10

Synthetic Organic Chemicals

Guo-Shuh J. Lee,* James H. McCain** and
Madan M. Bhasin**

Synthetic organic chemicals can be defined as products derived from naturally occurring materials (petroleum, natural gas, and coal), which have undergone at least one chemical reaction, such as oxidation, hydrogenation, or sulfonation.

The volume of synthetic organic chemicals produced in the United States increased from about 42 billion lb in 1958 to more than 270 billion lb in 1990 and continues to increase steadily. The growth in production for the past 35 years is shown in Fig. 10.1. The effect of the economic slowdowns in 1974/75 and in the early 1980s on chemical output is reflected very clearly. Although the total volume increased from 1989 to 1990, the sales value actually decreased, presaging the slowdown of the early 1990s. Up until the mid-1960s, most of the phenomenal growth reflected the replacement of "natural" organic chemicals. Since that time, growth for synthetic materials has been dictated by the expansion of present markets and the development of new organic chemical end uses. It is not certain that this rate of growth can be maintained as the uses of many products become strongly affected by environmental concerns. In fact, the future may see more emphasis on chemicals that can be produced from renewable raw material sources.

Those synthetic organic chemicals (excluding polymers) having production volumes of greater than four billion pounds in 2000, according to the Stanford Research Institute (SRI) Chemical Economics Handbook, are listed below. Note that the production of 5 chemicals alone totaled more than 100 billion lb, and 15 totaled 190 billion lb/year.

Ethylene dichloride	30.0 billion lb/year
MTBE	19.0
Methanol	18.7
Vinyl chloride	18.1
Ethanol	16.9
Styrene	12.6
p-Xylene	12.3
Terephthalic acid/DMT	10.1
Formaldehyde (37%)	10.0
Ethylene oxide	8.8
Cumene	8.6
Ethylene glycol	7.5
Oxo chemicals	7.1
Linear alfa olefins	5.2
Propylene oxide	5.2
Total	190.1

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*The Dow Chemical Co., Midland, MI.
**The Dow Chemical Co., South Charleston, WV.

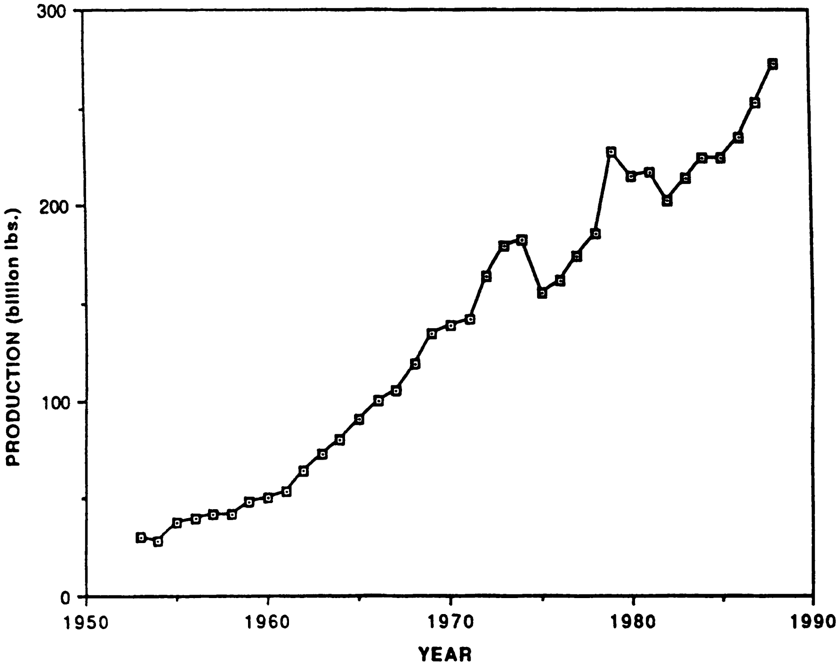


Fig. 10.1. Total production of synthetic organic chemicals, 1953–1990. (*U.S. International Trade Commission, December 1991.*)

Almost three thousand organic chemical products are currently derived from petrochemical sources. The commercial syntheses for all these products, however, can be traced back to one of six logical starting points. Consequently, this chapter has been subdivided according to the six major raw material sources: chemicals derived from methane, those from ethylene, propylene, "C_4s," higher aliphatics, and the aromatics.

A number of general references at the end of the chapter may be consulted for an overview of the subject.

CHEMICALS DERIVED FROM METHANE

Methane is readily available as the major component of natural gas, and its primary use is as fuel. It is also found in coal mines and as a product of anaerobic biological decay of organic materials in swamps and landfills. It is possible to make many chemicals from methane in a laboratory. However, methane is relatively inert chemically and is truly useful as a raw material for only a few commercial chemicals. These conversions generally require high temperatures and pressures or very aggressive chemicals such as chlorine, and usually are operated on a very large scale. Here, only those materials that are currently made from methane in commercial quantities are considered. The most important of these are shown in Fig. 10.2.

Synthesis Gas

The most important route for the conversion of methane to petrochemicals is via either hydrogen or a mixture of hydrogen and carbon monoxide. The latter material is known as synthesis gas. The manufacture of carbon monoxide–hydrogen mixtures from coal was first established industrially by the well-known water–gas reaction:

$$C + H_2O \rightarrow CO + H_2$$

Two important methods presently are used to produce the gas mixture from methane. The first is the methane–steam reaction, where methane and steam at about 900°C are passed through a tubular reactor packed with a promoted iron oxide catalyst. Two reactions are

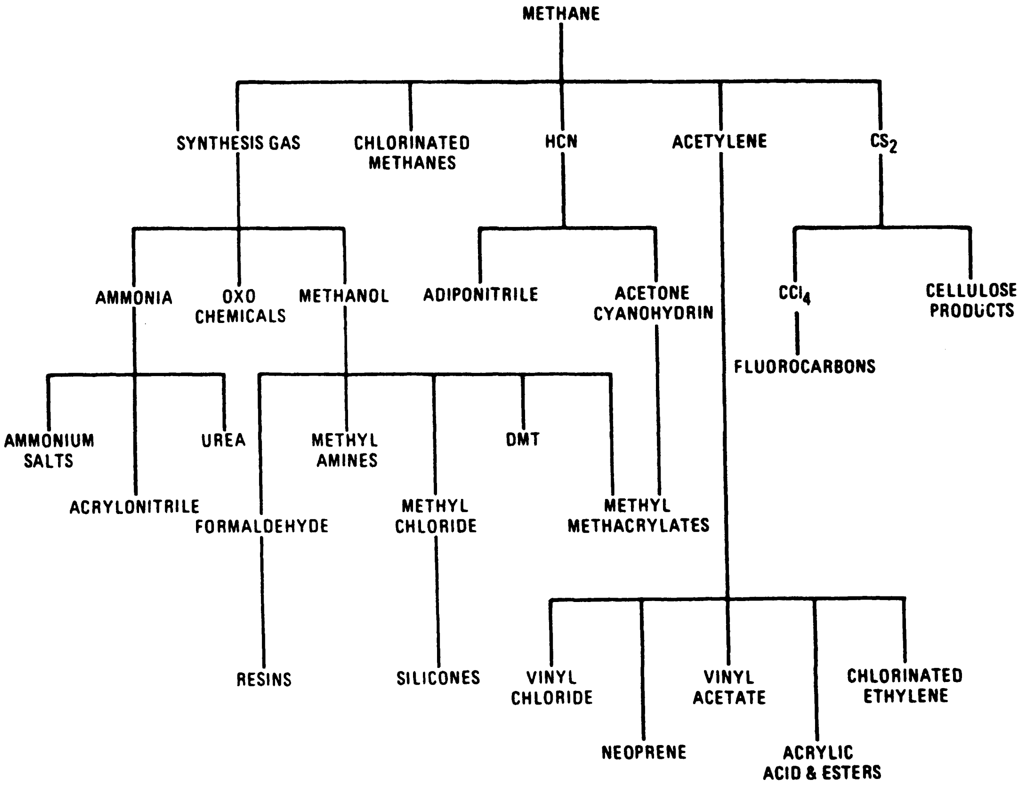


Fig. 10.2. Some important synthetic chemicals derived from methane.

possible, depending on the conditions:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

The second commercial method involves the partial combustion of methane to provide the heat and steam needed for the conversion. Thus the reaction can be considered to take place in at least two steps, the combustion step:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

followed by the reaction steps:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

The process usually is run with nickel catalysts in the temperature range of 800–1000°C. Steam reforming usually is used on the lighter feedstocks, and partial oxidation is used for the heavier fraction.

Synthesis gas is the starting material for the manufacture of ammonia and its derivatives and also for methanol, as well as for other oxo-synthesis processes. It also is a source of carbon monoxide in the manufacture of such chemicals as acetic acid. And it is also a source of hydrogen for petroleum refining processes. However, shortages and corresponding high prices of natural gas and naphtha have generated interest in other synthesis gas feedstocks such as coal and residual oil.

Ammonia. Although ammonia is not an organic chemical, it is one of the largest-volume synthetic petrochemicals. From it many reactive organic chemicals are derived such as urea, acrylonitrile, caprolactam, amines, and isocyanates. Almost all of the 40.6 or more billion lb of ammonia produced in 1999 in the United States was based on hydrogen from petroleum and natural gas. Detailed descriptions of ammonia processes are found in Chapter 29.

Methanol. Methanol was once known as wood alcohol because it was a product of the destructive distillation of wood. All American methanol was produced in that way before 1926. That year, however, marked the first appearance in the world of German synthetic methanol. Today, almost all of the approximately 10 billion lb/year of methanol made in the United States comes from large-scale, integrated plants for conversion of natural gas to synthesis gas to methanol (Fig. 10.3). World consumption has reached 57 billion lb in 2000.

In principle, methanol, because it is derived from synthesis gas, can be made not only from convenient natural gas but also from any source of reduced organic carbon such as coal, wood, or cellulosic agricultural waste. It then can be used as a readily stored fuel or shipped for use as fuel or raw material elsewhere. As petroleum and natural gas become more difficult to recover, alternative carbon sources such as these will be used more. An example involving methanol is a coal-based acetic anhydride facility started in the 1980s in the United States. Another example is the use of some of the natural gas formerly wasted during recovery of Middle Eastern oil to make methanol and other chemicals. Direct use of methanol as a motor vehicle fuel is being studied, but it is not known when or even if such use will be significant in terms of methanol usage or decreased petroleum usage.

Methanol synthesis resembles that of ammonia in that high temperatures and pressures are used to obtain high conversions and rates. Improvements in catalysts allow operation at temperatures and pressures much lower than those of the initial commercial processes. Today, "low-pressure" Cu–Zn–Alminium oxide catalysts are operated at about 1500 psi and 250°C. These catalysts must be protected from trace impurities that the older "high-pressure" (5000 psi and 350°C) and "medium-pressure" (3000 psi and 250°C) catalysts tolerate better. Synthesis gas production technology has also evolved so that it is possible to maintain the required low levels of these trace impurities.

Methanol is used as a solvent, an antifreeze, a refrigerant, and a chemical intermediate. The greatest chemical uses for methanol as of 1998 were formaldehyde, 33 percent; MTBE, 27 percent; acetic acid, 7 percent; and chloromethane, 5 percent. Other chemicals derived from methanol include methyl methacrylate, methylamines, and dimethyl terephthalate.

Formaldehyde. Formaldehyde may be made from methanol either by catalytic vapor-phase oxidation:

$$CH_3OH + \tfrac{1}{2}O_2 \rightarrow CH_2O + H_2O$$

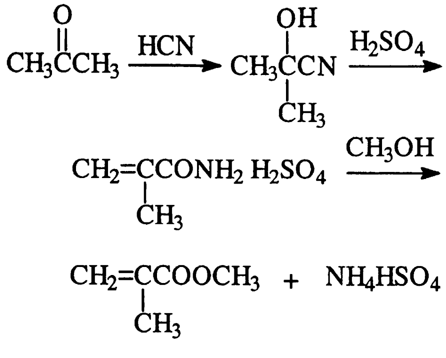
or by a combination oxidation–dehydrogenation process:

$$CH_3OH \rightarrow CH_2O + H_2$$

It also can be produced directly from natural gas, methane, and other aliphatic hydrocarbons, but this process yields mixtures of various oxygenated materials. Because both gaseous and liquid formaldehyde readily polymerize at room temperature, formaldehyde is not available in pure form. It is sold instead as a 37 percent solution in water, or in the polymeric form as paraformaldehyde [$HO(CH_2O)_nH$], where n is between 8 and 50, or as trioxane $(CH_2O)_3$. The greatest end use for formaldehyde is in the field of synthetic resins, either as a homopolymer or as a copolymer with phenol, urea, or melamine. It also is reacted with acetaldehyde to produce pentaerythritol [$C(CH_2OH)_4$], which finds use in polyester resins. Two smaller-volume uses are in urea–formaldehyde fertilizers and in hexamethylenetetramine, the latter being formed by condensation with ammonia.

U.S. production of formaldehyde in 2000 was approximately 10 billion lb of 37 percent formaldehyde, amounting to about 85 percent of capacity. Usage is expected to grow at about 3 percent/year through 2005.

Methyl Methyacrylate. Methyl methacrylate is formed in a three-step process from methanol, acetone, and HCN:



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}CH_3} \xrightarrow{HCN} \mathrm{CH_3\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}CN} \xrightarrow{H_2SO_4}$$

$$\mathrm{CH_2{=}\underset{\underset{CH_3}{|}}{C}CONH_2\ H_2SO_4} \xrightarrow{CH_3OH}$$

$$\mathrm{CH_2{=}\underset{\underset{CH_3}{|}}{C}COOCH_3} + \mathrm{NH_4HSO_4}$$

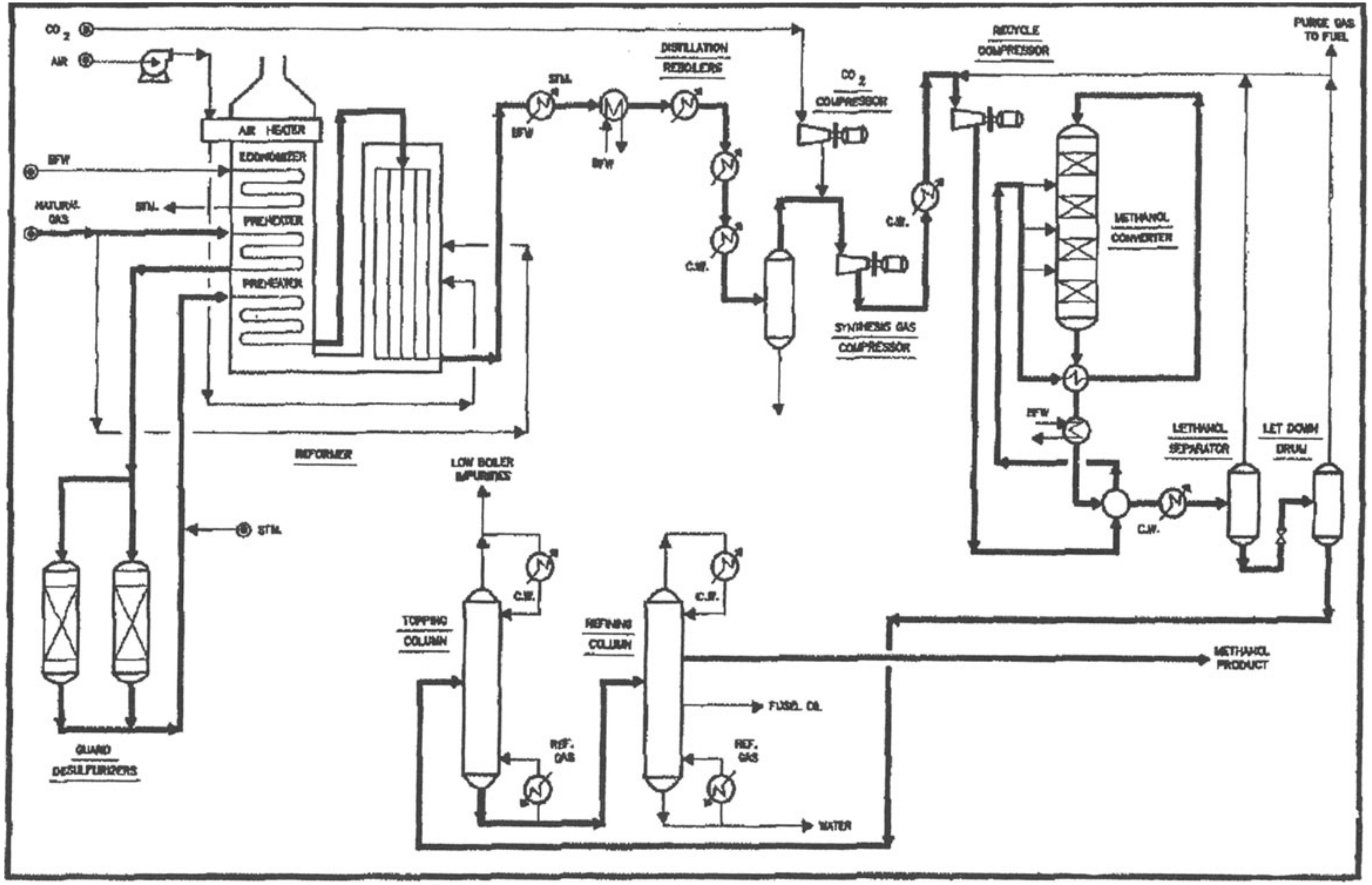


Fig. 10.3. Methanol via natural gas reforming. (*Chem Systems Report No. 93-1. Copyright Nexant Chem Systems, Inc. and used by permission of the copyright owner.*)

Although this is the major process in operation, there also is at least one commercially operated process for converting isobutylene and/or tert-butanol to methacrylic acid followed by esterification with methanol. A new process based on acetone cyanohydrin also has been reported. It avoids corrosive sulfuric acid and byproduct salts while coproducing formamide, which can be converted to HCN for recycle to the process.

U.S. production of methyl methacrylate in 1999 totaled 1.4 billion lb, which is about 82 percent of world capacity. Its uses are almost exclusively based on polymerization to poly(methyl methacrylate), which, because of its physical strength, weathering resistance, optical clarity, and high refractive index, has major uses in cast and extruded sheet (33%), molding powders and resins (16%), and surface coatings (22%).

Acetic Acid. The worldwide production of acetic acid was reported to be 15.7 billion lb in 1998. Acetic acid is a global product with about one third of production capacity now outside the United States, Western Europe, and Japan. The majority buildup is in Asia. In the future, the capacity in Asia will continue to increase substantially.

Acetic acid is produced by methanol carbonylation (the dominant process) as well as by acetaldehyde oxidation, ethanol oxidation, and light hydrocarbon oxidation. When methanol carbonylation was first practiced in the United States and West Germany, a cobalt iodide catalyst was used, and the process required up to 10,000 psia pressure. The technological breakthrough that allowed methanol carbonylation to become the leading acetic acid process was the discovery of rhodium–iodine catalysts, which can be operated at moderate pressure (500 psia) and at a methanol selectivity of 99 percent to acetic acid. Figure 10.4 is a schematic of the process. The recent advancement is the implementation of the low water technology. It significantly reduces the production cost by increasing productivity and lowering utility and capital cost.

In the United States, 5.3 billion lb of acetic acid was consumed in 1998. The applications, in decreasing order were: vinyl acetate (which alone accounts for more than 40 percent of U.S. acetic acid consumption), dimethyl terephthalate/terephthalic acid, acetate esters, cellulose acetate, other acetic anhydride uses, textiles, monochloroacetic acid, and several smaller uses. Growth projections are close to 3 percent from 1999 to 2003. The growth is tied largely to vinyl acetate monomer manufacture and to a lesser extent terephthalic acid manufacture.

Methyl t-Butyl Ether (MTBE). In 1980, MTBE was the fastest-growing derivative of methanol. This is a result of its only significant use, which is as an antiknock agent replacing lead in gasoline. In 1990, it was the fastest-growing chemical in the world. The world production has reached 48 billion in 1999. The U.S. production was about 30 billion lb, which was 63 percent of world capacity.

Because of its high miscibility in water and its increased use over the last several years, MTBE is now being found in many areas of the United States in groundwater reservoirs. This problem received national attention in June 1996, after MTBE was discovered in the drinking water supply of the city of Santa Monica, California. This incident led to many legislative initiatives in California and culminated in an Executive Order issued by California Governor Davis on March 25, 1999 to remove MTBE from all gasoline sold in California at the earliest possible date, but not later than December 31, 2002. Large declines in MTBE production and use are expected in the next few years.

MTBE is made by reacting methanol with the isobutylene contained in mixed-C_4 refinery streams. This is possible because butanes, the other butanes, and butadiene are inert under the mild conditions used. The process is catalyzed by acidic ion exchange resins.

Oxo Chemicals. The so-called oxo process combines carbon monoxide and hydrogen with olefins to make saturated aldehydes having one more carbon atom than the olefins have. The earliest such reaction studied used ethylene to produce both an aldehyde and a ketone.

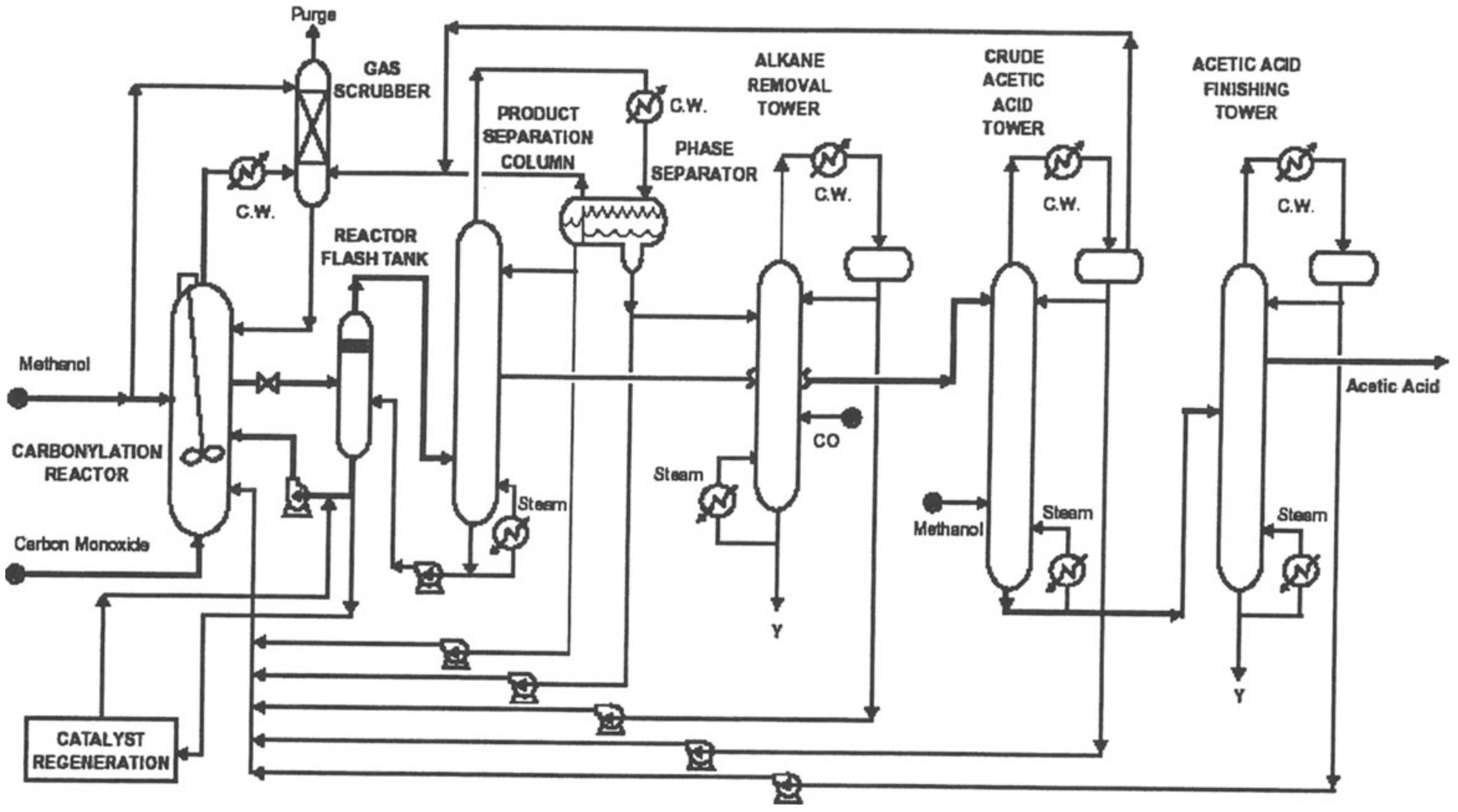


Fig. 10.4. Acetic acid via methanol carbonylation. (*Chem Systems Report No. 99/00 S5. Copyright Nexant Chem Systems, Inc. and used by permission of the copyright owner.*)

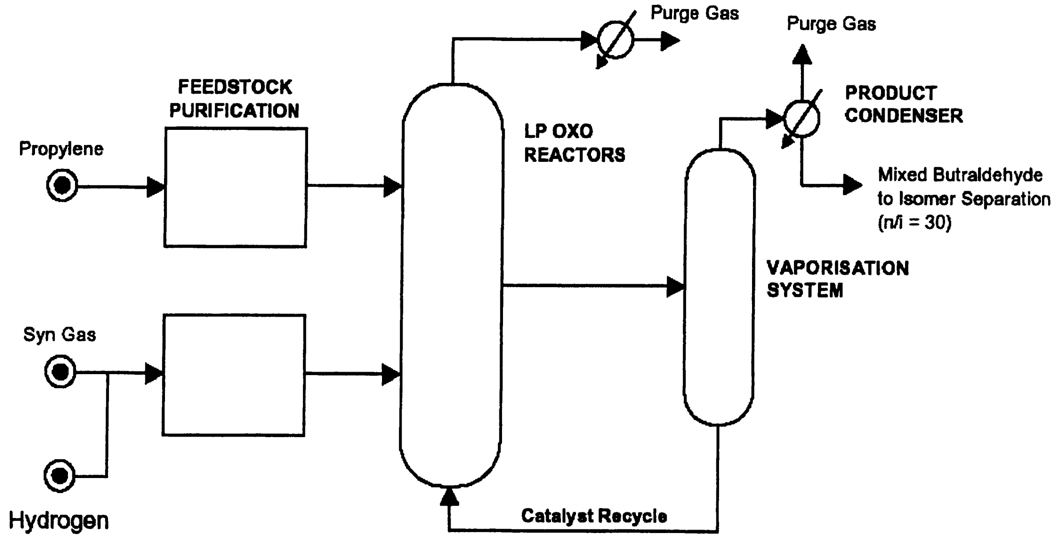


Fig. 10.5. Low-pressure oxo process. (*Chem Systems Report No. 98/99 S13. Copyright Nexant Chem Systems, Inc. and used by permission of the copyright owner.*)

Thus, the reaction was named "oxo" after the German *oxierung*, meaning "ketonization."

The low-pressure oxo process based on rhodium complex catalysts has largely replaced the older, high-pressure process, which used cobalt carbonyls as catalyst. The low-pressure process is operated at about 100°C and 200 psig. A new generation oxo process with bisphosphite modified rhodium catalyst is shown schematically in Fig. 10.5.

Oxo chemicals include butyraldehyde (*normal-* and *iso-*) and the corresponding alcohols, 2-ethylhexanol (from n-butyraldehyde), propionaldehyde, and n-propyl alcohol, and lesser amounts of higher aldehydes and alcohols derived from C_5 through C_{17} olefins. The total volume of products derived from oxo chemistry exceeds a billion pounds a year. Volumes and applications are given later in this chapter for the most important products.

