for Flexicoking is shown in Fig. 15.16. The first two vessels are typical of Fluid coking, in which part of the coke is burned in the heater in order to have hot coke nuclei to contact the feed in the reactor vessel. The cracked products are quenched in an overhead scrubber where entrained coke is

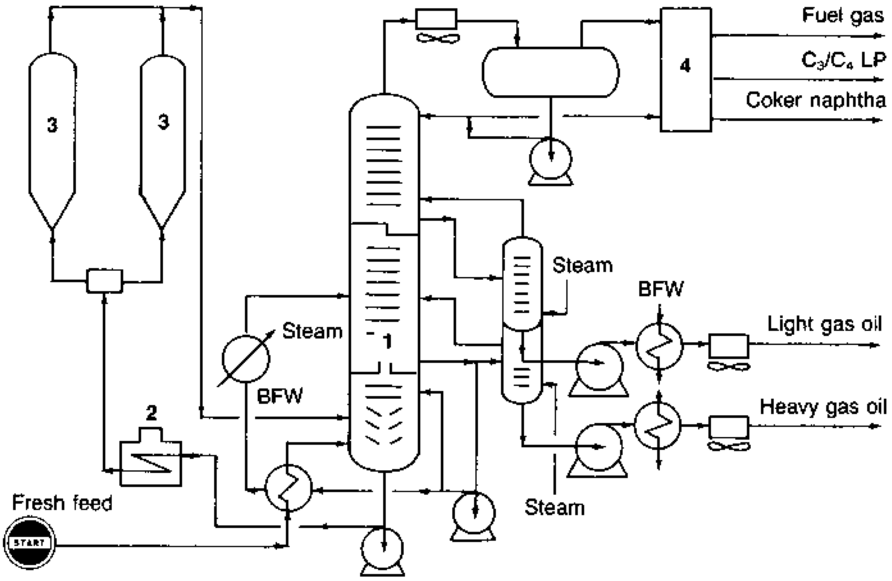


Fig. 15.15. Delayed coking—ABB Lummus Crest Inc. Includes: feed/product fractionator (1), heater (2), coke drums (3), and vapor recovery unit (4). (Hydrocarbon Processing, *69, no. 11, p. 106, Nov. 1990; copyright 1990 by Gulf Publishing Co. and used by permission of the copyright owner.*)

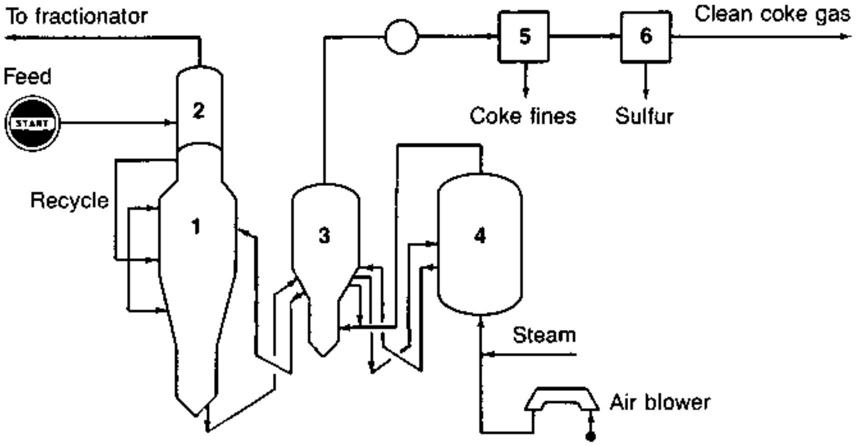


Fig. 15.16. Fluid coking (Flexicoking)—Exxon Research and Engineering Co. Includes: reactor (1), scrubber (2), heater (3), gasifier (4), coke fines removal (5), and hydrogen sulfide removal (6). (Hydrocarbon Processing, *69, no. 11, p. 106, Nov. 1990; copyright 1990 by Gulf Publishing Co. and used by permission of the copyright owner.*)

returned to the reactor. Coke from the reactor circulates to the heater where it is devolatilized to yield a light hydrocarbon gas and residual coke. A sidestream of coke is circulated to the gasifier, where, for most feedstocks, 95 percent or more of the gross coke product from the reactor is gasified at elevated temperature with steam and air. Sulfur that enters the unit with the feedstock eventually becomes hydrogen sulfide exiting the gasifier and is recovered by a sulfur removal step.

Hydrocracking

Before the late 1960s, most hydrogen used in processing crude oil was for pretreating catalytic reformer feed naphtha and for desulfurizing middle-distillate products. Soon thereafter, requirements to lower sulfur content in most fuels became an important consideration. The heavier fractions of crude oil were the hardest to treat. Moreover, these fractions were the ones offering additional sources of light products. This situation set the stage for the introduction of hydrocracking.

A typical flow diagram for hydrocracking is shown in Fig. 15.17. Process flow is similar to hydrotreating in that feed is pumped to operating pressure, mixed with a hydrogen-rich gas, heated, passed through a catalytic reactor, and distributed among various fractions. Yet the hydrocracking process is unlike hydrotreating in several important ways. Operating pressures are very high, 2000 to 3000 psia. Hydrogen consumption also is high, 1200 to 1600 scf of hydrogen per barrel of feed, depending on the extent of the cracking.[14] In fact, it is not uncommon to see hydrocrackers built with their own hydrogen manufacturing facilities nearby.

The catalysts for hydrocracking have a dual function. They give both hydrogenation and dehydrogenation reactions and have a highly acidic support to foster cracking. The hydrogenation–dehydrogenation components of the catalysts are metals such as cobalt, nickel, tungsten, vanadium, molybdenum, platinum, palladium, or a combination of these metals. The acidic support can be silica–alumina, silica–zirconia, silica–magnesia, alumina–boria, silica–titania, acid-treated clays, acidic-metal phosphates, or alumina, to name some given in the literature.[23]

Great flexibility is attributed to most hydrocracking processes. Under mild conditions, the process can function as a hydrotreater. Under more severe conditions of cracking, the process produces a varying ratio of motor fuels and middle distillates, depending

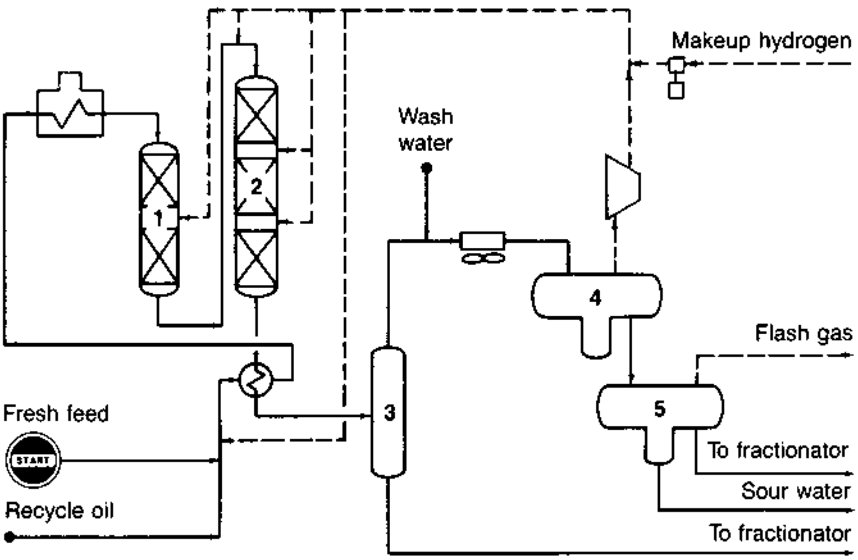


Fig. 15.17. Hydrocracking—UOP. Includes: staged reactors (1, 2), gas separator (3), hydrogen separator (4), and product washer (5). (Hydrocarbon Processing, *69, no. 11, p. 102, Nov. 1990; copyright 1990 by Gulf Publishing Co. and used by permission of the copyright owner.*)

on the feedstock and operating variables. Even greater flexibility is possible for the process during design stages when it can be tailored to change naphthas into liquefied petroleum gases or convert heavy residues into lighter products.

Because the hydrocracker is viewed as both a cracker and a treater, it can appear in refining process schemes in a number of different places. As a cracker, it is used to convert feeds that are too heavy or too contaminant-laden to go to catalytic cracking. As a treater, it is used to handle heating-oil fractions that need to be saturated to give good burning quality. But it is the trend to heavier feeds and lighter high-quality fuels that causes hydrocracking to offer advantages to future refining, even though the hydrocracking units are much more expensive to build and to operate.

The principle of an ebulliating catalyst bed is embodied in some proprietary designs, in contrast with the fixed-catalyst beds used in other versions of hydrocracking. The H-Oil process of Hydrocarbon Research, Inc. and the LC-Fining process jointly licensed by ABB Lummus Crest Inc., Oxy Research & Development Co., and Amoco Corp. are examples of hydrocracking processes that use an ebullient bed instead of a fixed bed of catalyst.

Polymerization

This process usually is associated with the manufacture of plastic films and fibers from light hydrocarbon olefins, with products such as polyethylene and polypropylene. As a gasoline manufacturing process, the polymerization of light olefins emphasizes a combination of only two or three molecules so that the resulting liquid will be in the gasoline boiling range.

For early polymerization units, the catalyst was phosphoric acid on a quartz or kieselguhr support. Many of these units were shut down when the demand for gasoline with increased octane numbers prompted the diversion of the olefin feeds to alkylation units that gave higher octane number products. Yet some refinery balances have more propylene than alkylation can handle, so a newer version of polymerization was introduced.[24] It is the Dimersol process of the Institut Français du Pétrole, for which the flow diagram is shown in Fig. 15.18.

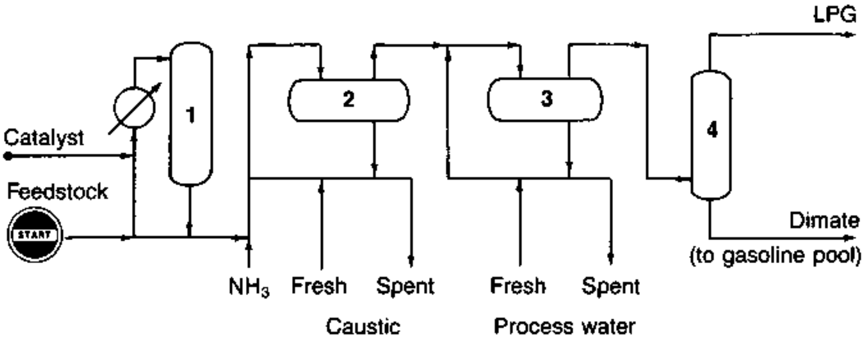


Fig. 15.18. Polymerization (Dimersol)—Institute Français du Pétrole. Includes: a reactor (1) of several in series, catalyst removal using a caustic wash (2), water wash (3), and distillation (4). (Hydrocarbon Processing, *69, no. 11, p. 134, Nov. 1990; copyright 1990 by Gulf Publishing Co. and used by permission of the copyright owner.)*

The Dimersol process uses a soluble catalytic complex injected into the feed before it enters the reactor. The heat of reaction is taken away by circulating a portion of the bottoms back to the reactor after passing it through a cooling water exchanger. The product goes through a neutralizing system that uses caustic to destroy the catalyst so that the resulting polymer is clean and stable. Typical octane number ratings for the product are 81 Motor and 96.5 Research, unleaded.

Alkylation

This is another process that increases the total yield of gasoline by combining some of the gaseous light hydrocarbons to form bigger molecules boiling in the gasoline range. Alkylation combines isobutane with a light olefin, typically propylene and butylene. A flow diagram for an alkylation unit using sulfuric acid as a catalyst is shown in Fig. 15.19.

Common catalysts for gasoline alkylation are hydrofluoric acid or sulfuric acid. The reaction is favored by higher temperatures, but competing reactions among the olefins to give polymers prevent high-quality yields. Thus, alkylation usually is carried out at low temperatures in order to make the alkylation reaction predominate over the polymerization reactions. Temperatures for hydrofluoric acid–catalyzed reactions are approximately 100°F, and for sulfuric acid they are approximately

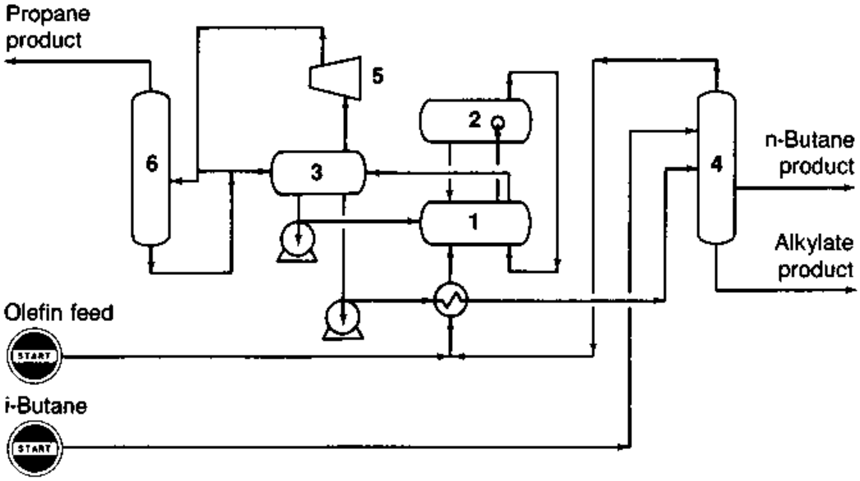


Fig. 15.19. Alkylation—Stratco, Inc. Includes: contactor (1), acid settler (2), flash drum (3), deisobutanizer (4), compressor (5), and depropanizer (6). (Hydrocarbon Processing, *69, no. 11, p. 132, Nov. 1990; copyright 1990 by Gulf Publishing Co. and used by permission of the copyright owner.)*

TABLE 15.10 Typical Alkylate Octane Numbers[25]

	Feed olefin			
	C_2	C_3	$C_3 + C_4$	C_4
Research octane number, clear	101.5	90.5	93	96.5
Motor octane number, clear	93	89	91	95.5

50°F. Since the sulfuric acid–catalyzed reactions are carried out below normal atmospheric temperatures, refrigeration facilities are included.

Alkylate product has a high concentration of 2,2,4-trimethyl pentane, the standard for the 100 rating of the octane number scale. Other compounds in the alkylate are higher or lower in octane number, but the lower octane number materials predominate so that alkylate has a Research octane number in the range of 92 to 99. Developments are under way to slant the reactions in favor of the higher-octane materials.[25] Random samples of alkylate quality reported in the literature[26] are summarized in Table 15.10.

Ether Processes

Cooperative studies between automobile manufacturers and gasoline producers established the relationship of some gasoline components to automobile engine emissions. It has been shown that the use of gasolines containing some oxygenated compounds, such as alcohols or ethers, will cause the gasoline-fueled engine to emit less carbon monoxide.[27]

The favored alcohols are low molecular weight ones, methanol and ethanol. Commercial technology exists for making either alcohol from a variety of raw materials; namely, natural gas, petroleum crude oil, coal, or agricultural grain. A higher molecular weight alcohol, tertiary butyl alcohol (TBA), is another suitable gasoline blending compound. The major drawback in using alcohols in gasolines is that it creates a new set of conditions for safe fuel handling and efficient engine design. On the other hand, the alcohols could be used to make ethers. These have been shown to have fewer blending problems than alcohols and were more compatible with existing gasoline blends.

Another environmentally imposed restriction on gasoline blends was to reduce vapor pressure. The restriction was imposed to control hydrocarbon evaporative losses during gasoline storage and automobile refueling. The consequence of this restriction was to reduce the amount of C_4 hydrocarbons included in the gasoline blends.

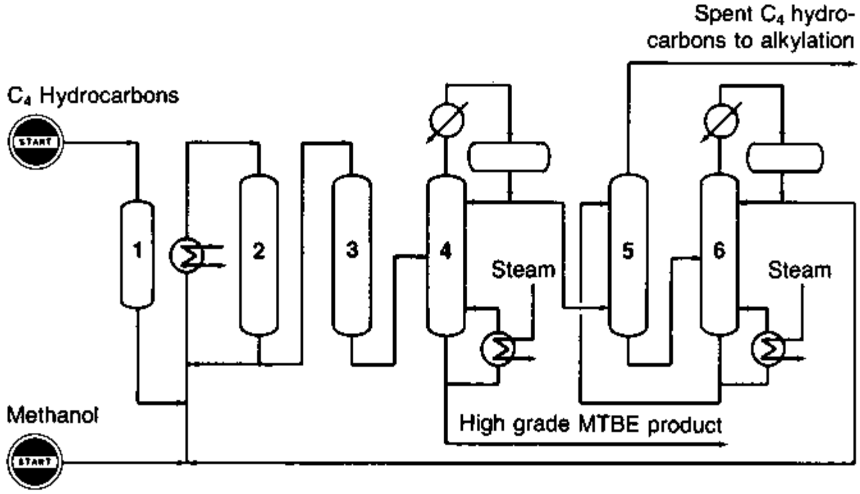


Fig. 15.20. Ethers—Huels AG and UOP. Includes: guard bed (1), reactors (2, 3), butene column (4), and water wash (5, 6). (*Hydrocarbon Processing, 69, no. 11, p. 128, Nov. 1990; copyright 1990 by Gulf Publishing Co. and used by permission of the copyright owner.*)

A common second feed to the ether manufacturing process, in addition to an alcohol, is isobutylene. Isobutylene is not only one form of the C_4 hydrocarbons, but it can be made from the other C_4 homologs. So not only is ether manufacture a way to make a desirable oxygenated compound for gasoline blending, but the ether process gives a way to use the C_4 hydrocarbons to enhance the antiknock quality of the gasoline without causing the blend to exceed the vapor pressure restriction.

Methyl tertiary butyl ether (MTBE) is the more popular ether blending compound. It is made by reacting methanol with isobutylene. A flow diagram of a typical process is shown in Fig. 15.20.

Other desirable ether compounds for gasoline blending can be made in a similar process. For example, ethyl tertiary butyl ether (ETBE) is made from ethanol and isobutylene. Tertiary amyl methyl ether (TAME) is made from methanol and isoamylene.

FUTURE PROCESSING

The manufacture of fibers, films, construction materials, and many synthetic organic chemicals made from petroleum is evolving at such a rapid rate that these subjects are covered in other, separate chapters of this book. Yet the greatest use for petroleum and its products now is to furnish fuels for heat and mobility.

There is an ever-changing economic balance between the need for energy fuels and that for other petroleum-derived products. Many decades have been spent in perfecting technology to give the least expensive fuels for the most efficient energy consumption. Future processing technology will add another dimension: increased concern about the relation of increased energy use to environmental changes. We are only beginning to identify and to quantify how future energy needs might be satisfied in environmentally compatible ways.

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16

Natural Gas

R. N. Maddox* and R. E. Cannon**

CHARACTERISTICS

Natural gas is a naturally occurring mixture of simple hydrocarbons and nonhydrocarbons that exists as a gas at ordinary pressures and temperatures. In the raw state, as produced from the earth, natural gas consists principally of methane (CH_4) and ethane (C_2H_6), with fractional amounts of propane (C_3H_8), butane (C_4H_{10}), and other hydrocarbons, pentane (C_5H_{12}) and heavier.

All of the ethane and heavier components of natural gas are easily separated from the gas stream and liquefied under moderate pressure, and most of these components are recovered for their added value as separate products. Raw natural gas may be described as "rich" ("wet") or "lean" ("dry"), depending on the amounts of liquefiable heavier components contained.

In addition to hydrocarbon components, raw natural gas from some reservoirs may contain varying amounts of nonhydrocarbon contaminants or diluents, such as hydrogen sulfide (H_2S), carbon dioxide (CO_2), water (H_2O), nitrogen (N_2), and helium (He). The first two of these compounds, hydrogen sulfide and carbon dioxide, are termed "sour" or "acid" gases; acid-free natural gas is described as "sweet."

Although some natural gas is suitable for use as a fuel as produced, virtually all undergoes some processing to produce a merchantable gas whose composition is principally methane and ethane. Water and acid gas components are removed to prevent freezing, corrosion, or other operating problems in transmission or utilization. Diluents that exist in significant quantities usually are removed to improve the heating properties of the gas. Much of the ethane and propane and all of the butanes and heavier hydrocarbons are removed for their greater value as separate liquid products.

Table 16.1 is a tabulation of typical raw gas compositions; Table 16.2 shows the physical properties of the principal constituents of natural gas; and Table 16.3 depicts typical specifications for pipeline quality, or "merchantable," natural gas.

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TABLE 16.1 Typical Raw Gas Compositions (Water-Free Basis)

	Casinghead (Wet) Gas		*Gas Well (Dry) Gas*		*Condensate Well Gas*	
	Mol %	*Gal/mcf*	*Mol %*	*Gal/mcf*	*Mol %*	*Gal/mcf*
Carbon dioxide	0.63					
Nitrogen	3.73		1.25		0.53	
Hydrogen sulfide	0.57					
Methane	64.48		91.01		94.87	
Ethane	11.98		4.88		2.89	
Propane	8.75	2.399	1.69	0.463	0.92	0.252
iso-Butane	0.93	0.303	0.14	0.046	0.31	0.101
n-Butane	2.91	0.914	0.52	0.163	0.22	0.069
iso-Pentane	0.54		0.09		0.09	
n-Pentane	0.80		0.18		0.06	
		0.777		0.203		0.103
Hexanes	0.37		0.13		0.05	
Heptanes plus	0.31		0.11		0.06	
	100.00	4.393	100.00	0.875	100.00	0.525

Source: Gas Processors Association.

The common unit of measurement for natural gas is the cubic foot in the English system and the cubic meter in the metric system, each expressed at pressures and temperatures standard to the system. In the United States, the cubic foot is expressed in the English system at standard conditions of 14.73 pounds per square inch (psi) and 60 degrees Fahrenheit (°F), although a number of other standard conditions are specified by various regulatory and state agencies. In metric units, the cubic meter is commonly defined at one atmosphere (101.325 kPa) and 15 degrees Celsius (°C).

Another common unit of measurement for natural gas is its heating value, expressed in British thermal units (Btu) per cubic foot in the English system, and in Joules or calories in the metric system. Commercially used natural

TABLE 16.2 Properties of Natural Gas and Natural Gas Liquids

	Chemical Formula	*Molecular Mass*	*Boiling Point @14.496 psi, °F*	*Vapor Press. @100°F, psia*	*Gas Density Air = 1*	*Heating Value Btu/cf Gas*
Methane	CH_4	16.043	−258.73	(5000)*	0.554	1010.0
Ethane	C_2H_6	30.070	−127.49	(800)*	1.038	1769.6
Propane	C_3H_8	44.097	−43.75	188.64	1.523	2516.1
i-Butane	C_4H_{10}	58.123	10.78	72.58	2.007	3251.9
n-Butane	C_4H_{10}	58.123	31.08	51.71	2.007	3262.3
i-Pentane	C_5H_{12}	72.150	82.12	20.45	2.491	4000.9
n-Pentane	C_5H_{12}	72.150	96.92	15.57	2.491	4008.9
Hexane	C_6H_{14}	86.177	155.72	4.96	2.976	4755.9
Heptane	C_7H_{16}	100.204	209.16	1.62	3.460	5502.5
Octane	C_8H_{18}	114.231	258.21	0.54	3.944	6248.9
Carbon dioxide	CO_2	44.01	−109.26		1.520	0
Hydrogen sulfide	H_2S	34.08	−76.50	394.59	1.177	637.1

Source: Gas Processors Association Standard 2145.

TABLE 16.3 Typical Pipeline Quality Natural Gas

	Minimum	*Maximum*
Major and Minor Components, Mol %		
Methane	75	—
Ethane	—	10
Propane	—	5
Butanes	—	2
Pentanes and heavier	—	0.5
Nitrogen and other inerts	—	18
Carbon dioxide	—	3
Hydrogen	—	5
Total unsaturated hydrocarbons	—	0.5
Carbon monoxide	—	0.1
Trace Components		
Hydrogen sulfide	—	0.25 gr/100 scf
Mercaptan sulfur	—	0.50 gr/100 scf
Total sulfur	—	1.0 gr/100 scf
Water vapor	—	7.0 lb/mmcf
Oxygen	—	10 ppmv
Other Characteristics		
Heating value, Btu/scf—gross saturated	950	1150
—gross dry	967	1170
Relative density	0.530	0.740

Liquids: Free of liquid water and hydrocarbons at delivery temperature and pressure.

Solids: Free of particulates in amounts deleterious to transmission and utilization equipment.

gas, after processing, yields about 950 to 1050 Btu/cubic foot. Also used as a unit of measurement is the therm, equivalent to 100,000 Btu, or the nominal heat content of 100 standard cubic feet of natural gas.

The most common unit of measurement in the English system is the MCF, or thousand cubic feet. Larger volumes, used to express production or pipeline volumes, are noted as BCF, or billion (10^9) cubic feet; even larger volumes, such as reserve figures, usually are expressed as TCF, or trillion (10^{12}) cubic feet.

OCCURRENCE OF NATURAL GAS

Natural gas occurs in three principal forms: associated gas, nonassociated gas, and gas condensate. The first two of these are depicted in Fig. 16.1, which includes a simplified schematic of the flow of natural gas from the well through various stages of processing.

Associated gas is found in crude oil reservoirs, either dissolved in the crude oil or in conjunction with crude oil deposits. Dissolved or associated gas provides the driving force or reservoir pressure necessary to produce oil from a reservoir. Dissolved gases are produced from oil wells along with the oil and separates, or is separated, from the crude oil at the well head. Such gas also may be called "casinghead gas" or "oil well gas." In the beginning of the industry, virtually all utilized natural gas was associated gas from oil wells. Much of the very large gas reserves of some Persian Gulf countries and the Prudhoe Bay reserves of Alaska is associated gas.

Nonassociated gas occurs in reservoirs separate from those of crude oil. It is commonly called "gas well gas," and contains much less of the heavier, or condensable, hydrocarbons found in associated gas. Today, because of the wide demand for natural gas, most utilized gas is nonassociated gas.

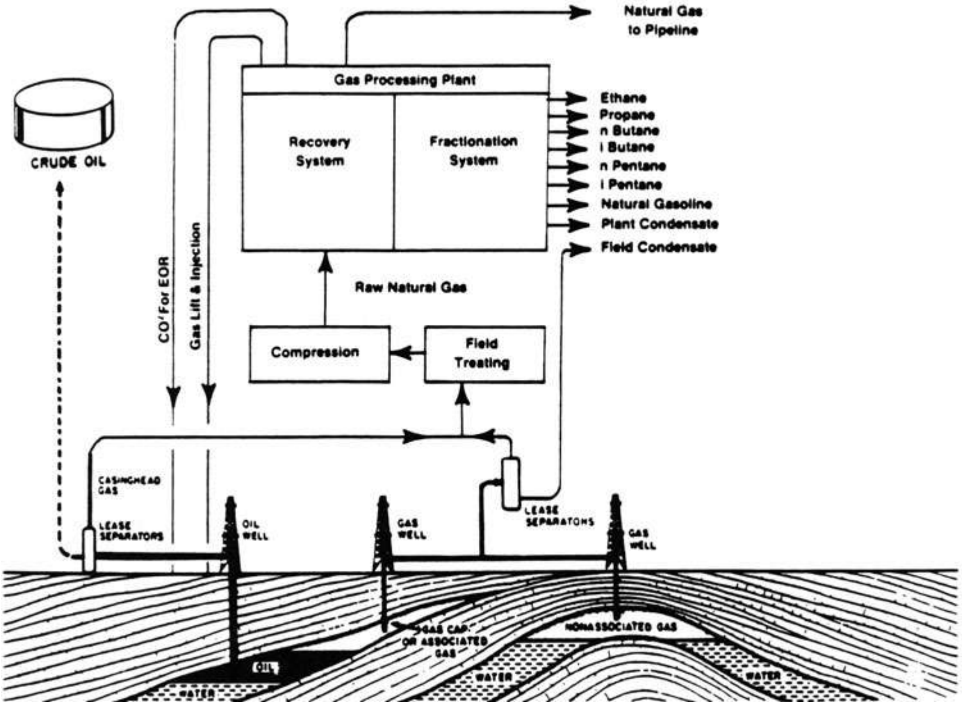

Fig. 16.1. Schematic flow of natural gas from well through processing.

The third form in which natural gas reserves occur might be called a two-phase fluid, as it is neither a true gas nor a true liquid. It is not a gas because no surface boundary exists between gas and liquid. These reservoirs, called "gas condensate" reservoirs, usually are found in moderately deep formations, have very high pressures, and pose special problems in production and processing.

EVOLUTION OF THE U.S. NATURAL GAS INDUSTRY

Although natural gas is the predominant product (98%) of the gas industry today, its utilization evolved out of the production and use of manufactured gas, and its major expansion came about through utilization of early "town gas" systems originally installed to distribute manufactured gas.

Manufactured gases are those obtained by destructive distillation of coal, by the thermal decomposition of oil, or by the reaction of steam passing through a bed of heated coal or coke. Prior to the development of large natural gas reserves, manufactured gas was used widely for illumination in the "gaslight" era of the United States.

Following the discovery of major oil and gas reserves in the early twentieth century, associated gas became plentiful in oil-producing areas, and natural gas began to displace manufactured gas in town systems. However, early natural gas utilization was confined largely to areas at or very near the source of supply because methods and materials for transporting the gas had not yet been developed.

Natural gas is relatively difficult to transport and store and is extremely bulky compared to other forms of energy. At atmospheric pressure, one cubic foot of natural gas contains about two-tenths the energy content of a cubic foot of solid or liquid fuel. Thus, it is necessary to transport natural gas through pipelines at very high pressures, typically 900 to 1000 psi. The development of high-strength, thin wall pipe and modern welding techniques in the mid-1930s permitted the construction of numerous long-distance, high-pressure gas transmission lines from the large and growing reserves of the southwestern United States to the major industrial and population centers of the country.

In rapid succession, a number of long-distance pipelines were laid during the period from 1930 to 1940, including three pioneer 1000-mile lines from large reserves in the Southwest to major markets in the North and the Northeast. Spurred by abundant and inexpensive gas reserves, the U.S. natural gas industry expanded rapidly following 1945, and natural gas virtually replaced the more expensive manufactured gas in city distribution systems.

In 1930, marketed production of natural gas totaled 1.9 trillion cubic feet; following early pipeline expansion, total consumption by 1940 had risen to 2.7 trillion cubic feet. Then, in the decade between 1940 and 1950, gas consumption more than doubled to 6.3 trillion cubic feet, and it doubled again to 12.8 trillion cubic feet by 1960. Marketed production in the United States peaked at 22.7 trillion cubic feet in 1973, followed by significant declines resulting from conservation efforts. The current marketed production of natural gas is about 18 trillion cubic feet per year, and is increasing steadily because of its convenience and qualities as an environmentally desirable fuel.

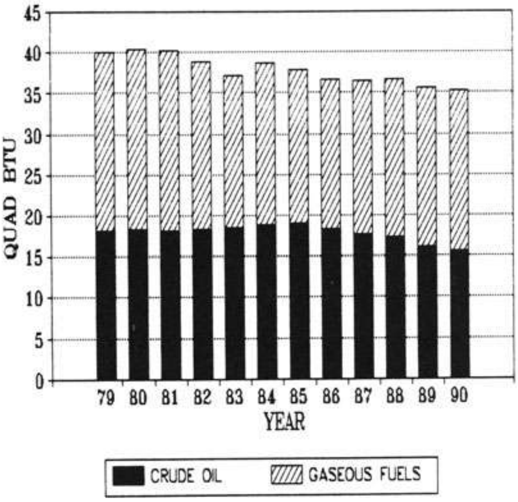

Fig. 16.2. U.S. petroleum energy production by year. (*Data from U.S. Department of Energy.*)[1,2]

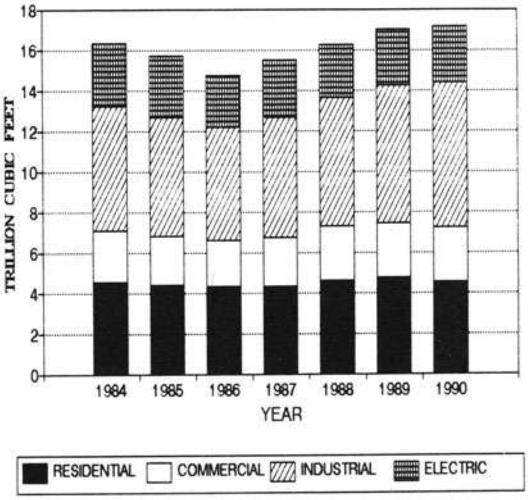

Fig. 16.3. U.S. marketed natural gas production by year. (*Data from U.S. Department of Energy.*)[1]

U.S. MARKETED PRODUCTION

Natural gas accounts for well over one-half of total U.S. petroleum energy production, as illustrated in Fig. 16.2. Its major market segments, shown in Fig. 16.3, are residential and commercial fuels, industrial fuel and feedstock, and electric power generation.

Residential consumption is predominantly for space heating, cooking, and water heating. Commercial use includes space heating and other fuel needs for commercial establishments such as stores, hotels, and restaurants.

Industrial use, accounting for about 36 percent of total gas consumption, includes fuels for manufacturing operations, industrial boiler fuel, and process heat. Oil refineries are major consumers of natural gas for refining operations. In addition, natural gas is the prime feedstock for the manufacture of ammonia fertilizers, methanol, and other basic chemical derivatives. Figure 16.4 is a simplified schematic of some of the principal chemical and products derived from natural gas.

Fuel for electric power generation accounts for about 15 percent of marketed natural gas production. This market segment is extremely

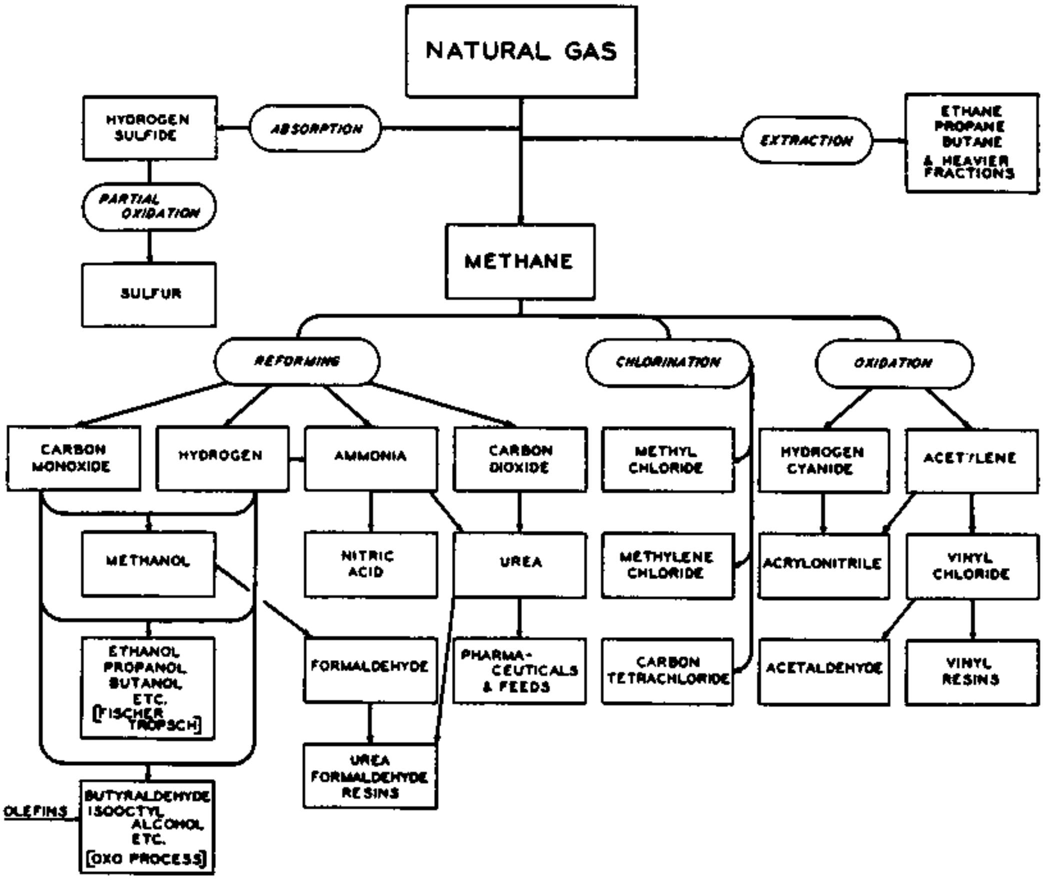

Fig. 16.4. Some petrochemical products derived from natural gas. (*From Crockett, L. O., and Widgery, R., "Natural Gasoline Producers' Stake in Chemical Manufacturing," 34th Annual Convention, Gas Processors Assoc., 1955.*)[7]

price-sensitive and competes directly with fuel oil and coal. Given the current environmental emphasis on reduction of air pollutants, the use of cleaner-burning natural gas is expected to increase significantly in the foreseeable future.

In addition to what is termed "marketed production" for these uses, approximately 1.6 trillion cubic feet of natural gas is consumed annually in lease, processing plant, and pipeline fuels.

At current production levels, about 56 percent of U.S. petroleum energy production consists of the gaseous fuels natural gas and natural gas liquids. Moreover, since peak production in 1985, U.S. crude oil has declined by about 18 percent, while gaseous fuel production has increased about 6 percent. These trends suggest that the U.S. petroleum economy will become even more dependent on the gaseous fuels in the future.

NATURAL GAS LIQUIDS

Included in the gaseous fuels segment of U.S. petroleum energy production depicted in Fig. 16.2 are the natural gas liquids extracted from natural gas as produced. These natural gas liquids, commonly terms "NGLs" are ethane, propane, butanes and pentanes, and higher hydrocarbons.

The recovery and separation of natural gas liquids from raw natural gas is a relatively simple operation, which relies principally on the differences in boiling points and vapor pressures of the various components. (These differences are shown in Table 16.2.) The two most prevalent recovery processes are the absorption and cryogenic turboexpander processes. Together, they account for approximately 90 percent of total U.S. natural gas liquids production. The bulk of U.S. gas liquids is produced as a raw mix stream in some 700 gas processing plants located in or near major gas-producing provinces. The raw mix streams are transported by an extensive pipeline network to large central fractionator complexes where the mixed stream is fractionated into its components ethane, propane, butanes, and pentanes.

The total U.S. recovery of natural gas liquids in 1990 was approximately 566 million barrels, or about 31 barrels per million cubic feet of marketed natural gas. The total NGL supply is supplemented by about 200 million barrels per year of refinery production, which equates to about 4 percent of the total crude oil charge to refineries. Thus, the total U.S. production of NGLs in 1990 was about 766 million barrels, or some 2 million barrels per day. As a point of reference, this was about 20 percent of total U.S. liquid petroleum production in 1990. The total NGL supply in 1990, including some 70 million barrels of imports, mostly from Canada, was about 836 million barrels, or 2.30 million barrels per day.

The trend of total U.S. NGL supply is depicted in Fig. 16.5. Major demand segments are shown in Fig. 16.6, which indicates that around to 35 to 40 percent of gas liquids, principally ethane and propane, are consumed as cracking feedstocks for ethylene manufacture. Some of the chemical derivatives obtained from ethane and propane are shown in Fig. 16.7.

Traditionally, a major demand for natural gas liquids, mainly butanes and pentanes, has been in the manufacture of motor gasolines. However, the recent phaseout of leaded gasoline and the current, ongoing reduction in motor gasoline volatility have drastically reduced demand for pentane and butanes as gasoline blending stocks. On the other hand, these same measures, enacted to reduce air pollutants from the automobile, have resulted in an increased demand for these products as prime feedstocks for the formulation of clean-burning reformulated gasolines.

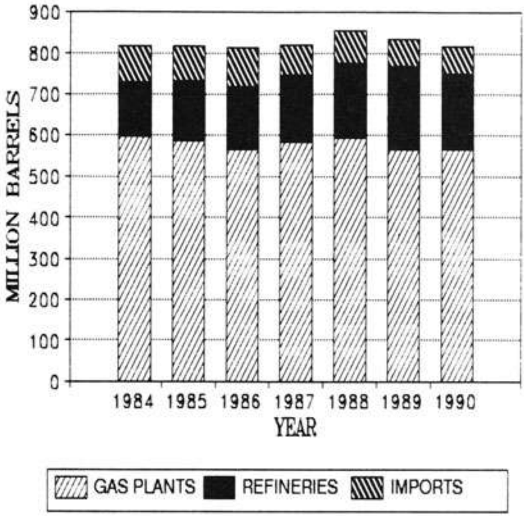

Fig. 16.5. U.S. NGL supply by year. (*U.S. Department of Energy.*)[2]

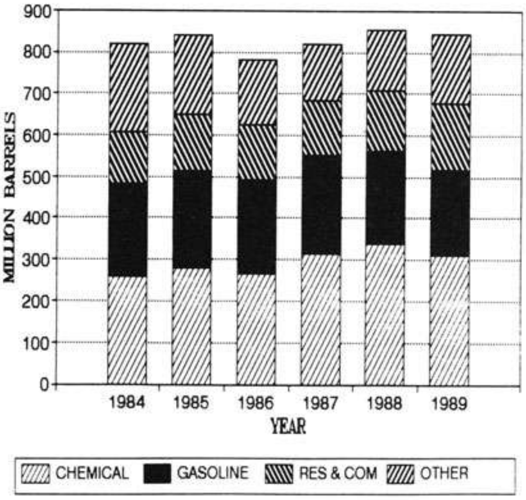

Fig. 16.6. U.S. NGL demand by year. (*"Sales of Natural Gas Liquids and Liquefied Refinery Gases," American Petroleum Institute, Gas Processors Association, and National Propane Gas Association.*)[6]

A third major market is consumption of propane as residential and commercial fuels, principally in rural areas beyond the reach of natural gas distribution systems.

Additional major uses indicated in the "other" category of Fig. 16.6 include consumption as internal combustion engine fuels and numerous agricultural uses such as crop drying.

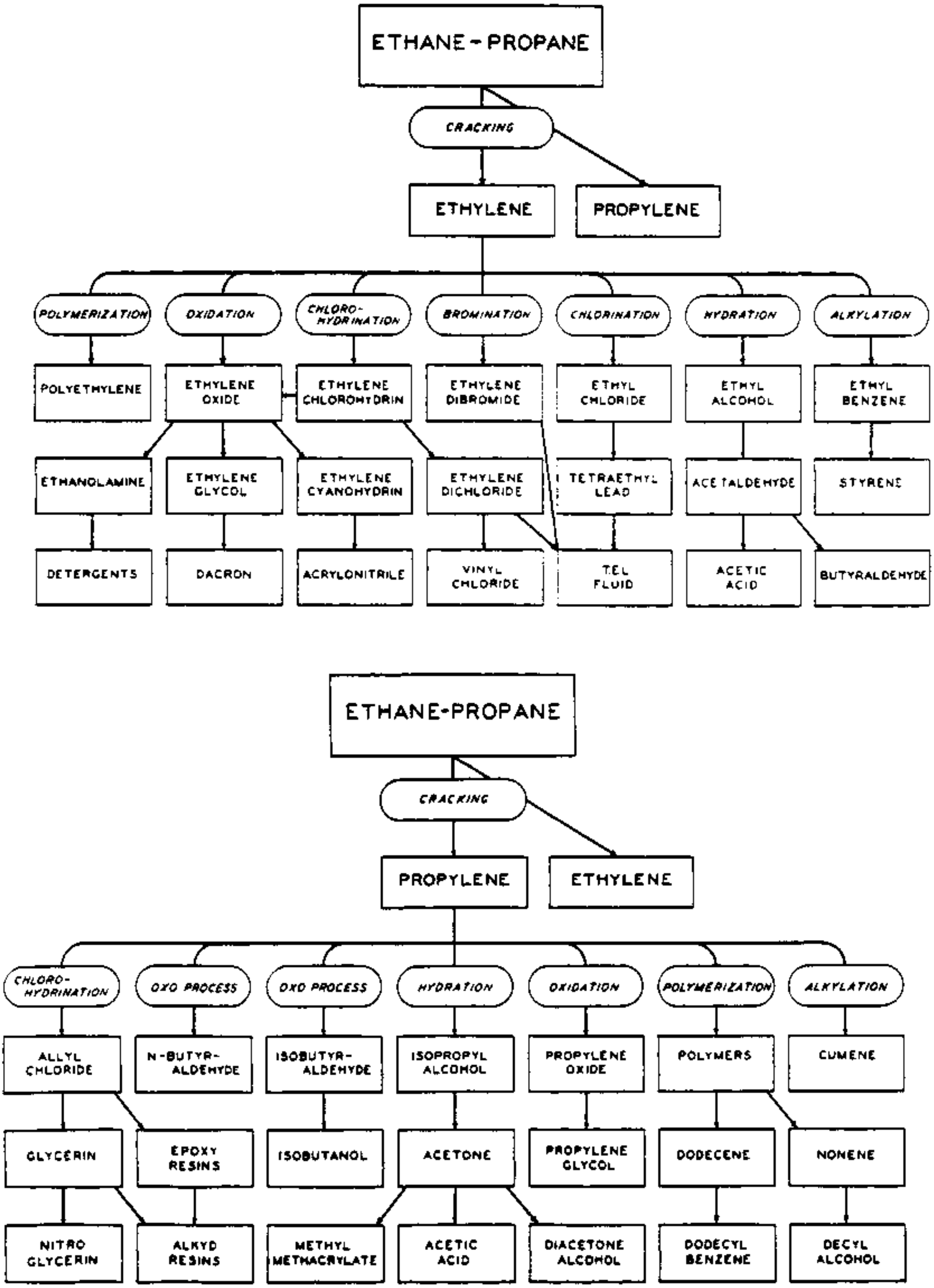

Fig. 16.7. Some products derived from ethane and propane. (*Crockett, L. O., and Widgery, R., Natural Gas Producers' Stake in Chemical Manufacturing," 34th Annual Convention, Gas Processors Association, 1955.*)[7]

U.S. NATURAL GAS RESERVES

Figure 16.8 is a graphical representation of proven U.S. natural gas reserves over time, which indicates approximately 10 years of indigenous supply at current consumption rates. Proven reserves estimates are subject to constant change, either up or down, depending on reservoir operating experience, field extensions resulting from additional drilling, and revised estimates. For example, an unusually large reduction in proven reserves is shown for 1988; this resulted from downward revisions in estimated gas reserves on the north slope of Alaska.

Not included in reserves data are undiscovered but probably recoverable reserves in unexplored or unproven provinces. Currently, these probable reserves are estimated by the U.S. Department of Energy at 307 to 500 trillion cubic feet, much of which almost certainly will become proven reserves when they become economically feasible.

Whatever the ultimate recoverable reserves may be, current estimates of proven reserves of natural gas comprise about 52 percent of U.S. proven reserves of total petroleum energy.

STRUCTURE OF THE U.S. NATURAL GAS INDUSTRY

The natural gas industry in the United States is made up of four major segments: production, processing, transmission, and distribution. The industry is physically interconnected by a pipeline network that extends through the lower 48 states and across international borders into Mexico and Canada.

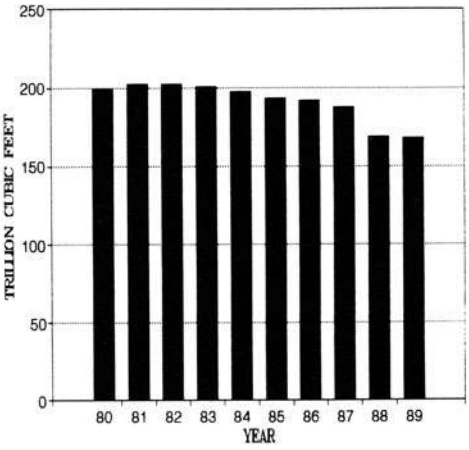

Fig. 16.8. Proven U.S. natural gas reserves.[5]

The production function is a large part of the oil-producing industry, and most of the same firms are dominant in both oil and gas. Exploration and drilling technologies for both oil and gas are identical. Production from both oil well gas and gas well gas is introduced into large field gathering systems for delivery to the processing function. A typical gathering system may include 2000 miles of gathering lines connected to a thousand producing wells.

The gas processing function includes the gathering and delivery of gas streams from a field or fields into a central processing facility. Approximately 750 gas processing plants are in operation in the United States. In these plants the raw natural gas is dehydrated to remove moisture, treated for removal of contaminants, and compressed to pipeline pressure. During treating, most raw gas also is processed for recovery of liquid products, including ethane, propane, butanes, and natural gasoline, which are sold for petrochemical and gasoline feedstocks and other fuel uses.

The transmission function transports the processed pipeline quality gas from the gas plant to major markets. About two-thirds of U.S. marketed gas production reaches the ultimate consumer through a network of some 250,000 miles of pipelines. Other deliveries may be made directly to industrial consumers or to city distribution systems.

The distribution function receives natural gas from the transmission pipeline at the city gate of the local distribution system and delivers it to the ultimate consumer through a network totaling some 600,000 miles of distribution pipelines.

WORLD NATURAL GAS

Natural gas, in recent years, has become an international commodity fuel. Current world reserves of natural gas, depicted in Fig. 16.9,

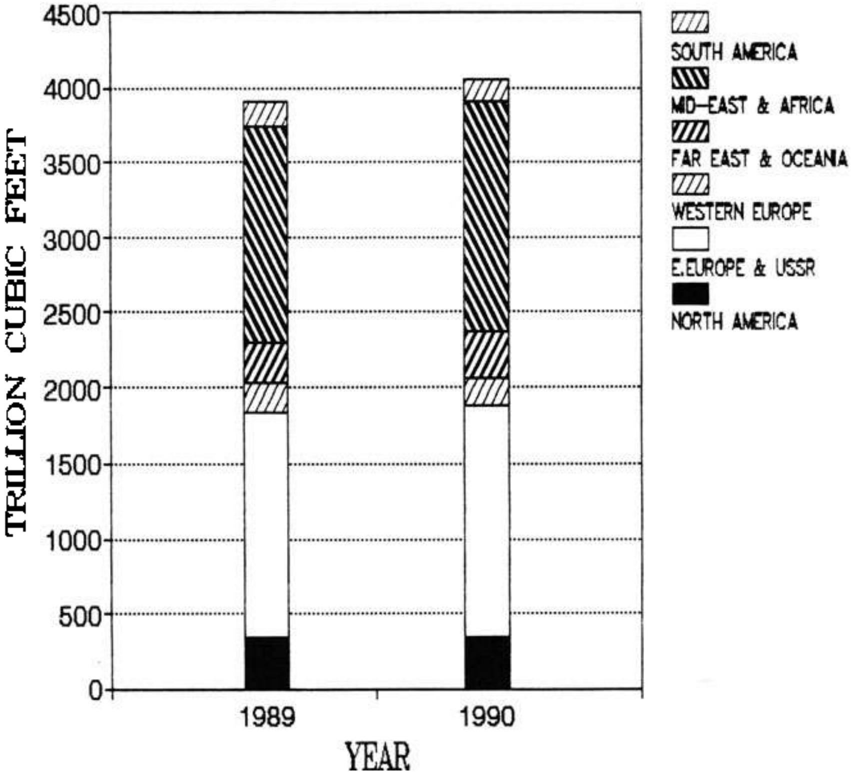

Fig. 16.9. Estimated world natural gas reserves. (*U.S. Department of Energy.*)[4]

are estimated at about 4000 trillion cubic feet, the equivalent of about 42 percent of world petroleum energy reserves. About 38 percent of these reserves are in remote regions of the Former Soviet Union and about 31 percent are located in the Persian Gulf countries of the Middle East.

The location of these reserves, far from the major populations of consuming countries, suggests that the world natural gas industry is in a development stage very similar to that of the U.S. industry in the mid-1930s. Approximately 1.5 trillion cubic feet per year of gas from the Gröeningen field of the Netherlands, together with about 1 trillion cubic feet per year from Norway and the North Sea, is flowing by pipeline into industrialized western Europe. In addition, nearly 2 trillion cubic feet per year of natural gas is piped from the Former Soviet Union into western Europe, along with another 1.5 trillion cubic feet into eastern Europe.

Additional international movements of natural gas are in the form of liquefied natural gas (LNG), principally from Algeria into Europe (about 1 trillion cubic feet per year) and from Oceania into Japan (about 1.6 trillion cubic feet per year).

It is a certainty that world use of natural gas will increase dramatically in the immediate future as industrialized countries replace coal-fired facilities with cleaner-burning natural gas. In addition, a number of countries remote from major markets are in the process of installing world-scale plants for utilization of natural gas and gas liquids for production of fertilizers, methanol, premium gasoline blending stocks, and other basic petrochemical derivatives that will result in higher-value products from natural gas and gas liquids for which these are no local markets.

Already, the gaseous fuels account for approximately 40 percent of world petroleum energy production (Fig. 16.10) and nearly

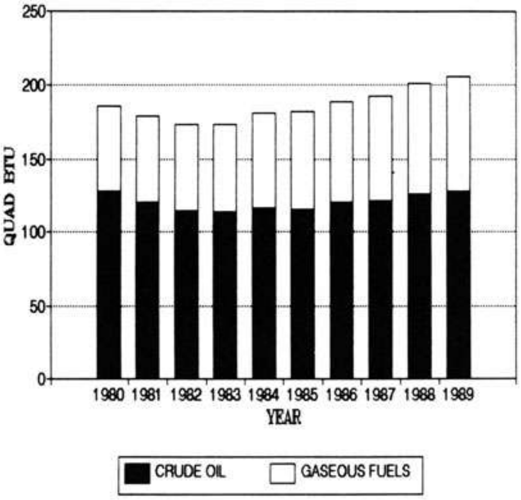

Fig. 16.10. World petroleum energy production. (*U.S. Department of Energy.*)[4]

one-half of world petroleum energy reserves. And, as illustrated in Fig. 16.11, the growth of world natural gas consumption is already increasing rapidly.

Despite a world surplus of crude oil capacity for the foreseeable future, it seems certain that the world has entered the "Age of Gaseous Energy," and that natural gas and gas liquids will continue to move into a position of petroleum energy dominance in the next decade.

PREPARING NATURAL GAS FOR TRANSMISSION AND SALE

To make a product suitable for sale, the various contaminants and undesirable constituents contained in the raw gas must be removed. The first step is to separate the gas from any liquids and/or solids. This initial separation is usually carried out in near proximity to the producing well. The separators used depend primarily upon the difference in density between the gas and the liquid for separating the two phases. These separators may be classified as vertical, horizontal, or spherical, depending on their geometry and physical orientation.[8]

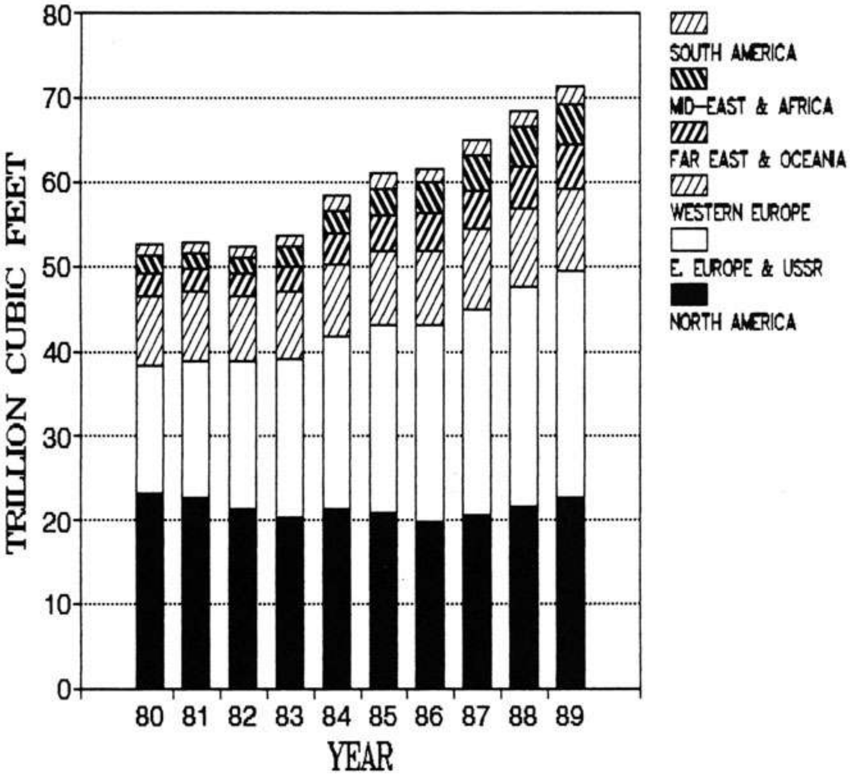

Fig. 16.11. World gas consumption. (*U.S. Department of Energy.*)[4]

The liquids produced are sold as oil or condensate, depending upon the type of reservoir from which the production is obtained. The natural gas stream after this first stage of separation contains only gaseous components, though some of these may be liquefied by later processing.

Typical compositions for gas streams at this point are shown in Table 16.1. (The compositions in Table 16.1 are on a water-free basis.) As typically produced, each of the gas streams would be saturated with water vapor. Developing the technology for handling gas streams that contain significant quantities of water vapour was one of the keys necessary to development of the natural gas industry as it exists today.

In the presence of water, natural gas can—under the proper conditions of temperature and pressure—form hydrates. To the naked eye the hydrates are similar in appearance to snow; and they can result in plugging of pipelines and flow systems. Hydrates can form at temperatures well above the freezing point of water. In the early days of pipelining natural gas under pressure, shutdowns of the lines during the winter months frequently were caused by plugging with hydrates.

A hydrate is a type of chemical compound called a clathrate, defined as a type of solid molecular compound in which one component is trapped in cavities of cagelike crystals of another component. In the natural gas hydrate, water forms the "cage," and hydrocarbon molecules are the trapped component.

Hydrate formation can be prevented or avoided in two ways: (1) by dehydration, in which water is removed from the gas stream so that under conditions of processing or transmitting, no liquid water will condense; and (2) by inhibition, which involves injecting into the gas stream a component that will interfere with the ability of the water to form hydrates with the gas. Both procedures are widely used in the gas industry.

Of the wide variety of materials that can effectively depress the hydrate-forming tendency of a natural gas, two—methyl alcohol and ethylene or diethylene glycol—are used almost exclusively. Ethylene glycol (a polyhydroxy alcohol) is a high-boiling point material that mixes in all proportions with water and remains predominantly in the liquid phase. At temperatures approaching the freezing point of water, solutions containing more than 50 percent by weight ethylene glycol have viscosities approaching 10 cp. This limits their utilization in some low-temperature applications.

Methyl alcohol has a much lower boiling point and consequently a much higher vapor pressure than ethylene glycol. Hence procedures used for estimating the amount of methyl alcohol required must take into account the amount of methyl alcohol that vaporizes into the gas phase.[9,13,14] Although the vaporization requires the injection of greater quantities of methanol, it does have potential advantages. If the gas phase were cooled in further processing or transmission, one would expect methanol to condense along with additional water and/or hydrocarbons. This would provide a safety factor for hydrate prevention that does not exist with the glycols.

Dehydration of the gas can be accomplished through the use of either a liquid or a solid desiccant. The solid desiccants most often employed include alumina, silica gel, and molecular sieves. The liquid desiccant most frequently used is triethylene glycol.

Any of the solid materials used as desiccants must be regenerated periodically; so there must be at least two adsorption towers if dehydration of the gas is to be continuous. A schematic of a typical two-tower adsorption plant is shown in Fig. 16.12.[9] The adsorbent must be heated to high temperature (ca. 400°F, 200°C) to remove the water and regenerate the solid desiccant. This usually is accomplished by heating a slip stream of the gas and circulating the heated gas through the adsorbent bed.

Figure 16.13 shows a schematic flow sheet for a typical triethylene glycol dehydration system. The lean glycol is pumped to the top of an absorber column and flows downward in countercurrent contact with the water-wet gas entering the bottom of the tower. The absorber may contain either plates or packing. Dehydrated gas leaves the top of the absorber,

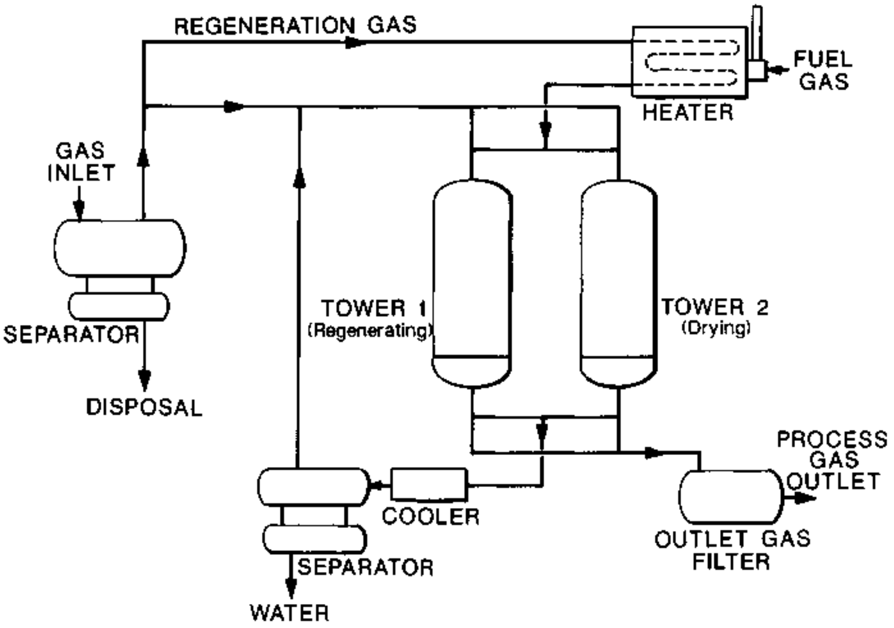

Fig. 16.12. Two-tower adsorption dehydration unit.

and the glycol enriched by the absorbed water flows from the bottom into a regenerator. After the absorbed water is stripped from the triethylene glycol solution, it is recirculated to the absorber. The concentration of the glycol leaving the reboiler will be approximately 98.5 to 98.7 percent by weight triethylene glycol if the reboiler operates at 400°F (205°C) and one atmosphere pressure.

Normal contract specfication for gas to be transmitted through a high pressure pipeline is a water content of 7 lb of water per million standard cubic feet of natural gas. This is approximately the water content of natural gas in equilibrium with water at the freezing point when the gas is under a pressure of 1000 psia.

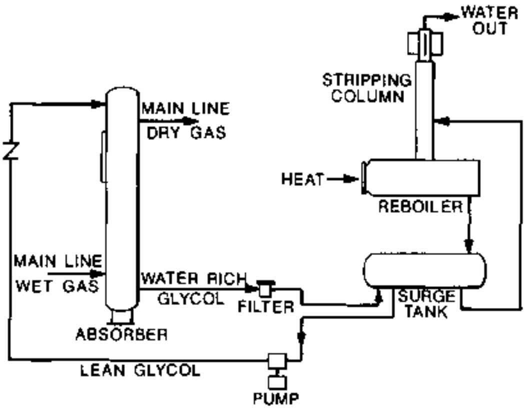

Fig. 16.13. Glycol dehydration unit.

The solid desiccants offer much lower water contents for the dried gas. With proper design and operation, molecular sieve dehydrators can satisfactorily prepare gas for total liquefaction at temperatures as low as -263°F (-165°C). Lower outlet water dew points can be obtained with triethylene glycol if the concentration of glycol going to the absorber is increased. This can be accomplished by using vacuum in the reboiler or by introducing another material into the reboiler to lower the required partial pressure of the water vapor above the glycol. Proper design and operation of such glycol systems can produce outlet water dew points in the -40°F (-40°C) range, or lower.

Natural gas pipelines normally operate at elevated pressures. In many instances the gas is available at low pressures so must be pumped or compressed to higher pressure. If the volume of the gas stream is small, reciprocating compressors must be used. For larger

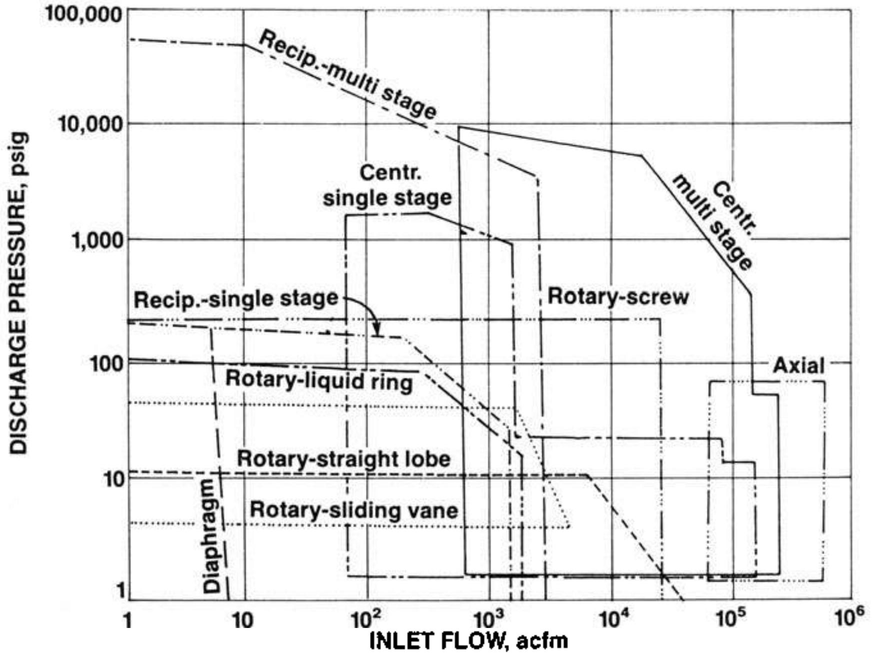

Fig. **16.14.** Approximate range of application for compressors. (GPSA Engineering Data Book, *10th ed., Gas Processors Suppliers Association, Tulsa, OK, 1987.*)

gas volumes, rotary compressors of various types are available. Figure 16.14[10] shows pressure and flow rate ranges in which different types of compressors currently available are used.

If the natural gas stream contains objectionable quantities of hydrogen sulfide and/or carbon dioxide, they must be removed in order to make the gas suitable for transmission and sale. The details of removal of H_2S and CO_2 from natural gas streams are beyond treatment here, but excellent discussions are available.[10,12] There are many different processes available, depending upon the contaminants to be removed and their concentration in both the sour and the sweetened gas. The dominant treating process is still the use of an alkanolamine. A typical flow sheet for an amine sweetening installation for removal of hydrogen sulfide in carbon dioxide from a natural gas stream is shown in Fig. 16.15.[12]

Environmental restrictions and controls will not permit release of the hydrogen sulfide or its incineration to sulfur dioxide. As pointed out by Maddox,[12] the least undesirable alternative is conversion of the hydrogen sulfide to sulfur. Again, there are many different processes available, several of which are discussed in the book by Maddox. The dominant method is by use of the Claus process, which involves partial combustion of the hydrogen sulfide to sulfur dioxide and catalytic combination of the hydrogen sulfide and sulfur dioxide to produce sulfur. Detailed discussions of the Claus technology as well as other techniques of converting hydrogen sulfide to sulfur are available.[10,12]

Figure 16.16 is a sketch of a "once-through" Claus process using a hot gas bypass for reheat. Sufficient air is used to burn one-third of the H_2S and all hydrocarbons. Steam usually is generated in the waste heat boiler, where the combustion products are cooled, and sulfur is condensed. The gas must be heated before introduction to the reactor to prevent sulfur condensation in the reactor

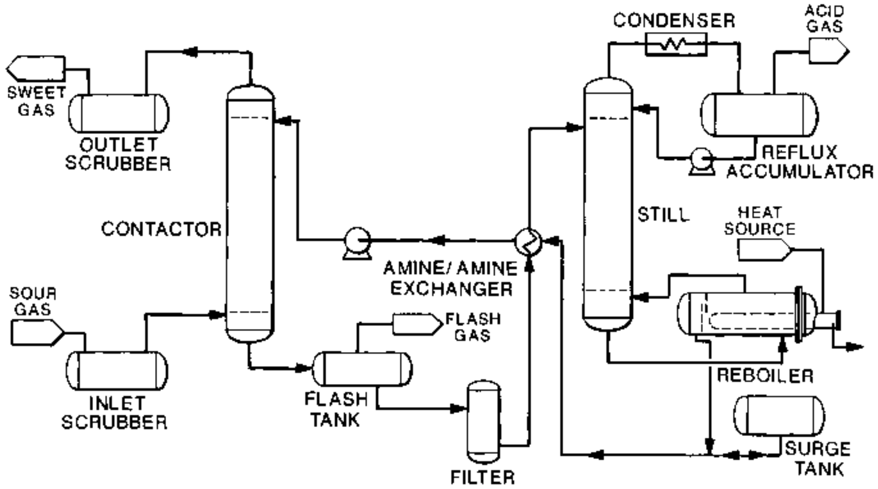

Fig. 16.15. Typical ethanolamine sweetening unit.

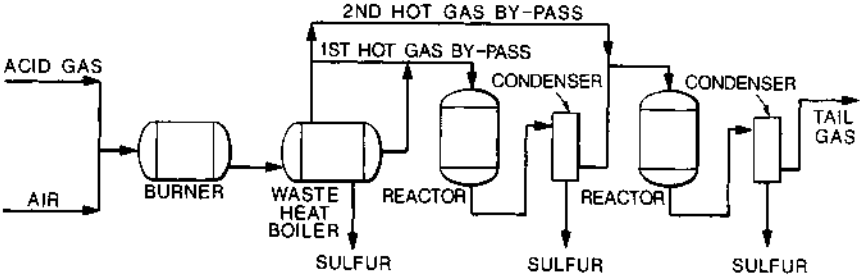

Fig. 16.16. Once-through Claus sulfur unit.

bed. Tail gas usually is sent to a tail gas cleanup unit to minimize sulfur emissions.