Chloromethanes

The four chlorinated methanes are methyl chloride (CH_3Cl), methylene dichloride (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4). The U.S. production levels were about 520, 500, 450, and 750 million lb respectively, in 1990. Due to environmental regulation, there were some major changes. The 2000 levels were 1267, 290, 792, and 40 million lb, respectively.

Methyl chloride is the only chlorinated methane with good growth. The principal use for methyl chloride is in the manufacture of chlorosilanes (89%) for the silicone industry. Other smaller uses are for methyl cellulose ether, quaternary ammonium compounds, herbicides, and butyl rubber.

Methyl chloride is produced by two methods: by the reaction of hydrogen chloride and methanol and by the chlorination of methane. Due to increasing demand for methyl chloride, the more selective methanol hydrochlorination has become increasingly important, whereas the nonselective methane chlorination route has declined. The hydrochlorination process also has the advantage that it utilizes, instead of generating, hydrogen chloride, a product whose disposal has become increasingly difficult. The methanol hydrochlorination process can be carried out in either liquid or gas phase. The gaseous phase reaction is carried out at 250–280°C. It uses a smaller reactor but requires extra energy to vaporize aqueous HCl.

$$CH_3OH + HCl \rightarrow CH_3Cl + H_2O$$

Methylene chloride and chloroform can be made, along with the other products, by the direct chlorination of methane. It is much more common, however, to produce them by the chlorination of methyl chloride. This can be done either thermally (350–450°C) or photochemically. The HCl byproduct can be recycled back into a hydrochlorination process for production of the methylene chloride starting material.

Methylene chloride is used primarily as a solvent for degreasing and paint removal, and it is also used in aerosols and foam-blowing agents. Since 1985, new environmental regulation has had a major impact on this chemical. The consumption of methylene chloride has been reduced by 60 percent due to recycling and product substitutions.

Chloroform is used to produce chlorodifluoromethane (HCFC-22), which is used as a refrigerant (70%) and to synthesize the monomer tetrafluoroethylene (30%). Fluoropolymers that use HCFC-22 as a feedstock are strong. But the uses for refrigerant will be phased out beginning 2010. The major uses for carbon tetrachloride were to make aerosol propellants such as dichlorodifluoromethane (CFC-12) and trichlorofluoromethane (CFC-11). The volume of carbon tetrachloride decreases to almost zero as CFC-11 and 12 will be phased out.

Acetylene

In the early days of the chemical industry, acetylene was a key starting material for many important products. Initially it was obtained for chemical purposes by reaction of calcium carbide with water; but that practice has given way to acetylene recovery from hydrocarbon cracking, so that now 86 percent of acetylene used in chemical manufacturing is made in this way. Owing to difficulty in its safe collection and transport, it is almost always used where it is prepared.

Acetylene still is a preferred raw material for some products, but it has been largely replaced by ethylene for many others. Chemicals once produced from acetylene by processes now considered outdated include: vinyl chloride, vinyl acetate, acetaldehyde, acrylonitrile, neoprene, and chlorinated solvents.

1,4-Butanediol. In 2000, 164 million lb of 1,4-butanediol were made from acetylene in the United States. It is the largest consumer of acetylene.

The Reppe process is used to make 1,4-1 butanediol from acetylene. In this process, acetylene and formaldehyde are reacted in the presence of a copper–bismuth catalyst. The resulting intermediate, 2-butyne-1,4-diol is hydrogenated over a Raney nickel catalyst:

$$HC{\equiv}CH + 2HCHO \rightarrow \underset{\text{2-butyne-1,4-diol}}{HOCH_2C{\equiv}CCH_2OH}$$

$$\underset{\text{2-butyne-1,4-diol}}{HOCH_2C{\equiv}CCH_2OH} + H_2 \rightarrow \underset{\text{1,4-butanediol}}{HO(CH_2)_4OH}$$

The use of acetylene to make vinyl chloride (VCM) is now considered outdated and it is a minor process compared to the production of VCM from ethylene. Only 120 million lb of 16 billion lb VCM was made from acetylene.

Applications of 1,4-butanediol include the manufacture of THF (tetrahydrofuran), used as a solvent, and of poly(butylene terephthalate), used in thermoplastic resins.

Hydrogen Cyanide

Most of the hydrogen cyanide used today is prepared, as illustrated in Fig. 10.6, by ammoxidation of methane over a platinum catalyst. Absorption in water and distillation give pure hydrogen cyanide. Although all new hydrogen cyanide capacity is based on this technology, it also can be made from coke-oven gas, from acidification of inorganic cyanides, and by dehydration of formamide. A significant amount of material is obtained as a byproduct of ammoxidation of propylene in acrylonitrile manufacture. This amounts to about 25 percent of the demand. Because hydrogen cyanide is very toxic, the producers use much of it on-site to minimize the potential for human exposure during shipping.

The U.S. demand in 2000 was about 1.6 billion lb. Uses for hydrogen cyanide include: adiponitrile (for nylon 6/6), 47 percent; methyl methacrylate, 27 percent; sodium cyanide, 8 percent; methionine, 6 percent; and chelating agents, 2 percent.

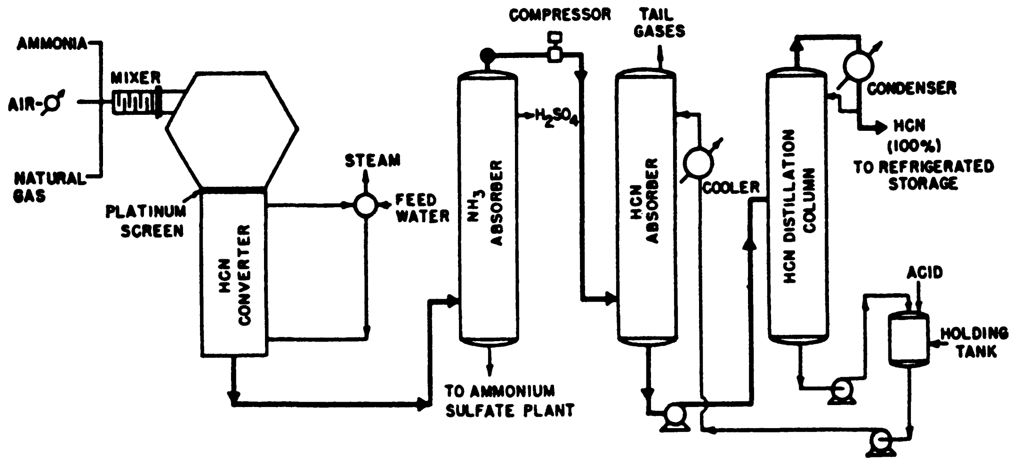


Fig. 10.6. The hydrogen cyanide process. (*Reprinted from Ind. Eng. Chem.,* **51**, *no. 10, 1235, 1959; Copyright 1959 by the American Chemical Society and reprinted by permission of the copyright owner.*)

Carbon Disulfide

Carbon disulfide is made by the catalytic reaction of methane with sulfur vapor. This can be thought of as analogous to oxidation of methane with oxygen, giving carbon dioxide. Carbon disulfide is used as raw material for making rayon (43%), agricultural chemicals (36%) and cellophane (3%). The total U.S. consumption in 2000 was about 160 million lb.

CHEMICALS DERIVED FROM ETHYLENE

Ethylene surpasses all other organic petrochemicals in production and in the amount sold. It is used as raw material for a greater number of commercial synthetic organic chemical products than is any other single chemical. Figure 10.7 shows the more important derivatives of ethylene. Ethylene consumption has grown explosively since 1940 when 300 million lb were used, mostly for making ethanol and ethylene oxide. During World War II, styrene use grew markedly, and polyethylene was developed as insulation for the then-new radar electronics. These materials later found a multitude of applications, which were responsible in large part for ethylene consumption reaching nearly 5 billion lb in 1960. Strong growth in ethylene dichloride and ethylene oxide contributed to over 18 billion lb of ethylene consumption in 1970. Continued growth raised this figure to 27 billion lb in 1978 and over 58 billion lb in 2000, which is almost two hundred times the 1940 volume. The overall growth for 48 years averaged a remarkable 10 percent/year.

Ethylene is manufactured by cracking hydrocarbons. A discussion of hydrocarbon cracking as a route to ethylene is found in Chapter 18.

Polyethylene

The largest consumers of ethylene are the various types of polyethylene: Low Density Polyethylene (LDPE), High Density Polyethylene (HDPE), and Linear Low Density Polyethylene (LLDPE). Chapter 15 gives detailed discussions of preparation of the various types of polyethylene.

LDPE is produced by high-pressure, high-temperature radical polymerization of pure ethylene. When improved properties are required, copolymers with one or more other vinyl monomers such as ethyl acrylate, vinyl acetate, or acrylic acid are used. LDPE has a relatively branched molecular structure, and the branches are relatively long. It is used for a multitude of purposes because of its properties and economics. Some important uses include: films for packaging of food and other merchandise; shipping trays and pallets; lightweight, flexible water- and chemical-resistant containers or barriers; and temporary coverings as in construction and agriculture.

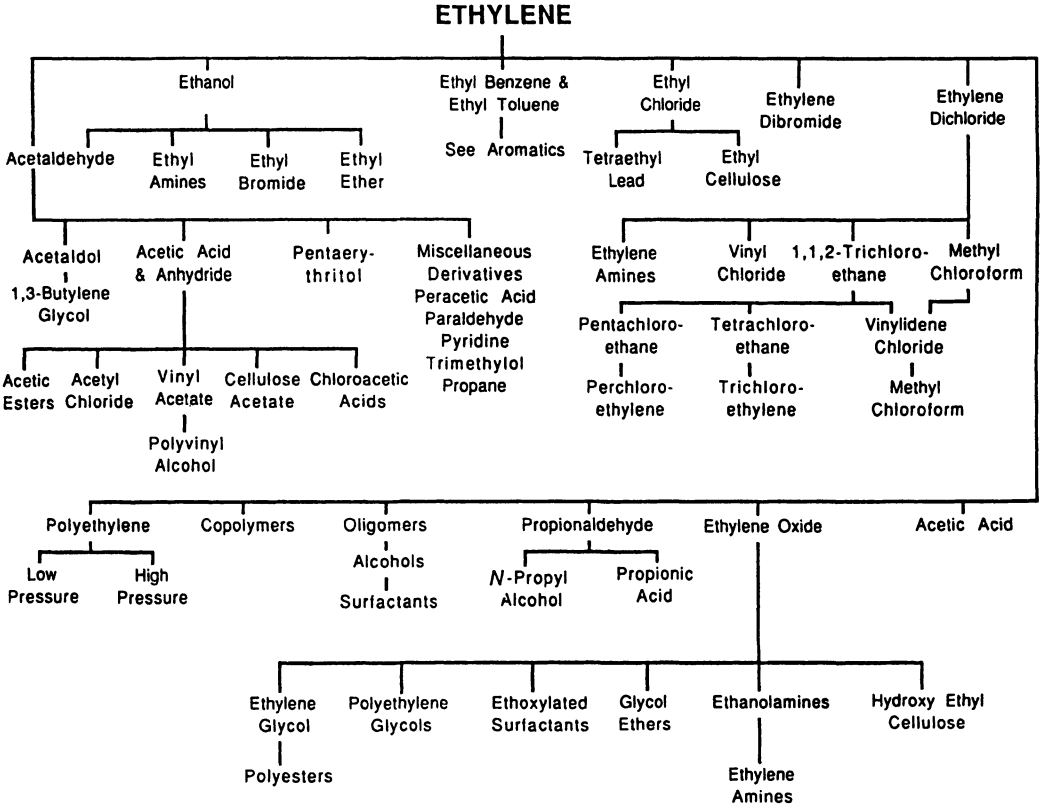


Fig. 10.7. Important derivatives of ethylene.

HDPE is produced by a low-pressure polymerization process in which highly pure gaseous ethylene is converted by proprietary catalysts to solid polyethylene particles. It has a very linear molecular structure. HDPE is stronger, tougher, and more rigid than LDPE, so it is used where such properties are advantageous. The major uses for HDPE are in blow-molded bottles, cans, and tanks for products such as milk, bleach, detergent, and fuel and in grocery sacks and other paper-replacement markets.

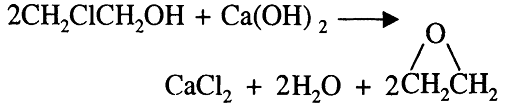
LLDPE is made by a catalytic process very similar to that for HDPE, but it is a softer polyethylene than HDPE with properties similar to those of LDPE. Its properties are achieved by inclusion of comonomers such as butene or hexene. A relatively disordered crystalline state is obtained by introducing many short branches into an otherwise highly linear molecule. Thus, the less expensive equipment of the HDPE process can be used to make a product having the greater flexibility and impact strength characteristic of LDPE.

In 2000, world capacity for polyethylene was nearly 112 billion lb.

Ethylene Oxide

Ethylene oxide was discovered in 1859 by Wurtz. He stated that ethylene oxide could not be made by direct oxidation of ethylene, and it was nearly 80 years before this was disproved. Wurtz made ethylene oxide by the method known today as the chlorohydrin process, in which ethylene is reacted in turn with hypochlorous acid and base. This process was commercialized during World War I in Germany, and until 1985 was still used commercially in the United States.

$$CH_2{=}CH_2 + HOCl \longrightarrow CH_2ClCH_2OH$$



$$2CH_2ClCH_2OH + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O + 2\,CH_2\overset{O}{\wedge}CH_2$$

Since 1985, processes for the direct oxidation of ethylene using either air or oxygen and

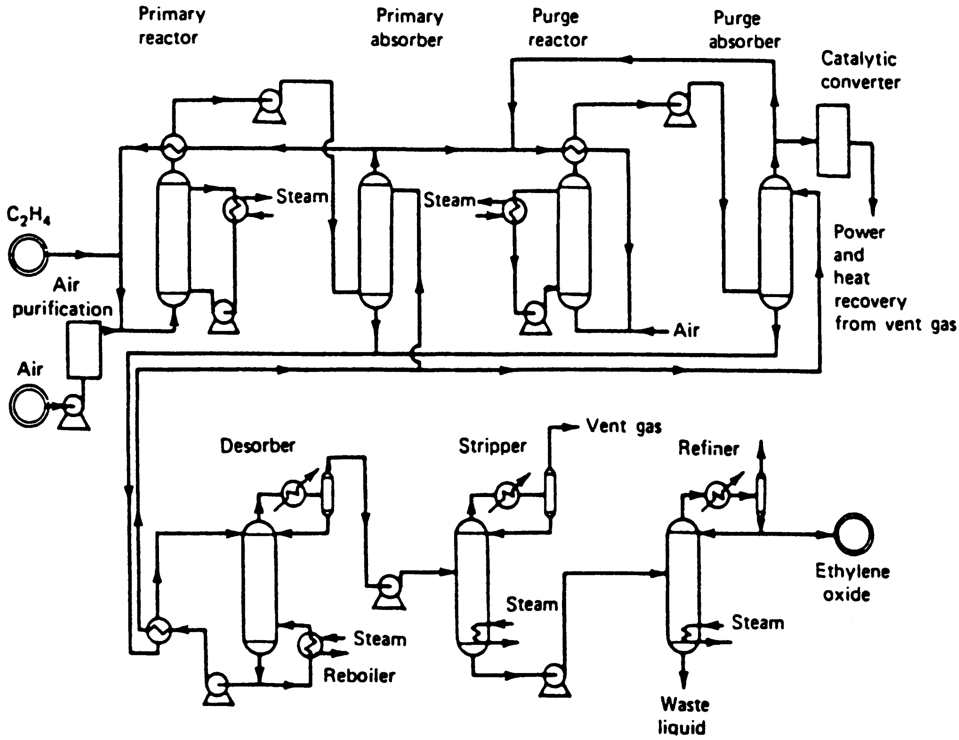


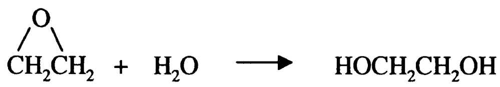
Fig. 10.8. Air-based direct oxidation process for ethylene oxide. (*Encyclopedia of Chemical Technology, Kirk and Othmer, Web site ed., ethylene oxide, manufacture, 2002. Copyright by John Wiley & Sons, Inc. and reproduced by permission of the copyright owner.*)

a silver catalyst have been the only remaining commercial processes for ethylene oxide production in the United States. Figure 10.8 illustrates an air-based process, and Fig. 10.9 an oxygen-based process. In this very exothermic conversion, oxygen and ethylene combine on a silver catalytic surface to make ethylene oxide. Oxygen and ethylene concentrations are controlled at low levels to avoid creating explosive mixtures.

The competing reactions of total combustion to carbon dioxide and isomerization must be avoided. Ethylene oxide plants in which air is used as source of oxygen require additional investment for purge reactors and associated absorbers. This investment is offset by the need, in the oxygen-based process, for an oxygen production plant and a carbon dioxide removal system. In general, the oxygen-based process is thought to be more economical, and all the plants built since the mid-1970s have been oxygen-based.

In 1999, U.S. ethylene oxide capacity was 9.1 billion lb with production of 8.2 billion lb. Major uses in that year were: ethylene glycol, 57 percent; nonionic surfactants, 11 percent; ethanolamines, 11 percent; glycol ethers, 7 percent; diethylene glycol, 5 percent; and triethylene glycol, 2 percent. The remaining 7 percent of ethylene oxide consumption included PEGs (poly(ethylene glycol)), urethane polyols, and exports. In the following sections, several of these derivatives are discussed in more detail.

Ethylene Glycols. Monoethylene glycol or ethylene glycol is the major derivative of ethylene oxide. Ethylene glycol was initially made commercially by hydrolysis of ethylene chlorohydrin. Today, hydrolysis of ethylene oxide is the preferred route.



$$\overset{O}{CH_2CH_2} + H_2O \longrightarrow HOCH_2CH_2OH$$

Reaction of ethylene oxide with water is accomplished using a large molar excess of water to favor ethylene glycol formation over

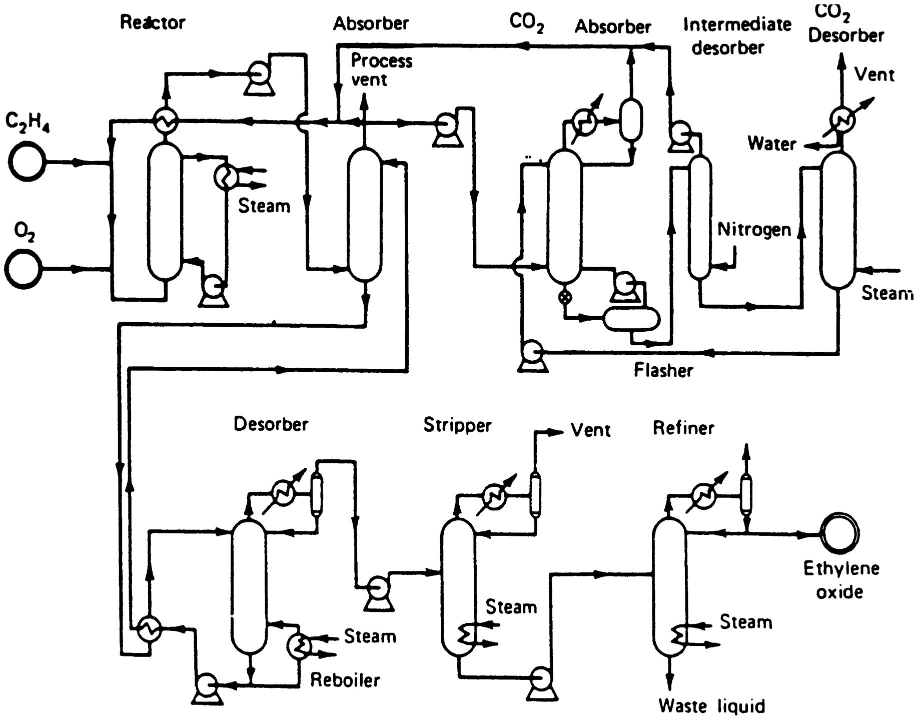


Fig. 10.9. Oxygen-based direct oxidation process for ethylene oxide. (*Encyclopedia of Chemical Technology, Kirk and Othmer, Web site ed., ethylene oxide, manufacture, 2002. Copyright by John Wiley & Sons, Inc. and reproduced by permission of the copyright owner.*)

that of diethylene glycol and triethylene glycol, as the glycols are more reactive with ethylene oxide on a molar basis than is water. A multiple-effect distillation scheme is used to recycle the unreacted excess water. The major product, ethylene glycol, is recovered between light impurities and the heavier glycol byproducts.

In 1999, U.S. consumption of ethylene glycol totaled 5.5 billion lb. Of that, 1.5 billion lb (28%) was used in the production of polyester bottles, primarily for soft drinks. Polyester fiber applications accounted for 1.4 billion lb (26%), primarily for the textile industry. Polyester film and miscellaneous applications consumed another 0.4 billion lb (7%). Antifreeze applications have held steady at approximately 1.6 billion lb over the last 20 years, and have become relatively less important with time than the polyester applications. This trend is expected to hold in the future. Increased demand for polyester bottles is expected to fuel growth in the United States, and bottle and textile applications are expected to fuel growth in other areas of the world.

Diethylene glycol usage is about 800 million lb/year in the United States. Major uses are unsaturated polyester resins (21%), polyurethane resins (21%), and antifreeze blending (10%). Other applications include use as raw materials for triethylene glycol (7%) and for morpholine (7%). Diethylene glycol is also used for dehydration of natural gas and in textile conditioning.

Triethylene glycol consumption is approximately 115 million lb/year in the United States. The major use, natural gas drying, depends on the low volatility and strong affinity of triethylene glycol for water. Lesser amounts are used as intermediate for vinyl plasticizers, polyester resins, and polyols. Additional direct applications include solvent and humectant uses.

Polyethylene glycols are produced by base-catalyzed addition of ethylene oxide to a low molecular weight glycol such as diethylene glycol. These glycols are higher-molecular-weight analogs of mono-, di-, and triethylene glycol but differ from the latter compounds in that they are not pure substances but rather consist of distributions of low molecular weight polymers. With average molecular weights beginning at about 200 (that of tetraethylene glycol) and going up to about 1000, these materials are liquids at ambient temperature. They are used as plasticizer intermediates, dispersant media, lubricants, and humectants. Above an average molecular weight of 1000, the polyglycols become waxy solids and find use in ointments, cosmetics, and lubricants taking advantage of their oil and water compatibility and low toxicity. At very high molecular weights, homopolymers of ethylene oxide are used for thickening, for water-soluble films, and for reducing friction in, for example, water delivery in fire hoses. Their value in this last application is that a given size hose can be made to deliver a greater flow of water.

Surfactants. Ethylene oxide-containing surfactants are generally of nonionic or anionic classes. The nonionic materials are made by base-catalyzed addition of ethylene oxide to either fatty alcohols or alkylphenols. Sulfation can be used to convert these compounds to the sulfated anionic surfactants. The products contain from a few to many ethylene oxide molecules per alcohol. The chain of poly(ethylene oxide) in a nonionic product acts as the hydrophile, and the alkyl or alkaryl residue is the hydrophobe. A sulfate salt group adds to the hydrophilicity of an anionic surfactant.

Surfactants based on aliphatic alcohols are used as cleaners in both domestic and industrial applications. They provide excellent properties such as wetting, dispersion, and emulsification. The ethoxylates derived from alkylphenols are chemically stable and highly versatile, finding more use in industrial practice than in domestic applications. They are used both as processing aids and as components in various products. Their applications include metal cleaning, hospital cleaners and disinfectants, agricultural chemical formulation surfactants, insecticides and herbicides, oil-well drilling fluids, and many others.

In the United States in 1999 for surfactant applications, 340 million lb of ethylene oxide were consumed in the production of alkylphenol ethoxylates, and 600 million lb were consumed in the production of ethoxylates of aliphatic alcohols.

Ethanolamines. Ethanolamines are manufactured by reacting ethylene oxide and ammonia. The

$$\begin{aligned} NH_3 &\xrightarrow{C_2H_4O} HOC_2H_4NH_2 \\ &\xrightarrow{C_2H_4O} (HOC_2H_4)_2NH \\ &\xrightarrow{C_2H_4O} (HOC_2H_4)_3N \end{aligned}$$

relative amounts of the three amines will depend primarily on the ammonia-to-oxide feed ratio. The three products are separated by distillation. Over the years, the relative demand for the three products has varied greatly. Thus, operational flexibility must be maintained.

The ethanolamines are water-miscible bases from whose properties stem their major uses as neutralizers in aqueous formulations such as metalworking fluids. Monoethanolamine is used in detergents, in "sweetening" (removing carbon dioxide and hydrogen sulfide from) natural gas, for removing carbon dioxide from ammonia during its manufacture, and as a raw material for producing ethyleneamines by reductive amination. Diethanolamine finds use in detergents and as an absorbent for acidic components of gases, as well as its major use as a raw material for surfactant diethanolamides of fatty acids. Triethanolamine's main end uses are in cosmetics and textile processing.

In the United States in 1999, ethylene oxide consumed in the production of ethanolamines totaled approximately 900 million lb. Approximately 300 million lb went into each of monoethanolamine, diethanolamine, and triethanolamine.

Glycol Ethers. In the same way that water reacts with one or more molecules of ethylene oxide, alcohols react to give monoethers of ethylene glycol, producing monoethers of diethylene glycol, triethylene glycol, and so on, as by-products.

$$\begin{aligned} ROH &\xrightarrow{C_2H_4O} ROC_2H_4OH \\ &\xrightarrow{C_2H_4O} RO(C_2H_4O)_2H \\ &\xrightarrow{C_2H_4O} RO(C_2H_4O)_3H \end{aligned}$$

Since their commercial introduction in 1926, glycol ethers have become valuable as industrial solvents and chemical intermediates. Because glycol monoethers contain a $-OCH_2CH_2OH$ group, they resemble a combination of ether and ethyl alcohol in solvent properties. The most common

$$2ROC_2H_4OH \xrightarrow{H_2SO_4} ROC_2H_4OC_2H_4OR + H_2O$$

alcohols used are methanol, ethanol, and butanol. Principal uses for the glycol ethers are as solvents for paints and lacquers, as intermediates in the production of plasticizers, and as ingredients in brake fluid formulations. Condensation of the monoethers produces glycol diethers, which are also useful as solvents.

Solvent characteristics of glycol ethers are enhanced by esterifying with acetic acid. The resulting acetate esters are used extensively in coating formulations, especially those formulations in which their high solvent power allows a decreased total solvent usage in compliance with volatile organic compound (VOC) emission standards.

In the United States in 1999, ethylene oxide consumption for production of glycol ethers was approximately 560 million lb.

Other Uses of Ethylene Oxide. About 2 percent of ethylene oxide is consumed in miscellaneous applications, such as its use as a raw material in manufacture of choline, ethylene chlorohydrin, hydroxyethyl starch, and hydroxyethyl cellulose and its direct use as a fumigant/sterilant. Production of 1,3-propanediol via hydroformylation of ethylene oxide was begun on a commercial scale in 1999. 1,3-Propanediol is a raw material for polytrimethylene terephthalate, which finds uses in fibers, injection molding, and in film. Use of ethylene oxide in making 1,3-propanediol is expected to be as much as 185 million lb by 2004, up from 12 million lb in 1999.

Chlorinated Ethanes and Ethylenes

A number of important large-volume petrochemicals are obtained through the chlorination of ethane and ethylene. The largest-volume chlorinated derivative is 1,2-dichloroethane (18 billion lb/year); most of it is used to make vinyl chloride. It has about 4 percent growth rate in the past decade. Because of their unique solvent and chemical intermediate properties, the market for chlorinated ethanes and ethylenes (exclude 1,2-dichloroethane) grew steadily until it reached a peak in 1980. Owing to environmental problems, particularly in the solvent area, the demand for some of the end uses has been declining steadily since then. The 1999 annual production rates for tetrachloroethylene, trichloroethylene, and 1,1,1-trichloroethane are at about 300, 210, and 250 million lb. Figure 10.10 shows the possible production routes to the major chlorinated derivatives.