PROCESSING FOR LIQUIDS RECOVERY

The first time that liquids were recovered from a natural gas stream, it probably happened more by accident than by design. Any time a gas stream from a liquid-gas separator is either cooled or compressed, liquids will form. This simple statement still provides the basis for nearly all hydrocarbon liquid recovery systems from natural gas. Figure 16.17[11] shows schematically the flow through a simple compression liquids-recovery facility. Replacing the water cooling after the second stage of compression with refrigeration would increase liquids recovery. If the gas had not been dehydrated, there would be danger of hydrate formation at this point.

As the natural gas industry developed and expanded, so did the demand for liquids recovered from natural gas. One way of recovering additional liquids is through the use of a heavy absorption oil that has good solubility characteristics for the propane and heavier hydrocarbon components in the gas stream. As in the case of dehydration, the solvent must be regenerated. Figure 16.18[11] shows the absorption–stripping section of an absorption-type hydrocarbon liquids recovery facility. The absorbent is circulated to the top of the absorber and flows downward, absorbing liquefiable components from the gas stream. It then is heated in the stripper, with the stripped components being cooled and condensed while the stripped absorption oil is recirculated. The liquid hydrocarbon stream typically would flow through a fractionation train for separation into the individual components or mixtures that could be sold.

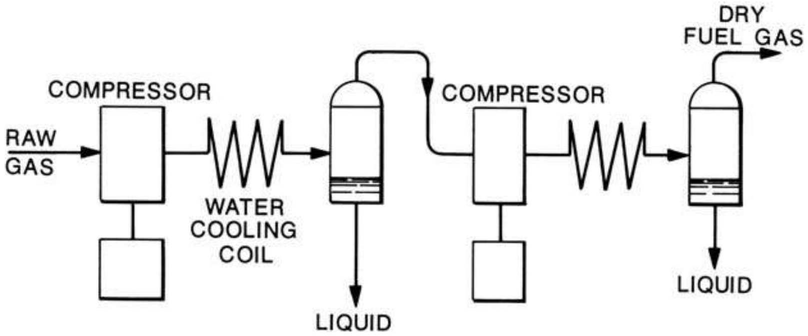

Fig. 16.17. Liquid hydrocarbon recovery by compression and cooling. (*Adapted from Huntington, R. L.,* Natural Gas and Gasoline, *McGraw-Hill, New York, 1950.*)

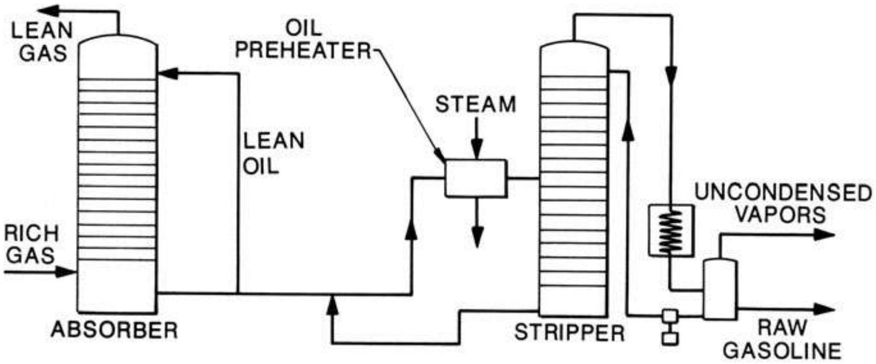

Fig. 16.18. Absorption-stripping unit. (*Adapted from Huntington, R. L.,* Natural Gas and Gasoline, *McGraw-Hill, New York, 1950.*)

Combining refrigeration with oil absorption allowed for additional liquid recoveries and greater economy of operation. Using temperatures as low as −40°F (−40°C), refrigerated oil absorption plants were capable of recovering 70 percent or more of the propane present in the natural gas stream. Recoveries for the butane and heavier constituents were essentially 100 percent.

Development of the turbo-expander process allowed design and construction of plants for recovery of liquid ethane, as well as the heavier hydrocarbon components. The turbo-expander extracts work from the gas during expansion from a high pressure to a lower pressure. Because of the work extraction the gas is cooled, and, by means of suitable heat exchange, temperatures as low as −150°F (−100°C) can easily be achieved. The separation at low pressure gives higher relative values of the vapor–liquid equilibrium constant for nitrogen and methane than for ethane and heavier hydrocarbons. The result is that the process shown in Fig. 16.19[13] can recover as much as 75 percent or more of the ethane contained in the gas as the demethanized product. In some cases the process will be run

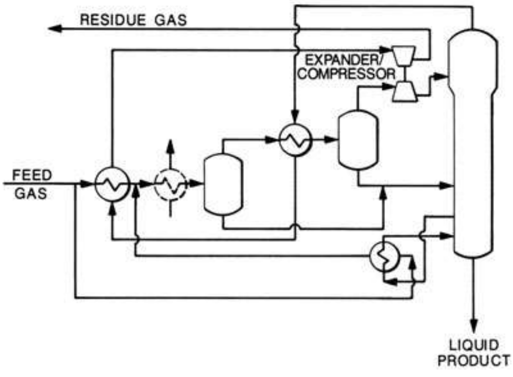

Fig. 16.19. Turbo-expander process flow.

to produce a deethanized product that contains essentially all of the propane in the feed gas. The liquid product from the facility either can go to on-site fractionation into salable products or, more typically, be introduced into a pipeline and transported to a central fractionation facility near the point of ultimate use for the liquid product.

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17

Coal Technology

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INTRODUCTION

Coal represents over 90 percent of the U.S proven reserves of fossil fuels, and can serve as a source of synthetic fuel for the petrochemical industry as well as a source of electric power production and process heat generation. About one-third of the world's coal reserves are present in the United States. The recoverable reserves of U.S. coal have been estimated to be 250 billion tons. Eastern U.S. coals are generally bituminous with a heating value of 10,000 to 15,000 Btu/lb. Bituminous coals comprise nearly one-half of the total U.S. coal reserves. The western as well as southwestern U.S. coals are mainly subbituminous (with a heating value of 9000–12,000 Btu/lb) and lignite (with a heating value of 8000–10,000 Btu/lb).

Historical interest in coal technology has been cyclic, primarily because of the varying economics of petroleum. Coal dominated the U.S. energy picture until the discovery of petroleum. Each subsequent threat to oil supplies spurred a temporary renewal of interest in coal, which rapidly faded as each new major oil strike was made. The threat to oil supplies in 1973 produced the historic response pattern in all respects except one: although exploration for oil and gas increased because of the price increases, few major new oil reserves have been found. Coal use for electric power generation has increased in recent years, but the economic conversion of coal to clean fuels still stands as one of the key technical challenges of our time.

The number of publications on the subject of coal composition, structure, and usage has grown enormously during the last few years, as funds for coal research have increased markedly. Indeed, the future of coal science looks brighter than ever as a new generation of researchers grapple with, and overcome the obstacles to, making meaningful contributions toward the elucidation of the structure, composition, and physiocochemical behavior of coal. The objective of this chapter is to provide a brief review of the state of the art of coal science and technology.

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(1) Texaco Research and Development: Coordinating author plus Introduction and sections on Coal Production and Consumption, Origin and Classification, Coal Composition and Structure, Pyrolysis, and Gasification; (2) Center for Applied Energy Research, University of Kentucky: Coal Mining and Preparation; (3) Advanced Fuel Research: Combustion; (4) Center for Applied Energy Research, University of Kentucky: Direct Coal Liquefaction; (5) Eastman Chemical Company: Petrochemical Feedstocks.

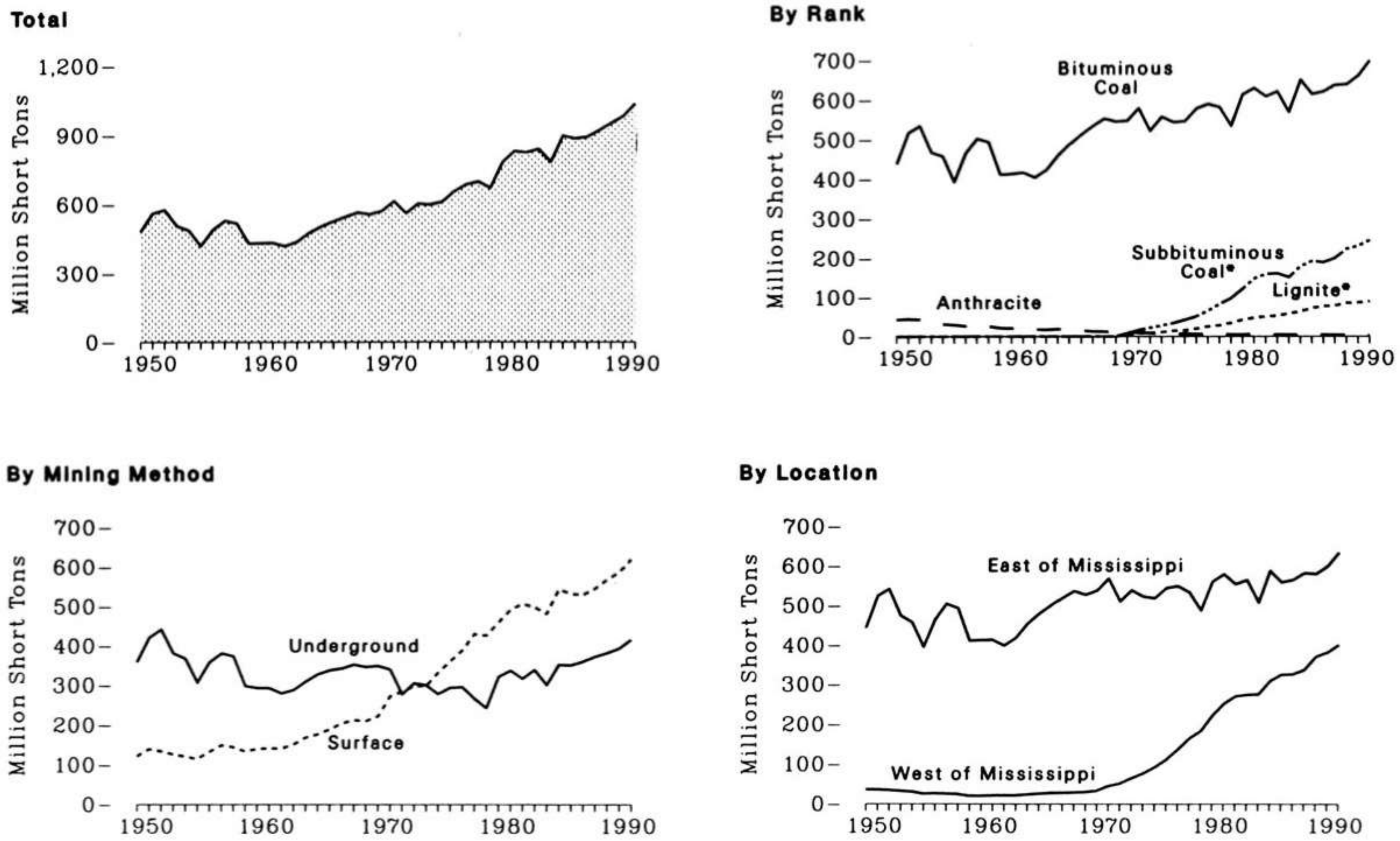

Fig. 17.1. U.S. coal production, 1949-90. (Annual Energy Review, *Energy Information Administration, U.S. Department of Energy, DOE/EIA-0384 (90).*)[1]

COAL PRODUCTION AND CONSUMPTION

Bituminous coal accounts for, by far, the largest share of all coal produced in the United States. In 1990, production of all types of coal totaled over 1 billion short tons, of which 943 million tons were subbituminous and bituminous coals (Fig. 17.1). Despite its clean burning characteristics, anthracite accounts for a diminishing share of total coal production. Most anthracite is mined in northeastern Pennsylvania. In 1949, anthracite accounted for 9 percent of total coal production; by 1990 its share was reduced to less than one-half of 1 percent. Figure 17.2 presents data on coal consumption in the United States.

Although more coal is mined to the east of the Mississippi than in the West, the share of western production has increased significantly since 1965. In 1965, production of western coal was 27 million tons (5% of the total). By 1990, western production had increased by almost 15 times, to 401 million tons (39% of the total). The growth in western coal, due in part to environmental concerns, led to an increased demand for low-sulfur coal, which is concentrated in the West. Also, surface mining, with its higher than average productivity, is much more prevalent in the West than the East.

The average productivity of all types of mines in the United States increased each year after 1949, reaching 2.4 tons per miner per hour in 1969. In 1989, average productivity reached an all-time high of 3.7 tons per miner hour.

Electric utilities are the dominant consumers of coal. Their consumption grew from 84 million tons in 1949 (a 17% share) to 772 million tons (an 86% share) in 1990. In contrast, consumption by all other sectors in 1990 was lower than it had been in 1949. The most dramatic declines occurred in the transportation sector (as railcars switched to petroleum) and the residential and commercial sectors. In 1949, those two sectors accounted

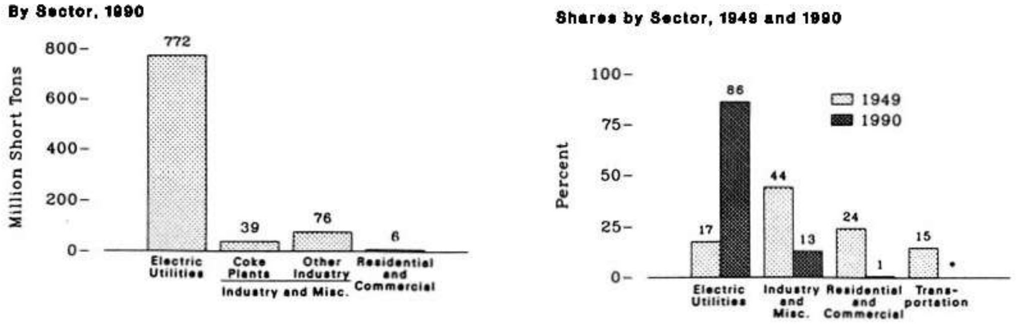

Fig. 17.2. U.S. coal consumption by sector. (*U.S. Department of Energy, DOE/EIA-0384 (90).*)[1]

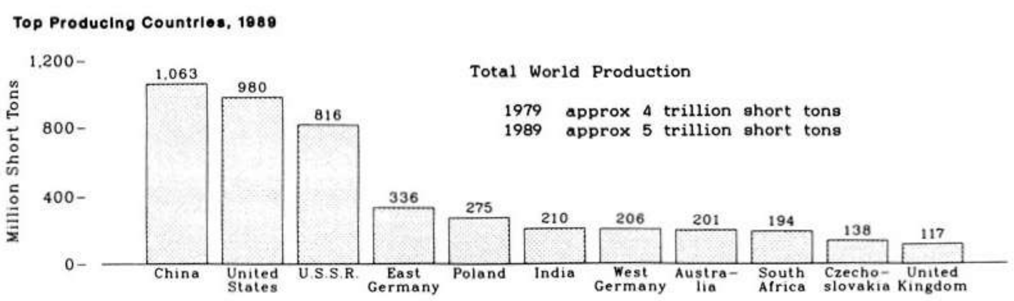

Fig. 17.3. World coal production in 1989. (*U.S. Department of Energy, DOE/EIA-0384 (90).*)[1]

for 187 million tons (39% of the total); but in 1990, their consumption totaled 6 million tons, less than 1 percent of U.S. consumption. Coal consumption by the industrial sector trended downward after the mid-1960s. Industrial consumption fell to about 112 million short tons in 1986 from 205 tons in 1966. During 1988 and 1989, coal consumption rose to 118 tons, but it declined to 115 tons in 1990 during an economic slowdown in the United States. As shown in Fig. 17.3, the United States is the second largest producer of coal in the world, right behind China.

ORIGIN AND CLASSIFICATION OF COAL

Coal originated from the remnants of various forms of plant life (trees, bushes, ferns, mosses, vines, etc.) that flourished in swamps and bogs millions of years ago during prolonged periods of abundant rainfall. Peat, the precursor of coal, was formed by bacterial and chemical action on accumulations of plant debris. Given[2] has presented an excellent review on the origin and formation of coal.

Accumulations of plant debris and sediments compressed and solidified the deposit, thus initiating coalification. Exclusion of oxygen from the peat by overlying water retarded the rate of decay, and the extent of coalification (which determines the coal rank) depended largely on the temperatures existing during this process. When the prevailing temperature was relatively low (corresponding to a depth of only a few hundred feet below the surface), coalification was relatively slow and resulted in low-rank coal. At increased depths, higher temperatures in the organic masses improved the coalification process, producing higher-rank coals (bituminous and anthracite). Intrusions of igneous rocks sometimes accelerated these increases. The chemical changes that occur during coalification are decreases in hydrogen and oxygen content and an increase in carbon content.

Coal is an "organic rock," being grossly characterized by layers or bands having glossy or dull appearances. The glossy layers are composed mainly of vitrinite, formed from woody parts of plants: trunks, limbs, branches, twigs, and roots. The dull bands consist of finely divided material, formed from leaves, pollen, spores, seeds, and resins (collectively termed exinite), in addition to fine vitrinite and more coalified micrinite and fusinite. Besides these banded coals, there are two types of dull, nonbanded coals: (a) cannels, which are rich in spores, and (b) bogheads, which contain abundant remains of algae.

Coals can be classified by rank and/or type. Table 17.1 presents a classification of coals in the United States according to rank. The main rank classes seen in this table are grouped according to certain chemical and physical properties. The factors determining rank, or degree of coalification, are moisture, volatile matter (material that is volatilized when coal is heated at a certain temperature and for a certain length of time), fixed carbon (the residue after the loss of volatile matter), heating value, caking, and weathering properties.

The reflectance of vitrinite (a commonly used rank indicator for high-rank coals) is measured by comparing the intensity of a beam of light incident on a polished surface of vitrinite with the light reflected directly back from that surface.

An international classification of coal (Table 17.2) classifies high-rank coals according to their volatile-matter content, calculated on a dry, ash-free (d.a.f.) basis. Because volatile matter is not a suitable parameter for coals containing more than 33 percent volatile matter, the calorific value on a moist, ash-free basis is included as a parameter for such coals. The resulting classes of coal, based on volatile-matter content and calorific value, are grouped according to their plastic properties, by employing either the free-swelling or the Roga test. They are then subgrouped according to plastic properties, by using either the Audibert-Arnu or the Gray-King test. A three-figure cost number is used to classify a coal. The first figure indicates the class of the coal, the second figure the group, and the third figure the subgroup.

TABLE 17.1 Classification of Coals by Rank[a]

		Fixed Carbon Limits, percent (Dry, Mineral-Matter-Free Basis)		*Volatile Matter Limits, percent (Dry, Mineral-Matter-Free Basis)*		*Calorific Value Limits, Btu per pound (Moist,[b] Mineral-Matter-Free Basis)*		
Class	*Group*	*Equal or Greater Than*	*Less Than*	*Greater Than*	*Equal or Less Than*	*Equal or Greater Than*	*Less Than*	*Agglomerating Character*
I. Anthracitic	1. Meta-anthracite	98	—	—	2	—	—	—
	2. Anthracite	92	98	2	8	—	—	—
	3. Semianthracite	86	92	8	14	—	—	Nonagglomerating[c]
II. Bituminous	1. Low volatile bituminous coal	78	86	14	22	—	—	
	2. Medium volatile bituminous coal	69	78	22	31	—	—	Commonly agglomerating[e]
	3. High volatile *A* bituminous coal	—	69	31	—	14,000[d]	—	
	4. High volatile *B* bituminous coal	—	—	—	—	13,000[d]	14,000	
	5. High volatile *C* bituminous coal	—		—	—	11,500	13,000	
						10,500	11,500	Agglomerating
III. Subbituminous	1. Subbituminous *A* coal	—	—	—	—	10,500	11,500	Nonagglomerating
	2. Subbituminous *B* coal	—	—	—	—	9,500	10,500	—
	3. Subbituminous *C* coal	—	—	—	—	8,300	9,500	—
IV. Lignitic	1. Lignite *A*	—	—	—	—	6,300	8,300	—
	2. Lignite *B*	—	—	—	—	—	6,300	—

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[a] This classification does not include a few coals, principally nonbanded varieties, which have unusual physical and chemical properties and which come within the limits of fixed carbon or calorific value of the high-volatile bituminous and subbituminous ranks. All of these coals either contain less than 48 percent dry, mineral-matter-free fixed carbon or have more than 15,500 moist, mineral-matter-free British thermal units per pound.

[b] Moist refers to coal containing its natural inherent moisture but not including visible water on the surface of the coal.

[c] If agglomerating, classify in low-volatile group of the bituminous class.

[d] Coals having 69 percent or more fixed carbon on the dry mineral-matter-free basis shall be classified according to fixed carbon, regardless of calorific value.

[e] It is recognized that there may be nonagglomerating varieties in these groups of the bituminous class, and there are notable exceptions in high volatile *C* bituminous group.

TABLE 17.2 International Classification of Coals by Type (Courtesy Bureau of Mines, U.S. Department of the Interior)

GROUPS (determined by caking properties)			CODE NUMBERS										SUBGROUPS (determined by coking properties)		
GROUP NUMBER	ALTERNATIVE GROUP PARAMETERS		The first figure of the code number indicates the class of the coal, determined by volatile-matter content up to 33% V. M. and by calorific parameter above 33% V. M. The second figure indicates the group of coal, determined by caking properties. The third figure indicates the subgroup, determined by coking properties.										SUBGROUP NUMBER	ALTERNATIVE SUBGROUP PARAMETERS	
	Free-swelling index (crucible-swelling number)	Roga index												Dilatometer	Gray-King
3	>4	>45	▨	▨	▨	▨	435	535	635	▨	▨	▨	5	>140	$>G_8$
			▨	▨	▨	334	434	534	634	▨	▨	▨	4	>50-140	G_5-G_8
			▨	▨	▨	333	433	533	633	733	▨	▨	3	>0-50	G_1-G_4
			▨	▨	▨	332 a 332 b	432	532	632	732	832	▨	2	≤ 0	E-G
2	2½-4	>20-45	▨	▨	▨	323	423	523	623	723	823	▨	3	>0-50	G_1-G_4
			▨	▨	▨	322	422	522	622	722	822	▨	2	≤ 0	E-G
			▨	▨	▨	321	421	521	621	721	821	▨	1	Contraction only	B-D
1	1-2	>5-20	▨	▨	212	312	412	512	612	712	812	▨	2	≤ 0	E-G
			▨	▨	211	311	411	511	611	711	811	▨	1	Contraction only	B-D
0	0-½	0-5	▨	100 A B	200	300	400	500	600	700	800	900	0	Nonsoftening	A
CLASS NUMBER →			0	1	2	3	4	5	6	7	8	9	As an indication, the following classes have an approximate volatile-matter content of: Class 6 33-41% volatile matter 7 33-44% " " 8 35-50% " " 9 42-50% " "		
CLASS PARAMETERS	Volatile matter (dry, ash-free) →		0-3	>3-10 >3-6.5 >6.5-10	>10-14	>14-20	>20-28	>28-33	>33	>33	>33	>33			
	Calorific parameter [a] →		—	—	—	—	—	—	>13,950	>12,960-13,950	>10,980-12,960	>10,260-10,980			
			CLASSES (Determined by volatile matter up to 33% V. M. and by calorific parameter above 33% V. M.)												

Note: (i) Where the ash content of coal is too high to allow classification according to the present systems, it must be reduced by laboratory float-and-sink method (or any other appropriate means). The specific gravity selected for flotation should allow a maximum yield of coal with 5 to 10 percent of ash.

(ii) 332a . . . >14-16% V. M.
332b . . . >16-20% V. M.

[a] Gross calorific value on moist, ash-free basis (30 C , 96% relative humidity) B t u./ lb.

COAL COMPOSITION, ANALYSES, AND STRUCTURE

Coal Composition and Analyses

Coal is an "organic rock" composed of carbon, hydrogen, oxygen, nitrogen, sulfur, and mineral matter. These components can vary considerably both chemically and structurally, depending on the rank of the coal and even within coals of the same rank. Of these parameters, sulfur and mineral matter exhibit the greatest variation for coals of the same rank. For coals of different ranks the greatest characteristic variations occur in the carbon and hydrogen values.

There are two major types of coal analysis—proximate and ultimate. In addition, there are a number of miscellaneous analyses. Many of the tests are empirical, requiring strict adherence to specified conditions. In the United States, the American Society for Testing and Materials (ASTM) develops these methods. International standards are developed by the International Organization for Standardization.

Proximate analysis includes the determination of moisture, ash, and volatile matter (the fixed carbon by difference). These values, in addition to total sulfur and heating values, usually are sufficient to provide the information necessary for process heating, steam generation, and coking considerations. The ultimate analysis includes the determination of carbon, hydrogen, nitrogen, and total sulfur (ith oxygen being calculated by difference). Numerous other analyses are conducted, the scope of which varies widely. These include not only standard methods such as heating value, free-swelling index, and ash analysis but also those procedures used to determine trace elements, mineral phases, surface patameters, conversion potential, and plastic properties.

The standard analyses are described in ASTM and Bureau of Mines publications. Many of the procedures, however, are not standard methods and must be acquired from one or more of the many publications dealing with the specific area of interest. For example, plastic properties of coal, which are important considerations in any process design, can be characterized by various techniques. Each technique has its own advantages and disadvantages (Table 17.3).

Figure 17.4 shows the proximate analyses of coals selected to represent the various ranks of coal (reported on an ash-free basis). Analyses listed by coal bed, county, and state can be found in a number of publications, such as the data bank developed by the U.S. Department of Energy and the Pennsylvania State University Coal Bank, Bureau of Mines bulletins, Illinois State Geological Survey circulars, and the Argonne National Laboratory Coal Data Base (on a limited number of coal samples).

The heating value (usually reported in Btu/lb) is the high-heat value (HHV), also referred to as the gross heating value. This quantity is defined as the heat produced by combustion of a unit quantity, at a constant volume, under specified conditions. The low-heat value (LHV) is calculated from the HHV by deducting 1030 Btu for each pound of water originally present or formed during combustion. The high-heating value can be reasonably calculated from a number of formulas using determined values for carbon (C), hydrogen (H), oxygen (O), sulfur (S), and additional data as deemed necessary.

Coal Structure

An obstacle to progress in coal technology is that most scientists are accustomed to working with homogeneous species of good purity, but there is no such thing as pure coal. The composition and the structure can vary dramatically between coals of different ranks, or even between coals of the same rank. However, some structural features are common to all coals.[88]

In general, coals are composed of aromatic and hydroaromatic building blocks or layers, with a variety of substituent groups and some cross-linking between adjacent units. Some of these units are not strictly planar because of the presence of heteroatoms (oxygen, nitrogen, or sulfur) or hydroaromatic portions. The structure of graphite consists of extensive parallel layers of carbon atoms arranged

TABLE 17.3 Summary of Various Techniques to Characterize the Plastic Properties of Coal

	Description	*Advantages*	*Disadvantages*
Free-Swelling Index/Grey-King	Visual comparison of cokes carbonized under well-defined conditions, with standard conditions.	Inexpensive, rapid, reproducible.	Lack of flexibility; transition phenomena from coals to coke not known.
Hot-Stage Microscopy	Morphological changes observed by optical microscopy.	Appropriate to supply the changes in macerals when heated.	Provides qualitative information "subjective."
Foxwell/Gas Flow Method	Measures the resistance of the gas flow through a bed of coal during continuous heating.	Indirectly measures the fluidity of the plastic mass by the pressure differences between the inlet and outlet ports.	Requires highly purified (oxygen-free) gas to avoid oxidation.
Plastometer a. Constant torque b. Variable torque	a. Records the angular velocity of a rotating shaft through a bed of coal as a function of temperature. b. Records the changes in torque re-required to rotate a cylindrical retort (when coal is carbonized) at constant speed as a function of temperature.	Measures the changes in fluidity as a function of temperature; quite sensitive for determining extent of oxidation or weathering.	Does not provide data on swelling properties, limited heating rates (−3°C/min).
Dilatometer	Expansion, contraction, and volume change on resolidification measured as a function of temperature when heated.	Provides data on dilation parameters and transition temperatures; wide range of heating rates (<100°C/min).	Does not provide quantitative information on changes in fluidity of coal.

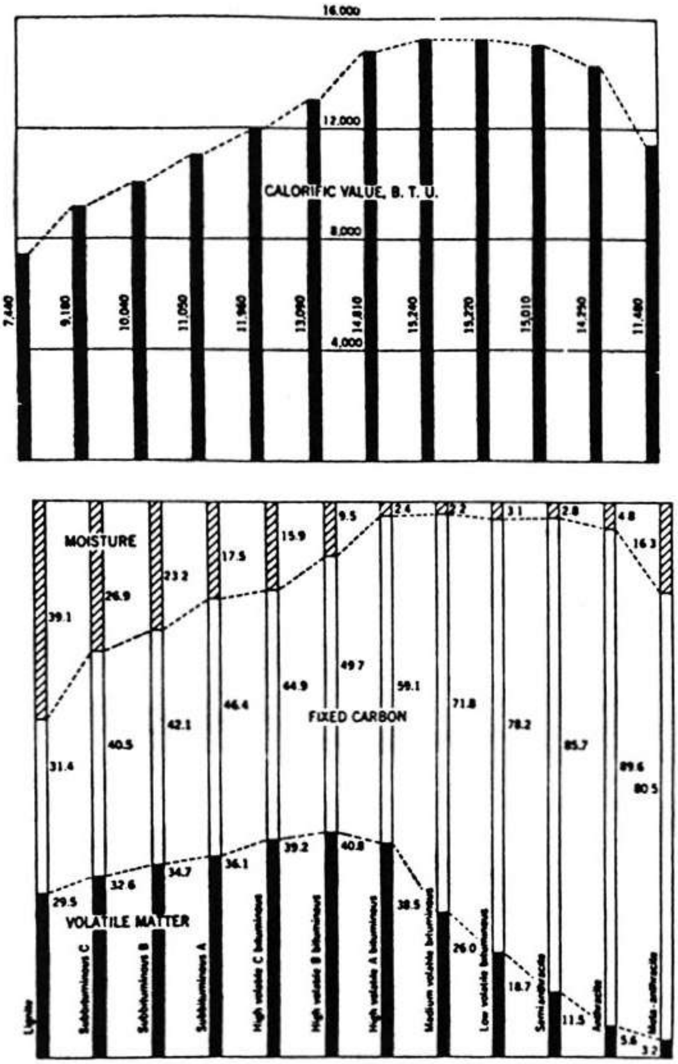


Fig. 17.4. Analysis of U.S. coals selected to represent the various ranks. (*Courtesy Bureau of Mines*).

in condensed layers mutually oriented and separated by a distance of 0.335 μm (the carbon–carbon distance of van der Waal). The parallel stacking of layers in coal is similar to this, but lacks mutual orientation between the layers, and the average spacing between layers is somewhat larger in coal than in graphite.

Low-rank coals are composed of small layers that are more or less randomly oriented and are connected by cross links. Thus, the structure is highly porous. Medium-rank coking coals shows a greater degree of orientation, and a greater tendency toward parallel stacking. These coals have fewer cross links and fewer pores than lignites. High-rank coals (primarily anthracites) show a growth of the individual layers, a marked increase in the degree of orientation, and the development of a new type of pore that is elongated parallel to the stacks of layers. These coals are considered to be the products of the highest degree of coalification.

The above classification of coal types must be used with caution. In essence, the heterogeneous chemical structures of the wide range of plant materials and chemicals that were the genesis of coal guarantee an almost unlimited range of chemical structures within the various types of coals. Therefore, coals have been considered as a variety of chemical entities; and this wide variety virtually dictates coal reactivity under specific conditions.

The identification of the constituents of a complex mixture such as coal by molecular type may proceed in a variety of ways, but it generally consists of three types of analysis: chemical techniques; spectroscopic techniques; and physical property methods, whereby structural parameters are derived from a particular property by a sequence of mathematical manipulations. Several good reviews on this subject are available.[3,4]

Relations between Elemental Composition of Coal and Environmental Concerns

Coals generate "a seemingly endless string of environmental hazards that are ubiquitous and pervasive."[5] It is well known that nitrogen and sulfur are the two primary pollutants (heteroatoms) in coal. Therefore, the structure of these compounds in coals, their evolution during thermal decomposition, and the distribution of these species in products are being investigated. The studies conducted in these areas suggest that nitrogen in coal is almost entirely contained in tightly bound ring structures. The nitrogen-containing structures evolve from coal without cleavage during pyrolysis. Coal-derived nitrogen compounds also result in the formation of materials that interfere with synthetic fuel processing. The latter problem results from the fact that most of these compounds are basic and thus serve as poisons for the acidic catalysts used in synthetic crude oil refining. The nitrogen present in coal is converted to NO_x compounds during combustion.

Sulfur is present in coal in several forms, such as pyrite, sulfates (small amounts), and organic-sulfur compounds. Pyrite (FeS_2) decomposes at a relatively low temperature (approximately 400°C), producing FeS, H_2S, and organic-sulfur compounds. Organic-sulfur compounds can be classified into three groups: loosely bound sulfur, tightly bound sulfur, and a category intermediate between these two forms. The tightly bound sulfur compounds decompose above 500°C, and loosely bound organic-sulfur decomposes at low temperatures (about 400°C). Some of the tightly bound organic-sulfur compounds are formed by incorporating pyritic sulfur into the ring structures.

Pollutant distributions between char, tar, and gases are expected to be a function of pyrolysis conditions and, hence, are process-dependent. Khan[6] developed models to predict the distribution of sulfur in the products based on pyrolysis data for 32 different coal samples devolatilized in a fixed-bed reactor. It was observed that the total sulfur content in the pyrolysis products at 500°C could be correlated with the total sulfur (weight percent of original coal) content. The relationships are as follows:

$$\text{Total sulfur in gas} = 0.31 \times S_{\text{coal}}$$
$$[R^2 = 0.93, F = 425, P = 0.0001]$$

$$\text{Total sulfur in tar} = 0.06 \times S_{\text{coal}}$$
$$[R^2 = 0.85, F = 175, P = 0.0001]$$

$$\text{Total sulfur in char} = 0.61 \times S_{\text{coal}}$$
$$[R^2 = 0.98, F = 1{,}475, P = 0.0001]$$

where R^2 is the coefficient of determination, F is the mean square of the model divided by the mean square of error, and P is the significance value. When $P < 0.05$, the effect usually is termed significant.

Multivariate analysis demonstrated that the organic sulfur content of coal plays a stronger role in determining the sulfur content of tar or gases, whereas the pyritic sulfur content plays a key role in determining the sulfur content of the char, at the low-temperature (500°C) devolatilization conditions. With increasing peak devolatilization temperature, however, the gaseous sulfur yield increases at the expense of char sulfur.[6]

COAL MINING AND PREPARATION

Coal mines fell into two general classifications, surface and underground. Production of coal

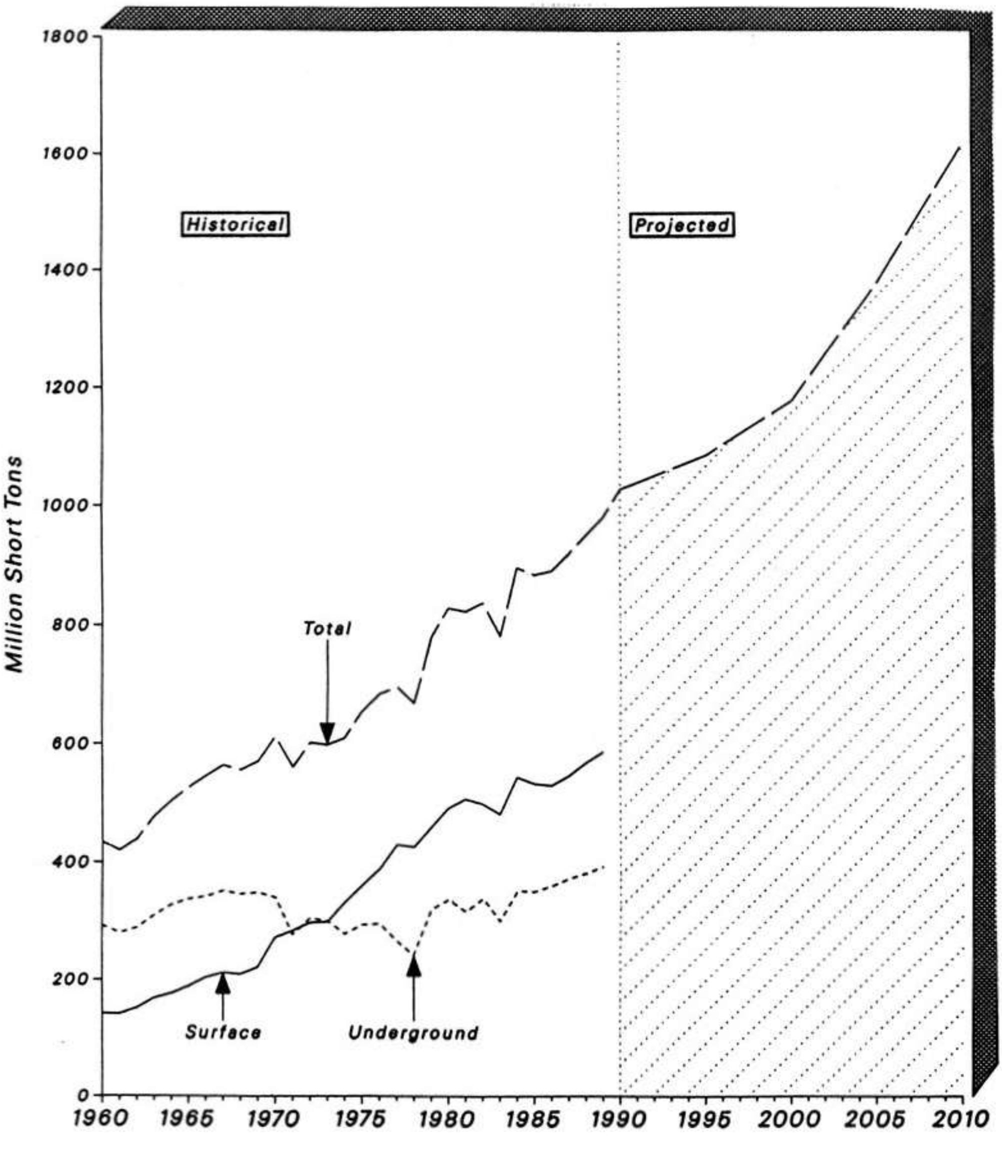


Fig. 17.5. U.S. coal production by methods of mining. (*Sources: DOE/EIA* Annual Energy Review *1989*, Annual Energy Outlook *1991*, *and* Coal Data.)

by type of mining for the United States is shown in Fig. 17.5.

Surface Mining

Surface mining techniques are used when the coal is present near the surface, and the overburden is thin enough. These techniques include contour mining, strip mining, and auger mining.

Contour mining is used in hilly countryside areas where the slope of the surface will permit only a narrow bench to cut around the side of a hill; the excavation is backfilled immediately after the removal of coal. It is the only method that can be used on slopes of 15 degrees or higher.

Strip mining is used in flat or gently rolling lands on the Midwest and West where large and efficient equipment can be used. In this technique, the coal is exposed by removing the overlying strata, or overburden. Blast holes are drilled, and explosives are loaded into these holes to shatter the rock cover; earth-moving equipment is used to remove the soil and the shattered rock. The coal then is collected with power shovels or other coal-digging machines and loaded directly into trucks.

Auger mining is a supplementary method used to reach coal in stripped areas where the overburden has become too thick to be removed economically. Large augers are operated from the floor of the surface mines and bore horizontally into the coal face to produce some reserves not otherwise minable.

For a coal deposit where the seam is near the top of a hill, the entire hilltop can be removed to expose the coal.

Underground Mining

Underground mining techniques are somewhat more labor-intensive than surface mining and are used to remove coal located below too much overburden for surface mining; but here, too, machines are used in most instances to dig, load, and haul the coal. Access to the coal seam is through a drift (horizontal passage), a slope, or a shaft (Fig. 17.6), depending on the location of the coal seam.

A *drift mine* is one that enters a coal seam exposed at the surface on the side of a hill or mountain. The mine follows the coal horizontally.

A *slope mine* is one where an inclined tunnel is driven through the rock to the coal, with the mined coal removed by conveyors or truck haulage.

A *shaft mine* is one where a vertical shaft is dug through the rock to reach the coal, which may be at great depth below the surface. The coal then is mined by horizontal entries into the seam, with the resulting coal hoisted to the surface through the vertical shaft.

Two general mining systems are used in underground mining, namely, room-and-pillar and longwall.

Room-and-pillar mining is an open-stopping method where mining progresses in a nearly horizontal or low-angle direction by opening multiple stopes or rooms, leaving solid material to act as pillars to support the vertical load. This system recovers about 50 percent of the coal and leaves an area much like a checkerboard. It is used in areas where the overlying rock or "roof" has geologic characteristics that offer the possibility of good roof support. This system was used in the old mines where the coal was hand-dug. Two current methods for extracting the coal from the seam are the conventional method, where the coal is undercut and blasted free (Fig. 17.7), and the continuous method, where a machine moves along the coal face to extract the coal instead of blasting it loose (Fig. 17.8). Roof control is the major problem of the room-and-pillar method of mining.

Longwall mining uses a machine that is pulled back and forth across the face of the coal seam in larger rooms. It is not a major mining method in the United States at this time. Coal recovery using this method is greater than in room-and-pillar mining and

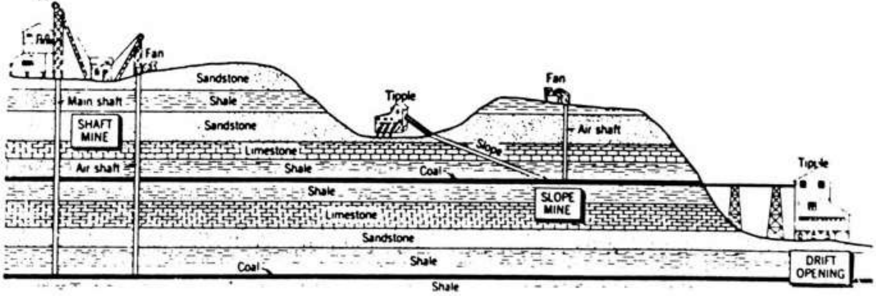


Fig. 17.6. Three types of entrances to underground mines—shaft, slope, and drift. (*Courtesy Bureau of Mines.*)

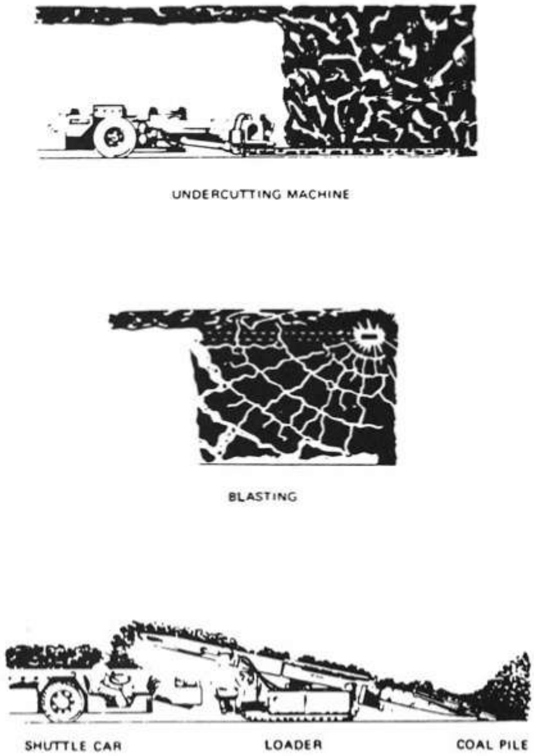


Fig. 17.7. Basic steps in conventional mining. (*Courtesy Bureau of Mines.*)

can be used where roof conditions are fair to poor. Strong roof rock, however, can be a problem. The seam should be over 42 inches thick to accommodate this type of operation and the large coal cutter or plow that is used. A large reserve is necessary.

A modification of this method, using a continuous mining machine on faces up to 150 feet long, is known as *sortwall mining.* It uses the room support system of self-advancing chocks developed for longwall operations.

Coal Preparation

"Coal preparation" is a term applied to upgrading of coal to make it suitable for a particular use. It includes blending and homogenization, size reduction, and beneficiation or cleaning. It is this last aspect, as well as the degree to which it is required, that most significantly governs the cost of coal preparation. Figure 17.9 shows levels of cleaning in terms of broad categories.

Only about one-third of the 3.3×10^9 metric tons of coal produced every year is at present cleaned by breaking, crushing, screening, and wet and dry concentrating processes. This section will briefly describe the processes utilized for coal cleaning.

Coal generally is cleaned by physical methods to remove mineral matter consisting of rock, slate, pyrite, and other impurities. In general, processes for the removal of mineral matter utilize either differences in density or surface chemical properties of coal and mineral matter. For convenience, coal cleaning can be divided into three parts: coarse-coal cleaning, medium-coal cleaning, and fine-coal cleaning. Figure 17.10 shows various coal cleaning methods and corresponding size ranges of coal treated.

The first step in most of the coal cleaning operations is size reduction, the main objective being to liberate mineral matter from coal. Size reduction equipment for coal application ranges from heavy-duty crushers and breakers, capable of crushing lumps of up to a meter cube in size, to coal pulverization equipment capable of milling coal to a fine powder. The hardness and the softness of the coal is defined in terms of the Hardgrove Grindability Index (HGI). A high (>80) HGI indicates soft coal,

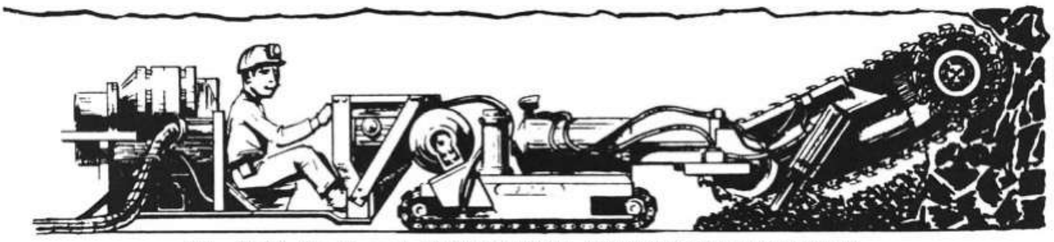


Fig. 17.8. Continuous mining machine. (*Courtesy Bureau of Mines.*)

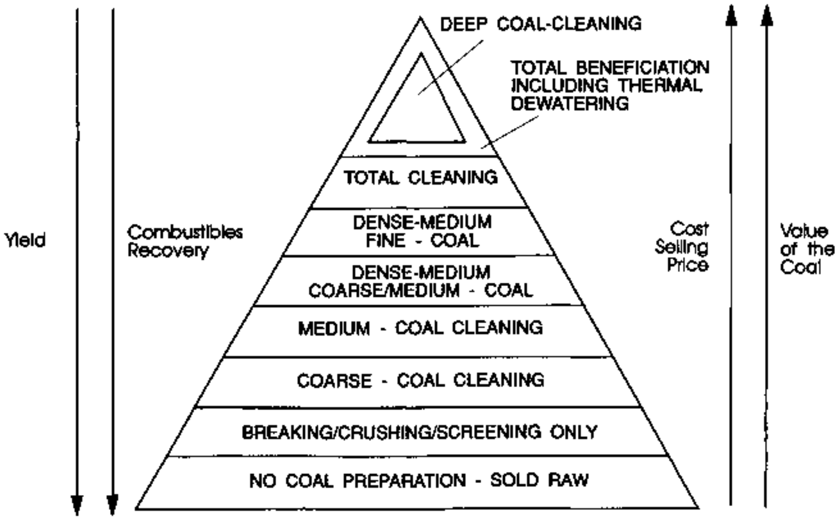


Fig. 17.9. Different levels of coal cleaning and their effect on coal recovery and economics.

easy to grind, and a low (~35) HGI indicates difficult-to-grind coal.

After the coal is crushed, it generally is screened to separate the raw coal into various sizes for cleaning operations. Screening of coal above 12 mm size usually is carried out dry. Double-deck vibrating screens commonly are used for this purpose. For sizing below 12 mm, wet screening is done, using either high frequency vibrating screens or the Sieve Bend. Details on size reduction can be found in various books on coal preparation.[7,8]

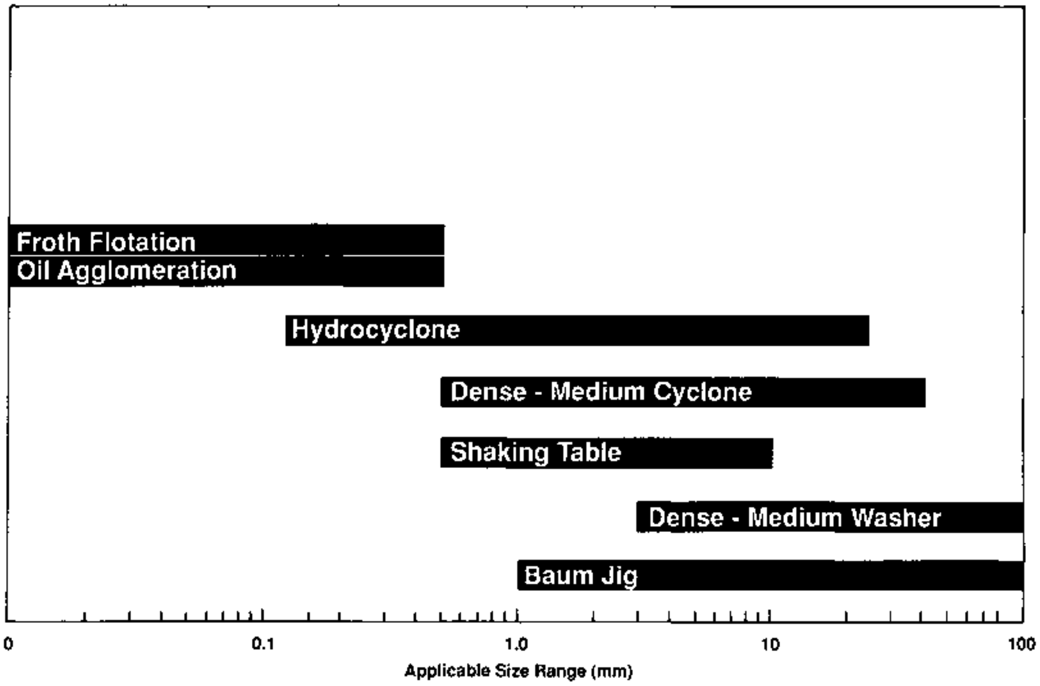
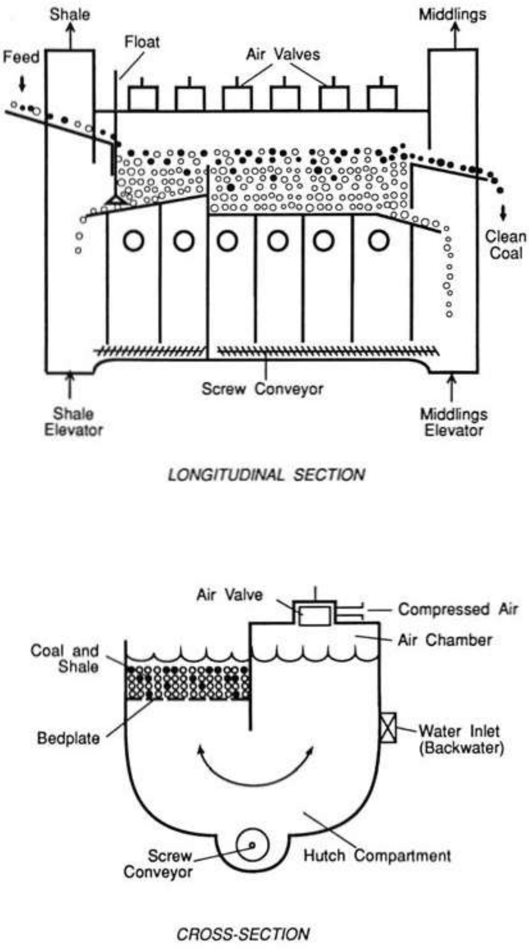


Fig. 17.10. Coal cleaning equipment in common use in the coal industry with respect to the coal size processed.

Coarse-Coal Cleaning

Jigging and dense-medium separation generally are used for coarse coal cleaning.

Jigging. Jigging is among the oldest of mineral processing methods and one of the first adopted for coal cleaning. The separation of coal from mineral matter is accomplished via a fluidized bed created by pulsing a column of water, which produces a stratifying effect on the raw coal. Water is pulsated through the perforated bottom of an open-top rectangular box. The lighter coal particles rise to the top, overflow at the end of the jig, and are removed as clean product. The denser mineral matter settles on a screen plate and is removed as refuse. Most jigs are of the Baum type (Fig. 17.11), in which the pulsations are generated by air pressure.



LONGITUDINAL SECTION

CROSS-SECTION

Fig. 17.11. Sections of a typical Baum jig.

Dense-Medium Washing. Dense-medium separations include processes that clean raw coal by immersing it in a fluid medium with a density intermediate between the density of clean coal and that of reject. Most dense-medium washers use a suspension of fine magnetite in water to achieve the desired density. The process is very effective in providing a sharp separation and is relatively low in capital and operating costs.

Medium Coal Cleaing

Medium-size coal includes coal ranging in size from 3/4 inch to 28 mesh (0.5 mm). The principal techniques utilized are the wet concentrating tables, the dense-medium cyclone, the hydrocyclone, and spirals. All of these equipment types are widely used in the coal industry.

Wet Concentrating Table. This is also known as a shaking table and works much like the classical miner's pan. The shape of the table is usually a parallelogram, and the deck of the table is sloped (or sloping) slope with rubber riffles on it. The upper side of the desk contains a feed box and a wash water box. The deck is vibrated longitudinally with a slow forward stroke and a rapid return. Normal decks are 5 meters long along the longest edge and 2.5 meters wide at right angles to the length. Such a machine can process up to 12 to 15 tons of coal/hour.

Dense-Medium Cyclone. The essential features of a cyclone are shown in Fig. 17.12. A mixture of raw coal and a dense medium (magnetite suspension) enters the cyclone tangentially near the top, producing free-vortex flow. The refuse moves downward along the wall and is discharged through the underflow orifice. The clean coal moves radially toward the cyclone axis, passes through the vortex finder to the overflow chamber, and is discharged from a tangential outlet.

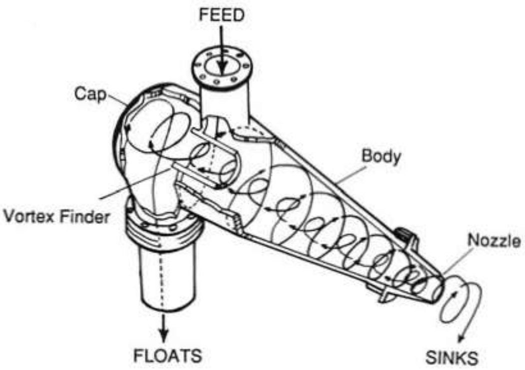


Fig. 17.12. Heavy-medium cyclone separator.

Cyclones are available in various diameters; a 500-mm-diameter unit can process up to 50 tons of coal/hour, whereas one of 750 mm diameter can process up to 120 tons/hour.

Some other forms of the heavy-medium cyclone are the Vorsyl Separator, the Larcodems, the Dynawhirlpool, and the Tri-flo Separator. Each of these units utilizes cyclonging principles.

Hydrocyclone. When only water is used in a cyclone for cleaning coal, it is called a hydrocyclone. Hydrocycloning has been applied even to process coal finer than 0.5 mm. Its design differs from that of the dense-medium cyclone by having a greater cone angle and a longer vortex finder.

Spiral Separator. The spiral separator is usually 8 to 10 feet in height and consists of a trough going downward in a spiral. The coal slurry is fed in at the top, and as it follows the spiral down, centrifugal force separates the coal from the denser mineral matter. A splitter box at the bottom of the spiral can be adjusted to obtain the desired separation.

Fine Coal Cleaning

Froth Flotation. Coal below 0.5 mm in size, classified as fine coal, generally is processed by surface chemical methods such as froth flotation. In the froth flotation process, the fine coal slurry, to which a small amount of flotation agents—usually fuel oil and a short-chain alcohol (methyl isobutyl carbinol)—is added, is processed through a flotation cell. In the cell, fine bubbles are generated by using either forced air or suction. The coal, being hydrophobic, attaches to the air bubbles and rises to the top where it is removed as froth. The refuse, being hydrophilic, remains in the water and is removed from the bottom. The process is very effective in recovering high-grade coal at moderate cost.

The reagents used in froth flotation of coal are classified as collectors, frothers, and modifying agents. Collectors (kerosene or No. 2 fuel oil) provide a thin coating of oil on the coal and promote attachment of air bubbles to it. The frother (methyl isobutyl carbinol) promotes a stable froth. Modifying agents have several functions such as depressing unwanted material, altering the surface of the particles to aid attachment of air bubbles, and providing acidity ot alkalinity to the flotation pulp.

An advanced froth flotation technique called columm flotation has been shown to be superior in obtaining a low-ash clean coal with high recovery of combustible. It has been proved effective in recovering ultra-fine (minus 74 microns) coal.[9,10] A schematic diagram of the column flotation process is shown in Fig. 17.13.

The basic difference between the conventional and the column flotation system is in the design, which provides quiescent flotation conditions in the column, thus effectively recovering fine coal. Also, gentle washing of froth at the top of the column removes entrained impurities from the froth, providing a low-ash clean coal product. The colums also have been effective in removing high amounts of liberated pyritic sulfur. In 1989 the University of Kentucky Center for Applied Energy Research designed four 2.4-meter-diameter columns that were installed at the Powell Mountain Coal Company, St. Charles, Virginia, for recovery of fine coal from refuse streams.

Recently, an air sparged cyclone developed at the University of Utah was tested on a pilot scale. In this technique, flotation is performed inside a cyclone that has porous walls through which air is injected.

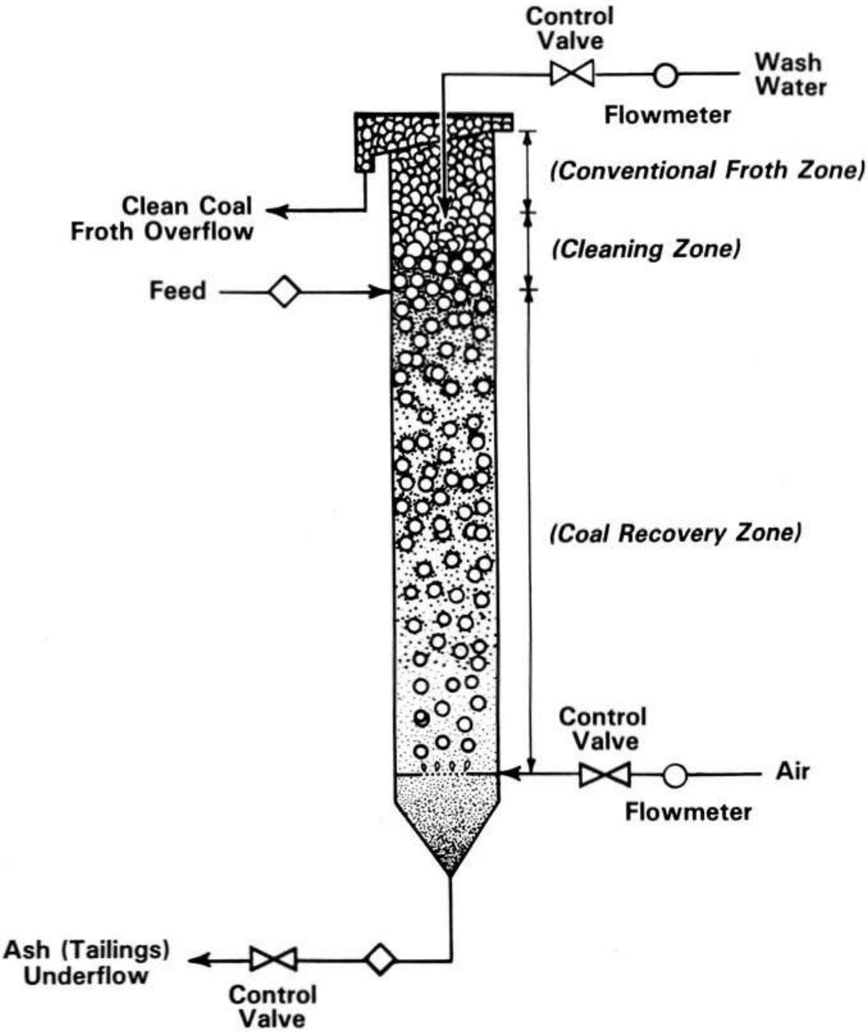


Fig. 17.13. Schematic diagram of column flotation.

Other Processes. An oil agglomeration process that utilizes oil or other hydrocarbon to agglomerate coal, leaving mineral matter in aqueous suspension, has been tested on pilot and commercial scales. The Otisca process utilizes pentane as an agglomerant, which is recovered from clean coal and recycled back in the process. The NRCC process from Canada utilizes fuel oil as an agglomerant. Another process, the high-gradient magnetic and electrostatic cleaning process, utilizes differences in magnetic and electrical charge properties of the mineral matter present on coal. Both of these process have achieved limited success.

Chemical cleaning processes utilize alkali or acid to leach the impurities present in the coal. TRW's Gravimelt process, which has been tested on a pilot scale, utilizes molten caustic to leach mineral matter. The major drawback of a chemical cleaning process is the economics.

The chemical methods are not effective in removing major amounts of organic sulfur. Thus, removal of total sulfur to produce a clean-burning fuel is very difficult. It is envisioned that the optimum desulfurization of coal will include physical, chemical, and microbial treatment. The raw coal will be ground fine to liberate most of the pyritic sulfur and then processed by using the column flotation process to remove most of the liberated mineral matter. Then the clean coal will be treated chemically and finally by microbes to remove organic sulfur from the coal.

Fine Coal Drying

One of the biggest problems in processing fine-size coal is dewatering the drying. Conventional mechanical dewatering devices are effective in dewatering coarse and medium-size coal. For dewatering of fine-size coal, especially if a substantial amount is in the 74-micron range, the conventional techniques provide a dewatered product containing about 30 percent moisture.[11]

Filtration devices that utilize high pressure forces, such as Andaritz Hyperbolic and Ama's KDF filters, have the capability of reducing moisture in the filter cake to about 20 percent. However, the capital and operating costs are high for these devices. Other newly developed techniques that have been tested on a pilot scale include an ultrahigh-*g* centrifuge, which generates forces up to 4000 *g* in the centrifuge, and an electro-acoustic technique that utilizes the synergistic effect of electric, ultrasonic, mechanical, and surface chemical forces to remove moisture from the cake.

COAL UTILIZATION—PYROLYSIS

Technology and Relation to Other Coal Conversion Schemes

In a strict sense, coal pyrolysis means heating of coal in an inert atmosphere. When heated, coal undergoes thermal decomposition, which results in the evolution of gases and tars. In all coal conversion and utilization processes (including gasification, combustion, and liquefaction), some form of coal pyrolysis occurs. Because coal pyrolysis by itself is an important coal utilization process for making coke and oil, a vast amount of literature exists on this topic. By carefully varying the pyrolysis conditions and by adding reactive atmospheres (such as hydrogen), one can optimize production of a desired product (i.e., solid, liquid, or gas). Gasification is closely related to pyrolysis in that when coal is gasified by reacting it at a high temperature with steam and an oxidant (air or oxygen), pyrolysis is the first stage of the reaction as the coal is heated to the reaction temperature. Depending on the type of gasifier, the condensable hydrocarbon gases may be completely destroyed or may be collected as a by-product. Similarly, pyrolysis occurs at the first stage of combustion, but hydrocarbons are destroyed by oxidation. In direct liquefaction, some pyrolysis may occur because of the high temperature utilized when solvents are reacted with the coal, but the dominant process normally is a dissolution of the coal structure, due to solvent chemistry.

Mild gasification is a pyrolysis-based process designed to produce a product slate of alternative fuels by decomposing coal at relatively mild conditions of temperature and pressure. The idea is to produce the most profitable combination of products with a given feedstock and associated operating, distribution, and capital costs.[81,89]

History

Coal pyrolysis is a very old technique (dating back to the eighteenth century) that allows separation of the hydrocarbon fuels and uses relatively inelegant technology. Most pyrolysis systems in use in the late 1800s and early 1900s were in Europe and had as their objective the production of smokeless fuel (char) for domestic use. However, within a short time it was realized that the coal tar fraction contained valuable chemical products. For example, the olefins were described as having potential wealth similar to "Ali Baba's cave." Subsequently, interest faded because of the abundance of inexpensive petroleum. A detailed review has been published.[12]

Interest in pyrolysis was rekindled by the oil embargo of 1973, and emphasis was placed on developing processes that would achieve a maximum yield of liquid products. Several processes were developed to the pilot-plant stage in the 1970s, only to be placed in mothballs when oil prices softened in the early 1980s.

Comparison of Pyrolysis Processes

Based on the reactor configuration, pyrolysis can be conveniently divided into two broad groups: advanced (contemporary) and early processes. A simplified classification of various pyrolysis procedures is provided in Table 17.4.

Coal pyrolysis processes generally are regarded as low temperature when the process temperature does not exceed 700°C, or high temperature if the temperature of the process is at or exceeds 900°C. Some processes operate at temperatures between these extremes. It needs to be emphasized that the pyrolysis conditions used determine the extent to which coal is carbonized and the nature of the liquid and gaseous products. A number of reviews on the advanced pyrolysis processes are available.[13,14] Only a brief comparison of various contemporary devolatilization processes is given in Table 17.5.

Factors Affecting Coal Pyrolysis

During pyrolysis, the yield of gases and liquid products may vary from 25 to 70 percent by weight. The yield depends on a number of variables, such as coal type, gas atmosphere, final pyrolysis temperature, time–temperature history, and pressure. A certain operating condition may lead to increased product yield, but achievement of this process condition often is obtained at added expense.

Depending on the desired products, one may choose to operate a given process in a particular time and temperature mode. Many excellent reviews (e.g., those of Howard,[15] Gavalas,[4] and Solomon and Serio[16]) have been published that discuss the factors affecting coal pyrolysis and product composition. In the following sections, major conclusions presented in the literature are discussed (as summarized in Table 17.6).

Temperature and Heating Rate. The effect of pyrolysis temperature on the yield of products is relatively straightforward. Coal undergoes a large variety of physical and chemical changes when heated gradually from ambient temperature to approximately 1000°C

TABLE 17.4 Simplified Classification of the Various Pyrolysis Procedures

Pyrolysis Process	*Final Temperature °C*	*Products*	*Processes*
		Early Schemes (Slow Heatup)	
Low temperature	500–700	Relatively more reactive coke.	Rexco (700°C; cylindrical units). Coalite (650°C) made in vertical tubes.
Medium temperature	700–900	Relatively more reactive coke with high gas yield, or domestic briquettes.	Town gas and gas coke (obsolete). Phurnacite, low-volatile coal, pitch-bound briquettes carbonized at 800°C.
High temperature	900–1050	Hard unreactive coke for metallurgical use.	Furnace coke (950–1050°C).
		Advanced Techniques (Rapid Heatup)	
Low temperature	500–700	Relatively higher tar yield (20–35 wt.) compared to gas (5–15 wt. %).	COED (fluid bed); Occidental flash (entrained flow) pyrolysis.
Medium temperature	700–900	Lower tar yield compared to that obtained in low-temperature operation.	Clean Coke Process; oxidized clean coal (in fluid bed).

TABLE 17.5 Representative Operating Conditions and Yields for Contemporary Coal Pyrolysis, Hydropyrolysis, and Extraction Processes

Process	*Status*	*Reactor Type*	*Reactor Temperature °(C)*	*Reactor Pressure (MPa)*	*Residence Time (s)*	*Coal*	*Yield, Mass Percent Dry Coal*				*Size of Facility (in 1000 kg/day Coal)*
							Char	*Tar/Oil*	*Gas*	*Water*	
COED, FMC Corporation	Developed	Multiple fluidized-bed	290–565	0.12–0.19	1200[1]	Bituminous	62	21	14	3	32
TOSCOAL	Developed	Rotating horizontal retort	520	0.1	300–600	Subbituminous	69	13	9	9	23
Lurghi-Ruhrgas	Commercial	Mechanical (twin screw) mixer	595	0.1	~3	Subbituminous	50	~32[2]	11	~7[2]	1600
Occidental Flash Pyrolysis	Developing	Entrained flow	610	0.3	1.5	Bituminous	56	35	7	2	3
Clean Coke, U.S. Steel	Developing	Fluidized-bed	~800	~0.8	~3000	—	66	14	15	—	—
Rockwell/Cities Service Flash Hydropyrolysis	Developing	Entrained flow	845	3.5	~0.1	Bituminous	46	38	16	—	22
Supercritical Gas Extraction, NCB[3]	Developing		400	10	1800	Bituminous	63	33[4]	2	2	—

[1] In pyrolysis stages.
[2] Water plus tar/oil sum 39%, individual values estimated.
[3] NCB: National Coal Board, United Kingdom.
[4] Tar extract, softening point 70°C.
Source: Adapted from Probstein and Hicks.[13]

TABLE 17.6 Summary of Advantages and Limitations of Pyrolysis Process Conditions and Feedstock Characteristics

Heating Rate

- High heating rate increases liquid/gas yield and reduces char yield.
- The tar obtained at a high heatup rate is of poorer quality (i.e., lower H/C ratio) than that obtained at a slower heating rate.[13,15]
- High heating rate increases open char structure and char reactivity (in reactive gases).
- Sophisticated (often exensive) systems needed to achieve high heating rate.
- High heating rate increases the thermoplastic (softening and swelling) behavior of coal.

Temperature

- Low-temperature operation (500–700°C) improves liquid yield.
- Affects heteroatom distribution among char, liquid, and gas.
- At elevated temperatures ($>$ 1,300°C), inorganics are removed as slag.
- Longer residence time needed for reaction to be completed at lower temperatures.

Pressure

Inert Gas Atmosphere:

- Higher pressure operation reduces reactor size needed (i.e., increases throughput).
- Higher pressure reduces tar yield.
- Coal feeding, product separation are more difficult at high pressure.
- Better gas-solid heat transfer is achievable at higher pressure.

H_2 Atmosphere:

- Cost of H_2 must be considered versus the quality of the product generated.
- Improves yields of liquid and light products.
- Requires sophisticated pressure systems.
- May increase the undesirable agglomerating properties of coal.[17]

Other Atmospheres (H_2O, CO_2, CO, CH_4, CS_2):

- Probably improve liquid/gas yield.
- Not much information is available.

Vacuum:

- Plastic behavior of coal is reduced.[17]
- Increases liquid/gas yield.[17]
- It is difficult to achieve gas–solid heat transfer (solid–solid heat transfer feasible).
- Not much information is available.

Particle Size

- Smaller particle size improves product (gas/liquid) yield.
- Smaller particle size reduces secondary reactions.
- Grinding cost increases with the reduction in size.

Coal Rank

- High Volatile A (HVA) bituminous coals produce largest quantities of tar.
- Lignites are rich in oxygen functional groups which lead to overall reduction in the calorific value of the product.
- Types of sulfur (pyritic versus organic) present in various coals can influence its distribution in products.

Some changes are observed before the inset of thermal decomposition (i.e., carbon–carbon bond scission and the like), which occurs above 350°C. When heated to approximately 100°C, the physically sorbed moisture is liberated. For low-rank coals such as lignites that contain appreciable carboxylic functions as part of the coal structure, heating will liberate carbon dioxide by thermal decarboxylation. Over 50 percent of the carboxylic acid functions are lost as carbon oxides in the temperature range of 100 to 250°C. As the temperature of thermal treatment increases to the range of 200 to 400°C, coals may lose a number of lower molecular weight organic species (especially aliphatic compounds), which are believed to arise from moieties (components) that are loosely bound to the more thermally stable part of the coal structure. At a higher temperature (375–700°C), depending on the heating rate, thermal destruction of the coal structure occurs, which is reflected by the formation of a variety of hydrocarbons including methane (and other alkanes), polycyclic aromatics, phenols, and nitrogen-containing compounds. In this temperature range, bituminous coals soften and become plastic (thermoplastic) to varying degrees. At a still higher temperature (600–800°C), depending on the heating rate, the plastic mass undergoes repolymerization reactions, forming semicoke (solid coke still containing significant volatile matter). At temperatures exceeding 600°C, semicoke hardens to form coke with the evolution of methane, hydrogen, and traces of carbon oxides. Pyrolysis of coal is essentially complete at approximately 1000°C. The temperature at which the maximum devolatilization rate occurs depends on the heating rate. For a slow heating rate (about 5°C/sec), the maximum occurs around 400°C, whereas for a rapid heating rate (about 10°C/sec), it might occur at 900°C.[18] Soaking coal at the final temperature normally would increase the yield because decomposition of char is a relatively slow process.

Since the changes and reactions described above do not occur at sharply defined temperatures, it is to be expected that heating rate will have a marked effect on the nature and distribution of pyrolysis products resulting from a given process. The general situation is as shown below:

Temperature	*Changes/Reactions*
100°C	Physically sorbed water is liberated.
100–250°C	Thermal decarboxylation of low-rank coals liberates CO_2.
200–400°C	Lower molecular weight organic species, especially aliphatic compounds, are lost.
375–700°C	Thermal destruction of coal structure occurs; there is formation of methane and other alkanes, polycyclic aromatics, phenols, and nitrogen-containing compounds.
1000°C	Pyrolysis is essentially complete.

Solomon and coworkers conducted extensive work on the kinetics of coal devolatilization, and many reviews are available.[19]

Coal Type. The type of coal utilized strongly influences its pyrolysis behavior. Low-rank coals (e.g., lignites) contain oxygen functional groups that evolve upon pyrolysis, primarily as water and oxides of carbon. The high-rank bituminous coals contain lesser amounts of oxygen; consequently, these coals produce significantly lower volumes of water and carbon oxides than hydrocarbon gases (primarily tars) when pyrolized. The nature of the tar produced also is dependent on coal rank. Bituminous coal tars tend to be more aromatic in nature (and relatively more thermally stable) than the tars generated from lignites. The type of coal pyrolyzed also determines its physical behavior when pyrolyzed. When heated, bituminous coals soften, become plastic, and swell to varying degrees. Lower-rank coals generally do not become plastic. However, at rapid heating rates (about 10°C/min) or at elevated gas pressure, certain lower-rank coals may melt and demonstrate some plastic and swelling characteristics.

Other Factors. Several other factors influence the nature of the pyrolysis process and the direction it takes, some to a lesser extent and others to a greater extent. These include the size of the coal particles, size and configuration of the coal bed, pressure (or vacuum) under which the process is operated, presence of various inorganic materials in the coal, secondary reactions, and others.[86] Although it is beyond the scope of this chapter to consider these items, interested readers can find additional information in the literature. These sources include reports on pressure effects,[15,20] effects of vacuum,[17] effects of inorganics,[21,86] and a potentially reactive gas atmosphere.[17,22]

Pyrolysis Products: Utilization and Characterization

Efficient utilization of all generated solid, liquid, and gaseous products is vital for the overall process economics of a pyrolysis system. A number of viable alternatives can be considered for utilization of these products, some of which are discussed below. The generated products may require varying degrees of treatment before they become usable. For example, the stream exiting the pyrolyzer unit will require separation of gas, liquid, and particulates. The unit operations (e.g., hot dust removal cyclones, quench/particulate scrubber towers, and venturi scrubbers to remove tar mist) required for separation may be similar to those used for a fixed-bed gasifier (e.g., cold gas cleanup). The gas stream may require, depending on its end usage, a sulfur removal process. In addition, a pyrolysis plant also will require processes for wastewater treatment. Finally, environmental factors such as toxicology of the coal pyrolysis liquids (CPL) need to be considered. Mutagenicities of CPL are strongly dependent on the conditions of pyrolysis (e.g., temperature, coal type, and gas atmosphere).

Tar Utilization. Markets tend to have product specifications of various liquid fuels that do not vary widely. However, the characteristics of CPL can vary greatly, depending on the coal type and the operational conditions chosen. In general, the H/C (atomic) ratio for CPL is lower than that for various petroleum feedstocks. This ratio varies from 1.8 to 1.9 for No. 2 fuel oil, and from 1.7 to 1.8 for No. 6 fuel oil. In comparison, the H/C (atomic) ratio for CPL ranges from 0.9 to 1.5. In addition, CPL appear to be significantly more aromatic (e.g., 50–70%) than petroleum-based fuels.

The uses of CPL can be crudely divided, for convenience, into two broad categories: (a) direct combustion applications (uses that do not require extensive upgrading), and (b) transportation fuels and chemicals (uses requiring upgrading, extensive processing, or both). Because of the high aromaticity of CPL, one may consider converting them into gasoline (high proportion of branched-chain alkanes and lighter aromatics) rather than diesel (straight-chain alkanes with heavier aromatics). A lot of attention in low-temperature tar processing was devoted to hydrogenative techniques (hydrotreating, hydrocracking, or both). The primary objectives have been to: (a) reduce viscosity, (b) reduce the polynuclear aromatics content, and (c) remove heteroatoms (sulfur, nitrogen, and oxygen) in converting these tars into usable fuels and chemicals.

The cost of H_2 still is the primary impediment in tar upgrading. Low-temperature tars can be used as chemicals: phenols and phenolic chemicals, road tars, preservatives, and carbon binders, to name a few. These usages, however, do not constitute a large-enough market in themselves to support a major industry.

Char Utilization. Char produced in the pyrolysis process can have a range of applications to offset the cost of producing liquid fuels. One obvious application is on-site combustion to generate heat for the pyrolysis process itself. Alternatively, chars can be used for combustion in electric power plants. Char can also be gasified to produce hydrogen for use in the pyrolysis plant if the process requires hydrotreatment (e.g., tar upgrading or hydropyrolysis). Other applications include production of activated carbon and molecular sieves.

In general, the volatile matter content of char is significantly lower than that of the parent coal. It was demonstrated, however, that the reactivity of several low-temperature chars (prepared at 500°C) was greater than that of the parent coal.[23]

Economic and Process Considerations

Using current coal technology, coal pyrolysis can produce liquid fuels that are potentially directly usable as fuels, or fuels that can be upgraded for such uses. However, it does not appear to be economical at present to produce solely liquid fuels as a substitute for their petroleum counterparts. Plant designs for coal pyrolysis projects aimed solely at this purpose generally require more sophisticated processing steps than their petrochemical counterparts to produce liquid hydrocarbons that can meet required specifications, while at the same time minimizing waste production. Steps involving upgrading and refining of tars by hydrogenation and hydrocracking to produce premium fuels require massive amounts of expensive hydrogen. These costly endeavors can be justified only in situations where assurances of ample supplies will take precedence over any economic considerations, as was the case in World War II Germany.

The economics of a coal pyrolysis process to cream-off the liquids, utilizing mild conditions (less sophisticated and thus less expensive systems than direct or indirect liquefaction processes) before char is combusted or gasified, can be quite attractive. A number of process streams can be considered for efficient use of all generated solid, liquid, and gaseous products. For example, chars can be sold to offset the production costs of pyrolysis liquids. The gases produced can be combusted to supply the heat generated for the pyrolysis process.

COAL UTILIZATION-GASIFICATION

History

Coal gasification is an old, established technology that has been rediscovered and is gaining favorable interest. A large number of coal gasifiers operated commercially in this country and in Europe to produce industrial and residential fuel gas during the last and the early part of this century. By the mid-1950s, however, the availability of inexpensive natural gas and petroleum had led to the abandonment of most coal gasification processes.[93]

In the years since 1973, the price of petroleum has increased. In addition, the capability of integrated gasification combined cycle power plants to effectively compete with direct coal combustion for electric power generation has significantly increased the attractiveness of coal gasification.

Coal was first gasified in England by William Murdock in 1792, and the world's first coal gas company was chartered in England in 1812. Coal gas was first produced in America in 1816 in the city of Baltimore. However, by 1850, over 55 commercial coal gasification plants were generating gas for lighting and heating in the United States. In the early 1930s there were over 11,000 coal gasifiers operating in the United States, consuming about 12 million tons of coal and producing 500 million Btu/day of coal gas. Most of the early gasifiers were moving-bed units operating with sized coal charged with steam and air to produce a "product gas" (150 Btu/scf). Operation of the moving-bed gasifier in a cyclic mode (blowing the gasifier first with air, followed by steam to gasify) increased the heating value of the product "water gas" to 300 Btu/scf. Coke oven gas was used as "town gas," while co-firing of oil with water in the moving bed process produced "carburetted water gas."

Coal gasification plants continued to be built on a limited scale in certain areas of the world including the United States, Europe, and countries with a limited supply of petroleum. Extensive large-scale development work was done in the United States in the late 1940s to mid-1950s, including: (a) development of a 100 ton/day Texaco entrained-flow gasifier at Morgantown, West Virginia, by Texaco and Olin Matheson; (b) demonstration of a 360 ton/day Babcock and Wilcox entrained gasifier at Belle, West Virginia; (c) development of a 24 ton/day Koppers-Totzek entrained gasifier at Louisiana, Missouri.

During the 1950s and 1960s a significant contribution to domestic energy use was made by coke oven gas, which is roughly similar to the gas generated in moving-bed gasifiers.

New interest in coal gasification since 1973 has led to a number of large-scale demonstration projects for the following processes:

- Texaco
- British Gas Lurgi/Slagger
- Kilngas
- Shell and Dow gasifiers

Development of these coal gasification processes assures the potential for coal gasification technology.[94]

Reaction Fundamentals

The initial steps in a coal gasification process involve grinding and/or pretreatment of the coal. In a gasifier, the coal is heated in the presence of reactive gases whose composition depends on the product desired. The first event that occurs in the gasifier is pyrolysis or devolatilzation. Walker[24] has presented extensive reviews of gasification reaction fundamentals.

During gasification, coal undergoes some or all of the following reactions/changes:

- Pyrolysis (devolatilization)
- Char–oxygen reaction
- Char–CO_2 reaction
- Char–H_2O reaction
- Char–H_2 reaction

In the manufacture of synthetic natural gas, all of the above reactions occur to varying degrees; however, in synthesis gas (CO/H_2 mixtures) production, the char–H_2 reaction is suppressed.

Coal char can resemble graphite, depending on the conditions under which it is formed. Coal-char gasification systems generally are bounded by equilibria obtained by considering the carbonaceous solids to be equivalent to graphite. Therefore, it is common to consider char as similar to graphite in a thermodynamic sense.

Char formed in pyrolysis has a higher degree of crystallinity than the starting coal but is significantly less ordered, in terms of crystallinity, than graphite. In the case of the latter, the carbon atoms located at the edges of crystallites have unpaired sigma electrons that are most susceptible to reaction. The concentration of active edge sites depends on crystallite size and concentration of defects such as vacancies and dislocations. In the case of coal chars, the concentration of defects depends on the coal type and pyrolysis conditions. In general, bituminous coal chars have lower active site concentration and thus lower reactivity.

Heteroactoms such as O, N, and S can play a role during gasification. Hydrogen sites are presumed to increase char reactivity by preferential oxidation with subsequent production of nascent carbon active sites of high activity. Nitrogen and sulfur also could encourage ring attack owing to concentration of pi electrons.

The pore structure can markedly affect char reactivity. Most coals in general, and coal chars in particular, are highly porous and contain a polymodal pore size distribution. Pores normally are classified into macropores (>500 Å in diameter), transitional pores (20–500 Å in diameter), and micropores (<20 Å in diameter). Upon pyrolysis, pores in coals open up but still contain microporosity. Coal chars, in general, and lignitic chars, in particular, retain the polymodal pore distribution. The surface areas of coal chars can range between 100 and 800 m^2/g. Most of this surface area and therefore the active surface area resides inside the char particles; so the accessibility of the reactive gases to the active sites is very important.

The fundamental reactions involved during gasification can be described by the Langmuir-Hinchelwood mechanism and the Rideal-Eley mechanism. The Langmuir-Henshelwood mechanism involves three different steps: (a) adsorption of the gas onto the solid surface; (b) surface reaction/migration; (c) desorption of the product species from the solid surface. In the Rideal-Eley mechanism, the basic steps involved are: (a) reaction between the gas molecular and surface atoms by direct collision; (b) desorption of formed product(s).

These mechanisms describe the intrinsic reaction rate, which would be the upper limit of the achievable gasification rate. The actual gasification rate in a gasifier would be equal to or lower than the intrinsic rate. Determination of the intrinsic reaction rate for pure carbon, in general, and coal chars, in particular, currently is not possible because nearly all coal chars and most carbons are ill-defined and/or impure.

Because coal chars are highly microporous, most of the gasification reaction take place inside the char particles. Therefore, they require diffusion of gas into and diffusion of products out of the porous particles. The overall diffusion process can be described by the following steps: (a) diffusion of reactant from the bulk gas to the solid surface (film diffusion); (b) diffusion of reactant from the surface to the interior (internal diffusion); (c) diffusion of product from the interior to the surface (internal diffusion); (d) diffusion of product from the surface to the bulk gas (film diffusion).

Film diffusion coefficients normally are large and have very low temperature dependency ($T^{0.5-1.5}$). Internal diffusion coefficients can be activated (for pores 5–7 Å in diameter with E_{act} of about 5 to 10 kcal) or nonactivated. For pores in the transitional size range, internal diffusion is of the Knudsen type with a low temperature dependency ($T^{0.5}$).

One can calculate the rates of internal and film diffusion if the pore diameter and process conditions are well defined. The temperature dependency of the rate can be presented in the form of an Arrhenius plot (i.e., log rate versus reciprocal temperature). Gasification rates can be divided into three zones, I, II, III, depending on various flow and diffusion condition. To determine the overall gasification rate in a gasifier when gas diffusion controls the overall rate, it is necessary to model the actual gasifier.

C–O_2 Reaction. This is the most common and the fastest gasification reaction and is highly exothermic. The primary reaction products, as shown below, are CO and CO_2:

$$C_s + O_2 = CO_2 \qquad -94.1\ \text{kcal/gmole}$$

$$C_s + 0.50_2 = CO \qquad -26.45\ \text{kcal/gmole}$$

The equilibrium constants, K_p, for both reactions are >1 up to 3500°C, and, as a result, both reactions are essentially irreversible up to 3500°C. The CO/CO_2 should increase with lower pressure and high temperature, as pressure does not influence the equilibrium of the first reaction, and the forward reaction (second reaction) is not favored under pressure.

The postulated elementary reactions for the carbon–oxygen reaction are:

$$2C_f + O_2 \rightarrow 2C_f(O)$$

$$C_f(O) \leftrightarrow C_{fs}(O)$$

$$C_f(O) \rightarrow CO$$

$$C_f(O) + C_f(O) \rightarrow CO_2 + C_f$$

In the above, C_f stands for a free active site, $C_{fs}(O)$ represents a stable oxygen surface complex, and $C_f(O)$ is a transient oxygen surface complex.

Above 2300°K the reaction gas dissociates very quickly, but above 1700°K the active sites are quickly annealed. Thus the reaction rate increases with temperature (the exception being between 1700 and 2300°K).

C–H_2O Reactions. The carbon-steam reaction is an endothermic reversible reaction:

$$C_{(s)} + H_2O \leftrightarrow CO + H_2 \qquad 31.4\ \text{kcal/gmole}$$

Mechanism I:

$$H_2O + C_f \leftrightarrow H_2 + C(O)$$

$$C(O) \rightarrow CO + C_f$$

Mechanism II:

$$H_2O + C_f \rightarrow H_2 + C(O)$$

$$C(O) \rightarrow CO + C_f$$

$$C_f + H_2 \rightarrow C_f(H_2)$$

The following presents the rate expression based on either mechanism:

$$\text{Rate} = \frac{A \cdot P_{H_2}O}{1 + B \cdot P_{H_2} + C \cdot P_{H_2O}}$$

In the above expression, A, B, and C are constants, and P_{H_2O} and P_{H_2} are partial pressures of H_2O and H_2. The reaction rate is not favored by high pressure. Both H_2 and H_2O inhibit the reaction.

The carbon–steam reaction has a side reaction, called the water–gas shift reaction, shown below:

$$CO + H_2O = CO_2 + H_2$$

This reaction, which is very rapid, is catalyzed by various impurities and surfaces.

CO_2–Solid Reactions. The equilibrium for the carbon-CO_2 reaction is favored at high temperatures and at lower pressures:

$$C_2 + CO_2 = 2CO(g) \qquad 41.2\ \text{kcal/mol}$$

Two mechanisms have been proposed for this reaction:

Mechanism I:

$$CO_2 + C_f \leftrightarrow CO + C(O)$$
$$C(O) \rightarrow CO + C_f$$

Mechanism II:

$$CO_2 + 2C_f \rightarrow C(CO) + C(O)$$
$$C(O) \rightarrow CO + C_f; \quad C(O) \leftrightarrow C_f + CO$$

In mechanism II, CO inhibits by adsorbing onto the active sites. In mechanism I, CO does not adsorb on the active sites, but the reaction is inhibited by CO because of its reaction with the oxygen complex.

Both reaction mechanisms yield a similar kinetic expression for the reaction:

$$\text{Rate} = \frac{A \cdot P_{co_2}}{1 + B \cdot P_{co} + C \cdot P_{co_2}}$$

In the above expression, A, B, and C are constants, and P_{co} and P_{co_2} are partial pressures of CO and CO_2. The reaction rate becomes significant above 900°K. Chemisorption of CO_2 on carbon occurs even at 625°K. H_2 strongly inhibits the reaction, presumably by adsorbing on the active sites.

Types of Coal Gasifiers

All gasification processes can be separated into three generic types of reactors: (a) moving-bed or countercurrent reactors; (b) fluidized-bed or back-mixed reactors; (c) entrained-flow reactors (not back-mixed).

Figure 17.14 shows the generic types of gasification reactors together with temperature profiles and locations of reactants and products. Table 17.7 summarizes the important characteristics of each type of gasification process, Table 17.8 presents the overall status of various coal gasification technologies, and Table 17.9 presents the performance characteristics of selected gasifiers on Illinois No. 6, Pittsburgh No. 8, and West Kent coals.

Moving-Bed Gasifiers. Moving-bed gasifiers consist of a downward-moving bed of coal being contacted by upward-flowing gases that move through the bed. The coal sequentially undergoes drying, devolatilization, gasification, combustion, and ash cooling.

In the drying zone at the top of the bed, coal is dried by the upward-flowing hot gases. As the coal moves farther down the bed, its temperature increases, and at about 600 to 900°F pyrolysis occurs, liberating tars/oils and gases. The devolatilized coal, or char, is gasified by reaction with steam, carbon dioxide, and hydrogen to produce a mixture of carbon monoxide, hydrogen, and methane, along with unreacted steam and carbon dioxide, as char descends farther through the gasifier. The final composition of the gases produced and the rates of the reactions are strongly influenced by the gasifier temperatures and pressure of operation, as discussed above.

The peak temperature within the gasifier (occurs in the combustion zone) is controlled by the relative proportions of steam and oxygen (air) added to the gasifier. If dry ash is desired, sufficient steam is added to offset the exothermic oxidation reactions with endothermic steam–carbon reactions and to maintain temperatures in the combustion zone safely below the ash-fusion temperature. Slagging gasifiers operate at higher temperatures and remove ash in a molten state.

Moving-bed gasifiers require sized coal for proper operation; typically coal between $\frac{1}{4}$ inch and 2 inches in diameter is used. The countercurrent flow of gases and solids leads to high thermal efficiencies, with exit gas temperatures usually in the range of 500 to 1000°F. The raw product gas contains fines

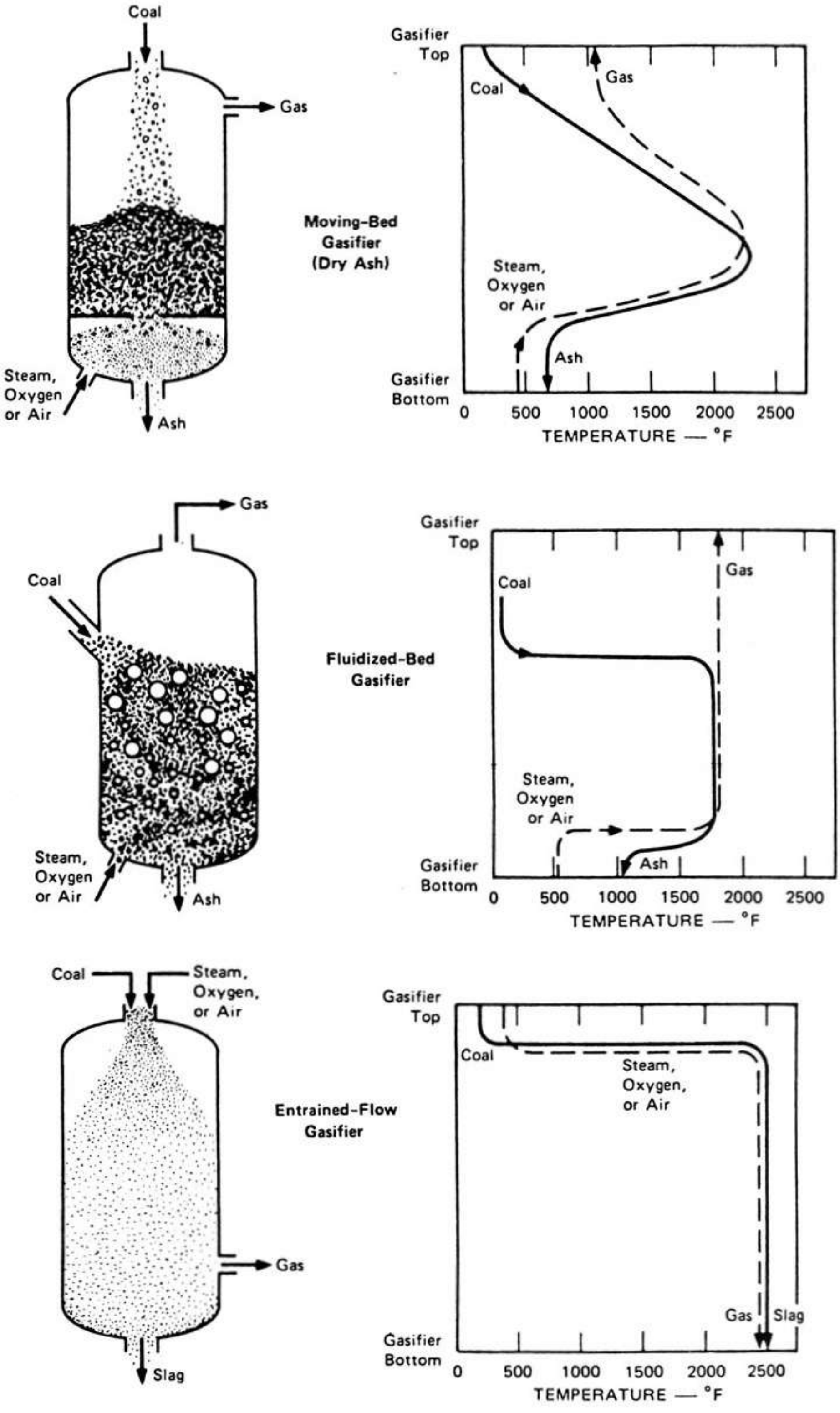


Fig. 17.14. Generic coal gasification reactors. (*Source: Electric Power Research Institute and Synthetic Fuels Associates, Inc.*)

TABLE 17.7 Features of Fixed-Bed, Fluidized-Bed, and Entrained-Bed Gasifiers

	PARAMETERS	
Moving Bed	*Fluidized Bed*	*Entrained Bed*
Gravitating moving bed of coal.	Fluidized beds arranged in one or more zones.	Up flow or down flow suspension gasifications.
Mechanical grates/distributors.	Uniform temperature and compositions throughout each fluidized zone.	High temperature–high rate process.
Discrete zones: • Preheating-drying devolatilization • Gasification • Combustion	Moderate process response.	Fast process response.
	ADVANTAGES	
Moving Bed	*Fluidized Bed*	*Entrained Bed*
High carbon conversion efficiency.	High degree of process uniformity.	Handles all types of coal—no pretreatment.
Low ash carryover.	Excellent solids/gas contact.	Low steam consumption.
Low-temperature operation.	Lower residence time than fixed bed gasifier.	Excellent solids/gas contact.
Lowest air/oxygen requirement.	Higher coal throughput per unit volume of reactor.	No tar formation.
		No phenol formation.
		Ability to slag ash.
		High capacity per unit volume of reactor.
		Produces inert slagged ash.
	DISADVANTAGES	
Moving Bed	*Fluidized Bed*	*Entrained Bed*
Sized coal required.	Sized coal required.	Requires finely crushed coal.
Coal fines must be briquetted.	Dry coal required for feeding.	Small surge capacity requiring close control.
Low offgas temperature.	Requires complicated gas distributor.	

and tar/oil produced during gasification. These materials are removed prior to downstream processing.

Moving-bed gasifiers can be operated at atmospheric pressure or can be pressurized: with either air or oxygen as the oxidant; with either dry ash or molten ash removal; with or without stirrers to prevent agglomeration.

Figure 17.15 illustrates the mechanical configuration for a Lurgi gasifier, and Table 17.10 shows the characteristics of several moving-bed gasifiers.

Fluidized-Bed Gasifiers. In a fluidized bed gasifier, reactant gases are introduced through a distributor at the bottom of the bed at velocities sufficient to suspend the incoming particles. The result is a bed of highly mixed solids in intimate contact with the gas phase. The agitation leads to uniform temperatures throughout the bed, and the high degree of mixing results in reaction rates that are generally higher than those experienced in moving-bed gasifiers. Fluidized-bed gasifiers generally do not achieve the high thermal efficiencies associated with moving-bed gasifiers.

Exit gas temperatures for fluidized-bed gasifiers usually are higher than those for moving-bed gasifiers. Therefore, the product

TABLE 17.8 Status of Various Gasification Technologies

Gasifier	*Project or Company*	*Location*	*Coal Throughput, tonnes/day*	*Product (final)*	*Start-up*
2nd generation gasification plants in commercial operation					
Texaco	Tennessee Eastman	Tennessee, USA	820	methanol	1983
Texaco	Cool Water	California, USA	910	IGCC	1984
Texaco	Ube Industry	Ube, Japan	1500	ammonia	1984
Texaco	Ruhrkohle/Ruhrchemi	Oberhausen, FRG	1720	oxo chemicals	1986
HTW[1]	Kemira Oy	Oulu, Finland	600	ammonia	1988
2nd generation gasification plants in demonstration operation					
Ruhr 100	Ruhrgas	FRG	100–200	fuel & synthesis	1979
BG/Lurgi	British Gas	Westfield, UK	500	fuel & synthesis	1984
Kiln Gas	Allis-Chalmers	Illinois, USA	540	fuel gas	1983
U-Gas	IGT	Chicago, USA	27	fuel & synthesis	1974
KRW[2]	Kellog-Rust-Westinghouse	Pennsylvania, USA	14–27	fuel gas	1975
HTW	Rheinbraun	Berrenrath, FRG	720	methanol	1985
VEW[3]	VEW	Dortmund, FRG	240	fuel & synthesis	1985
PRENFLOW[4]	Koppers-Totzek	Furstenhausen, FRG	48	fuel & synthesis	1986
Shell	Shell	Texas, USA	230–260	fuel & synthesis	1987
Dow	Dow	Louisiana, USA	2200	IGCC	1987
Saarberg-Otto	Saarberg-Otto	Furstenhausen, FRG	260	fuel & synthesis	1979
MIP[5]	Humboldt/Sumitomo (MEFOS)	Lulea, Sweden	240	fuel & synthesis	1986
2nd generation gasification plants under construction or planned					
NEDO[6]	NEDO	Chiba, Japan	20–50	hydrogen	1991
NEDO	NEDO	Iwaki, Japan	200	IGCC	1991
KRW	Appalachian project	Pennsylvania, USA	440	IGCC	1990
U-Gas	CCC-FWPSC	Virginia, USA	450	IGCC	1990

Acronyms:

1. HTW: High Temperature Winkler.
2. KRW: Kellogg-Rust-Westinghouse.
3. VEW: Vereinigte Elektrizitatswerke.
4. PRENFLO: Pressurized Entrained Flow Gasification.
5. MIP: Molten Iron Pure Gas.
6. NEDO:New Energy and Industrial Development Organization Japan.

Source: Takematsu, T., and Maude, C., "Coal Gasification for IGCC Power Generation," International Energy Agency, IEA CR/37, Mar. 1991.

gas contains much lower levels of tar/oil produced during pyrolysis. Particle attrition in the gasifier, however, generally leads to higher levels of fine/dust carryover. Particles and ash are removed in fluidized-bed systems as dry solids. Pretreatment of coal is required to handle strongly caking coals.

Fluidized-bed gasifiers can be operated at atmospheric pressure or pressurized. Fluidizing gases can be mixtures of steam with either air or oxygen and, in some cases, mixtures of hydrogen with other gases.

Table 17.11 summarizes the characteristics of several fluidized-bed gasifiers presently under development, as well as the Winkler gasifier, which is commercially available. There are several Winkler gasifiers at various installations worldwide, and the largest unit processes 650 tons of coal/day. The Winkler gasifier is illustrated in Fig. 17.16.

Entrained-Flow Gasifiers. Entrained-flow gasifiers consist of finely ground coal entrained in a flow of reactant gases. Contact between

TABLE 17.9 Performance Characteristics of Selected Gasifiers on Illinois No. 6, Pittsburgh No. 8, and West Kent Coals*

Parameters	*Lurgi dry ash*	*Lurgi slagger*	*Texaco*	*Shell*	*KRW (PDU, TP-034-2)*	*KRW design estimate*	*U-Gas*
		Illinois No. 6 coal			*Pittsburgh No. 8 coal*		*West Kent coal*
T, °F	1600	2700	2700	3000	1793	1850	1831
p, psia	315	300	600	365	230	600	15
H_2O/coal, mole/mole	2.42	0.298	—	0.027	0.43	0.29	1.34
O_2/coal, mole/mole	0.286	0.259	0.463	0.435	0.44	0.30	0.45
C conversion, %	99.3	99.5	99	99.3	76.0	89.6	93.8
Gas composition (dry)							
CO	15.36	58.05	51.69	61.46	43.38	51.5	26.1
CO_2	31.4	1.94	10.6	1.65	35.30	9.3	23.4
H_2	42.9	30.41	35.1	30.6	18.04	25.9	37.4
CH_4	8.78	7.76	0.09	0.04	1.83	10.4	2.8

*Shinner, R., Fourth Technical Meeting of COGARN, presented in "Coal Gasification: Direct Applications and Synthesis of Chemicals and Fuels: A Research Needs Assessment," by Penner, S. S., and others for US DOE.[25]

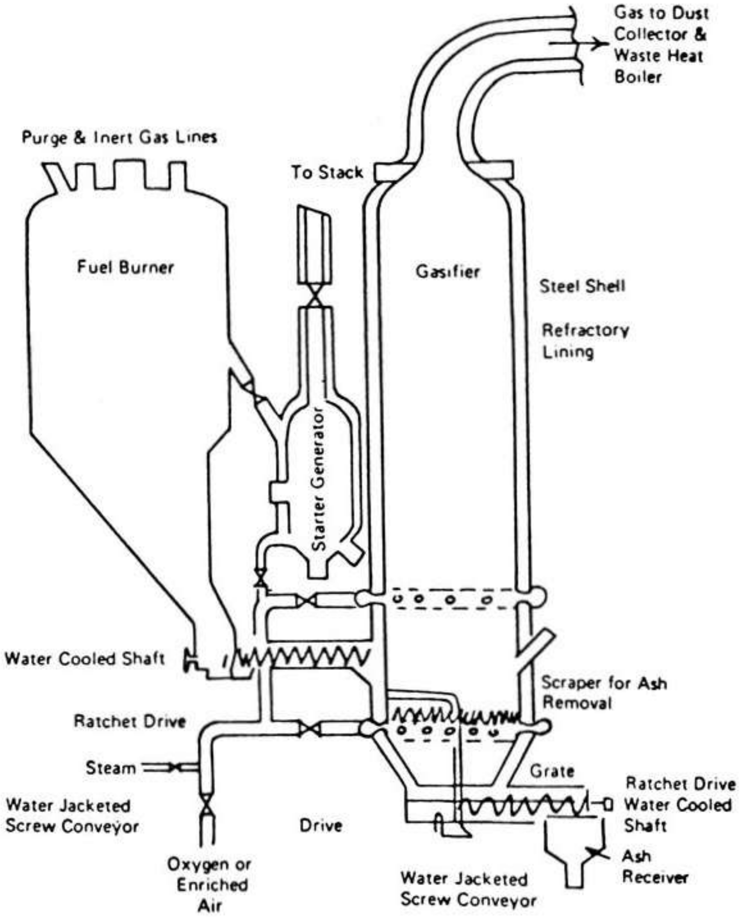


Fig. 17.15. Typical Lurgi gasifier. (*"Comparative Study of Coal Gasification Processes—Koppers-Totzek, Lurgi and Winkler," Koppers Co., Pittsburgh, PA.*)

TABLE 17.10 Characteristics of Moving-Bed Gasifiers

	Operating Pressure	*Oxygen or Air*	*Agglomeration Prevention*	*Status*
		Dry Ash, Single Stage		
GEGAS	To 500 psig	Air	Stirrer paddles	5-ft-diameter test unit
Lurgi	To 450 psi	Oxygen or air	Rotating blades	Commercial
MERC	to 105 psi	Air	Spiraling stirrer	42-in.-diameter test unit
Riley-Morgan	40 in. H_2O	Air	Agitator in rotating bed	10.5-ft test unit
Wellman-Galusha	10 in. H_2O	Air	Spiraling arms	Commercial
Wilputte	Atm	Air	Rotating arm	Commercial
		Dry Ash, 2-Stage		
ATC/Wellman (Incandescent)	Atm	Air	None	Commercial
FW/Stoic	Atm		None	Commercial
Ruhr-100	1500 psi	Oxygen	Stirrer blades	3–7 ton/hr test unit
Woodall-Duckham	40 in. H_2O	Air or oxygen	None	Commercial
		Slagging		
BGC/Lurgi	To 400 psi	Oxygen	Stirrer	6-ft-diameter test unit
GFERC	To 400 psi	Oxygen	Stirrer	16-in.-diameter test unit

Source: Bodle, W. W., and Schora, F. C., "Coal Gasification Technology Overview," *Symposium Papers: Advances in Coal Utilization Technology*, pp. 11–34, Institute of Gas Technology, Louisville, KY, May 14–18, 1979.

TABLE 17.11 Characteristics of Fluidized-Bed Gasifiers

	Developer	*Oxygen or Air*	*Pressure*
Winkler	Davy Powergas	Oxygen or Air	ATM
Rheinbraun	Rheinische Braunkohlenwerke	Oxygen	150 PSI
CO_2 Acceptor	Conoco Development	Air	150 PSI
Hygas	IGT/GRI/DOE	Oxygen or Air	1200 PSI
Synthane	DOE/PETC	Oxygen	1000 PSI
Westinghouse	Westinghouse Electric/DOE	Air	225 PSI
U-Gas	IGT/DOE	Oxygen or Air	350 PSI
Cogas	Cogas Development Co.	Air	10 PSIG
Catalytic	Exxon	None	500 PSI

Source: Bodle, W. W., and Schora, F. C., "Coal Gasification Technology Overview," *Symposium Papers: Advances in Coal Utilization Technology*, pp. 11–34, Institute of Gas Technology, Louisville, KY, May 14–18, 1979.

the solids and gases is cocurrent, with little or no batch-mixing occurring. This type of gasifier may be either single-stage or two-stage.

In general, high temperatures, 2200 to 3200°F, are used to completely gasify the coal in mixtures of steam and oxygen (air). Because of the high temperatures employed, gasification rates are considerably higher than those achieved with either fixed-bed or fluidized-bed gasifiers. These gasifiers can handle all coals, including those that are strongly caking, without pretreatment. The high temperatures of operation produce a gas devoid of both methane and tars/oils. Two-stage gasifiers are those in which the incoming coal first is entrained with reactant gases to produce gas; the resultant char is gasified further in a second stage, which may or may not be entrained. As is the case with fluidized-bed

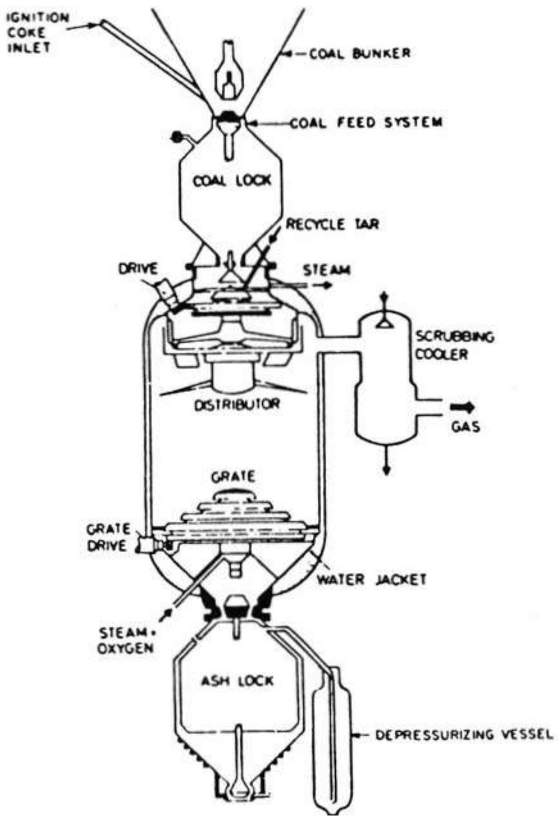


Fig. 17.16. A Winkler gasifier. (*"Comparative Study of Coal Gasification Processes—Koppers-Totzek, Lurgi and Winkler," Koppers Co., Pittsburgh, PA.*)

gasifiers, stage operation enables better overall thermal efficiencies to be achieved without sacrificing higher gasifier throughputs, as the more reactive incoming coal can be gasified at lower temperatures than the less reactive chars. Entrained-flow gasifiers can be operated at atmospheric pressure or pressurized, and ash may be removed either dry or molten.

GASIFICATION FOR POWER GENERATION

Numerous studies confirm that gasifiers coupled with gas turbine/steam turbine combined cycles represent one of the most promising technologies for future coal-based power generation systems. Integrated Gasification Combined-Cycle (IGCC) technologies offer the potential for high electrical conversion efficiencies and economies of scale, which can be achieved in sizes below 1000 MW.

Compared to coal-combustion plants, IGCCs have lower capital and operating costs, resulting in lower net electricity costs. High reliability and low capital/operating costs (and minimal environmental impacts) are requirements for gasification systems proposed for utility applications. Operating costs can be minimized with a gasifier that is capable of operating on run-of-the-mine coals, including caking coals as well as fines. The gasifier should achieve high thermal efficiencies and high carbon utilization.

High efficiencies are obtained in the combined-cycle operation because efficient combustion turbines are combined with steam turbines. The gas turbine converts high-temperature (2300°F) heat efficiently, while the steam turbine utilizes low-temperature heat efficiently in the form of steam (1050°F).

Environmental impacts are minimized if the gasifier is designed and operated in such a

TABLE 17.12 Design and Actual Performance for the CW CGP*

Performance Parameter	*Design*†		*Actual Performance*	
			Illinois	*Pittsburgh*
Coal type	*SUFCO*	*SUFCO*	*No. 6*	*No. 8*
Sulfur content (wt%)	0.48	0.4	3.1	2.9
HHV (Btu/lb)	12,300	12,300	12,800	13,700
Coal-feed rate (TPD)	1000	1000	1000	1000
Oxygen consumption (TPD)	962	908	885	979
Gross power production (MWe)	114	116	120	125
Byproduct sulfur produced (TPD)	4.6	3.8	30	27
Coal/water slurry concentration (wt% solids)	60	60	64	62
Carbon conversion (%)	98.3	98.3	96.6	99.1
Gasifier/syngas cooler efficiency (%)	90.3	91.5	88.5	91.6
Gasifier refractory life (yr)	1.0	2.6	1.1	‡
Overall heat rate (Btu/kWh)§	11,500	11,300	12,000	11,600
Efficiency (%)	29.7	30.2	28.4	29.4

†Design parameters based on SUFCO coal.

‡Data not yet available.

§The heat rates were not optimized and are expected to be reduced by ~2500 Btu/kWh in future plants.

*"Coal Gasification: Direct Application and Synthesis of Chemicals and Fuels; A Research Needs Assessment," by Penner, S. S., and others for US DOE, Office of Energy Research; prepared under contract No. DE-AC01-85ER30076, NTIS-PR-360.[26]

way that tars are not formed. Low pollutant emission levels result from the combustion of a clean fuel. Pollutants are removed before combustion by using gas purification systems. Ash leaving the system should be in a benign form for disposal. On balance, coal gasification systems are environmentally superior to other alternative coal utilization technologies and will meet rigorous environmental standards for sulfur, nitrogen, and particulates.

A well-designed IGCC system can accept many types of feedstocks including lignites and petroleum coke. Gasification systems may be configured to produce other industrial chemical products, which adds flexibility. Table 17.12 presents design and actual performance data for the Cool Water Coal Gasification Process, which operated in the IGGC mode for five years.

Descriptions of Gasification Processes

General Electric Moving Bed. General Electric is operating a one-ton-per-hour, air-blown, advanced moving-bed gasifier in Schenectady, New York. The unit operates at 300 psig and is equipped with a mechanical stirrer to enable caking coals to be gasified. The fact that the volume of coal in the gasifier at any time is large compared to the steam and air injection rates allows considerable flexibility in handling feed interruptions. Figure 17.17 shows a diagram of the GE moving-bed gasifier.

Rotary-Kiln Gasifier. The rotary-kiln gasifier developed by the Allis-Chalmers Corporation consists of a tumbling bed of solids moving countercurrently to the flow of hot gases (Fig. 17.18). Reaction zones in the kiln parallel those in a moving-bed gasifier with the coal sequentially dried, devolatilized, gasified, and combusted. Steam and air are injected into the kiln through ports located beneath the tumbling solids. Although rotary kilns are commercially available, the gasifier is still in the development stage with a 600 ton/day demonstration plant being planned.

Westinghouse Fluidized-Bed Gasifier. Westinghouse has successfully operated a 15 ton/day air (or oxygen)-blown, fluidized-bed gasifier (Fig. 17.19). The untreated coal

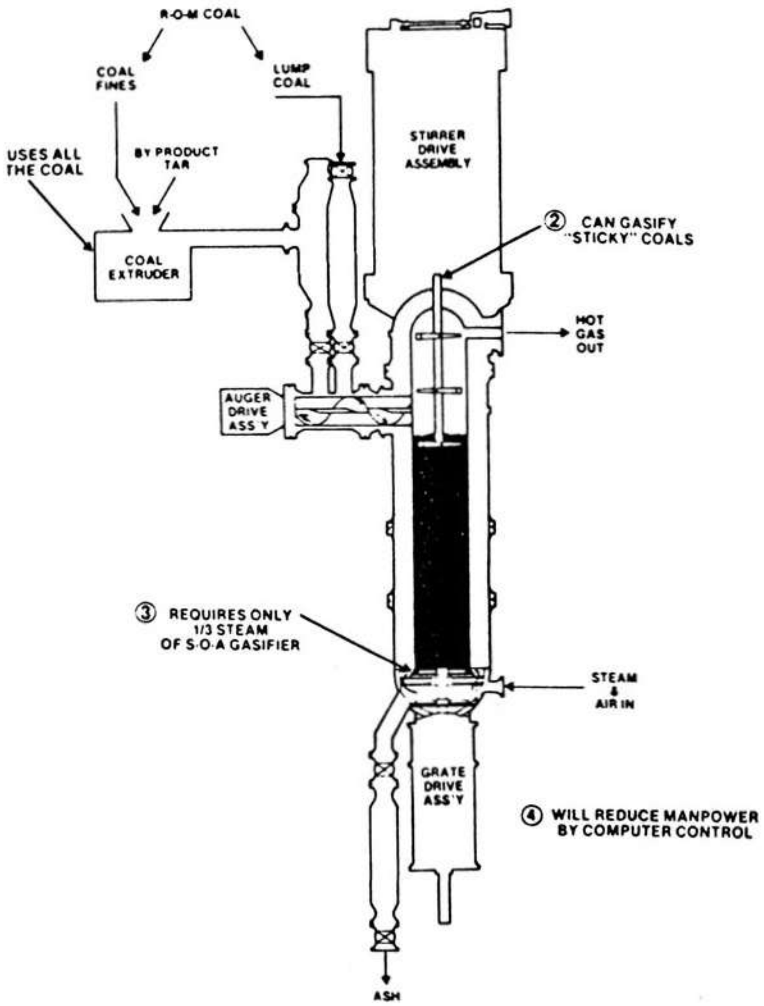


Fig. 17.17. General Electric GEGAS-D advanced gasifier. (*Courtesy General Electric Co.*)

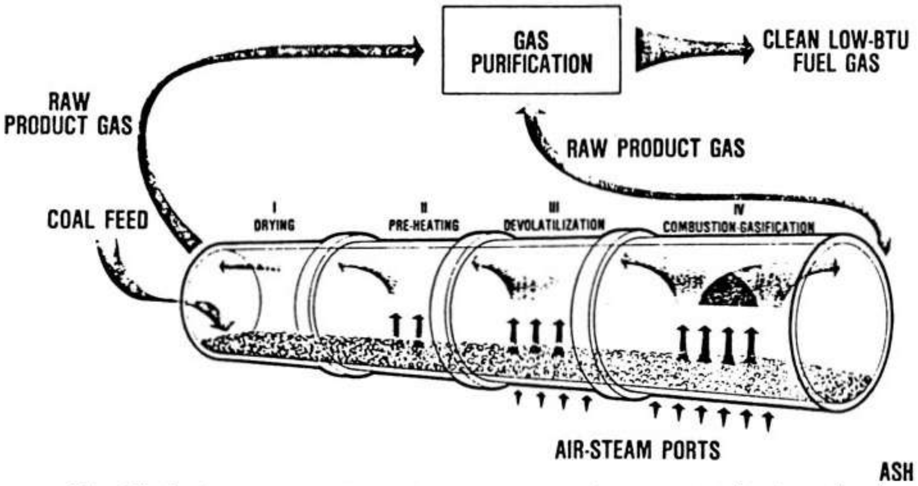


Fig. 17.18. Rotary ported kiln gasification process. (*Courtesy Allis-Chalmers Corp.*)

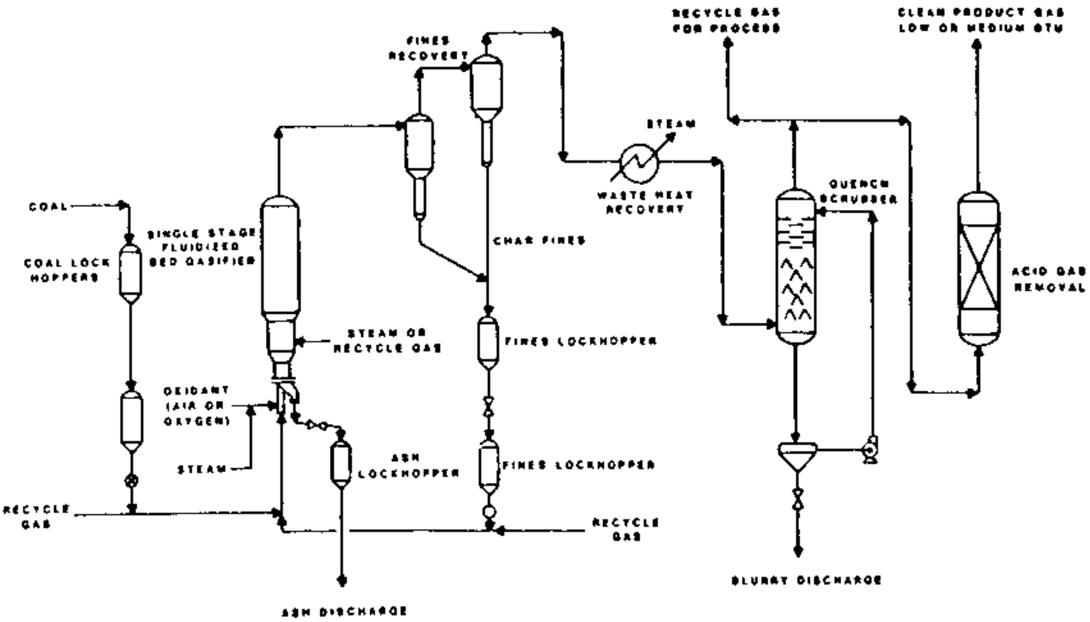


Fig. 17.19. Westinghouse pressurized fluidized-bed gasification system. (*Courtesy Westinghouse Electric Corp.*)

is fed to the gasifier where it is combusted in a stream of air or oxygen through the central feed tube. Steam fed with the air or oxygen and in the grid zone of the gasifier reacts with the coal and char to form hydrogen and carbon monoxide. As the bed of char circulates through the jet, the carbon in the char is consumed, leaving particles that are rich in ash.

Texaco Coal Gasification Process. The Texaco process (TCGP) offers the following design features: downward-loading, pressurized entrained-flow slagging reactor; air- or oxygen-blown process; high operating temperatures; flexible feedstocks and products; system coupling for cogeneration. The TCGP is designed to operate at pressures between 20 and 80 atm and temperatures between 1200 and 1500°C. High points in its development history are indicated in Table 17.13. Figure 17.20 shows a direct quench gas cooling configuration for the TCGP. The coal is wet-ground and mixed with water to make a slurry containing from 60 to 70 wt. % solids. The slurry is mixed with oxygen or air in the gasifier burner. By properly adjusting the oxygen/slurry ratio, temperatures are maintained above fluid ash temperatures.

The gases are cooled after leaving the gasifier, either by direct contact with quench water, as in Fig. 17.20, or by passage through a radiative cooler followed by a convection cooler. The former method is preferred when the output is NH_3 or H_2, as the required shift reactor is easily integrated in the quench mode. The cooled gases next go to a scrubber to remove char and ash. The product gases leaving the scrubber contain H_2, CO, CO_2, H_2O, and traces of Ar, N_2, CH_4, H_2S, and COS. Spencer and others have reported on the performance of the TCGP.[27,28]

Various products have been prepared in commercial plants, including H_2, NH_3, fuel gas for electricity generation, and synthesis gas (CO and H_2) for production of methanol and other oxo products.

Any carbonaceous material that can be formed into a concentrated, pumpable slurry can be gasified in this process. For example, petroleum coke is converted to synthesis gas in a 30-ton/day plant in Ube City, Japan,

TABLE 17.13 Development of the TCGP

Owner	*Type of Plant*	*Location*	*TPD*	*Start-up*	*Gas Cooling*	*Product*
Texaco, Inc.	Pilot	California	15	1973	d.q.^{1}	—
Texaco, Inc.	Pilot	California	15	1978	d.q./h.r.^{2}	—
Texaco, Inc.	Pilot	California	15	1981	d.q.	—
RAG/RCH	Demonstration	W. Germany	165	1978	h.r.	Oxo-chemicals
Dow Chemical	Demonstration	Louisiana	400	1979	—	Synthesis gas for electric power
TVA	Demonstration	Alabama	190	1982	d.q.	Ammonia
Tennessee-Eastman	Commercial	Tennessee	900	1983	d.q.	Acetic anhydride
Southern California Edison Co., etc. (Cool Water)	Commercial	California	1000	1984	h.r./d.q.	Synthesis gas for electric power
Ube	Commercial	Japan	1650	1984	d.q.	Ammonia
SAR	Commercial	W. Germany	800	1986	d.q./h.r.	Oxo-chemical/H_2
IHI	Pilot	Japan	15	1989	d.q./h.r.	—
Lntong	Pilot	China	15	1991	d.q.	—
LuNan	Demonstration/ commercial	China	360	1991	d.q.	Ammonia
Shogang	Commercial	China	1100	1993	h.r.	Steel products

*^{1}d.q. = direct quench; ^{2}h.r. = heat recovery.

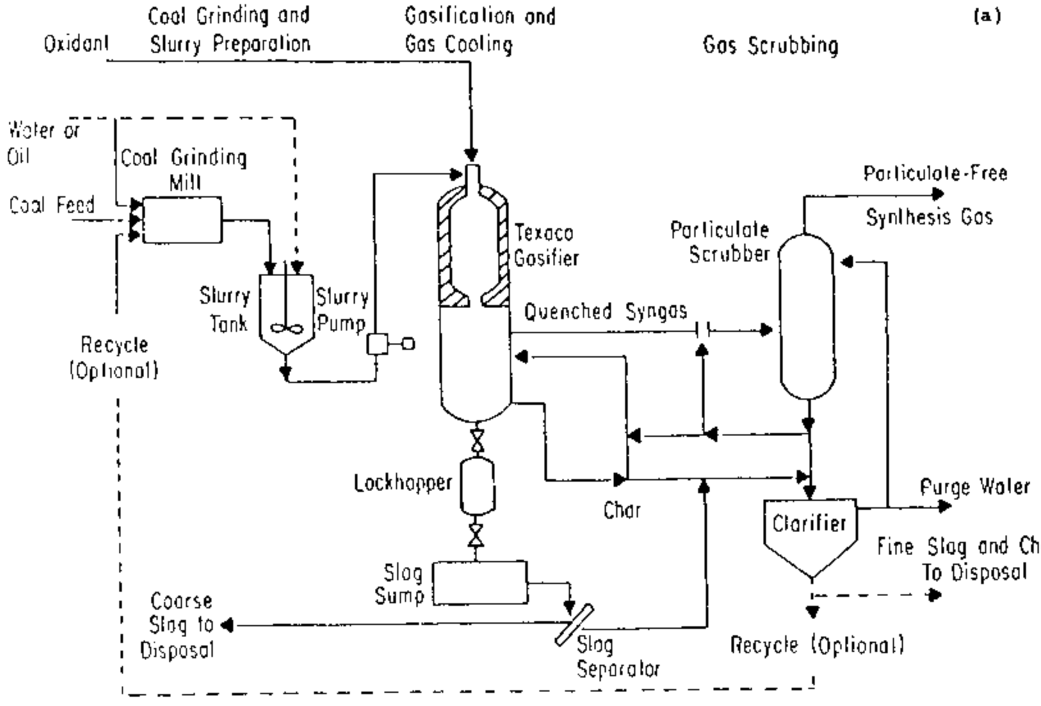


Fig. 17.20. Flow diagram for the Texaco Coal Gasification Process utilizing direct quench of gases leaving the gasifier. (*Courtesy Texaco.*)

which has been operating since 1982. In 1991, a mixture of coal and sewage sludge was successfully gasified.

KBW Process. In the KBW process (Fig. 17.21), powdered coal is entrained with steam and oxygen and, under slight pressure, is fed into the gasifier where gasification at about 2800°F. The slagged ash drops into a water seal, from which it is removed by a continuous scraper conveyor. The high temperature reportedly results in production of a gas mixture rich in the desirable constituents of CO and H_2, with no methane and only limited amounts of CO_2. Characteristically, coal yields a gas of 50 to 55 percent CO and 30

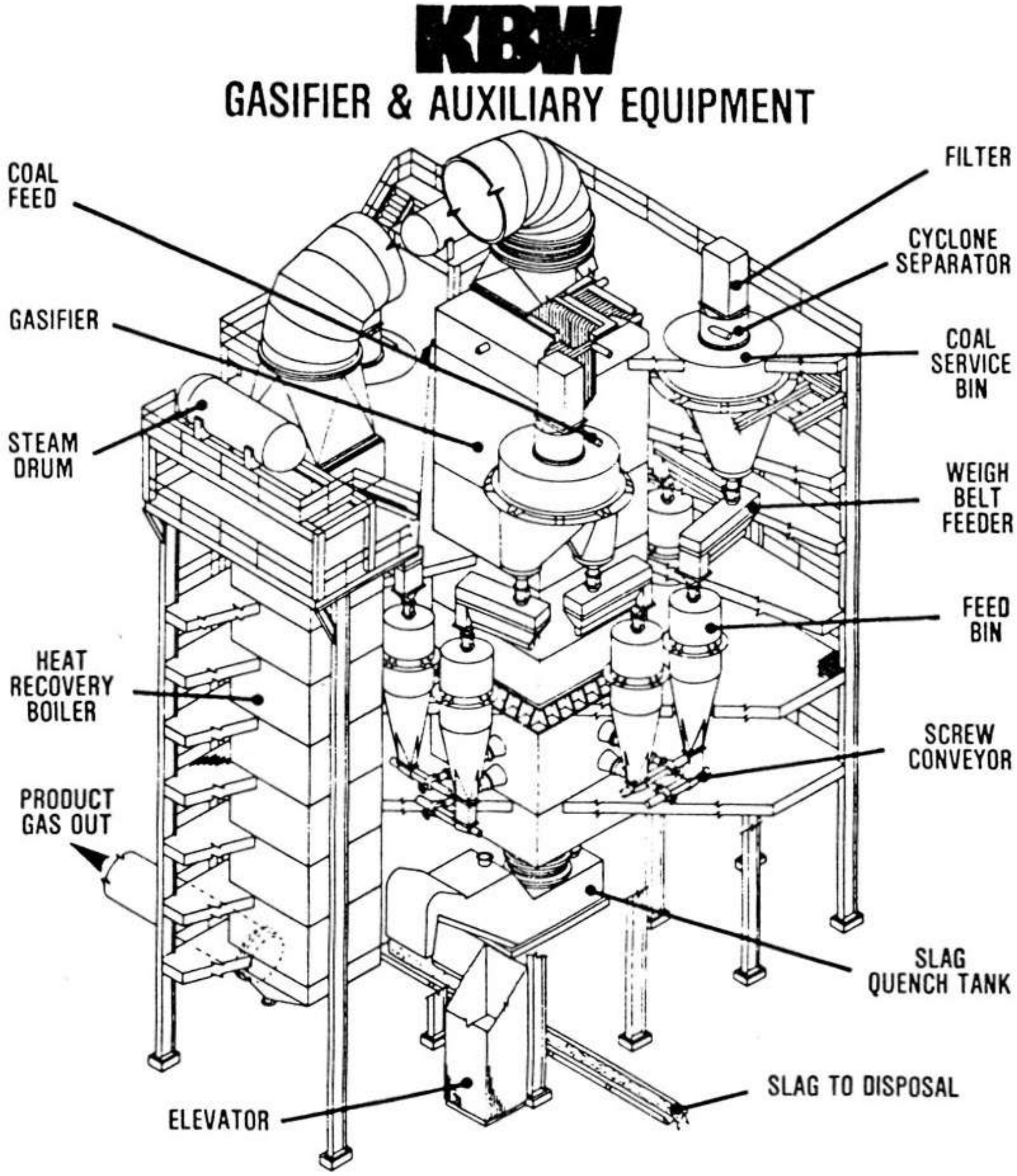


Fig. 17.21. Koppers Totzek gasifier. (*"Comparative Study of Coal Gasification Processes—Koppers-Totzek, Lurgi and Winkler," Koppers Co., Pittsburgh, PA.*)

to 35 percent H_2, on a dry basis. The exit gas is cooled to about 400°F in a waste heat boiler and cleaned to remove particulate matter.

COMBUSTION

In the United States, approximately three-quarters of the annual coal consumption is burned in boilers to generate steam for turboelectric plants in the electric utility industry. On a worldwide basis this figure is closer to one-half. However, the use of coal in small-scale combustion devices for direct heating is significant outside the United States. A summary of the most important direct combustion processes for coal is given in Table 17.14.

The use of coal in combustion processes has drawn increasing criticism from environmentalists because of concerns over its contribution to acid rain (from oxides of sulfur and nitrogen) and global warming (from its high CO_2 production per unit of energy), as well as associated emissions of particulates and trace elements.[31] Despite increasing environmental regulations, which account for about 30 percent of the cost of a new plant, coal is still the fuel of choice for new plants by electrical utilities in the United States.[32] In addition, the amount of coal used for combustion is likely to increase steadily over the next decade in developing countries such as China. The combustion of coal is also important in several eastern European economies, such as Poland. Consequently, there is a strong impetus for development of so-called clean coal technologies that are also highly efficient.

Combustion Technology

Remarkable advances have been made in the energy efficiency of electric utility plans because of improvements in the steam-generating equipment and turbines. A method of expressing the efficiency of the conversion of coal to electricity is the heat rate, which is a measure of the pounds of coal required to generate one kilowatt-hour of electricity. Of course, the heat rate depends on the heating value of the coal, and the numbers usually are based on an assumed value of 12,500 Btu/lb, which is common for a bituminous coal. On this basis the heat rate of a modern, well-maintained plant in 1990 was about 0.7 lb. This is compared to average values of 1.4 lb in 1937 and 0.8 lb in 1968. Some new designs project heat rates close to 0.6 lb of coal per kilowatt-hour, which corresponds to an overall thermal efficiency of 45 percent, based on coal having an as-fired heating value of 12,500 Btu/lb.[33]

Further improvements in thermal efficiency may be achieved with new systems of power generation now being developed. One such technology, known as MHD (magnetohydrodynamics), is expected to have a thermal efficiency of between 50 and 60 percent if coal is used as a fuel.[34] The principle of MHD is to burn the fuel under conditions that will give a combustion gas temperature of about 4900°F, add an easily ionizable salt such as potassium carbonate (seeding) so that the gas will have a relatively high concentration of free ions and electrons, and then pass this conducting gas through a magnetic field and draw off electrical energy through electrodes placed in the path of the gas. By analogy, the hot conducting gas moving through a magnetic field behaves like the armature in a conventional turbogenerator. A coal-fired MHD generator would discharge less sulfur and nitrogen oxides to the atmosphere than a conventional plant of equivalent size because the seeding salt would absorb these oxides, which would be recovered during regeneration of the seed. The higher thermal efficiency would also reduce the amount of CO_2 evolved per unit of energy produced.

However, there are still some major technical obstacles to overcome before a commercial MHD plant can be built.[33,34] One problem is the selection of materials to withstand the extreme temperatures in the gas and meet the requirements that two walls in the duct must be conductors, and the other two walls must be insulators. A second problem is recovery of the potassium used as the feeding material; some estimates indicate that economical

TABLE 17.14 Summary of Direct Combustion Coal Process (Smoot)*

Process Type	*Description*	*Extent of Coal Use In U.S. (% of Total Used)*	*Commercial Use*	*Scale Size (TPD)*[a]	*Coal Types*	*Coal Size*
Power station	Commercial electricity production	78–80%				
Pulverized	Rapid burning of finely grained goal		Common	1000–10,000	All	0.01–0.025 mm
Fluidized-bed[b]	Well-stirred combustion		Pilot plant	2000–8000	All	0.15–0.6 cm
Stoker	Mechanically fed fixed bed		Small	100	Noncaking	1–5 cm
MHD	Combustion energy capture by magnetic fields		Laboratory	800–4000		
Coal/oil mixture (COM)	Burning coal/oil mixtures in oil furnaces		Demonstration			
Industrial heat/steam	Industrial plant power	8–11%				
Pulverized			Small	1–100		
Fluidized-bed			Pilot	1–100	same as above	
Stoker			Common	1–100		
COM			Demonstration	1–100		
Domestic/commercial	Hand-stoked space heating	1%		0.005–0.05	Noncaking	3–10 cm
Transportation	Fuel for railroads	0.01–0.02%		0.1–1	Noncaking	

[a] TPD = tons/day.

[b] Very adaptable, exhibits high heat transfer in bed as well as low-level pollutant products.

**Source*: Excerpted from Smoot, L. D. in *Fossil Fuel Combustion*, William Bartok and Adel F. Sarafin (Eds.). John Wiley & Sons, New York, 1991. Copyright © 1991 by John Wiley & Sons, Inc. and used by permission of the copyright owner.

operation will require 99 percent recovery. The U.S. DOE supports a research program on MHD that includes tests on prototype MHD components and the use of MHD exhaust gases for steam generation.[32] This five-year program is intended to prove the feasibility of the concept by the end of 1993. Research on the MHD concept also is being actively pursued in other countries such as the Former Soviet Union, China, Japan, Poland, Italy, and India. The work in Russia has progressed to the pilot-plant scale.