Chlorinated Ethanes. Of the nine possible chlorinated derivatives of ethane, only three are of commercial importance: ethyl chloride, 1,2-dichloroethane (ethylene dichloride), and 1,1,1-trichloroethane (methyl chloroform). The other compounds have no important end uses and are produced either as intermediates or as unwanted by-products. They normally are converted to useful materials by a cracking process (for trichloroethylene) or by perchlorination (for carbon tetrachloride and tetrachloroethylene).

Ethyl Chloride. Most of the ethyl chloride is made by the exothermic hydrochlorination of ethylene, in either the liquid or the vapor phase:

$$CH_2{=}CH_2 + HCl \xrightarrow{AlCl_3} CH_3CH_2Cl$$

A much smaller amount is produced by the thermal chlorination of ethane. This direct chlorination may be run in conjunction with another process, such as oxychlorination, which can use the byproduct HCl as feed.

Ethyl chloride rose to commercial importance because of the automotive industry. It was the starting material for tetraethyllead, at one time the most commonly used octane booster. Demand has been cut drastically because of the conversion from leaded to unleaded gasoline for environmental reasons. Other uses for ethyl chloride are in the production of ethyl cellulose, as an ethylating agent, as a blowing agent, and in solvent extraction.

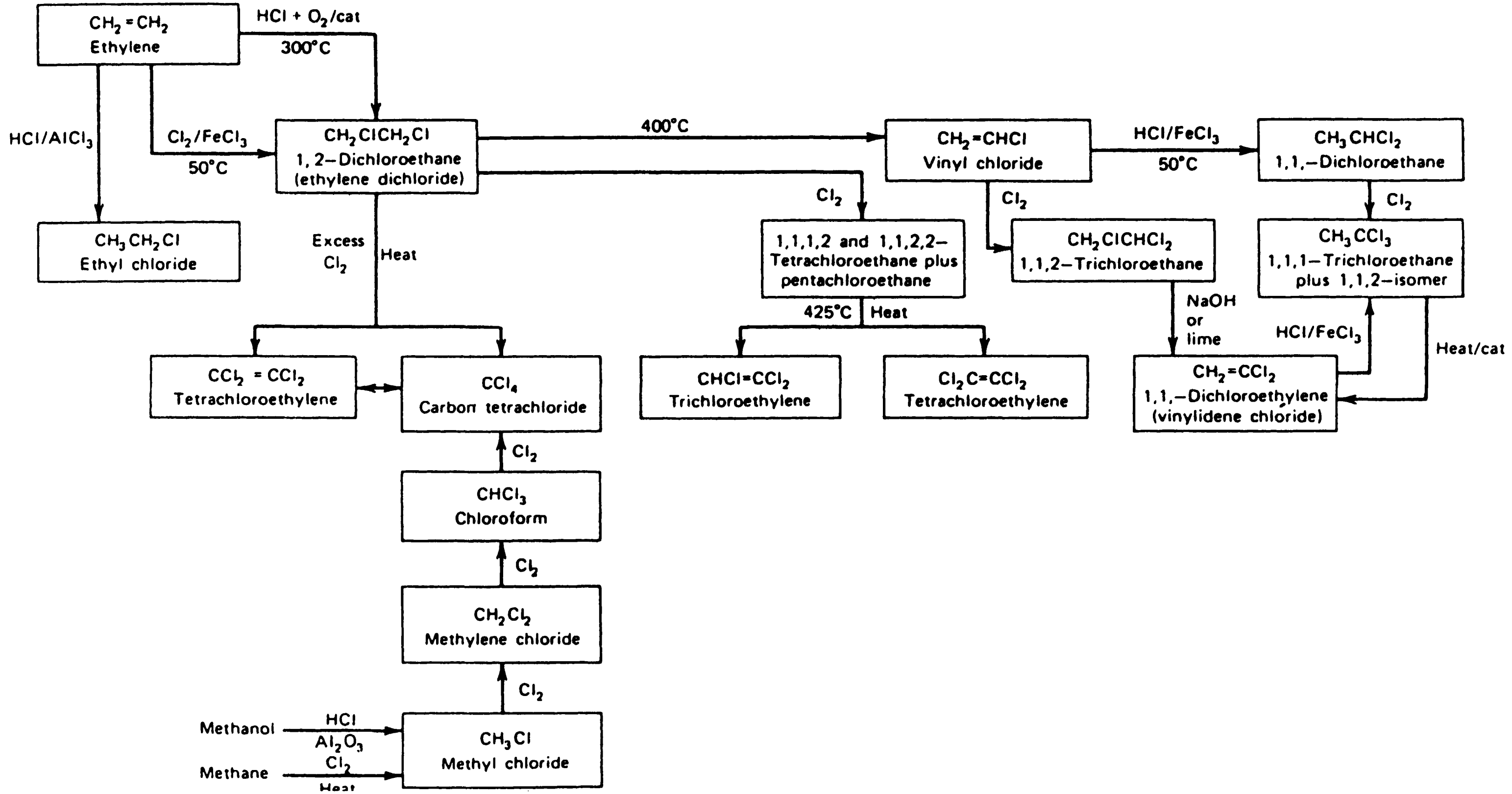


Fig. 10.10. Manufacturing processes for C_1 and C_2 chlorocarbons. (*Encyclopedia of Chemical Technology, 3rd ed., Vol. 5, p. 671. Copyright by John Wiley & Sons, Inc. and reproduced by permission of the copyright owner.*)

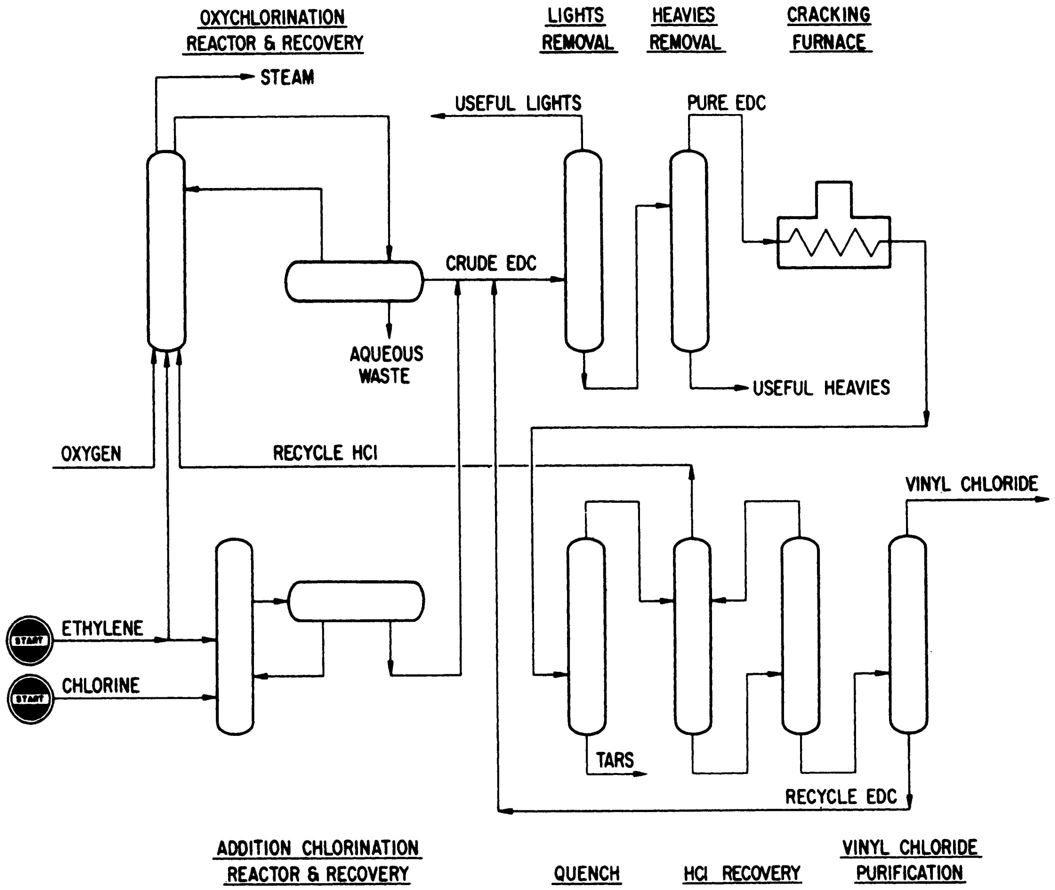


Fig. 10.11. Integrated EDC/vinyl chloride process. *(Hydrocarbons Processing, p. 174, 1985 November. Copyright Gulf Publishing Company and used by permission of the copyright owner.)*

1,2-Dichloroethene (Ethylene Dichloride). Ethylene dichloride (EDC) is one of the truly major petrochemicals. The U.S. production exceeded 18 billion lb in 1999. Almost 95 percent of this went into the manufacture of vinyl chloride monomer.

Figure 10.11 shows an integrated plant for producing EDC and vinyl chloride from ethylene, chlorine, and air. In this process, vinyl chloride (VCM) is produced by the thermal cracking of EDC. The feed EDC may be supplied from two sources. In the first source, ethylene and chlorine are reacted in essentially stoichiometric proportions to produce EDC by direct addition. In the second source, ethylene is reacted with air and HCl by the oxychlorination process. Ideally, both processes are carried out in balance, and the oxychlorination process is used to consume the HCl produced in the cracking and direct chlorination steps. The chemical reactions are as follows.

$$CH_2{=}CH_2 + 2HCl + 1/2O_2 \rightarrow ClCH_2\text{–}CH_2Cl$$

$$CH_2{=}CH_2 + Cl_2 \rightarrow ClCH_2\text{–}CH_2Cl$$

$$ClCH_2\text{–}CH_2Cl \rightarrow CH_2{=}CHCl + HCl$$

Thus the overall reaction for the integrated plant is:

$$4CH_2{=}CH_2 + 2Cl_2 + O_2 \rightarrow 4CH_2{=}CHCl + H_2O$$

The direct chlorination of ethylene usually is run in the liquid phase and is catalyzed with ferric chloride. High-purity ethylene normally is used to avoid product purification problems. The cracking (pyrolysis) of EDC to VCM typically is carried out at temperatures of 430–530°C without a catalyst. The hot gases are quenched and distilled to remove HCl and then VCM. The unconverted EDC is returned to the EDC purification train. The oxychlorination step is the heart of the process and has two major variables, the type of reactor and the oxidant. The reactor may be either a fixed bed or a fluidized bed, and the oxidant is either air or oxygen. The temperature is in the range of 225–275°C with a copper chloride-impregnated catalyst.

Profitable disposal of the byproduct HCl once was the major restriction to the growth of EDC. The advances in the oxychlorination, which uses the HCl and air to produce ethylene dichloride, opened the door for the rapid replacement of the acetylene-based routes.

Almost 95 percent of all EDC goes to make VCM. Of that, less than 20 percent actually is isolated as EDC. Smaller uses are as a solvent and as a raw material for other chlorinated hydrocarbons such as trichloroethylene and perchloroethylene. Also a small amount is used to produce ethylene diamines.

Vinyl Chloride. Approximately 16.5 billion lb of VCM were produced in the United States in 1999, making it one of the largest-volume petrochemicals. It has been reported that more than 35 percent of the global production of chlorine goes to the manufacture of VCM. Although most of the VCM comes from EDC by the route described previously, it can be obtained from other sources, including its production in the catalytic hydrochlorination of acetylene and as a byproduct in the synthesis of other chlorinated hydrocarbons.

More than 95 percent of all VCM is used to produce polyvinyl chloride (PVC), an important polymer for the housing and automotive industries. (A detailed description of PVC is included in Chapter 15.) The rest of the VCM goes into the production of chlorinated solvents.

1,1,1-Trichloroethane (Methyl Chloroform). 1,1,1-Trichloroethane was a major solvent, particularly for cold and vapor degreasing. It was phased out for emissive uses in the United States in 1996 because of its ozone depletion potential. The only application left is as chemical precursor for HCFC-141b and HCFC-142b. However, both are subject to phaseout schedule of the Montreal Protocol, and their production has been frozen at the 1996 level. The U.S. consumption has fallen from 700 million lb in 1988 to about 200 million lb in 1999.

1,1,1-Trichloroethane can be produced by three methods: by chlorination of 1,1-dichloroethane, from 1,1,2-trichloroethane via 1,1-dichloroethylene, and by direct chlorination of ethane. In the United States the first route produces about 70 percent. In this process the EDC feedstock is rearranged to 1,1-dichloroethane via cracking to VCM, followed by addition of HCl in the presence of a catalyst. For the final step, the dichloroethane is thermally or photochemically chlorinated. The reactions are as follows:

$$\mathrm{ClCH_2{-}CH_2Cl \rightarrow CH_2{=}CHCl + HCl}$$

$$\mathrm{CH_2{=}CHCl + HCl \rightarrow CH_3{-}CHCl_2}$$

$$\mathrm{CH_3{-}CHCl_2 + Cl_2 \rightarrow CH_3{-}CCl_3 + HCl}$$

Chlorinated Ethylenes. VCM is by far the largest-volume chlorinated ethylene derivative. The others of commercial interest are tetrachloroethylene (perchloroethylene), trichloroethylene, and 1,1-dichloroethylene (vinylidene chloride).

Tetrachloroethylene (Perchloroethylene). Perchloroethylene historically has been the dominant solvent in the dry-cleaning industry because of its good stability and low flammability. Environmental concerns reduced its usage in dry-cleaning from 500 million lb in 1988 to less than 100 million lb in 1999. However, increasing quantities of perchloroethylene are being used to make alternative chlorofluorohydrocarbons, such as HCFC-123 and HCFC-134a. The total production volume in 1999 was 318 million lb.

Most perchloroethylene has been coproduced with carbon tetrachloride by the chlorination of propylene and/or chloropropanes. After the phaseout of CFC-11 and -12, the market for carbon tetrachloride disappeared. Producers have modified their units to shift the production to perchloroethylene.

An oxychlorination/oxyhydrochlorination process for the production of perchloroethylene and trichloroethylene is shown in Fig. 10.12.

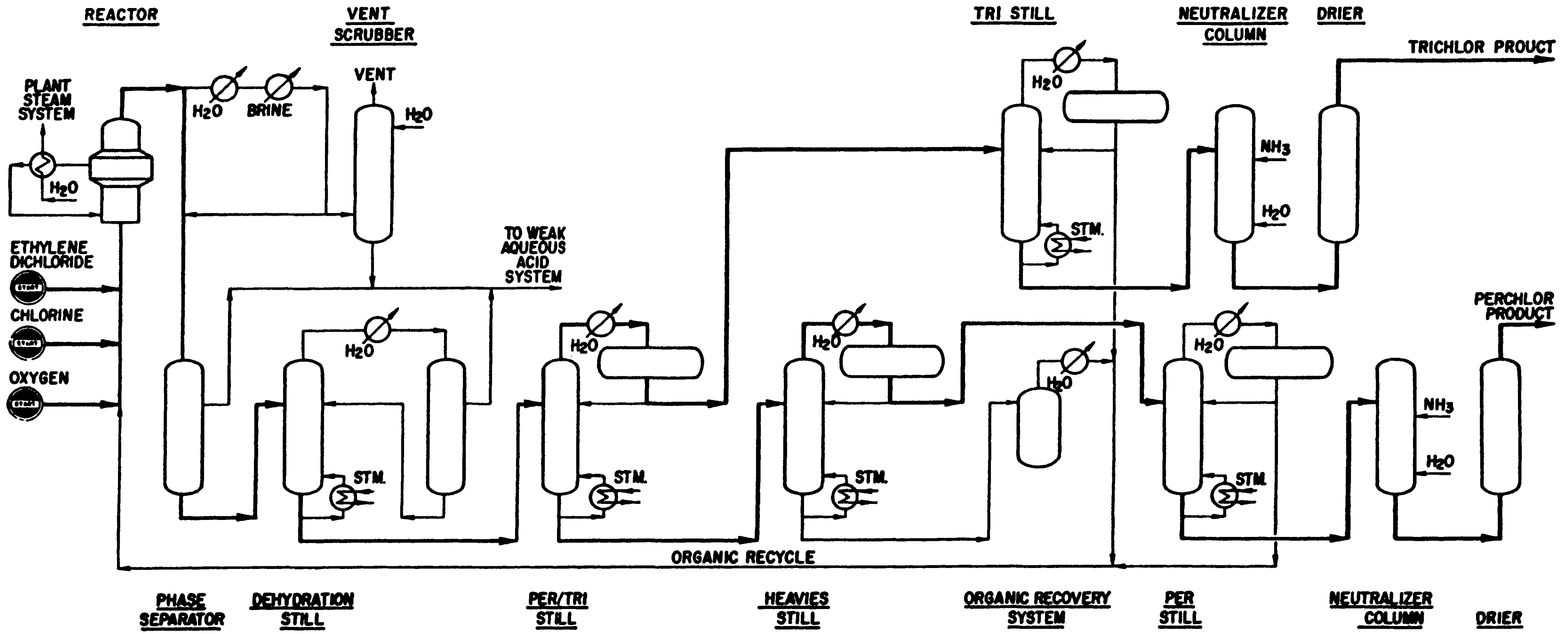


Fig. 10.12. Perchloroethylene/trichloroethylene plant. (*Reproduced from Hydrocarbon Processing, p. 154, 1985 November. Copyright by Gulf Publishing Co. and used by permission of the copyright owner.*)

The process can accept a wide range of low-cost feedstocks, such as ethylene, chlorinated C_2 hydrocarbons, and by-product streams from VCM chloromethanes, methyl chloroform, and EDC plants. The product ratio of trichloroethylene to perchloroethylene can be adjusted over a wide range.

Other Chlorinated Ethylenes. Trichloroethylene was a major solvent for degreasing in the late 1960s and early 1970s. Since that time, its production has decreased from 500 million lb to 100 million lb in 1993 because of environmental pressures on the solvent users and replacement by 1,1,1-trichloroethane. Recently, trichloroethylene has recovered market share in metal cleaning due to the phasing out of 1,1,1-trichloroethane in 1996. Also, the use as precursor for HFC-134a synthesis continues to increase. The production volume in 1998 was 245 million lb.

Although 1,1-dichloroethylene (vinylidene chloride) is a relatively small-volume product, it provides a way of upgrading the unwanted 1,1,2-trichloroethane by-product from the manufacture of EDC and 1,1,1-trichloroethane. Its major use is as an intermediate for polyvinylidene chloride and its copolymers, which are important barrier materials for food packaging.

Ethanol

Ethanol is made by both ethylene hydration and fermentation of starches and sugars. In this section the synthetic route will be discussed. The fermentation route is covered in Chapters 32 and 33.

In the World War II era, 72 percent of U.S. ethanol was derived from molasses fermentation. By 1978 the balance was 90 percent from direct catalytic hydration and the rest from fermentation. In 1998 the balance had returned to the dominance of fermentation, with 83 percent of the 10 billion lb of U.S. ethanol made in this way. The recent swing toward fermentation is due to the use of 90 percent of the fermentation ethanol as motor fuel, as a result of post-oil-embargo U.S. government policy.

Direct hydration of ethylene is by far the major route to synthetic ethanol. It is accomplished under pressure at 250–300°C over an acidic catalyst. Ethylene and high temperature steam are mixed and passed over an acidic catalyst, usually phosphoric acid on a support. A modest conversion is achieved even with the severe conditions. Cooling of the exit stream and passage through a separations system give ethylene and water for recycle. Ethanol is made either as a 95 percent azeotrope with water or as an anhydrous material from a drying system.

Synthetic ethanol has the following uses: as a chemical intermediate (for ethyl acetate, ethyl acrylate, glycol ethers, ethylamines, etc.), 30 percent; in toiletries and cosmetics, 20 percent; as a coatings solvent, 15 percent; as a raw material for vinegar, 10 percent; in household cleaners, 7 percent; in detergents, 5 percent; in pharmaceuticals, 5 percent; in printing inks, 3 percent; and in miscellaneous uses, 5 percent.

Ethylbenzene

Ethylbenzene is used almost exclusively (99%) as a raw material for producing styrene. The remainder is used as solvent and in the manufacture of diethylbenzene. The world and U.S. demand were 44.7 and 12.6 billion lb, respectively. A growth of about 3 percent/year was expected for the next few years.

Over 90 percent of all ethylbenzene is produced by alkylation of benzene with ethylene in the presence of an acidic catalyst such as aluminum chloride or an acidic zeolite. Figure 10.13 shows a liquid phase alkylation process with zeolite catalyst.

$$C_6H_6 + CH_2{=}CH_2 \rightarrow C_6H_5CH_2CH_3$$

Conversion to styrene is accomplished either by dehydrogenation:

$$C_6H_5CH_2CH_3 \rightarrow C_6H_5CH{=}CH_2 + H_2$$

or by a sequence of oxidation to ethylbenzene hydroperoxide, reduction to methyl phenyl carbinol (by a process that also oxidizes propylene to propylene oxide), and dehydration of the methyl phenyl carbinol to styrene.

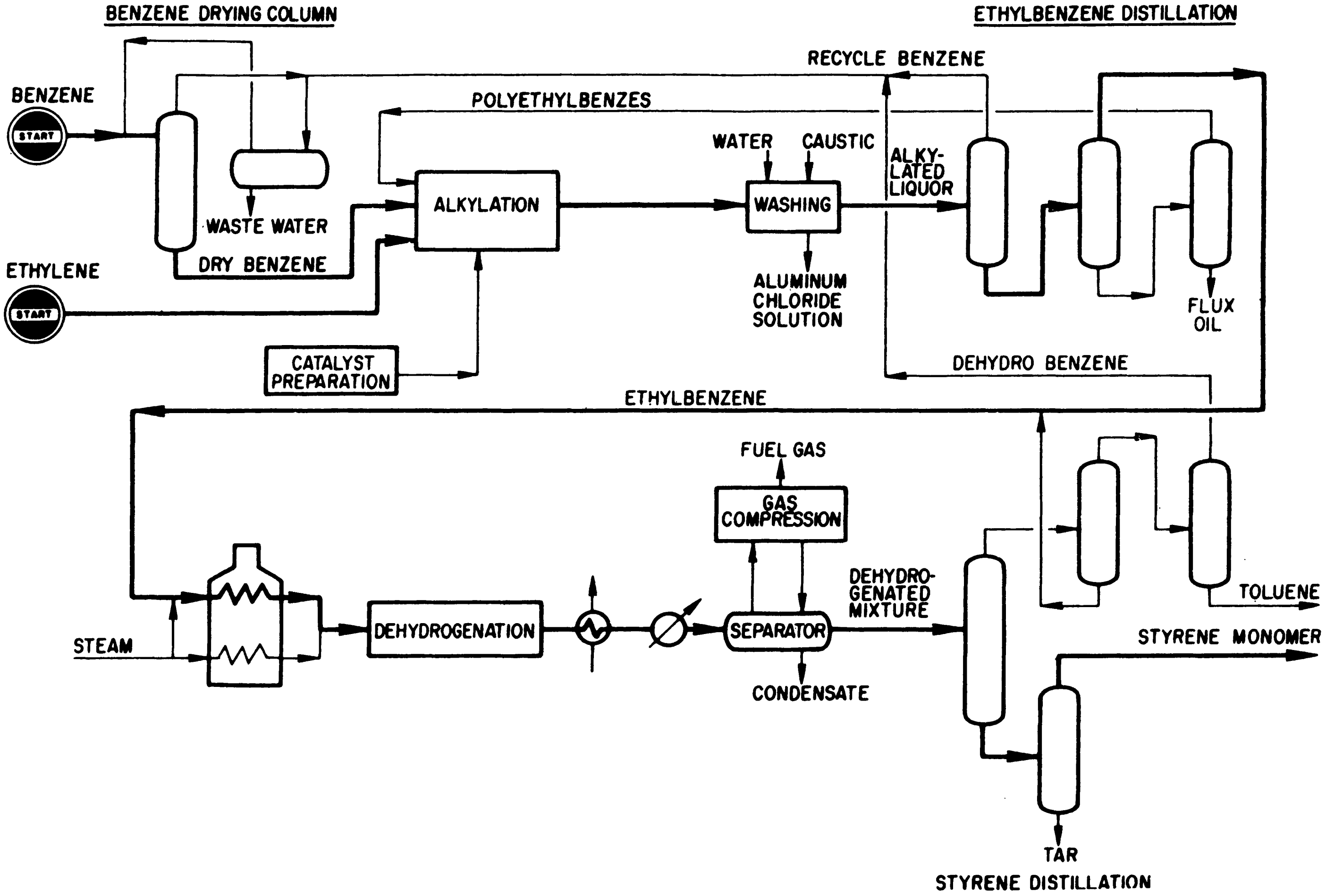


Fig. 10.13. Integrated plant for manufacture of ethylbenzene and styrene. (*Reproduced from Hydrocarbons Processing, Petrochemical Handbook, p. 169, 1985 November. Copyright Gulf Publishing Co. and used by permission of the copyright owner.*)

Acetaldehyde, Acetic Acid, Acetic Anhydride, Vinyl Acetate

Acetaldehyde. Acetaldehyde has been made from ethanol by dehydrogenation and by catalytic hydration of acetylene. Today direct oxidation of ethylene in the liquid phase catalyzed by palladium and copper has replaced these earlier methods. Figure 10.14 shows an ethylene-to-acetaldehyde unit based on this last route.

Acetaldehyde once was widely used as raw material for a variety of large-volume chemical products such as acetic acid and butanol. U.S. usage peaked in 1969 at 1.65 billion lb. Today, most of the former uses have been superseded by routes based on C_1 or other chemistry such as methanol carbonylation to acetic acid and butanol from propylene by oxo chemistry. Of the remaining uses, which totaled about 400 million lb in the United States in 2000, pyridine and substituted pyridines are the major consumers at 40 percent. It is also used as a raw material for peracetic acid, pentaerythritol, and 1,3-butylene glycol.

Acetic Acid. Acetic acid used to be derived from ethylene with acetaldehyde as an intermediate. The relatively high price of acetaldehyde compared to methanol and carbon monoxide, however, caused a shift away from this route. Although most acetic acid is currently produced by methanol carbonylation, as discussed earlier, a new route directly from ethylene was commercialized in 1997. This route employs a palladium-containing catalyst and combines ethylene directly with oxygen to produce acetic acid with approximately 86 percent selectivity. Figure 10.15 is a schematic diagram of the process.

Acetic Anhydride. A total of 1.9 billion lb of acetic anhydride was produced in the United States in 1999. Commercial production of acetic anhydride is currently accomplished through two routes, one involving ketene and the other methyl acetate carbonylation. A former route based on liquid phase oxidation of acetaldehyde is now obsolete.

In the ketene process, acetic acid is thermally dehydrated at 750°C to ketene. The ketene is separated from byproduct water and reacted with another mole of acetic acid to produce acetic anhydride. Figure 10.16 is a schematic diagram of this process.

The methyl acetate carbonylation process was successfully started and operated in the early 1980s. In this process, methyl acetate, itself the product of a one-step esterification

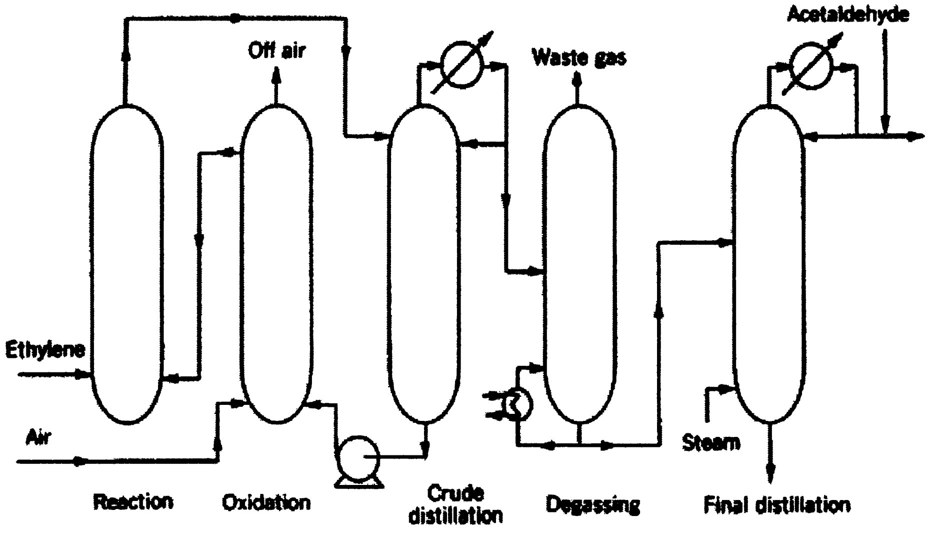


Fig. 10.14. Two-stage acetaldehyde process. (*Encyclopedia of Chemical Technology, Kirk and Othmer, Web site ed., acetaldehyde, manufacture, 2002. Copyright by John Wiley & Sons, Inc. and reproduced by permission of the copyright owner*)

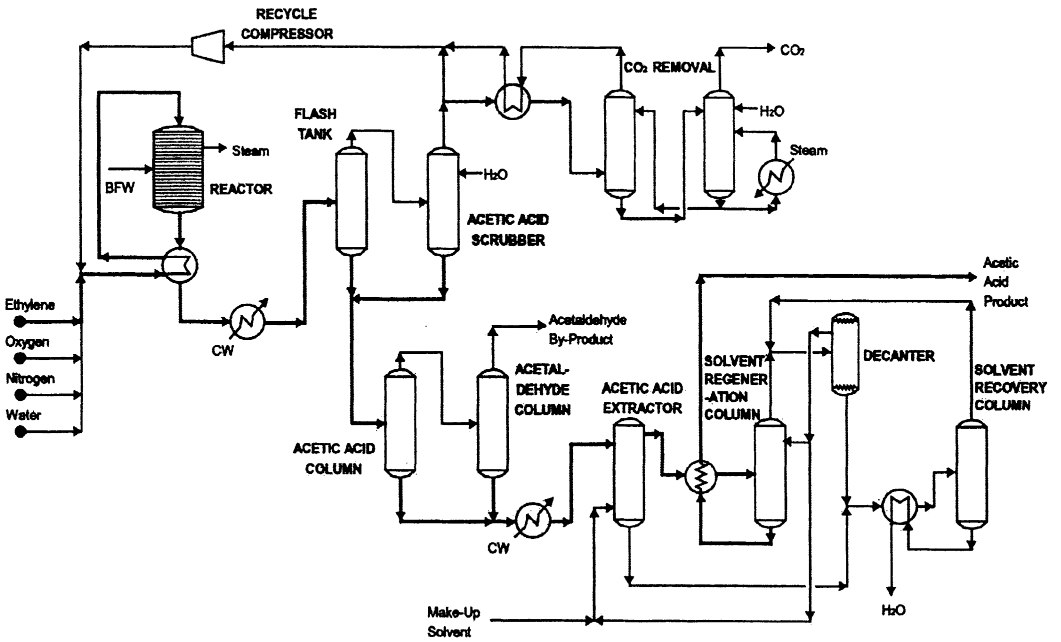


Fig. 10.15. Acetic acid via direct ethylene oxidation. (*Chem Systems Report No. 99/0055. Copyright Nexant Chem Systems, Inc. and used by permission of the copyright owner.*)

of acetic acid and methanol, is reacted with carbon monoxide in the presence of a promoted rhodium-iodide catalyst. Figure 10.17 illustrates this process exclusive of esterification to make methyl acetate.

The greatest use of acetic anhydride is in esterifying cellulose to cellulose acetate for application as cigarette filter tow and in textiles. In the United States, acetic anhydride is manufactured by cellulose acetate manufacturers and largely used internally. Other products using acetic anhydride as a raw material are mostly mature with low growth rates; they include triacetin, plastic modifiers and intermediates for pharmaceuticals, herbicides, pesticides, and dyes for polyolefins. Growth in production was projected to be 0.8 percent/year in the United States through 2003.

Vinyl Acetate. Vinyl acetate (VAM, for vinyl acetate monomer) production is the largest consumer of acetic acid worldwide. In North America, vinyl acetate production in 2000 was 1.7 billion lb. Growth in North America in the period 2000–2005 is expected to be 1.0 percent/year and for the world, 2.4 percent/year.

Production of vinyl acetate is based primarily on vapor phase oxidative addition of acetic acid to ethylene. Figure 10.18 illustrates the process.

VAM finds exclusive use as a monomer or raw material for polymers and copolymers; and latex paints are the largest use for poly(vinyl acetate) (PVA) emulsions. Because latex paints cure without appreciable solvent emissions, regulatory pressures against such emissions favor the use of latex paints over solvent-based coatings. Adhesives are the second largest consumers of PVA emulsions, with a range of applications from packaging and wallboard to consumer "white" glue.

In the second major use of VAM, PVA is converted to poly(vinyl alcohol) (PVOH) by a transesterification reaction with methanol, giving methyl acetate as coproduct. PVOH finds its major end use in textile sizing and adhesives. Further reaction of PVOH with butyraldehyde or formaldehyde gives polyvinyl butyral (PVB) or polyvinyl formal, which together constitute the third largest consumption of VAM. PVB is used almost exclusively in the adhesive laminating inner layer in safety glass.

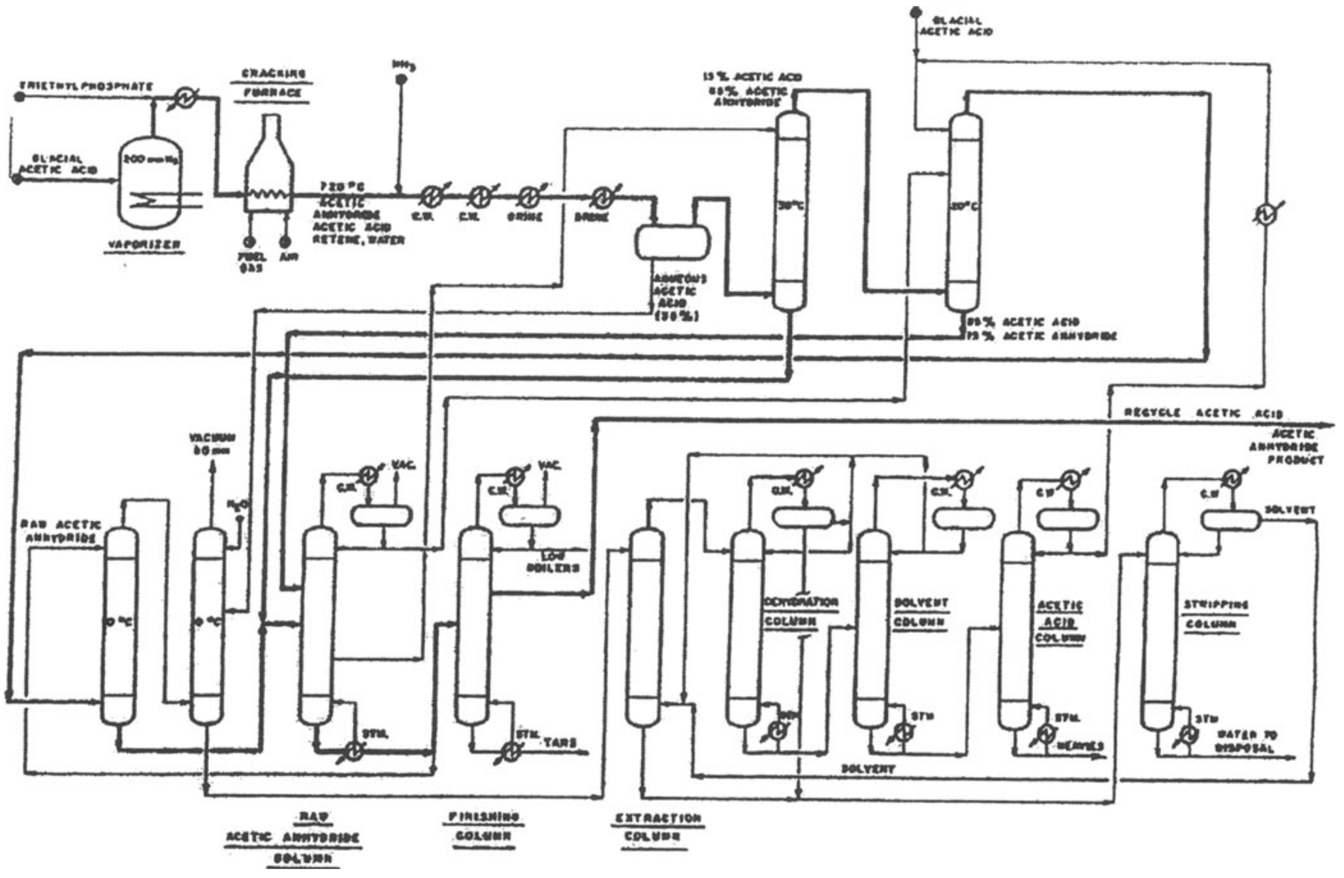


Fig. 10.16. Acetic anhydride from acetic acid ketene process. (*Chem Systems Report No. 97/98-1. Copyright Nexant Chem Systems, Inc. and used by permission of the copyright owner.*)

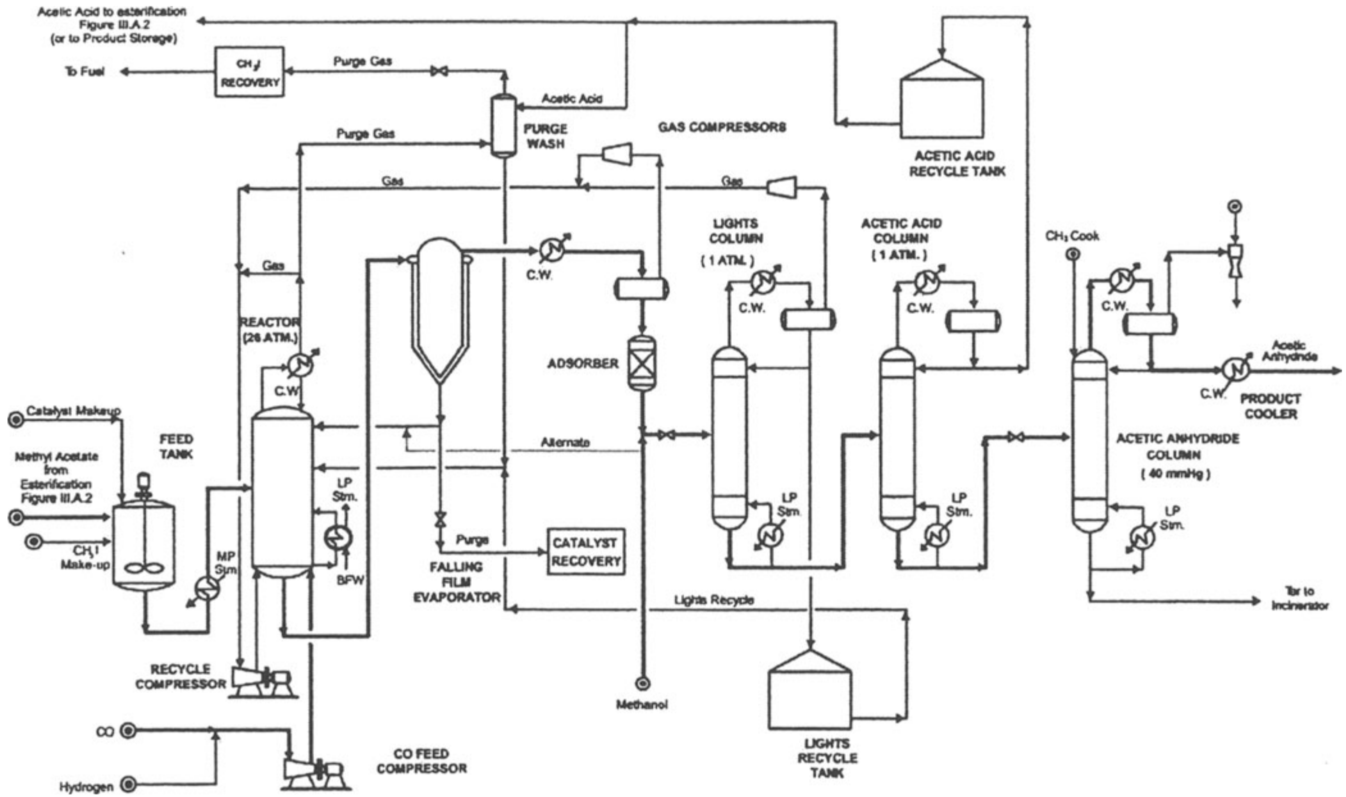


Fig. 10.17. Acetic anhydride by carbonlyation of methyl acetate. (*Chem Systems Report No. 97/98-1. Copyright Nexant Chem Systems, Inc. and used by permission of the copyright owner.*)

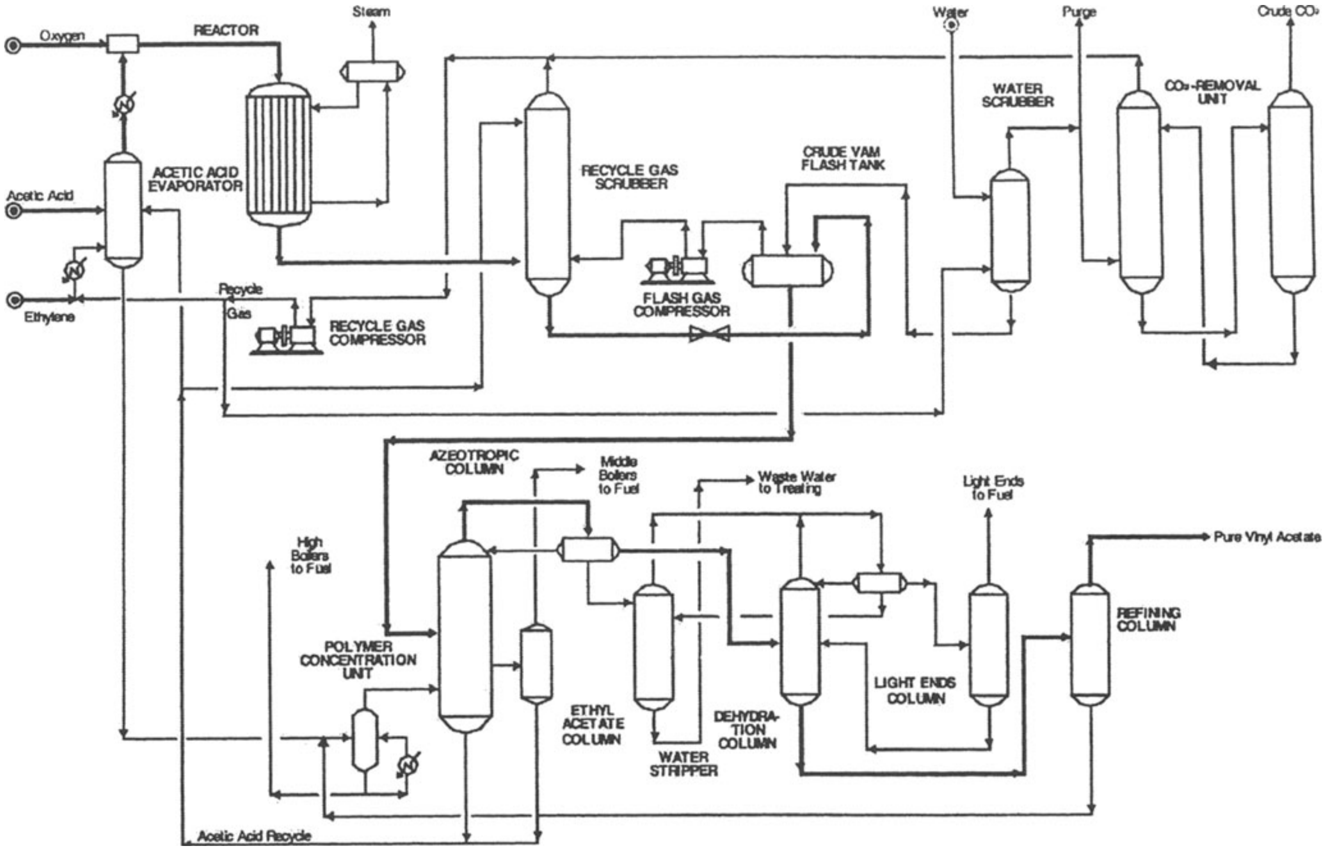


Fig. 10.18. Vapor phase vinyl acetate from ethylene process. (*Chem Systems Report No. 98/99-S3. Copyright Nexant Chem Systems, Inc. and used by permission of the copyright owner.*)

Ethylene Oligomers (Alpha Olefins) and Linear Primary Alcohols

Linear primary alcohols and alpha olefins in the C_6–C_{18} range have enjoyed remarkable growth in the last three decades. As esters, the C_6–C_{10} alcohols are used for plasticizing PVC. In the C_{12}–C_{18} range, the alcohols are used to make readily biodegradable surfactants of various types such as ethoxylates (nonionic), alcohol sulfates, and sulfates of ethoxylates (anionic). Alpha olefins are used as polyethylene comonomer (33%) and as raw materials for detergent alcohols (22%), oxo alcohols (10%), and lubricants and lube oil additives (18%).

Production of linear primary alcohols and production of alpha olefins are accomplished by similar reactions in which ethylene is oligomerized by organometallic catalysts based on aluminum alkyls such as triethylaluminum. The two processes are distinguished by the way in which the growing hydrocarbon chain is removed from the catalyst center. In the case of the alpha olefin products, ethylene growth to a hydrocarbon chain of a few or many two-carbon units is interrupted when the hydrocarbon on aluminum is displaced as an alpha olefin by exchange with fresh ethylene. Thus the aluminum alkyl is regenerated, and chain growth starts again. In production of alpha alcohols, the hydrocarbon group on the aluminum catalyst is cleaved by oxygen at the sensitive carbon–aluminum bond to give aluminum oxide and an alcohol. Figures 10.19 and 10.20 illustrate production schemes for alpha alcohols and alpha olefins, respectively.

Demand for alpha olefins in North America in 1999 totaled nearly 2.7 billion. The rate of growth through 2004 is expected to be 5.7 percent/year.

Ethylene–Propylene Elastomers

Ethylene propylene copolymer and terpolymer rubbers (EPRs) are produced at the rate in excess of two billion pounds per year worldwide. Of this, 41 percent is in North America, 27 percent in Western Europe, and 23 percent in Japan.

EPR is produced by polymerization of a mixture of ethylene and propylene and optionally a small amount of a nonconjugated diene such as ethylidene norbornene, norbornene, 1,4-hexadiene, or dicyclopentadiene. Two processes, one a solution and the other a suspension process, are employed. They use organometallic catalysts, the most common being products of combining (organo)vanadium halides with alkyl aluminum or alkyl aluminum halides. The resulting catalysts are deactivated by water and alcohols.

The comonomer diene confers sulfur vulcanizability on the elastomer. Otherwise, a peroxide cure is required for cross-linking. The polymers are readily oil-extended with 20–50 percent oil for many applications. Some uses result from the ability of these products to resist oxidation by ozone.

Applications of ethylene–propylene copolymers and terpolymers include: automotive (the major use area), thermoplastic olefin elastomers, single-ply roofing, viscosity index improvers for lube oils, wire and cable insulation, hose, appliance parts, and polymer modification.

Propionaldehyde

Propionaldehyde is produced by the oxo reaction of ethylene with carbon monoxide and hydrogen. n-Propyl alcohol is produced by hydrogenation of propionaldehyde, and propionic acid is made by oxidation of propionaldehyde.

n-Propyl alcohol is used as solvent in printing inks and as an intermediate in the preparation of agricultural chemicals. Propionic acid is used as a grain preservative as, for example, in preventing spoilage of wet corn used as animal feed. The use of propionic acid as a grain preservative is an alternative to drying by heating, which consumes fuel, and is considered mostly when fuel is expensive.

Other Ethylene Uses

Some lesser-volume ethylene uses are in:

- *Agriculture*, as a ripening agent for fruits and vegetables
- *Vinyl toluene* for use in unsaturated polyester resins

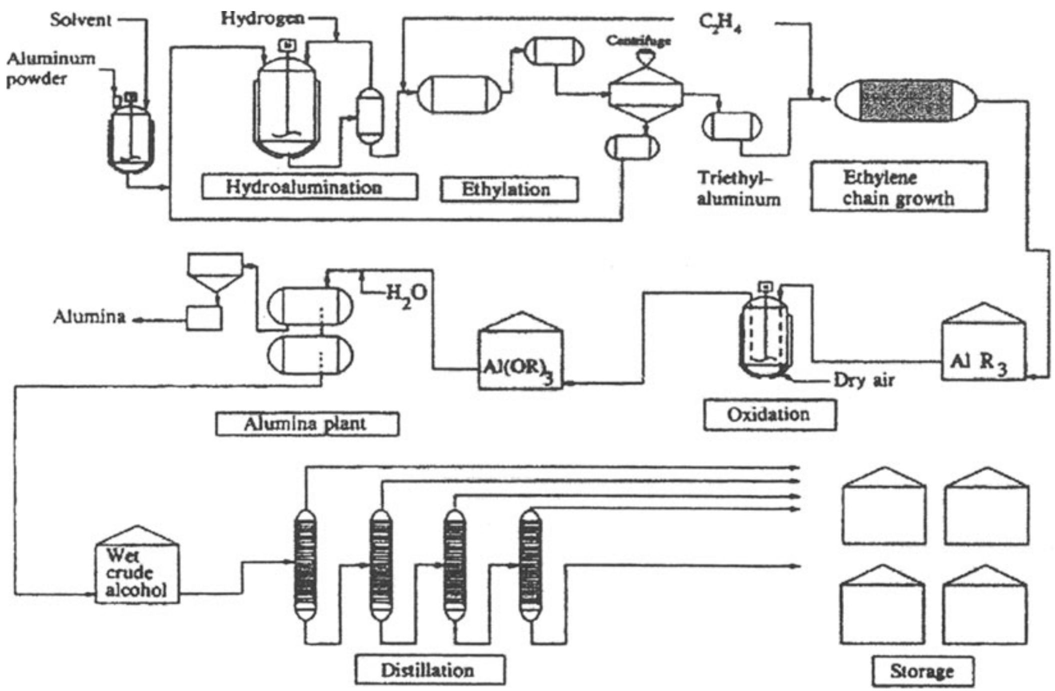


Fig. 10.19. Flow diagram of a process for primary alcohols from ethylene. (*Encyclopedia of Chemical Technology, Kirk and Othmer, Web site ed., alcohols, higher aliphatic, synthetic processes, manufacture, 2002. Copyright by John Wiley & Sons, Inc. and reproduced by permission of the copyright owner.*)

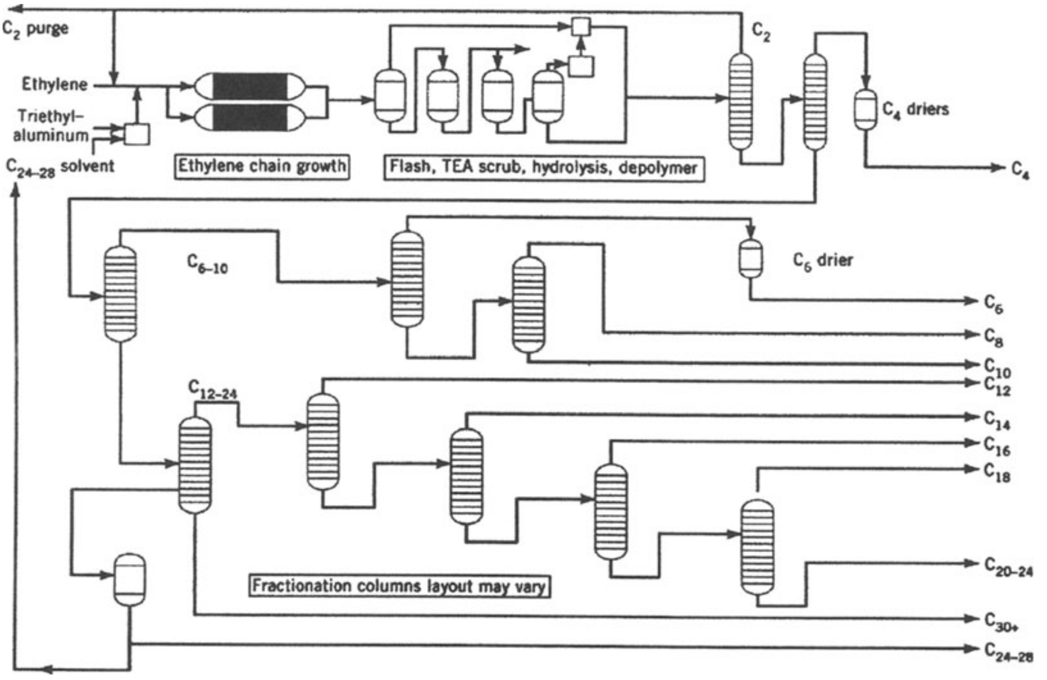


Fig. 10.20. Flow scheme of a process for alpha-olefins from ethylene. (*Encyclopedia of Chemical Technology, Kirk and Othmer, Web site ed., olefins, higher, manufacture, 2002. Copyright by John Wiley & Sons, Inc. and reproduced by permission of the copyright owner.*)

- *Aluminum alkyls* used in making organometallic catalysts and as initiators for processes such as ethylene–propylene rubber, polybutadiene, low-pressure polyethylene, and ethylene oligomerization to make alpha-olefins and C_6–C_{18} alcohols
- *Diethyl sulfate* made from sulfuric acid and ethylene and used as an alkylating agent in many applications
- *Alkylation of anilines* for chemical intermediates used in pesticides, pharmaceuticals, dyes, and urethane comonomers

CHEMICALS DERIVED FROM PROPYLENE

Propylene consumption for chemical synthesis in 1998 in the United States was 30 billion lb. This demand was exceeded by that of only one other synthetic organic chemical, ethylene. The demand was projected to grow at about 4.7 percent/year through 2003. Major uses of propylene are in polypropylene, acrylonitrile, propylene oxide, and cumene. A breakdown of propylene consumption by product is:

Polypropylene	45%
Acrylonitrile	12
Propylene oxide	11
Cumene	8
Oxo alcohols	8
Isopropyl alcohol	4
Oligomers	4
Acrylic acid	5
Export, other	3

Propylene is produced as a coproduct of ethylene cracking and is a product of petroleum refinery operations.

Polypropylene

More than 40 years after its introduction, polypropylene is the largest chemical consumer of propylene in the United States. It is produced primarily by a bulk or gas phase process, with the older slurry process still used by some. Because of its greater stiffness relative to polyethylene, polypropylene is used for more demanding applications. This stiffness is not without a drawback in the form of increased brittleness, which can be moderated through incorporation of ethylene by copolymerization. Its major uses are in fibers and injection molding. Chapter 15 reviews polypropylene in some detail.

Acrylonitrile

In 1960, almost all of the 260 million lb annual production of acrylonitrile was based on acetylene. Ten years later, the volume had risen to 1.1 billion lb, which was based almost entirely on an ammoxidation process with ammonia, propylene, and air as feeds. However, in the latter 1980s the growth rate had slowed considerably.