A second promising technology is the combined-cycle plant, in which both a gas turbine and a steam turbine are used to generate electricity. In one version of this concept, the coal first is gasified to produce fuel gas, which is cleaned and then burned in a gas turbine. An example of such a plant is shown in Fig. 17.22. The hot exhaust gases subsequently are used to generate steam that drives a steam turbine. A second type of combined-cycle plant uses a pressurized fluidized-bed combustor (PFBC) to generate the hot gas for the gas turbine.[35,36] However, because of the relatively low maximum temperature limit on the PFBC (see below), the thermal efficiency is lower than for the gasifier-based plant. An important advantage is that the thermal efficiency of a combined-cycle plant exceeds 40 percent, whereas that of a conventional pulverized coal-fired boiler

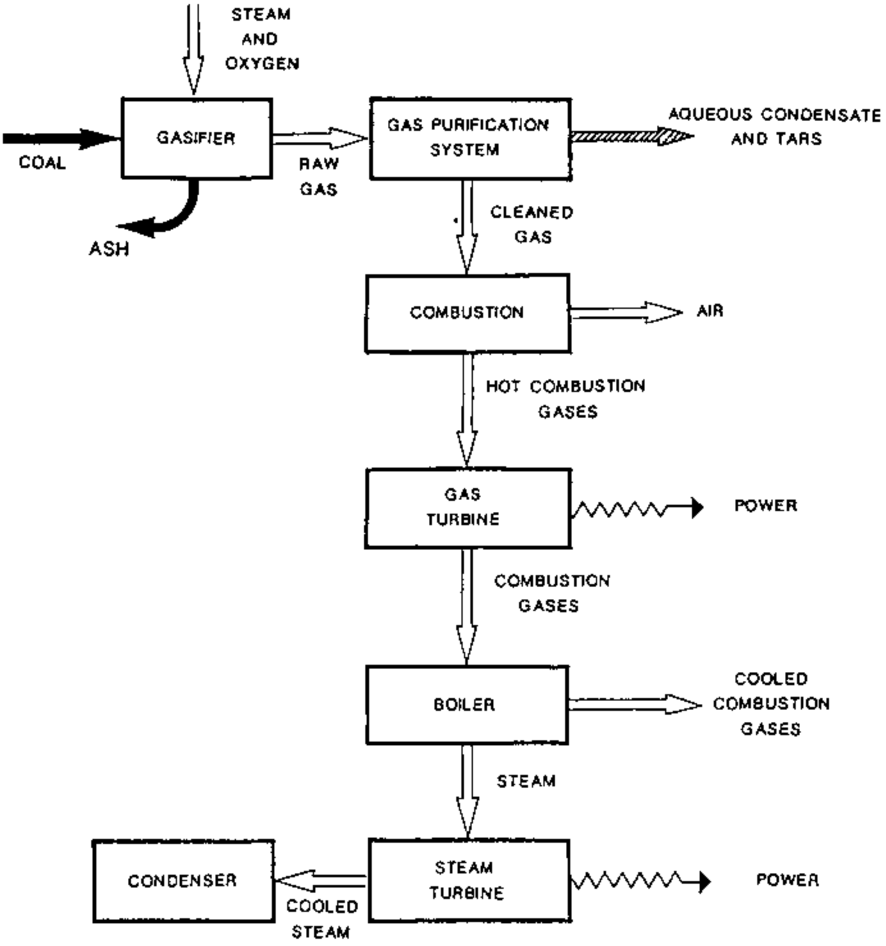


Fig. 17.22. A combined-cycle plant in which the coal is first gasified prior to combustion. (Reprinted with permission from Schobert, H. H., *Coal: The Energy Source of the Past and the Future*, American Chemical Society, Washington, D.C., 1987. Copyright 1987, American Chemical Society.)

equipped with flue gas desulfurization is about 35 percent. The development of more advanced gas turbines, which allow higher gas inlet temperatures, will significantly increase the efficiency advantage of combined-cycle plants. A second aspect of these plants is the requirement for a clean gas system for the gas turbine. This is a technical challenge in terms of the development of processes to remove trace amounts of impurities from gasifier effluents without having to cool down the gas stream. However, this feature is also an advantage because the pollutants can be removed from a much lower volume of gas when compared to the stack and, in most cases, are in a form that is more easily removed. Another advantage of combined-cycle plants is their modular nature, which offers flexibility in construction and the ability to add capacity in smaller increments. The feasibility of the combined cycle plant was demonstrated at Southern California Edison's Cool Water station, which utilized a Texaco gasifier to generate the fuel gas.[27]

The use of coal slurries, either coal–oil mixtures (COM) or coal–water mixtures (CWM), has been the subject of considerable research because of its potential to replace fuel oil in boilers.[37,38] The recent work has shifted in favor of CWM over COM, as the cost savings for the latter were not enough to offset the conversion costs. CWM is typically composed of 60 to 75 percent coal, 24 to 39 percent water, and 1 percent chemical additives. The advantages of CWM compared to dry pulverized fuel are ease and safety of handling, transporting (e.g., via pipeline), and injection of the fuel. It is possible that the manufacture of CWM can be integrated into coal beneficiation processes such as froth flotation. The potential problems with the replacement of CWM for oil are: (1) limited flame stability and turndown; (2) incomplete combustion; and (3) slagging and fouling caused by inorganic constituents. This technology is still in the development stage, and work has slowed considerably since 1986 because of low oil prices. Several demonstration projects have been completed or are still under way.[38]

Combustion Equipment

Industrial and electric utility boilers are fired with either stokers, pulverized-coal-fired burners, or cyclone burners, the choice depending on the kind of coal and the amount of steam needed. Table 17.15 gives the kinds of coal that can be burned with the various kinds of firing. Although good results usually will be obtained with the respective coal and firing equipment, this table should be used only as a rough guideline, and final equipment selection should be based on a sound engineering analysis.

Stoker Firing. Stokers are the oldest continuous coal combustion devices, having been in operation for more than 150 years. They are still used to fire small-capacity boilers. Table 17.16 gives the approximate range of capacity for each kind of stoker. There are several types of stokers, which are classified by the method of coal feeding and the relative direction of the fuel and air. The three main

TABLE 17.15 Burning Equipment for Various Coals[99]

	Stokers				
Fuel	*Under Feed*	*Traveling or Chain Gate*	*Spreader*	*Pulverized-Coal burner*	*Cyclone Burner*
Anthracite		X		X	
Bituminous:					
17–25% volatile	X		X	X	X
25–35% volatile				X	X
strongly coking	X	X	X	X	X
weakly coking		X	X	X	X
Lignite		X	X	X	X

TABLE 17.16 Approximate Range of Capacity of Stokers[99]

Type	*Steam, M lb/hr*	*Grate Heat Release, M Btu/hr sq. ft. (max)*
Single retort	5–50	200
Multiple retort	40–300	300
Traveling or chain grate	10–300	300
Spreader	10–300	1000

types are underfeed, crossfeed, and overfeed. Both fuel and air have the same direction in retort stokers; this arrangement is called underfeed burning. The fuel moves across the air direction in chain- or traveling-grate stokers; this design is called crossfeed burning. The spreader stoker approximates overfeed burning, the incoming fuel moving toward the air. Except for certain types of coal gasifiers, in which lump coal moves downward toward a grate against air (or oxygen and steam) coming through the grate, no conventional combustion system operates purely in the overfeed mode.

An example of a crossfeed chain-grate stoker being used to heat a fire-tube boiler is given in Fig. 17.23. This stoker consists of an endless track of grate bars that pass over rotating sprockets at each end, similar to a conveyor belt. Coal is fed onto one end of the grate, using a hopper, to a depth of about 4 inches. The coal burns as it moves along the grate, and, at the far end of the grate, only the ash remains. The ignition of the coal is assisted by radiant heat from a refractory lining.

Pulverized-Coal Firing and Cyclone Firing. Electric utility and large industrial plants favor pulverized-coal-fired and cyclone-fired furnaces because of their inherent flexibility regarding the kind and quality of coal, their comparatively good availability, their quick response to load changes, and their extremely high steam-generating capacity. Recent units

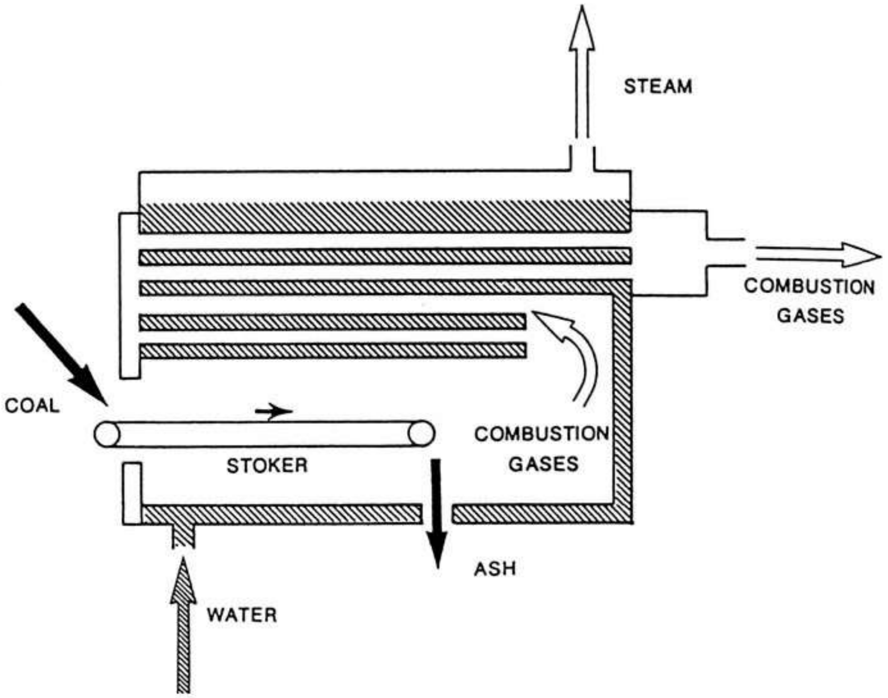


Fig. 17.23. Example of a chain-grate stoker equipped with a five-tube boiler. (Reprinted with permission from Schobert, H. H., *Coal: The Energy Source of the Past and the Future*, American Chemical Society, Washington, D.C., 1987. Copyright 1987, American Chemical Society.)

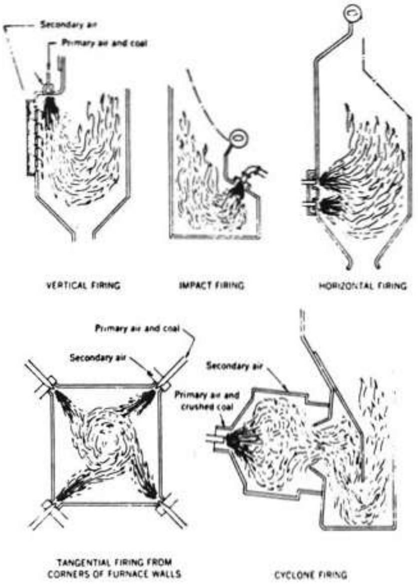


Fig. 17.24. Methods of firing pulverized and crushed coal. (*Courtesy Bureau of Mines.*)

generate as much as 9.5 million lb of steam/hour at 3500 psig and 1000°F.

The burner and furnace configurations for the main type of pulverized-coal firing (often called suspension firing), and cyclone firing are shown in Fig. 17.24. There are some design variations in vertical, impact, and horizontal suspension firing, but these schematic drawings serve to illustrate the principles.

Coal-fired boilers are further differentiated by the operating mode: the "dry bottom" or "wet bottom" (slagging) mode. Most modern pulverized coal-fired boilers are of the dry bottom type, in which the ash is cooled before contacting any surface.[39] Wet bottom firing provides a more convenient method of ash disposal but has several disadvantages that have led to its virtual elimination in the United States.[35] The disadvantages include less flexibility in fuel selection, higher incidence of fouling and corrosion, and higher levels of NO_x formation.

The first suspension-fired furnace in the United States was designed like the one shown for vertical firing in Fig. 17.24. Pulverized coal (about 70% through a 200-mesh screen) is transported to the burner with primary air, the amount of this air being about 20 percent of that needed for complete combustion. The balance of the air, known as secondary air, is admitted through openings in the furnace wall. Because a large percentage of the total combustion air is withheld from the fuel stream until it projects well down into the furnace, the ignition stability is good.[40] This type of firing is well suited for coals that are difficult to ignite, such as those with less than 15 percent volatile matter. Although no longer used in central-station power plants, this design, with delayed admission of secondary air, may find favor again if low-volatile chars from various coal-conversion processes are burned for heat and power.

The other types of suspension firing use burners in which the primary air and coal and the secondary air are mixed just before or immediately after entering the furnace. With tangential firing, the burners are arranged in vertical banks at each corner of a square, or nearly square, furnace and directed toward an imaginary circle in the center of the furnace. This produces a vortex with its axis on the vertical centerline. The burners consist of an arrangement of slots, one above the other, admitting through alternate slots the primary air–fuel mixture and the secondary air. The burners can be tilted upward or downward 30 degrees from the horizontal plane, enabling the operator to control superheat and to permit selective utilization of furnace heat-absorbing surfaces. Basically, the turbulence needed for mixing the fuel and air is generated in the furnace instead of in the burners.

Cyclone firing is a form of two-stage wet bottom firing in which the coal is not pulverized as for suspension firing but is crushed to 4-mesh size and admitted tangentially with primary air to a water-cooled cylindrical chamber called a cyclone furnace. The finer particles burn in suspension, and the coarser ones are thrown by centrifugal force to the furnace wall. The wall, having a sticky coating of molten slag, retains the coal until it burns. The secondary air, which is admitted tangentially along the top of the furnace, completes the combustion of the coarse particles. Slag drains continuously into the main boiler furnace. The main advantage of cyclone firing is the ability to use larger coal particles. However, being a wet bottom technique, it suffers from the disadvantages discussed above.

Fluidized-Bed Combustion. In the past 20 years, fluidized-bed combustion (FBC) has advanced from the laboratory and pilot-plant scale to commercial status worldwide.[36,39,41,42] Although this technology is not yet widely used in the electrical power industry, the potential advantages of this burning mode are clear: (a) The fuel-bed temperature is low, about 1550°F, which means less formation of nitrogen oxides, and retention of some of the sulfur in the ash of certain coals. (Adding dolomite or limestone to the fuel bed greatly improves sulfur retention.) It is equally important that there is less volatilization of sodium and potassium in the coal; consequently, there are fewer deposits on and corrosion of furnace, superheater, and reheater tubes. (b) Heat-transfer rates from the fluidized bed for immersed heat-transfer surfaces are relatively high, as much as 100 Btu/hour/ft^2/°F. Temperature control is easier, as the bed temperature is more uniform because of the rapid mixing in the bed. (c) The FBC has the capability to burn many kinds of coal and is less sensitive to changes in coal heating value or ash characteristics than other combustion methods. (d) The FBC is adaptable to several kinds of power generation cycles (e.g., cogeneration or combined cycle) can operate at atmosphere or elevated pressure, and can use bubbling or circulating beds with in-bed or external heat exchangers. This versatility allows engineers to develop FBC systems that are tailored to specific applications, which can result in significant cost savings when compared to other technologies.[39]

It is believed that the application of fluidized-bed boilers to electric-utility stations will reduce operating costs and increase efficiency compared with conventional pulverized-coal fired plants of the same capacity that are equipped with emission controls. The principle of the fluidized-bed combustor is illustrated schematically in Fig. 17.25.

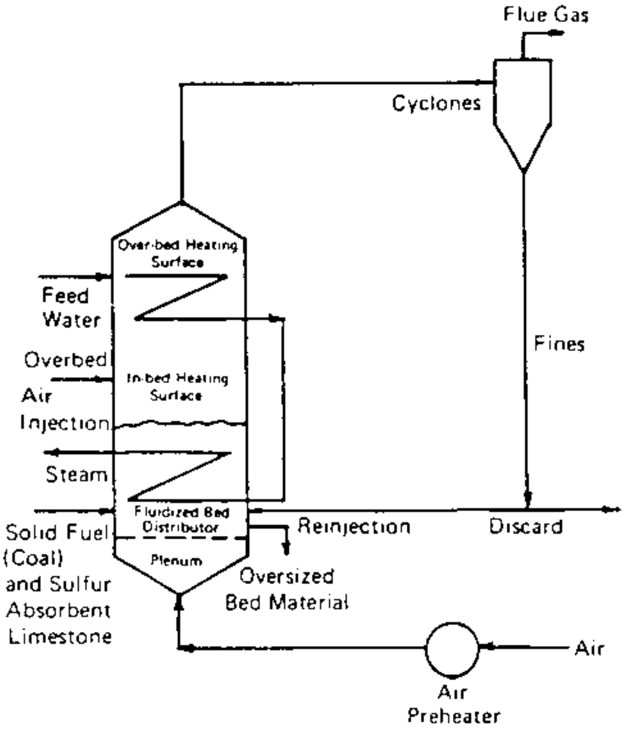


Fig. 17.25. Basic components of a fluidized bed combustor. (*Shang, J. Y., Department of Energy, Morgantown WV.*)

The current trends in the area of FBC are as follows:[39] There is more interest in running units at elevated pressures (6–15 atm) in order to reduce equipment size, lower emissions, reduce sorbent requirements, and increase the thermal efficiency by the use of a gas turbine in addition to a steam turbine in the combined-cycle concept. There is also a trend away from bubbling beds and toward "circulating" beds, which use finer solids and higher velocities and are able to use sorbents more efficiently.[42]

Several large-scale demonstration projects of FBC technology for electrical power generation are now under way. These include a 110 MWe atmospheric pressure circulating fluidized-bed boiler at the Colorado–Ute Electric Association's Nucla Station, which began operation in August 1988. A second project is the American Electric Power Tidd 70 MWe pressurized fluidized-bed combustor/combined-cycle demonstration, which began generating power in December 1990. Both projects were partly funded by the Clean Coal Technology Program.[43]

Boiler Types

There are various kinds of industrial and utility boilers, broadly classified as fire-tube and water-tube. In the former, the hot combustion gases pass through tubes, and heat is transferred to water outside the tubes. The most common and least expensive boiler of this type is the horizontal return tubular (HRT) boiler. However, because of the design and construction of fire-tube boilers, there is a definite limitation to their size and the pressure that they can tolerate.

Water-tube boilers may be broadly classified at straight-tube and bent-tube types, the latter having several variations in design and being preferred for applications where higher capacities and steam pressures are required. In both types, heat is transferred by radiation or convection to the outside of the tubes, and water flows inside the tubes as a result of thermal circulation, or in the case of certain bent-tube boilers, as the result of forced circulation. A comparatively new version of the forced-circulation, bent-tube boiler for central station power plants is the "once through" type. The feed-water passes progressively through the heating, evaporation, and superheater sections; no drum is used for separating the steam from the boiler water as in other boilers, so the ratio of water circulated in the boiler to steam generated is unity. The data in Table 17.17 approximate the range of steam capacities and pressures for the principal types of boilers.

Pollution Controls

The emission of sulfur and nitrogen oxides and particulates from coal combustion has become a problem of increasing concern and regulation.[31,32] The combustion of coal contributes about 25 percent of the particulate matter, 25 percent of the sulfur oxides, and 5 percent of the nitrogen oxides in the atmosphere.[33] A major concern about the particulate matter, most of which is inorganic matter derived from the mineral content of

TABLE 17.17 Approximate Range of Capacities of Various Types of Industrial and Utility Boilers[99]

Type	*Capacity, lb Steam/hour*	*Maximum Design Pressure, psig*
Fire tube (HRT)	1000–15,000	250
Water tube		
straight	15,000–150,000	2000
bent, 3-drum, low-head	1000–35,000	400
2-drum, vertical	1000–350,000	1000
electric utility	up to 9,000,000	3500

the coal, is that the smallest particles are respirable and may pose a health hazard. The collection of particulate matter is done in most power plants by the use of electrostatic precipitators, which have been developed to very high efficiencies (>99%). Other techniques for particulate removal include baghouses and cyclone collectors.

The significant reduction of SO_2 and NO_x emissions from coal combustion by the year 2000 is a major part of the 1990 Clean Air Act. The achievement of these goals will be assisted by a U.S. DOE program known as the Clean Coal Technology Program, which provides government funding for a range of advanced pre-combustion and post-combustion technologies.[43] The current technology for removal of SO_2 is Flue-Gas Desulfurization (FGD), in units known as scrubbers. The most common scrubbers use a slurry of lime or limestone to capture the sulfur oxides, and the product is a sludge containing calcium sulfite and calcium sulfate. However, the disposal of sludge is another environmental problem. A more favorable solution for newer plants is to use fluidized-bed combustion with a sulfur capture agent or a combined-cycle system where the sulfur can be more easily removed from the gasification stream.

The major component of nitrogen oxides emitted from coal is nitrogen oxide (NO). Most of the nitrogen formed from combustion of coal does not originate from the coal but from the reaction of nitrogen and oxygen in the air that is used to burn the coal. Consequently, the control of nitrogen oxides can be most easily achieved by changing the conditions of the combustion process. This usually involves the use of staged combustion where the coal first is burned in a fuel-rich flame that subsequently is made fuel-lean. This is made a viable option for an existing plant by changing the burner design or by the addition of natural gas.

Several techniques are being developed for post-combustion scrubbing of NO_x, such as selective catalytic reduction. This technique now is used in Japan and Germany but is not yet widely used in the United States because of its high cost.[31] The use of a fluidized-bed combustor where the combustion is carried out at lower temperature in the presence of a sorbent will reduce both nitrogen oxides and sulfur oxides.

DIRECT COAL LIQUEFACTION

The primary purpose of any coal liquefaction process is to produce a liquid product with an increased hydrogen-to-carbon ratio, a reduced heteroatom (e.g., S, O, N) content, and a minimal inorganic content. This has been accomplished by a variety of methods, which can be divided into the three categories of pyrolysis, indirect liquefaction, and direct liquefaction.[96]

Direct coal liquefaction (DCL) refers to the process of converting coal to liquid products by mixing the coal with a recycle process solvent or petroleum-derived residual oil and reacting it under hydrogen at 750 to 850°F (400–450°C) and 1000 to 2500 psig (7–17 MPa). The process involves the breakdown of the coal structure into soluble products promoted by hydrogenation. The solubilized products, consisting mainly of aromatic compounds, then may be upgraded by conventional petroleum refining techniques. For information on the early history of DCL see Wu and Storch,[44] Donath and Hoering,[45] and Ministry of Fuel and Power.[46]

The success of any DCL method is highly dependent on the type of coal used in the process. Coal rank has been shown to influence both the overall conversion and the product distribution. Lower-rank coals have been reported to give birth higher and lower conversions than bituminous coals,[47] with most evidence supporting the latter. However, the liquid products from subbituminous coals are generally more volatile and of lower molecular weight[48] than those for higher-rank bituminous coals.

After the end of World War II, the United States adopted much of the technology developed by Germany in the construction of a 200 to 300 bbl/day plant at Louisiana, Missouri, operated by the Bureau of Mines from 1949 to 1954.[44] Although the Germans had demonstrated the commercial-scale operation of DCL plants, coal-derived liquids could be produced only at high cost. Research in the United States was limited prior to the 1970s, primarily because of the availbility of vast reserves of inexpensive oil discovered in the Middle East in the late 1940s. However, the 1973 oil embargo created a surge in interest in coal liquefaction as one of a number of routes to produce petroleum substitutes from indigenous resources. From this renewed effort in the early 1970s, four major processes evolved: the H-Coal process, the Exxon Donor Solvent (EDS) process, and two Solvent Refined Coal (SRC-I and SRC-II) processes. All were single-stage processes that attempted to convert coal to liquids in a single reaction stage. By the late 1970s and early 1980s these processes were being developed on the pilot-plant scale. This section discusses these processes as well as two-stage processes and future research in DCL.

The H-Coal Process

The H-Coal process was an adaptation of the H-Oil process used in the petroleum industry to convert heavy oil residues to lighter fractions using a catalytic ebullated bed reactor.[49] Research on the H-Coal process began in 1964 at Hydrocarbon Research, Inc. (HRI) on a bench-scale unit, and by 1973 the design of a 200- to 600-ton/day pilot plant was under way. Construction of the plant was completed in early 1980. Located adjacent to the Ashland Oil refinery in Cattletsburg, Kentucky, it operated succesfully from startup in May 1980 until shutdown in November 1982.

H-Coal employed a single catalytic stage to produce a synthetic crude oil.[50,51] Figure 17.26 shows a schematic of the H-Coal process. The coal is crushed, dried, and mixed with a recycle oil and hydrogen gas before being preheated to approximately 850°F (454°C). The preheater effluent then is fed to the bottom of the ebullated bed reactor. During operation, fresh catalyst (an extruded cobalt–molybdenum catalyst) is fed to the top of the reactor while spent catalyst is removed from the bottom of the reactor to maintain constant inventory. The constant upward flow of the coal slurry causes the catalyst to remain in a fluidized state. The products are removed from the top of the reactor, and the various fractions are separated by conventional techniques.

The H-Coal products had a high H/C ratio and a low heteroatom content, as shown in Table 17.18. The process design allowed for a high throughput rate. However, the use of high temperatures in the reactor caused excessive thermal cracking, resulting in high gas yields and, correspondingly, low hydrogen utilization efficiency. Typically, between 14,000 and 20,000 standard cubic feet of hydrogen were required for each ton of coal processed.

The H-Coal process produced approximately 3 to 3.5 barrels of liquid product for each ton of coal feed.[49] Testing showed that the process was best suited for high-volatile bituminous coal feeds; the use of low-rank coals reduced throughput and distillate yields considerably. The demonstrated success of the ebullated bed reactor in this system led to its future use in two-stage systems.

The Exxon Donor Solvent Process

Research on the Exxon Donor Solvent (EDS) process began at Exxon in 1966 and by 1975 had progressed from investigations using 100 cm^3 batch units to a continuous $\frac{1}{2}$-ton/day pilot plant.[52] With the help of external funding, a 250-ton/day pilot plant was designed and constructed. The Exxon Coal Liquefaction Plant (ECLP) at Baytown, Texas began operations in April 1980, and was shut down and dismantled in late 1982.[51]

A schematic of the EDS process is shown in Fig. 17.27.[50,51] The coal is ground and mixed with a hydrogenated distillate recycle solvent before entering the liquefaction reactor. Hydrogen is added to the slurry in a tubular thermal reactor, which operated at 800 to 880°F (425–470°C) and 1500 to 2000 psig (10–14 MPa). The total reactor product is set to a distillation unit, where it is separated into gas, naphtha, distillates, and a vacuum

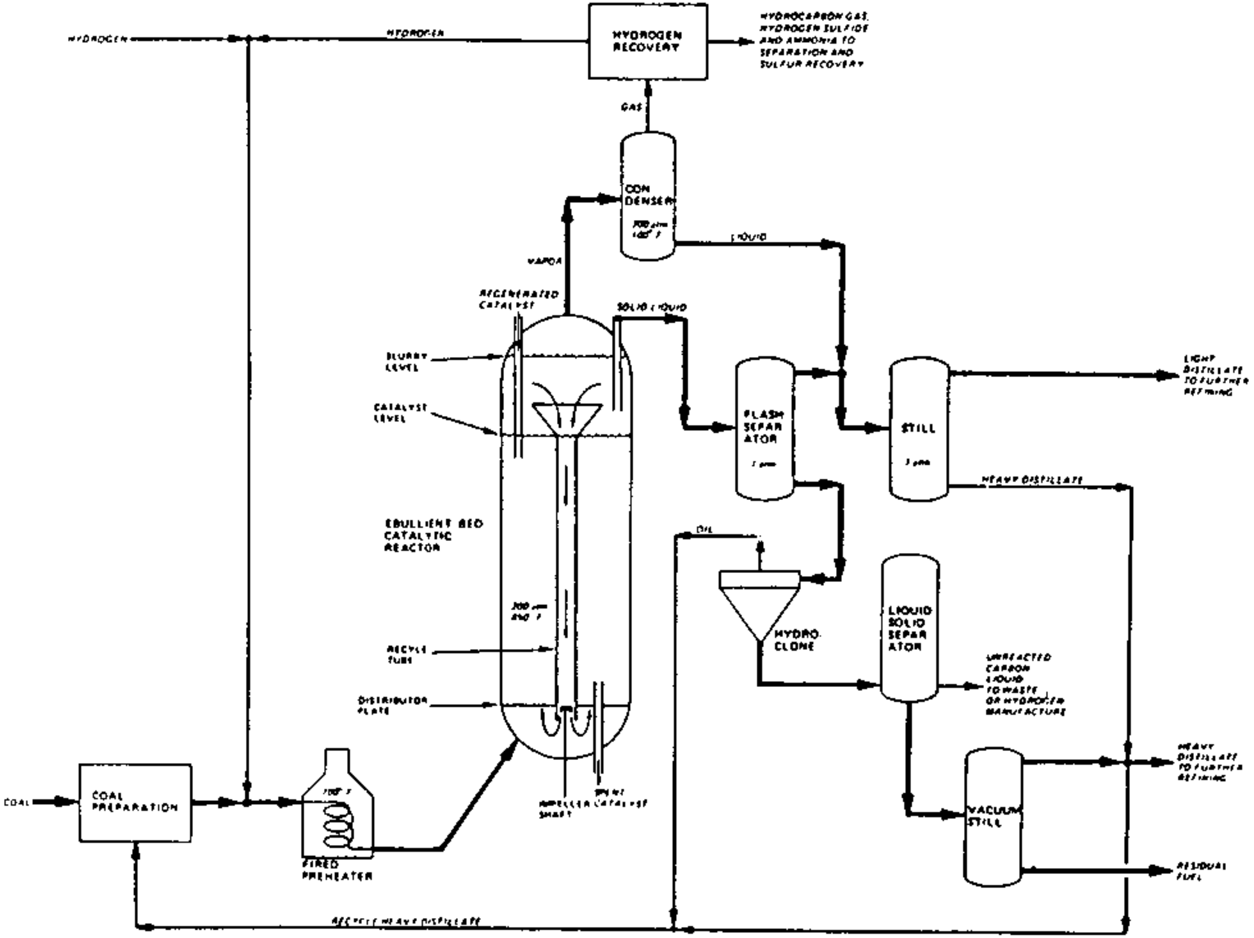


Fig. 17.26. Schematic of H-Coal process. (*Courtesy The Pace Company, Denver, CO.*)

TABLE 17.18 Heteroatom Content of Product Streams from Various Direct Liquefaction Processes

Process	*Wt. % in Naphtha* (C_5—*390°F*)				*Wt. % in Distillate (400–975°F)*			
	O	*N*	*S*	*H*	*O*	*N*	*S*	*H*
H-Coal	0.6	0.2	0.07	13.79	1.1	0.5	0.08	9.52
EDS	2.42	0.23	0.28	12.03	2.0	0.6	0.3	8.97
SRC-II	3.51	0.42	0.26	10.46	3.63	0.99	0.25	9.27
ITSL	0.41	0.14	0.015	13.78	0.56	0.20	0.015	10.21

bottoms slurry. The 400 to 850°F (204–455°C) distillate fraction is sent to a fixed-bed catalytic solvent hydrogenation unit to generate a hydrogenated H-donor recycle solvent, which supplies hydrogen to the coal in the liquefaction reactor. The use of an external reactor to hydrogenate the recycle solvent distinguished the EDS process from other single-stage processes.[53] Additional hydrogen is supplied from the gas phase. The production of distillates is achieved by thermal cracking and hydrogenation in the liquefaction reactor. Although this process used a separate solvent hydrogenation unit, it is considered a single-stage process because both dissolution of the coal and upgrading of the dissolution products took place in the same reactor.

The operating conditions for the EDS process were similar to those of the H-Coal process, and, similarly, it was found that the process worked best with bituminous coals. The product distribution was slightly worse than obtained in the H-Coal process, and the distillate yield was lower, around 2.5 to 3 barrels of liquid product per ton of feed. The rather inferior performance was probably attributable to the absence of a catalyst in the liquefaction step of the EDS process. However, because the reactor was less complicated for the EDS process and the solids removal was simpler, the economics of the processes were roughly equivalent.[50]

The EDS process suggested that coal could be adequately hydrogenated in the absence of added catalyst. However, a later modification used vacuum bottoms recycle, in addition to the normal distillate solvent recycle, and displayed improved operating characteristics and higher distillate yield, particularly for low-rank coals. The increased residence time

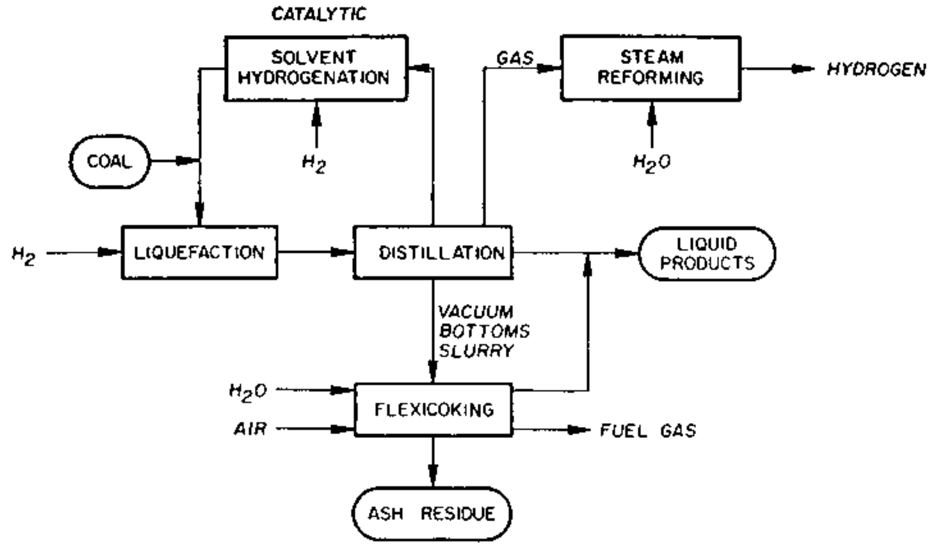


Fig. 17.27. Schematic of Exxon Donor Solvent process. (*Courtesy The Pace Company, Denver, CO.*)

of the resid in the reactor increased the yield of naphtha range materials.[54] In addition, the ash in the bottoms recycle may have contributed some catalytic effect, resulting in increased conversion for lignite and subbituminous coals.[55] The recognition of these factors also was important to the development of the later two-stage liquefaction concept.

The Solvent Refined Coal Processes

The solvent refined coal (SRC) process began as a study on the feasibility of coal de-ashing by Spencer Chemical in 1962.[50] The aim was to produce a cleaned combustible fuel that was solid at room temperature. A 50-ton/day plant, located in Fort Lewis, Washington, operated in the SRC mode from its completion in October 1974 until it was modified in late 1976. It later was shut down in 1981. With this change came the new designation SRC-II, and the original process was sometimes designated as SRC-I. In 1972, another 6-ton/day pilot plant was built, in Wilsonville, Alabama, by Catalytic Inc. for EPRI and Southern Company Services Inc. This plant began operation in January 1974, and it is the only DCL plant currently in operation in the United States, although its present form is a highly modified configuration of the original.

Figure 17.28 shows a schematic of the SRC-I process. The feed coal is crushed and mixed with a recycle solvent and hydrogen prior to entering the preheater. The preheater effluent, at 700 to 750°F (370–400°C), then is fed to the dissolver unit, or thermal liquefaction unit (TLU), which operates at 840 to 870°F (450–465°C). There is no upgrading step, as the desired product is a solid at room temperature and not a distillate. The solids removal from the liquid slurry is accomplished by critical solvent de-ashing (CSD). The solids-free resid from the CSD was separated by vacuum distillation into a recycle solvent (the light fraction) and a solvent refined coal product (the bottoms).

The primary product of the SRC-I process was a low-sulfur, low-ash, solid boiler fuel

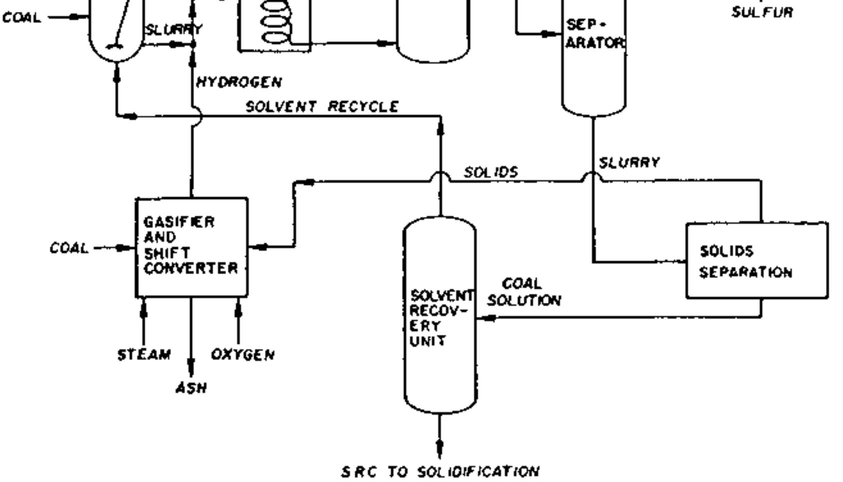


Fig. 17.28. SRC-I process for solvent refined coal. (*Courtesy The Pace Company, Denver, CO.*)

with a melting point of approximately 300°F (150°C), a Btu content of 16,000 Btu/lb, and an H/C ratio approximately the same as that of coal. Although this was considered to be a thermal liquefaction process, it was most successful using bituminous coals with high native pyrite content. Its beneficial effects certainly can be attributed to the now well-known catalytic properties of iron sulfides.

The SRC-I process suffered from a number of problems. Among them was the fact that the distillate solvent was a poor hydrogen transfer medium, and components of the solvent were incorporated into the resid, making it virtually impossible to maintain solvent balance.[51] Problems with hydrogen transfer often led to problems with retrograde reactions (i.e., coking), particularly in the preheater section. Attempts to correct this problem by moderating the conditions led to excessive quantities of toluene insolubles precipitating downstream in the CSD.

The SRC-II process was again a thermal process, relying only on the native mineral matter in the coal as a catalyst. However, in SRC-II part of the product from the dissolver was included with the recycle solvent, without first de-ashing. This helped maintain a high mineral matter concentration in the reactor, which must have augmented the extent of catalytically promoted reactions. The other changes in the SRC-II process can be seen in Fig. 17.29.

The SRC-II process operated under more severe conditions than SRC-I and gave primarily a distillable product, although gas yields also were high. This poor selectivity resulted in excessive hydrogen consumption. More than the other single-stage liquefaction processes, SRC-II was limited to the use of bituminous coals with high catalytic mineral matter content. Processing of subbituminous coals was possible only with the use of additional pyrite catalyst added to the feed stream.[48]

Two-Stage Processes

During the late 1970s and early 1980s, there was an increasing awareness that the process of direct coal liquefaction proceeded in two loosely defined steps, each requiring different reaction regimes. The first step involves coal dissolution, in which the coal is converted to a soluble form with high molecular weight and relatively little change in average composition from that of the coal. The second involves upgrading, in which the dissolved

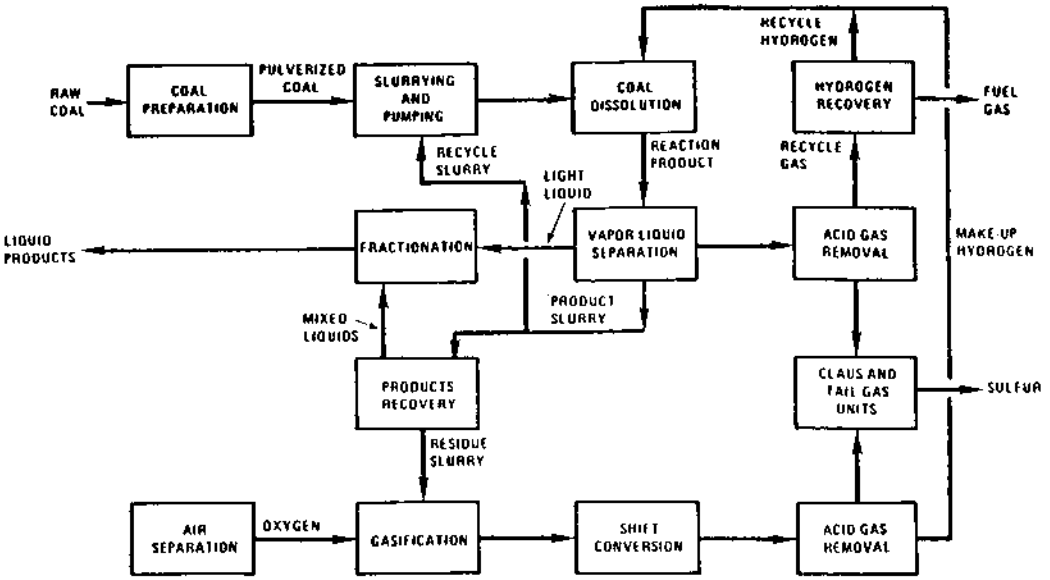


Fig. 17.29. SRC-II process for solvent refined coal. (*Courtesy The Pace Company, Denver, CO.*)

products are converted to lower-boiling liquids with reduced heteroatom content.[56] Studies have shown that the conversion to tetrahydrofuran (THF) solubles can occur in one to five minutes, and that further reaction generally leads to unwanted hydrocarbon gas production.[50] It also was found that in the dissolution stage most of the hydrogen is supplied by the solvent rather than the gas. Therefore, the use of a short contact time (SCT) thermal liquefaction reactor followed by a catalytic upgrading reactor should optimize conditions for both reactions, leading to higher yield, more efficient use of hydrogen, and a better product distribution. These studies were the beginning of the two-stage liquefaction process.

The first process that attempted to separate the two steps was the nonintegrated two-stage liquefaction (NTSL) process.[57] This involved the use of a second-stage upgrading reactor placed downstream of an SRC-I dissolution reactor. Because of the high ash content of the dissolution product, which could cause plugging and rapid deactivation of the catalyst, a fixed-bed catalytic upgrading reactor could not be used.[58] The use of a variation of the ebullated bed type reactor, called the LC-Finer, installed at the Wilsonville facility, allowed the upgrading of a portion of the SRC-I resid, but the process still was considered inefficient, primarily because of the poor hydrogen transfer ability of the distillate solvent. Distillate yields were only about 40 percent (maf coal).[59] Use of the term "nonintegrated" stems from the fact that the hydrotreater does not contribute solvent to the first-stage reactor, as shown in Fig. 17.30.

Lummus Integrated Two-Stage Liquefaction Process

Several companies began work on integrating the two stages of the liquefaction process by recycling part of the hydrogenated resid. Around 1975, the Lummus Company began work on one such process, called integrated two-stage liquefaction (ITSL).[58,60] The process, shown in Fig. 17.31, consists of an SCT thermal liquefaction reactor followed by an LC-Finer, similar to the NTSL process. Aside from the recycle, the unique feature of this process configuration is the use of the Lummus antisolvent de-ashing (ASDA) unit, originally located between the SCT reactor and the LC-Finer, to remove ash from the resid prior to upgrading. The liquid product of this process is a below-650°F (343°C)

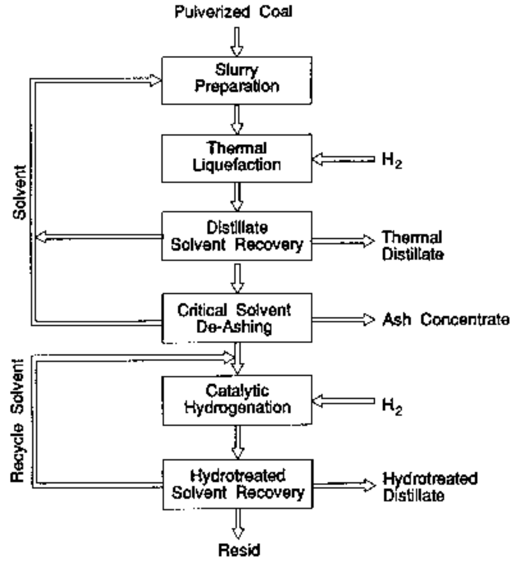


Fig. 17.30. Schematic of nonintegrated two-stage liquefaction process.

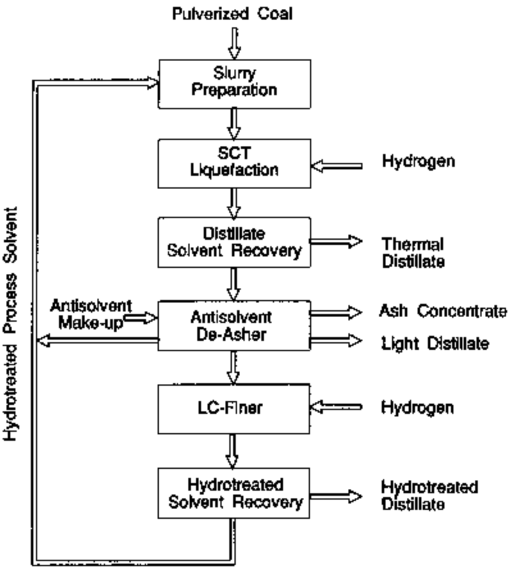


Fig. 17.31. Schematic of Lummus ITSL process.

distillate, with the above-650°F (343°C) residue being recycled as solvent.

The SCT reactor is essentially equivalent to the preheater in the SRC-I process. The coal slurry, consisting primarily of liquid products, solids (ash and unconverted coal), and gas, exits the reactor after a residence time of 2 to 12 minutes, depending on the feed coal rank, at 800 to 840°F (425–450°C) and 1500 to 2500 psig (10–17 MPa). The short contact time resulted in lower hydrogen consumption, similar conversion, and a resid that was more reactive to upgrading at milder conditions than SRC-I.[61]

The ASDA unit removed the ash and heavy components of the resid by agglomeration with process-derived naphtha. The process required the solids content of the reject stream to be less than 55 percent in order for it to be pumpable.[50] As mentioned, the ASDA originally was placed between the SCT reactor and the LC-Finer. Subsequent studies showed that, by placing the ASDA after the upgrading stage, the conversion yields were increased.[60] In studies with subbituminous coal, additional improvements in yield were achieved by recycling part of the ASDA feed to the SCT reactor. Relevant to future process development was the finding that the catalyst in the upgrading stage was not deactivated by the ash in the SCT reactor effluent.

The LC-Finer, also known as the hydrotreater (HTR), was used to upgrade the resid from the SCT reactor and to produce a hydrogenated recycle solvent. The low temperature of 700 to 750°F (370–400°C) and pressure of 2500 to 2700 psig (17–19 MPa) in the HTR prevented excessive gas production, but still allowed adequate hydrogenation to take place. The catalyst also was less prone to deactivation by coking at these low temperatures. Distillate yields of 52 percent (maf coal) were achieved by this process on a PDU scale.[58] The liquid product produced by the ITSL process had a better quality, as shown in Table 17.19, and was more easily upgraded by conventional petroleum reforming techniques than the single-stage process products.

The Kerr-McGee Company developed a similar ITSL process.[50,60] The conditions in the SCT reactor were more severe than in the Lummus ITSL, resulting in significant distillate production in the SCT reactor. Bench-scale studies showed that the high temperature in the SCT reactor also increased gas production.

Although the first stage of this system was considered a thermal reactor, it was found that the addition of 2 wt. % Fe_2O_3, with dimethyldisulfide (DMDS), to a bituminous coal feed resulted in a significantly increased yield. This is attributed to catalysis by the iron sulfides formed during the reaction.

Wilsonville Integrated Two-Stage Liquefaction Process

By the mid-1980s, the configuration of the 6-ton/day plant at Wilsonville, Alabama, had been significantly modified from the original SRC-I mode. The Kerr-McGee company supplied a CSD to replace the filtration units previously in use. In 1981, HRI, Inc. installed

TABLE 17.19 Distillate Yields from Various Direct Liquefaction Processes

Process	*Configuration*	*Distillate wt. % maf coal*	*Yield, bbl/ton maf coal*	*Distillate Quality, gravity °API*	*Heteroatoms wt. %*		
					N	*O*	*S*
SRC-II (1982)	one-stage noncatalytic	41	2.4	12.3	1.0	2.33	0.33
H-Coal (1982)	one-stage noncatalytic	52	3.3	20.2	0.50	1.0	0.20
Wilsonville (1985)	ITSL thermal-catalytic	62	3.8	20.2	0.25	1.9	0.23
Wilsonville (1986)	CC-ITSL catalytic-catalytic	70	4.5	26.8	0.16	<1	0.11

an H-Oil ebullated bed reactor. This allowed, for the first time, the testing of the TSL concepts on a large scale. The plant piping was changed to test the Lummus ITSL process configuration.[50,57,60] The TLU was bypassed, leaving just the preheater, and the de-asher was installed before the second stage. This configuration resulted in a total conversion of 88 percent (maf coal) with a distillate yield of 54 percent (maf coal). To reduce the rejection of organic material with the ash in the CSD, the TLU was reinstalled. This meant that most of the conversion would take place in the first stage, with the second stage serving as a solvent hydrogenation unit, resulting in easier solid–liquid separation. With this change, a distillate yield of 57 percent (maf coal) was reported with an Illinois #6 bituminous coal.[62]

Reconfigured Integrated Two-Stage Liquefaction Process

Research at Lummus showed that moving the ASDA unit downstream of the HTR increased the distillate yield.[50] The Wilsonville plant was modified to operate in the reconfigured integrated two-stage liquefaction (RITSL) mode by moving the CSD unit downstream of the second stage, as shown in Fig. 17.32.[57] In this configuration, the de-ashed resid and some hydrotreated distillate were combined as recycle solvent. As indicated by the Lummus research, no detrimental effects to the catalyst in the HTR were seen due to the ash-containing feed. The process originally achieved a distillate yield of 62 percent (maf coal). A further increase in distillate yield to 63 percent (maf coal) was accomplished by using an ash-containing recycle. The primary gain from this configuration was the reduction of CSD feed by 50 percent, thereby reducing the load on the unit and the amount of organics rejected with the ash.

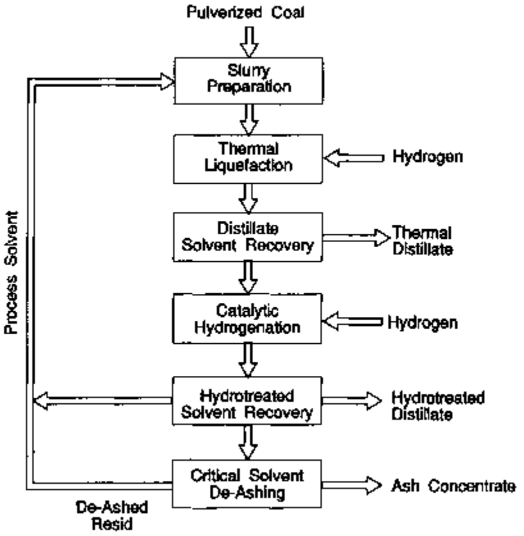


Fig. 17.32. Schematic of reconfigured ITSL process.

Close-Coupled Integrated Two-Stage Liquefaction Process

The purpose of the close-coupled integrated two-stage liquefaction (CC-ITSL) process was to minimize the residence time between reactors, thereby improving the thermal efficiency, reducing the potential for retrograde reactions, and producing a higher-quality solvent.[50,62,63] Also, because the CSD had been moved downstream of the HTR, there was no need for pressure letdown followed by repressurization between the first and the second stages.[57] The CC-ITSL configuration, shown in Fig. 17.33, demonstrated that the inclusion of the gases and light oils from the TLU in the HTR feed did not adversely affect the process. Distillate yields from the CC-ITSL of up to 64 percent (maf coal) were reported for Illinois #6 bituminous coal.[62]

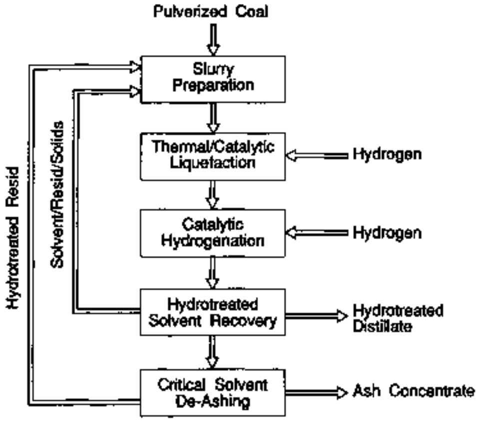


Fig. 17.33. Schematic of close-coupled ITSL process.

Catalytic Two-Stage Liquefaction Process

HRI began research on a catalytic two-stage liquefaction (CTSL) process in 1982.[50] In this process the first and second stages were close-coupled catalytic ebullated bed reactors, originally using supported $CoMo/Al_2O_3$ catalysts.[60] The temperature of the first stage was lowered to 750°F (400°C) to permit a closer balance between hydrogenation and cracking rates. This also allowed in situ solvent hydrogenation. In contrast to the ITSL, the temperature of the CTSL second stage was higher (around 825°F, 440°C), than that of the first stage. This was intended to promote hydrocracking of the resid in the HTR, and to produce an aromatic recycle solvent. Later, the $CoMo/Al_2O_3$ catalyst was replaced in the first stage with a $NiMo/Al_2O_3$ catalyst, while the second stage continued to use the cobalt-molybdenum catalyst. The product from the second stage had effectively been catalytically hydrogenated twice and was much lighter than the product from previous processes. Therefore, pressure filtration was used for solids removal, with a higher efficiency for solid–liquid separation than could be achieved by CSD. The distillate yield for the CTSL process was as high as 68 percent (maf coal) for an Illinois #6 bituminous coal.[60]

The Amoco Oil Company developed an ITSL process very similar to HRI's CTSL process.[60] The main differences were the use of a higher-temperature, smaller-volume, thermal first-stage TLU and a lower temperature in the catalytic hydrotreater. This process was tested on HRI's bench-scale unit. The higher temperature in the TLU (820–850°F, 438–455°C) resulted in a 30 percent higher gas yield than HRI's CTSL process, whereas the lower temperature in the HTR (ca. 700°F, 370°C) contributed to longer catalyst life. However, the distillate yield for the Amoco process was considerably lower than that of HRI's CTSL process.

In 1985, the Wilsonville plant installed an additional ebullated bed reactor to replace the existing TLU.[50] This allowed the plant to operate without (Thermal/Catalytic, T/C CC-ITSL) or with (Catalytic/Catalytic, C/C CC-ITSL) a first-stage catalyst.[57] It is important to note that in the T/C CC-ITSL runs with subbituminous coal, iron oxide and dimethyldisulfide were added to the feed slurry as disposable catalysts, although the operational mode is still termed "thermal." This addition also was used for some bituminous coal runs, resulting in improved overall conversion and distillate yield.[57] The Wilsonville C/C CC-ITSL is slightly different from the HRI CTSL in two ways: the temperature in the first stage reactor is 800 to 820°F (425–438°C), and the second stage is 760 to 795°F (404–424°C). This allows solvent hydrogenation in the second stage rather than the first stage, similar to the ITSL process.

The second deviation from the HRI CTSL is the continued use of the CSD unit to remove the ash and solids. Improvements in the CSD unit have reduced organic rejection to the same levels that HRI achieves with filtration. These changes have allowed the Wilsonville plant to achieve distillate yields of up to 77 percent (maf coal) with a cleaned Ohio #6 bituminous coal.[64] More typical yields of 70 percent (maf coal) were found with Illinois #6 bituminous coal.[64] Recent studies demonstrated the beneficial effects on the distillate yield of deep-cleaning the coal, achieving a distillate yield of 74 percent with a Pittsburgh #8 bituminous coal.[65]

Research in DCL is not limited to the United States. Currently the British Coal Corporation (BCC) has constructed a 2.5-ton/day PDU at Point of Ayr, North Wales.[66,67] The facility, using a two-stage liquefaction process called Liquid Solvent Extraction (LSE), is supported by the United Kingdom Department of Energy, European Economic Community, Ruhrkohle, and Amoco. In the LSE process, dried crushed coal is slurried with a high-grade recycle solvent, pressurized to 300 psig (2 MPa), heated to 770°F (410°), and fed to the thermal first-stage reactor. The low pressure in the first stage is possible because of the excellent hydrogen donor properties of the recycle solvent. Solids are removed from the dissolved coal stream by filtration, producing a low-ash solids-free filtrate called the coal extract solution. The coal extract solution is pressurized to 3090 psig (21 MPa), mixed with hydrogen gas, and fed to the catalytic, ebullated-bed, second stage, where it is hydrocracked at 750 to 850°F (400–450°C).

DCL and the Future

Like that of the past, future research primarily will be driven by economic considerations. The use of large-scale commercial DCL will be feasible only when the costs of coal-derived products are comparable to those of petroleum-derived products. Special circumstances, such as those present in Germany during World War II, may occasionally make DCL economically feasible, but these situations are usually temporary. Two recent studies[50,60] reported that, at an equivalent crude petroleum cost of around $35/bbl, coal liquefaction would be economically advantageous. However, with the current (1992) cost of crude oil closer to $20/bbl, the viability of a large-scale DCL operation is tenuous, to say the least. Current research is focused on improving the economics of DCL. Several approaches to reducing the cost are currently under investigation.

Reducing the cost associated with hydrogen production will greatly improve the economics of any coal liquefaction scheme. This may be done either by improving the hydrogen-generation methods or by improving the efficiency of hydrogen use (e.g., minimizing hydrocarbon gas make). Minimizing the severity of the reaction conditions, while maintaining a high yield, will reduce both equipment costs and gas production, thereby reducing hydrogen consumption.

Coal beneficiation, which involves the separation of some of the ash from the coal prior to liquefaction, may yield several benefits. Primarily it will reduce the load on the solid–liquid separator, thereby reducing the amount of organics rejected with the ash. Another benefit will be in the reduction of wear on plant components and better utilization of reactor volume. However, removal of mineral matter prior to reaction will eliminate any beneficial catalytic effect that the mineral constituents may contribute.

Improved catalysts, in both stages of a two-stage liquefaction system, probably represent the area of greatest potential benefit to the process economics.[68] Coal conversion reactions are generally slow, and any improvement in reaction kinetics could result in a large economic return. Currently research is being devoted to developing a dispersed slurry phase, as well as supported, catalysts that are more active and selective, and resistant to deactivation in the presence of high-boiling feeds.

The use of less expensive western U.S. subbituminous coals as feedstocks could further improve the process economics. It has been shown that they can produce lower-boiling and higher-quality liquids,[44,48,55] and that they cause less rapid deactivation of the second-stage catalyst.[60] The main problem is their lower rate and extent of conversion, which causes inefficient use of reactor space and the loss of additional product on solids separation. The different behavior of low-rank coals is believed to relate to their thermal sensitivity and high propensity for cross-linking. Dissolution promoted by an effective slurry-phase catalyst may be able to counter this tendency through increasing the effectiveness of hydrogenation.

The solution to the problems of making DCL economically viable may exist as one, or any combination, of the above techniques. There is also the possibility of discovering approaches that represent a radical departure from conventional techniques. Meanwhile, research is continuing to move toward the ultimate goal of an inexpensive alternative to imported petroleum.

PETROCHEMICAL FEEDSTOCKS

Feedstocks for the petrochemical industries now are produced mainly from crude oil (Chapter 15) and natural gas (Chapter 16). About 90 percent of all organic chemicals are manufactured from only six feedstocks: synthesis gas, ethylene, propylene, butadiene, benzene, and *p*-xylene, with synthesis gas accounting for 56 percent of these feedstocks. Synthesis gas (a designation for various mixtures of carbon monoxide and hydrogen) now is produced by steam reforming of natural gas or light oils and is used in the manufacture of ammonia, methanol, and other chemicals. However, synthesis gas also may be produced by the gasification of coal.

There are many references that discuss and evaluate processes for the production of chemicals from coal.[7,90,95,98] A typical flow sheet for a plant is shown in Fig. 17.34. This "Coal Refinery" used hydroliquefaction, pyrolysis, and gasification and produces a product slate as shown in Fig. 17.35. The acronym POGO refers to Power Oil Gas Other, a project of the U.S. Department of Energy.

Most basic chemicals currently produced from oil can be produced from coal using demonstrated technology. The broadest range of synthesized products is available by conversion of coal to synthesis gas and utilization of existing processes for production of chemicals such as ammonia, methanol, and acetyl derivatives. Advances in the chemistry of synthesis gas are rapidly expanding the array of chemicals obtainable from coal by this route.[69-71] Many other chemicals can be separated from the by-products of gasification and pyrolysis. In fact, the foundation of the modern chemical industry was built on processes utilizing coal hydrogenation and pyrolysis to obtain a variety of chemicals including dyes, solvents, fuels, and pharmaceuticals.[72] However, in the 1950s the wide availability and low cost of petroleum pushed coal into the background as a raw material.

Today, the choice of feedstock for chemicals production depends on complex technical, economic, environmental, and political factors. Clearly, not all chemical products are suitable for production from coal with current technology. Some factors that must be considered in the evaluation of the appropriate feedstock for a particular chemical product are: (1) the correspondence between the carbon/hydrogen ratio in the chemical and the feedstock, (2) the delivered cost of alternative raw materials, (3) capital costs, (4) environmental protection, and (5) the reliability of supply. Except for special situations, the manufacture of chemicals from coal at present coal prices relative to the prices of petroleum and natural gas does not provide sufficiently attractive economic benefits. Special situations typically are a result of the concurrence of several favorable factors, such as the location of manufacturing facilities very close to coal mines with coal types that closely match the needs of the desired operation, coupled with the use of a process that can best utilize the composition of such coal with minimal conversion toward the hydrogen-to-carbon ratio of competing feedstocks. Alternatively, other situations arise because of political considerations where government subsidies or a closed economy provide the incentives for development of a synthetic fuels or a coal-based chemicals industry.

Chemicals from Coal

The use of coal as a raw material started with the discovery of the first coal tar color by Sir William Perkins in 1856. Prior to this time the liquid by-products of coal coking were regarded as wastes. Perkins's discovery revealed that valuable materials could be isolated or made from coal tar and ultimately led to the establishment of the modern chemical industry. Coke ovens rapidly came to be important as sources of chemicals such as benzene, naphthatlene, ammonia, and hydrogen. Coal tar became an important source for aromatic and heterocyclic chemicals for the dye and pharmaceutical industries.

Chemical by-products from coke manufacture amount to roughly 4 percent of the coal feed. Although this yield initially supplied adequate amounts of chemicals for developing end uses, the growth of the industry eventually required additional sources of chemicals. The advent of technology for producing calcium carbide and acetylene in 1892 provided a means for conversion of coke to chemical products.[73] Also, this technology stimulated the growth of an independent chemical industry by allowing the manufacture of chemicals to be pursued apart from the manufacture of coke for steel production.

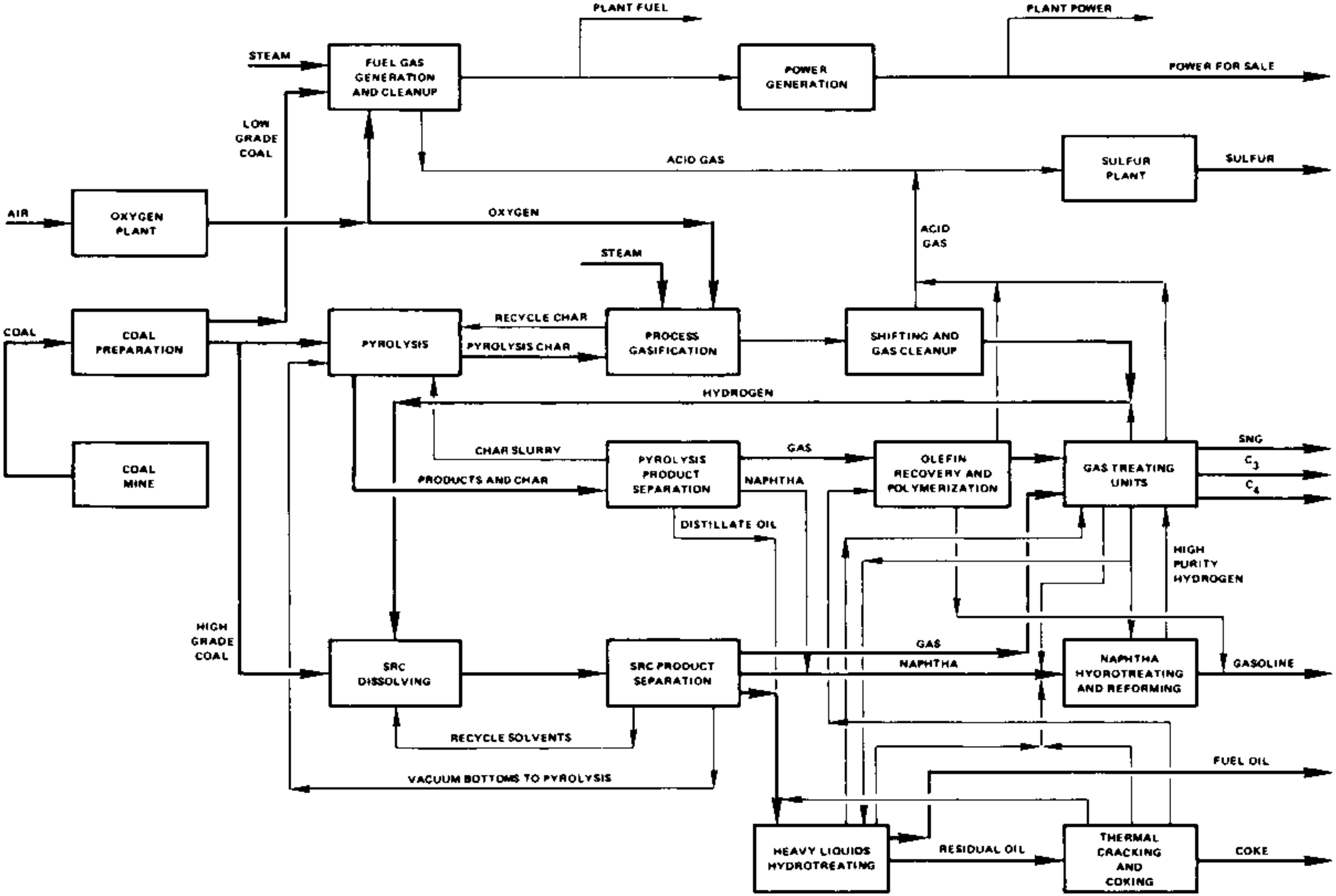


Fig. 17.34. Simplified block diagram of the POGO complex. (*O'Hara, J. B., Klumpe, H. W., Bela, A., and Jentz, N. E., "Project POGO—A Coal Refinery,"* Chem. Engr. Prog., **74**, 8, *pp. 49–63, Aug. 1978. By permission.*)

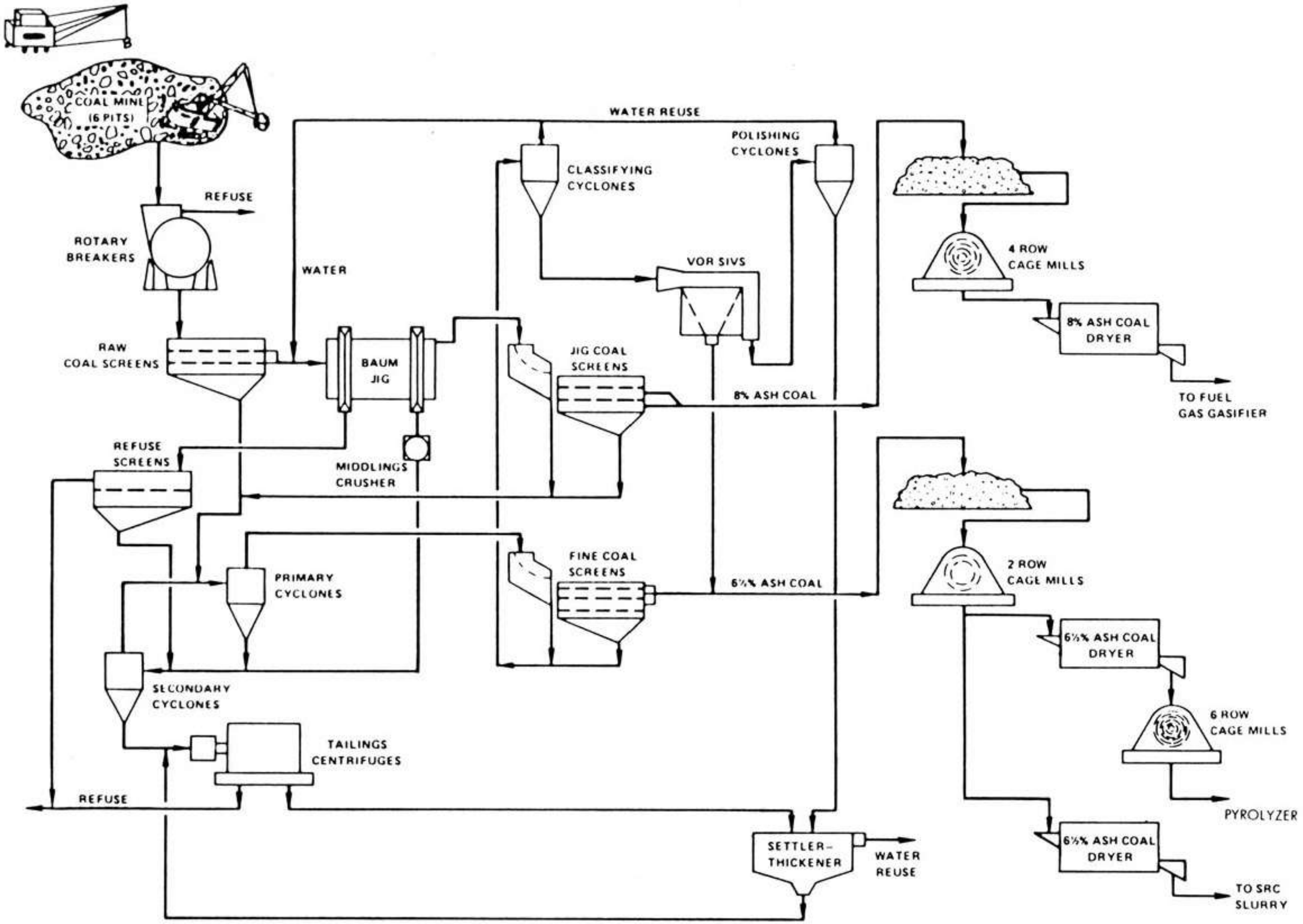


Fig. 17.35. Projected POGO plant yields. (*O'Hara, J. B., Klumpe, H. W., Bela, A., and Jentz, N. E., "Project POGO—A Coal Refinery,"* Chem. Engr. Prog., **74**, 8, *pp. 49–63, Aug. 1978. By permission.*)

In Germany, shortages of petroleum during World Wars I and II prompted industry to develop processes for the conversion of coal into liquids for use as motor fuels. The two most important processes developed and implemented to meet wartime requirements were the Bergius coal liquefaction process and the Fischer-Tropsch process.[74] The Bergius process is a direct liquefaction process involving high-pressure catalytic hydrogenation. The Fischer-Tropsch process is an indirect liquefaction method in which synthesis gas reacts over a metal catalyst to form a range of hydrocarbon products including oxygenates and olefins. Because of the reactive nature of the olefinic and oxygenated coproducts, the Fischer-Tropsch process is particularly appropriate for coproduction of fuels and chemical intermediates. The history of chemicals production from coal shows that coal chemicals typically have been obtained as by-products from processes primarily designed to produce such products as motor fuel, town gas, or coke. Except under certain favorable conditions, economics still suggest that the production of chemicals must be coupled with the manufacture of other end products.

Coke production remains the most important demonstrated technology associated with the direct production of chemicals from coal. Industrial chemicals currently obtained in significant amounts from this source include benzene, toluene, xylene, naphthalene, anthracene, phenanthrene, phenol, ammonia, ammonium sulfate, sulfur, and carbon dioxide. The vast majority of aromatics production from coal occurs in Eastern Europe, India, and Japan.[75]

The combination of chemical and fuel production results in a type of synergism that can benefit the economics of both end products. Thus, some chemicals that cannot be produced economically as primary products from coal may be obtained as revenue-generating coproducts that enhance the overall economics of fuel production. This concept has prompted efforts at Great Plains and Sasol to increase the recovery of chemical by-products from these facilities. At Great Plains, ammonia and sulfur now are recovered, but facilities are being added to recover phenol from gasification liquids and a krypton/xenon mixture from the air separation plant. R&D efforts are in progress to enable economical recovery of other by-products.

In recent years several commercial plants have been constructed for conversion of coal to synthesis gas for chemical manufacturing. These include the Eastman acetic anhydride plant, the Ube ammonia plant, and the SAR oxo chemicals plant. Of these, the Eastman plant is the only one still operating exclusively on coal. Feedstock changes at the other plants illustrate the vulnerability of coal conversion processes to a changing economic climate. The fact that the Eastman process remains competitive under changing conditions is due to a set of special circumstances that favor a coal-based process. The success of the Eastman Chemicals from Coal complex demonstrates that synthesis gas from coal is a viable feedstock for some industrial chemicals, given a specific set of conditions.

Clearly, the slate of chemicals produced from coal-derived synthesis gas will expand as new technologies are developed, and supplies of petroleum and natural gas dwindle. The most likely such chemicals are those for which existing processes have been demonstrated but which presently lack economic merit. Relatively small improvements in technology, shifts in feedstock availability, capital costs, or political factors could enhance the viability of coal-based processes for the production of methanol, ethanol, and higher alcohols, vinyl acetate, ethylene glycol, carboxylic acids, and light olefins.

Developing technologies presently exist for the partial oxidation of coal to organic acids, for plasma pyrolysis of coal to produce acetylene and other small molecules,[76] and for the manufacture of additional chemicals such as acetaldehyde from synthesis gas.[77] Also, the use of coal tar for the manufacture of high-temperature engineering plastics[78] and bioconversion of coal to aromatics, organic acids, alcohols, and methane[79] have been reported. Innovative strategies are being considered that offer potential for reducing the costs of energy and chemicals produced from coal by taking avantage of waste disposal credits through gasification of coal mixed with carbon-containing waste streams.[80]

Mild gasification is another emerging technology being pursued. The objective of this technology is to produce an optimum combination of products, including fuel and chemicals, at conditions considerably less severe than required for synthesis gas generation.[81] The optimum product mix varies with the coal type. Benzene and phenol are large-volume chemicals potentially available from mild gasification of eastern coals, and several high-value carbon products are available from the char produced using western coals.[82]

Indirect Coal Liquefaction

In indirect coal liquefaction, a synthesis gas first is produced in a suitable gasifier by reaction with oxygen and steam. Then this gas is treated to remove sulfur compounds, and the ratio of CO to H_2 is fixed by means of the water-gas shift reaction. The purified, adjusted synthesis gas then is reacted to produce the desired liquid products.

Fischer Tropsch—The SASOL Complex. Fischer-Tropsch synthesis is the best-known indirect liquefaction method. It was developed in 1925 by German chemists Franz Fischer and Hans Tropsch. In this process, synthesis gas is reacted over an iron or cobalt catalyst at 350 psi and 330°C to produce largely aliphatic hydrocarbons, including gasoline, jet fuel, diesel oil, middle distillates, heavy oil, and waxes. The Germans used this technology during World War II to produce nearly 15,000 barrels/day of military fuels.

The South Africans have applied the Fischer-Tropsch technology in their SASOL facility. The Sasol (South African Coal, Oil and Gas Corporation) installation is the world's largest synfuel plant based on coal. It converts an inferior high-ash (35%) coal into a broad spectrum of products, which may include ethylene, propylene, butylene, gasoline, and long straight-chain alcohols and hydrocarbons. The Sasol plant has been operating for over 35 years.

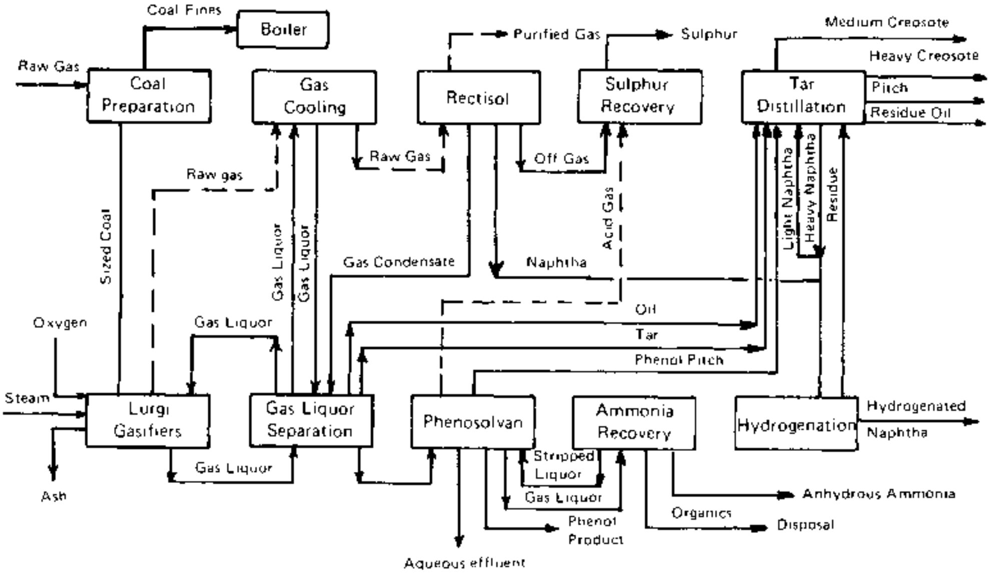
South Africa has substantial deposits of coal but no oil and obtains 75 percent of its energy from coal. The plant at Sasolburg is located on a huge coal field. SASOL I, the existing synthetics plant, is part of a versatile chemical complex that supplies much of South Africa's needs for materials such as nitrogen fertilizers, plastics, and pipeline gas. Consumption of coal at Sasol is 5 million tons/year. Coal is gasified in Lurgi reactors with steam and oxygen under pressures of about 20 atmospheres. Principal products are H_2, CO, CO_2, and CH_4. The key components are H_2 and CO, and their ratio can be adjusted by changing the amounts of H_2O and O_2 used in the gasification. Constituents present in addition to the major gaseous products include NH_3, H_2S, and other sulfur-containing substances. The raw products are purified by cooling the gas, condensing out water and phenolic-type substances, and passing the remaining gas through three absorption trains using very cold methanol. This removes essentially everything except H_2, CO, and CH_4. Sulfur in the purified gas amounts to less than 1×10^{-8}. This guarantees relative freedom from sulfide poisoning of catalysts and a low sulfur content in the final products. A flow sheet is shown in Fig. 17.36.

In October 1973, a large-scale plant, SASOL II, designed primarily to produce gasoline, was authorized by South Africa. In 1978, another major sythetic fuel plant was started. These two new plants were designed for zero emissions of liquid wastes and were intended to produce over 100,000 barrels of coal-derived liquids/day. The total cost of these projects was over $7 billion.

In 1980, Sasol introduced a second generation of its Fischer-Tropsch technology (the Synthol process), and in 1989 a third generation. Each new generation has utilized improved engineering design and has enhanced the utilization of the chemicals generated. At Sasol, the process is operated to produce primarily gasoline and diesel fuels, but it can be modified by using different catalysts and reaction conditions to ehance the yield of oxygenated products that can be separated for chemical uses.[74,83] Some of the oxygenates available

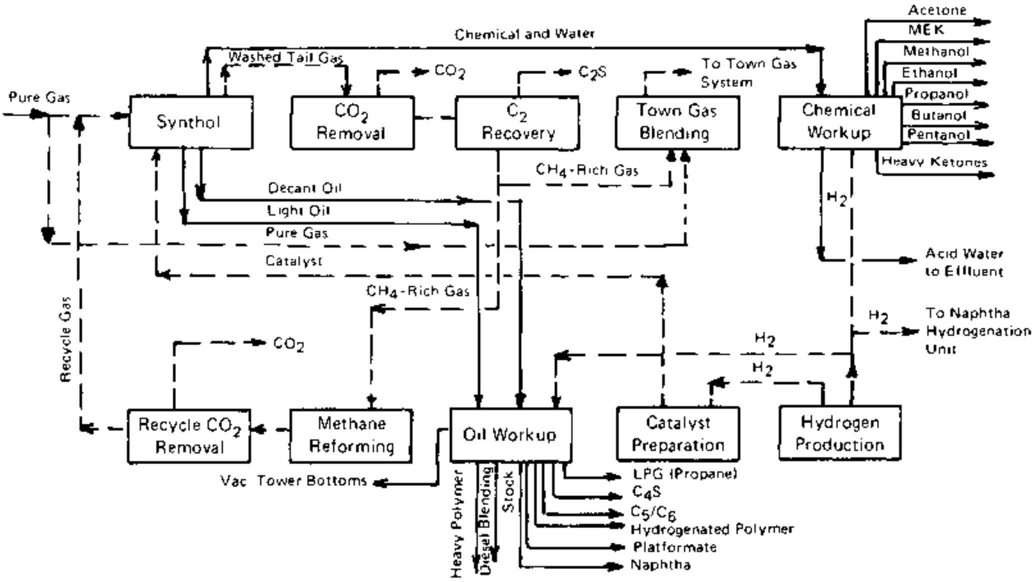
Sasol's Two Main Coal-Into-Oil Processes

Coal gasification and purification flow diagram



(a)

Fischer-Tropsch Synthesis Flow Diagram



(b)

Fig. 17.36. Sasol's two main coal-into-oil processes. (*Reprinted from* Encyclopedia of Chemical Processing Design, *pp. 310, 320, by courtesy of Marcel Dekker, Inc., 1979.*)

from the process are methanol, ethanol, propanol, butanone, and higher alcohols and ketones. Fischer-Tropsch olefins can be separated and used for production of oxo chemicals, synthetic rubber, and alkylbenzene sulfonate detergents. Hydrocarbon waxes produced in the reactors have found a variety of uses. Also, by-products from the Sasol Lurgi coal gasifiers are recovered for chemical and solvent applications. These products include phenol, cresols, toluene, xylenes, ammonia, and sulfur. A recent addition to the spectrum of chemical products from Sasol is polypropylene. Also, Fischer-Tropsch ethane now is being cracked to supplement ethylene production for sale to polyethylene producers. Additional work is in progress to evaluate the recovery of organic acids from aqueous waste streams.

Methanol. Methanol is a water-soluble, low molecular weight alcohol that may be of increasing importance as a low-sulfur fuel, a chemical feedstock, and perhaps an intermediate for the production of gasoline. The synthesis of methanol is accomplished by the catalytic conversion of synthesis gas containing two moles of hydrogen for each mole of carbon monoxide. Methanol synthesis is widely practiced in industry on a commercial scale and will not be discussed further here.

Chemicals from Coal at Eastman Chemical Company

In 1983 Eastman Chemical Company (Division of Eastman Kodak Company) became the first U.S. manufacturer to produce a modern generation of industrial chemicals, with acetic anhydride as the key product, using coal as the feedstock.[84] This production was made possible by successful completion of facilities at Tennessee Eastman Division. in Kingsport, Tennessee. The start-up of this chemical plant was the result of more than a decade of work done to identify, develop, and assemble the numerous technologies needed for a viable commercial venture.

Commercial facilities constructed include a coal gasification plant for synthesis gas manufacture, raw gas cleanup and separation facilities, a sulfur recovery unit, a coal-fired steam plant, and chemical plants to produce methanol, methyl acetate, acetic acid, and acetic anhydride. In the 1980s, these plants gasified approximately 900 tons of coal/day to produce annually over 500 million lb of acetic anhydride, 150 million lb of acetic acid, 390 million lb of methyl acetate, 365 million lb of methanol, and 15 million lb of sulfur. An expansion in 1991 more than doubled the capacity for methyl acetate, acetic acid, and acetic anhydride. Approximately one billion lb of acetic anhydride, one of Eastman's key raw materials, is used each year in making photographic film base, Tenite cellulosic plastics, Estron acetate for filter tow, textile yarns, and coatings chemicals.

A flow sheet of Eastman's chemicals from coal plant is shown in Fig. 17.37. A simplified description of the main plants in the complex follows.

A. *Coal gasification.* In the mid-1970s Eastman engineers and scientists studied modern coal gasification technologies and the modifications necessary to produce chemical feedstocks. After all factors were considered, the Texaco coal gasification process was chosen to provide synthesis gas from the local coal. In this process, oxygen and coal slurry are introduced into the gasifier at elevated temperature and pressure. The Texaco-licensed process operates at sufficiently high temperatures to avoid producing environmentally undesirable by-products. The slag from this process is suitable for disposal in nonhazardous landfills. The energy recovery arrangement produces medium- and low-pressure steam, which is well suited for use by other processes in the complex. The product gas is mainly carbon monoxide and hydrogen, making this unit particularly suitable for the production of chemical feedstocks. Because the raw gas is generated at elevated pressures, the size of the gas cleanup equipment is reduced, and the need to compress the product gas prior to its use as a chemical feedstock is minimized.

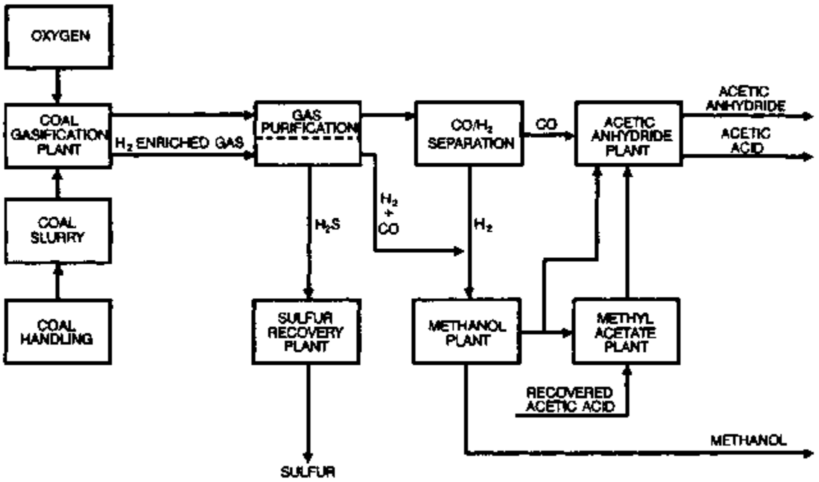


Fig. 17.37. Overall block flow diagram for coal gasification–acetic anhydride complex.

The gasifier product is scrubbed with water to cool the gas and remove any ash particles. A portion of the gas stream is sent to a water–gas shift reaction to increase the hydrogen content. Finally, low-pressure steam is generated as the product gas is cooled before additional purification. The full recovery of this heat increases the thermal efficiency of the process and is important for economical operation of the chemical processes that utilize the steam.

B. *Synthesis gas refinement.* Following the gas scrubbing, shift reaction, and cooling operations associated with the gasifier, the product gas streams are treated to remove hydrogen sulfide in a Rectisol process by utilizing Linde, A. G., technology. In this process, the sulfur in the coal, which is converted to hydrogen sulfide during the gasification process, and carbon dioxide are absorbed by a cold methanol wash. Further processing cryogenically purifies the carbon monoxide and hydrogen streams in a "cold box," also provided by Linde. The cryogenic separation provides a carbon monoxide feed for the acetic anhydride plant and a hydrogen-rich stream suitable for methanol production. These processes are uniquely integrated to improve the overall thermal efficiency of their operation.

C. *Sulfur recovery.* The hydrogen sulfide removed from the product gas streams is further processed into elemental sulfur. Conversion of the sulfide to elemental sulfur results in 99.7 percent of the sulfur originally contained in the coal being recovered and sold as a by-product. This conversion is accomplished using the Claus process followed by a Shell Claus Off-Gas Treating unit (SCOT).

D. *Methanol production.* Methanol is produced from carbon monoxide, carbon dioxide, and hydrogen. The proper gas-feed composition for methanol production is formed by combining the hydrogen-enriched syngas from the shift reactor and the hydrogen–carbon monoxide stream from the gas separation unit. The refined syngas streams, which contain a proper combination of hydrogen and carbon oxides, are fed to a low-pressure, gas-phase catalytic methanol process that is very energy-efficient, both in the method of control of the reactor and in subsequent refinement of the methanol. This process and the proprietary items of equipment were provided by Lurgi, A. G.

E. *Gasification system venting.* Additional efficiency was achieved by providing for combustion of process vent gas streams having fuel value in a nearby powerhouse. Emergency venting of the syngas is directed to one of the two flare systems provided to avoid the development of undesirable or hazardous conditions during process upsets.

F. *Methyl acetate production.* Methanol made from synthesis gas is reacted with by-product acetic acid from cellulose esters manufacturing to form methyl acetate in an Eastman patented process (U.S. Patent 4,435,595). The principal component of this process is a reactor-distillation column in which acetic acid and methanol flow countercurrently, reacting and flashing at each stage. The acetic acid serves the dual functions of reactant and extractive agent to remove water and methanol from their methyl acetate azeotropes.

G. *Production of acetic anhydride and acetic acid.* In the final step of the process, purified carbon monoxide from the gas separation plant is reacted with methyl acetate to form acetic anhydride by using a proprietary catalyst system and process developed by Eastman (U.S. Patent 4,374,070). Part of the acetic anhydride is reacted with methanol to coproduce acetic acid. The methyl acetate resulting from this reaction is recarbonylated in the acetic anhydride reactor system. The acetic acid and acetic anhydride are refined in the distillation section of this plant. A reactor liquid purge stream removes high molecular weight by-products, and a catalyst recycle process recovers and regenerates the catalyst from the purge stream (U.S. Patent 4,388,217).

The Eastman Chemicals from Coal Plant has been demonstrated to provide an economically attractive process for commercial production of acetic anhydride. It is instructive to recapitulate some of the factors that contribute to this situation.

A. *Plant configuration.* (1) The hydrogen-to-carbon monoxide ratio of the syngas is well suited to combined production of methanol and acetic anhydride. Although the hydrogen is not needed for production of acetic anhydride via carbonylation, it is used to decrease the hydrogen deficiency in the feed gas and thus minimizes use of the water–gas shift reactor. (2) The methyl acetate and acetic anhydride plants are highly energy-efficient, and they use medium and low-pressure steam produced by cooling the gasifier product. (3) The acetic anhydride is used in existing processes to make cellulose acetate. The reaction produces by-product acetic acid that can be recycled to the methyl acetate plant to react with methanol. This combination of processes obviated the need to construct an acetic acid plant.

B. *Coal feedstock advantages.* (1) The operating cost is less than for a natural gas or petroleum-based plant. (2) The coal cost is closely related to mining and delivery costs and is less subject to unstable political environment than that of petroleum. (3) The plant location near Appalachian coal fields minimizes delivery costs. (4) Coal gasifiers can use less expensive high-sulfur coal, and the sulfur can be recovered and sold to further improve the economics.

C. *Environmental advantages.* (1) No tar or other hydrocarbon waste streams are produced in the high-temperature (over 2500°F) gasifier. (2) The molten slag is converted to inert granular pellets that qualify for nonhazardous landfill. (3) Wet grinding of the coal to form a slurry eliminates dust problems. (4) Because the sulfur in the coal is converted to hydrogen sulfide in the gasifier, more than 99.7 percent is eventually recovered as elemental sulfur. (5) Aqueous streams containing hydrocarbons from the chemical plants are recycled to the gasifier for slurry and quench water makeup. (6) Tail-gas streams from the chemical plants are burned for heat recovery in existing boilers and furnaces.

Methanol to Gasoline—The Mobil Process. Mobil Research and Development Corporation, under a contract with the U.S. Department of Energy, developed a process that catalytically dehydrates and polymerizes methanol to produce a high octane unleaded gasoline. The catalyst is one of a new family of synthetic zeolites designated ZSM-5 by Mobil. These new zeolites have a unique channel structure, different from previously known

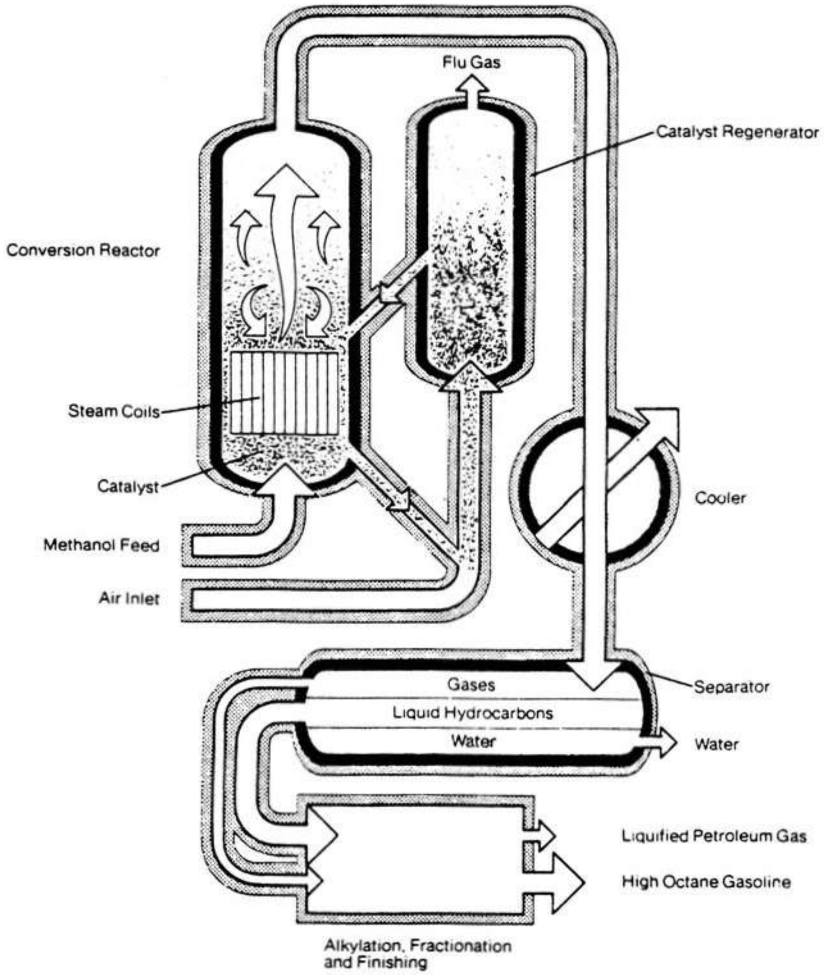


Fig. 17.38. Mobil's fluid-bed MTG process uses a unique zeolite catalyst in converting methanol directly to high octane, unleaded gasoline. (*Courtesy The Pace Company, Denver, CO.*)

wide-pore (9–10 Å in diameter) and other narrow-pore (5 Å) zeolites. One of these new zeolites converts methanol into a mixture of hydrocarbons corresponding to high-quality gasoline. The mass balance shows 0.44 lb of gasoline and 0.56 lb of water from each pound of methanol, and the heating value of the gasoline is 95 percent of that in the methanol feed. A schematic diagram of the process is shown in Fig. 17.38. Crude methanol is vaporized at the bottom of the reactor and passes through the dense fluidized bed at 775°F and 25 psig. The methanol is converted to hydrocarbons and water. The catalyst is removed from reaction products in a disengager section at the top of the reactor, the reactor effluent is condensed, and the water and hydrocarbon products are separated. To make additional gasoline, propene and butenes can be alkylated with isobutane by conventional petroleum technology. The reactor is 25 feet long and 4 inches in diameter.

Portions of the catalyst powder are periodically removed from the reactor and regenerated with air. The regenerated catalyst is transferred back to the reactor. Small amounts of carbon monoxide, carbon dioxide, and coke are formed as by-products.

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18

Rubber

T. C. Bouton*

INTRODUCTION

The word "rubber" immediately brings to mind materials that are highly flexible and will snap back to their original shape after being stretched. In this chapter a variety of materials are discussed that possess the characteristics describing this class of materials. Originally rubber meant the gum collected from a tree growing in Brazil. The term "rubber" was coined for this material by the English chemist Joseph Priestley, who noted that it was effective for removing pencil marks from paper. Today, in addition to Priestley's natural product, many synthetic materials are made that possess these characteristics and many other properties. The common features of these materials are that they are made up of long polymer chains that are amorphous (not crystalline), they have a high degree of flexibility such that they do not stiffen until temperatures well below ambient are reached, and the chains can form a three-dimensional network in some manner.

It is difficult, indeed almost impossible, to visualize a modern society without rubber products. The development of synthetic rubber began out of the need for countries to establish independence from natural products that grew only in tropical climates. In times of conflict the natural product might not be available, and its loss would seriously threaten national security. Synthetic rubber, then, became a strategic concern during World Wars I and II.[1] Beyond the security issue, the need for materials with better performance also provided a strong impetus for the development of new rubbery materials. In particular, improvements in oil resistance, high temperature stability, and oxidation and ozone resistance were needed.[2] Research today is driven to develop materials with even better performance in these areas.

The demand for rubber was estimated to be 15.845 million metric tons for 1990.[3] Of this demand, 67 percent is synthetic rubber of various kinds. Rubber has been classified by use into general purpose and specialty. The major general purpose rubbers are natural rubber, styrene-butadiene rubber, butadiene rubber, isoprene rubber, and ethylene-

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*Firestone Synthetic Rubber & Latex Co., Division of Bridgestone/Firestone, Inc., Akron, OH.

propylene rubber. These rubbers are used in tires, mechanical goods, and similar applications. Specialty elastomers provide unique properties such as oil resistance or extreme heat stability. Although this differentiation is rather arbitrary, it tends also to classify the polymers according to volumes used. Styrene-butadiene rubber, butadiene rubber, and ethylene-propylene rubber account for 75 percent of all synthetic rubber consumed.

The 1990 estimated synthetic rubber capacity by type is presented in Table 18.1, and Table 18.2 lists the U.S. rubber consumption by type in 1989.

TABLE 18.1 Synthetic Rubber Production by Type (Excludes Centrally Planned Economy Countries)

Type	*Description*	*Capacity Metric Tons*
SBR-solid	Styrene/butadiene rubber (emulsion plus solution)	2,430,000
SBR-latex	Styrene/butadiene emulsion rubber–latex	315,000
BR	Butadiene rubber	968,000
IR	Isoprene rubber	129,000
CR	Chloroprene (or neoprene) rubber	308,000
EPDM	Ethylene/propylene terpolymer	573,000
NBR	Nitrile or acrylonitrile/butadiene rubber	262,000
Others		595,000

Worldwide Rubber Statistics 1990, International Institute of Synthetic Rubber Products, Inc.

TABLE 18.2 U.S. Rubber Consumption, 1989 (Metric Tons)

Total new rubber	2,917,836
Natural	866,870
Total synthetic	2,050,966
SBR	769,579
Nitrile	65,645
Polybutadiene	374,793
EPDM	288,855
Butyl polyisoprene, polychloroprene, silicone, and others	612,094
% Natural	29.7
% Synthetic	70.3

"RMA Statistical Report," Rubber Manufacturers Association, 1400 K Street, NW, Washington, DC 20005.

RUBBER CONCEPTS

Several key principles (outlined below) greatly help interested persons in understanding the performance of elastomeric materials. This outline should present these concepts well enough for use in the following discussions of specific polymer types. However, the reader should consult the references for a more complete understanding of these principles. The concepts are classified as those that relate to polymer structure, those that relate directly to physical properties, and those that relate to the use of the material, as listed below.

1. Polymer structure
    a. Macrostructure
        - Molecular weight
        - Molecular weight distribution
        - Branching
    b. Microstructure
    c. Copolymer composition
    d. Network structure
2. Rubber properties
    a. Glass transition temperature
    b. Crystallinity
3. Rubber use
    a. Compounding
    b. Processing

POLYMER STRUCTURE

Macrostructure

Molecular Weight. The single most important property of any polymer is the size or length of the molecule. The polymerization process consists of combining many of the simple monomer molecules into the polymer chain. Most of the monomers used to produce rubbers are either gases or low-viscosity liquids under normal conditions; upon polymerization they form liquids whose viscosity increases to extremely high values as the chain length is increased. At very low chain length, this increase is linear with molecular weight until the chains are long enough to become entangled. Above the entanglement molecular weight, the viscosity increases to the 3.4–3.5th power of molecular weight increase.[4] In addition to viscosity, a great many other physical properties of any polymer depend upon the molecular weight.[5]

Molecular Weight Distribution. A given polymer sample is composed of many polymer chains, which in most cases are not of the same length. This variability can be a result of the synthesis process or of possible random scission and cross-linking that can occur upon processing. For economic reasons, it is not possible to separate the various polymer chains by length prior to use; so it is important to characterize this distribution in order to describe the polymer and understand its performance. As with any distribution, no single number is a totally satisfactory descriptor.

The commonly used molecular weight parameters[6] are the number, weight, and z average molecular weight, which are defined, respectively, as:

$$Mn = \Sigma N_i M_i / \Sigma N_i$$

$$Mw = \Sigma N_i M_i^2 / \Sigma N_i M_i$$

$$Mz = \Sigma N_i M_i^3 / \Sigma N_i M_i^2$$

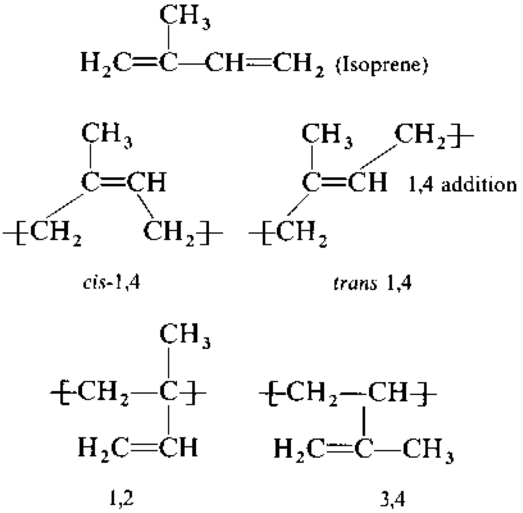
where N_i is the number of moles of species i, and M_i is the molecular weight of species i.

Although there are many different statistical ways to describe any population, the above parameters have been widely used because they are readily understood in physical terms, and they can be measured directly in the laboratory.[7] A fourth parameter, the dispersion index, frequently is used to characterize the breadth of the distribution. This parameter is simply the ratio of the weight to the number average molecular weight, with 1.0 being the lowest possible number (i.e., all chains of exactly the same length). Typical values for commercial polymers are in the 2 to 5 range, with those under 2 considered relatively narrow and those over 2.5 considered broad in distribution. The measurement of these molecular weight averages once was a time-consuming task, but with the development of gel permeation chromatography (GPC), also referred to as size exclusion chromatography, the measurement of these distributions has become commonplace.[8] Units are even available that automatically sample polymerization reactors, process the sample, and perform all necessary calculations to provide data for process control. These units can have multiple detectors, thereby providing compositional distribution as a function of molecular weight.

Branching. The concept of a polymer chain implies two ends per chain. However, because of the nature of the process used to form the polymer, the chain may contain one or more branch points, resulting in multiple ends per chain. These chain ends can have an adverse effect on polymer performance. Branching, molecular weight, and molecular weight distribution have been shown to affect processability as well.[9] The optimum macrostructure often represents a compromise between processing and ultimate performance.

Microstructure

In the formation of elastomers from diolefin monomers such as butadiene or isoprene, there are a number of possible structures. As the control of these structures is critical in obtaining optimum properties, this area has received great attention from the synthesis chemist. The possible isoprene structures are:



Vinyl addition

For butadiene (no methyl group) the 3,4 form does not exist. The 1,2 addition is referred to as vinyl addition.

The polymer in natural rubber (from the *Hevea brasiliensis* tree) is pure *cis* polyisoprene; gutta percha and balata are composed of the *trans* isomer.

Copolymer Composition

Many of the commercial synthetic elastomers are synthesized from more than one monomer, such as styrene-butadiene and ethylene-propylene rubbers. The properties of the resultant polymer depend on the ratio of the two monomers in the polymer and upon the distribution of the monomers within the chain.

If the monomers are uniformly distributed within the polymer chain, the ratio of monomers will define the flexibility of the polymer chain.[10] Because many properties depend on this chain mobility, polymer composition is carefully controlled. In addition to chain mobility, polymer composition also defines the solubility parameter of the polymer, which is a critical property relative to the type of solvents in which the polymer is soluble, the ability of the polymer to accept and hold oil, and the relative compatibility of the polymer with other polymers.[11] Basically, these properties all involve polymer/solvent interaction, with the difference being the increasing molecular weight of the solvent.

In addition to the relative ratio of the monomers, the arrangement of the units in the chain is important. This arrangement is referred to as the copolymer sequence distribution. In the previous discussion, the assumption was made that the comonomer units were well mixed in the polymer chain. If this is not the case, parts of the chain can reflect properties of the corresponding homopolymer. It is thus possible to produce polymers that have significantly different properties in different parts of the polymer chain. A most dramatic example of this can be found in styrene-butadiene-styrene or styrene-isoprene-styrene thermoplastic elastomers. These triblock polymers behave as cured elastomers at room temperature. The polystyrene blocks have sufficiently different solubility from the polydiene portions that they phase-separate into domains. These polystyrene domains, having multiple chains entering each one, serve as temporary cross-links, in that it is very difficult to pull a styrene block out of the polystyrene domain, and at the same time the domains act as fillers because of their size and hardness. However, once the polymer is heated above the softening point of the domain, the chain can easily be pulled out of the domains, allowing for polymer processing.[12]

In production of most copolymers, the composition incorporated into a polymer chain is generally not the same as that of the monomer ratio, owing to the relative reactivity of different species. As the active chain species can be from either of the two monomers, and either of the monomers can add to any growing end, the following four equations are required to describe the system:

$$-A^* + A \rightarrow -A - A^* \qquad (k_{AA})$$

$$-A^* + B \rightarrow -A - B^* \qquad (k_{AB})$$

$$-B^* + A \rightarrow -B - A^* \qquad (k_{BA})$$

$$-B^* + B \rightarrow -B - B^* \qquad (k_{BB})$$

where the * designates the growing chain end and the k's are the corresponding reaction rate constants. Two relative rate constants, r_A and r_B, called the reactivity ratios, can be used to characterize the nature of the copolymerization, where r_A is defined as k_{AA}/k_{AB} and r_B as k_{BB}/k_{BA}. The copolymer composition will be the same as the monomer mixture only if $r_A = r_B = 1$, which is relatively rare. If r_A and r_B approach zero, the units will tend toward alternation, whereas if $r_A \times r_B = 1$, the copolymer composition is dependent on the monomer composition and will vary with conversion. Tables of reactivity ratios are published, covering many monomer pairs and polymerization conditions.[13] More detailed discussions of copolymerization kinetics can be found in the references.[14,15]

Network Structure

A critical requirement for obtaining engineering properties from a rubbery material is its existence in a network structure. Charles Goodyear's discovery of vulcanization changed natural rubber from a material that became sticky when hot and brittle when cold into a material that could be used over a wide range of conditions. Basically, he had found a way to chemically connect the individual polymer chains into a three-dimensional network. Chains that previously could flow past one another under stress now had only limited extensibility, which allowed for the support of considerable stress and retraction upon release of the stress. The terms "vulcanization," "rubber cure," and "cross-linking" all refer to the same general phenomenon.

For most rubber systems the network is formed after the polymer is compounded and molded into the desired final shape. Once cross-linked, the material no longer can be processed. If cross-linking occurs prior to compounding or molding, the material is referred to as gelled, and it cannot be used. Most rubber is used in a compounded and cured form.

The one general class of polymers that fall outside this concept is the thermoplastic elastomers, one example of which was discussed previously. These materials can be processed (and reprocessed) at high temperature, yet they maintain properties of cured rubber at use temperatures. This system functions by the formation of either hard plastic, crystalline, or ionic domains that, at use temperature, act as cross-link sites because multiple chains are involved in the domains. Upon heating, the integrity of these domains breaks down, and the polymer chains can easily flow past one another. It should be noted that at use temperatures these systems have a three-dimensional network. Such systems tend to show more creep and stress relaxation than cured systems, as the network is formed via weaker secondary effects rather than primary chemical bonds. These problems become more severe as the use temperature is increased because ultimately the network cannot remain intact at processing temperatures. For any network, its structure is important in defining the performance of the final product. Such properties as modulus, hardness, and tensile strength are dependent on the network density.[16]

RUBBER PROPERTIES

Glass Transition Temperature

In order for a polymer to behave as a rubbery material, it is necessary for the chain to have great mobility. As the temperature is lowered, the ability of the chain segments to move decreases until a temperature is reached where any large-scale motion is prevented. This temperature is referred to as the glass transition temperature. Below this temperature the rubber becomes a glassy material—hard and brittle; above this temperature amorphous plastics, such as polystyrene, can exhibit rubbery character if the molecular weight is sufficiently high. All rubbery materials, then, must have glass transition temperatures below room temperature. For good low-temperature properties, it obviously follows that a low glass transition temperature polymer is required. The control of the glass transition temperature of the polymer is critical for many properties other than low temperature use. For example, the wet traction and wear of a passenger tire have been shown to depend directly on the polymer glass transition temperature.[17]

Control of this property is possible by controlling the structure of the polymer chain. Monomers with bulky side groups restrict chain mobility and thus raise the glass transition temperature. The composition of copolymers and the ratio of polymer blends often are determined by the desired glass transition temperature of the final product.

Crystallinity

Polymer chains can exist in spatial arrangements that are orderly enough to allow the chains to form crystalline structures. The existence of strong interchain interactions via polar forces, hydrogen bonding, or ionic groups can facilitate crystallization. The existence of crystallization is very important for many plastics and fibers, but crystallinity cannot be appreciably present in rubbery materials, as the corresponding restriction in chain mobility could preclude the very chain mobility needed for rubbery properties. Rubbery materials must have both their melting temperature (if they have a crystalline point) and their glass transition temperature below the use temperature.

Crystallinity can be reduced by disruption of the order in the chain by copolymerization.[18] For example, both polyethylene and polypropylene are crystalline plastics, whereas ethylene/propylene rubber produced at about a 50/50 ratio is an amorphous elastomer. Compositional excursions much outside this range lead to crystalline materials.[19] For some materials, such as natural rubber, that are close to crystallizing, stretching the chains can align them sufficiently for crystallization to occur. Such polymers can exhibit excellent gum properties and improved strength in the uncured state that greatly facilitate processing. Attempts have been made with some success to produce other polymers that exhibit this property of natural rubber. Although the melting temperature can be matched by appropriately disrupting the crystallizable structure through controlled introduction of another monomer, an exact match is not possible because the extent of crystallinity and the kinetics of crystallization will differ.

RUBBER USE

Compounding

The rubber industry began when Charles Goodyear developed the first useful rubber compound: natural rubber plus sulfur. The concept of mixing materials into rubber to improve performance is still of primary importance today. Without compounding, few rubbers would be of any commercial value. Any given rubber application will have a long list of necessary criteria in addition to cost, encompassing appearance, processing, mechanical, electrical, chemical, and thermal properties. Developing such compounds requires a broad knowledge of material science and chemistry combined with experience. The use of designed experiments (see Chapter 4) can greatly facilitate selecting the optimum compound formulation.

The major components in a compound are curatives, reinforcing agents, fillers, plasticizers, and antidegradants.

Curatives. The function of curatives is to cross-link the polymer chains into a network; the most common ones are the sulfur type for unsaturated rubber and peroxides for saturated polymers. Chemicals called accelerators may be added to control the cure rate in the sulfur system; these materials generally are complex organic chemicals containing sulfur and nitrogen atoms. Stearic acid and zinc oxide usually are added to activate these accelerators. Metal oxides are used to cure halogenated polymers such as polychloroprene or chlorosulfonated polyethylene.

Reinforcing Agents. Carbon black and silica are the most common reinforcing agents. These materials improve properties such as tensile strength and tear strength; also, they increase hardness, stiffness, and density and reduce cost. Almost all rubbers require reinforcement to obtain acceptable use properties. The size of the particles, how they may be interconnected (structure), and the chemical activity of the surface are all critical properties for reinforcing agents.

Fillers. Fillers are added to reduce cost, increase hardness, and color the compound. They generally do not provide the dramatic improvement in properties seen with reinforcing agents, but they may have some reinforcing capability. Typical fillers are clays, calcium carbonate, and titanium dioxide.

Plasticizers. These materials are added to reduce the hardness of the compound and can reduce the viscosity of the uncured compound to facilitate processes such as mixing and extruding. The most common materials are petroleum-based oils, esters, and fatty acids. Critical properties of these materials are their compatibility with the rubber and their viscosity. Failure to obtain sufficient compatibility will cause the plasticizer to diffuse out of the compound. The oils are classified as aromatic, naphthenic, or paraffinic according to their components. Aromatic oils will be more compatible with styrene-butadiene rubber than paraffinic oils, whereas the inverse will be true for butyl rubber. The aromatic oils are dark colored and thus cannot be used where color is critical, as in the white sidewall of a tire. The naphthenic and paraffinic oils can be water-white and are referred to as nonstaining.

Antidegradents. This group of chemicals is added to prevent undesirable chemical reactions with the polymer network. The most important are the antioxidants, which trap free radicals and prevent chain scission and cross-linking. Antiozonants are added to prevent ozone attack on the rubber, which can lead to the formation and growth of cracks. Antiozonants function by diffusion of the material to the surface of the rubber, thereby providing a protective film. Certain antioxidants have this characteristic, and waxes also are used for this purpose.

Processing

A wide range of processes are used to convert a bale of rubber into a rubber product such as a tire. The first process generally will be compounding. Typical compounding ingredients were discussed previously. In many compounds more than one rubber may be needed to obtain the performance required. Uncured rubber can be considered as a very high-viscosity liquid; it really is a viscoelastic material possessing both liquid and elastic properties. Mixing materials into rubber requires high shear, and the simplest method is a double roll mill in which the rubber is shear-mixed along with the other compounding ingredients in the bite of the mill. Large-scale mixing is most commonly done with a high-shear internal mixer called a Banbury. This mixing is a batch process although continuous internal mixers also are used.

The compounded rubber stock will be further processed for use. The process could be as simple as injection- or transfer-molding the stock into a hot mold where it is cured. Extrusion of shaped stock frequently is used to make hose or tire tread material. Another common process is calendering, in which a fabric is passed through rolls where rubber stock is squeezed into the fabric, to make rubber fabric for roofing membranes or body plies containing the cord for tire construction. The actual construction of the final product can be very complex. For example, a tire is built of many different rubber stocks and components. Different compounds are used for sidewalls, treads, body plies, and bead areas. Steel or fiber cords are required for the tire body, and steel is required to provide the strength needed in the bead area, which holds the tire to the rim. All of these components must be assembled with high precision so that the final cured unit can operate smoothly at high speeds. Tires must perform at hot and cold temperatures under wet and dry conditions for 30,000 or more miles. Although tires appear to be simple round black objects, they obviously are complex high-technology composite structures.[20–22]

NATURAL RUBBER

More than 500 years ago, the people of Central and South America were using a product that they collected from certain trees to make balls and to coat fabric to make it waterproof. This material they called *cauchuc*, which means "weeping wood." Today we know the tree as the *Hevea brasiliensis* and the material as natural rubber. Although a number of plants produce rubber, the only significant commercial source is the *Hevea* tree. Natural rubber had only limited applications until 1839, when Charles Goodyear found that when combined with sulfur and heated, the material changed into cured rubber with properties much as we know them today. The development of the pneumatic tire in 1845 combined with the dramatic growth of the automotive industry led to a rapid increase in the demand for natural rubber.

Although the tree was indigenous to Brazil, seeds were taken to England where they were germinated, and the plants were sent to the Far East. Rubber plantations were in existence by the late 1800s, and in the 1920s plantations were begun in West Africa. Because of a leaf blight disease, essentially all natural rubber now comes from plantations in Africa and the Far East rather than Central and South America.[21]

The production process starts with the trees. Over the years considerable biological research has been done to produce trees that grow faster, produce more latex, and are resistant to wind and disease damage. Once such an improved tree has been identified, buds are grafted from the tree onto root stock. All such trees are referred to as clones and will have the same characteristics. It typically takes 6 to 7 years of growth before a tree is ready for rubber recovery. Peak rubber production is reached at 12 to 15 years of age. Another major development in improving tree performance has been the use of tree stimulants, which have resulted in an overall yield increase of 30 percent without adverse effects on the trees.

The production process of natural rubber in the tree is not yet fully understood. However, it involves a long series of complex biochemical reactions that do not involve isoprene as a monomer, even though the resulting polymer is 100 percent *cis* 1,4 polyisoprene. Because the tree makes the product, the rubber production process is really one of recovery.

The recovery process starts with tapping of the tree, which involves manually removing thin sections of bark at an angle so that as the latex is exuded from the damaged living latex cells, it will flow down to be collected in a cup. The depth of the cut is critical, as a too-shallow cut will not allow optimum latex yield, and too deep a cut will damage the tree. The damaged latex vessels will seal off after several hours. A preservative is added to the collection cup to prevent coagulation of the latex. The tapper then collects the latex and takes it to a collection station, from which it is shipped to the rubber factory. Additional preservative is added at the collection station to assure stable latex. The latex contains around 30 to 45 percent rubber. Approximately 3 percent of the solid material is nonrubber materials, consisting primarily of proteins, resins, and sugars.

The latex is processed in one of several ways, depending on the desired final product. If it is going to be used in the final product application in the latex form (such as for dipped goods and adhesives), it will be concentrated to 60 percent or higher solids. The most common process is centrifugation. The latex separates into the high-solids product and a low-solids skim material that contains a much higher percentage of the nonrubbery components; rubber produced from skim is generally of a lower quality because of these impurities. A variety of chemicals can be added to the latex to provide the necessary preservation and mechanical stability. As the final use of the latex will involve destabilizing the rubber particles, care must be taken not to overstabilize the latex concentrate. Being a natural product, the latex tends to change upon aging, a factor that also must be compensated for in the process.

Dry rubber is produced from the latex first by dilution, then by coagulation with organic acids, and finally by formation into sheets or crepe. Rubber smoked sheets are made by working the coagulated sheets between rolls to remove as much of the nonrubbery components as possible, followed by drying for up to a week in a smokehouse. The smoke serves as a fungicide that prevents biological attack of the rubber. To provide a more well-defined uniform product, Technically Specified Rubber (TSR) processes have been developed. These processes involve converting the coagulated rubber into rubber crumb, which is further washed, dried, and baled. Constant-viscosity grades of natural rubber have been developed by chemically reacting the aldehyde groups, which otherwise would lead to cross-linking upon storage. In the pale crepe process the latex is carefully selected for colored bodies (from carotene) and treated with sodium bisulfite to stop enzyme activity. The rubber is extensively washed through rollers to remove serum, as this can lead to yellowing. The wet crepe is dried under carefully controlled temperatures and in the absence of light to assure optimum properties. The previously described processes involve considerable investment and are practical only for plantation operations. Small shareholders may allow their latex to coagulate naturally and sell it to processors. Such a product will vary greatly, depending on the specific history of each rubber slab.[23]

Uses

The largest use of natural rubber is in the manufacture of tires. Over 70 percent of its consumption is in this area. The next largest use is as latex in dipped goods, adhesives, rubber thread, and foam. These uses account for approximately another 10 percent. The remainder is used in a variety of applications such as conveyor belts, hoses, gaskets, footwear, and antivibration devices such as engine mounts.

Because of the high stereoregularity of natural rubber, the units in the polymer chain can form very orderly arrangements, which result in crystallization upon storage at low temperatures or upon stretching. Stored crystallized rubber may be converted to its original amorphous state by heating. Several crystalline forms are reported, with melting points varying from 14°C to 36°C.[24] Although crystallization upon storage can be a problem to users, the ability to crystallize reversibly upon stretching accounts for many of the unique properties of natural rubber. Specifically, the ability of natural rubber to be used as a gum polymer (unfilled vulcanizate) depends on this property. The crystallites that form act both as filler and as temporary cross-links, providing high tensile properties.[24] In tire fabrication this property is reflected in natural rubber stocks possessing high green (uncured) strength and excellent building tack. In the final product, strain-induced crystallization provides tear and cracking (cut growth) resistance.

Although many other polymers can crystallize, only natural rubber has been found to have the necessary combination of rate of crystallization, degree of crystallization, and melting point to provide all of the properties discussed above. Natural rubber has good flexibility and resilience. In truck and bus tires, it is used extensively with blends of polybutadiene to give the low heat buildup needed as well as wear and cut growth resistance. In passenger tires, natural rubber is used in the sidewalls and carcass areas. These areas require the building tack, ply adhesion, and hot strength properties that it imparts. Synthetic rubber is used almost exclusively in passenger tire treads.

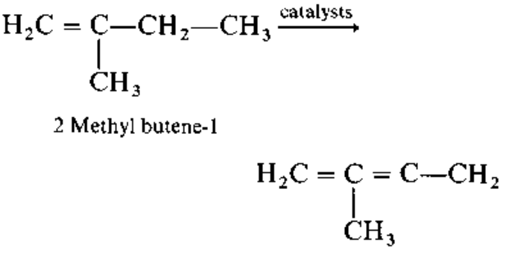
The largest use of natural rubber latex is in the dipped goods area. Products include balloons, surgical and examination gloves, and prophylactics. The rapid spread of AIDS has led to a dramatic increase in the surgical and examination glove market. Latex also is used to make adhesives, rubber thread, and foams. However, natural rubber is being replaced in these two latex areas by urethanes and synthetic rubber latex. Although natural rubber latex is a mature product, research continues on improving its uniformity, stability, and performance.[26]

POLYISOPRENE

Faraday discovered in 1826 that natural rubber was composed of a hydrocarbon with a ratio of five carbons to eight hydrogen atoms; and in 1860, G. Williams isolated isoprene by collecting the distillate from the heating of natural rubber. By 1887, scientists in France, England, and Germany had converted isoprene back into a rubbery material. Because this offered a potential for manufactured "natural" rubber, research was undertaken to find ways to obtain isoprene from sources other than rubber itself.[27]

Monomer Production

The primary source of isoprene today is as a by-product in the production of ethylene via naphtha cracking. A solvent extraction process very similar to that used for butadiene is employed. Much less isoprene is produced in the crackers than butadiene, so the availability of isoprene is much more limited. Isoprene also may be produced by the catalytic dehydrogenation of amylenes, which are available in C-5 refinery streams:



$$H_2C = \underset{\displaystyle CH_3}{\underset{|}{C}}—CH_2—CH_3 \xrightarrow{\text{catalysts}} H_2C = \underset{\displaystyle CH_3}{\underset{|}{C}} = C—CH_2$$

2 Methyl butene-1

Isoprene

It also can be produced from propylene by a dimerization process, followed by isomerization and steam cracking. A third route involves the use of acetone and acetylene, produced from coal via calcium carbide. The resulting 2 methyl butyn-3-ol-2 is hydrogenated to methyl butanol and subsequently dehydrogenated to give isoprene. The plants that were built on these last two processes have been shut down, evidently because of the relatively low cost of the extraction route.

Polymer Production Process

The free-radical catalysts were found to produce a product that did not have the tack, green strength, or gum tensile of natural rubber. Whereas natural rubber is an essentially pure *cis*-1,4 structure, the emulsion product was of mixed microstructure. This precluded the ability of the latter to undergo stress-induced crystallization, which is required to obtain many of the desired natural rubber properties.

In 1955 investigators from the Firestone Tire and Rubber Company and the B. F. Goodrich Company announced the synthesis of polyisoprene with over 90 percent *cis*-1,4 structure. The work at Firestone was based on lithium metal catalysts, whereas the work at Goodrich was the result of using Ziegler-Natta type coordination catalysts.[28,29]

Use

Although considerable interest was generated by these discoveries, their commercial success has been rather limited. The lithium-based polymers were found to produce up to 94 percent *cis*, which still was not high enough to provide the properties of natural rubber. Polymers made with the coordination catalysts have *cis* contents of up to 98 percent, providing products that can more closely serve as replacements for natural rubber than the lithium-based polymers. In comparison with natural rubber, they offer the advantage of very high rubber content and excellent uniformity in quality. For economic reasons, polyisoprene has seen only limited success. Several of the plants built to produce polyisoprene have been either shut down or converted for use to produce other polymers. In terms of synthetic rubber production in 1988, only 129,000 metric tons were produced (excluding centrally planned economy countries), which represented only 3 percent of total synthetic rubber production. Since that time an additional 45,000-metric-ton plant has been closed. In comparison, in 1989 natural rubber usage was 4,114,000 metric tons.[30] Evidently because of its strategic importance, the former Soviet Union continues to rely heavily on polyisoprene, with a 1990 capacity of 960,000 metric tons.[31]

STYRENE-BUTADIENE RUBBER

The largest-volume synthetic rubber consumed is styrene-butadiene rubber (SBR). In 1990, SBR solid rubber accounted for 35 percent of all synthetic rubber. If SBR latex and carboxylated SBR latex are included, its share increases to 55 percent. The major application of solid SBR is in the automotive and tire industry, accounting for approximately 70 percent of the use. Therefore, SBR has been tightly tied to the tire business.[32]

Initially, SBR was developed as a general purpose alternate material to natural rubber. In the United States the thrust came early in World War II when the U.S. supply of natural rubber was cut off. The basic technology was developed in Germany in the late 1920s, and by 1939 Germany had 175,000 metric tons of capacity in place. The first U.S. production was 230 metric tons in 1941, but by 1945 more than 850,000 metric tons of capacity were in place. Basically, in a period of five years the emulsion SBR business as we know it today was put in place. By 1973 U.S. capacity had increased to almost 1,400,000 metric tons, but in 1989 it had contracted to 881,000 tons—close to the 1945 capacity.[33]

Monomer Production

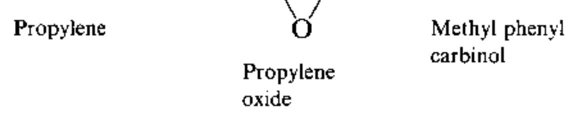
The production of butadiene monomer is discussed below in the polybutadiene section. Styrene is producted by two processes: The largest volume process involves the alkylation of benzene with ethylene to give ethyl benzene, which is then dehydrogenated to give styrene.[34]

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Ethylene}}{C_2H_4} \longrightarrow \underset{\text{Ethyl benzene}}{C_6H_5CH_2CH_3}$$

$$C_6H_5CH_2CH_3 \longrightarrow \underset{\text{Styrene}}{C_6H_5CHCH_2} + H_2$$

The second process involves the coproduction of propylene oxide.[35] Ethylbenzene is oxidized to its hydroperoxide, which is reacted with propylene to give the coproduct propylene-oxide and methyl phenyl carbinol, which is then dehydrated to styrene.

$$C_6H_5CH_2CH_3 + O_2 \longrightarrow \underset{\substack{\text{Ethylbenzene}\\\text{hydroperoxide}}}{C_6H_5CHOOHCH_3}$$



$$C_6H_5CHOOHCH_3 + \underset{\text{Propylene}}{CH_3CHCH_2} \longrightarrow \underset{\substack{\text{Propylene}\\\text{oxide}}}{CH_3\underset{O}{CHCH}_3} + \underset{\substack{\text{Methyl phenyl}\\\text{carbinol}}}{C_6H_5CHOHCH_3}$$

$$C_6H_5CHOHCH_3 \longrightarrow \underset{\text{Styrene}}{C_6H_5CHCH_2} + H_2O$$

Polymer Production Process

SBR is produced by two different processes, emulsion and solution. The emulsion process involves a free radical mechanism, whereas solution SBR is based on alkyllithium catalysis.

Emulsion Process

The formula developed to provide SBR during World War II was standardized, with all rubber plants owned by the U.S. government. The standard recipe is listed below:[36]

Component	*Parts by Weight*
Butadiene	75
Styrene	25
n-Dodecyl mercaptan	0.5
Potassium peroxydisulfate	0.3
Soap flakes	5.0
Water	180

Initiation occurs through reaction of the persulfate with the mercaptan, as shown below:

$$\underset{\substack{\text{Potassium}\\\text{persulfate}}}{K_2S_2O_8} + \underset{\text{Alkylmercaptan}}{2RSH} \longrightarrow \underset{\substack{\text{Mercaptyl}\\\text{free radical}}}{2RS\cdot} + KHSO_4$$

$$RS\cdot + \underset{\text{monomer}}{M} \longrightarrow RSM\cdot$$

Chain propagation occurs by the growing-chain free radical attacking either butadiene or styrene monomer. The active radical chain can react with mercaptan to form a new mercaptyl radical and a terminated chain. The mercaptyl radical then can initiate an additional chain. The molecular weight of the chain P can be controlled by the concentration of mercaptan via this chain transfer mechanism.

$$P\cdot + RSH \rightarrow PH + RS\cdot$$

$$RS\cdot + M \rightarrow RSM\cdot$$

Termination also can occur by the reaction of two free radicals, through either combination or disproportionation reactions.

$$P\cdot + P\cdot \rightarrow P\text{-}P \qquad \text{Combination (bimolecular coupling)}$$

$$P\cdot + P\cdot \rightarrow P\text{-}CH = CH_2 + PH \qquad \text{Disproportionation (hydrogen free radical transfer)}$$

The mercaptyl radical also can react with growing chains, to lead to termination.[37]

Polymerization is carried out at 50°C until conversion of 70 to 75 percent is reached, at which time the polymerization is terminated by the addition of a free radical scavenger such as hydroquinone. Polymerization beyond this point results in excessive free radical attack on the polymer chains. Products made under such conditions have poor properties due to excessive branching and gelation. Unreacted butadiene and styrene are removed by flashing and steam stripping. Antioxidant is added to the latex, followed by coagulation with the addition of polyelectrolytes and salt-acid. The coagulated crumb then is washed, dried, baled, wrapped, and packaged for shipment. Because of the soap and other chemicals in the formulation, most emulsion polymers will contain about 7 percent of nonrubber residues. The emulsion process flow sheet is shown in Fig. 18.1.

It soon was discovered that polymers made at lower temperatures had significantly better properties, especially tire threads, because they contained less low molecular weight material. Attempts simply to lower the polymerization temperature were unsuccessful because of the resulting low polymerization rate. Success finally was achieved through the use of a "redox" system. This system involves an oxidizing agent such as peroxides or hydroperoxides and a reducing agent such as water-soluble transition metal salts. These systems are very active, even at temperatures as low as 0°C.

Mercaptans again are used as chain transfer agents to provide a mechanism for molecular weight control. Commercially these types of polymerization are carried out at 5°C and are referred to as "cold" polymerizations to differentiate them from the previously discussed "hot" systems. A typical formula is listed below.[38]

Component	*Parts by Weight*
Butadiene	71
Styrene	29
tert-Dodecyl mercaptan	0.18
p-Methane hydroperoxide	0.08
Ferrous sulfate heptahydrate	0.03
Trisodium phosphate decahydrate	0.50
Tetrasodium ethylenediaminetetraacetate	0.035
Sodium formaldehyde sulfoxylate	0.08
Rosin acid soap	4.5
Water	200

The improved wear properties of cold polymerization SBR led to the very rapid replacement of hot SBR for most applications. This change was relatively easy to make, as all of the equipment could be used with the only modification required being the addition of reactor cooling, which is achieved with either the reactor jacket, internal coils, or both.

It later was found that even more improvements could be realized by polymerizing to very high molecular weights and then adding petroleum-based oils to the latex prior to coagulation. The oil is absorbed by the rubber, which upon coagulation produces oil-extended polymers. For tread applications, oils of higher aromatic content were preferred because of their excellent compatibility with the rubber. Typically 37.5 parts of oil are added although grades containing up to 50 parts have been produced. Very high molecular weight polymers thus can be processed

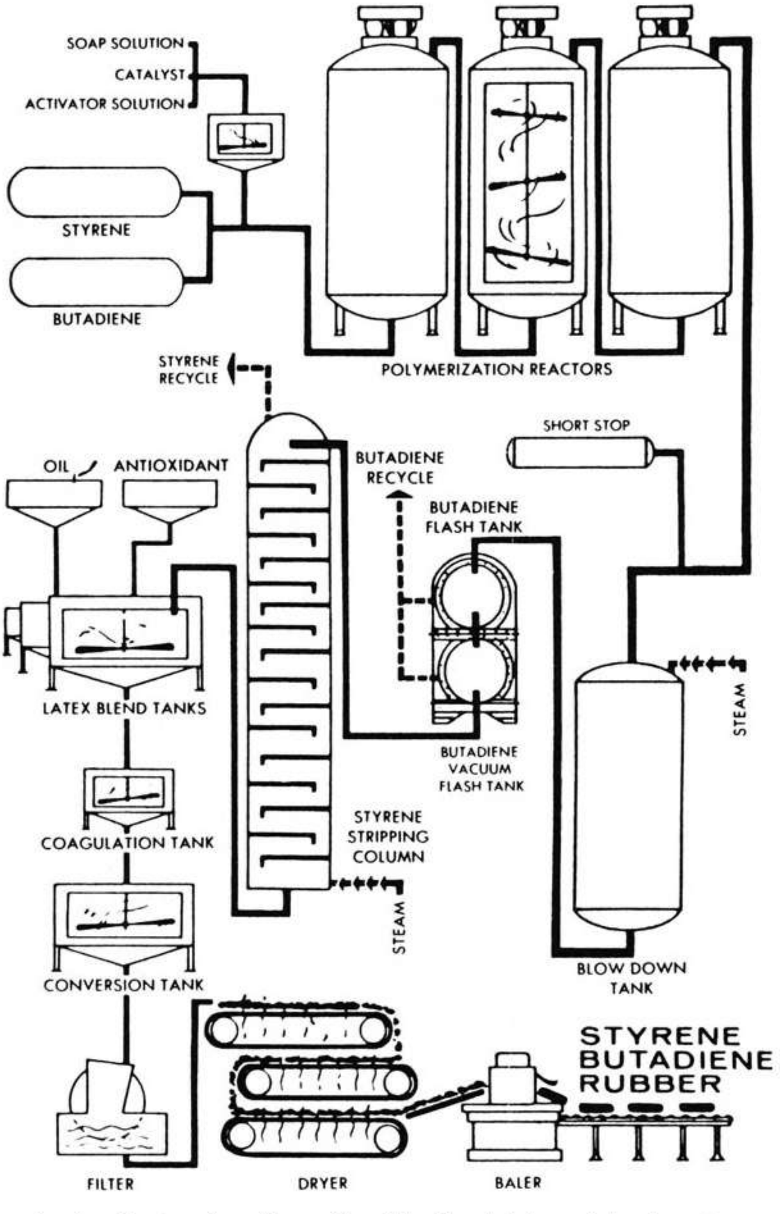


Fig. 18.1. The production of styrene-butadiene rubber. (*Reprinted with permission from* The Vanderbilt Rubber Handbook, *13th ed., R. F. Ohm, Ed. Copyright 1990, the R. T. Vanderbilt Company, Inc.*)

without requiring excessive energy to mix them and avoiding polymer degradation. Carbon black masterbatches also are produced. In this process carbon black is added to the latex prior to coagulation, and the black, along with oil, is incorporated into the latex in the coagulation step. These products offer the user the advantage of not having to handle free black in their mixing operation, and can provide additional compounding volume for manufacturers with limited mixing capacity.

Not all emulsion SBR is converted to dry rubber for use. There are a variety of applications where the latex can be used directly in the final fabrication process. This technology logically grew out of the latex technology developed for natural rubber. For latex applications the particle size distribution can be critical because of its impact on viscosity as well as possible performance variables, as when used to provide impact strength in plastics such as ABS.[39] Careful control of the mechanical stability of the latex also is critical, as these systems must destabilize under relatively mild conditions such as those in a coating operation. A number of processes have been developed to control particle size via partial destabilization of the latex. Among the commercial methods are: careful control of a freeze–thaw cycle, controlled shear agitators, high pressure colloid mills, and the addition of chemicals such as hydrocarbons or glycols.

A special variation of SBR latex containing terpolymerized vinyl pyridine is used in the tire industry to provide adhesion of organic fiber tire cords to rubber stock. The vinyl pyridine SBR latex is combined with resins and coated on the fiber by a dipping process, followed by a controlled temperature and tension process to set the adhesive as well as to control the shrinkage properties of the cord.

Solution Process

The discovery of the ability of lithium-based catalysts to polymerize isoprene to give a high *cis* 1,4 polyisoprene was rapidly followed by the development of alkyllithium-based polybutadiene. The first commercial plant was built by the Firestone Tire and Rubber Company in 1960. Within a few years the technology was expanded to butadiene/styrene copolymers, with commercial production under way toward the end of the 1960s.

The copolymerization with alkyllithium to produce uniformly random copolymers is more complex for the solution process than for emulsion because the reactivity ratios differ greatly. For nonpolar solvent systems values for r_B of 14 and r_S of .07 are reported.[39] Although the product of the reactivity ratios is close to one and the process thus is random from a statistical basis, the actual composition is not uniform in the polymer chain. Because of the extremely high rate of reaction of the styryllithium anion with butadiene, the polymerization very heavily favors the incorporation of butadiene units as long as reasonable concentrations of butadiene are present. This observation initially was somewhat confusing because the homopolymerization rate of styrene is seven times that for butadiene. However, the cross-propagation rate is orders of magnitude faster than either, and it therefore dominates the system. For a 30 mole percent styrene charge the initial polymer will be almost pure butadiene until most of the butadiene is polymerized. Typically two-thirds of the styrene charged will be found as a block of polystyrene at the tail end of the polymer chain.

Several methods have been proposed to overcome this problem. In one, the styrene and part of the butadiene are charged initially with butadiene metered at a rate equivalent to its incorporation into the chain. A second approach involves adding both monomers at a relatively slow rate so that the equilibrium monomer concentration reaches a pseudo-steady state that will produce polymer at the desired composition.[40] This process can be done in either a batch or a continuous mode.[41]

In addition to these reaction engineering approaches to produce uniformly random copolymer, the chemistry may be changed by the addition of polar agents such as amines and ethers. This action results in bringing the reactivities much closer together. The change in chemistry also is reflected in the microstructure of the butadiene portion of the polymer. Whereas in the nonpolar system the vinyl content of the butadiene portion is around 10 percent, in polar systems vinyl contents of 30 to 40 percent typically are obtained when a 20 percent styrene polymer is randomized. Higher styrene contents require higher modifier levels, resulting in even higher vinyl contents. An added complication with polar modifiers is their ability to react with the growing chain, resulting in undesired termination.[42]

In spite of these complications, all recent U.S. expansions or announced plants for SBR have been for solution polymers. This fact is even more surprising, considering the significant excess emulsion SBR capacity in existence.

The driving force toward solution SBR is its improved properties for passenger tire treads. As the polymerization recipe consists of monomer, solvent, possibly trace polar agents, and trace initiator, the polymer contains essentially all-rubber hydrocarbon. The only major nonrubber constituent will be the antioxidant added to all unsaturated polymers. In addition to the high rubber hydrocarbon content, solution polymers can offer more linear chains and narrower molecular weight distributions than emulsion polymers.[43] Advantage also can be taken of the relatively stable growing chain end to chemically modify the polymer to improve its interaction with carbon black in tire compounds. This modification can lead to a dramatic reduction in rolling resistance, which is critical for automotive manufacturers who must meet government-mandated fuel-economy targets. One study comparing an emulsion polymer, its solution counterpart, and a chemically modified version of the solution polymer showed a 23 percent hysteresis reduction in going from emulsion to solution and an additional 15 percent reduction for the chemically modified polymer, to provide an overall reduction of 38 percent.[44] To date, this type of control has not been demonstrated for the emulsion technology.

POLYBUTADIENE

Next to SBR, polybutadiene is the largest-volume synthetic rubber produced. Consumption was approximately 1,140,000 metric tons in 1990 (excluding centrally planned economy countries).[45]

Monomer Production

Butadiene monomer can be produced by a number of different processes. The dominant method of production is as a by-product from the steam cracking of naphtha to produce ethylene. The butadiene is recovered from the C-4 fractions by extractive distillation.[46] "On-purpose" butadiene is generally produced by dehydrogenation or oxidative dehydrogenation of four-carbon hydrocarbons.[47,48]

Polymer Production Process

Polybutadiene is produced by free-radical emulsion, alkali metal solution, and transition metal coordination solution processes. Most production is based on the solution processes because of the ability to obtain preferred microstructures by these routes.

Alkali-metal-based polymer (usually organolithium) produces a product with about 36 percent *cis*, 54 percent *trans*, and 10 percent vinyl. The polymerization process is conducted in an aliphatic hydrocarbon under an inert atmosphere in either a batch or a continuous mode. Because of the characteristics of this polymerization system, polymers of extremely narrow molecular weight distribution and low gel can be produced.[49] The narrowest distribution is produced via batch polymerization.