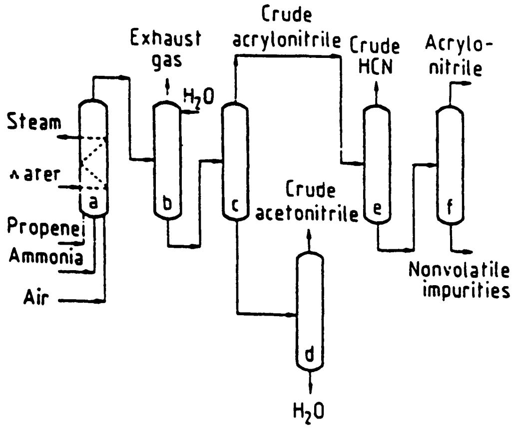
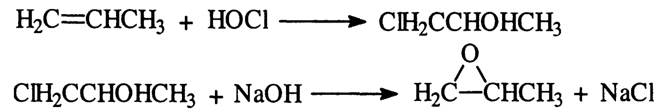


Fig. 10.21. Simplified diagram of the Sohio acrylonitrile process: (a) fluidized-bed reactor; (b) absorber column; (c) extractive distillation column; (d) acetonitrile stripping column; (e) lights fractionation column; (f) product column. (*Patrick W. Langvardt, Ullmann's Encyclopedia of Industrial Chemistry, W. Gerhartz (Ed.), 5th ed. Vol. A1, p.179, 1985. Copyright Wiley-VCH Verlag GmbH & Co KG. Used with permission of the copyright owner and the author.*)



$$H_2C{=}CHCH_3 + HOCl \longrightarrow ClH_2CCHOHCH_3$$

$$ClH_2CCHOHCH_3 + NaOH \longrightarrow H_2\overset{O}{C{-}C}HCH_3 + NaCl$$

The air, ammonia, propylene process for acrylonitrile is shown in Fig. 10.21. The main reaction is given below.

$$2H_2C{=}CHCH_3 + 2NH_3 + 3O_2 \rightarrow 2H_2C{=}CHCN + 6H_2O$$

In this process the highly exothermic oxidation is performed in a fluidized bed to facilitate heat removal. Note also that acetonitrile and hydrogen cyanide are byproducts. In the case of hydrogen cyanide, this source is of major commercial importance.

Acrylic fibers are by far the major end use for acrylonitrile. They find use primarily in fabrics for clothing, furniture, draperies, and carpets. The second largest consumer of acrylonitrile is acrylonitrile–butadiene–styrene (ABS) and styrene acrylonitrile (SAN) resins. ABS is useful in industrial and construction applications, and the superior clarity of SAN makes it useful in plastic lenses, windows, and transparent household items.

Propylene Oxide

Propylene oxide (PO) is one of the most important organic chemicals from the propylene family. The global capacity was almost 11 billion lb in 1998. PO production in the United States reached 4.2 billion lb in 1998. Polyurethane polyether polyols are the largest usage, which contributed to about 60 percent of domestic PO consumption. It is also used to make propylene glycol, glycol ethers, polyglycols, glycerine, surfactants, and amino propanols.

PO was manufactured by the chlorohydrin route first during World War I in Germany by BASF and others. This route (below) involves reaction of propylene with hypochlorous acid followed by treatment of the resulting propylene chlorohydrin with a base such as caustic or lime. The products of the second reaction are PO and sodium or calcium chloride (Fig. 10.22).

Until 1969, the chlorohydrin process was the only PO process, and The Dow Chemical

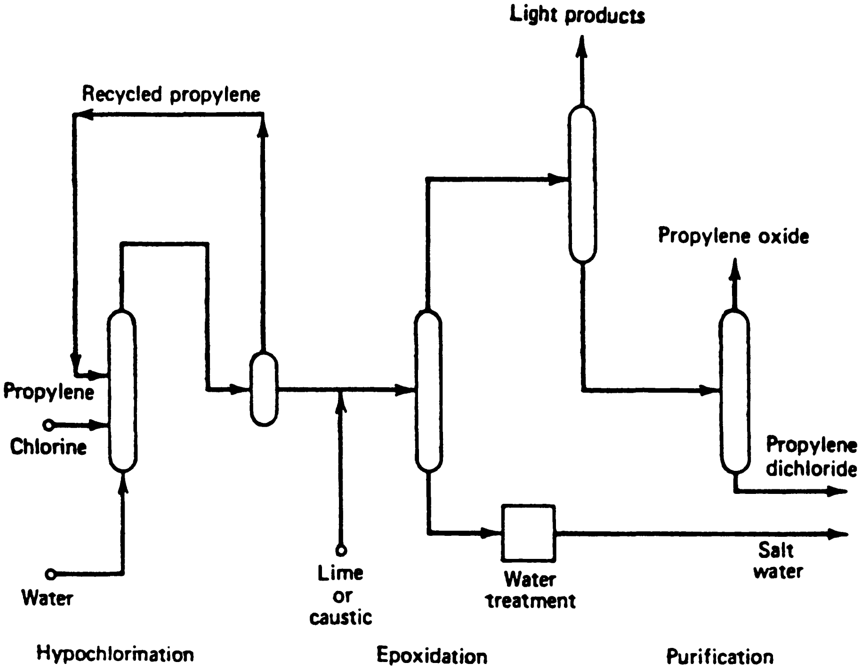
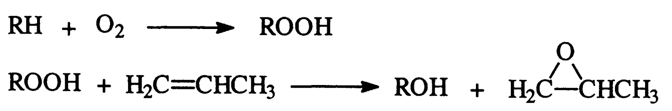


Fig. 10.22. Chlorohydrin process. (*Encyclopedia of Chemical Technology, Kirk and Othmer. 3rd ed., Vol. 19, p. 255, 1980. Copyright by John Wiley & Sons, Inc. and used by permission of the copyright owner.*)

Company was the largest producer. In that year, Oxirane brought on stream the first peroxidation process involving catalyzed epoxidation of propylene with tert-butyl hydroperoxide. In 1977, Oxirane (later Arco Chemical) commercialized a process which employed ethylbenzene hydroperoxide as the epoxidizing agent and produced PO and styrene (Fig. 10.23).



$$RH + O_2 \longrightarrow ROOH$$

$$ROOH + H_2C{=}CHCH_3 \longrightarrow ROH + H_2C\overset{O}{—}CHCH_3$$

The peroxide processes convert propylene to its epoxide while reducing the hydroperoxide to the corresponding alcohol (e.g., tert-butyl alcohol or phenyl methyl carbinol). Because the processes produce the alcohols in larger amounts than PO, their success depends upon finding uses for the alcohols. tert-Butyl alcohol can be dehydrated to isobutylene and hydrogenated to isobutane for recycle to the PO process. It can also be converted to MTBE. Phenyl methyl carbinol can be dehydrated to styrene, making this process a more involved conversion of ethyl benzene to styrene than is direct dehydrogenation.

Propylene Glycols. PO is converted to mono-, di-, and tri-glycols by a hydrolysis. It is similar to the hydrolysis of ethylene oxide to mono- and di-ethylene glycol. The propylene glycols are used for many of the same applications as the corresponding products derived from ethylene oxide. Because of their very low toxicity, they also can be used for pharmaceutical, cosmetic, food applications, liquid detergent, tobacco humectant, deicing fluid, and antifreezes. In 1999, the U.S. consumption for mono-, di-, and tri-propylene glycols were 1.08 billion lb, 125, and 16 million lb, respectively.

Isopropyl Alcohol

Isopropyl alcohol (IPA) has been called the first petrochemical. Both historically and today, it is

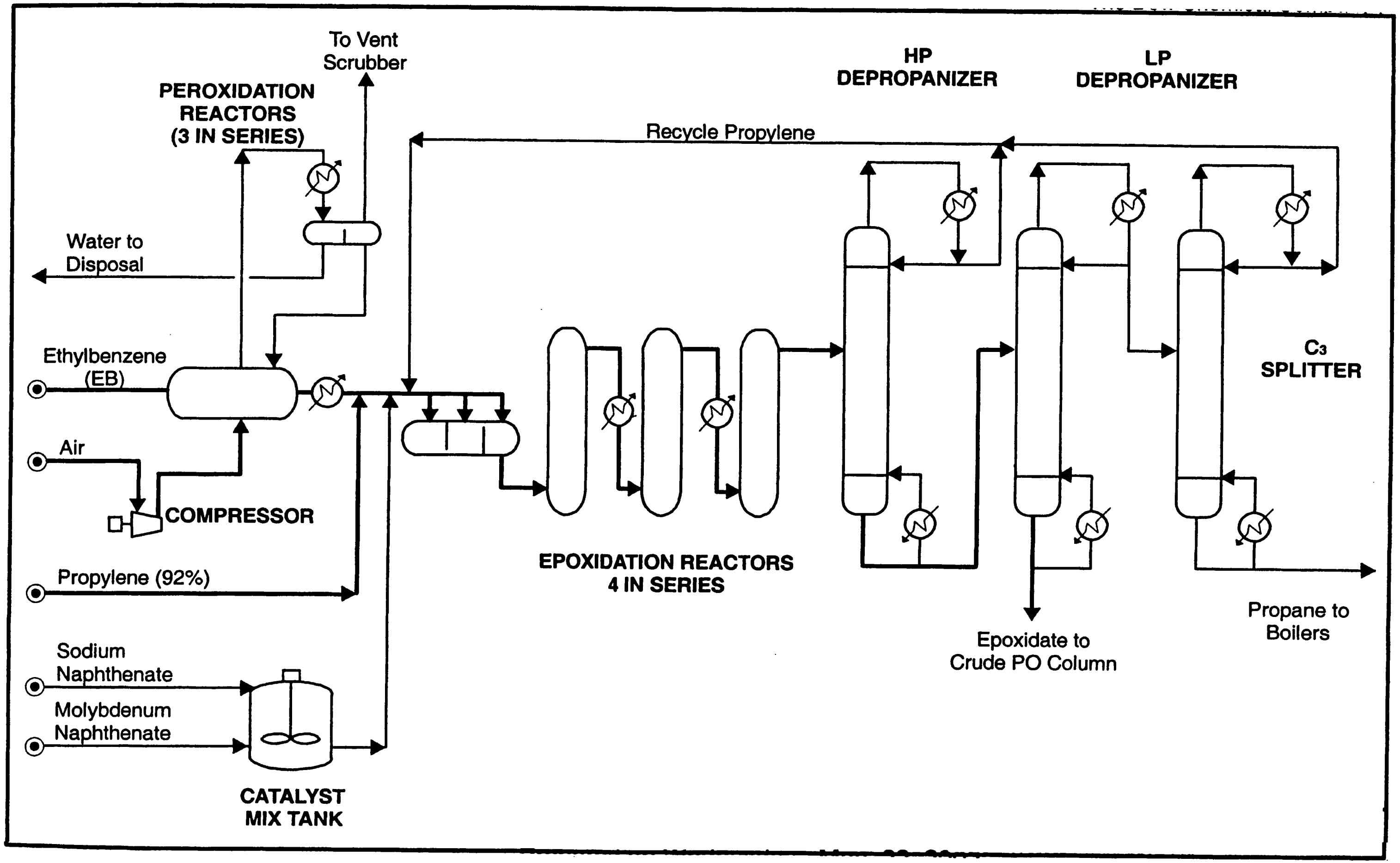


Fig. 10.23. Styrene/PO via peroxidation and epoxidation. (*Chem Systems Report No. 97/98-7. Copyright Nexant Chem Systems, Inc. and used by permission of the copyright owner.*)

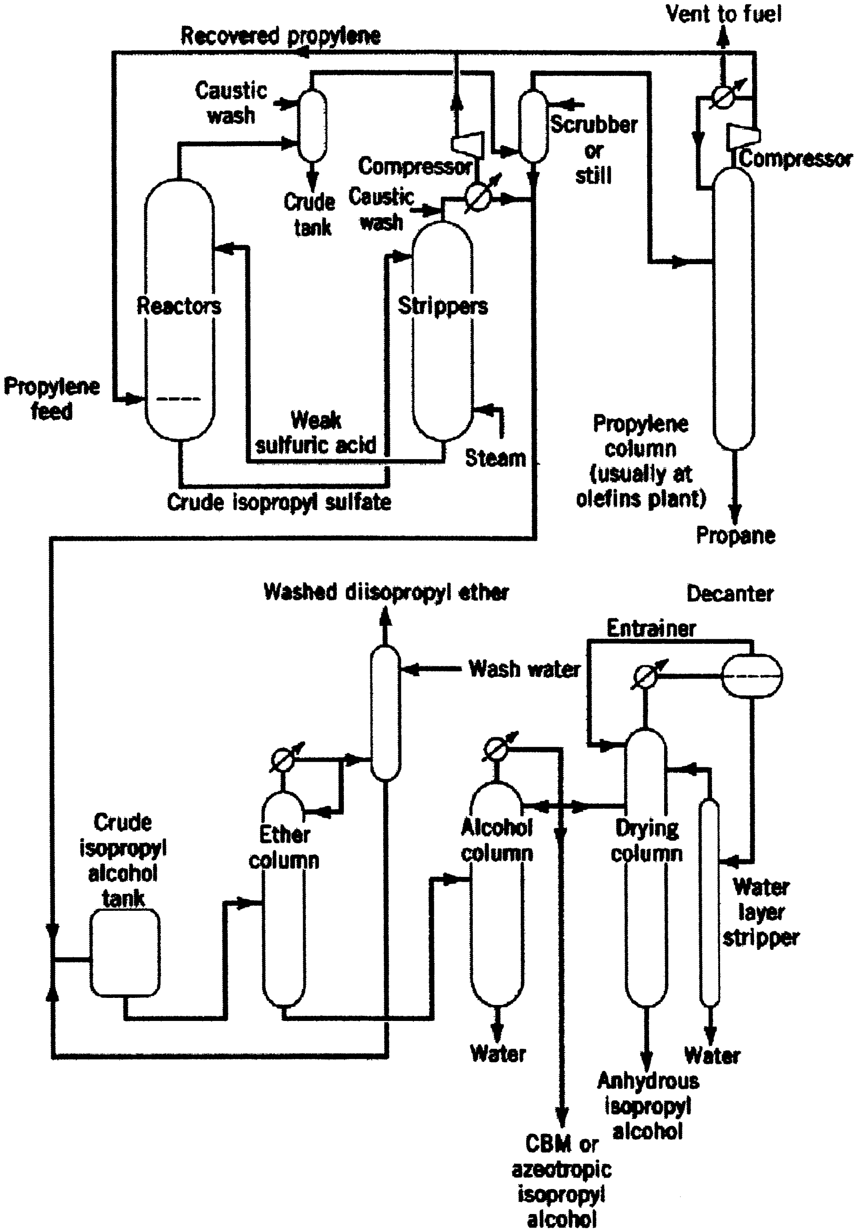


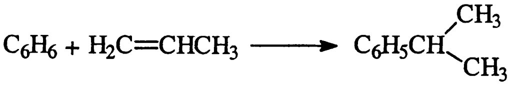
Fig. 10.24. Flow scheme of a process for isopropanol. (*Encyclopedia of Chemical Technology, Kirk and Othmer, Web site ed., isopropyl alcohol, manufacture, 2002. Copyright by John Wiley & Sons, Inc. and reproduced by permission of the copyright owner.*)

prepared by sulfuric acid-mediated indirect hydration of propylene (see Fig. 10.24). Originally it was the source of most of the acetone used in the world. Now, this route must compete with acetone derived from the cumene oxidation process, in which cumene is converted to equimolar amounts of phenol and acetone. The amount of IPA used for producing acetone declined from 47 percent in 1978 to 7 percent in 2001. IPA can also be made by hydrogenation of acetone, but the large capacity for IPA by indirect hydration is a disincentive for this application. Direct hydration of propylene in a vapor-phase, catalytic process is also commercially practiced. This is similar to hydration of ethylene to make ethanol. Relative to the sulfuric acid-mediated process, it offers the advantage of decreased corrosion. However, it suffers from a requirement for a pure propylene feed, whereas the former process can be used with a dilute, refinery stream.

Isopropyl alcohol is an excellent solvent with a blend of polar, nonpolar, and hydrogen-bonding character that makes it useful in a broad spectrum of applications. Its moderate volatility makes it convenient for uses involving evaporation or recovery by distillation. Thus, it is no surprise that much of IPA's consumption is for solvent uses. In North America in 1999 about 1.2 billion lb of IPA were consumed. Major uses were: solvent applications, 47 percent; isopropylamines, 15 percent, esters and ketones, 20 percent; and others, including pharmaceuticals, 18 percent. The total demand in 1999 was significantly less than the 1.9 billion lb recorded for 1978. This downward trend is not unique to IPA and is primarily a result of regulatory pressure in the United States to decrease emissions of VOCs in coating and other applications.

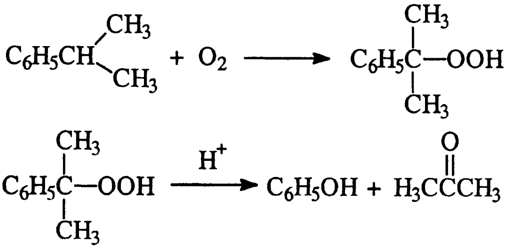
Cumene

Cumene manufacture consumed about 10 percent (2.2 billion lb) of the propylene used for chemicals in the United States in 1998. It is prepared in near stoichiometric yield from propylene and benzene with acidic catalysts (scheme below). Many catalysts have been used commercially, but most cumene is made using a "solid phosphoric acid" catalyst. Recently, there has been a major industry shift to zeolite-based catalyst. The new process has better catalyst productivity and also eliminates the environmental waste from spent phosphoric acid catalyst. It significantly improves the product yield and lowers the production cost. Cumene is used almost exclusively as feed to the cumene oxidation process, which has phenol and acetone as its coproducts.



$$C_6H_6 + H_2C{=}CHCH_3 \longrightarrow C_6H_5CH(CH_3)_2$$

Acetone. Acetone in commerce is derived mostly from cumene oxidation. This is a two-step process involving oxidation of cumene to the hydroperoxide followed by acid catalyzed decomposition to acetone and phenol:



$$C_6H_5CH(CH_3)_2 + O_2 \longrightarrow C_6H_5C(CH_3)_2{-}OOH$$

$$C_6H_5C(CH_3)_2{-}OOH \xrightarrow{H^+} C_6H_5OH + H_3C\overset{O}{\overset{\|}{C}}CH_3$$

The 1998 U.S. use of acetone was about 2.6 billion lb. Its major uses are methacrylic acid and esters (44%); solvent (17%); bisphenol-A (20%); and aldol chemicals (such as methyl isobutyl ketone) (13%).

Oxo Chemicals

About 8 percent of the propylene converted into chemicals is used to make oxo alcohols such as 1-butanol and 2-ethylhexanol, which are called oxo alcohols because they are derived from olefins by the oxo process, which converts them to aldehydes. (The oxo process was described earlier in this chapter.)

Butyl Alcohols and Aldehydes. Hydroformylation of propylene gives a mixture of n-butyraldehyde and isobutyraldehyde. This mixture is formed approximately in the ratio of 2 : 1 from the high-pressure, cobalt-catalyzed oxo process. There has always been a much greater demand for the linear n-butyraldehyde than the iso product, so it has been necessary to find uses for the latter.

The low-pressure, rhodium-catalyzed oxo process has made the product mix conform to the relative demand for the two aldehydes. This process gives a 10 : 1 ratio of n-butyraldehyde to isobutyraldehyde.

Each aldehyde can be hydrogenated to the corresponding alcohol for use as a solvent or an intermediate for plasticizers and resins. n-Butyraldehyde is also converted to 2-ethylhexanol by sequential condensation and hydrogenation. 2-Ethylhexanol is used to make the phthalate ester, which finds wide use as a plasticizer of PVC.

Propylene Oligomers: Dodecene and Nonene

The manufacturing processes for these materials are very similar to the one for cumene. When nonene is the desired product, additional fractionation is required, the extent of which is determined by product specifications.

In the reactor portion of this process, the olefin stock is mixed with benzene (for cumene) or recycle lights (for tetramer). The resulting charge is pumped to the reaction chamber. The catalyst, solid phosphoric acid, is maintained in separate beds in the reactor. Suitable propane quench is provided between beds for temperature control purposes because the reaction is exothermic.

Dodecene is an intermediate for surfactants, mainly through two routes. One, the larger user, produces dodecylbenzene sulfonate for anionic detergents. The other goes through the oxo process to tridecyl alcohol, which then is converted into a nonionic detergent by the addition of alkylene oxides.

Nonene has two major outlets, the larger being the oxo production of decyl alcohol which is used in the manufacture of esters, and so forth, for plasticizers. The other significant use for nonene is in the manufacture of nonylphenol, an intermediate for the important series of ethoxylated nonylphenol nonionic surfactants.

Acrylic Acid and Esters

Acetylene once was the raw material for commercial production of acrylic acid and esters, but in 1970 production of acrylic acid by oxidation of propylene was first practiced commercially. In a few years, the new process had essentially replaced the old. In 2000, acrylic acid production in the U.S. was of the order of 2.0 billion lb, and that of acrylate esters was of the order of 1.8 billion lb.

The oxidation of propylene is carried out in two stages (Fig. 10.25). Acrolein exiting the first-stage converter can be isolated, or it can be further oxidized to acrylic acid in the second converter. The process is operated with two reaction stages to allow optimum catalyst and process conditions for each step.

$$H_2C{=}CHCH_3 + O_2 \rightarrow H_2C{=}CHCHO + H_2O$$

$$H_2C{=}CHCHO + \tfrac{1}{2}O_2 \rightarrow H_2C{=}CHCO_2H$$

$$H_2C{=}CHCO_2H + ROH \rightarrow H_2C{=}CHCO_2R + H_2O$$

Acrolein is very reactive and has some use as a chemical intermediate, as well as direct use

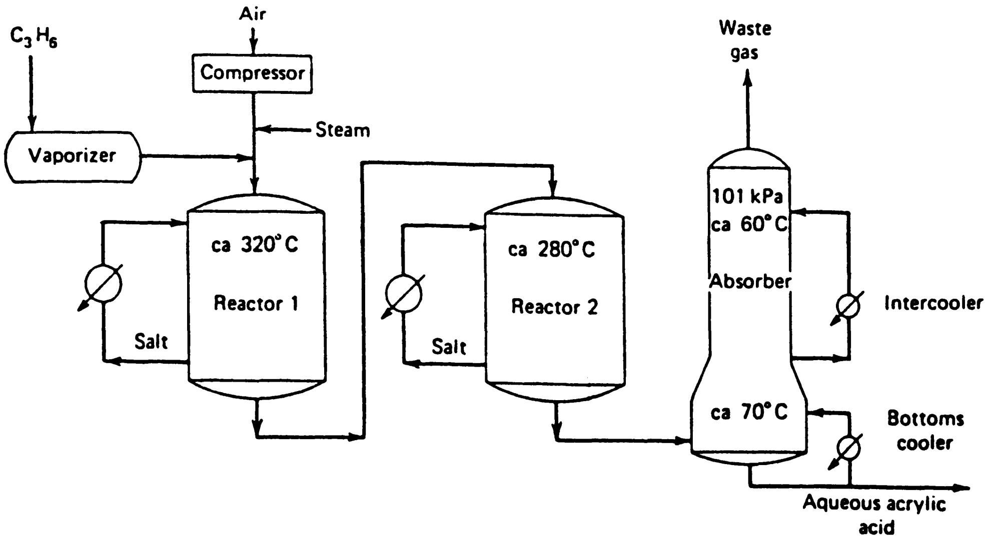


Fig. 10.25. Acrylic acid from oxidation of propylene. (*Encyclopedia of Chemical Technology, Kirk and Othmer, 3rd ed., Vol. 1, p. 339, 1980. Copyright by John Wiley & Sons, Inc. and reproduced by permission of the copyright owner.*)

as an aquatic pest control agent. Most acrolein is converted without isolation to acrylic acid.

Acrylic acid is almost exclusively used directly, or after conversion to an ester, as a monomer. Acrylate esters are produced by normal esterification processes. However, in dealing with acrylic acid, acrolein, or acrylates, unusual care must be taken to minimize losses due to polymerization and other side reactions such as additions of water, acids, or alcohols across the reactive double bond. Polyacrylic acids find use in superabsorbers, dispersants, and water treatment. The polyesters are used in surface coatings, textile fibers, adhesives, and various other applications.

Epichlorohydrin

Epichlorohydrin (ECH) is made from propylene, the majority is via allyl chloride intermediate. Total consumption in 1999 was about 600 million lb. Uses for ECH include epoxy resins (65%), synthetic glycerin (22%), and others (paper treatment, specialty ionic exchange resin, glycerol, and glycidol derivatives).

The key reaction in this manufacturing process is the hot chlorination of propylene, which fairly selectively gives substitution to methyl group rather than the addition to the double bond. In this chlorination step, fresh propylene is first mixed with recycle propylene. This mixture is dried over a desiccant, heated to 650–700°F, and then mixed with chlorine (C_3H_6 to Cl_2 ratio is 4 : 1) and fed to a simple steel tube adiabatic reactor. The effluent gases (950°F) are cooled quickly to 120°F and fractionated. The yield of allyl chloride is 80–85 percent.

Hypochlorous acid is then reacted with the allyl chloride at 85–100°F to form a mixture of dichlorohydrins. The reactor effluent is separated, the aqueous phase is returned to make up the hypochlorous acid, and the nonaqueous phase containing the dichlorohydrins is reacted with caustic or a lime slurry to form ECH which is steam-distilled out and given a finishing distillation.

ECH is used to manufacture epoxy resins for surface coating, castings, and laminates. It is hydrolyzed in 10 percent caustic to make synthetic glycerin (see "Glycerin"). ECH is also employed as a raw material for the manufacture and glycidol derivatives used as plasticizers, stabilizers, surface active agents, and intermediates for further synthesis. The polyamide/ECH resin (which is used in the paper industry to improve the wet strength) has had very good growth in the past few years. The average growth rate for ECH for the period 1990–1999 is about 3 percent and the trend is expected to continue.

Glycerin

Glycerin can be prepared from propylene (via ECH) or as a byproduct from fat and oil hydrolysis of the soap industry. Before 1949 all glycerin was obtained from hydrolysis of fatty triglycerides. In the past 50 years, the synthetic glycerin is to serve the portion of demand not satisfied by natural glycerin. In 1998, the U.S. production for natural versus synthetic is about 2.4 : 1. The diagram of different routes for the manufacture of glycerin is in Fig. 10.26.

In 1998, glycerin consumption in the United States was about 380 million lb. The average annual growth for 1990–1998 is about 2.3 percent/year. About 80 percent of U.S. usage of glycerin is in foods, pharmaceuticals, personal care, cosmetics, tobacco, and similar applications. This reflects its extremely low toxicity, sweet taste, and moisturizing and lubricating properties. Chemical uses for glycerin include use as a "starter" alcohol for polyols made by alkoxylation with propylene oxide and ethylene oxide, and as raw material for alkyd polymers, plasticizers, and explosives.

Glycerin by the Epichlorohydrin Process. In the ECH process, synthetic glycerin is produced in three successive operations, the end products of which are allyl chloride, ECH, and finished glycerin, respectively. Glycerin is formed by the hydrolysis of ECH with 10 percent caustic. Crude glycerin is separated from this reaction mass by multiple-effect evaporation to remove salt and most of the water. A final vacuum distillation yields a 99+ percent product.