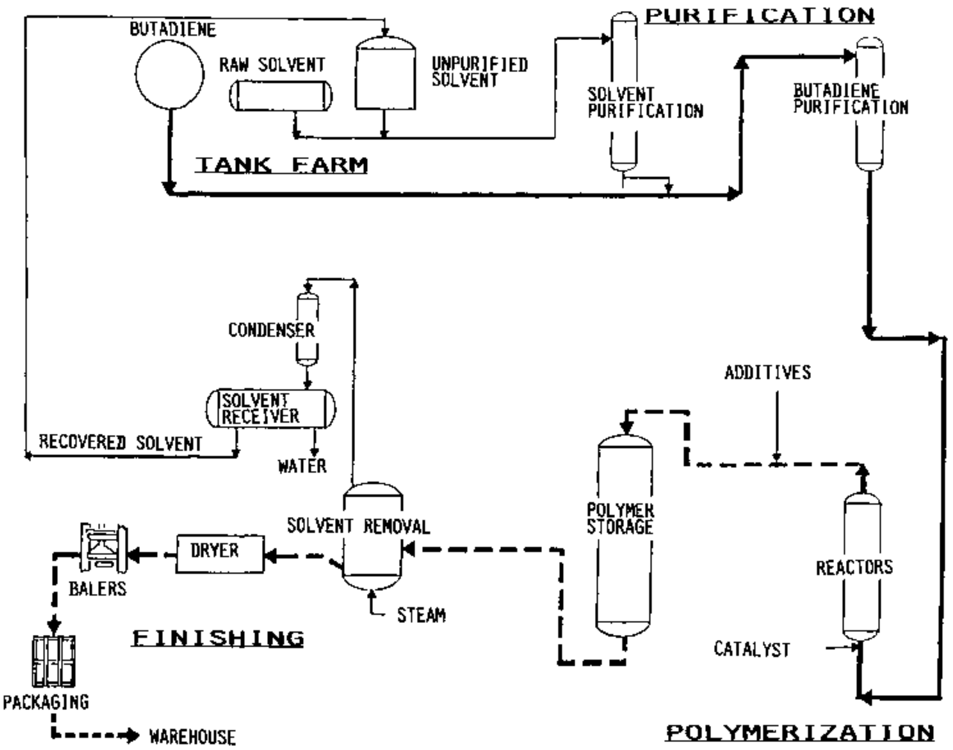
Upon the addition of polar agents, such as ethers or amines, the organolithium initiators can produce polybutadienes with vinyl contents up to 100 percent.[50] The vinyl content can be controlled by the ratio of modifier to catalyst and the polymerization temperature, with lower temperatures favoring increased vinyl formation. Even at the high vinyl contents such polymers do not crystallize, because of the atactic nature of the vinyl units.

High *cis* polybutadiene is produced via solution processes using Ziegler-Natta type transition metal catalysts. The major commercial catalysts of this type are based on titanium, cobalt, nickel, and neodymium.[51] Typically the transition metal is used in the form of an organometallic compound, which is reacted with an organoaluminum or organoaluminum halide as a reducing agent to give the active species at the desired transition state. The cobalt catalysts appear to require aromatic solvents, whereas aliphatic hydrocarbons can be used for the others. Because of the active nature of transition metals, the polymer solutions are treated to deactivate or remove such materials from the final product. All of these catalysts produce products with 95 percent or higher *cis* content. The neodymium system is reported to produce the highest *cis* (98–99%).[52]

All of the solution processes require high efficiency in recovering the solvent. The most widely used process consists of termination of the polymerization and the addition of antioxidant to the polymer solution. The solution may be treated to remove catalyst residue and then transferred into an agitated steam stripping vessel in which unreacted monomer and solvent are flashed off, leaving the rubber as a crumb slurry in water. The water/crumb slurry then is dewatered and dried. The recovered monomer/solvent is recirculated to a series of distillation columns to recover monomer and purify the solvent. As both the anionic and the coordination catalyst systems are highly sensitive to impurities such as water, the purification system is very critical for satisfactory process control. (Fig. 18.2).

Oil-extended polybutadiene also is produced. The production process is basically the same with the exception that a higher molecular weight polymer is produced, which upon oil extension has about the same bulk viscosity as the nonextended polymers. The oil is added to the polymer solution prior to the desolventization step. Oil carbon black masterbatches also are produced. In these processes the carbon black must be ground or debeaded in some mechanical manner and then transferred as a slurry, either in solvent or water, to the polymer solution.

The emulsion polybutadiene process is similar to that described for emulsion SBR.



SOLUTION POLYBUTADIENE

Fig. 18.2. Flow diagram for a typical solution process for manufacture of polybutadiene. (*Courtesy Firestone Synthetic Rubber and Latex Co.*)

Uses

The major use for polybutadiene is in tires, with over 70 percent of the polymer produced used by the tire industry. Cured polybutadiene has excellent low-temperature properties, high resiliency, and good abrasion resistance due to its low glass transition temperature. However, this same fundamental property also leads to very poor wet skid resistance. For this reason, polybutadiene is blended with other polymers such as natural rubber and SBR for use in tread compounds. In general, polybutadiene is a poorer-processing polymer than SBR, but this is generally not a problem as it is blended with other polymers in use. The very high *cis* polymers have the potential for strain-induced crystallization, which can lead to improved green strength and increased cut growth resistance in the cured product. High *cis* polybutadiene is reported to have a melting point of 6°C.[53]

The other major use for polybutadiene is as an impact modifier in plastics, in particular high impact polystyrene (HIPS) and acryolonitrile-butadiene-styrene resin (ABS). In the HIPS application the rubber is dissolved in the styrene monomer, which is then polymerized via a free radical mechanism. A complex series of phase changes occurs, resulting in small rubber particles containing even smaller polystyrene particles being incorporated into a polystyrene matrix. The rubber is added to impart impact strength. Because of the unique morphology that is formed, low levels of rubber (typically around 7%) provide rubbery particles having a volume fraction of 30 to 40 percent. This morphology leads to high impact at very low rubber levels, providing for good stiffness and hardness.[54]

Polybutadiene may be used in a similar manner in ABS production via a mass process. However, most is emulsion-polymerized for use as a latex in the emulsion ABS process.

ETHYLENE/PROPYLENE RUBBER

There are two general types of polymers based on ethylene and propylene: ethylene/propylene rubber (EPM) and ethylene/propylene terpolymer (EPDM). EPM accounts for approximately 20 percent of the polyolefin rubber produced. Comprising a totally saturated polymer, these materials require free radical sources to cross-link. EPDM was developed to overcome this cure limitation. For EPDM a small amount (less than 15%) of a nonconjugated diene is terpolymerized into the polymer. One of the olefinic groups is incorporated into the chain, leaving its other unsaturated site free for vulcanization. This ensures that the polymer backbone remains saturated, with corresponding stability, while still providing the reactive side group necessary for conventional cure systems. The nonconjugated dienes used commercially are ethylidene norbornene, 1,4 hexadiene, and dicyclopentadiene. The selection of the termonomer is made on the basis of the reactivity of the termonomer, both in polymerization and in vulcanization. The estimated 1990 worldwide consumption (excluding CPEC) was 593,000 metric tons.

Monomer Production

Ethylene and propylene are produced primarily by the cracking of naphtha. They also are available from the fractionation of natural gas.

Ethylidene norbornene is produced by reacting butadiene with cyclopentadiene. 1,4 Hexadiene is produced from butadiene and ethylene:

$$CH_2{=}CH{-}CH{=}CH_2 + CH_2{=}CH_2 \longrightarrow \underset{\text{1,4 Hexadiene}}{CH_2{=}CH{-}CH_2{-}CH{=}CHCH_3}$$

Dicyclopentadiene is obtained as a byproduct from the cracking of heavy feedstocks to produce ethylene.

Polymer Production

There are two processes used to produce EPM/EPDM: solution and suspension. In either case a Ziegler-Natta type catalyst is used (aluminum alkyl or aluminum alkyl chlorides and a transition metal salt). The most generally used transition metal is vanadium in the form of the tetrachloride or the oxytrichloride.[55] The solution process is similar to that used for other solution polymers. The polymer cement can be finished by stream stripping and drying of the resulting crumb.[56]

In the suspension process, the polymer is suspended in the monomer propylene. This process offers the advantages of being able to operate at higher solids (owing to the lower viscosity of a suspension than that of a solution at comparable solids), simple heat removal by the evaporative cooling of the propylene, more uniform reactor temperature profile, and ease of production of high molecular weight or semicrystalline polymers, as a polymer solution is not required.[57]

Announcement recently was made of the use of a specially developed titanium-based catalyst in the suspension process for EPM and EPDM where the termonomer is low-boiling. The advantages claimed, in addition to those characteristic of the suspension process, are better structural control and high catalyst efficiency, resulting in a high-purity product without requiring catalyst removal.[58]

The polymer composition for both EPM and EPDM is usually in the 40/60 to 60/40 ethylene/propylene ratio. Outside these ranges, the polymer will start to crystallize because of either polyethylene or polypropylene blocks.

Use

EPM/EPDM polymers exhibit outstanding resistance to heat, ozone, oxidation, weathering, and aging due to the saturated backbone. They have low density, accept aliphatic and naphthenic oils well, and maintain acceptable properties at high filler loadings. They are used in single-ply roofing, wire and cable installation, automotive parts, impact modification of polypropylene, and viscosity index additives for automotive oils and in producing thermoplastic olefin elastomers by blending with polypropylene, which may be partially grafted or cross-linked by dynamic vulcanization. Although at one time EPDM was expected to become the major polymer for tires, this market has not materialized for a variety of processing and performance reasons.[59]

BUTYL RUBBER

Butyl rubber is one of the older synthetic rubbers, having been developed in 1937. Because of the saturated nature of a polyolefin elastomer, the commercial polymer is actually a copolymer of isobutylene and isoprene. The isoprene is added to provide cure sites. In addition, halogenated (bromo or chloro) derivatives are available. The halogenated products improve the mixing and cure compatibility with the more common unsaturated rubbers such as natural or styrene-butadiene rubber.

Monomer Production

Isobutylene is obtained as a by-product from petroleum and natural gas plants. The monomer must be highly purified to assure high molecular weight.

Production Process

Butyl rubber is produced at very low temperature (below −90°C) to control the rapid exotherm and to provide high molecular weight. The process consists of charging isobutylene along with isoprene (2–4%) with an inert diluent such as methyl chloride to a reactor to which a Friedel-Crafts catalyst is added. The polymerization is very rapid, and the polymer forms in a crumb or slurry in the diluent. Heat is removed via a jacket by evaporating materials such as ethylene. The slurry is steam-stripped to remove all volatiles. The catalyst is neutralized, and antioxidants are added to the slurry prior to drying.[60,61]

The halogenated derivatives are produced by the direct addition of the halogen to a solution of the isobutylene-isoprene polymer.

Properties and Use

The most important characteristic of butyl rubber is its low permeability to air. This property accounts for its major use in inner tubes and tire inner liners. Because of the poor compatibility of butyl with other rubbers (with respect to both solubility and cure), the halobutyls are preferred.

Other uses for butyl rubber are automotive mechanical parts (due to the high damping characteristics of butyl), adhesives, mastics, and sealants.[62]

NITRILE RUBBER

Nitrile rubber was invented at about the same time as SBR in the German program to find substitutes for natural rubber.[63] These rubbers are copolymers of acrylonitrile/butadiene, containing from 15 to 40 percent acrylonitrile. The major applications for this material are in areas requiring oil and solvent resistance. The estimated worldwide consumption in 1990 (excluding CPEC) was 252,000 metric tons.[64]

Monomer Production

The production of butadiene is discussed in the polybutadiene section. Although several routes have been developed to produce acrylonitrile, almost all now is produced by the catalytic fluidized-bed ammoxidation of propylene:

$$\underset{\text{Propylene}}{CH_2{=}CHCH_3} + \underset{\text{Ammonia}}{NH_3} + O_2 \rightarrow \underset{\text{Acrylonitrile}}{CH_2{=}CHCN} + H_2O$$

Polymer Production

The polymerization process parallels the emulsion process used for styrene-butadiene rubber. Either a hot or a cold process can be used, with the cold polymerization providing the same improved processing and vulcanizate properties as seen in SBR. Polymerizations are carried to 70 to 80 percent conversion and terminated to avoid gel formation. The latex must be stripped to remove unreacted butadiene and acrylonitrile.

Properties and Use

As the acrylonitrile content increases in the polymer chain, properties change predictably. The glass transition temperature increases approximately 1.5°C for each percent increase in acrylonitrile. Properties such as hysteresis loss, resilience, and low temperature flexibility will correspondingly change. The oil resistance increases with increased acrylonitrile content, as does the compatibility with polar plastics such as PVC. The major market for nitrile rubber is in the automotive area because of its solvent and oil resistance. Major end uses are for hoses, fuel lines, O-rings, gaskets, and seals. In blends with PVC and ABS, nitrile rubber acts as an impact modifier. Some nitrile rubber is sold in latex form for the production of grease-resistant tapes, gasketing material, and abrasive papers. Latex also is used to produce solvent-resistant gloves.[65] A hydrogenated nitrile rubber has been developed and commercialized that provides both better oil resistance and high-temperature resistance.[66]

CHLOROPRENE RUBBER

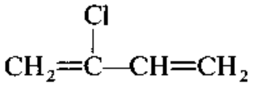
Chloroprene rubber (Neoprene-trade name of Du Pont) was one of the earliest synthetic rubbers, first commercialized in 1932. It has a wide range of useful properties but has not become a true general purpose synthetic rubber, probably because of its cost. It does possess properties superior to those of a number of general purpose polymers, such as oil, ozone, and heat resistance; but for these properties other specialized polymers excel. Polychloroprene thus is positioned between the general purpose elastomers and the specialty rubbers.

Monomer Production

Chloroprene monomer production starts with the catalytic conversion of acetylene to monovinylacetylene, which is purified and subsequently reacted with aqueous hydrogen chloride solution containing cuprous chloride and ammonium chloride to give chloroprene.[67]

$$\underset{\text{Acetylene}}{CH{\equiv}CH} \longrightarrow \underset{\text{Monovinylacetylene}}{CH{\equiv}C{-}CH{=}CH_2}$$

$$CH{\equiv}C{-}CH{=}CH_2 + HCl \longrightarrow$$



$$CH_2{=}\overset{\displaystyle Cl}{\overset{|}{C}}{-}CH{=}CH_2$$

Chloroprene

Production Process

Polychloroprene is produced by using an emulsion process. Two general types of processes are used: sulfur modified and unmodified. In the sulfur modified process, sulfur is dissolved in monomer and is incorporated into the polymer chain. Upon the addition of thiuram disulfide type materials and under alkaline conditions, some of the sulfur bonds are evidently cleaved to give the soluble polymer. In the unmodified process chain transfer agents are used. If neither the sulfur modified nor the chain transfer system is used, the resulting polymer is a gelled tough material. Typical polymerization systems consist of rosin acid soap emulsifier and persulfate catalyst. Conversions of 80 to 90 percent are obtained. Polymerizations are run at around 40°C. For the modified polymer, the thiuram disulfide is added after polymerization, and the latex is aged to allow the peptization reaction to occur. Acidification stops the peptization reaction. The latex is vacuum-stripped and coagulated by acoating a cold drum, with a thin frozen film continuously formed and scraped from the drum. The coagulated rubber is washed and dried.

The polymerization produces primarily *trans* 1,4 polychloroprene. The *trans* content can be increased somewhat by lowering the polymerization temperature.[68,69]

Properties and Uses

Polychloroprene is stable to oxidation and ozone. It also has flame resistance, and its oil resistance is better than that of general purpose rubbers. Its major disadvantage, other than cost, is relatively poor low-temperature properties. Because of the high stereoregularity, polychloroprene will strain crystallize, giving good tensile to unfilled stocks. At low temperatures the polymer can crystallize, making processing more difficult. Polymer made at lower temperatures will show higher unfilled tensile properties and more rapid crystallization due to the higher *trans* content (i.e., less disruption of the crystal structure). The major end uses are for conveyor belts, V-belts, hoses, and mechanical goods such as wire insulation, O-rings, and gaskets. It also has found use in single-ply roofing and adhesives.[70]

SILICONE ELASTOMERS

Silicone elastomers represent a rather unique group of polymers in that they consist of alternating silicon–oxygen bonds to form the polymer chain backbone. Side groups off the silicon atoms are selected to provide very specific properties that differentiate one type from another. The most common side group is the dimethyl structure. Replacement of small amounts of the methyl group with vinyl provide sites for cross-linking. Phenyl groups are used to improve low-temperature properties. Fluorosilicones are produced by replacing the methyl with trifluoro-propyl units. The addition of bulky phenyl side groups leads to an increase in the glass transition temperature. However, the disruption caused by such groups leads to the desired reduction or elimination of crystallization, which is critical for low-temperature properties. Such polymers have glass transition temperatures around −110°C, which is the range of the very best of the carbon-backbone polymers for low glass transition temperatures.

Monomer Production

The actual polymerization process involves a ring-opening reaction of dimethyl-substituted cyclic siloxanes. The preparation of the cyclic materials starts with the production of pure silicon via the reduction of quartz with coke in an electric arc furnace. The silicon metal then is reacted with methyl chloride to give a mixture of silicones, from which dimethyldichlorosilane is removed by distillation.[71] Subsequent hydrolysis gives the cyclic dimethylsiloxane.

$$\underset{\text{Quartz}}{SiO_2} + \underset{\text{Coke}}{C} \longrightarrow \underset{\text{Silicon metal}}{Si}$$

$$Si + CH_3Cl \longrightarrow \underset{\text{Dimethyldichlorosilane}}{(CH_3)_2SiCl_2}$$

$$(CH_3)_2SiCl_2 + H_2O \longrightarrow \underset{\text{Cyclic dimethylsiloxane}}{[(CH_3)_2\text{—}SiO]_x}$$

Polymer Production

The polymerization process involves an equilibrium ring-opening reaction carried out in the bulk state, which can be catalyzed by acids or bases.

Uses

Silicone rubber offers a set of unique properties to the market, which cannot be obtained by other elastomers. The Si–O backbone provides excellent thermal stability and, with no unsaturation in the backbone, outstanding ozone and oxidative stability. The very low glass transition temperature, combined with the absence of low-temperature crystallization, puts silicones among the materials of choice for low-temperature performance. The fluorosubstituted versions provide solvent, fuel, and oil resistance along with the above-mentioned stability advantages inherent with the silicone backbone.

The gum polymer has rather poor tensile properties when cured, but these properties can be greatly improved by the use of silica reinforcing agents. These systems exhibit some of the greatest improvements in properties by filler addition; and because this improvement is significantly higher for silica than for other reinforcing agents, it is assumed that direct bonding occurs between the silica and the polymer. The silicone materials also may have very low surface energy, which accounts for their nonstick characteristics. Because of the inherent inertness of the materials, they have been widely used for medical purposes within the body. The largest use of silicone is in sealant and adhesive applications.

Several different methods have been developed to cure silicones. Free radical cures are possible for those polymers containing vinyl groups. The largest-volume process, however, involves room-temperature vulcanizations, which can employ either a one-component or a two-component system. In the one-component system, a cross-linking agent such as methyltriacetoxysilane is used. With exposure to moisture, hydrolysis of the cross-linking agent leads to the silanol reactive cure site; so such materials must be compounded and stored free of moisture.[72]

POLYURETHANE RUBBER

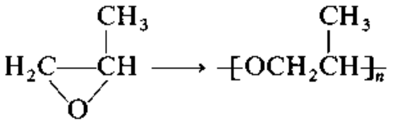
A wide range of materials is included in this class. The common feature is the use of chain extension reactions to provide products with acceptable commercial properties. The chain extension reaction effectively reduces the actual number of chain ends, thereby eliminating the generally poor properties observed when very low molecular weight polymers are cross-linked. The chain extension step involves the reaction of a difunctional polymeric polyol with difunctional organic isocyanates to give the polyurethane:

$$\text{–NCO} + \text{HO—R}'\text{—OH} \rightarrow \text{–NHCOO—R}'\text{—OCONH–}$$

The most used polyols have a polyester or a polyether backbone. A wide variety of isocyanates are used, with toluene di-isocyanate, *m*-phenylene di-isocyanate, and hexamethylene di-isocyanate the most common.

Raw Materials

The largest-volume polyether used is obtained from propylene oxide polymerized under basic conditions:



Propyleneoxide Polypropyleneoxide

Polyester polyols are produced from a number of different materials involving diacids and diols to give the ester linkage. Aliphatic polyesters generally are used for elastomers to impart chain flexibility.

$$\underset{\text{Ethylene glycol}}{HO(CH_2)_2OH} + \underset{\text{Adipic acid}}{HOOC(CH_2)_4COOH} \longrightarrow \text{Polyesterglycol}$$

The production of isocyanates is based on the reaction of phosgene with primary amines. Toluene di-isocyanate is the most frequently used di-isocyanate.

$$\underset{\text{Toluene diamine}}{CH_3C_6H_4(NH_2)_2} + \underset{\text{Phosgene}}{COCl_2} \rightarrow \underset{\text{Toluene di-isocyanate}}{CH_3C_6H_5(NCO)_2}$$

Use

The urethane elastomers are complex segmented or block polymers. Soft, noncrystalline blocks are provided by the polyether or aliphatic polyester long chains, whereas stiff, hard blocks are produced by the reaction of aromatic di-isocyanates with low molecular weight materials such as diols or diamines. The hard blocks can phase-separate to provide a physical rather than a chemical cross-link, similar to those discussed for the butadiene styrene thermoplastic elastomers although the domain size is much smaller for the polyurethanes. Chemical cross-links can be introduced by using trifunctional materials or by adjusting the stoichiometry to allow additional reactions with the urethane or urea structures to give allophanate or biuret linkages.

Polyurethane rubbers can have high tensile strengths, excellent tear strength, and good abrasion and chemical resistance. The greatest disadvantage is the hydrolytic instability of the urethane linkage. A major use is in automotive bumpers and facia. These materials are made in a reaction injection molding process. Castable urethanes are used to produce solid rubber wheels and printing rolls. Millable urethanes can be processed on conventional rubber equipment. Unsaturation can be introduced to allow the use of conventional rubber cure systems. Cures also are possible by reaction of the active hydrogens with materials such as high molecular weight polyfunctional isocyanates that are nonvolatile at cure temperatures.

Thermoplastic polyurethane elastomers are processed by injection molding and other processes used for thermoplastics. Small gears, seals, and even automotive fender extensions can be produced by this means.

By selecting from the large number of possible reactions and stoichiometry, properties can be tailored to meet a very wide range of applications.[73-75]

PLASTICIZED POLYVINYL CHLORIDE

Generally one thinks of polyvinyl chloride as a rigid plastic—which it is, with a glass transition temperature around 85°C. The addition of polar chemicals such as dioctyl phthalate can reduce the glass transition temperature below room temperature, producing a rubbery material.

Monomer Production

Vinyl chloride is produced primarily from ethylene, which is converted to ethylene dichloride by either chlorination or oxychlorination. The ethylene dichloride is cracked to give vinyl chloride and hydrogen chloride.

$$\underset{\text{Ethylene}}{H_2C{=}CH_2} + Cl_2 \longrightarrow \underset{\text{Ethylene dichloride}}{ClCH_2CH_2Cl}$$

$$ClCH_2CH_2Cl \longrightarrow \underset{\text{Vinyl chloride}}{H_2C = CHCl} + HCl$$

Production Process

Polyvinyl chloride is produced by the free radical polymerization of vinyl chloride. Bulk, emulsion, solution, and suspension polymerization processes have been used.

The plasticized product can be produced by mixing the polymer and plasticizers at elevated temperatures, by dry blending in which the plasticizer is absorbed into the resin and then heated to flux, by solution blending, and by the plastisol process, in which fine polyvinylchloride powder is dispersed in the plasticizer and is relatively stable until it is heated.

Properties and Use

Plasticized polyvinyl chloride can be regarded as the first thermoplastic elastomer, as it it used in an uncross-linked form. Because of the lack of cross-linking, this material exhibits high rates of creep and stress relaxation. As with other thermoplastic elastomers, these disadvantages worsen as the temperature is increased. Although the polymer is saturated, it must be stabilized for use to prevent dehydrochlorination at processing temperatures. Because of the high chlorine content, polyvinyl chloride has excellent flame resistance as well as good electrical properties. Even at high plasticizer levels, these materials have marginal elasticity when compared to most other elastomers. Despite their shortcomings, they are used in many areas where they compete with other rubbers.

One of the larger uses is for wire and cable insulation. The flame resistance makes this the material of choice for residential wiring, extension cords, and so on. Inexpensive garden hose represents another large-volume use. Sports balls can be produced by rotational molding of plastisols. The low fabrication cost allows such products to dominate the lower-price-range market.[76,77]

MODIFIED POLYETHYLENE RUBBERS

Elastomeric polymers can be produced by the chlorination or chlorosulfonation of polyethylene. Both products start with polyethylene, either in solution or in aqueous suspension, which then is reacted to give the specified degree of substitution to obtain the desired properties. Sufficient substitution is achieved to disrupt the regularity of the polymer chain, changing it from the crystalline polyethylene plastic into amorphous elastomers.

Chlorinated Polyethylene

The chlorinated products contain around 40 percent chlorine. These materials must be stabilized with metal salts, like other chlorinated elastomers and plastics. Peroxide cross-linking generally is used. Being saturated, the materials have excellent weather and ozone resistance and can be used over a temperature range of −65°F to 300°F. The high chlorine content imparts oil resistance and relatively slow rates of burning. Typical applications where this combination of properties is required include hoses for chemical or oil resistance, tubing, and belting. In comparison with plasticized PVC, these materials have better low-temperature properties and do not suffer a loss of plasticizer because none is required.

Chlorosulfonated Polyethylene

Reaction with sulfur dioxide in addition to chlorine introduces into the polymer sites that are suitable for cross-linking. Sulfur contents in the range of 1.0 to 1.5 percent are used, with chlorine contents of 25 to 40 percent. Curing is accomplished by using metallic oxides, sulfur-bearing organic compounds, and epoxy resins. These materials have outstanding ozone resistance and show little color change upon light exposure. Good resistance to oils, heat, oxidation, weather, and corrosive materials also is exhibited. Applications include pond and pit liners, coated fabrics, light-colored roofing membranes, wire and cable insulation, chemical hose, and belting.[78,79]

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19

Synthetic Resins and Plastics

Jerome K. Knapczyk* and Robert H. M. Simon**

INTRODUCTION

The emergence of the synthetic resins and plastics industry from primitive beginnings a century ago to an international multibillion dollar per year industry today has profoundly changed the way people live. Plastics can perform in ways that are not possible with traditional materials and therefore have become an essential component in our technologically based society. For many applications, such as videotape and heart valves, plastics are the only feasible material. In the United States alone, 61.5 billion lb of resins were sold in 1990.[1] The upward trend in U.S. production of resins is illustrated in Fig. 19.1.[2] The expectation of continued consumer demand, as well as industry profits, supports a large research and development effort that promises even better materials for the future.

Though most plastic and resin products are derived from petroleum, they account for less than 3 percent by weight of total consumption of oil and gas for both material and energy consumption.[3] The amount of energy required to fabricate a finished plastic is generally less than that required for materials such as aluminum, steel, and glass. Weight and design advantages result in further energy savings. Formability means fewer parts, fewer fasteners, and fewer steps needed to put together complex assemblies such as auto dashboards, airplane seats, and boat hulls. This translates directly into lower production cost. Moreover, a lighter product means less fuel consumption when the finished product is transported or finds its way into cars or airplanes, for example.

The commercial history of synthetic resins and plastics can be traced to about 1869, when John Wesley Hyatt and his brother Isaiah, who were seeking a substitute for ivory, developed a practical process for converting cellulose nitrate into useful products.[4] It was mixed with camphor and molded into dentures, billiard balls, toothbrushes, combs, dolls, and collars. This material, which was called celluloid, was one of the developments that made the early motion picture industry possible, as it also could be cast into transparent films of good optical quality. Because of its flammability and poor dur-

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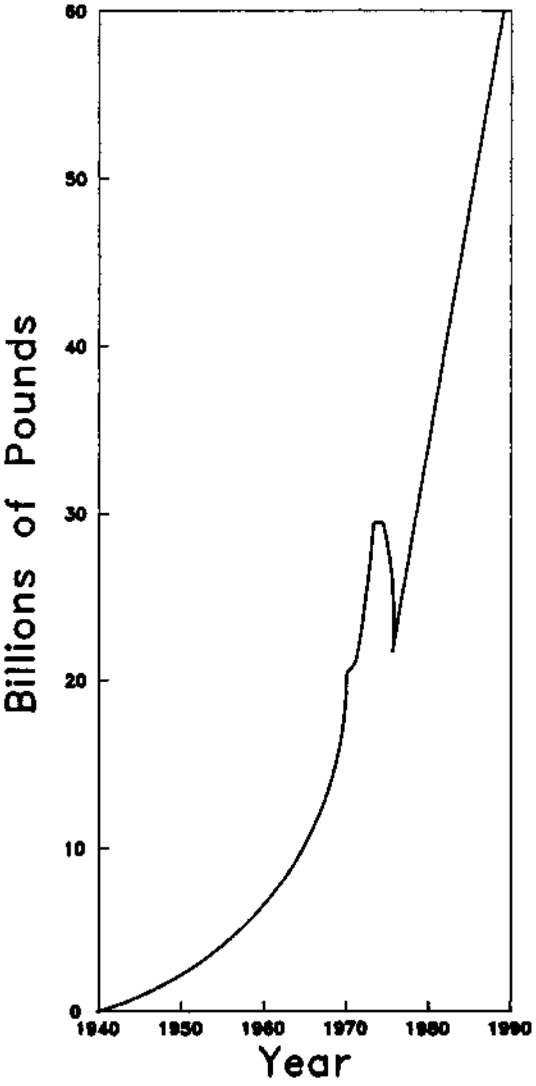


Fig. 19.1. U.S. resin sales, 1940–90.

ability, celluloid has been largely replaced by other plastics, though it is still used for table tennis balls.

During the first decade of the twentieth century, Leo Baekeland developed the first practical process for making molded objects from phenol-formaldehyde resins. The company he formed was named General Bakelite Co. and he called his product bakelite. The development of these early materials was largely an art because very little was known about the chemistry and physical changes that led to the final products. In the mid-1920s Hermann Staudinger hypothesized that plastics owe their properties to the very large size of the molecules that compose them. Then, within ten years, contributions by Wallace Carothers, Herman Mark, Paul Flory, and others led to the incontrovertible conclusion that the chemistry and physical dynamics that lead to the formation and characteristic properties of polymers are the same as those for smaller molecules when account is made for size and complexity.[5] This very fundamental understanding has led to the synthesis and modification of thousands of new polymeric materials and to the development of the modern plastics industry.[6]

The word "plastic" was originally used as an adjective to denote formability. In the 1920s it began to be used as a noun to refer to synthetic materials such as bakelite and celluloid. Now it is used generically to refer to a large class of manufactured organic polymeric materials (Fig. 19.2). The American Society for Testing Materials (D 1695–77) has defined a plastic as "a material that contains as an essential ingredient an organic substance of large molecular weight, is solid in its finished state, and, at some stage in its manufacture or in its processing into finished articles, can be shaped by flow."

Though the words "plastics" and "resins" sometimes are used interchangeably, workers in the polymer industry generally make a distinction between them. Originally "resin" referred to the natural exudates of plants and trees such as rosin, copal, amber, elemi, kaure, manila, mastic, and batu. Later the word also became to be used for resin-like substances of animal origin such as shellac and casein.

In the synthetic polymer field, "resin" also refers to unblended, synthetic polymeric raw materials from which a finished adhesive, coating, or plastic product is made. In the manufacture of a polyethylene irrigation pipe, for example, the raw product synthesized from ethylene monomer is called a resin. It is considered a plastic material after the resin is blended with fillers, pigments, antioxidants, or other substances, and then extruded.

Besides plasticizers and stabilizers, other additives used in plastics include other resins, minerals, dyes, fibers, biocides, processing

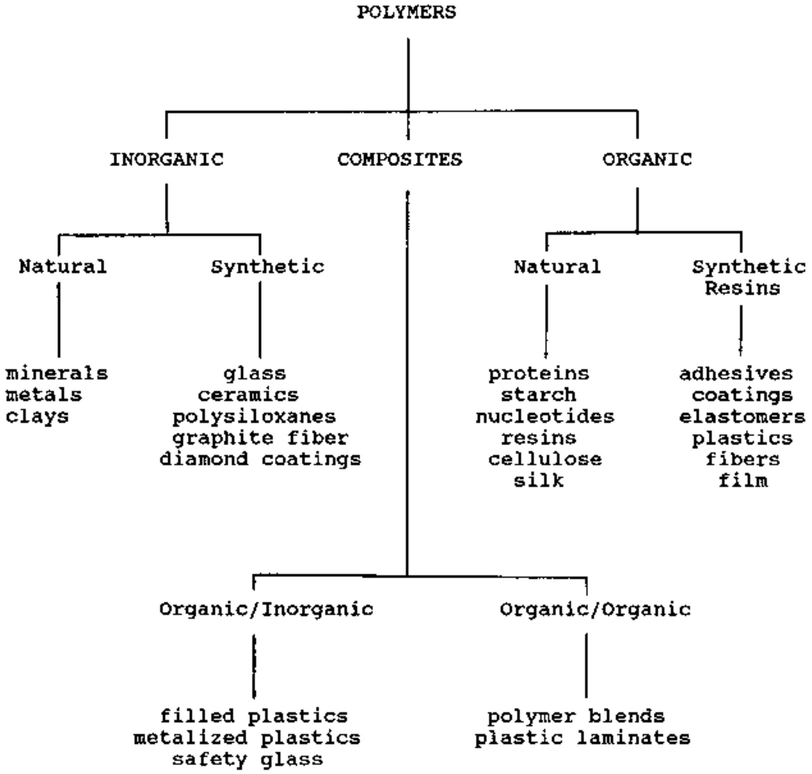


Fig. 19.2. A classification of polymeric substances.

aids, flame retardants, antistats, ultraviolet absorbers, rubbers, or any other substance needed to meet the requirements of the manufacturing process and the product's end use.[7]

The ability, or inability, of a resin to react under certain conditions is an important property. Many resins, such as polyethylene, are relatively unreactive and are used primarily for the physical properties they impart to the finished product. Other resins are synthesized with reactive sites so that they can be made to react further. Ion exchange resins fall into this category; so do the polymeric components of reactive coatings, and adhesives, and reactively processed elastomers and plastics.

Resins and plastics also can be combined with inorganic substances to make hybrid materials that combine the desirable properties of the dissimilar materials. Examples include safety glass (glass/polyvinylbutyral/glass laminate), carbon fly rods (carbon fiber/epoxy resin composite), snack food packaging (aluminum/multilayer plastic film laminate), and computer circuit boards (glass cloth/polyimide composite).[8]

Plastics and resins can be classified in several different ways. They can be grouped according to chemical composition (polyolefin, polyacrylate); according to physical characteristics (elastomeric, thermoplastic, thermoset); according to form (sheet, film, fiber); and according to function (packaging film, structural adhesive, engineering thermoplastic).

Although these classifications are useful, it often is difficult to make a clear distinction between chemistry, form, and function. The distinctions often are arbitrary, and consequently the literature often is confusing. For example, "plastic" sometimes is used generically to cover all solid polymer products whether they are rigid or not. However, the term "elastomer" often is reserved for polymeric materials with elastic properties. Elastomers sometimes are defined as polymers that can be stretched to at least twice their original length, and, when the stress is withdrawn, will rapidly retract to the original length.[9] When a distinction is made between plastics and elastomers, "plastics" refers to less resilient organic materials used for their structural rigidity.

This chapter will discuss some fundamental characteristics of resins and plastics technology. It will cover some important aspects of structure, properties, and processing. More thorough discussions of elastomeric materials, adhesives, coatings, and textiles will be found in other chapters.

POLYMER STRUCTURE AND NOMENCLATURE

Plastics and resins are polymeric substances derived from monomeric precursors. The monomeric units can be put together in many ways. The chain can be linear (even though it may be tightly coiled), branched, or cross-linked (Fig. 19.3). When the polymer is derived from a single monomer, it is called a homopolymer. When the polymer contains two or more different monomeric components, it is called a copolymer. Depending on the monomers and other reactants used in the synthesis, and the polymerization conditions, the monomeric units can be arranged in various ways. They can alternate randomly or in a regular way. They also can be arranged in blocks and in branches that radiate from the main chain (Fig. 19.4).

A polymer is named by enclosing within parenthesis the name of the repeating unit, or name of the monomer(s), from which it is derived, preceded by the prefix poly. The

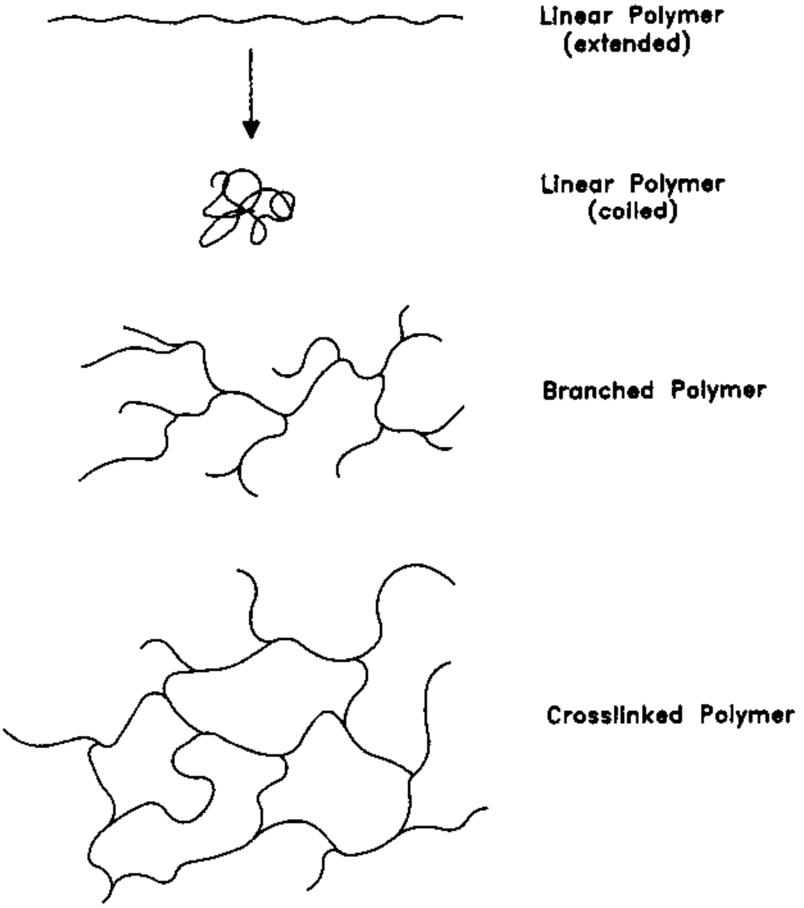


Fig. 19.3. Some polymer chain configurations.

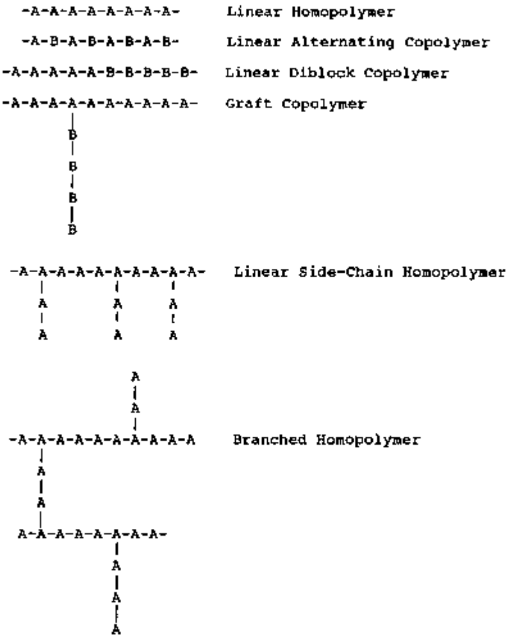


Fig. 19.4. Some polymer backbone structures.

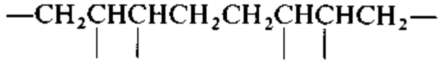
systematic name, or name approved by the International Union of Pure and Applied Chemistry (IUPAC), is derived from the IUPAC designation of the repeating units.[10] Trivial, semisystematic, or trade names often are used, and for simple polymers the parenthesis frequently is dropped. Table 19.1 gives names and a structural representation for a selection of polymers.[11]

Sometimes polymers with identical repeating units have different common names. This reflects different modes of synthesis. For example, both polyethylene and polymethylene have the same backbone structure, which can be represented by either —(CH_2CH_2)— or —(CH_2)—. By convention, however, the former is used to signify a polymer prepared from ethylene, whereas the latter is used for a polymer made from a monomer with only one carbon, such as diazomethane. Polymers like these, with the same repeating units, but made in different ways, can have quite different physical properties. The name given to a polymer says something about its repeating units, or the molecules from which it is synthesized, but it does not characterize it with respect to molecular weight, polydispersity, stereochemistry, or chemical and physical properties.

Unsymmetrical monomers such as propylene link together in what is called a head-to-tail manner; that is, regions such as

$$\text{—}CH_2\underset{|}{C}HCH_2\underset{|}{C}HCH_2\underset{|}{C}HCH_2\underset{|}{C}H\text{—}$$

will predominate over regions such as



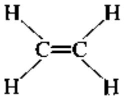
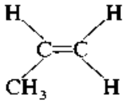
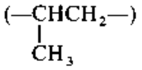
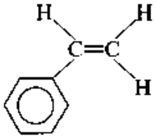
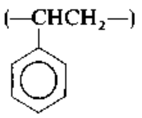
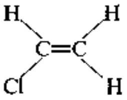
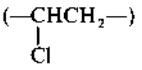
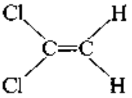
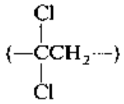
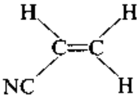
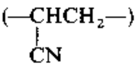
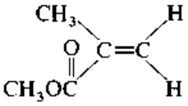
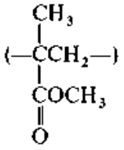
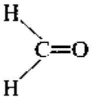
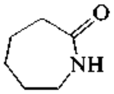
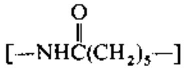
$$\text{—}CH_2\underset{|}{C}H\underset{|}{C}HCH_2CH_2\underset{|}{C}H\underset{|}{C}HCH_2\text{—}$$

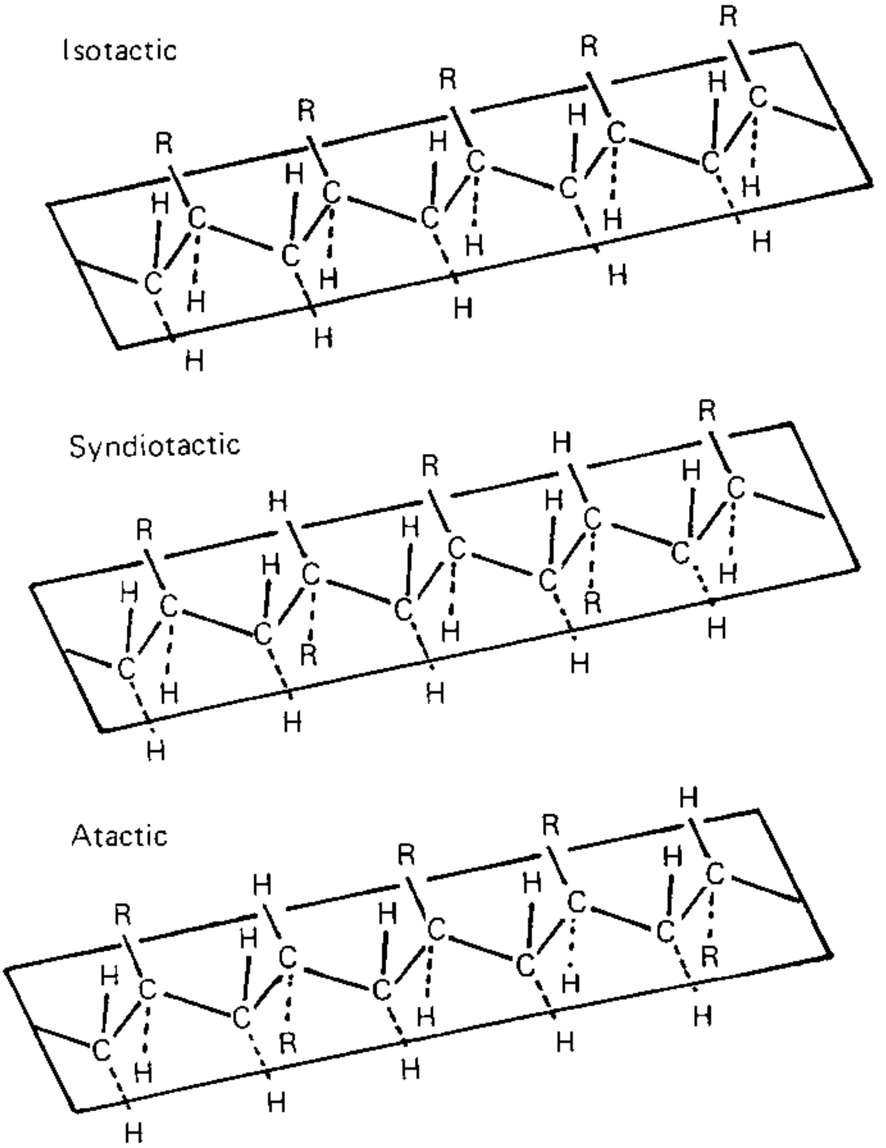
Unsymmetrical monomers can produce polymers with various stereochemical arrangements. When the carbons bearing the methyl group in polypropylene, for example, have the same configuration, the polymer is called isotactic; when alternate carbons with the methyl group have the same configuration, the polymer is called syndiotactic; and when there is a random distribution of configurations, the polymer is called atactic (Fig. 19.5). The stereochemistry of a polymer will strongly influence its properties. When a thermoplastic polymer is stereoregular, the individual polymer strands can more easily align in an orderly way. Thus a stereoregular polymer will tend to be more crystalline than an atactic one.

Molecular weights can be very low or very high, depending on the degree of polymerization. When the degree of polymerization is relatively small, usually less than 100, the polymer is called an oligomer. In practice it is very difficult to carry out a polymerization so that all the molecules produced have exactly the same molecular weight. Thus, there is a distribution of molecular weights in a polymer.

Unlike nonpolymeric molecules, the molecular weight obtained for a polymer will be an average one, and will depend on the way that molecular weight is measured. Molecular weight determinations that depend upon counting numbers of macromolecules of each weight, such as by chromatographic, osmotic pressure, boiling point elevation, and melting point depression methods, produce what is called number average molecular weights, M_n. If light scattering or centrifugation methods are chosen to obtain molecular weights, larger

TABLE 19.1 Nomenclature of Some Common Monomers and Polymers

Monomer	*Repeating Unit*	*Names*
 Ethylene	$(-\mathrm{CH_2CH_2}-)$	Polyethylene
 Propylene	 $(-\underset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{HCH_2}-)$	Polypropylene Poly(propylene)
 Styrene		Polystyrene Poly(1-phenylethylene)
 Vinyl chloride	 $(-\underset{\mathrm{Cl}}{\mathrm{C}}\mathrm{HCH_2}-)$	Polyvinyl chloride Poly(vinyl chloride) Poly(1-chloroethylene)
 Vinylidene chloride	 $(-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{C}}}\mathrm{CH_2}-)$	Polyvinylidene chloride Poly(vinylidene chloride) Poly(1,1-dichloroethylene)
 Acrylonitrile	 $(-\underset{\mathrm{CN}}{\mathrm{C}}\mathrm{HCH_2}-)$	Polyacrylonitrile Poly(1-cyanoethylene)
 Methyl methacrylate	 $(-\overset{\mathrm{CH_3}}{\underset{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{COCH_3}}}{\mathrm{C}}}\mathrm{CH_2}-)$	Poly(methyl methacrylate) Poly[1-(methoxycarbonyl)-1-methylethylene]
 Formaldehyde	$(-\mathrm{CH_2O}-)$	Polyformaldehyde Poly(oxymethylene)
 Caprolactam	 $[-\mathrm{NH}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}(\mathrm{CH_2})_5-]$	Nylon 6 Polycaprolactam Poly(ε-caprolactam) Poly[imino(1-oxohexamethylene)]



Isotactic

Syndiotactic

Atactic

Polypropylene configurations.

Fig. 19.5. Homopolymer backbone configurations resulting from addition polymerization of an unsymmetrical monomer.

size molecules make a bigger contribution to the average value obtained. The molecular weight obtained by these techniques is called weight average molecular weight, M_w. Weight average molecular weights are always larger than number average molecular weights. In the rare cases where all of the molecules have the same molecular weight, the ratio M_w/M_n is unity. This ratio, called the polydispersity index, is a measure of the molecular weight distribution in a polymer. The greater the range of molecular weights in a polymer, the larger will be the index.

Molecular weight and polydispersity often can be manipulated. The degree of control over these properties will depend on the polymerization mechanism, conditions during polymerization, and final processing conditions. Polymers with low polydispersity have higher and sharper melting points than those with large polydispersity. Other properties such as clarity, hardness, melt flow behavior, solvent resistance, and strength also depend on polydispersity.

PROPERTIES OF RESINS AND PLASTICS

There are unlimited combinations of polymer structure, molecular weight, and conformation possible, and each has a unique set of chemical and physical properties. For this reason properties of a given polymer type can vary greatly. Most plastics are used for their material properties and not for the chemical reactions that they might undergo. Important material properties include density, melting point, glass transition temperature, rheology, hardness, abrasion resistance, conductivity, tensile strength, gas permeability, chemical and radiation resistance, color, clarity, surface energy, and so on.

Polymers would be low-viscosity fluids if they were not highly tangled or otherwise bonded together. When intermolecular interactions are weak (e.g., entanglement, hydrogen bonds, dipole–dipole interactions, and Van der Waals bonds), the polymer is called a thermoplastic. When the entire polymer matrix is linked together by covalent bonds into a single three-dimensional network, the polymer is called a thermoset. Thermosets are said to be cross-linked.

If a thermoplastic solid is heated to sufficiently high temperatures, the bonds that make it rigid at lower temperatures begin to weaken. Individual chains start to untangle and slip by each other, and the mass begins to soften and flow. The plastic can be cast, extruded, or thermoformed at this stage. When the viscous shaped material cools, the mass becomes rigid again, as intermolecular bonds re-form. In principle this cycle can be repeated indefinitely, but in practice thermal and oxidative degradation may take place at the elevated temperatures needed for processing. This limits the number of cycles that can occur before the plastic's desirable properties are altered.

At sufficiently high temperatures all organic materials degrade as bonds begin to fragment, rearrange, or oxidize. Even at ambient conditions, oxidation and other changes caused by photochemical reactions, or by moisture, acids, and other contaminants in the air, may occur. These aging processes often are accompanied by cross-linking, the formation of lower molecular weight substances, and colored by-products. Over a period of time the product may weaken, become brittle, and change color. Thus, many plastics are formulated with antioxidants and light stabilizers to minimize degradation during processing and to promote durability during use.

In most cases, the weak intermolecular bonds of thermoplastics allow them to be dissolved in a solvent or blended with other substances. A solution of thermoplastic in a volatile solvent is called a lacquer. Higher molecular weight nonvolatile, nonreactive components such as plasticizers or other resins also may be soluble in a thermoplastic to some degree. Plasticizers dilute a resin and reduce intermolecular forces between molecules. They are added to soften a resin or make it flexible, or to make it easier to process. Vinyl upholstery, some films used in packaging, and many other plastics are made with high levels of plasticizer.

The weak intermolecular forces that make thermoplastics easy to process can lower resistance to abrasion, chemical attack, or etching by a solvent, and may restrict their use at higher temperatures where they can soften or creep. In contrast, thermoset plastics do not melt or dissolve in a solvent, and they often are more resistant to thermal deformation and chemical attack than are thermoplastics. The degree of rigidity under thermal and mechanical stress is related to the amount of cross-linking. Highly cross-linked thermosets retain their shape at elevated temperatures and under strong deformation forces, whereas lightly cross-linked thermosets are easily deformed or elastomeric.

Molecular order in a thermoplastic depends on intrinsic factors such as stereoregularity, branching, polydispersity, and polarity of the repeating units, and, to some degree, on extrinsic factors such as the polymer's purity and the way it is isolated and processed.

Highly ordered arrangements are said to be crystalline. Crystallinity in a polymer is unlike that for low molecular weight organic compounds such as sucrose; complete crystallinity seldom is attained. Instead, crystalline order occurs in domains called crystallites, which are regions of the polymer matrix where orderly packing of the individual polymer strands takes place. Crystallites alternate with highly disordered, or amorphous, regions (Fig. 19.6). Such polymers are referred to as semicrystalline. Because the size of the crystalline regions may be large enough to scatter light, and their refractive index is generally different from that of the amorphous regions, semicrystalline polymers such as polyethylene often are translucent or opaque.

The distribution of the amorphous and crystalline regions in a polymer can be random (Fig. 19.6a) or oriented (Fig. 19.6b). When semicrystalline thermoplastics are drawn into filament, or stretched into film at elevated temperatures, the long axes of the crystallites align in the direction of drawing (Fig. 19.6b). If this orientation is frozen in by quenching the hot drawn polymer, the orientation is set, and some material properties become anisotropic. Properties such as refractive index, elongation, and tensile strength will differ in the polymer's three dimensions. In practice, the tensile strength in the draw direction is improved by one or two orders of magnitude; and this improvement is used to advantage in the production of packaging film and fiber, where enhanced strength is needed to compensate for the small cross-sectional areas of the product.

In general, highly crystalline thermoplastics have a higher density, are more resistant to solvents, and melt more sharply at higher temperatures than amorphous polymers or polymers with low crystallinity. Although highly crystalline polymers have greater stiffness, they usually are more brittle or less resilient to shock than amorphous polymers. Thus, in applications where stiffness and solvent resistance are important, a highly crystalline polymer is a likely choice, but where clarity and resilience are needed, an amorphous polymer might be used. Often a balance between amorphous and crystalline regions is needed to produce the combination of strength and flexibility required for a given application.

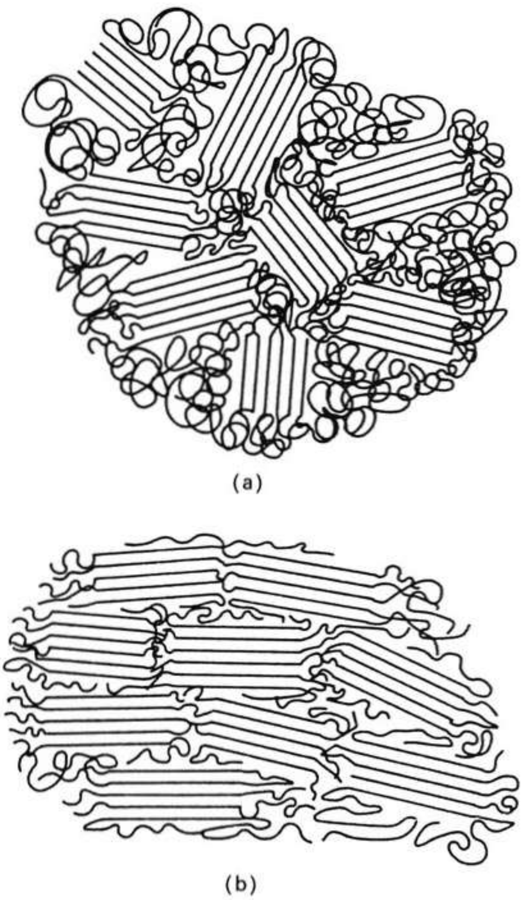


Fig. 19.6. Crystalline and amorphous regions in a semicrystalline thermoplastic polymer. (a) Unoriented. (b) Oriented.

Another property that determines a plastic's usefulness is its modulus. Modulus is related to stiffness; high stiffness corresponds to high modulus. Modulus is defined as the ratio of stress (deforming force per unit cross-sectional area) to strain (increment of deformation) for elastic deformation (Fig. 19.7). Its dimensions are the same as those of pressure or tensile strength.

The modulus obtained for a material depends on the way that it is measured. When the term "modulus" is used without qualifiers, the slope of the steepest part of the stress–strain

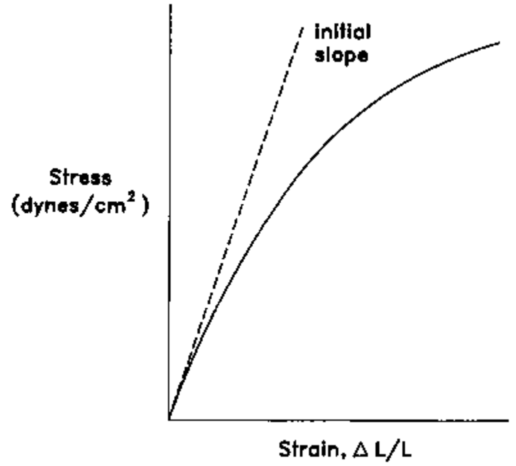


Fig. 19.7. Stress–strain relationship. The initial slope defines the modulus.

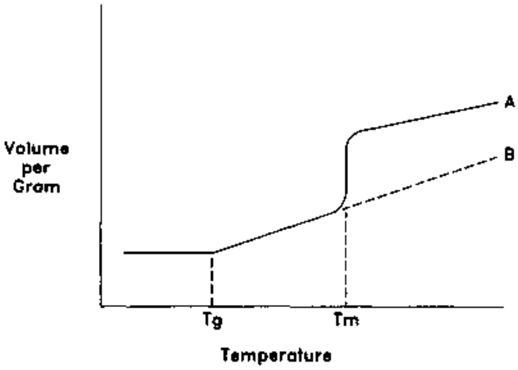


Fig. 19.8. Volume–temperature changes for semi-crystalline (*A*) and amorphous (*B*) polymers.

curve, or initial modulus, is meant. Tensile modulus corresponds to the initial slope of the stress–strain curve generated when a specimen is clamped at one end and pulled at the other. Torsional modulus is the torque required to twist a specimen clamped at one end through a specified angle. Modulus usually decreases with plasticizer content and increases when fillers and reinforcing fibers are added.

A polymer's modulus may strongly affect its glass transition temperature, T_g, which is the temperature at which segments of the polymer chain, about 10 to 30 units long each, acquire enough energy to move around, about fixed positions in the matrix. Below T_g a polymer is rigid or glasslike. Above T_g, segmental motion sweeps out increasingly larger volumes than the volume of the atoms that make up the segments (Fig. 19.8). As this so-called free volume increases, the polymer's density and modulus decrease.[12] In addition to its becoming less rigid, other properties such as impact strength and elongation also change substantially.

In contrast to small crystalline molecules, where changes from a solid to a liquid take place over a narrow temperature span, amorphous polymers do not exhibit well-defined melting points. As temperature increases above T_g, the polymer becomes less rigid as the chains become more and more mobile and begin to slip by each other. Viscosity decreases gradually, and the polymer eventually begins to flow.

A semicrystalline polymer is more rigid above T_g than a comparable amorphous polymer. For example, a crystalline polymer such as polyethylene, with a T_g well below ambient temperature, will retain useful structural properties above ambient temperature. Crystallites serve as inter-chain crosslinking sites that retard the mobility of polymer chains above T_g until the crystallites begin to melt, at a temperature called the crystalline melting point, T_m. Table 19.2 lists T_g of some common polymers.

A polymer's T_g and T_m can be determined in several ways. A convenient method is thermal analysis. Measurements are carried out in a calorimeter that scans temperature and measures the quantity or rate of heat absorbed by a substance compared to a standard. Scans for an amorphous and a semicrystalline polymer are shown schematically in Fig. 19.9.

The influence of T_g on the mechanical properties of polymers can be dramatic. Properties such as refractive index, abrasion and solvent resistance, thermal conductivity, and response to mechanical shock may show step changes at T_g. On heating through T_g, the modulus of an amorphous polymer may decrease by two to five orders of magnitude.

In Fig. 19.10, the effect of increasing the molecular weight of a hypothetical amorphous oligomer is to cause a shoulder in the modulus

TABLE 19.2 Approximate Glass Transition Temperatures (T_g) for Some Common Polymers

Polymer	$T_g(°C)$
Poly(dimethyl siloxane)	−123
Polyethylene (LDPE)	−122
Polybutadiene	−85
cis-Polyisoprene	−70
Poly(butyl acrylate)	−63
Poly(propylene oxide)	−62
trans-Polyisoprene	−53
Polychloroprene	−50
Poly(ethylene adipate)	−48
Polypropylene (atactic)	−20
Poly(vinyl acetate)	28
Poly(ethylene terephthalate)	70
Poly(vinyl chloride)	80
Polypropylene (isotactic)	100
Polystyrene	100
Poly(methyl methacrylate)	105
Polyacrylonitrile	105
Poly(tetrafluoroethylene)	115
Cellulose triacetate	197

curve at about 10^6 dynes/cm^2. As molecular weight increases, a plateau of increasing height and length is produced, as entanglement begins to retard slippage between polymer chains. The temperature–modulus plateau at $T > T_g$ corresponds to a state where a polymer exhibits the resilient properties of a viscous solid, often referred to as viscoelastic properties.[13] These properties are discussed further below, in the section on "Polymer Rheology."

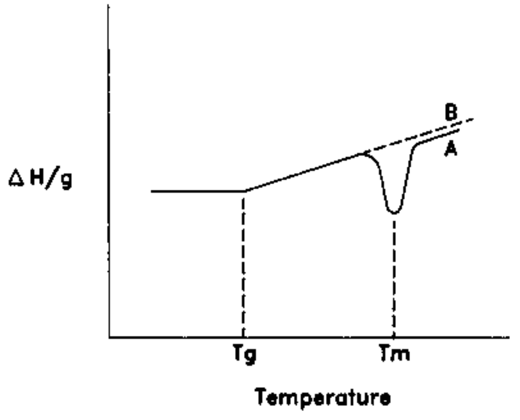


Fig. 19.9. Differential thermal scan showing discontinuities in heat absorption ($\Delta H/g$) for the semicrystalline (A) and amorphous (B) polymers in Fig. 19.8.

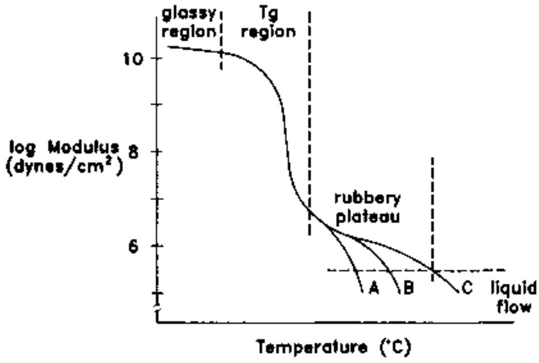


Fig. 19.10. Generalized modulus–temperatures curves for low (A), moderate (B), and high (C) molecular weight amorphous thermoplastic polymers.

The effect of temperature on the modulus of a semicrystalline resin is shown in Fig. 19.11. The modulus change is less dramatic near T_g because backbone rigidity is provided by the crystallites. When the temperature becomes high enough to melt the crystallites, the polymer is free to flow.

Figure 19.12 compares the modulus–temperature response of an amorphous thermoplastic polymer with thermosets that are lightly and highly cross-linked. Cross-links in thermosets do not melt out like crystallites in semicrystalline thermoplastics; so the modulus–temperature curve is flatter up to the point of thermal decomposition. Modulus above T_g is strongly dependent on the number of cross-links per unit volume, or

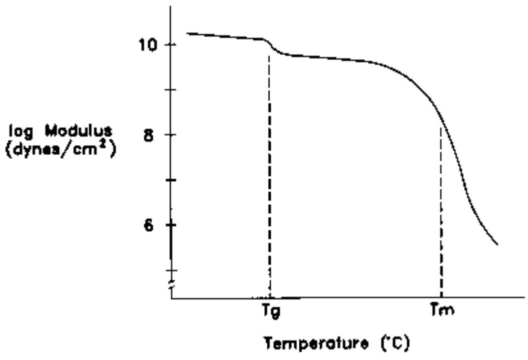


Fig. 19.11. Modulus–temperature curve for a semicrystalline polymer.

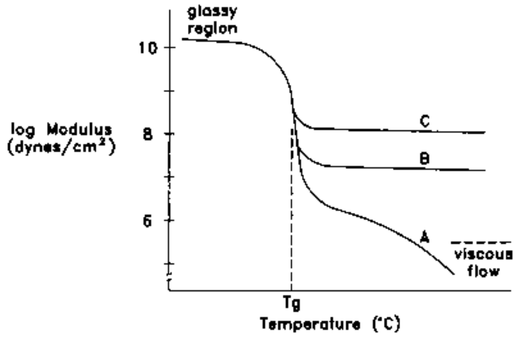


Fig. 19.12. Generalized modulus–temperature curve for an amorphous thermoplastic (*A*) and for thermosets that are lightly (*B*) and highly (*C*) cross-linked.

molecular weight between cross-links. For example, if the molecular weight between cross-links is between 2500 and 5000, modulus will be in the vicinity of 5 to 10×10^6 dynes/cm^2. This is the range for elastomers where there are large threadlike segments to coil and stretch. The glass transition temperatures of flexible thermosets such as rubbers, sealants, and pressure-sensitive adhesives are below room temperature. In phenol-formaldehyde plastics and some other thermosets, where the degree of cross-linking is very high, a modulus greater than 10^8 dynes/cm^2 may be exhibited above T_g.

T_g depends on some of the same chemical and steric factors that affect crystallinity. It also depends to some degree on how it is measured. When obtained with oscillating stress–strain response methods, T_g will increase with the rate of applied stress (Fig. 19.13).

As might be expected, other viscoelastic properties will show a time–temperature dependency. For example, if an indenter is used to measure the hardness of a thermoplastic, the time that the indenter is impressed on the surface is a measurement variable. Over a long impression time the polymer may yield under the stylus point, allowing it to sink deeper into the surface. Thus the polymer will appear to be less hard than it seems if the impression time is short. This time–property relationship also is exhibited during impacts. At temperatures above T_g a polymer might exhibit ductile properties when deformed at low rates and brittle fracture at high deformation rates.

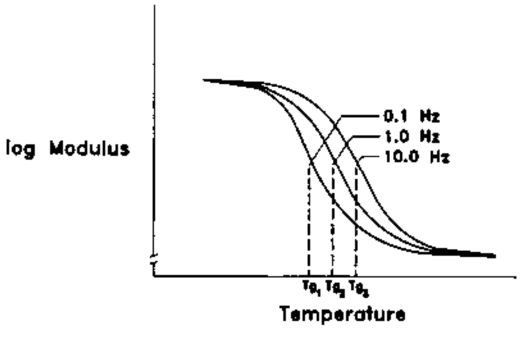


Fig. 19.13. Generalized modulus–temperature curves showing the effect that periodic strain rate has on T_g.

The creep behavior of a plastic is an important consideration in its use. Under static loads thermoplastics may deform at temperatures below a T_g measured under dynamic conditions. A useful way to express creep behavior is by what is called the heat deflection temperature (HDT). HDT is the minimum temperature that results in a specified deformation, usually 0.01 inch under a static load, usually 1.82 or 0.46 N/mm^2 (264 or 66 psi, respectively).[14] For an unreinforced plastic, this is around 20°C below the T_g determined at a frequency of one oscillation per second.

IMPORTANT CLASSES OF PLASTICS AND RESINS: THERMOPLASTICS

Because of their versatility and processing ease, thermoplastics account for about 85 percent of the domestic resins market of about 61 billion lb/year.[1] Some of the more important members of this class of resins are discussed below.

Polyolefins

Polyolefins, particularly polyethylene and polypropylene, are the largest-selling class of resins. Domestic sales volume in 1990 for polyethylene was 20 billion lb, and for polypropylene and its copolymers it was 8 billion lb.[1] The large volume of polyolefins sold reflects a broadly useful property spectrum, ease of fabrication, and low cost. Lower cost is a result of a favorable raw material supply and continuing improvement in manufacturing processes. (See below, "Polymerization Methods" in section on "Polymer Synthesis.")

Polyethylene. Polyethylene accounts for about 32 percent of domestic resin sales. It is a high molecular weight, semicrystalline polymer prepared from ethylene. Depending on its manufacturing process, its degree of polymerization will vary from about 500 to 500,000. The monomer is prepared in large quantities by the cracking of natural gas and light petroleum.

Polyethylene was first manufactured in England in 1939.[15] The first applications of polyethylene—which took advantage of its relative inertness, moisture resistance, and good electrical insulating properties—were in marine and radar cable insulation. At room temperature polyethylene is resistant to most chemicals except strong oxidants. Currently, the largest uses for polyethylene are for containers and packaging film. This includes kitchen food wrap and store packaging for fruits, vegetables, and other food products, and heavy-duty sacks for fertilizers and other bulk products.

Commercial polyethylene is available in various molecular weights and branching, resulting in different mechanical properties and processibility. The various grades can be divided into two principal categories, low density polyethylene (LDPE) and high density polyethylene (HDPE). The density of LDPE varies from about 0.90 to 0.94 g/cm^3, and HDPE varies from 0.95 to 0.97 g/cm^3. Density is related inversely to the average frequency and length of molecular chain branching. As polyethylene density increases, impact strength and elongation tend to drop off, while tensile strength, abrasion resistance, hardness, rigidity, and heat distortion temperature increase.

There are two types of low density polyethylene, a highly branched type made by a high pressure process (HP-LDPE) and one prepared at much lower pressures that has higher molecular weight, less branching, and fewer periodic short side chains than the former type. The latter is called linear low density polyethylene (LLDPE).

HP-LDPE is prepared at pressures of 1000 to 3000 atmospheres and at temperatures from about 150 to 250°C. Polymerization takes place by a free radical mechanism initiated by molecular oxygen or peroxides such as benzoyl peroxide. If lower pressures were used, the polymer formed this way would have an excessively low molecular weight. This is so because molecular weight is determined largely by the rates of chain growth and chain termination, and for the growing polyethylene radical the rate of termination is very high. High pressures increase the concentration of reactants and the probability that the growing chain will encounter a monomer before termination can occur.

Elevated reaction temperatures and highly reactive propagating free radicals result in competing chain transfer reactions. Chain transfer occurs when a hydrogen atom is picked off the backbone of a growing intermediate by another free radical center (see below, under "Free Radical Addition Polymerization"). Because chain transfer reduces molecular weight and causes branching, the polymer made this way is highly branched. Branching prevents close packing, making crystallization more difficult. Typical HP-LDPE exhibits crystallinity of about 20 to 55 percent, compared to 60 to 90 percent for unbranched polyethylene. Control over molecular weight to produce various grades of LDPE is carried out by adding chain transfer agents to the monomer feed.

LDPE accounts for about 55 percent of U.S. sales of polyethylene. It supplies 41 percent of the 6.5 billion lb polyethylene film market,[16] 53 percent of the 850 million lb injection molding market, and the majority of the extrusion, wire-and-cable, and shrink-wrap markets.[17] HP-LDPE is widely used for higher-clarity applications. Its low melting point allows it to be coated or extruded at relatively low temperatures and higher rates than LLDPE. Extrusion coatings on paper and board are used to provide moisture resistance. Coated milk cartons and multiwalled paper bags are examples. It is used for power and cable insulation, and is extruded into irrigation piping and monofilament for rope, nets, and lawn chairs. It is injection-molded into buckets, bottles, drums, baskets, toys, and laboratory ware.

HDPE and LLDPE are prepared at lower pressures by non–free radical chemistry. The Phillips process, for example, uses proprietary chromium or molybdenum oxide catalysts on finely divided silica or silica–alumina supports.[18] Polymerization occurs between 70 and 200°C and at pressures in the range of 30 to 40 atmospheres.

A competing low pressure process uses what are called Ziegler-Natta catalysts.[19] Polymerization with these catalysts take place at temperatures below 100°C and pressures in the neighborhood of 2 to 4 atmospheres. These catalysts were developed in the early 1950s through the discoveries of Karl Ziegler in Germany and Giulio Natta in Italy, and their importance brought Ziegler and Natta the Nobel Prize in chemistry in 1963. Since then many related polymerization catalysts have been prepared.[20]

Both heterogeneous and soluble Ziegler-Natta catalysts are used. They are formed by combining compounds of elements from Group IV to VII with organometallics from metals of Groups I and III. Typically they are combinations of aluminum alkyls and aluminum alkyl halides with Ti(III) and Ti(IV) halides. They can be adsorbed on finely divided mineral supports to provide a large surface area for heterogeneous processes. Though some of the details of how these catalysts function are not known, it is generally accepted that monomers form pi-complexes with the transition metal component and that additional monomers are inserted, one after another, into the polarized metal–carbon bond. The polymer grows from the catalytic site much as a blade of grass grows from its root.

Transition metal catalysts produce polyethylene resins with less branching than polyethylene made by high pressure processes. In turn, the polymer molecules can pack closer together, resulting in higher density and crystallinity. Crystallinity reduces clarity and increases modulus and tensile strength. The melting point of HDPE is about 20°C higher than that of LDPE.

HDPE accounts for about 42 percent of the domestic polyethylene market.[1] It is harder, more rigid, and less waxy in appearance than HP-LDPE. Its higher density gives it better gas barrier properties. Because it softens above 100°C, containers made with HDPE can be sterilized, but those made with LDPE cannot. It is extruded into pipe, trash bags, food packaging, multiwalled sack liners, wire and cable coverings, and thick industrial film. A large application is for blow-molded containers and housewares.

Though crystallinity up to 90 percent is achievable, high crystallinity makes the resin brittle. Its brittleness can be reduced, however, by copolymerization with small amounts of 1-butene or 1-hexene.[21] Copolymerization introduces structural irregularity without branching and reduces close packing and density. The increased segmental motion that results improves toughness and resistance to stress. These copolymers are the linear low density polyethylenes (LLDPE) (see above).

The greater toughness of LLDPE compared to HDPE is especially useful for higher-performance, low temperature applications. LLDPE is used widely for gas and water pipes and for other applications where a plastic needs to withstand high stress for long periods at moderate temperatures without failure. The properties of LLDPE are suitable for blown film, containers, and other packaging applications where film clarity is not important. It exhibits higher strength and puncture resistance, which allows the use of thinner films. About 3 billion lb of LLDPE are used annually for this purpose.

Polypropylene. Polypropylene and its copolymers account for about 13 percent of U.S. resin sales.[1] Its manufacture and properties have much in common with HDPE. Unlike polyethylene, however, isotactic, syndiotactic, Nomenclature").[22] Atactic polypropylene, and atactic configurations are possible as a consequence of the pendant methyl group (see above, under "Polymer Structure and which can be produced by free radical polymerization, is primarily obtained as a by-product from the manufacture of the isotactic stereoisomer as described below. Since the random arrangement of the pendant methyl groups along the polymer chain prevents crystallization, the atactic material is an amorphous, low melting waxy solid with reduced solvent resistance. It is used as a water barrier coating for wire and cable, roofing material, and laminated paper. Syndiotactic polypropylene has been prepared in the laboratory, but no commercial interest has developed for it.[23]

Commercial polypropylene is based on catalysts of the Ziegler-Natta type that produce a product with an isotactic content of 90 percent or more. The presence of the methyl groups restricts movement of the polymer molecules somewhat, and crystallization rarely exceeds 65 to 70 percent. The degree of stereoregularity depends on a multitude of factors, some of which are not well understood. Variables include the type of metals in the catalyst, their oxidation states and crystal structure, and the organic functionality in the complex. In some systems both the rate of reaction and the degree of stereoregularity are increased by the addition of electron pair donors such as amines.

Isotactic polypropylene is a colorless thermoplastic that has a density of 0.91 to 0.94 g/cm^3 and is one of the lightest commercial plastics. Its chemical and physical properties are similar in many ways to those of HDPE. Although its impact strength is somewhat lower than that of HDPE, it is clearer, glossier, and harder. It also has a higher softening point (140–155°C, compared to 122–130°C for HDPE). It has unusually high resistance to flexing stress, and thus is used in molded articles with built-in hinges.

As with HDPE, copolymerization is used to modify the mechanical properties of isotactic polypropylene. Up to about 7 percent ethylene may be added to form a random copolymer. The ethylene in the chain reduces crystallinity somewhat, resulting in improved elongation and toughness. Although increasing the atactic to isotactic ratio can have a similar effect, copolymerization accomplishes it more efficiently. Terpolymers of polypropylene also are available.[24]

For applications requiring even higher impact strength, especially at low temperatures, further increases in random copolymer ethylene level become unsuitable because other important properties such as stiffness and melting point are degraded. For these applications ethylene is substituted for the propylene feed during the course of the polymerization, resulting in a block copolymer with up to 40 percent ethylene. The polymer consists of a block of highly isotactic polypropylene bonded to a block of random ethylene–propylene copolymer. At even higher ethylene levels, the copolymer takes on elastomeric properties. These copolymers are known as EPR or EPM rubbers.

The tertiary carbons along the backbone of polypropylene are susceptible to oxidation in air. This is especially a problem at high process or use temperatures, in sunlight, or during mechanical stress. Formulation with antioxidants, peroxide decomposers, and UV stabilizers greatly reduces this problem.

Polypropylene is used in a large variety of applications. About 20 percent of it is injection-molded into furniture, appliance parts, bottles, battery cases, luggage, distributor caps, screw-on bottle caps, and housewares. Up to 40 percent filler can be used to stiffen it. Various grades of filled polypropylene are used in industrial and automotive applications.

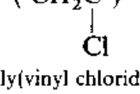
About 40 percent of polypropylene resin is extruded into fiber and filament, coatings, film, sheet, pipe, and wire insulation. The fiber does not absorb water and is stain- and abrasion-resistant. The largest market for polypropylene fiber is for carpet backing. The fiber also is used to make disposable diapers and other nonwoven fabrics. Because of its strength, lightness, and resistance to weathering and microorganisms, it has replaced natural fiber in rope and cord.

The strength and barrier properties of polypropylene film can be improved by stretching it during or just after extrusion, but before it has been cooled. This aligns the polymer chains in the direction of drawing. The orientation is set during quenching, thereby increasing strength in the draw direction. Film stretched in one direction is called uniaxially oriented film. Film that is stretched in both the machine direction and the transverse direction is referred to as biaxially oriented. Oriented polymers are stressed and have lower entropy than unoriented polymers. When the unconfined oriented material is reheated to sufficiently high temperatures, the polymer strands randomize and the material changes dimensions. Stress relaxation is used to advantage in shrink wrapping.

The barrier properties of polypropylene film to certain gases such as oxygen can be improved further by laminating it to film with better barrier properties such as poly(vinylidene chloride). If one of the film components has a sufficiently low melting point, the laminate may be heat-sealable. Laminated barrier films are widely used for wrapping meats, bakery goods, snack items, and frozen foods. Form-and-fill packaging is the largest use of polypropylene film. The package is formed, filled with product, and sealed in a continuous process.

Vinyl Resins

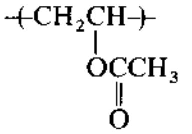
Vinyl resins are the second largest class of industrial polymers, accounting for about 10 billion lb or 16 percent of domestic resin sales.[1] This class includes poly(vinyl chloride), poly(vinylidene fluoride), poly(vinyl acetate), poly(vinyl alcohol), the poly(vinyl ethers), and a numbet of other related polymers and copolymers.



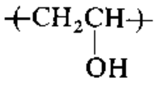
$$-\!\!(\mathrm{CH_2}\underset{\mathrm{Cl}}{\underset{|}{\mathrm{C}}})\!\!-$$

$-\!\!(\mathrm{CH_2CCl_2})\!\!-$

Poly(vinyl chloride) Poly(vinylidene chloride)

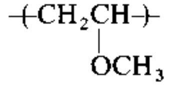


$$-\!\!(\mathrm{CH_2}\underset{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{OCCH_3}}}{\underset{|}{\mathrm{CH}}})\!\!-$$



$$-\!\!(\mathrm{CH_2}\underset{\mathrm{OH}}{\underset{|}{\mathrm{CH}}})\!\!-$$

Poly(vinyl acetate) Poly(vinyl alcohol)



$$-\!\!(\mathrm{CH_2}\underset{\mathrm{OCH_3}}{\underset{|}{\mathrm{CH}}})\!\!-$$

Poly(vinyl methyl ether)

These are among the most versatile resins, based on the diversity of uses for them. Poly(vinyl chloride) and its copolymers are the most important of these resins.

Polyvinyl Chloride. Poly(vinyl chloride), or PVC, initially was used as a replacement for cellulose nitrate. It is prepared by the polymerization of vinyl chloride under free radical conditions, most of it by suspension polymerization and the rest by emulsion and mass polymerization. The uncompounded resin is an atactic, amorphous, rigid material. The large dipole moment of the carbon–chlorine bonds produces strong intermolecular associations that result in high melt viscosity and good dimensional stability at room temperature. The high chlorine content gives it a high degree of flame and chemical resistance, which makes it suitable for pipes and fittings, tank linings, and packaging for corrosives. Although PVC is insoluble in most hydrocarbons, it is partially soluble in polar solvents such as ketones and chlorinated hydrocarbons. Its melting point and glass transition temperature depend on the method of preparation. It softens between 70 and 80°C, and when heated above 80°C it begins to degrade, eliminating hydrogen chloride from the polymer backbone.

The heat and light sensitivity of PVC and its processibility are greatly improved when the resin is compounded with antioxidants, UV absorbers, lubricants, fillers, pigments, and plasticizers. Stabilization with antioxidants and UV screeners has permitted its use in demanding exterior applications such as water hoses, siding for buildings, and sheeting for roofs. PVC is unusual because it can accept very large quantities of plasticizer and still retain desirable properties over a wide temperature range. At high plasticizer concentrations the type of plasticizer strongly influences properties. Plasticizers can be used to tailor the product for a specific application. For example, citrate esters impart flexibility for food contact applications; chlorinated hydrocarbons improve flame resistance and electrical properties; and the phthalic esters are lower-cost, general purpose plasticizers with good low-temperature properties.

The additives usually are mixed with the resin in two stages. Initially they are mixed at low shear to produce a good distribution. This is followed by roll milling or Banbury mixing, which homogenizes the mixture and forms a flux that is discharged to a mill for sheeting, or to an extruder for shaping. The molten sheet then can be calendered, compression-molded, or cooled and pelletized for packaging, storage, and shipment prior to fabrication.

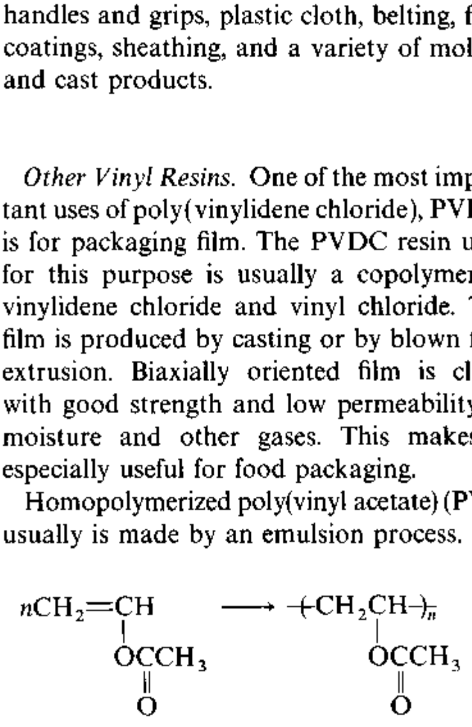
Over 60 percent of the PVC resin produced is extruded, much of it into pipe and conduit for water, gas, drainage, and sewerage. A large amount is extruded into siding, window profiles, window blinds, gutters, and downspouts. Calendered PVC is made into film, sheet, flooring, paneling, pool liners, upholstery, shower curtains, wall covering, electrical tape, packaging, and labels. PVC also is blow-molded into bottles. Laminates of PVC and cloth are used for upholstery fabrics, leather substitutes, and interior trim in domestic and automobile use. Because of its good electrical properties, stability, and toughness, PVC is used widely for both domestic and industrial wire and cable sheathing. Adding various-colored pigments aids in the identification of complex circuits.

PVC can be blended with other polymers to produce injection-molding compounds. Properties that make these blends suitable for appliance and business equipment housings such as computer monitors and keyboards include good impact strength, heat resistance, flame retardancy, and chemical and solvent resistance.[25]

Other important forms of PVC include plastisols, which are dispersions of the polymer in a plasticizer, and organosols, dispersions of polymer, plasticizer, and a volatile solvent. Dispersions are produced by spray-drying the polymer mixture made by emulsion or suspension polymerization. The friable powder produced this way is milled and then mixed with plasticizer and other additives. At ambient temperatures these mixtures are low-viscosity, easily handled liquids. When these dispersions are heated to temperatures above 125°C, any volatile solvents present evaporate, and the polymer and plasticizer fuse into a homogeneous solid. Organosols and plastisols are made into products by painting, dipping, molding, casting, and foaming. They are used in the production of handles and grips, plastic cloth, belting, film, coatings, sheathing, and a variety of molded and cast products.

Other Vinyl Resins. One of the most important uses of poly(vinylidene chloride), PVDC, is for packaging film. The PVDC resin used for this purpose is usually a copolymer of vinylidene chloride and vinyl chloride. The film is produced by casting or by blown film extrusion. Biaxially oriented film is clear, with good strength and low permeability to moisture and other gases. This makes it especially useful for food packaging.

Homopolymerized poly(vinyl acetate) (PVA) usually is made by an emulsion process.

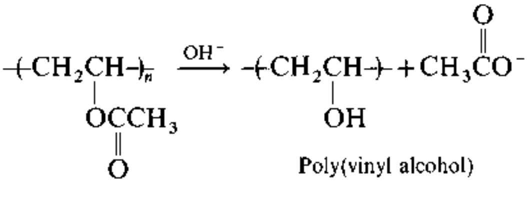


$$n\mathrm{CH_2{=}\underset{\underset{\underset{\displaystyle O}{\|}}{OCCH_3}}{\underset{|}{CH}}} \longrightarrow \mathrm{\text{-}\!\!(CH_2\underset{\underset{\underset{\displaystyle O}{\|}}{OCCH_3}}{\underset{|}{CH}}\text{-}\!\!)_n}$$

Vinyl acetate Poly(vinyl acetate)

The solid resins are clear, colorless, odorless, and tasteless, with a wide molecular weight distribution and a broad softening range. They are soluble in ketone and ester solvents and are readily plasticized. PVA is used in coatings and adhesives, as a chewing gum base, and as an intermediate in the production of poly(vinyl alcohol), PVOH.

PVOH is made by basic hydrolysis of PVA.

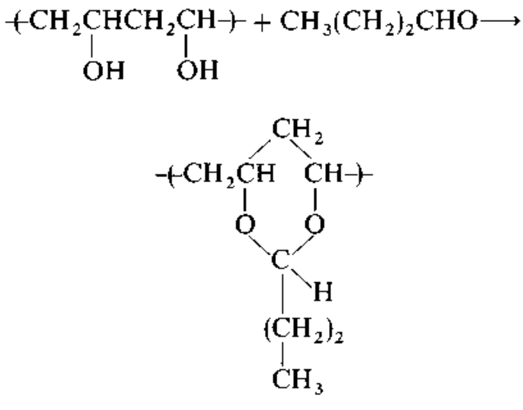


$$\mathrm{\text{-}\!\!(CH_2\underset{\underset{\underset{\displaystyle O}{\|}}{OCCH_3}}{\underset{|}{CH}}\text{-}\!\!)_n} \xrightarrow{OH^-} \mathrm{\text{-}\!\!(CH_2\underset{OH}{\underset{|}{CH}}\text{-}\!\!) + CH_3\overset{\overset{\displaystyle O}{\|}}{C}O^-}$$

Poly(vinyl alcohol)

Its solubility in water depends on how it is prepared. It is used for packaging film, as a thickening agent, as a component in adhesives, in the manufacture of controlled-dosage film sachets, and for the production of poly(vinyl butyral) (PVB).

PVB is made from hydrolyzed PVA by reaction with butyraldehyde.



Poly(vinyl butyral)

It has excellent optical properties, and, when plasticized, has good toughness and adhesion to glass. The largest use of plasticized PVB is for a safety glass inner layer. Its properties are adjusted to cushion the impact of an automobile occupant with the windshield during an accident. It also adheres to shards of glass broken during a collision or when a stone hits the windshield.

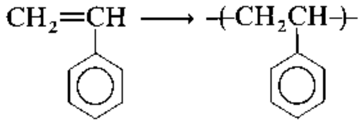
A variety of resin products are prepared from copolymers of ethylene and vinyl acetate. Though the proportion of ethylene can vary greatly, the most important ethylene vinyl acetate (EVA) copolymers contain less than 50 percent vinyl acetate. EVA copolymers with low vinyl acetate content are more crystalline than those with higher vinyl acetate content. In general, the more amorphous copolymers have higher impact strength, greater elasticity, and better resistance to stress cracking than LDPE. EVAs find use in packaging film and in a variety of adhesive products.

The hydrolyzed derivative of EVA is ethylene vinyl alcohol copolymer (EVOH). EVOH resins have high strength and elasticity. The films are glossy and clear and have good oxygen, nitrogen, and carbon dioxide barrier characteristics. Much EVOH is used for food packaging. Because the gas barrier properties of EVOH are reduced under humid conditions, it often is coextruded with nonpolar resins such as polyethylene or polypropylene to form multicomponent laminates.

For packaging applications that demand it, the moisture and gas barrier properties of the laminated film are further enhanced by metallizing one of the components. Because a continuous metal layer is much less porous than plastic, the rate of diffusion of gases thus is significantly reduced. The metallizing process is carried out in a high vacuum chamber where a very thin coating of aluminum is evaporated onto the surface of the plastic film. The development of multilayer films with exceptional barrier properties has made packaging of foods with nitrogen gas possible. This has substantially improved the quality and shelf life of many packaged food products.

Polystyrene and Styrene Copolymers

Polystyrene and its copolymers account for about 10 percent of the domestic resin market.[1] In its unmodified state, polystyrene is a hard, crystal-clear thermoplastic with relatively poor impact strength. Styrene is one of only a few vinyl monomers that can be polymerized by free radical, cationic, anionic, and Ziegler-Natta processes.



Styrene Polystyrene

When prepared by free radical and ionic processes, it is an atactic, amorphous solid. Isotactic polystyrene has been prepared by Ziegler-Natta polymerization.[20] It is an opaque, semicrystalline material that has a higher T_g and melting point and lower solubility than the more common amorphous atactic stereomer. The syndiotactic form also has been made.[26] However, no commercial interest has yet been shown for the stereoregular materials.

Amorphous atactic polystyrene softens at 90 to 95°C and becomes a mobile liquid at 140°C. It has good electrical properties and good resistance to strong acids and bases. It is soluble in esters and aromatic and chlorinated hydrocarbons and insoluble in aliphatic hydrocarbons and lower alcohols.

A large number of grades of polystyrene have been made for specific purposes, most of them by manipulating molecular weight and molecular weight distribution and by adding lubricants and plasticizers. The resins can be injection-molded, extruded into sheet and film, and made into foam. The electrical and heat-resistant grades are used as electrical insulation for capacitors and transformers and as housings for electrical appliances. Other grades are used for packaging, jars and tumblers, combs and hairbrushes, coat hangers, food canisters, and tubs. Foamed polystyrene is used as thermal insulation for refrigerators, coolers, trays, and cups; for mechanical shock insulation in molded packaging for cameras, small appliances, and radios; and for flotation in life preservers, buoys, and docks.

Toughened or rubber modified polystyrene blends are prepared by incorporating up to 10 percent by weight of polybutadiene or styrene–butadiene copolymer rubbers into the resin. The dispersed rubber particles decrease the plastic's brittleness by interrupting the crack propagation process. Unlike the unblended polymer, rubber modified polystyrene is translucent. The volume of rubber modified polystyrene made is roughly the same as that of general purpose polystyrene.

Good adhesion between the dispersed rubber phase and the continuous polystyrene phase is one requirement for improving the impact strength of rubber modified blends. Adhesion can be improved by compatibilization. There are several ways that this can be done. One way is to add molecules to the resin mixture that interact with, or have molecular similarities to, both phases. These are called compatibilizers. Another way to improve adhesion is to graft reactive substituents onto the molecules of one or both phases. Properly chosen, these grafted units interact with molecules of the other phase to improve the adhesive bond strength.

Rubbers are incorporated by mechanical blending and by polymerizing styrene monomer containing dissolved rubber. The latter process usually results in better impact strength due to efficient grafting between the growing polystyrene chains and the rubber. Strength and toughness are closely tied to the particle size of the rubber phase. Rubber-modified products made this way often are referred to as high impact polystyrene (HIPS).

Some HIPS plastics are extruded into sheet for subsequent thermoforming, which is done by heating the sheet above its softening point and forcing it against a mold by applying vacuum, air, or mechanical pressure (see below, "Thermoforming" in section on "Fabrication of Plastics"). Thermoforming of HIPS sheet for refrigerator door liners was one of the developments that helped to promote the growth of rubber-modified materials. HIPS is used in a variety of other products, including dinnerware, dairy containers, cold drink cups, and camper/trailer covers. In packaging applications, HIPS frequently is coextruded with a vinylidene chloride copolymer. The HIPS component provides structural strength and thermoformability, and the vinylidene chloride copolymer provides good gas barrier properties. In some packaging applications, such as yogurt containers, HIPS is coextruded with clear polystyrene, which adds a glossy surface that improves the package's visual appeal.

Styrene Copolymers. Copolymerization is another way to improve the mechanical properties and chemical resistance of polystyrene. Acrylonitrile, butadiene, alpha-methylstyrene, methyl methacrylate, divinylbenzene, maleic anhydride, and other monomers have been copolymerized with styrene to produce commercially important copolymers. Some of the most widely used of these are those prepared with acrylonitrile and butadiene. Styrene copolymerized with butadiene (SBR) is one of the more important elastomeric materials used today. (See Chapter 18.)

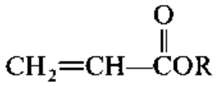
Styrene–acrylonitrile (SAN) is produced by mass, suspension, and emulsion polymerization. The copolymer has better chemical and mar resistance than the homopolymer. Properties vary with the ratio of the monomers; in general, an increase in the acrylonitrile content improves toughness and chemical resistance, but also increases color and melt viscosity. SAN is used for cups, handles, housings, and appliance parts. Low-color resins with high light transmittance are now available. Good optical properties make SAN useful for tumblers, serving dishes, canisters, and some disposable medical products.[27]

Acrylonitrile–butadiene–styrene (ABS) blends have become an important class of structural polymers. Like HIPS, ABS is a two-phase system in which the rubber is dispersed in the rigid SAN copolymer matrix. It is prepared by grafting SAN onto polybutadiene or butadiene copolymer. Properties can be modified by altering the ratio of the three ingredients and by manipulating rubber particle size, morphology, and the degree of grafting. ABS has high impact strength, toughness, and hardness and better resistance to outdoor weathering conditions than HIPS and SAN. Added protection from ultraviolet radiation can be obtained by adding pigments, stabilizers, and fillers.

ABS has good melt strength and little tendency to orient or develop mechanical anisotropy during molding. It can be made into uniformly tough molded and thermoformed objects. Moldings and extrusions with high gloss can be painted, metallized, and electroplated. ABS is extruded into pipes for plumbing and liquid transportation. Its high strength and heat and chemical resistance make it suitable for TV, telephone, computer, and camera housings, and for refrigerator linings, safety helmets, fascia, and dashboards in autos and many other applications.

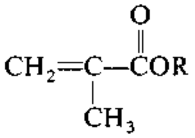
Acrylics

Acrylic resins are prepared by addition polymerization from acrylic or methacrylic acids and their ester, nitrile, and amide derivatives.



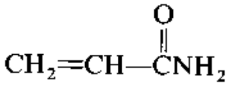
$$CH_2{=}CH{-}\overset{\overset{\Large O}{\|}}{C}OR$$

$R{=}H$ Arylic acid
$R{=}CH_3$ Methyl acrylate



$$CH_2{=}\underset{\underset{\large CH_3}{|}}{C}{-}\overset{\overset{\Large O}{\|}}{C}OR$$

$R{=}H$ Methacrylic acid
$R{=}CH_3$ Methyl methacrylate



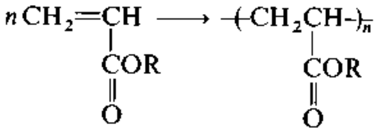
$$CH_2{=}CH{-}\overset{\overset{\Large O}{\|}}{C}NH_2$$

Acrylonitrile

$CH_2{=}CH{-}C{\equiv}N$

Acetonitrile

They are produced by a variety of processes including bulk, solution, emulsion, and suspension polymerization.



$$n\,CH_2{=}\underset{\underset{\underset{\underset{\large O}{\|}}{COR}}{|}}{CH} \longrightarrow {-}\!\!\left(CH_2\underset{\underset{\underset{\underset{\large O}{\|}}{COR}}{|}}{CH}\right)\!\!{-}_n$$

Because of the electronic effect of the carbonyl group, acrylates and methacrylates readily take part in both free radical and anionic addition polymerization reactions. The type of substituent attached to the double bond significantly affects polymer properties, and because these monomers readily undergo copolymerization, considerable property diversity can be designed into the polymers that are formed.

Polymers derived from acrylic and methacrylic acid esters are noted for waterlike clarity and color and for excellent stability during aging. Depending on the nature of the ester group and polymerization conditions, the polymer can be tacky, rubbery, or glasslike.

Thus, acrylics are used for such diverse products as pressure-sensitive and structural adhesives, coatings, and rigid plastics. Because of their low T_g, poly(ethyl acrylate) and poly(butyl acrylate) are used in acrylate-based rubbers.

The most important acrylic plastic is polymethyl methacrylate (PMMA). It also was the first acrylic to be produced commercially. It is an amorphous thermoplastic polymer that can be thermoformed, molded, or extruded above 150°C. It is soluble in ketones, esters, and chlorinated hydrocarbons, but is resistant to attack by dilute acids and bases. Compared to polymethyl acrylate, PMMA is more stable to exterior aging, has lower moisture absorption, and is more resistant to alkalies.

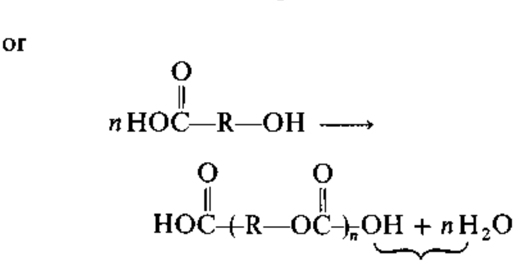
Applications for PMMA take advantage of its combination of weather resistance, clarity, light weight, impact strength, hardness, and formability. It has a visible light transmission of about 92 percent, which is somewhat higher than that of glass. Consequently it is used as a substitute for glass in some applications, including bank teller windows, skylights, archways, exterior signs, corrugated roofing, storm doors, and bath and shower enclosures. It also is used for interior applications such as appliance housings, tumblers, and instrument panels. One of its major disadvantages compared to glass is low abrasion and solvent resistance. For applications where abrasion and solvent resistance are important, PMMA sheet is available with a thin hard coating that improves its durability considerably.

The high degree of intermolecular interaction between the polar nitrile groups in poly(acrylonitrile) restricts bond rotation and produces a stiff polymer. As a result, poly(acrylonitrile) has a high melting point and is soluble in only a few solvents. It cannot be melt-processed because of extensive decomposition. However, copolymerizing acrylonitrile with other monomers produces a more easily processible material. Much of the commercial output of acrylonitrile monomer is used for fiber and for structural plastics such as SAN and ABS.

Some of the properties of polyacrylic acid, polymethyacrylic acid, and polyacrylamide are similar. They are hard, brittle, transparent, and hygroscopic solids; they are soluble in water and polar organic solvents, and insoluble in nonpolar solvents. They are used as thickeners, binders, adhesives, and suspending and flocculating agents, but the volume used is comparatively small. Several applications for polyacrylamide and partially hydrolyzed derivatives rely on their ability to flocculate solids in aqueous suspensions. Thus, they are used for water purification, especially in paper making and mining operations. They also are used to improve the flow properties of water, to adjust the dry strength of paper, and in secondary and tertiary oil recovery.

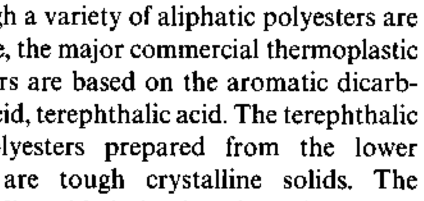
Polyesters

Polyesters are a class of resins with repeating ester linkages in the polymer backbone. Nominally, they are derived from the condensation of dicarboxylic acid monomers with diol monomers, or by self-condensation of hydroxycarboxylic acids.



$$n\,\mathrm{HO\overset{O}{\overset{\|}{C}}{-}R{-}\overset{O}{\overset{\|}{C}}OH} + n\,\mathrm{HO{-}R'{-}OH} \longrightarrow \mathrm{HO\overset{O}{\overset{\|}{C}}\!\left(R{-}\underbrace{\overset{O}{\overset{\|}{C}}O}_{\text{ester linkage}}{-}R'\right)_{\!n}OH} + n\,\mathrm{H_2O}$$

or



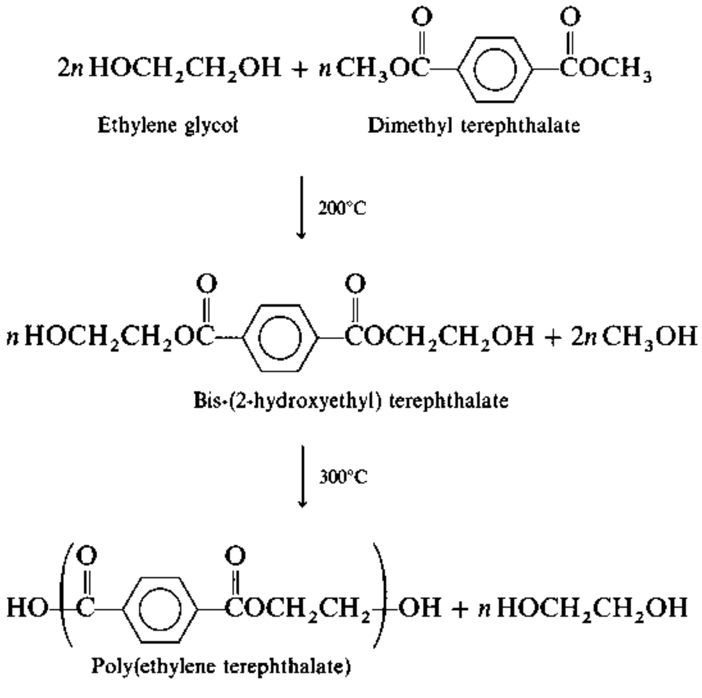
$$n\,\mathrm{HO\overset{O}{\overset{\|}{C}}{-}R{-}OH} \longrightarrow \mathrm{HO\overset{O}{\overset{\|}{C}}\!\left(R{-}O\overset{O}{\overset{\|}{C}}\right)_{\!n}}\underbrace{\mathrm{OH} + n\,\mathrm{H_2O}}$$

Though a variety of aliphatic polyesters are available, the major commercial thermoplastic polyesters are based on the aromatic dicarboxylic acid, terephthalic acid. The terephthalic acid polyesters prepared from the lower glycols are tough crystalline solids. The isophthalic acid derivatives have lower T_g's than other members of the group and are amorphous, or crystallize with difficulty. This illustrates the importance that molecular symmetry in the repeating units has on the physical characteristics of polymeric materials.

Poly(ethylene terephthalate) (PET) the most important of this group, was commercialized in the early 1950s, and has found a broad range of uses. The largest uses are in fiber staple; photographic film; video, magnetic, and computer tape; electrical insulation; bottles; and engineered products. Its advantages for these applications include its high melting point, low water absorption, good surface gloss, dimensional stability, and good control over properties.

PET can be prepared in several ways. In a widely used batch procedure, dimethyl terephthalate is mixed with excess glycol and a basic catalyst, and the mixture is heated to temperatures around 200°C. Methanol and excess glycol are removed to produce the intermediate bis-(2-hydroxyethyl) terephthalate. In a second stage, the temperature is increased to near 300°C under a slight vacuum to carry off residual volatiles produced in the final condensation step. The reaction is terminated when the viscosity increases to a predetermined value. The product is cooled and converted into granules for packaging and shipping.

Resin with an average molecular weight of 35,000 to 40,000 is used for film and fiber. Fiber is made from the resin by spinning, and film is manufactured by extrusion. Both processes orient the polymer molecules in the direction of drawing. Film is generally also stretched in the cross-machine direction to make a biaxially oriented product. Such films have improved strength and modulus as well as better optical properties. The hot film is quenched after annealing under tension for a predetermined period of time to allow further crystallization to take place. This yields a product with controlled clarity, strength, and modulus. Orientation also will improve heat resistance and barrier properties. Once the material has been fine-tuned to this degree, it becomes temperature-sensitive. Heating to near the T_g makes the polymer strands more mobile and causes additional crystallinity, loss of clarity, and dimensional changes. When this is done intentionally to stabilize a plastic, it is called annealing.



Resin with a molecular weight of about 70,000 is used for molded parts. Although the low rate of crystallization is helpful in making film, it is a problem for making castings and injection-molded engineered products. However, when the melt is allowed to crystallize under controlled temperature conditions in the presence of finely divided inorganic nucleating agents, thick materials can be produced with the desired morphology.

When tetramethylene glycol is used in place of ethylene glycol, poly(butylene terephthalate) (PBT), a material with a lower T_g and melting point (220–235°C), is obtained. Because PBT crystallizes more rapidly than unmodified PET, its mold cycle times are faster. It also has good strength and rigidity and has found use in precision parts for electronic devices, office appliances, and automobiles. Its material properties can be further modified with a variety of additives. The inclusion of glass fiber increases its modulus and its heat deflection temperature.

PET and PBT are more expensive than commodity plastics, but they have many advantages in structural applications, including rigidity, surface hardness, machinability, and higher service temperatures. Though they have been mentioned here, structural grades of the polyesters can be classified as engineering thermoplastics.

Engineering Thermoplastics

Engineering plastics have been defined as "thermoplastics that maintain dimensional stability and most mechanical properties above 100°C and below 0°C."[28] Compared to metal, wood, glass, and ceramic materials that they might replace, engineering plastics offer the advantages of corrosion resistance, weight reduction, and fabrication ease. For example, a large market for engineering plastics is developing in the transportation industry where weight reduction, impact resistance, design flexibility, corrosion resistance, and cost savings from parts consolidation are incentives for materials to replace steel.

An engineering plastic is expected to function when it is subject to high mechanical stress, temperature extremes, and hostile environments. In contrast, commodity thermoplastics such as the polyolefins, polystyrene, and PVC lose important mechanical properties when temperatures approach 100°C.

The engineering plastics group includes the polyamides, polyimides, polyacetals, polycarbonates, polyethers, polysufones, polysulfides, fluoropolymers, some of the polyesters, some grades of ABS, and the so-called high performance plastics. Together they account for about 5 percent of the plastics market. The higher-performance segments of this class cost more than conventional engineering plastics, but they retain mechanical and electrical properties during continuous use at temperatures above 150°C. Table 19.3 lists some of the major representatives of this group, the relative quantities sold, and approximate continuous use temperatures.[29]

Some of these resins, such as the polyacetals, nylons, and polyether ether ketones, are highly crystalline. The crystalline resins are more resistant to solvents and grease and are used for parts such as gears, bearings, and petroleum product containers, and parts that need resistance to aggressive solvents and grease. However, in applications where clarity and toughness are important, such as security glazing, clear piping, or protective housings, an amorphous material such as polycarbonate might be used. The crystalline materials tend to be more dimensionally stable under stress

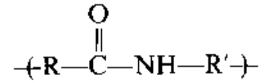
TABLE 19.3 Engineering Thermoplastics

	Approximate Continuous Use Temperature (°C)	*% of Total*
Polyamides	80	36
Polycarbonates	120	27
Polyacetals	80	16
Polyphenylene oxide	90	10
PET/PEB	130	9
High performance resins		2
Polyphenylene sulfide	200	
Polysulfone	150	
Polyether sulfone	180	
Polyether ketone	250	
Polyether ether ketone	240	
Polyetherimide	170	

but shrink more in molding operations than the amorphous ones.

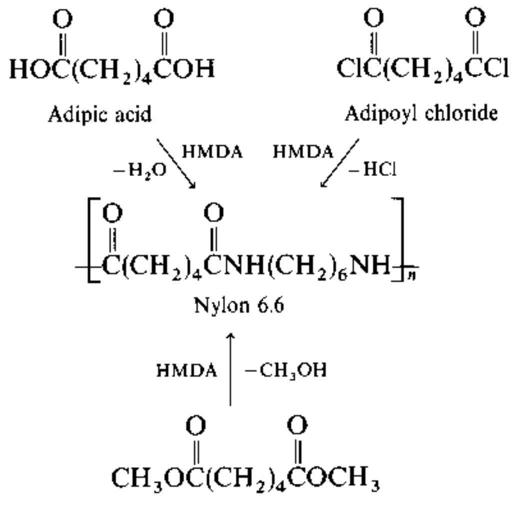
Engineering thermoplastics can be fabricated by conventional means into mechanically functional parts or structural components. They often are modified by adding stabilizers, fire retardants, fillers, and reinforcement materials. Only a few members of this diverse class of resins will be discussed here.

Polyamides and Polyimides. The polyamides are a class of polymers characterized by repeating amide links in the polymer backbone:



$$-\!\!\left(\!R-\overset{\overset{\displaystyle O}{\|}}{C}-NH-R'\!\right)\!\!-$$

They include natural polymers such as silk and synthetics such as nylons. Nylon polymers first were synthesized by Wallace Carothers and coworkers at Du Point in the late 1920s and 1930s. They are derived from carboxylic acid and amine precursors by both condensation and ring opening polymerization. They are commonly named by adding to the word nylon, a number equal to the number of carbons in the parent compounds. Thus, nylon 6.6 is the product of the condensation reaction between hexamethylenediamine, $NH_2(CH_2)_6NH_2$, or HMDA, and adipic acid or its acid halide and methyl ester.



$$\underset{\text{Adipic acid}}{HO\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}OH} \qquad \underset{\text{Adipoyl chloride}}{Cl\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}Cl}$$

$$\xrightarrow[-H_2O]{HMDA} \qquad \xleftarrow[-HCl]{HMDA}$$

$$\underset{\text{Nylon 6.6}}{\left[\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}NH(CH_2)_6NH\right]_n}$$

$$\uparrow HMDA \mid -CH_3OH$$

$$\underset{\text{Dimethyl adipate}}{CH_3O\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}OCH_3}$$

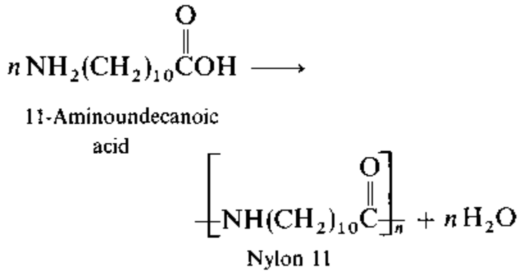
Adipic acid

Adipoyl chloride

Nylon 6.6

Dimethyl adipate

Nylons also can be made by the self-condensation of amine-substituted carboxylic acids. Nylons 7, 9, and 11 are made this way.

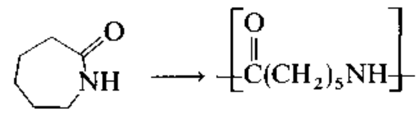


$$n\,NH_2(CH_2)_{10}\overset{\overset{O}{\|}}{C}OH \longrightarrow \left[NH(CH_2)_{10}\overset{\overset{O}{\|}}{C}\right]_n + n\,H_2O$$

11-Aminoundecanoic acid

Nylon 11

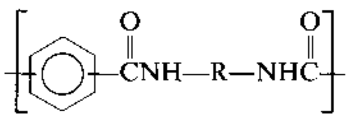
Nylons also are prepared by the ring-opening addition polymerization of certain lactams. The most important of these ring-opening processes is the polymerization of caprolactam to give nylon 6.



Caprolactam

Nylon 6

Of the many nylons available, nylons 6.6, 6, 11, and 12 are the most widely used. Nylons prepared from the terephthalic acids have very high melting points and are called aramides. The aramides are used in fiber applications where high thermal stability and high tensile strength are important. The repeating unit (R) can be derived from aliphatic or aromatic diamines.



Aramides

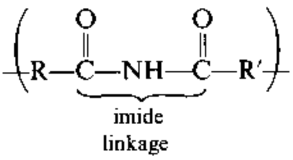
Most nylons are highly crystalline and undergo a sharp transition from a tough, rigid solid to a low-viscosity melt. This makes them easy to process. Nylons having an even number of carbon atoms between the amide groups pack better and therefore have a higher melting point than comparable nylons with odd numbers of carbon atoms. The crystalline nylons are translucent and have good chemical and hydrolytic stability.

Though the nylons originally were developed for their fiber-forming characteristics, their first commercial application was for toothbrush bristles, and shortly thereafter they were used for women's stockings. Not only are they drawn into monofilament and spun into fiber; they are extruded into film and tubing, blow-molded into bottles, injection-molded into numerous products, and used in coatings and adhesives. Large quantities of nylon are used for surgical suture, rope, tire cord, carpet stable, and brush bristles. Their advantages for these applications include durability, tensile strength, toughness, and flexibility.

The nylons were among the first engineering thermoplastics produced on a large scale. In these applications use is made of their toughness, high melting point, chemical resistance, and self-lubricating properties. When nylons are fiber-reinforced, their heat deflection temperatures approach the crystalline melting point, and because they retain toughness and flexibility at low temperatures, they can be used over a wide temperature range. Examples include pipes, gears, bearings, cams, housings, impeller blades, casters, and door catches.

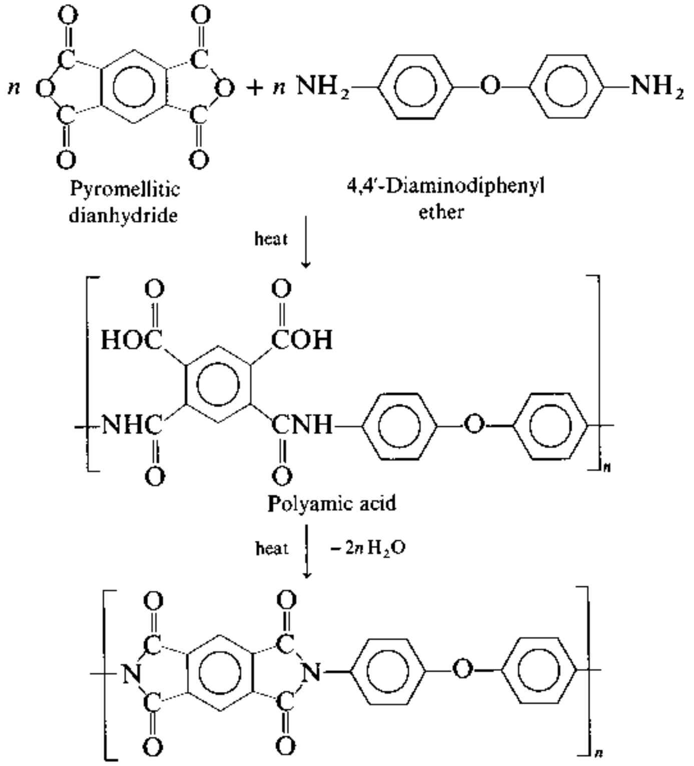
Nylons can reversibly absorb up to about 10 percent moisture. The moisture uptake changes dimensions and mechanical properties. Nylons 11 and 12, which have a higher proportion of hydrophobic methylene groups than nylon 6, for example, have a lower moisture uptake. Nylons can be mineral-filled or reinforced with fiber. Modifications of this kind significantly decrease water uptake and increase modulus, impact strength, temperature stability, and fire retardancy. Heat distortion temperature and creep also are improved this way. Filled nylons have replaced metals in applications such as door handles, hinges, window and door fasteners, and oil dipsticks.

Related to the polyamides are the polyimides, which contain the characteristics imide linkages in the backbone:



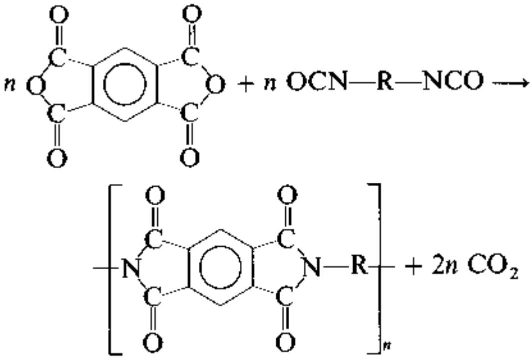
$$\left(\mathrm{R}-\underbrace{\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{NH}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}}_{\text{imide linkage}}-\mathrm{R'}\right)$$

Although polyimides can have an open-chain structure, cyclic polyimides have found more use because they are more thermally stable than open-chain polyimides.[30] The polyetherimide prepared from pyromellitic dianhydride and 4,4′-diaminodiphenyl ether has found use in high temperature coatings, adhesives, and structural plastics. The reaction involves rapid formation of the polyamide, called polyamic acid, followed by a high-temperature ring closure step.



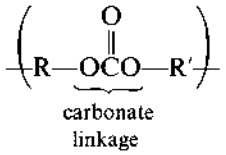
Thermodynamic factors favor ring formation over competing cross-linking reactions. These steps usually are carried out in stages, with ring closure driven to completion at higher temperatures. The polyamic acid produced during the first stage can be applied as a melt or in some cases as a solution, in a solvent such as dimethylformamide or dimethyl sulfoxide. This varnish can be used to impregnate glass fabrics or to bond composites. Once it is applied to the substrate, the temperature is increased to drive off solvents and complete ring closure. The final article then may be finished by machining.

Many types of polyimides are possible, although those derived from aromatic precursors are most important because they are the most resistant to hydrolysis and have excellent thermal and oxidative stability at temperatures up to 300°C or more. The resistance of polyimides to abrasion and solvents is good, and filled grades are available for load-bearing applications. Polyimide foams can be made by the reaction of dianhydrides with diisocyanates. The carbon dioxide that is produced acts as a blowing agent.[31]



Polyimides are good insulators and particularly resistant to electrical and radiation damage. They are used as structural adhesives, for electric motor insulation, for high performance cable and wire coatings, and for printed circuit boards.

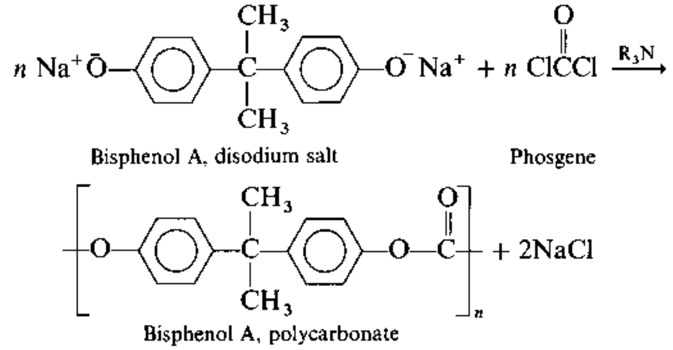
Polycarbonates. Polycarbonates are polyesters derived from carbonic acid and have the backbone structure:



$$\left(R - \underbrace{O\overset{O}{\overset{\|}{C}}O}_{\text{carbonate linkage}} - R' \right)$$

Although aliphatic polycarbonates have been produced, the term "polycarbonate" usually refers to the bisphenol A esters and copolymers of carbonic acid. Bisphenol A polycarbonate has been made by transesterifying diphenyl carbonate with bisphenol A, but most now is manufactured by interfacial polymerization of bisphenol A with phosgene.

In the interfacial process, bisphenol A is dissolved in the aqueous sodium hydroxide phase of a two-phase system with methylene chloride. As phosgene is pumped into the mixture, the sodium chloride condensation by-product dissolves in the aqueous phase, and the growing polymer dissolves in the organic phase. A tertiary amine is used as the catalyst. When the reaction is complete, the methylene chloride solution is extracted with acid to remove basic components and then washed with water. The solvent is then flashed off and recycled, leaving the solid.



Bisphenol A, disodium salt

Phosgene

Bisphenol A, polycarbonate

It is an amorphous material that exhibits unusually high impact strength over a broad temperature range. Though its T_g approaches 150°C, it can exhibit ductile failure at temperatures as low as -200°C. This is unusual for an amorphous material, as most thermoplastics are brittle below T_g.

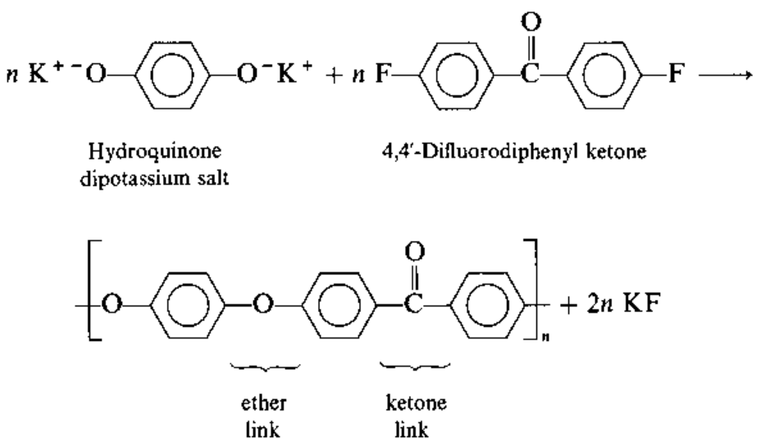
In its fused form polycarbonate has glasslike clarity with 89 percent transmission of visible light, high thermal resistance, and good processibility. Material with an average molecular weight of 22,000 to 50,000 softens above 220°C. It can be injection-molded and extruded between 270 and 320°C at pressures between 10,000 and 20,000 psi. The resin must be dried prior to processing in order to prevent thermally induced hydrolysis.

Polycarbonate is resistant to dilute acids, aliphatic hydrocarbons, alcohols, and oils, but is attacked by alkalis, aromatic and chlorinated hydrocarbons, ketones, and esters. Methylene chloride and pyridine are good solvents. Scratches and crazing by solvents and chemicals substantially lower its impact strength. For applications where this can be a problem, sheet is available with an abrasion-resistant coating that significantly improves resistance to abrasion and solvents. Polycarbonate cannot be used for extended periods outdoors without UV-absorbing coatings because photodegradation reduces its strength and causes it to discolor.

A large fraction of the polycarbonate made is used by the electronics industry. It has electrical insulating properties that are nearly independent of environmental conditions. This includes high surface and volume resistivity and good dielectric properties. Capacitors are made from metallized grades. A large outlet for high grade polycarbonate is compact disks. The transparency and impact resistance of polycarbonate has led to its use for motorcycle windshields, high-speed aircraft windows, ophthalmic lenses, helmets, and security glazings for banks, offices, and armored vehicles. It also is used in medical appliances, auto head- and tail-light housings, fan blades, and machine parts. It is extruded into film for packaging and pressure-activated switch protectors.

Both random and block copolymers of polycarbonate have been made. Copolymers with terephthalic and isophthalic acid units are used in glazing applications. Polymerization with mono- or difunctional poly(dimethylene) oxide gives, respectively, ABA and $(AB)_n$ block copolymers with improved heat distortion temperature. Blends with ABS exhibit good toughness and electrical properties. Polycarbonate-ABS blends are used for dashboard panels, spoilers, wheel caps, housings for lamps, and office equipment.

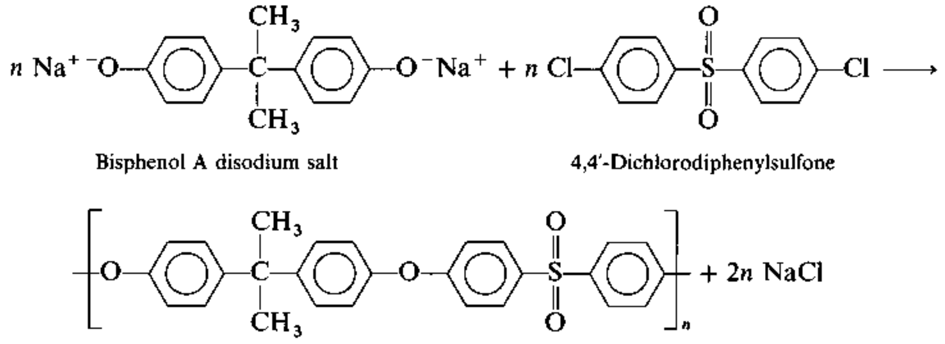
Polyetherether Ketones, Polysulfones, and Acetal Resins. The poly(etherether ketones), or PEEK, can be prepared by condensation of the dipotassium salt of hydroquinone or bisphenol A with 4,4′-difluorodiphenyl ketone at temperatures in excess of 300°C.



They are crystalline resins with T_g's in excess of 140°C and melting points of around 320°C. Their heat deflection temperature can be increased to near their melting point by incorporating glass filler. They have excellent solvent resistance and stability at 200°C and can be heated to near 300°C for short periods with no serious effect on their properties. Like other resins with the photosensitive aromatic backbone, they are not suitable for extended use outdoors.

PEEK can be processed into filament, tubes, sheet, and profiles by conventional methods at melt temperatures near 370°C. The largest user of the resin is the electronics industry, which uses it for cable insulation, connectors, and flexible circuit boards. It also is used for valve seals and compressor plates.

Polysulfone resins are prepared by a process similar to that used to prepare polyether ketones, except that the displacement occurs on a halogen-substituted aromatic sulfone.



They are amorphous, yellow, transparent, rigid resins with T_g's over 180°C and very good resistance to thermal oxidation. Like PEEK, they have good electrical properties. They are inherently resistant to burning, and for most applications do not require fire retardants. They also can be used in applications requiring long exposure to steam or hot water. Because they are transparent to microwaves, they are suitable for microwave cookware. Other uses include appliance parts, gas separators, medical devices, and electrical components.

The acetals, which have the $(\text{—}CH_2O\text{—})_n$ ether repeating unit, are prepared by ionic polymerization of formaldehyde and its oligomers. Initiators include alkoxide, amine, and phosphine bases, and both mineral and Lewis acids.

Initiation by bases, B^-:

$$B^- + CH_2{=}O \rightarrow B{-}CH_2{-}O^-$$

$$B{-}CH_2{-}O^- + n\,CH_2{=}O \rightarrow$$
$$B{-}CH_2{-}(O{-}CH_2)_n{-}O^-$$

Initiation by acids, A^+:

$$A^+ + CH_2{=}O \rightarrow A{-}OCH_2^{+}$$

$$A{-}OCH_2{}^+ + n\,O{=}CH_2 \rightarrow$$
$$A{-}O{-}(CH_2{-}O)_n{-}CH_2{}^+$$

Up to 15 percent ethylene oxide may be used as a comonomer to provide flexibility and stability. At one or both chain ends is a hydrolytically unstable $\text{—}OCH_2OH$ hemiacetal group. In moist environments or at elevated temperatures, formaldehyde is split off, generating another hemiacetal group.

$$\text{-}\!\!\underbrace{(CH_2O)_n CH_2{-}OH}_{\text{unstable hemiacetal end group}} \xrightarrow{\text{heat}}$$

$$\text{-}\!\!(CH_2O)_{n-1}CH_2OH + CH_2{=}O$$

This unzipping, which is essentially the reverse of the polymerizing reaction, can be prevented by esterifying or alkylating the hydroxyl end group.

$$\text{-}\!\!(CH_2O)_n CH_2{-}\underbrace{O\overset{\overset{O}{\|}}{C}CH_3}_{\text{stable acetate ester end group}}$$

The acetals are translucent, crystalline materials with good solvent resistance. Parts made from them exhibit high stiffness, good tensile strength, and dimensional stability. Like the nylons with which they compete, they are self-lubricating, but unlike the nylons, they retain dimensional stability under ambient moisture conditions. They have good fatigue resistance, but relatively low impact resistance. As in other polymeric systems, their impact resistance is increased significantly when they are reinforced with fibers.

The melting points of the homopolymer and ethylene oxide copolymer are around 175°C and 165°C, respectively. Typical of highly crystalline resins, liquid flow temperatures are about 10°C higher. They are injection-molded and extruded. Their utility is based on lower cost and improved performance in applications that were formerly met by zinc, brass, aluminum, and cast steel parts. Examples include fuel pump and filter housings, fuel caps, bearings, gears, cranks, springs, pens, integral hinges, zippers, and solvent containers.

IMPORTANT CLASSES OF PLASTICS AND RESINS: THERMOSETS

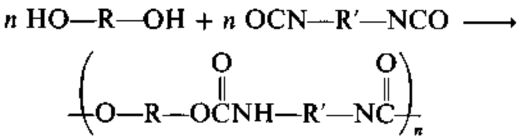
Cross-linking makes thermosets infusible and insoluble. The cross-linked network can form during polymerization when multifunctional monomers are present. Thermosets also are formed when resins with reactive functionality are caused to react with cross-linking co-reactants. Alternately, a cross-linked network will be produced when thermoplastic resins are irradiated or vulcanized or undergo autoxidation.

Thermoset plastics can be cross-linked to various degrees; they can be soft, flexible, elastomeric materials, or hard and structurally rigid. Though thermosets account for only about 15 percent of the plastics market, they are an extremely important segment.[1] The most important thermosets are derived from polyurethane, phenolic, unsaturated polyester, and epoxy resins.[32]

Polyurethanes

The polyurethanes, a versatile class of polymers that were discovered by Otto Bayer and coworkers in 1937,[33] are characterized by repeating carbamate units (—OCONH—) in the polymer backbone. They generally possess good toughness and abrasion and chemical resistance, and are made into film, sheet, foam, fiber, coatings, adhesives, and sealants. They also find extensive use in mechanical, sound, and thermal insulation, and for medical applications such as catheters and artificial blood vessels.[34]

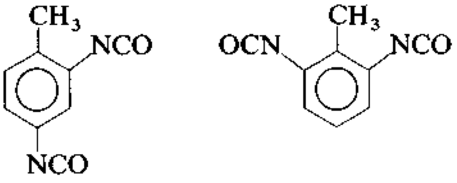
Polyurethanes are prepared by the addition of polyols to polyfunctional isocyanates.



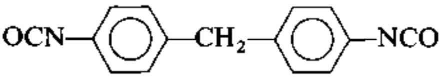
$$n\,\text{HO—R—OH} + n\,\text{OCN—R}'\text{—NCO} \longrightarrow \left(\text{O—R—O}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{NH—R}'\text{—N}\overset{\overset{\text{O}}{\|}}{\text{C}}\right)_n$$

Polyurethane backbone

Commonly used isocyanates include:



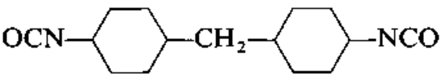
Toluene diisocyanate (TDI)
(a mixture of 2,4- and 2,6-isomers)



4,4′-Diphenylmethane diisocyanate (MDI)

$$\text{OCN—(CH}_2)_6\text{—NCO}$$

Hexamethylene diisoyanate (HDI)

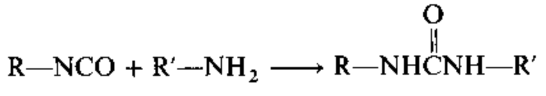


Dicyclohexylmethane diisocyanate (DCHDI)

Because the functionality, equivalent weight, and backbone structure of the reactants can be varied over a wide range, a broad spectrum of properties can be produced. The products will be thermoplastic if the functionality of the monomeric ingredients are two or less, or thermoset if functionality is greater than two. By far the largest class of industrial polyurethanes are thermosets derived from aromatic isocyanates.

In addition to alcohols, isocyanates can react with other substances with polar hydrogens. Examples include:

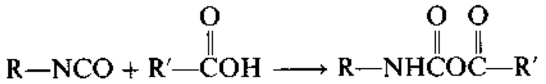
1° and 2° amines



$$\mathrm{R{-}NCO + R'{-}NH_2 \longrightarrow R{-}NH\overset{O}{\overset{\|}{C}}NH{-}R'}$$

A urea

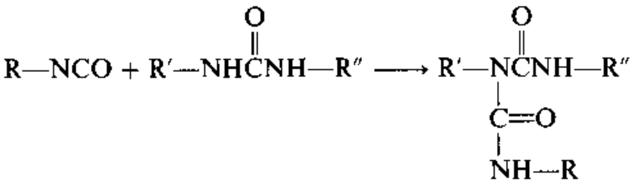
Carboxylic acids



$$\mathrm{R{-}NCO + R'{-}\overset{O}{\overset{\|}{C}}OH \longrightarrow R{-}NH\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}{-}R'}$$

An anhydride

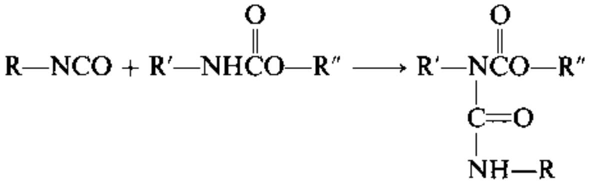
Ureas



$$\mathrm{R{-}NCO + R'{-}NH\overset{O}{\overset{\|}{C}}NH{-}R'' \longrightarrow R'{-}\underset{\substack{|\\ C=O\\ |\\ NH-R}}{N}\overset{O}{\overset{\|}{C}}NH{-}R''}$$

A biuret

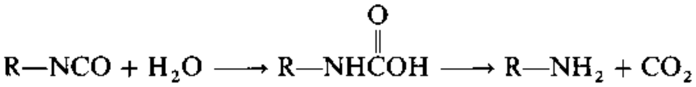
Urethanes



$$\mathrm{R{-}NCO + R'{-}NH\overset{O}{\overset{\|}{C}}O{-}R'' \longrightarrow R'{-}\underset{\substack{|\\ C=O\\ |\\ NH-R}}{N}\overset{O}{\overset{\|}{C}}O{-}R''}$$

An allophanate

Water



$$\mathrm{R{-}NCO + H_2O \longrightarrow R{-}NH\overset{O}{\overset{\|}{C}}OH \longrightarrow R{-}NH_2 + CO_2}$$

A carbamic acid

Hence, care must be exercised in the choice of reagents, solvents, and reaction conditions to prevent unwanted side reactions during the production of polyurethanes. Reagents must be dry and free of unwanted alcohols. The relative rates at which the various isocyanate reactions proceed are as follows: aromatic isocyanates > aliphatic isocyanates. Also: aliphatic amines > aromatic amines > primary alcohols > water > secondary alcohols > tertiary alcohols > phenols > carboxylic acids > urethanes. These reactions are catalyzed by tertiary amines and a variety of metal salts. The most active catalysts are organo-tin compounds such as dibutyl tin dilaurate.[35]

An important fabrication process that takes advantage of the high reactivity of the catalyzed isocyanate–polyol reaction is called reaction injection molding (RIM). In RIM, precise amounts of the reactive components are metered to a mixing head, where the liquid streams are mixed and injected into a mold. Bulky, complex shapes and thin-walled articles can be produced in this way. Reaction times of a few seconds are possible, and mold residence times of one or two minutes have been achieved. RIM consumes less energy and uses less expensive equipment than conventional injection-molding processes. The process is used to make fascias, bumpers, and other flexible automotive parts.[36] Fillers may be incorporated in the components to lower cost and increase rigidity. This fabrication technique is discussed further in the section on "Fabrication of Plastics" under "Injection Molding."

Polyurethane foams are produced by synthesizing the polymer concurrently with gas evolution from a blowing agent. Bubbles or gas are trapped in the reacting mixture to form a cellular structure. Commercial nitrogen-forming blowing agents include azobisformamide and azobisisobutyronitrile. In some processes water is deliberately added to generate carbon dioxide. The amine by-product produced this way reacts further with unreacted isocyanate to generate biuret cross-links. In rigid foams, low-boiling halogenated alkanes such as trichlorofluoromethane have been used. Foams produced this way are very good insulators because the halocarbon blowing agents trapped in the cells have low thermal conductivity. However, concern about ozone depletion is causing the elimination of many halocarbon blowing agents.

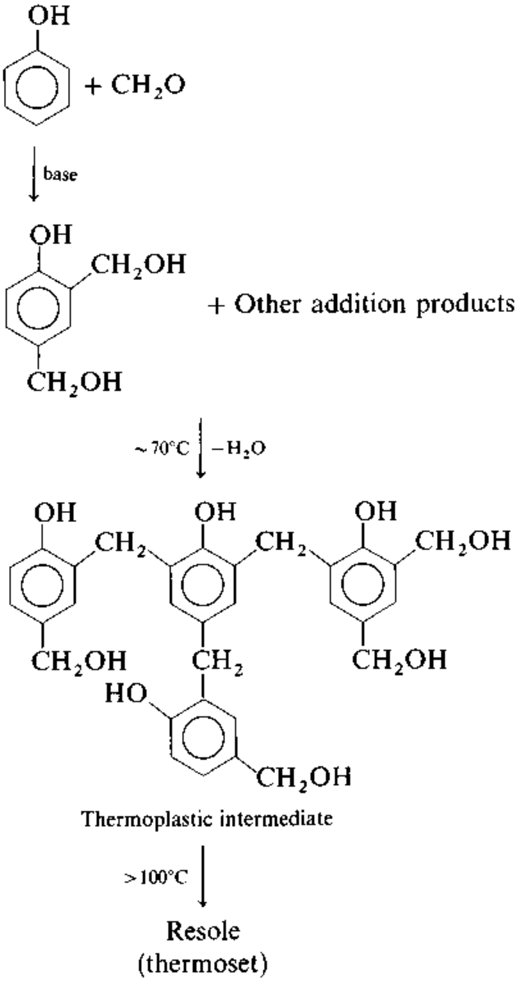
Foams usually are made with a mixture of aliphatic polyether or polyester diols and triols. A typical formulation also will contain an aromatic diisocyanate such as toluene diisocyanate or diphenylmethane diisocyanate, a catalyst, surfactants, and foam stabilizers. The inclusion of trifunctional reactants makes varying degrees of cross-linking possible. Lightly cross-linked foams are flexible, whereas those more highly cross-linked are rigid. Flexible foams generally have an open cell structure; most rigid foams are made with closed cells.

Polyurethane foams have dry heat stability to about 150°C and are resistant to many solvents. Because more than 90 percent of a low density foam consists of gas, these materials exhibit low thermal conductivity and are good acoustical insulators. Compared to polyether foams, polyester foams are stiffer and more resistant to dry-cleaning fluids. Thus polyester foams are preferred in such applications as textile laminates and shoulder pads. Polyether polyols produce a foam that is more resilient and less subject to hydrolysis than other foams; so polyether foams are preferred for upholstery, bedding, and carpet backing where cushioning is important. Rigid foams are used for lightweight insulated construction panels, packaging, and flotation equipment. Further information is included in the section on "Fabrication of Plastics" under "Foamed Plastics."