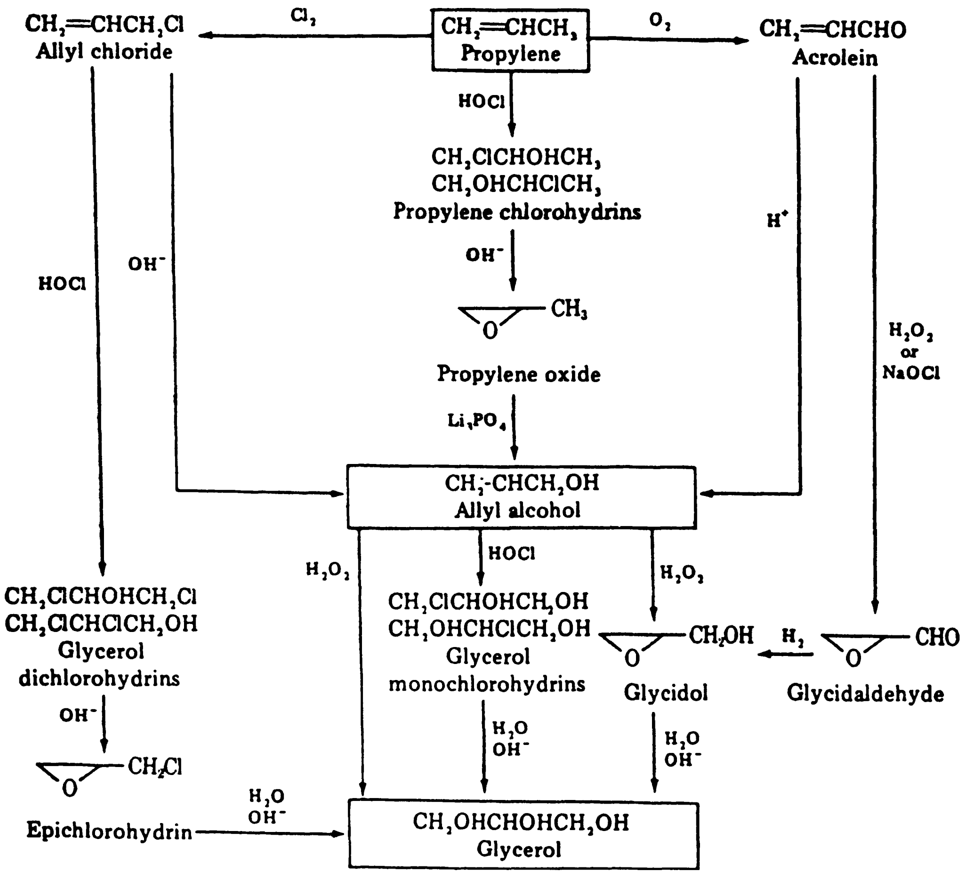


Fig. 10.26. Routes for the manufacture of glycerin. (*Encyclopedia of Chemical Technology, 3rd ed., Vol. 11, p. 923, 1980. Copyright by John Wiley & Sons, Inc. and reproduced by permission of the copyright owner.*)

CHEMICALS DERIVED FROM BUTANES AND BUTYLENES

Saturated four-carbon hydrocarbons (butanes) occur in natural petroleum products such as crude oil and the heavy vapors in wet natural gas. The saturated C_4s are also produced from other hydrocarbons during the various petroleum refining processes. The butylenes—unsaturated C_4s—do not occur in nature, but are derived from butanes or other hydrocarbons either deliberately or as by-products. The complex interrelationships of C_4 hydrocarbons, including their production and use, are described in Fig. 10.27.

The chemical uses of the C_4 hydrocarbons still account for only a small fraction of the available material. To put the volume of C_4s used in chemical manufacture in perspective with the amount used for fuel, one finds that approximately 12 percent of the butanes and about 30 percent of the butylenes were used as chemical raw materials. The trends that affect availability of C_4 hydrocarbons for chemical and energy end uses are determined by the natural gas processors, petroleum refiners, and, to a growing extent, ethylene manufacture.

Changes in technology and in the availability of optimum feedstocks have far-reaching effects on the entire product mix. For example, when the availability of LPG and ethane for ethylene manufacture has decreased, n-butane and the higher crude cuts have been used, and the proportion of by-product butadiene has increased.

The spectrum of products which can be derived from the four-carbon hydrocarbons is shown in Fig. 10.28. Several of these can also

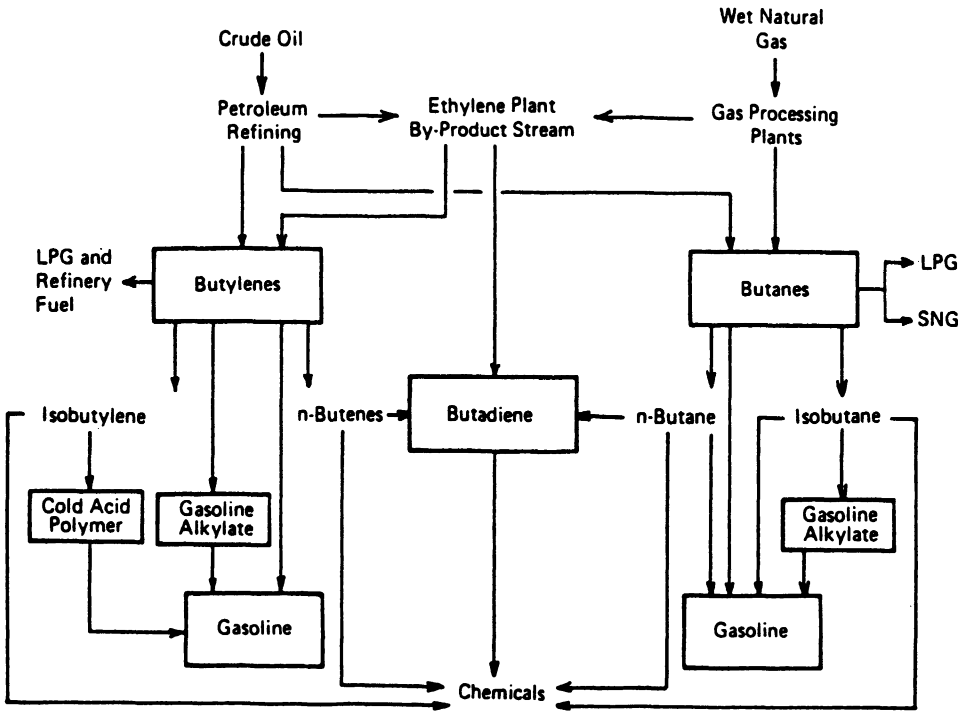


Fig. 10.27. Origins, interrelationships, and end uses of C_4 hydrocarbons. (*Reproduced from Chemical Economics Handbook, p. 300200A,* Stanford Research Institute, Menlo Park, CA, 1980, March.)

be produced from other raw materials and are described elsewhere in this chapter.

n-Butane Derivatives

n-Butane can be obtained from natural gas and from refinery hydrocracker streams. Most of the n-butane goes into fuel additive uses. The major chemical use is as a feedstock for ethylene production by cracking. The other important chemical uses for butane are in oxidation to acetic acid and in the production of maleic anhydride. In the past, butane also was the main feedstock for the production of butadiene by dehydrogenation, but it has been replaced by coproduct butadiene obtained from ethylene production.

Ethylene. The largest potential chemical market for n-butane is in steam cracking to ethylene and coproducts. n-Butane is a supplemental feedstock for olefin plants and has accounted for 1–4 percent of total ethylene production for most years since 1970. It can be used at up to 10–15 percent of the total feed in ethane/propane crackers with no major modifications. n-Butane can also be used as a supplemental feed at as high as 20–30 percent in heavy naphtha crackers. The consumption of C_4s has fluctuated considerably from year to year since 1970, depending on the relative price of butane and other feedstocks. The yield of ethylene is only 36–40 percent, with the other products including methane, propylene, ethane, and butadiene, acetylene, and butylenes. About 2–3 billion lb of butane are consumed annually to produce ethylene.

Acetic Acid. Acetic acid is the most important carboxylic acid produced industrially. The annual production in the United States in 1999 was almost 15.7 billion lb. As with many compounds produced on a large scale, acetic acid has several different commercial processes. The carbonylation of methanol is now the dominant route. (This process was described earlier in this chapter in the section "Methanol".) The oxidation of acetaldehyde, ethanol, and butane are also important. The percent world capacity for virgin acetic acid

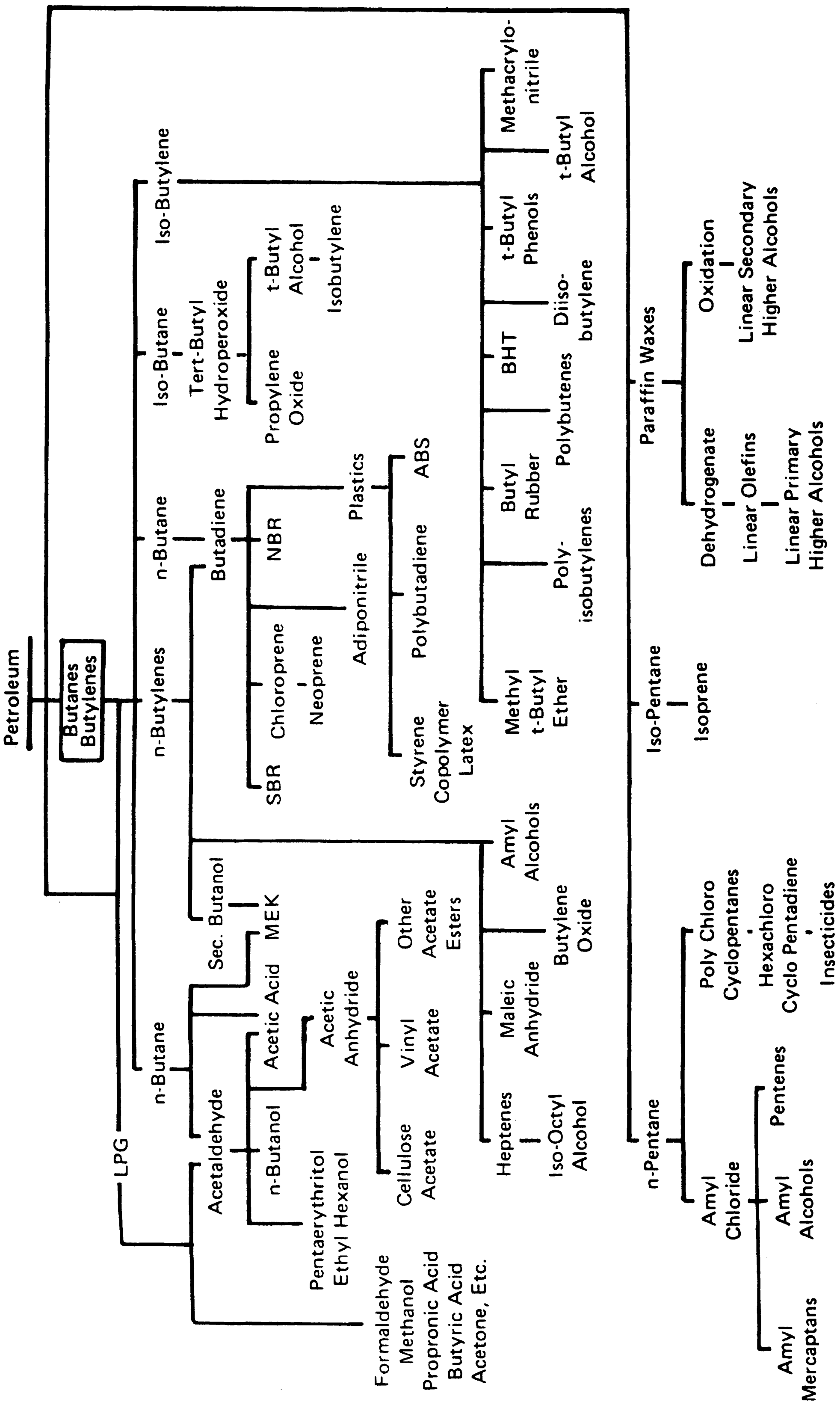


Fig. 10.28. Chemicals from butanes, butylenes, LPG, and higher aliphatic hydrocarbons.

by different starting materials are: methanol (60%), acetaldehyde (18%), ethanol (10%), and butane (8%).

The liquid-phase oxidation (LPO) of light saturated hydrocarbons yields acetic acid and a spectrum of coproduct acids, ketones, and esters. Although propane and pentanes have been used, n-butane is the most common feedstock because it can ideally yield two moles of acetic acid. The catalytic LPO process consumes more than 500 million lb of n-butane to produce about 500 million lb of acetic acid, 70 million lb of methyl ethyl ketone, and smaller amounts of vinyl acetate and formic acid. The process employs a liquid-phase, high-pressure (850 psi), 160–180°C oxidation, using acetic acid as a diluent and a cobalt or manganese acetate catalyst.

Figure 10.29 shows the flowsheet for this process. From the reactor, the product mixture is passed through coolers, and then through separators where the dissolved gases are released. The major components of the oxidized crude are acetic acid, methyl ethyl ketone, and various alcohols and acids. The initial reaction involves formation of butane-2 hydroperoxide, which is not isolated. Further oxidation and decomposition of the resultant radicals produce acetic acid.

Concurrently, the hydroperoxide may be converted to methyl ethyl ketone (MEK). If the initial radical attack is at the primary rather than the secondary carbon, the process makes propionic and formic acids. Reaction conditions can be changed to produce more MEK at the expense of some acetic acid. The maximum acetic acid/MEK ratio is 6.5–7 on a weight basis. If ethyl acetate is also formed, the ratio can go down to acetic acid/(ethyl acetate + MEK) of 3.6–4, with MEK being about 55 percent of the byproduct.

A portion of the acetic acid, which is the major product, can be converted in a separate unit to acetic anhydride. Acetic anhydride may be produced from acetic acid, acetone, or acetaldehyde. With both acetic acid and acetone the initial product is ketene. The ketene is highly reactive and reacts readily

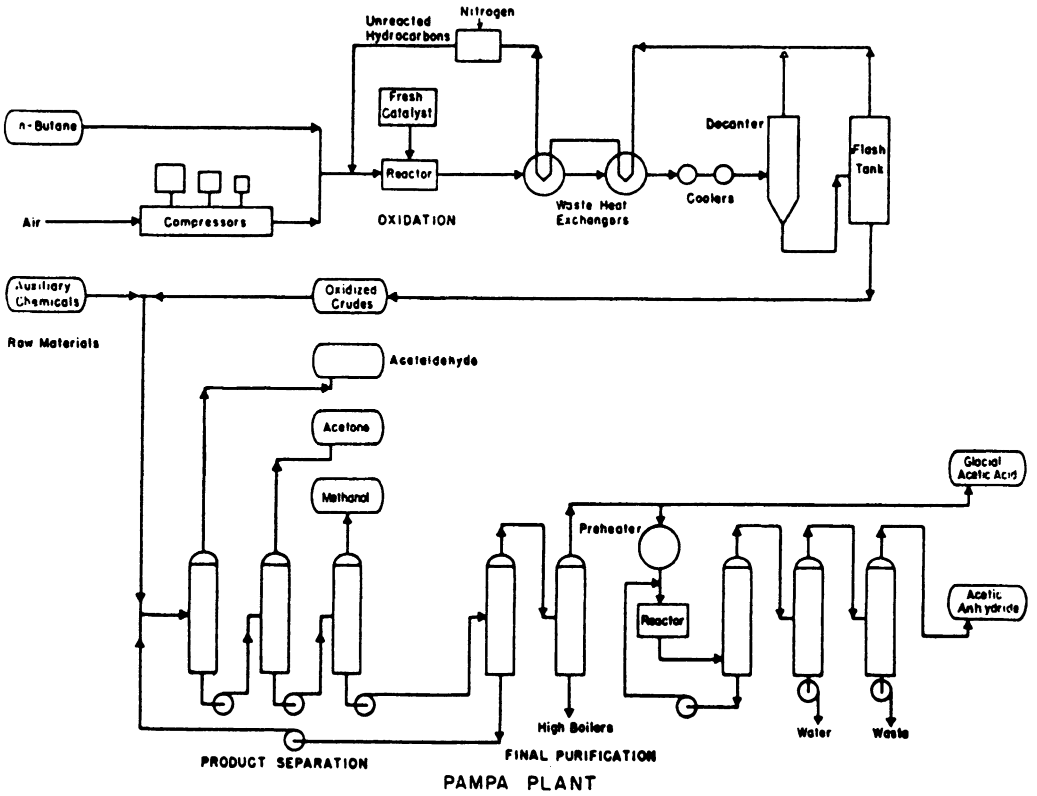


Fig. 10.29. Oxidation of butane. (*Pet. Ref.* **38**, *no. 11, 234, 1959. Copyright 1959 by Gulf Publishing Co.*)

with acetic acid to form acetic anhydride. All this takes place at 700–800°C in the presence of a triethyl phosphate catalyst. With acetic acid, the reactions are:

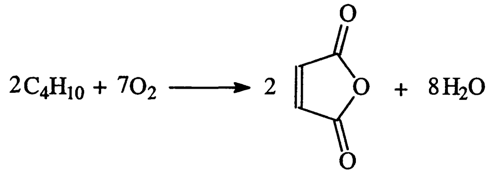
$$CH_3COOH \rightarrow CH_2{=}C{=}O + H_2O$$

$$CH_3COOH + CH_2{=}C{=}O \rightarrow (CH_3CO)_2O$$

Acetic anhydride is used to make acetic acid esters. It is especially effective in difficult acetylations, such as in the manufacture of aspirin and cellulose acetate.

Maleic Anhydride. Maleic anhydride is one of the fastest-growing chemical end-uses for butane. The demand in the United States was about 500 million lb in 2000. About 60 percent of the maleic anhydride produced goes into the manufacture of unsaturated polyester resins, used primarily in fiber-reinforced plastics for construction, marine, and transportation industries. It is also used to make lube oil additives, alkyd resins, fumaric and malic acids, copolymers, and agricultural chemicals.

Essentially all maleic anhydride is manufactured by the catalytic vapor-phase oxidation of hydrocarbons. Prior to 1975, benzene was the feedstock of choice. By the early 1980s, however, many producers had switched to n-butane for economic and environmental reasons. Although benzene as a feedstock for maleic anhydride is no longer used in the United States, it is still used in older plants in Latin America, Europe, and East Asia. The oxidation reaction to produce maleic acid from n-butane is as follows:



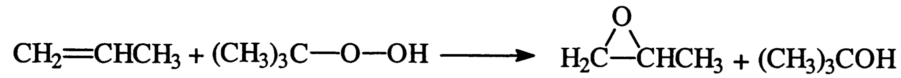
Until the late 1990s nearly all butane oxidation to maleic anhydride was conducted in a fluid bed or in a fixed bed multitubular, tube-shell heat exchanger type of reactors. After over a decade of intensive R&D efforts, DuPont was successful in commercializing a Circulating Fluid Bed Reactor (CFBR) catalyst system. CFBR has the advantage of providing 10–15 percent higher selectivity even at higher conversions, thereby significantly reducing raw material costs. A diagram of the fluid bed process in presented in Fig. 10.30.

Isobutanes

t-Butyl Alcohol/Propylene Oxide. An important use for isobutane is in the peroxidation of propylene with t-butyl hydroperoxide. The feedstocks are propylene and isobutane, and the process is similar to the PO/styrene plant. (See the section "Chemicals from Benzene" below.) In the two-stage conversion route, oxidation of isobutane with air yields a mixture of t-butyl hydroperoxide and t-butanol in a liquid-phase reaction at 135–144°C. After separation of products, a molybdenum-catalyzed reaction of the hydroperoxide with propylene at 110°C yields PO and t-butyl alcohol (TBA).

$$2(CH_3)_3CH + 3/2O_2 \longrightarrow (CH_3)_3{-}C{-}O{-}OH + (CH_3)_3COH$$

isobutane t-butyl hydroperoxide TBA



$$CH_2{=}CHCH_3 + (CH_3)_3C{-}O{-}OH \longrightarrow H_2C\overset{O}{-}CHCH_3 + (CH_3)_3COH$$

propylene t-butyl hydroperoxide propylene oxide TBA

The ratio of TBA to PO, and thus the isobutane requirement, can be adjusted from approximately 2 : 1 to 3 : 1. The U.S. capacity of PO in 1999 was about 1715 million lb. (The capacity for PO/styrene and chlorohydrin routes was 1120 and 2150 million lb, respectively). At this time, only one domestic PO producer is not using this process.

When this process was first introduced, TBA had a low value, so the TBA/PO ratio was kept to a minimum. Since the use for MTBE as oxygen enhancer in gasoline has became important, a higher TBA/PO value is used. Note, however, that changes in the

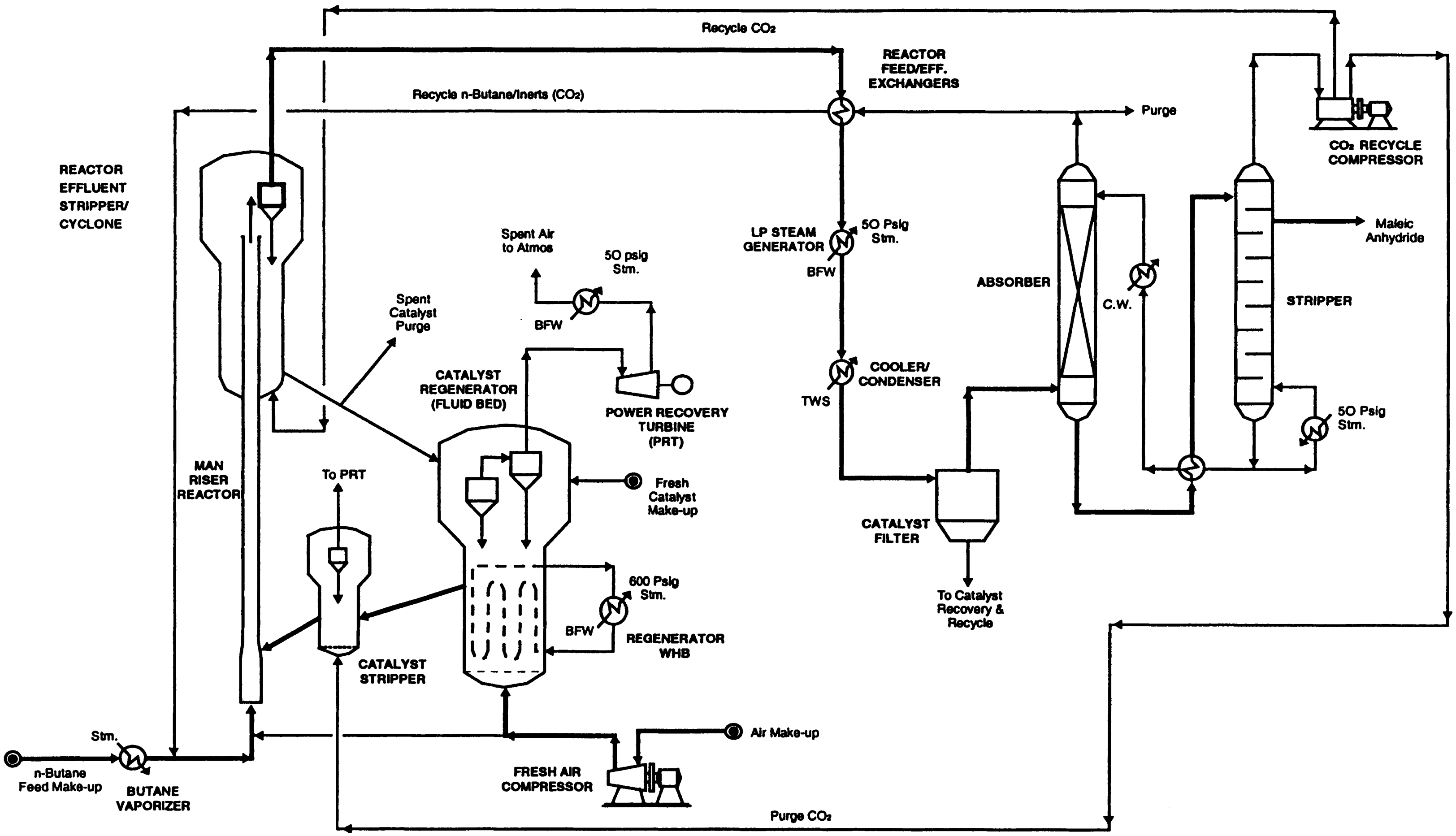


Fig. 10.30. Maleic anhydride DuPont process. (*Chem Systems Report No. 99/00-5. Copyright Nexant Chem Systems, Inc. and used by permission of the copyright owner.*)

MTBE picture also apply here—as discussed earlier. Dehydration of TBA yields high-purity isobutylene, which can be converted into MTBE with methanol. Today, almost 900 million lb of isobutylene is produced from TBA.

Other Isobutane-Based Chemicals. Isobutane can be directly dehydrogenated to isobutylene by a modification of the Houdry process. This can then be converted to MTBE. The estimated use is over 1 billion lb of isobutane. Because of their inertness and higher vapor pressures, high-purity propane and butanes have become the important substitutes for fluorocarbons as aerosol propellants. Isobutane can also be used as a solvent in polymer processing, and as a blowing agent for foamed polystyrene.

Butylenes

Butylenes are four-carbon monoolefins that are produced by various hydrocarbon processes, principally catalytic cracking at refineries and steam cracking at olefins plants. These processes yield isomeric mixtures of 1-butene, *cis-* and *trans*-butene-2, and isobutylene. Derivatives of butylenes range from polygas chemicals and methyl t-butyl ether, where crude butylenes streams may be used, to polybutene-1 and LLDPE, which require high-purity 1-butene. In 1997, the estimated consumption of butylenes (in billions of pounds) was: alkylation, 32.0; MTBE, 12.0; other, including polygas and fuel uses, 0.5.

The major chemical uses for n-butylenes are sec-butyl alcohol (and MEK), butadiene, butene-1, heptenes, and octenes. In 1978, butadiene accounted for almost 70 percent of the demand. At the present time sec-butanol and 1-butene are the largest chemical end-uses of butylene, consuming about four fifths of the total.

1-Butene. The largest chemical use of n-butenes is 1-butene used in production of LLDPE, which requires alpha-olefin comonomers. Various processes for the production of LLDPE and HDPE incorporate 1-butene as a comonomer. This accounts for about 70 percent of 1-butene use. The alpha-olefin comonomers control the density and physical properties of the polymer. About 20 percent of the 12,500 million lb of HDPE production in the United States in 1997 utilized 1-butene as comonomer, as did 45 percent of the 6900 million lb of LLDPE. Most of the remainder was split between 1-hexene and 1-octene.

The remaining 30 percent of 1-butene is divided among several uses. About 10–15 percent of the 1-butene is polymerized in the presence of a Ziegler-type catalyst to produce polybutene-1 resin. The markets for this resin are pipe, specialty films, and polymer alloys. Approximately the same volume of 1-butene is reacted with synthesis gas in an oxo reaction to produce valeraldehydes. These C_5 aldehydes are then hydrogenated to amyl alcohols or oxidized to valeric acid. Amyl alcohols are consumed in the production of lube oil additives and amyl acetate and in solvent uses. Valeric acid goes into lubricant base stocks and specialty chemicals.

Smaller uses of 1-butene are in 1,2-butylene oxide, butyl mercaptan, and butyl phenols. Butylene oxide, produced by the chlorohydrin process, is used as a corrosion inhibitor in chlorinated solvents. Butyl mercaptan is a precursor for organophosphate herbicides, pharmaceutical intermediates, and is used as a gas odorant.

sec-Butanol and Methyl Ethyl Ketone. The next-largest use for n-butenes is in the manufacture of sec-butanol. A refinery butanes–butylenes stream, usually rich in butene-2, is contacted with 80 percent sulfuric acid to produce the sec-butyl hydrogen sulfate. Dilution with water and steam stripping produce the alcohol. MEK is obtained in high yields at catalytic dehydration of the alcohol at 400–500°C.

Solvent applications account for almost 95 percent of all MEK consumption; the rest goes to chemical uses such as MEK peroxide and methyl ethyl ketoxime. The solvent applications include surface coatings, adhesives, lube oil dewaxing, magnetic tape manufacture, and printing inks. Production of MEK in 1999 totaled almost 690 million lb.

Heptenes and Octenes. Heptene and octene are oligomers produced by the polymerization of refinery streams containing C_3 and C_4 hydrocarbons. Originally these polygas units were developed to provide a source of high-octane blending components from refinery gases, but many have since been adapted to produce heptenes and octenes for chemical uses. Heptenes are used primarily to produce isooctyl alcohol which is a precursor for lube oil additives, diisooctyl phthalate (DIOP), other plasticizers, and herbicide esters. Isooctyl alcohol was once the predominant plasticizer alcohol, but development of plasticizers from competing alcohols such as 2-ethylhexanol and linear alcohols has eroded its market. Octenes are precursors of isononyl alcohol, which in turn is the raw material in the manufacture of diisononyl phthalate (DINP) plasticizers. These plasticizers compete directly with dioctyl phthalate in many applications. The total U.S. consumption of butylenes for production of heptenes and octenes was approximately 240 million lb in 1997.

Butene-2. Most butene-2 in the United States goes into production of gasoline alkylate. Some butene-2 is used in solvent applications, and it is also the intermediate in the disproportionation process for producing propylene from ethylene.

Isobutylene

Methyl t-Butyl Ether. By far the largest use of isobutylene is in the manufacture of methyl t-butyl ether (MTBE). Since its introduction in 1979, the demand for MTBE as an octane improver in gasoline has grown phenomenally. By 2000, production had reached 46 billion lb/year. MTBE use is exclusively as an octane booster/combustion promoter in gasoline. Use of MTBE in gasoline, at least in the United States, is expected to decline in the coming years for the reasons discussed earlier in this chapter. The decline of MTBE production is expected to have a significant impact on C_4 uses in the future.

MTBE is produced by reacting methanol and isobutylene under mild conditions in the presence of an acid catalyst. The isobutylene feed is either mixed butylenes, a butylenes stream from catalytic cracking, or a butylenes coproduct from ethylene production. The reaction conditions are mild enough to permit the n-butenes to pass through without ether formation. Figure 10.31 shows a typical process for making MTBE.

Another approximately 1.5 billion lb of isobutylene goes into other chemical uses. These applications include polybutenes and derivatives of high-purity isobutylene such as butyl rubber, polyisobutylenes, and substituted phenols. Isobutylene is more reactive than the n-butenes, but many of its reactions are readily reversible under relatively mild conditions.

Polybutenes. More than 900 million lb of butylenes are consumed in the production of polybutenes. The process involves the

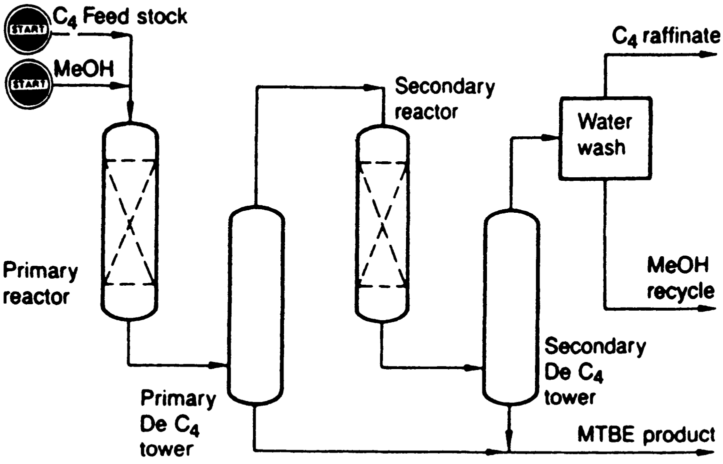


Fig. 10.31. Two-stage MTBE process. (*Bitar, L. S., Hazbun, E. A. and Piel, W. J., Hydrocarbons Processing, 63, no. 10, 54. 1984, October. Copyright Gulf Publishing Company and reproduced by permission of the copyright owner.*)

Friedel–Crafts polymerization of desulfurized C_4 refinery streams. Although the feed is a mixed butylenes stream, the polybutene product is essentially a polymer of isobutylene, with a few n-butene units occurring in the polymer chain. The optimum isobutylene concentration in the feed stream is reported to be in the 20–25 percent range. The polymerization reaction yields products with a molecular weight range of 300–3000.

The lowest-molecular-weight polymers (mol. wt. 300–350) are used for dielectric fluids and specialty lubricants. They comprise a very small part of the market. Polymers in the 700–750 range are precursors for caulks, sealants, and gasoline additives. Polymers with molecular weights of 900–1500 constitute the segment with by far the largest volume. They are used in the manufacture of lube oil additives via modification with phosphorus, amine, or succinimide groups. The resulting dispersants reduce oil consumption, restore compression, and improve oil viscosity. They are also used as gasoline additives and specialized plasticizers. The higher polymer fraction (mol. wt. 1500–3000) mainly is formulated into adhesives, caulks, and sealants. The use of polybutenes in gasoline detergents is expected to show continued growth.

Butyl Rubber. Almost two-thirds of the demand for high-purity isobutylene is for production of butyl rubber, which is produced by the cationic polymerization of high-purity isobutylene with isoprene (2–3% by weight) at low temperatures in the presence of a Friedel–Crafts catalyst. The isobutylene must be pure in order to obtain a high molecular weight product. The elastomer's outstanding property of impermeability to air and gas makes it particularly suitable for tire liners and tire bladders and valves. Other important butyl elastomers are the halogenated products, chlorobutyl and bromobutyl. Halogenated butyl rubbers, which are more compatible with other tire elastomers and can be cured faster than butyl rubber, have grown to be of more importance in recent years.

Polyisobutylenes. Polyisobutylenes are produced by the low temperature polymerization of high-purity isobutylene. The main commercial products have two molecular weight ranges: a 40,000–50,000 molecular weight polymer, and a polymer with molecular weight two to four times that of butyl rubber. The lower-weight polymer is used in binder systems, and in plasticizers and tackifiers for adhesives and sealants for electrical applications. The largest application for the higher-weight polymer is in the production of lube oil viscosity improvers. In 1997, about 50 million lb of high-purity isobutylene went to make polyisobutylenes.

Other Derivatives of Isobutylene. The production of many smaller-volume chemicals is based on high-purity isobutylene. The major chemicals are para-t-butylphenol, di-t-butyl-*p*-cresol (butylated hydroxytoluene, BHT), 2,6-di-t-butylphenol, t-butylamine, t-butyl mercaptan, and isobutyl aluminum compounds. Isobutylene usage by each of these six ranged from 8 to 18 million lb. The total volume of isobutylene that went for small-volume chemical production was about 140 million lb in 1997.

The substituted phenols and cresols constitute about half the total volume of this group. Para-t-butylphenol is produced by the alkylation of phenol with isobutylene. The principal applications for this derivative are in the manufacture of modified phenolic resins for the rubber industry and in surface coatings. BHT is obtained from isobutylene and *p*-cresol. Technical-grade BHT is an antioxidant for plastics and elastomers, and is a gum inhibitor in gasoline. Food-grade BHT is an antioxidant in edible oils, preserves, and many other foods. 2,6-Di-t-butylphenol is used to produce a wide range of plastics additives, antioxidants, and gasoline additives.

t-Butylamine is formed by the reaction of isobutylene with HCN in the presence of strong sulfuric acid. The intermediate t-butyl formamide is then hydrolyzed to form the amine and formic acid. This amine is used mainly to synthesize sulfonamide rubber accelerator compounds. The major use of n-butyl mercaptan is in odorant formulations for natural gas. The distributors of natural gas inject about one pound of odorant per million cubic feet. Isobutyl aluminum compounds are produced from high-purity isobutylene, hydrogen, and aluminum. Five distinctly different isobutyl aluminum compounds are produced in the United States. The principal end use for these compounds is as polymerization cocatalysts in the manufacture of polybutadiene, polyisoprene, and polypropylene. Other minor uses for high-purity isobutylene are in the manufacture of neopentanoic acid, methallyl chloride, and miscellaneous butylated phenols and cresols.

Butadiene

In the mid-1970s there were several major processes for making butadiene in the United States: steam cracking of naphtha, catalytic dehydrogenation of n-butene, dehydrogenation of n-butane, and oxidative dehydrogenation of n-butene. By 2000, more than 90 percent of all the butadiene was made as a coproduct with ethylene from steam cracking, and the only "on-purpose" production came from the dehydrogenation of butylene.

Thermal cracking of hydrocarbon feedstocks in the presence of steam at 700–900°C produces ethylene and several coproducts, including butylenes and butadiene. The yield of butylenes varies widely (to as high as 30%), depending on the feedstock and the severity of the cracking. The yield of butadiene is particularly high with naphthas and heavier feedstocks. Most ethylene producers recover a raw C_4 stream that contains butanes, butylenes, and butadiene. The butadiene is recovered by extraction, and the raffinate (containing butanes and butylenes) is used for gasoline blending or the production of chemicals.

The dehydrogenation process feed can be refinery streams from the catalytic cracking processes. This mixed C_4 stream typically contains less than 20 percent n-butenes. For use in dehydrogenation, however, it should be concentrated to 80–95 percent. The isobutylene generally is removed first by a selective extraction-hydration process. The n-butenes in the raffinate are then separated from the butanes by an extractive distillation. The catalytic dehydrogenation of n-butenes to 1,3-butadiene is carried out in the presence of steam at high temperature (>600°C) and reduced pressure. A typical catalyst could be a chromium-promoted calcium nickel phosphate. The oxidative dehydrogenation process for butadiene reacts a mixture of n-butenes, compressed air, and steam over a fixed catalyst bed of tin, bismuth, and boron.

Of the 17 billion lb of butadiene consumed in 1999, almost two thirds went into the production of elastomers (styrene–butadiene latex rubber (SBR), polybutadiene, nitrile, and polychloroprene). Adiponitrile, ABS resins, styrene–butadiene latex, styrene block copolymers, and other smaller polymer uses accounted for the remainder. The largest single use was for styrene–butadiene copolymers (SBR and latex). Most of it was made by an emulsion process using a free-radical initiator and a styrene–butadiene ratio of about 1:3. More detailed description of the rubber and polymer used can be found in Chapters 16 and 15.

HIGHER ALIPHATIC HYDROCARBONS

Cyclopentadiene

Cyclopentadiene is a product of petroleum cracking. It dimerizes exothermically in a Diels–Alder reaction to dicyclopentadiene, which is a convenient form for storage and transport. Dicyclopentadiene plus cyclopentadiene demand in the United States amounted to 270 million lb in 1998.

Dicyclopentadiene can be converted back to cyclopentadiene by thermally reversing the Diels–Alder reaction. Cyclopentadiene also undergoes the Diels–Alder reaction with other olefins, and this chemistry has been used to make highly chlorinated, polycyclic hydrocarbon pesticides. These pesticides are so resistant to degradation in the biosphere, however, that they are now largely banned from use. It is also used as a monomer and a chemical intermediate.

Isoprene

Isoprene is the basic repeating unit in natural rubber and in the naturally occurring materials known as terpenoids. It is a diene like butadiene and is useful as a building block for synthetic polymers. The most frequently used synthetic procedure for making isoprene is acid-catalyzed reaction of formaldehyde with isobutylene, giving a dioxolane intermediate that is thermally cracked to isoprene. Isoprene also can be recovered from petroleum refinery streams. A total of 360 million lb of isoprene was used in the United States in 2000.

Isoprene is converted to elastomers such as poly(*cis*-1,4-isoprene), which is tough, elastic, and resistant to weathering and is used mainly for vehicle tires. Recently, block copolymers of isoprene with styrene have been finding use as thermoplastic elastomers and pressure-sensitive adhesives.

n-Paraffins and Olefins

n-Paraffins are the unbranched fraction of hydrocarbons found in petroleum. They can be separated from the branched and aromatic hydrocarbons by a process using a shape-selective, controlled-pore-size adsorbent. In this process, the small pores exclude branched or aromatic materials and allow them to flow through a column more readily than the linear hydrocarbons, which become adsorbed into the narrow pore structure of the adsorbent. Linear, internal monoolefins are produced by dehydrogenation of n-paraffins.

Primary and Secondary Higher Alcohols

Linear internal monoolefins can be oxidized to linear secondary alcohols. The alpha (terminal) olefins from ethylene oligomerization, described earlier in this chapter, can be converted by oxo chemistry to alcohols having one more carbon atom. The higher alcohols from each of these sources are used for preparation of biodegradable, synthetic detergents. The alcohols provide the hydrophobic hydrocarbon group and are linked to a polar, hydrophilic group by ethoxylation, sulfation, phosphorylation, and so forth.

CHEMICALS DERIVED FROM BENZENE, TOLUENE, AND XYLENE

Until World War II, most of the commercial aromatic chemicals in the United States and other countries were derived from the coal industry. The high-temperature carbonization of coal to produce coke for the steel industry also generated a liquid stream that was rich in aromatics. Benzene, toluene, and xylene (BTX) and other aromatics could be recovered from the coal tar by extraction and distillation. Recently, the importance of this source has greatly diminished; now almost all of the BTX in the United States is based on petroleum (17 billion lb of benzene, 12.6 billion lb of toluene, and 12.3 billion lb of xylene).

There are two major sources for petroleum-based aromatics, catalytic reformate and pyrolysis gasoline. The catalytic reformate is a refinery product that occurs in the catalytic reforming of naphthenes and paraffins in low-octane naphtha to produce a high-octane product. The pyrolysis gasoline stream that results from the steam cracking of hydrocarbons to produce ethylene and propylene is a very large (and growing) source of benzene and other aromatics. Because the demand for toluene is considerably less than that for benzene, some toluene is converted back to benzene by high-temperature hydrodealkylation (HDA) or by catalytic toluene disproportionation (TDP). The amount of benzene produced by HDA at any given time depends on the relative economics of benzene and toluene. Recently, the ratio of benzene produced from HDA versus TDP process is about 1 : 3. The specific process details of these production routes can be found in Chapter 18.

Compared to the amount of BTX that goes into fuel, the volume of aromatic chemicals used as chemical building blocks is relatively small. About half of the benzene and more than 90 percent of the toluene and xylenes end up in the gasoline pool.

Chemicals from Benzene

Benzene is by far the most important aromatic petrochemical raw material. During 1999, some 2.8 billion gal were consumed in the United States. This ranks it close to propylene as a chemical building block. Benzene has a broad end-use pattern. Its most important uses are for: ethylbenzene (styrene), 55.6 percent; cumene (phenol), 22.4 percent; cyclohexane

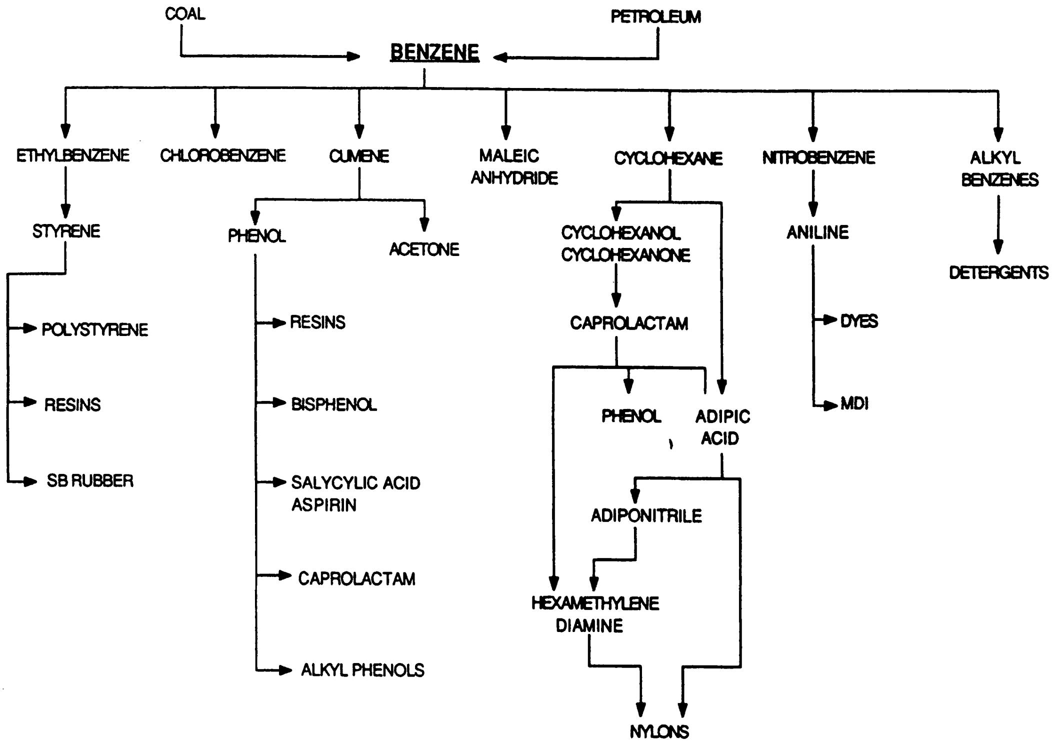


Fig. 10.32. Chemicals derived from benzene.

(nylon), 13.5 percent; nitrobenzene (aniline), 5 percent; and detergent alkylate, 3 percent. Other significant uses are for chlorobenzenes and maleic anhydride. Benzene is an excellent solvent, but it has been almost entirely replaced by less toxic materials. Some of the major end products are shown in Fig. 10.32.

Styrene. Styrene is the largest benzene derivative with annual consumption about 11.5 billion lb in the United States. It is produced mainly by catalytic dehydrogenation of high-purity ethylbenzene (EB) in the vapor phase. The manufacture process for EB is based on ethylene alkylation with excess benzene. This can be done in a homogeneous system with aluminum chloride catalyst or a heterogeneous solid acid catalyst in either gas or liquid-phase reaction. In the past decade, the liquid-phase alkylation with zeolite catalyst has won acceptance. Those processes have advantages of easier product separation, reducing waste stream, and less corrosion. In addition, it produces less xylene due to lower process temperature. Since certain xylene isomers have very similar b.p. as styrene, it is difficult to be separated.

The EB dehydrogenation can be done with various commercially available styrene catalysts. The fractionation train separates high-purity styrene, unconverted EB, and minor reaction byproducts such as toluene.

Styrene is also produced as coproduct from a PO process. In this route, EB is oxidized to its hydroperoxide and reacted with propylene to yield propylene oxide. The coproduct methyl phenyl carbinol is then dehydrated to styrene. For every pound of PO produced, up to 2.5 lb of styrene can be produced. In 2000, about 25 percent of styrene was produced by this process in the United States.

The largest use for styrene (over 70%) is to make homopolymer polystyrene. The U.S. production volume reached 6.3 billion lb in 1998. Other major uses are in plastics, latex, paints, and coatings, synthetic rubbers, polyesters, and styrene-alkyd coatings. In these applications styrene is used in copolymers such as ABS (8%), styrene–butadiene latex (8%) rubber (SBR) (4%), unsaturated polyester resins (6%), and other polymer applications.

Cumene (Phenol). Cumene has become the second largest chemical use for benzene. It is produced by alkylating benzene with propylene at elevated temperature and pressure in the presence of a solid acid catalyst. The U.S. production was more than 6.9 billion lb in 1999. Of this, about 96 percent then was converted to phenol.

Before 1970, there were five different processes used to make phenol in the United States: the sulfonation route, chlorobenzene hydrolysis, the Raschig process, cumene oxidation, and the benzoic acid route. By 1978, the first three processes had essentially disappeared, and 98 percent of the remaining plant capacity was based on cumene oxidation. The oxidation process is shown in Fig. 10.33.

In this process, cumene is oxidized to cumene hydroperoxide by air at about 100°C in an alkaline environment. The oxidation products are separated, and the bottoms are mixed with a small amount of acetone and sulfuric acid and held at 70–80°C while the hydroperoxide splits into phenol and acetone. Total domestic phenol capacity with this process is about 4.8 billion lb/year. In the much smaller-volume benzoic acid process, toluene is air-oxidized to benzoic acid with a cobalt catalyst. The benzoic acid then is converted to phenol by an oxidative decarboxylation reaction with air at about 240°C.

The three major uses for phenol are in the manufacture of phenolic resins, bisphenol A, and caprolactam.

Phenolic resins. Resins such as those made from phenol and formaldehyde now account for about one third of the phenol consumed in the United States. They are widely used in construction related use such as plywood adhesives, foundry resins, thermoformed plastics, and surface coatings.

Bisphenol. Bisphenol-A (4,4′-isopropylidene-diphenol) accounts for 35 percent of phenol consumption and is used mainly in the production of polycarbonates (55%) and epoxy resins (25%), two of the fastest-growing families of plastics. Other uses are in the manufacture of flame retardant such as tetrabromobisphenol-A, polysulfone resins, and polyacrylate resins. The consumption of bisphenol in the United States in 1999 topped 2.1 billion lb.

Bisphenol is obtained by the reaction of phenol and acetone with HCl or acid resin as catalyst. In the HCl catalyzed process (Fig. 10.34), phenol and acetone in a molar ratio of about 3 : 1 are charged to an acid-resistant stirred reactor. A sulfur-containing catalyst is added, and then dry HCl gas is bubbled into the reaction mass. The temperature is maintained at 30–40°C for 8–12 hr. At the end of the reaction, the mixture is washed with water and treated first with enough lime to neutralize the free acid. Vacuum and heat

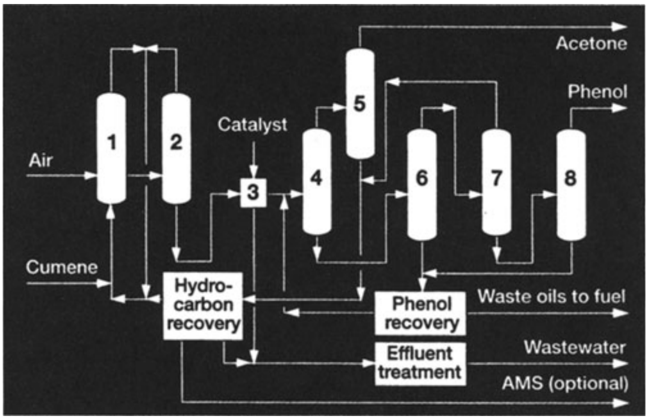


Fig. 10.33. Manufacture of phenol and acetone by oxidation of cumene. (*Hydrocarbon Processing. p. 117, 2001, March. Copyright 2001 by Gulf Publishing Co.*)

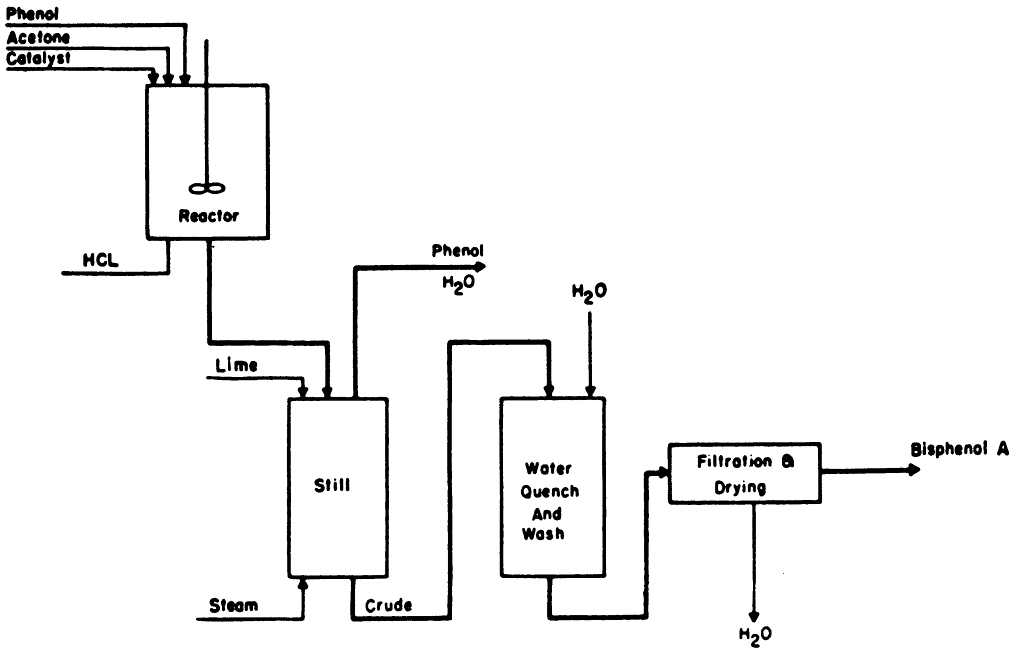


Fig. 10.34. Manufacture of bisphenol A. (*Pet. Ref.* **38**, *no. 11, 225, 1959. Copyright 1959 by Gulf Publishing Co.*)

are applied, and water and phenol are distilled separately from the mixture. The batch is finished by blowing the molten product with steam under vacuum at 150°C to remove the odor of the sulfur catalyst. The molten bisphenol is quenched in a large volume of water, filtered, and dried. All new bisphenol plants are based on the acid resin catalyst technology. The total capital investment for a resin plant is about half of a plant using HCl catalyst. The higher investment for the HCl-catalyzed process is due to the need for the corrosion resistant materials in the process equipment handling HCl and removing it after the reaction.

Other phenolics. Other major derivatives of phenol include caprolactam (14%), salicyclic acid (aspirin), alkylated phenols (3.6%), aniline (3.5%), and xylenols (3.5%).

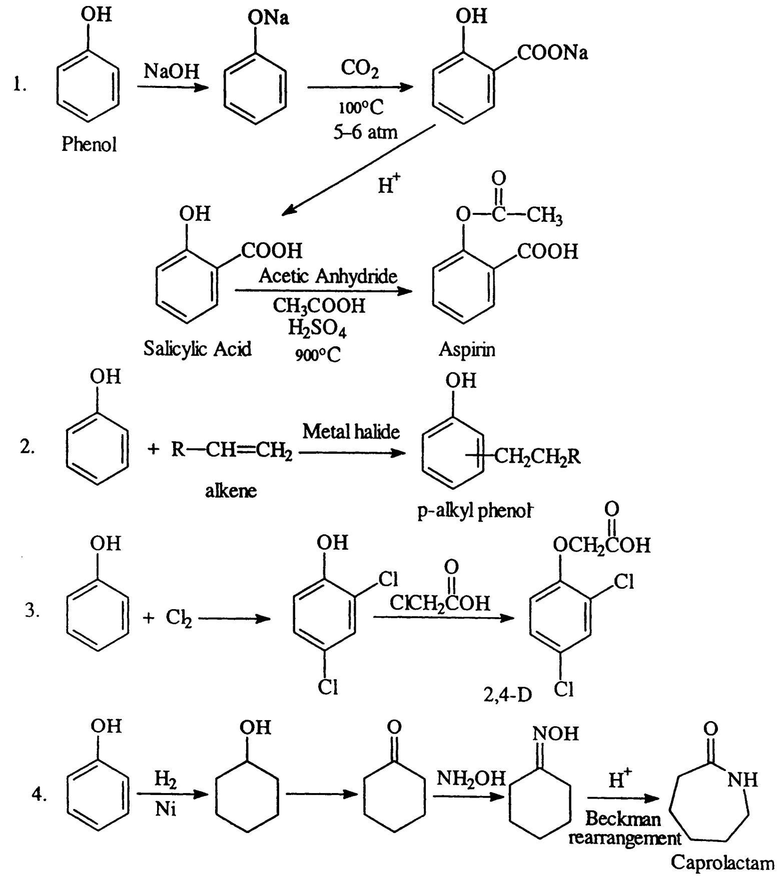
The uses of caprolactam are described in the section "Cyclohexane." Almost 60 percent of the 27 million lb of salicyclic acid went to aspirin, with remainder mainly going to salicylate esters and phenolic resins. Aspirin (acetyl salycylic acid) has long been recognized for its analgesic and antipyretic properties. It must now share this market with the competing pain relievers such as acetaminophen and ibuprofen.