Phenolic Resins

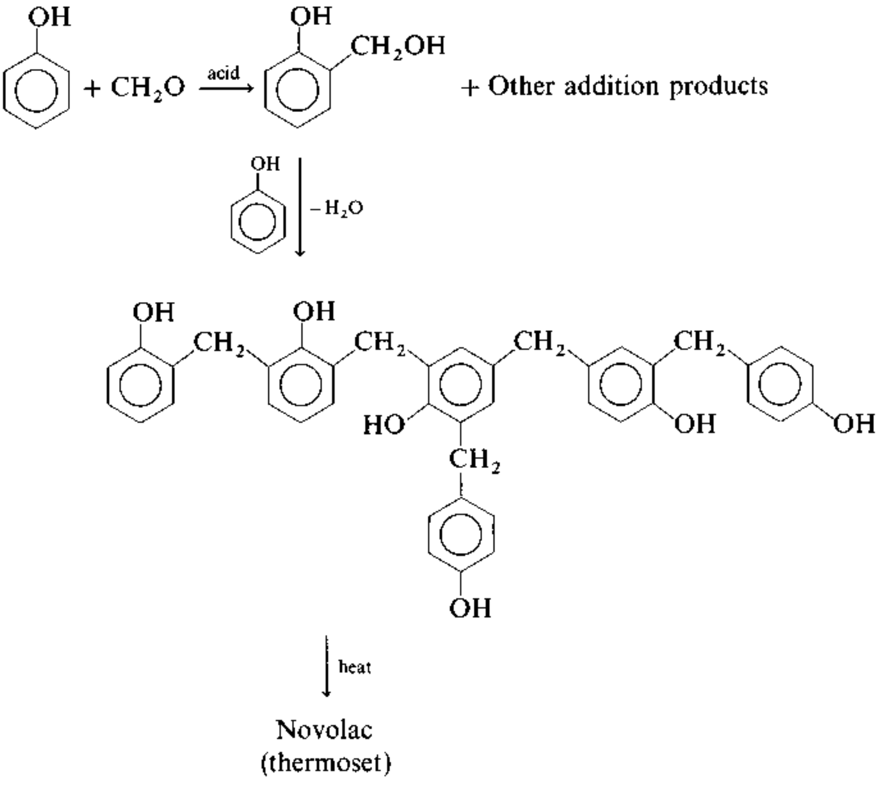
The phenolics were the first wholly synthetic plastic materials commercialized. The most important phenolic plastics are derived from the condensation of formaldehyde with phenol or its derivatives. Though this class of polymer was first made in the 1870s by von Baeyer, Leo Baekeland found early in the twentieth century that useful moldings can be made if the final stages of the curing reaction are carried out under heat and pressure.

The chemistry of the phenolics is complex. Polymerization involves heating the reactants with acidic or basic catalysts until condensation begins. Depending on the ratio of reactants and the catalyst type, materials with different properties are formed. If the molar ratio of formaldehyde to phenol is 1:1 or greater, and a basic catalyst such as sodium or calcium hydroxide is used, then a reactive resin called a resole is formed. The initial condensation step is carefully controlled to produce a resin that is easily handled during the final fabrication step.



The resole may be produced as a powder, a solution, or a dispersion. It can be compounded with fillers and other ingredients, cast into a mold, coated on a substrate, or used to impregnate a porous material. The thermosetting step then is carried out at temperatures up to 180°C.

If the phenolic reactant is present in excess during the initial condensation reaction, and an acidic catalyst such as sulfuric or oxalic acid is used, then a resin called a novolac is formed.



At molecular weights up to 1000, the novolacs are nearly linear; above 1000 branching becomes important. During the subsequent higher-temperature curing step, cross-linking occurs. Unlike the case of resoles, a curing agent that liberates formaldehyde or a readily condensable aldehyde needs to be added in order to convert the novolac to an infusible material. Paraformaldehyde and hexamethylenetetramine ("hexa") commonly are used for this purpose.

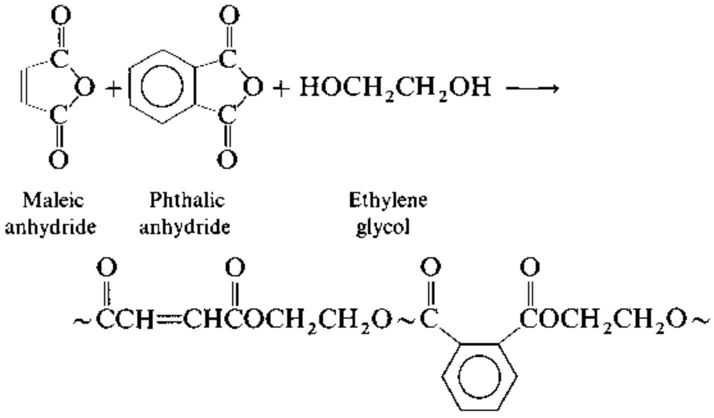
About 50 percent of the U.S. production of phenolic resin is used for the resole binder used in the manufacture of plywood. The laminates are made by heating the wooden panels coated with the resin under pressure. Phenolics also are used for electric coil varnishes, solvent-based adhesives, and molding powders. Wood fiber, mineral filler, and pigments can be added to the resin prior to the final curing and molding step. Parts such as automobile distributor housings and steering wheels, electrical plugs, and switches are produced from molding powders. Other applications include coatings, friction materials for break linings, and binders for abrasives and foundry molds.

Unsaturated Polyester Resins

Unsaturated polyesters are made by condensing polyols with unsaturated dicarboxylic acids or their anhydride derivatives. One or more unsaturated acid components may be used in the synthesis of the resin, but for economic reasons maleic anhydride is used most often. Fumaric acid produces materials with higher impact resistance, but is more expensive. Aliphatic, aromatic, and hydrogenated aromatic dicarboxylic acid or anhydride comonomers also may be added to the synthesis mixture to modify the product's properties. Phthalic acid often is used because it is inexpensive, improves solubility of the resin in styrene, and increases hardness and resistance to water. Isophthalic acid produces a better-performing product than phthalic acid but is more costly. Aliphatic dicarboxylic acids add flexibility but reduce resistance to water.

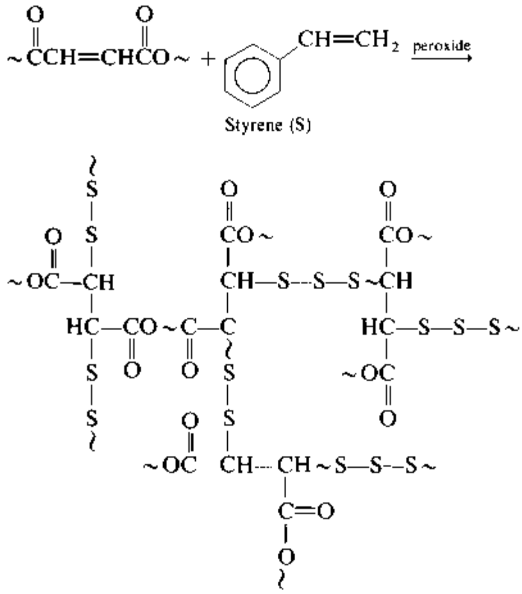
Like the dicarboxylic acid portion, a mixture of glycols may be used in resin synthesis. Commonly used are ethylene glycol, bisphenol A, trimethylolpropane, and the various polyethylene and polypropylene glycols. The selection depends on the properties needed in the intermediate resin and in the cured product.

Polymerization is carried out with the neat reactants at temperatures around 200°C and allowed to proceed until a predetermined viscosity or acid value has been attained.



Styrene-soluble, linear unsaturated polyester

Sixty to eighty percent solutions of the thermoplastic reaction product in monomer solvents such as styrene, vinyl toluene, or methyl methacrylate are packaged and distributed. The resins often are mixed with fillers, initiated with peroxide, and then cured into a hard thermoset material.



Free radical polymerization inhibitors such as hydroquinone usually are added to the resin mixture to prolong storage life. The presence of these inhibitors causes an induction period in the final curing step. The system will gel after about 1 percent cross-linking takes place, and then the rate of curing rapidly increases. Inability to remove the heat generated during this step is a problem in large, thick castings. If the temperature goes too high, the material may become brittle, cracked, and discolored. Up to 20 percent shrinkage can occur during polymerization.

The shrinkage, which causes stress and complicates the casting and lay-up process, can be reduced by using fillers.

The choice of initiator will depend on the fabrication requirements. For low-temperature curing, cobalt–peroxide combinations often are used. The benzoyl peroxide–tertiary amine system is used at low temperatures when oxygen inhibition is a problem. Higher-temperature processes generally rely on the uncatalyzed thermal initiation of initiators such as cumene hydroperoxide or dilauryl peroxide.

Oxygen can severely retard the free radical curing step. This is a major concern in coatings and other applications where the surface-to-volume ratio is high. Cure inhibition produces a tacky surface, or one with low hardness, and chemical and abrasion resistance. In these applications the tertiary amine–benzoyl peroxide accelerator–initiator combination has been found to be useful. Wax also may be added to the formulation. During curing the wax migrates to the surface to form a film that serves as an oxygen barrier. Other ways to minimize oxygen inhibition include thermal post-curing and the use of special resin formulations containing allyl ether or allyl ester functionality. These so-called allyl resins promote post-curing by an autoxidation process.

Flame-resistant products can be made by the inclusion of halogenated glycol or anhydrides in the preparation of the resin. Chlorendic anhydride or tetrabromophthalic anhydride also is used for this purpose. The hydrogen halide that is generated during burning serves as an oxidation inhibitor and promotes charring. The inhibition process is further enhanced by adding antimony oxide or trihalide to the formulation. Because the gases produced by these fire retardants are toxic, a great effort is being made to find nontoxic replacements.

Unsaturated polyesters are fabricated by casting, laminating, pultrusion, and coating. Except for some coating applications, most of these processes incorporate mineral fillers and/or glass fibers to improve strength and lower cost. Treating the glass fiber with an organosilane coupling agent such as 3-methacroylpropyltrimethoxy silane improves adhesion to the polyester and enhances strength and durability even more. Cast products include simulated marble, terrazzo, tile, electrical encapsulants, polymer cements, patching compounds, and bowling balls. Clear unsaturated polyester coatings are used in high-gloss furniture, wood panel, and flooring applications.

Gel coats are a large-volume application for unsaturated polyesters. These are reactive formulations containing pigments, fillers, and thixotropes to prevent sagging of the ungelled coating. The catalyzed resin formulation is sprayed onto a mold and allowed to gel, making an inner layer that forms the surface when the mold is separated. If the mold is glossy smooth, the surface of the coating will be glossy. Several coats may be applied in succession to build the coating thickness and produce special decorative effects. Following application of the surface layer to the mold, the coating is reinforced with a preshaped glass mat using a laminating binder. Alternatively, the reinforcement is applied by spraying a resin formulation containing chopped fibers. The binders used in these applications also might be unsaturated polyester resin formulations. Gel coats are used widely as exterior surfaces for boat hulls, bathroom fixtures, and recreational vehicles.

Filament winding on molds is used to produce large laminated tubes and storage tanks. The continuous glass fiber is guided into a tank filled with resin and then through an orifice to remove excess resin, and finally is wound onto a core. The part is cured in an oven, the core is removed, and additional finishing steps are completed.

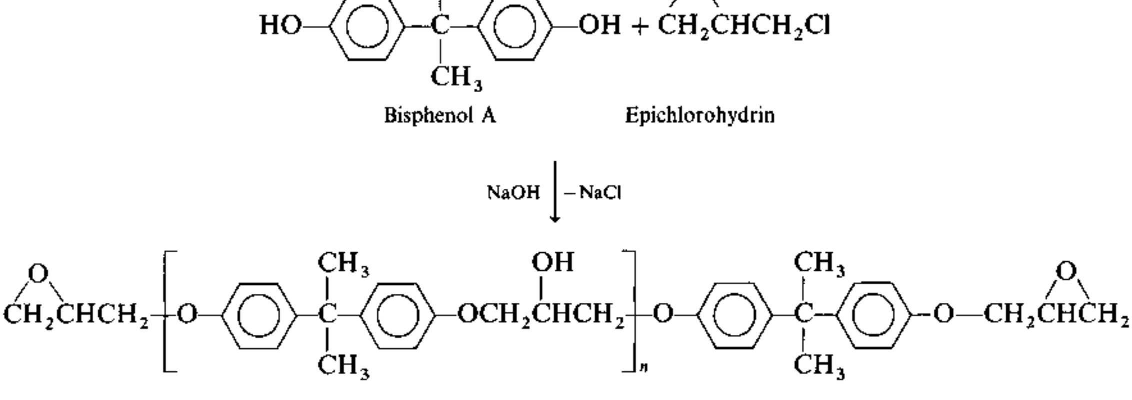
Pultrusion is a related process.[37] A continuous, resin-impregnated mat, or a bundle of reinforcing glass, Kevlar, or carbon fibers, is pulled through a heated die where shaping and curing take place. In addition to simple rods, tubing, and sheet, I-beams and complex profiles can be produced. Applications include ladders, reinforcement members for vehicles and buildings, window casements, and moldings of various kinds. There is further discussion of this process in the section "Fabrication of Plastics" under "Pultrusion."

Large panels are prepared with sheet molding compound (SMC). Typical SMCs contain a polyester resin of high fumaric acid content, calcium carbonate or clay fillers, chopped glass fibers, calcium, magnesium or zinc oxide thickeners, and high-temperature peroxide initiators. Rubbers or thermoplastic resins are used to reduce the amount of shrinkage during curing. SMCs can be compression-molded in minutes at high temperatures and moderate pressures to produce parts with paintable surfaces. Plastic auto and truck body panels are produced this way.[38]

Epoxies

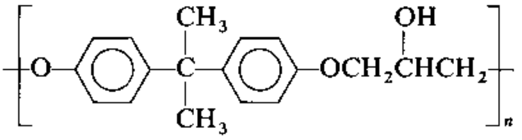
Epoxies are a broad class of reactive monomers and resins containing epoxy (oxirane) functionality. Introduced commercially at the end of World War II, they first were used for coatings, but soon began to be used for adhesives, cast products, and laminating binders. Cured epoxies have good chemical and corrosion resistance, high adhesion to a variety of substrates, and low shrinkage during curing.

The most widely used epoxies are those derived from the condensation of epichlorohydrin with bisphenol A. The degree of oligomerization, can be controlled by varying the epichlorohydrin/bisphenol A ratio. When this ratio is 2:1 or more, the major product is the diglycidyl ether monomer, where *n* is zero in the general formula.



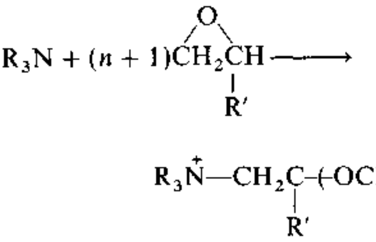
As the molar ratio of epichlorohydrin to bisphenol A declines, *n* and the molecular weight of the resin increase. Commercial liquid resins based on bisphenol A and epichlorohydrin have average molecular weights of under 1000. The solid resins are low-melting solids with average molecular weights below 4000, corresponding to an average *n* of 13. For each epoxy group that reacts, a hydroxyl group is generated. Thus *n* also corresponds to the number of hydroxyl groups in the molecule. When molecular weights are much higher than 4000, the high viscosity, limited solubility, and sluggish reactivity of the resin restricts its use for cross-linking reactions.

When the molar ratio of bisphenol A and epichlorohydrin approaches unity, resins with molecular weights greater than about 30,000 and *n* greater than about 40 are produced. These high molecular weight thermoplastics are called phenoxies:[39]



Because phenoxies are not cross-linked and have few unreacted epoxy groups remaining, they can be considered to be bisphenol A–propylene glycol polyethers. They are thermally stable, ductile polymers that can be processed in conventional molding, extruding, and thermoforming equipment. They are made into thermoplastic adhesives, coatings and sealants, film, and molded articles. The hydroxyl groups in the phenoxies can be esterified and used as reactive sites to prepare cross-linked coatings. The phenoxy esters exhibit excellent properties as paint primers.

With the exception of the phenoxies, most applications for epoxies require the solvent and chemical resistance and heat stability of thermosets. Because unmodified epoxies do not cross-link efficiently at convenient processing temperatures, a curing agent or a hardener is used. Curing agents can be catalytic or coreactive. The most common catalytic agents are Lewis acids such as boron trifluoride or Lewis bases such as tertiary amines. The Lewis acids weaken the carbon–oxygen bond of the epoxy ring by coordinating with the oxygen. This lowers the activation energy for ring opening enough to permit ready cross-linking by hydroxyl groups on other chains. Tertiary amines catalyze ring opening by the following scheme:

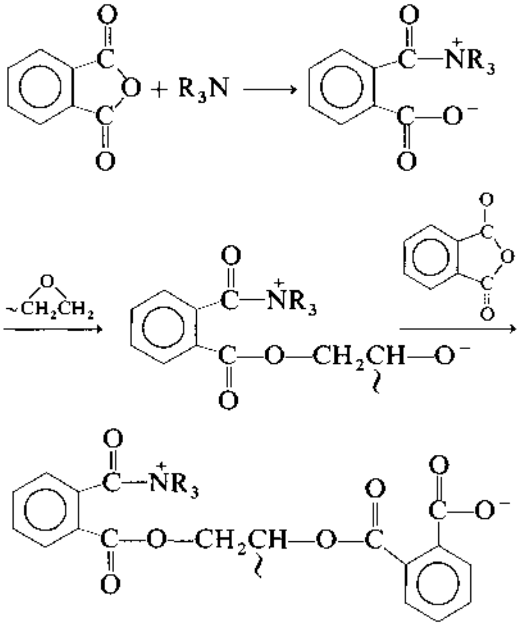


$$R_3\overset{+}{N}—CH_2\underset{R'}{C}\!-\!(OCH_2\underset{R'}{CH})_{n}O^-$$

Multifunctional primary and secondary aliphatic polyamines are used as coreactants. They add readily to the epoxy group at low temperatures to produce highly cross-linked networks. The aromatic amines are somewhat slower than the aliphatic amines, but provide higher heat stability. Examples of amine curatives include diethylenetriamine, triethylenetetramine, *N*-aminoethylpiperazine, and *m*-phenylenediamine.

Amine curing agents require special precautions. Unreacted amine can migrate to the surface of the product, resulting in odors and possible toxic reactions in sensitized people. To minimize these problems, multifunctional oligomeric amines often are used. Because they have higher molecular weight and functionality, they are less volatile and have a higher probability of being incorporated into the cured product than the lower molecular weight amines.

Mono- and dicyclic acid anhydrides also are widely used as curing agents. Examples include the solids phthalic anhydride and pyromellitic anhydride, and liquid anhydrides such as dodecenylsuccinic anhydride. The reaction rate between an epoxy resin and an anhydride is low, but it can be significantly improved by the addition of a catalytic amount of tertiary amine. Anhydride-promoted curing involves both anhydride and epoxy ring opening steps. The amine preferentially opens the anhydride to form the carboxylate group, which, in turn, reacts with the epoxide group.



One advantage of epoxy thermosets is that the amount of shrinkage that takes place during curing is low compared to that for vinyl addition and condensation polymerization. Low shrinkage means that the polymer has a lower degree of internal strain and retains better contact with a substrate to which it is bonded. Thus, epoxy coatings, adhesives, and encapsulants are noted for good adhesion.

Cured epoxy resins are rigid and brittle. Their impact resistance is improved by using oligomeric amine and polyol coreactants.

Because the equivalent weight per active amine is high in these products, there are fewer cross-link sites per unit. T_g is reduced along with hardness and modulus. Mineral fillers such as mica, quartz, glass, silica, marble powder, and alumina reduce shrinkage, lower thermal expansion, and reduce cost.

Coatings and laminating binders are among the largest uses for epoxies. In electronics they are used for potting and encapsulating and for impregnating cloth and fibrous mats for circuit boards. They also are used to bond carbon filament, high-strength fibers, and other components into aircraft and missile body components, chemical holding tanks, oil pipes, fishing poles, golf club handles, and other products where strength, water resistance, and resiliency are needed.

Silicone Resins

The basic chemical technology of silicones and silicone elastomers is covered in Chapter 18; so the discussion here is limited to silicone resins. These materials have many applications, including use in paints and varnishes, molding compounds, encapsulants, electrical insulation, pressure-sensitive adhesives, laminates, and release coatings. Their heat stability, water repellency, and resistance to solvents and weathering favor their use in these applications.

The production of these resins starts with a mixture that might include di-, tri- and tetrafunctional silanes, such as monomethyl-, dimethyl-, monophenyl-, diphenyl-, monovinyl-, and methylvinylchlorosilane, along with silicon tetrachloride. The tri- and tetrafunctional ingredients are cross-linkers. The resin properties will depend on the chlorosilane mixture, the degree of cure, and processing conditions.

The chlorosilane blend is mixed with inert solvents such as mineral spirits, toluene, or chlorinated hydrocarbons, or esters such as butyl acetate, and then hydrolyzed. Because the hydrolysis reaction can be complicated by the formation of insoluble gels, special care must be taken with respect to the choice and concentration of solvent, temperature, agitation level, sequential addition of the chlorosilanes, water concentration, and use of low molecular weight alcohol modifiers. These variables also affect the molecular structure of the hydrolysate and finished resin properties. The aqueous HCl solution formed by the hydrolysis is separated from the solvent phase, which contains the hydrolysate. The hydrolysate solution then is heated in the presence of catalysts such as metal soaps or acid-treated clays to promote partial condensation or "bodying." Some of the solvent may be stripped off during this step to achieve higher temperatures for more rapid condensation or to promote intermolecular silanol reactions. As the condensation reaction proceeds, the rate drops because of reduced silanol concentration, increased steric hindrance, and reduced molecular mobility. Curing generally is incomplete at the end of the bodying step. The resin then is filtered, curing catalyst is added along with solvent as needed to achieve the desired solids level, and the resulting solution is packaged.[46]

POLYMER SYNTHESIS

Unlike the properties of low molecular weight monomeric substances, the chemical and physical characteristics of high molecular weight polymers are strongly dependent on methods of synthesis. The chain-forming mechanism, polymerization conditions, and type of catalyst or initiator can significantly affect molecular weight, polydispersity, branching, stereochemistry, and end groups in the product. Condensation polymerization and addition polymerization are two major ways that monomers join to form polymers. New polymers also can be made by modifying existing ones.

Condensation polymerization occurs when monomers combine by displacing a small by-product molecule (D) for every new unit added to the growing oligomer:

$$nA + n\mathrm{B} \rightarrow \text{Polymer} + n\mathrm{D}$$

Water often is the by-product of condensation, but other condensation by-products can include methanol, phenol, and hydrogen chloride, depending on the polymerization reaction. In order for condensation polymerization to occur, the polymerizing molecules must have a functionality of two or more. When the monomers are difunctional, a linear polymer will be formed. If the monomers have a functionality of more than two, cross-linking is possible. Compared to addition polymers, the volume of condensation polymers sold is small. However, they constitute a diverse and important class of materials, which includes polyesters, polycarbonates, polyimides, polysulfides, polysulfones, the phenol-formalde-hyde and melamine resins, and a large percentage of the polyamides and polyurethanes. Examples of most of these materials were discussed in the preceding section.

A characteristic of addition polymerization is that monomers link together by forming new bonds without splitting off by-products. The repeating units have the same atoms as the monomers from which they were derived:

$$M + n\,M \rightarrow (M)_{n+1}$$

Both addition and condensation polymerization can take place by chain-growth and step-growth mechanisms. In chain-growth polymerization, chain extension can occur only after an initiation step has taken place. Only the initiating species and the propagating intermediate are capable of reacting with the monomer. One consequence of this is that high molecular weight species are generated early in the reaction, and the monomer still is present until very high conversions to the polymer have occurred.

Chain growth can be initiated by free radicals, acids and bases, and coordination compounds. Because the number of propagating species is never more than the number of initiating species, the average molecular weight of the product will depend in part on the concentration of the initiator. The higher the concentration of the initiating species, the higher the concentration of propagating intermediates, and the smaller the number of monomer units per growing intermediate.

Molecular weight also is determined by the frequency of terminating reactions. In free radical polymerization, the larger the number of initiating and propagating species present at any time, the greater the probability that coupling type terminations will occur. Thus, in polymerization where high molecular weight polymer is needed, small concentrations of initiator are used.

In step-growth polymerization an initiating species is not needed for chain extension, though catalysts may be effective. Monomers and intermediate oligomers have about the same reactivity because they share the same reactive end groups. Monomers react with other monomers and with oligomeric intermediates at nearly the same rate, so monomer concentration declines rapidly. Oligomeric intermediates, in turn, react along themselves and remaining monomer to give higher and higher molecular weight intermediates. However, unlike the case of chain polymerization, very high molecular weight polymer does not form until very late in the reaction.

In step-growth polymerization, the average degree of polymerization (DP), or number of monomer units per molecule, is given by the relationship $DP = 1/(1 - P)$, where P is the fraction of end groups consumed. The following table shows that when half the monomer molecules have reacted, the degree of polymerization is only 2, and it is only 20 when 95 percent have reacted. If a step-growth polymer requires a DP of 100 to have useful properties, 99 percent conversion of end groups is required.

P	DP
0.5	2.0
0.7	3.3
0.9	10
0.95	20
0.99	100
0.999	1000
1.0	∞

Monomer conversions of 99 percent or more often are required for good properties in step-growth polymers; so equilibrium processes must be driven to completion, and polymerization should be nearly free of competing side reactions. If these conditions are met, polymers with good properties can be made, and molecular weight control can be achieved by adjusting the ratio of the reactants.

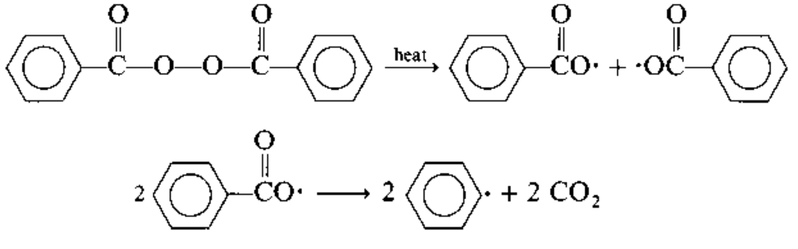
Many addition polymerizations are chain-growth processes involving the carbon–carbon double bond, and most condensation reactions are step-growth processes. However, there are notable exceptions. For example, polyurethanes are made by the step-growth addition of glycols and diamines to the carbon–nitrogen double bond of diisocyanates.

Free Radical Addition Polymerization

Free radical chain-growth addition polymerization of vinyl monomers is an important route to commercial polymers. The chain-growth mechanism involves three steps: initiation of a chain, propagation of the growing chain, and termination of the reactive intermediates.

Initiating free radicals can be generated by high-energy particles, oxygen, redox reactions, and thermal- or radiation-induced dissociation of initiators. Thus their sources include UV, electron beam, and autoxidative curing of coatings and adhesives; redox initiation in emulsion polymerization; and thermal decomposition of peroxides and azo compounds in solution, suspension, and bulk manufacturing processes.

Benzoyl peroxide is a frequently used thermal initiator, both for the manufacture of low density polyethylene resin and for unsaturated polyesters. At moderate temperatures benzoyl peroxide disassociates into a pair of benzoyl radicals that, in turn, further decompose into phenyl radicals $(I\cdot)$ and carbon dioxide.



These radicals add, in turn, to the double bond of an ethylene molecule to produce a carbon-centered monomer radical. The double bond becomes a single bond (saturated) and a new radical species is formed.

$$I\cdot + CH_2{=}CH_2 \rightarrow I{-}CH_2CH_2\cdot$$

Dissociation and subsequent addition of the initiator fragment to a monomer are together called the initiation step.

The new carbon radical formed during initiation quickly adds to another ethylene molecule. Then, in rapid succession, the chain propagates from the reactive chain end, adding thousands of units in a fraction of a second until all the monomer is consumed, or, what is more likely, a termination or chain transfer reaction intervenes.

$$I{-}CH_2CH_2\cdot + n\,CH_2{=}CH_2 \rightarrow I{-}CH_2CH_2(CH_2CH_2)_n\cdot$$

Termination can take place by coupling and by disproportionation reactions. Coupling occurs when two free radical centers bond to each other:

$$-CH_2CH_2\cdot + \cdot CH_2CH_2- \rightarrow -CH_2CH_2CH_2CH_2-$$

$$-CH_2CH_2\cdot + I\cdot \rightarrow -CH_2CH_2{-}I$$

Disproportionation can occur if a radical center of one intermediate abstracts a hydrogen atom from a carbon next to the radical center of another propagating intermediate. A double bond and a saturated carbon are produced at the expense of two reactive intermediates:

$$-CH_2CH_2\cdot + \cdot CH_2CH_2- \rightarrow -CH_2CH_3 + -CH{=}CH_2$$

Another way that a chain can stop growing is by chain transfer. During chain transfer, polymerization continues because a new propagating radical is generated. Chain transfer occurs when a propagating free radical abstracts a hydrogen, or some other atom, from a donor. The donor can be a monomer, polymer, initiator, solvent, or another propagating intermediate.

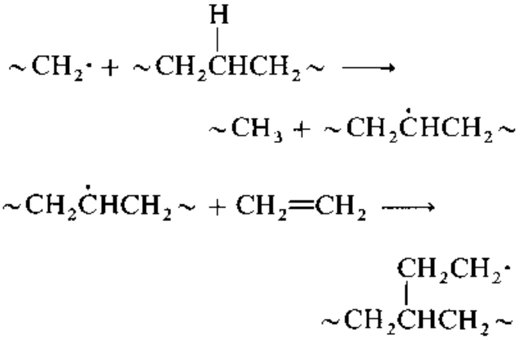
$$—CH_2CH_2\cdot + R—H \rightarrow —CH_2CH_3 + R\cdot$$

$$R\cdot + CH_2{=}CH_2 \rightarrow R—CH_2—CH_2\cdot$$

Chain transfers generally result in branching because hydrogens along a chain's backbone are more likely to be abstracted than hydrogens on a terminal carbon. There are two reasons for this. There are often more internal hydrogens than terminal hydrogens, so the probability of encountering an internal hydrogen is greater. Also, internal hydrogens usually are more weakly bonded than terminal hydrogens. The order of decreasing carbon- hydrogen bond strength is primary > secondary > tertiary > benzyl. Thus, the secondary hydrogens along the backbone of polyethylene are more readily abstracted than the terminal methyl hydrogens.

The highly branched structure of LDPE is a result of both intermolecular and intramolecular chain transfer reactions. Intramolecular chain transfer, called backbiting, takes place when the reactive center bends around and encounters one of its own backbone hydrogens. This often occurs at the fifth and sixth positions from the radical center.

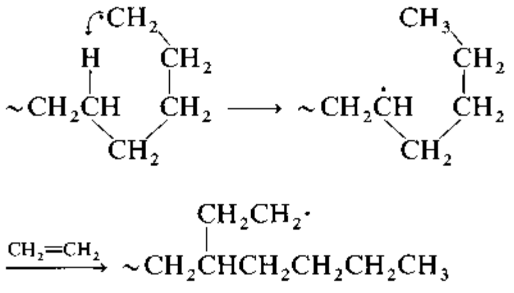
Intermolecular chain transfer



$$\sim CH_2\cdot + \sim CH_2\overset{\displaystyle H}{\overset{|}{C}}HCH_2\sim \longrightarrow \sim CH_3 + \sim CH_2\dot{C}HCH_2\sim$$

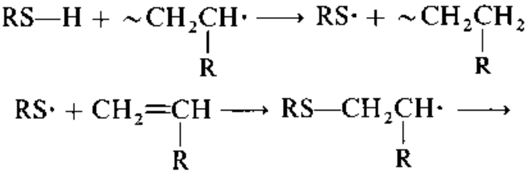
$$\sim CH_2\dot{C}HCH_2\sim + CH_2{=}CH_2 \longrightarrow \sim CH_2\overset{\displaystyle CH_2CH_2\cdot}{\overset{|}{C}}HCH_2\sim$$

Intramolecular chain transfer



$$\xrightarrow{CH_2=CH_2} \sim CH_2\overset{\displaystyle CH_2CH_2\cdot}{\overset{|}{C}}HCH_2CH_2CH_2CH_3$$

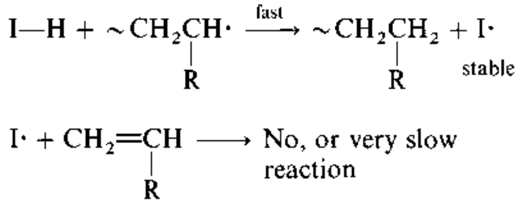
When chain transfer occurs, the degree of polymerization decreases. In some polymerization processes, substances called chain transfer agents are added to modify the molecular weight and structure of a polymer. When used in large concentrations, they produce low molecular weight polymers called telomers. Thiols are effective chain transfer agents because the hydrogen of the sulfur–hydrogen bond is easily abstracted by a carbon-centered free radical, and the resulting thiol radical readily adds to a carbon–carbon double bond to start a new chain.



$$RS—H + \sim CH_2\underset{\displaystyle R}{\underset{|}{C}}H\cdot \longrightarrow RS\cdot + \sim CH_2\underset{\displaystyle R}{\underset{|}{C}}H_2$$

$$RS\cdot + CH_2{=}\underset{\displaystyle R}{\underset{|}{C}}H \longrightarrow RS—CH_2\underset{\displaystyle R}{\underset{|}{C}}H\cdot \longrightarrow$$

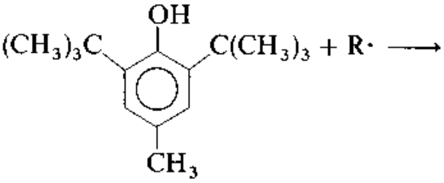
If a hydrogen is easily abstracted from a bond, but, for electronic or steric reasons, the newly generated free radical does not readily add to a monomer to continue the polymerization process, polymerization is inhibited. Substances that form very stable free radicals, such as hindered phenols and amines, fall into this class. Thus, the difference between a chain transfer agent and an inhibitor (I—H) in some instances is a matter of degree.



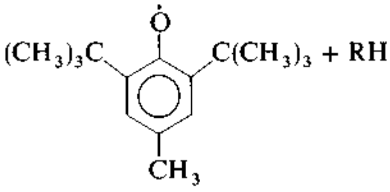
$$I—H + \sim CH_2\underset{\displaystyle R}{\underset{|}{C}}H\cdot \xrightarrow{\text{fast}} \sim CH_2\underset{\displaystyle R}{\underset{|}{C}}H_2 + \underset{\text{stable}}{I\cdot}$$

$$I\cdot + CH_2{=}\underset{\displaystyle R}{\underset{|}{C}}H \longrightarrow \text{No, or very slow reaction}$$

Inhibitors often are added to monomers to increase storage life and stabilize the resin during processing or the polymer during normal use. Some do this by scavenging initiating radicals and others by decomposing adventitious peroxides. Commercial hindered phenol and amine antioxidants couple with free radicals generated by autoxidative or thermal decomposition during polymer processing or product aging.



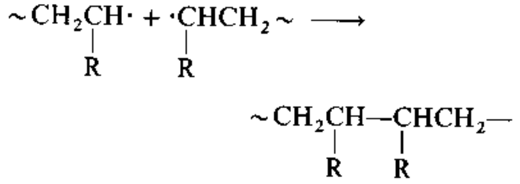
Di-*tert*-Butyl-*p*-cresol



Unreactive

Atmospheric oxygen, which can form peroxide and hydroperoxide initiators, also can serve as a potent polymerization inhibitor; so it is rigorously excluded from most free radical polymerizations. The rate of coupling between molecular oxygen and a free radical intermediate during polymerization is several orders of magnitude greater than the rate of propagation of the new oxygenated intermediate. Thus oxygen reduces the polymerization rate, lowers average molecular weight, and incorporates undesirable peroxide links in the product.

When an unsymmetrical monomer such as styrene or vinyl chloride is polymerized, two propagating species are possible. A combination of steric and electronic factors will favor one of the two possibilities and will determine the stereochemical course of the reaction (see above, section on "Polymer Structure and Nomenclature"). This results in "head-to-tail" linking. In coupling-termination reactions, however, head-to-head linking occurs.



$$\sim CH_2\underset{R}{\underset{|}{C}}H\cdot + \cdot\underset{R}{\underset{|}{C}}HCH_2\sim \longrightarrow \sim CH_2\underset{R}{\underset{|}{C}}H-\underset{R}{\underset{|}{C}}HCH_2-$$

Copolymerization is similar to homopolymerization, but the reactivity of the different monomers toward copolymerization and competing homopolymerization may differ considerably. For a system with two different monomers the following reactions are possible:

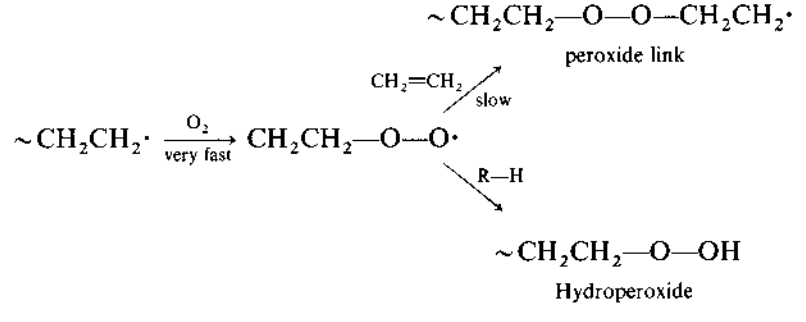
$$M_1\cdot + M_1 \xrightarrow{k_{11}} M_1-M_1\cdot$$

$$M_1\cdot + M_2 \xrightarrow{k_{12}} M_1-M_2\cdot$$

$$M_2\cdot + M_2 \xrightarrow{k_{22}} M_2-M_2\cdot$$

$$M_2\cdot + M_1 \xrightarrow{k_{21}} M_2-M_1\cdot$$

The first and third reactions are homopolymerizations, whereas the second and fourth are copolymerizations. The rates of these competing processes are given by the rate constants, k. A term called the reactivity ratio, r, where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, is a measure of the relative tendency of



the monomers to homopolymerize or copolymerize. If $r_1 > 1$, then M_1 tends to homopolymerize; whereas if $r_1 < 1$, copolymerization is preferred. If r_1 and r_2 are both equal to 1, there is no preference, and the resulting polymer will have a random distribution of monomer units. When r_1 and r_2 are both near zero, as is the case with maleic anhydride and styrene, an alternating copolymer is formed. There is a tendency toward alternation when the product of $r_1 r_2$ approaches 0, and a tendency to produce random copolymers when $r_1 r_2$ approaches one. When r_1 is much greater than one and r_2 is much less than one, as with styrene and vinyl acetate ($r_1 = 55$ and $r_2 = 0.01$), a nearly pure homopolymer of M_1 is produced. Table 19.4 is a partial list of reactivity ratios.[40] Reactivity ratios depend on the reaction temperature and on the reaction type; and they will also be different for free radical, anionic, and cationic copolymerizations.

Usually reactivity ratios fall between 0 and 1, so there is some tendency to alternate. Because the monomers in a copolymerizing batch reaction are seldom consumed at the same rate, the monomer composition of the reacting mixture will change rapidly. Thus, it is often necessary to adjust for compositional drift by adding monomers continuously to the reaction mixture.

TABLE 19.4 Some Free Radical Copolymerization Reactivity Ratios

	r_1	r_2
Ethylene		
1-Butene	3.60	0.16
Butyl acrylate	0.01	13.94
Propylene	3.20	0.62
Vinyl chloride	0.21	0.01
Methyl methacrylate		
Acrylamide	3.00	0.90
Isoprene	0.26	0.65
Maleic anhydride	5.20	0.02
Styrene	0.48	0.58
Vinyl acetate		
Methyl acrylate	0.03	6.38
Acrylonitrile	0.06	5.51
Ethylene	1.03	0.88
Vinyl chloride	0.25	1.64
Vinyl chloride		
Methyl acrylate	0.00	5.00
Isobutylene	2.12	0.27
Styrene	0.16	23.92
Vinylidene chloride	0.20	1.80

The relationship of the molar ratio of monomers in a copolymer, n, and in the monomer mixture from which the copolymer is formed at any instant, x, is given by:

$$n = [r_1 x + 1]/[(r_2/x) + 1]$$

Depending on the values of r_1 and r_2, there is a monomer composition that will yield a copolymer of the same composition. This composition, known as the azeotrope, can be derived from the above equation where $n = x$:

$$n_{az} = [M_1/M_2]_{az} = (1 - r_2)/(1 - r_1)$$

In principle, a pair of monomers at the azeotropic composition will produce a copolymer of the same composition throughout the batch reaction.

Copolymerization is an important way to produce properties that are not possible with homopolymers. For example, the homopolymer of vinylidene chloride is highly crystalline, and though it has excellent moisture and oxygen barrier properties, it does not produces very strong film or fiber. Copolymerization with 15 percent vinyl chloride disrupts the regular structure of the homopolymer to produce a stronger, clearer, more flexible material. The copolymer retains much of the barrier properties of the homopolymer and finds wide use for food packaging and filament. Other commercial copolymers include styrene–acrylonitrile, discussed above; vinylidene fluoride–hexafluoropropylene, a heat- and oil-resistant elastomer; styrene–butadiene rubber; ethylene–vinyl acetate hot melt adhesive; and 2-ethylhexyl acrylate–vinyl acetate–acrylic acid pressure-sensitive adhesives.

Ionic Chain Addition Polymerization

Some monomers can polymerize by ionic processes. Table 19.5 lists types of chain extension that some monomers undergo to produce homopolymer. Ionic polymerizations

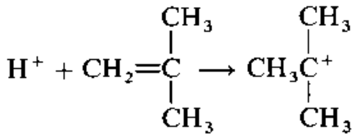
TABLE 19.5 Type of Initiation Suitable for a Select Group of Monomers toward Homopolymerization

Monomer	*Anionic*	*Cationic*	*Free Radical*	*Transition Metal Catalysis*
Acrylamide	Yes	No	Yes	No
Acrylic esters	Yes	No	Yes	No
Acrylonitrile	Yes	No	Yes	No
Butadiene	Yes	Yes	Yes	Yes
Caprolactam	Yes	Yes	No	No
Diallyl phthalate	No	No	Yes	—
Epoxies	Yes	Yes	No	No
Ethylene	No	No	Yes	Yes
Formaldehyde	Yes	Yes	No	No
Isobutene	No	Yes	Yes	Yes
Styrene	Yes	Yes	Yes	Yes
Tetrahydrofuran	No	Yes	No	No
Vinyl chloride	No	No	Yes	No
Vinyl esters	No	No	Yes	—
Vinyl ethers	No	Yes	No	—
Vinylidene chloride	No	No	Yes	—
Vinylidene fluoride	No	No	Yes	—

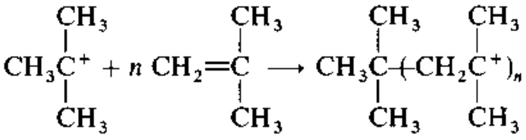
of vinyl monomers are similar in some respects to free radical chain polymerizations. One difference is that counterions are present during ionic polymerization. Depending on whether the counterion is weakly or strongly associated with the growing chain, it can markedly influence the rate of polymerization and the stereochemical result. Another difference is that the polarity of the solvent plays a larger role in ionic additions than it does in nonionic processes.

Cationic Polymerization. In cationic chain polymerization, the propagating center is positively charged. Protonic acids such as HCl and H_2SO_4 or Lewis acids such as BF_3, $TiCl_4$, I_2, and $AlCl_3$ have been used. Lewis acid catalysts usually require trace amounts of a cocatalyst such as water to be effective. Cationic polymerization also can be initiated photochemically by using onium salt photoinitiators. These substances generate protons during irradiation with UV light and are used in coating and adhesive applications.

When initiation takes place with an unsymmetrical monomer such as 2-methylpropene, addition occurs to the double bond to give the more thermodynamically stable carbonium ion. Propagation continues in like manner, always producing the more stable intermediate. As in free radical polymerization, this results in head-to-tail type chain growth.



$$\mathrm{H^+ + CH_2{=}\underset{CH_3}{\overset{CH_3}{C}} \longrightarrow CH_3\underset{CH_3}{\overset{CH_3}{C^+}}}$$



$$\mathrm{CH_3\underset{CH_3}{\overset{CH_3}{C^+}} + \mathit{n}\, CH_2{=}\underset{CH_3}{\overset{CH_3}{C}} \longrightarrow CH_3\underset{CH_3}{\overset{CH_3}{C}}\!\!\left(CH_2\underset{CH_3}{\overset{CH_3}{C^+}}\right)_{\!n}}$$

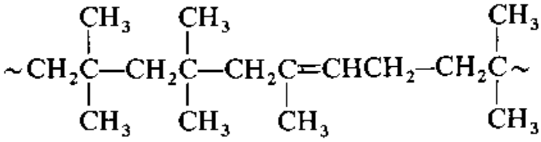
Reaction rates are determined by both electronic and steric factors; but unlike the case of free radical polymerization, rates are strongly dependent on the dielectric characteristics of the solvent and basicity of the counterion. Rates of addition to simple monomers are usually in the order of increasing stability of the carbonium ion intermediate. Methyl groups or substituents that can delocalize a positive charge undergo polymerization more rapidly; thus the following order of decreasing rates of vinyl polymerization is expected:

$$CH_2{=}CHOR > CH_2{=}CHPh > CH_2{=}C(CH_3)_2 > CH_2{=}CHCH_3 > CH_2{=}CH_2$$

Like free radical polymerization, cationic polymerizations undergo chain transfer and termination reactions. Chain transfers can take place by proton transfer to monomer, by hydride transfer from a chain, and by a variety of alkylations and cyclizations. Termination by coupling two cationic centers is not possible, but termination can occur when propagating centers react with water or other basic contaminants to give stable products.

Some rubbers, acetal resins, and a variety of polyethers are prepared on a commercial scale by cationic polymerization. Vinyl ethers are among the easiest monomers to polymerize by the cationic process. The carbonium ion is readily formed because the pendant oxygen participates in delocalization of the positive charge. When polymerization of isobutyl vinyl ether is carried out at temperatures in the range of −80°C using boron trifluoride etherate as initiator, isotactic crystalline polymer can be produced. Ethyl and isobutyl ethers produce polyvinyl ethers with low T_g's, and are used in pressure-sensitive adhesives.

Butyl rubber is made by low-temperature cationic copolymerization of isobutylene with 1 to 10 percent isoprene. The double bonds left in the polymer are cross-linking sites for subsequent vulcanization.



$$\sim CH_2\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}{-}CH_2\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}{-}CH_2\underset{\underset{\large CH_3}{|}}{C}{=}CHCH_2{-}CH_2\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}\sim$$

Because of its low permeability to gases, butyl rubber is used for inner tubes, gaskets, tubing, and sealants.

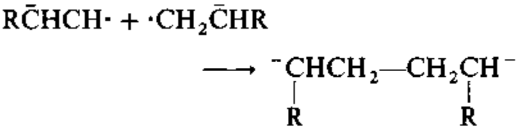
Other cationic processes include ring opening polymerization of epoxies, discussed below, and acid-catalyzed polymerization of aldehydes, discussed above.

Anionic Polymerization. Some monomers undergo chain extension when initiated by bases. As in cationic processes, both vinyl addition and ring opening chain extension can occur. The propagating species in these reactions are negatively charged. Monomer substituents attached to the carbon–carbon double bond that stabilize a negative charge, such as cyano, nitro, chloro, phenyl, and carbonyl groups, readily undergo anionic polymerization. Examples include acrylonitrile, methyl methacrylate, styrene, and butadiene, in order of decreasing reactivity. Rates are dependent on the basicity of the initiator, the ability of the solvent to solvate the reactants, and the counterion.

Alkali metals initiate anionic polymerization indirectly by an electron transfer process:

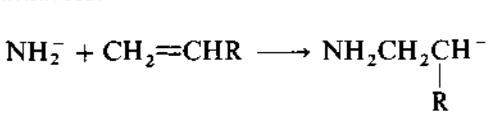
$$Na\cdot + CH_2{=}CHR \longrightarrow Na^+ + \cdot CH_2\bar{C}HR$$

The anion radical generated in the transfer step rapidly dimerizes to produce a dianion that serves as a difunctional initiator:



$$R\bar{C}HCH\cdot + \cdot CH_2\bar{C}HR \longrightarrow {}^-\underset{\underset{\large R}{|}}{C}HCH_2{-}CH_2\underset{\underset{\large R}{|}}{C}H^-$$

Strong bases such as imide, alkoxide, cyanide, and alkylate ions (e.g., butyl lithium) that add directly to the monomer's double bond constitute a second class of anionic initiators:



$$NH_2^- + CH_2{=}CHR \longrightarrow NH_2CH_2\underset{\underset{\large R}{|}}{C}H^-$$

For polymerization by amide ion, NH_2^-, the following order of rates of polymerization occurs:[41]

$$CH_2{=}CHCN > CH_2{=}CCO_2CH_3 > CH_2{=}CHC_6H_5 > CH_2{=}CHCH{=}CH_2$$

Like other chain-addition processes, anionic chain polymerization is complicated by competing chain transfer and termination steps. However, there are conditions where terminations are unfavorable. If there is rigorous exclusion of oxygen, water, carbon dioxide, and other substances that can quench the reactive intermediate, a "living polymer" is possible. When this occurs, all of the monomer has been consumed, and only the potentially reactive macroanions remain. If additional monomer is added at this point, propagation will resume.

The production of block copolymers involves synthesis of a living homopolymer, followed by addition of a second monomer. When the second addition is complete, a living diblock macroanion is formed. A third monomer can be added to the sequence, giving a triblock macroanion.

$$I^- + xM \longrightarrow \underset{\text{Homo-macro anion}}{I\text{-}(M)_x^-} \xrightarrow{yA} \underset{\text{Diblock macro anion}}{I\text{-}(M)_x(A)_y^-}$$

$$\xrightarrow{zN} \underset{\text{Triblock macro anion}}{I\text{-}(M)_x(A)_y(N)_z^-} \xrightarrow{H^+}$$

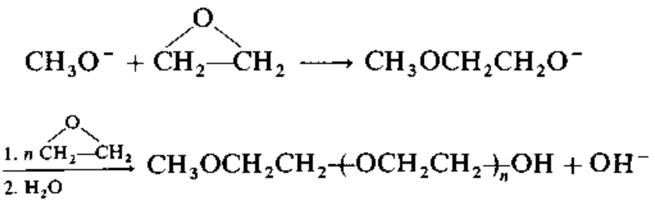
$$\underset{\text{Triblock copolymer}}{I\text{-}(M)_x(A)_y(N)_z H}$$

To generate the unreactive polymer, the macroanion intermediates can be quenched with a proton donor. Styrene–butadiene–styrene and other triblock copolymers are commercially available.

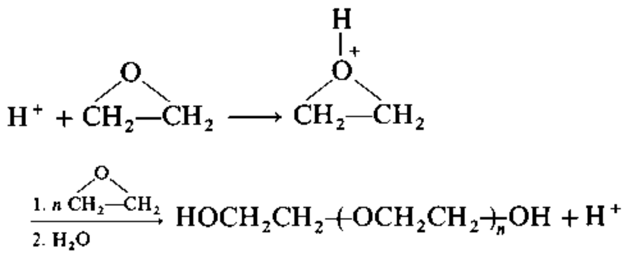
Ring Opening Addition Polymerization

Ring opening polymerizations also can occur by chain-growth and step-growth processes. Depending on the specific monomer, ring opening additions can be initiated by acids, bases, coordination catalysts, and free radicals. Because cyclic monomers can be highly strained, the driving force for the reaction is attainment of the more thermodynamically stable open-chain product. In addition to the epoxies already discussed above, other monomer classes that undergo ring opening addition polymerization include: tetrahydrofurans, trioxanes, episulfides, alkyleneimines, lactones, lactams, and cyclic siloxanes.

Commercial polyethers are made from ethylene oxide and propylene oxide by high-pressure, acid- or base-catalyzed processes. Initiation by base occurs by ring opening addition to the epoxy group and subsequent attack by the alkoxide ion generated on another monomer molecule. If sodium hydroxide is the initiator, the product is a diol. If an alkoxide is the initiator, one of the chain ends is an ether group, and the other is a hydroxyl group.

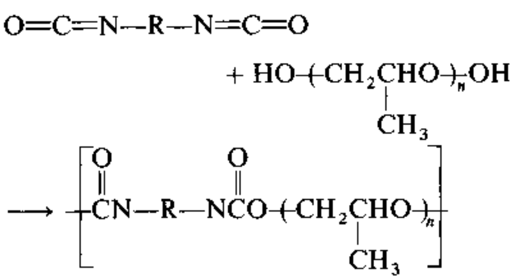


When a Bronsted acid initiator such as sulfuric acid is used, a low molecular weight polyethylene oxide diol is produced. Protonation of the cyclic ether oxygen is followed by ring opening displacement on the monomer.



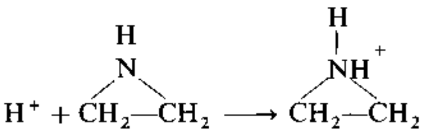
The lower molecular weight polyethylene oxides are viscous, water-soluble liquids or waxy solids used as surfactants, lubricants, humectants, and cosmetic and pharmaceutical formula bases. Metal oxides and organometallic initiators, such as aluminum and zinc alkyls, produce higher molecular weight polyethylene oxides. The resins are low-melting, easy-to-process solids that are soluble in a broad range of solvents. They find use as thickeners, water-soluble packaging, and latex stabilizers.

Propylene oxide undergoes similar ring-opening polymerization. The products are less soluble in water than the corresponding polyethylene oxides. They serve as toughening soft segments in polyurethanes when they are polymerized with oligomeric diisocyanates.

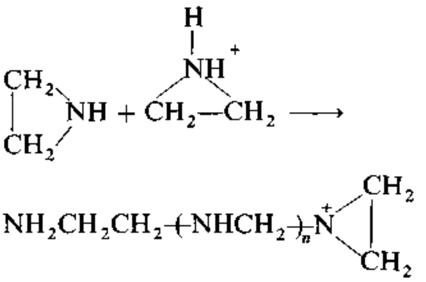


$$O{=}C{=}N{-}R{-}N{=}C{=}O + HO{+}CH_2\underset{CH_3}{\underset{|}{C}}HO{+_n}OH \longrightarrow \left[{+}\overset{O}{\overset{\|}{C}}N{-}R{-}N\overset{O}{\overset{\|}{C}}O{+}CH_2\underset{CH_3}{\underset{|}{C}}HO{+_n}{+}\right]$$

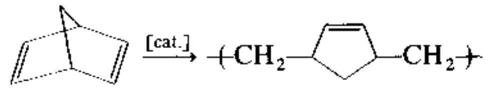
Alkylenimines take part in acid-catalyzed ring opening polymerization, like the epoxies. Coordination of a proton or Lewis acid with the ring nitrogen weakens the already strained carbon–nitrogen bond. Propagation occurs when the nucleophilic nitrogen of a monomer collides with a coordinated monomer to open up the ring.



Ethylenimene



A type of ring opening addition polymerization using transition metal catalysts not unlike Ziegler-Natta catalysts is called metathesis polymerization.[42] Metathesis polymers, first made in the 1960s, are called polyalkenamers. Polymers made from cyclooctadiene and norbornadiene have applications as specialty elastomers. The polymerization of norbornadiene can be summarized as follows:

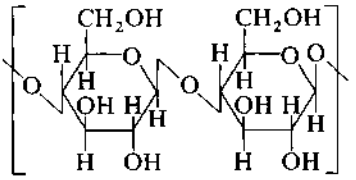


Norbornadiene

Polymer Modification

In principle, polymers can undergo the same reactions that simpler molecules undergo. Much use has been made of this capability to produce polymers that cannot be made directly from monomers. Substitutions and hydrolysis of pendant groups produce new functional groups, and controlled degradation reduces molecular weight. In addition, physical processes that change molecular orientation and morphology also can be thought of as polymer modifications. Some examples were provided in discussions about grafting, cross-linking, and film orientation; others are given here.

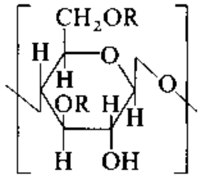
The conversion of cellulose into useful products is an illustration of how degradation, functionalization, and molecular orientation of a polymer can be applied to commercial advantage. Cellulose is the most common naturally occurring organic polymer. Over a trillion pounds of it are converted annually into paper and other cellulose-based products.



Cellulose

Although it is linear, and nominally thermoplastic, cellulose is not readily soluble and will not flow below its decomposition temperature.

The strong intermolecular hydrogen bonding in the polymer can be reduced by replacing one or more of the hydroxyl groups in the repeating unit by ester, ether, nitro, or xanthate groups.



where R =	
$-NO_2$	Nitrate
$=-\overset{\overset{O}{\|}}{C}CH_3$	Acetate
$=-CH_3$	Methyl ether
$=-\overset{\overset{S}{\|}}{C}-S^-Na^+$	Xanthate, sodium salt

The degree of substitution can vary from 0 to 3.

Several important products are made from cellulose this way. The insoluble polymer is dissolved by partially degrading it in alkali solution. In the viscose process, carbon disulfide is added to the basic aqueous mixture to convert some of the hydroxyl groups to xanthate groups. The solution produced this way is allowed to age until it thickens, and it then is extruded as filament into a bath that regenerates the free hydroxyl functionality. During processing the filament is stretched to orient the polymer and improve its strength. The yarn, called rayon, is used for textiles and tire cord. Cellophane is made when the viscose is cast onto a roll or extruded through a narrow slit into an acid bath, and then plasticized with glycerine.

The partially esterified acetate, propionate, and butyrate esters of cellulose also have proved to be useful. They can be made with a wide range of properties because of the latitude provided by varying molecular weight, ester content, and amount and type of plasticizer. The cellulose esters have been made into fiber, thickeners for coatings, and molded articles such as toys, combs, eyeglass frames, and cutlery handles. They have been extruded into pipe, formed into sheet, and used for a variety of decorative and protective laminates.

The methyl and ethyl ethers of cellulose have properties that are similar to those of the ester derivatives, and they have been used for related applications. Ethyl cellulose is injected-molded into parts with good low-temperature toughness and used as an additive in coatings and adhesives to improve flexibility. The methyl derivative is used as a thickener and emulsifier for paints, adhesives, food, and pharmaceutical products.

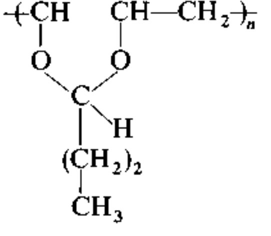
The conversion of polyvinyl acetate into a family of polyvinyl alcohol (PVOH) resins is an important modification of a synthetic polymer. PVOH cannot be made directly from vinyl alcohol because the stable form of vinyl alcohol is its tautomer, acetaldehyde:

$$CH_2{=}CHOH \rightarrow CH_3CH{=}O$$

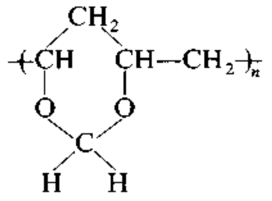
Thus, polyvinyl alcohol is made by basic hydrolysis of polyvinyl acetate.

The solubility of PVOH in water depends in a unique way on its degree of hydrolysis. Maximum solubility occurs at around 88 percent hydrolysis. At higher levels, the amount of intermolecular hydrogen bonding becomes high enough to reduce solubility. PVOH has a good combination of tensile strength and solvent resistance and has been spun into fibers, made into film, and used for coatings and adhesives.

Reaction of PVOH with butyraldehyde or formaldehyde gives products of commercial significance. Two of these are polyvinyl butyral (PVB) and polyvinyl formal. These are examples of useful resins made by modifying modified polymers. The latter is made into a varnish for coating wire and cable, and the former is extruded into sheet. Large quantities of PVB are used for the energy-absorbing layer in auto windshields.

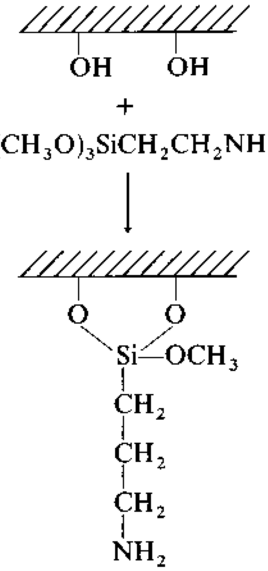


Polyvinyl butyral



Polyvinyl formal

There are many examples where a material's bulk properties are adequate for an application but its surface properties are not. Inks, coatings, or adhesives that do not adequately wet the surface of a substrate might cause printing problems and poor adhesion. Sometimes wetting and adhesion can be improved by the use of primers; but in some cases primers are not helpful, and it is necessary to modify the material's surface chemistry. If the polymer has hydroxyl functionality, coupling agents may be useful. Coupling agents such as 3-aminopropyltrimethoxysilane bind to the surface hydroxyls by forming silylether linkages. The other end of the coupling agent extends from the surface to bond with the coating.



In applications where coupling agents are not effective, other methods can be used to modify surfaces. Nonpolar surfaces can be converted to polar surfaces by chemical, radiation, and plasma-induced oxidations, or by plasma deposition of thin adhering coatings. Modifications such as this increase fabrication costs, but they produce uniquely suitable, high-value products.

Polymerization Methods

Bulk Polymerization. Bulk or mass polymerization is conducted with undiluted monomers and prepolymers. It is most successful in reactions where the monomer, like styrene and methyl methacrylate, will dissolve its polymer. The major difficulty associated with bulk polymerization is dissipating the exotherm that accompanies the process. For example, conversion of a carbon–carbon double bond to a single bond evolves about 30 kilocalories/mole of double bond. For polystyrene this amounts to about 290 calories/g, enough energy to severely overheat the mass if a way is not provided to transfer this heat from the polymerizing bulk.

Heat transfer is relatively simple to manage in small reaction vessels or in processes where the surface-to-volume ratio is high. Bulk polymerizations usually are successful for casting small objects, for making cast sheet, film, and coatings, or in reaction-injection molding. Large-scale bulk polymerization, however, must be carried out with specially designed equipment and processing methods. Heat removal generally can be done by a circulating coolant in a reactor jacket, cooling coils immersed in the reactants, and/or recirculating the reactant mixture through an external heat exchanger. If one or more of the monomers is sufficiently volatile (e.g., acrylonitrile), cooling by refluxing may be feasible if conversion to polymer does not get too high. This method can be very efficient. Adding cold feed to the reacting mass is often an effective means of controlling temperature.

The design and the operation of a bulk polymerization reactor and its agitation system go beyond considerations of temperature control and viscosity, however. The resultant mixing behavior also can affect molecular weight, reaction rate, and copolymer composition, for example. With continuous reactors the degree of backmixing is a very important consideration. In a completely backmixed reactor, for example, the contents are so thoroughly blended that their composition and conversion are uniform throughout. Such reactors often are employed to achieve a uniform copolymer composition, especially if that composition is nonazeotropic. However, a reactor of this type is not practical for operation at very high conversions, where the rate of polymerization is slow, as the reactor size becomes excessive. At the other end of the backmixing scale is the plug flow reactor, where conversion tends to increase continuously as the reactants pass through. Tubular reactors often permit a close approach to plug flow conditions. Plug flow reactors will be employed where a high-conversion effluent is required. Continuous processes may employ as many as three or more reactors in series, each designed to satisfy particular requirements as the reactant mass progresses to higher levels of viscosity and conversion. Multiple reactors with different design features often are encountered for analogous purposes with batch polymerizations.

Viscosity generally has little effect on the overall chain reaction rate until it reaches a value where an autoacceleration called the Trommsdorff or gel effect starts. The conversion at which this occurs, and its severity, will vary, depending on the polymerizing monomers, temperature, and other reaction variables. The gel effect takes place when the thermal motion of the bulky macromolecules has become so restricted that competing coupling termination reactions are hindered. However, because the monomers still can diffuse readily to the growing macromolecules, the reaction rate will accelerate. Dissipating the resulting heat surge can be difficult, especially in large reactors.

At higher conversions, the concentration of the diffusing monomer species starts dropping off. The reaction rate thus will tend to slow down, and heat generation diminishes. However, the higher viscosity that has developed increases the difficulty of agitation, so heat transfer problems still may persist. Agitators for high-viscosity reactants are slow-moving, to minimize power consumption (which can add significantly to the heat-removal load), and are intended primarily to achieve some blending and to avoid development of stagnant regions where reactants might degrade.

Reaction rates at high conversions ultimately will slow down so drastically that it generally is impractical to complete the polymerization in the reactor. Although post-curing may be carried out at some point downstream in the manufacturing process, unreacted monomers most often are removed by devolatilization. The devolatilized exiting polymer melt then is directly extruded to form pellets for subsequent fabrication steps. In some instances the melt may be fabricated directly into the final product.

Solution Polymerization. In solution polymerization, a solvent is used to maintain a homogeneous mixture of monomers, initiators, catalysts, and polymers throughout the reaction. Compared to bulk polymerization, the lower viscosities with this method generally allow improved heat and mass transfer, as well as faster reaction rates at high conversions.

There are a number of reasons why other methods might be preferred for the production of industrial resins. The use of solvents can lower initial reaction rates and reduce molecular weight to undesirable levels due to chain transfer reactions. In addition, solvents often are expensive, flammable, and toxic, and efficient means must be devised to recycle or dispose of them. Devolatilization with large-scale solution processes can be costly because of high capital and energy requirements.

There are, however, important solution polymerization processes. Examples include processes for making poly(vinyl acetate) and copolymers of vinyl chloride and of styrene. Another is the manufacture of unsaturated polyester resins, discussed above. In this case, the solvent for the resin, usually styrene, is a reactive diluent for subsequent polymerization. The styrene copolymerizes with the resin during the curing process, making it unnecessary to devolatilize the polymer or recycle solvent.

Emulsion Polymerization. Water, being nonflammable, nontoxic, and moderately volatile and having low viscosity, can be an excellent medium for carrying out polymerizations. Because most organic monomers are insoluble in water, suitable dispersal means are needed to utilize an aqueous medium. One way this can be done is by emulsifying the monomer and carrying out polymerization in the emulsified particles. This is done primarily via batch processes. The second method, suspension polymerization, is discussed in the next section.

When emulsifiers, such as soaps, alkyl sulfates, and alkyl sulfonates, are present in water above a minimum concentration called the critical micelle concentration, the emulsifier molecules aggregate into micelles. In micelles, the hydrophobic ends of the emulsifier are clustered at its center, and the hydrophilic ends extend into the aqueous phase. Micelles are spherical or lamellar with dimensions on the order of 2.5 to 5 nm, depending on the emulsifier used.[43] There may be 10^{17} to 10^{18} micelles/cm^3 of water. When monomer initially is added, a small fraction of the molecules is absorbed into the micelles, swelling them slightly. Most of the monomer is dispersed as droplets 1000 to 3000 nm in diameter, stabilized with emulsifier molecules along their surface. They number about 10^{10} to 10^{11} particles/cm^3 of water. These droplets serve as the monomer reservoir for the polymerization. A representation of emulsion polymerization early in the process is shown in Fig. 19.14.

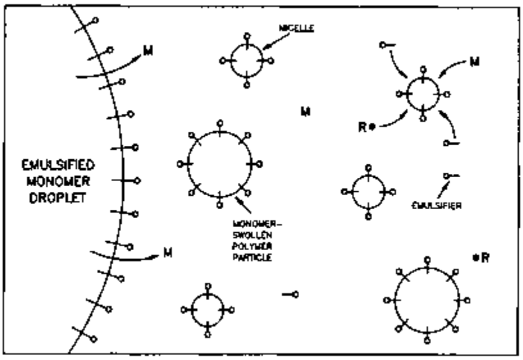


Fig. 19.14. Schematic representation of emulsion polymerization: M = solubilized monomer; R = initiator, monomer or low molecular weight polymer radical.

Once the monomer phase is dispersed into droplets, the rate of agitation does not ordinarily affect particle size or particle size distribution. The initiator, which is water-soluble, decomposes thermally in the aqueous phase, producing free radicals that diffuse into the micelles and initiate polymerization there. Termination reactions can occur in a number of ways, but because there are very few growing chains within a micelle, the probability for termination by coupling is low; thus the molecular weight of the polymer can become very high. Moreover, the emulsion has low viscosity throughout the polymerization, so efficient heat removal can be achieved, permitting high polymerization rates. Initiators, such as potassium persulfate, are effective at moderate temperatures, generally 70°C or less. Thus, the technique of emulsion polymerization offers a number of advantages. Also, the molecular weight can be lowered as needed with chain-transfer agents. The final product, called a latex, is a stable dispersion of solid polymer particles.

One of the limitations inherent in emulsion systems is difficulty in separating the polymer from the emulsifiers used in synthesis. Where the polymer is isolated from the latex, purification is done by adding an acid, salt, or some other substance that reduces the stability of the emulsion.[44] Except for washing the coagulated latex with water, polymers made in this way—such as some grades of styrene-butadiene copolymer and poly(vinyl chloride)—are not purified extensively. In many respects this lack of purification restricts their use because residual emulsifier in the polymer can impair the polymer's electrical properties, increase moisture sensitivity, and reduce clarity. Another difficulty is environmental: unreacted monomers and solvents used in the purification step need to be properly handled, and large quantities of water left from the coagulation step must be purified to meet local waste water regulations.

However, many products are formulated and used without isolating the polymer from the latex. These products include latex paints