Cyclohexane. Cyclohexane is the basic starting material for nylon fibers and resins via the intermediates adipic acid, caprolactam, and hexamethylenediamine. The world consumption was about 10 billion lb (with 3.5 billion lb in the United States) in 2000. Of these three derivatives, adipic acid and caprolactam account for over 90 percent of cyclohexane consumption. Cyclohexane is also used as a solvent and as a starting material for cyclohexanol and cyclohexanone. Although cyclohexane can be recovered from natural gasoline, most is made by liquid or vapor-phase hydrogenation of benzene. A nickel or platinum catalyst is generally used at elevated temperature and pressure.

Adipic acid. The world consumption for adipic acid was 4.6 billion lb in 1999. Nylon 66, produced from adipic acid and hexamethylenediamine (HMDA), is currently the largest-volume domestic nylon. About 86 percent of all adipic acid goes to make nylon 66 fibers and resins. Although HMDA can be made from adipic acid, a major source is from adiponitrile. The commercial synthesis of adipic acid is a two-step reaction starting with either cyclohexane or phenol. In both cases, a cyclohexanone/cyclohexanol mixture is formed as an intermediate. This mixture is then catalytically oxidized to the adipic acid product with nitric acid. It can also be manufactured as a byproduct of the caprolactam process.

Caprolactam. Essentially all caprolactam is used in the manufacture of nylon 6 fibers. In 1998, global demand reached nearly 7.3 billion lb with 1.7 billion lb used in North America. This is a fast-growing nylon with applications in carpets, textiles, and tires. Caprolactam can be produced from cyclohexane, phenol, and toluene via cyclohexanone. It is then reacted with hydroxylamine to give an oxime. The oxime undergoes an acid-catalyzed rearrangement to give caprolactam.

Although these nylon intermediates are derived mainly from cyclohexane, there are various other routes. For example, adipic acid can be made by butylene oxidation as well as by cyclohexane oxidation; HMDA can be made starting with butadiene, adipic acid, or acrylonitrile; and caprolactam is also produced from phenol. See Chapter 12 for a more detailed discussion of nylon fibers and resins.



Maleic Anhydride. Prior to 1975, benzene was the feedstock of choice for maleic anhydride manufacture. By the early 1980s, for economic reasons, many producers had switched to the n-butane process described in the section “n-Butane Derivatives”. By 1988, all of the maleic anhydride produced in the United States came from that process. However, about half of the maleic anhydride produced abroad still comes from benzene oxidation, with a small amount being recovered as a coproduct in phthalic anhydride manufacture.

Detergent Alkylate. Alkylbenzenes are major intermediates in the manufacture of synthetic detergents. If a straight-chain alkyl group is used, the resulting product is linear alkylbenzene (LAB), a "soft" degradable alkylate. Using a branched olefin (from propylene tetramer) gives branched alkylbenzene (BAB), a "hard" nondegradable alkylate. Approximately 960 million lb (mainly dodecyl- and tridecyl-benzene) of LAB were produced in 1998. The production of BAB was about 188 million lb in 1985; it declined to zero in 1998.

The production of LAB involves the liquid-phase alkylation of benzene with linear monoolefins or alkyl chlorides. Liquid HF is used as catalyst for linear monoolefins. And the $AlCl_3$ is used as the catalyst for alkyl chlorides. Nowadays, acidic zeolite catalyst is used for olefin alkylation which generates less waste and reduces manufacture cost. The alkylate is then sulfonated to produce linear alkylbenzene sulfonate for biodegradable detergents. The manufacture of detergents is described in detail in Chapter 27.

The majority of LAB has a chain length of 10–13. This method is also used to make longer-chain (C_{20}–C_{22}) alkyl derivatives of benzene. Those alkylates are used as lubricants.

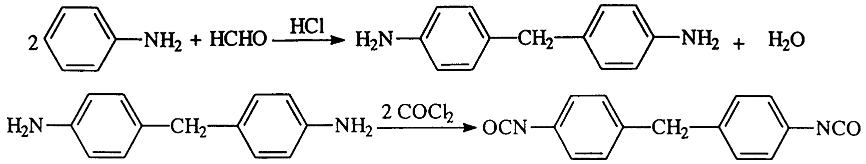
Nitrobenzene (Aniline). The U.S. nitrobenzene production was about 2 billion lb in 1999. Two types of manufacturing processes were used: the direct nitration and the adiabatic nitration process. In the direct nitration system, benzene is mixed with a mixture of nitric/sulfuric acid. The reaction can be carried out in either a batch or a continuous system. Those reactors require a cooling system to keep it at constant temperature. It also requires a separate system for sulfuric acid reconcentration. In the adiabatic process, water is flashed off under vacuum before the sulfuric acid/nitrobenzene separation. The advantage of the adiabatic process is to eliminate a separated sulfuric acid reconcentration unit. This also will provide a better heat integration. Recently, the disposal of nitrophenols has become a major issue for aniline manufacture. Small amounts of nitrophenols are always made during the benzene nitration. It is more of a problem for the adiabatic process due to higher process temperature. Now an improved adiabatic process has been developed. By using an enhanced mixing and a higher benzene/acid ratio it produces less nitrophenols and it still keeps the advantages of the adiabatic process.

In 2000, the aniline production in the United States was about 1.9 billion lb. Almost 98 percent of nitrobenzene is used for the production of aniline. Consequently many nitrobenzene plants are integrated with facilities for aniline production. The hydrogenation of nitrobenzene can be done in either the vapor over a copper–silica catalyst or in liquid phase over platinum–palladium catalyst. One of the smaller uses for nitrobenzene is the production of the pain reliever, acetaminophen.

Aniline can also be made by two other methods. In the first, nitrobenzene is reduced by reaction with scrap iron in the presence of a hydrochloric acid catalyst. The iron is oxidized to the ferrous state, and the coproduct aniline is separated. This route accounts for less than 5 percent of the current aniline production. The other process avoids nitrobenzene entirely and involves the vapor-phase ammonolysis of phenol, using an alumina catalyst. Aniline is formed with diphenylamine as a by-product. About 20 percent of the aniline is produced by this route.

Aniline is consumed as a raw material in the manufacture of a number of chemicals: *p,p*-methylene diphenyl diisocyanate (MDI), 65 percent; rubber-processing chemicals, 15 percent; herbicides, 5 percent; dyes and pigments, 4 percent; specialty fibers, 2 percent. Other uses are in pharmaceuticals and photo chemicals. Principal growth is occurring from demand for MDI and the small, rapidly growing specialty fibers.

Diisocyanates (MDI). The first step in the production of MDI (and polymeric "PMDI") is the condensation of aniline and formaldehyde to form diphenylmethylenediamine. The reaction conditions can be varied to change the isomer distribution of the product. This is followed by phosgenation to give an aromatic isocyanate product mix that corresponds to the starting polyaromatic amine.



Typically a mixture containing MDI and its dimer, trimer, and some tetramer is produced. Pure MDI can be separated by distillation. MDI is supplied in several grades, depending on the number of reactive units (-NCO groups) per molecule. The most common grade is polymeric MDI with a functionality of 2.3–3.0. The grades used in rigid foam production typically contain 40–60 percent pure MDI, with the balance being dimer and other isomers. Pure MDI is used mainly for RIM (reaction injection molding) systems.

The U.S. production of MDI was about 1.34 billion lb in 1998. Rigid polyurethane foams constitute the largest single use for MDI and its polymers, with total consumption of more than 850 million lb. Typical laminate and board foams contain more than 60 percent MDI, whereas pour systems and spray systems contain somewhat less. The main applications of rigid foam are in construction and in the manufacture of refrigerators and water heaters. Smaller uses are packaging, tank and pipe insulation, and transportation. A minor amount of polymeric MDI is used to make foundry sand binders. Pure MDI finds use in RIM systems, specialty coatings, thermoplastic resins, high-performance casting elastomers, and spandex fibers. A more detailed description of polyurethane polymers can be found in Chapter 15.

Other Uses for Aniline. Aniline currently is used as a raw material in most of the major groups of rubber-processing chemicals: accelerators, antioxidants and stabilizers, and anti-ozonants. The most important of these are the thiazole derivatives and substituted *para*-phenylenediamines. The demand for aniline in these rubber-processing uses is expected to grow at less than 1 percent/year. In agricultural chemicals, the major use for aniline is as a raw material in the manufacture of amide herbicides for controlling annual grasses and broadleaf weeds in various crops. More than 175 commercial dyes can be made from aniline, and many others are produced from aniline derivatives. This market, however, is not expected to show further growth. Since their introduction in 1979, the use of aniline in polyaramid specialty fibers has shown rapid growth. This trend is expected to continue in the future. Among the important pharmaceutical derivatives of aniline are the sulfonamides, a group of compounds used to combat infections.

Chlorobenzenes. Of the 12 different chlorobenzenes that can result from the chlorination of benzene, three are of most commercial importance: monochlorobenzene (MCB), *o*-dichlorobenzene (ODCB), and *p*-dichlorobenzene (PDCB). Chlorination of benzene can be done either batchwise or continuously in the presence of a catalyst such as ferric chloride, aluminum chloride, or stannic chloride. It is usually run as a three-product process; the current product distribution is about 52 percent to MCB, 17 percent ODCB and 31 percent PDCB. The pure compounds are separated from the crude by distillation and crystallization.

Production of monochlorobenzenes peaked in the 1960s with production volume at about 600 million lb. It was down to 152 million lb in 1998. The most significant cause for the decline is the replacement of monochlorobenzene by cumene as the preferred raw material for phenol manufacture. Other reasons include the elimination of the herbicide DDT, the change of diphenyl oxide process from chlorobenzene to phenol and a significant drop in solvent use. The production volume for ODCB and PDCB were 50 and 91 million lb, respectively, in 1998.

Monochlorobenzene. The largest use for monochlorobenzene, accounting for about 59 percent of the consumption, is in the production of chloronitrobenzenes. *p*-Nitrochlorobenzene (NCB) is converted into *p*-phenylenediamine for use as antioxidants in rubber processing. A smaller use for NCB is in the synthesis of the pain reliever, acetaminophen. *Ortho*-nitrochlorobenzene is a raw material for producing insecticides and several azo pigments. A large number of dyes also can be derived from either chlorobenzene or nitrochlorobenzene. About 13 percent of the monochlorobenzene is used as a solvent for pesticide formulation and in MDI processing. About 18 percent is used to make dichlorodiphenylsulfone, an intermediate in the manufacture of sulfone polymers.

Dichlorobenzenes. In 1998, approximately 16 million lb of the *o*-dichlorobenzene was converted into 3,4-dichloroaniline, the raw material for several major herbicides. Also a small amount (3 million lb) goes to various solvent applications. The major demands for *p*-dichlorobenzene come from uses in polyphenylene sulfide resins (50 million lb), room deodorants (16 million lb), and moth-control agents (11 million lb). Any future growth will have to come from the phenylene sulfide resins.

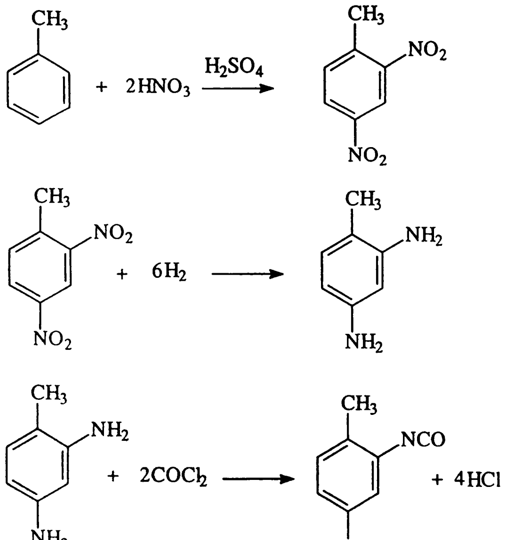
Trichlorobenzenes. A mixture containing trichlorobenzene is always obtained when chlorinating benzene. It can also be made through further chlorination of dichlorobenzene. Most trichlorobenzenes are produced as a mixture of 1,2,3-/1,2,4-trichlorobenzene. The 1,2,3-trichlorobenzene is sold as a raw material for pesticides. The 1,2,4-trichlorobenzene is used for the manufacture of the herbicide Banvel (dicamba). The estimated U.S. consumption was about 15 million lb in 1997.

Derivatives of Toluene

Although the bulk of the toluene is never isolated from the gasoline pool, approximately 12.6 billion lb of toluene was produced for nonfuel consumption in the United States in 2000. Approximately 80 percent of this toluene is used as feed stock for benzene and xylene. The second largest end-use of toluene is as a solvent for coatings, paints, and lacquers. Also of importance is the use of toluene as an intermediate in the manufacture of other chemicals, mainly toluene diisocyanate, and also benzoic acid and benzyl chloride.

Toluene is converted into benzene by a catalytic hydrodealkylation (HDA) process at elevated temperature and pressure. The importance of this process is influenced by the relative value and demand for benzene, as benzene from this source is normally more costly than that isolated directly from refinery reformate streams. Benzene (along with xylenes) can also be obtained by the catalytic TDP. It has became favorable in recent years. Toluene consumption for toluene disproportionation versus HDA has changed from about 1/5 in 1990 to 2/1 in 2000. The volume of toluene that finds use as a solvent is expected to show a continued decline because of regulations controlling the emission of VOCs.

Toluene Diisocyanate (TDI). TDI is manufactured from toluene by the route indicated in the following equations:



The synthesis of TDI begins with the nitration of toluene, using a nitric acid–sulfuric acid mixture. The nitration product typically contains at least 75 percent 2,4-dinitrotoluene with the balance mostly 2,6-dinitrotoluene, which is catalytically reduced to toluene diamine. Lastly, the diamine mixture is dissolved in chlorobenzenes and reacted with phosgene to produce the TDI. After phosgenation, the mixture is stripped of the solvent and separated by distillation. The final product is an 80 : 20 isomer mixture.

The annual U.S. production of TDI was 960 million lb in 1999. Most of the TDI is reacted with polyols to produce flexible polyurethane foams. These foams are widely used as cushioning materials in furniture, automobiles, carpets, and bedding. A small amount of TDI is used to make polyurethane coatings. Polyurethanes are discussed in detail in Chapter 15.

Benzoic Acid. Benzoic acid can be produced by the LPO of toluene using a catalyst such as cobalt or manganese. Domestic production of benzoic acid was about 130 million lb in 2000. Of this amount, about one half went to make phenol or phenolic derivatives. Other uses are in the synthesis of caprolactam and terephthalic acid, and as food additive, and as a plasticizer and resin intermediate.

Benzyl Chloride. The principal method for producing benzyl chloride involves the photochlorination of toluene, followed by neutralization and distillation. In 1999, 75 million lb of benzyl chloride were produced in the United States. About two-thirds was used to manufacture benzyl phthalates (mainly butyl benzyl phthalate), which are widely used as plasticizers. The other use was to make benzyl quarts. Benzyl chloride can also be used as raw material in the manufacture of benzyl alcohol, for use in photography, perfumes, and cosmetics. The production has increased considerably in Western Europe because of the greater use in solvents such as benzyl esters. But the U.S. production was stopped in 1999.

Chemicals from Xylene

Xylenes are obtained mainly (80%) from petroleum reformate streams in the form of "mixed xylenes." A typical composition of this stream is about 18 percent *p*-xylene, 40 percent *m*-xylene, 22 percent *o*-xylene, and 20 percent ethylbenzene. The major chemical uses of xylene, however, require the pure isomers. The purification process involves a number of steps. First the *o*-xylene is separated from the other aromatics by distillation, with the *meta* and *para* isomers going overhead along with the ethylbenzene. *p*-Xylene can be recovered by either adsorption or crystallization processes. The flow diagram in Fig. 10.35 depicts a two-stage crystallization process for recovery of high-purity *p*-xylene from mixed xylenes. In the adsorption process, the stream is charged to a fixed bed of molecular sieves, and the selectively adsorbed *p*-xylene is recovered by washing the bed with solvent. Because the demand for *p*-xylene is far greater than that for m-xylene, the raffinate usually is isomerized to form more of the *para* isomer. Toluene may also be disproportionated to form equivalent amounts of benzene and xylenes without any ethylbenzene. Recently, this TDP process became more favorable. Today, it contributes to 18.5 percent of xylene production.

In 1999, the total demand for the xylenes (12.3 billion lb) was roughly comparable to that for toluene. The volume of *o*-, *m*- and *p*-xylene were approximately 1.1, 0.27, and 9.9 billion lb, respectively. The principal uses of the three xylene isomers are the production of terephthalic acid (or di-methyl terephthalate), phthalic anhydride, and isophthalic acid, respectively.

Terephthalic Acid (Dimethyl Terephthalate). Terephthalic acid (TPA) and dimethyl terephthalate (DMT) are precursors for polyethylene terephthalate (PET), which in turn is used in the production of polyester fibers and film polyester thermoplastic PET bottles, and other resins. In 1999 the total U.S. production was more than 9 billion lb. In the past, the relative ease of producing high-quality DMT gave it the largest share of the terephthalate market. The trend is now toward TPA, as the result of technological advances that permit better purification of TPA and the use of the acid directly in polymer formation. The capacity is about 3 to 1 split in favor of TPA process.

One process for making TPA involves the air oxidation of a solution of *p*-xylene in acetic acid in the presence of a catalyst containing

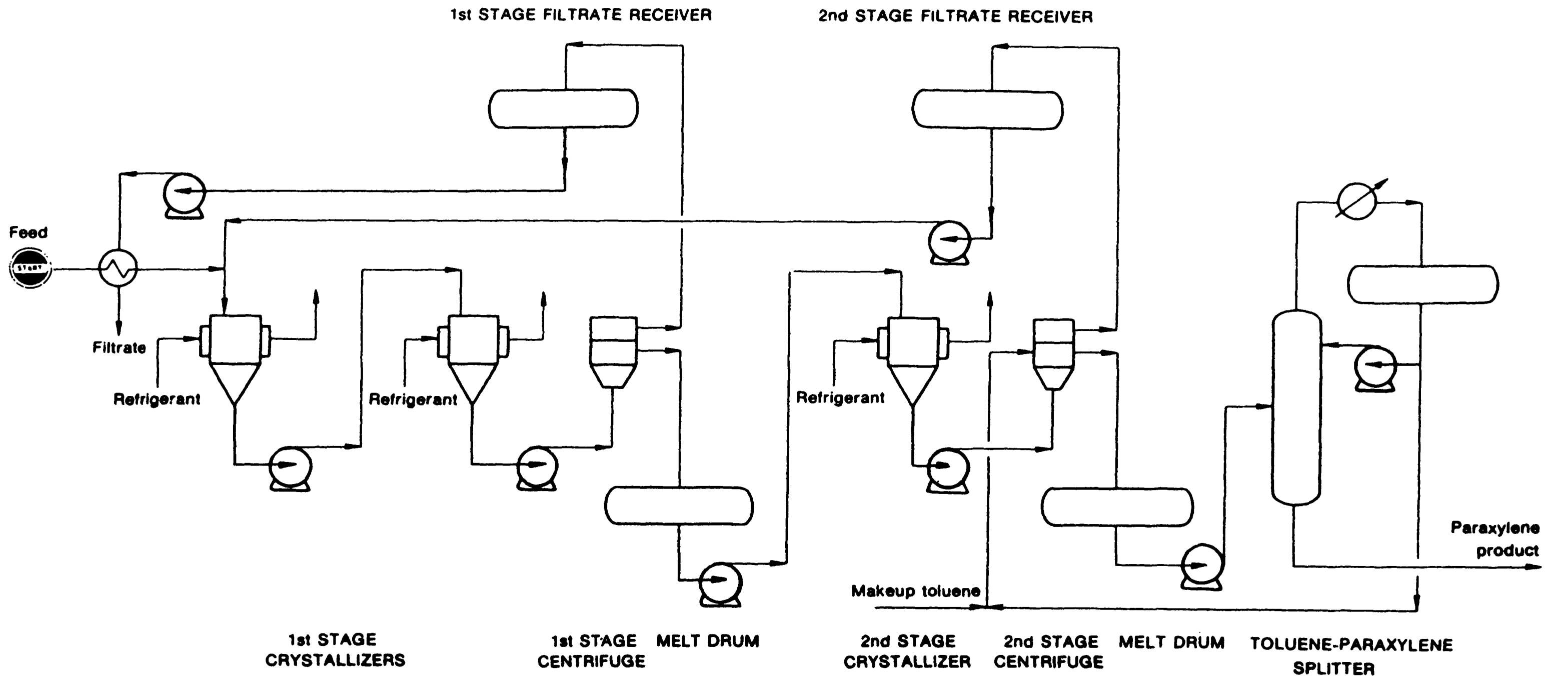


Fig. 10.35. Two-stage crystallization process for recovery of high-purity *para*-xylene from mixed xylenes. (*Reproduced from Hydrocarbon Processing, p. 175, Nov. 1985. Copyright 1985 by Gulf Publishing Co.*)

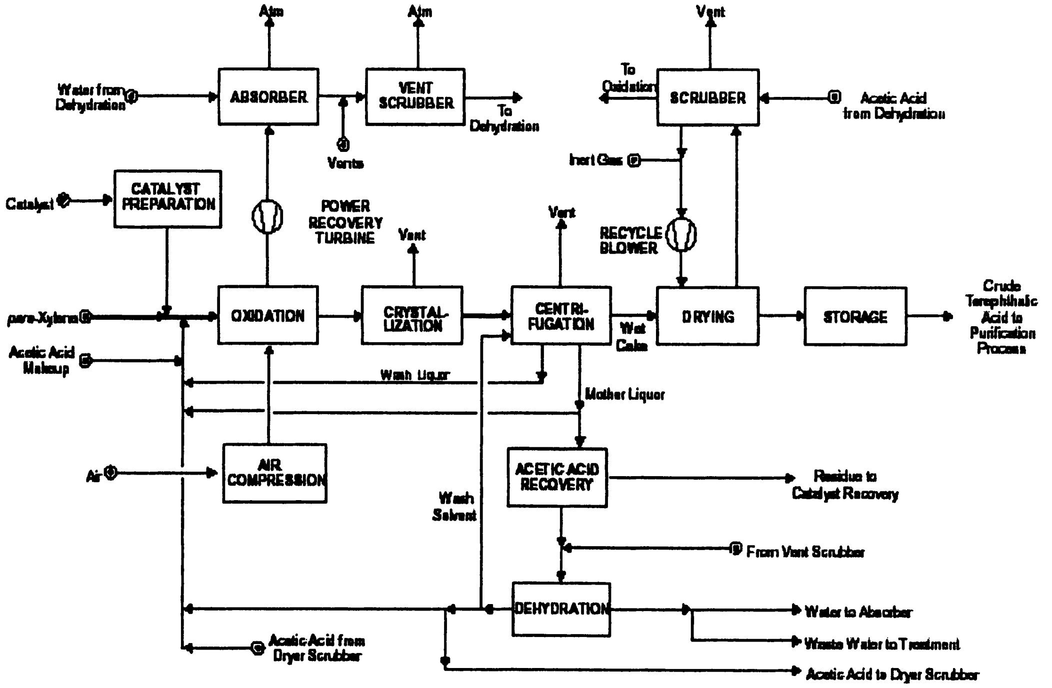


Fig. 10.36. Block flow diagram of generic crude TA process. (*Chem Systems Report No. 97/98-5. Copyright Nexant Chem Systems, Inc. and used by permission of the copyright owner.*)

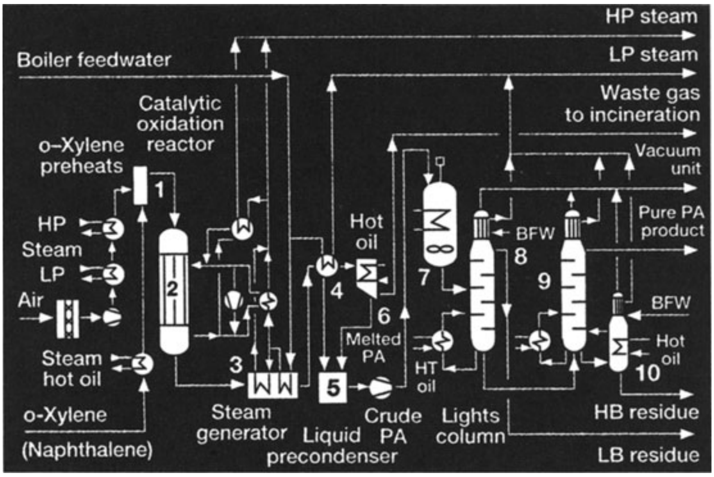


Fig. 10.37. Production of phthalic anhydride. (*Hydrocarbons Processing. p. 118, March, 2001.* Copyright 2001 by Gulf Publishing Co.)

cobalt, manganese, and bromide (Fig. 10.36). The liquid-phase reaction is conducted at about 200°C and 20 atm. pressure. The mixture is cooled to recover TPA by crystallization, dissolved in hot water, and hydrogenated to remove aldehydic by-products. Fiber-grade TPA is recovered by recrystallization.

Phthalic Anhydride. Although phthalic anhydride first was made commercially from the oxidation of naphthalene, by 1999, nearly 90 percent of the production had been converted to *o*-xylene as the feedstock. This is now essentially the only major use for the *o*-xylene. The flowsheet in Fig. 10.37 shows a typical process for making phthalic anhydride. The *o*-xylene is vaporized by injection into the hot gas stream and then passes through a catalyst-filled multitube reactor. The crude phthalic anhydride is desublimated, and any acid present is dehydrated in the predecomposer vessel. The crude is finally purified in two distillations. Although the fixed-bed process currently is important, there are a number of plants in which a fluidized-bed reactor is used.

About 1.1 billion lb of phthalic anhydride are produced annually in the United States. The major uses are in plasticizers, alkyd resins, and unsaturated polyester resins. The plasticizers are esters made by reacting two moles of an alcohol, such as 2-ethylhexanol, with one mole of phthalic anhydride. These plasticizers find major use in vinyl chloride polymers and copolymers. Alkyd resins are a type of polyester resin used in surface coatings. The most rapidly growing end use is in unsaturated polyester resins for reinforced plastics.

Isophthalic Acid. Although *m*-xylene is an abundant material, it has limited demand as a chemical raw material. The only major outlet is in the manufacture of isophthalic acid. More than 220 million pounds were produced in the United States in 1992, primarily for use in preparing alkyd resins and unsaturated polyester resins. Small amounts also are used in PET bottle applications.

Naphthalene Derivatives

The use of naphthalene for production of chemicals has been declining steadily, as it is being replaced by other petroleum-based materials. Current domestic consumption is only about 235 million lb. There are two commercial processes for producing naphthalene. One is the recovery of naphthalene from coal tar, and the other involves its recovery from certain aromatized petroleum fractions. Until the end of the 1950s, the only commercial source of naphthalene in the United States was coal tar. At that time petroleum-derived naphthalene became a commercial product and was quickly established as a desirable source of raw material for phthalic anhydride because of its quality, low sulfur content, and stable supply.

The oxidation of naphthalene to phthalic anhydride has long been its principal end use. In the last 30 years, however, *o*-xylene has supplanted naphthalene as the preferred raw material for phthalic anhydride, and it now accounts for about 90 percent of the PA production. The manufacture of phthalic anhydride is described above in the section "Chemicals from Xylene."

Presently the major end uses for naphthalene are phthalic anhydride (62%), carbaryl insecticide (15%), surfactants and dispersants (20%), and synthetic tanning agents (3%). Carbaryl (1-naphthyl, n-methylcarbamate) is a broad-spectrum insecticide. The major surfactants and dispersants are derivatives of naphthalene sulfonates; their principal applications are as commercial wetting agents, concrete additives, and rubber dispersants, and in agricultural formulations. The synthetic tanning agent are derivatives of naphthalene sulfonic acid and formaldehyde. Other smaller uses of naphthalene are in beta-naphthol and as a moth-repelling agent.

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