*Kirk-Othmer Encyclopedia of Chemical Technology.*

# ECONOMIC EVALUATION, SYNTHETIC ORGANIC CHEMICALS

The global synthetic organic chemicals industry produces a continual stream of innovative products and process technologies. Through technological interlinkage, these products and processes percolate throughout the industrial economy, touching upon and transforming a myriad of sectors, even those apparently far removed from chemical manufacture.

The synthetic organic chemicals industry supplies materials to a wide range of industrial operations. These include plastics, fibers, and solvents, biochemical agents, food chemicals, and materials for construction. Those sectors increasingly affected by organic chemicals include the fastest growing and pivotal industries operating in the early twenty-first century: electronics and telecommunications, the automotive and transportation industry, biotechnology, agriculture, environmental remediation, and the food sciences.

The first organic chemicals were naturally occurring materials derived either from animals or plant by products. These included dyes and textiles, herbbased medicinals, naval stores and solvents, cellulose-based products including paper goods, and a variety of resins and coatings for commercial applications.

The beginning of the modern synthetic organic chemical industry can be traced to the middle of the nineteenth century with the laboratory synthesis of the first dyes by William Perkin in England.

By the 1860s organic chemicals derived from coal-tar distillates had become an important branch of the chemical industry. Coal tar residues, when carefully distilled, supply basic aromatic building blocks for organic synthesis: benzene, toluene, and the xylenes. These materials were used as intermediates in the synthesis of dyes, medicinals, resins, and solvents. The development of improved ovens by the metallurgical industry for capturing increased volumes of coal tar distillates during the coking process helped spur the growth of the synthetic organic chemical industry (1,2). In the last quarter of the nineteenth century, the iron and steel industry was selling increasing volumes of these byproducts to local organic chemical producers (1,2).

At about this time, and continuing into the first part of the twentieth century, Germany took over from England as the world's dominant coal-tar-based organic chemical producing country. Germany obtained its raw materials mainly from its growing iron and steel industry. Also important to the future growth of the industry was Germany's ability to manufacture large volumes of high purity sulfuric acid, which was needed convert the coal tar intermediates into final products (2). Therefore, the emergence in the 1890s of the catalyst-based contact process for making high grade sulfuric acid, an innovation of the German firm Badische, proved a particularly critical development for the country's organics sector.

By the 1890s, the German chemical industry controlled nearly three-quarters of the world's coal tar chemicals markets. The major organic companies included Bayer, Badische, and Hoechst. In the 1920s, these and other of Germany's leading chemical producers would eventually combine into what would become the world's largest organic chemical company, I. G. Farbenindustrie. By the start of World War I, the German chemical industry supplied approximately 95% of total world output of synthetic organics. In 1914, German exported to the United States nearly $\$10 \times 10^6$ of coal-tar-based dyestuffs alone, or more than two and one half times the value of U.S. dye production (2).

## 1. Oil and Petroleum Refining

Coal tar distillates remained the dominant source of organics in Europe until the post World War II period. Even in the United States, coal tar held sway until the 1950s in the organics production of some major chemical producers, most notably, DuPont.

However, the prevailing trend for U.S. organics production after 1914 was the substitution of petroleum and natural gas for coal tars as the basis for synthetic organic chemical manufacture. This in turn resulted in the rising importance of U.S. organics vis-a-vis Germany. The U.S. petrochemical industry specialized in the industrial use of the olefins or aliphatics. The first and to this day most important organic intermediate was the olefin, ethylene, first obtained commercially by Union Carbide (Carbide and Carbon Chemicals Corporation) in the 1920s. The mass production and bulk utilization of ethylene was followed by the use of propylene and butenes. The butenes, for example, were converted to ketones and their derivatives, and applied for a variety of applications as solvents in the automotive and other industries (1–3).

These olefins were the basic building blocks of the U.S. petrochemical industry. Between 1926 and 1939, the number of industrial compounds derived from ethylene increased from 5 to 41. During the same period the number of compounds derived from propylene grew almost tenfold, from 7 to 68.

By the 1940s and 1950s, U.S. petrochemicals moved into other chemical groups, including the diolefins, acetylene, paraffins, and finally the aromatics, which competed successfully against the coal-tar based materials.

In the period up to 1950, petrochemical development was almost exclusively based in the United States. In the 1950s, petrochemicals production began to spread into Europe and Asia based on U.S. technology design. Since 1960, the petrochemicals industry has become global.

The emergence of petroleum refining during the twentieth century is closely linked with the growth and eventual world influence of the U.S. organic chemicals industry.

## 2. Oil as Feedstock

Structurally, oil is made up of hydrocarbon molecules containing various combinations of carbon and hydrogen. The configurations of these molecules depend on the number and arrangement of the carbon atoms. These may be linked in straight chains, branched chains, and circular, or ring formation. With respect to molecular weight, the lighter molecules (fewer carbon atoms) tend to be gases; the medium weight molecules are liquids; and the heavier (many carbon atoms) are heavy liquids and solids.

Hydrocarbons are divided into a variety of categories. Each category possesses a distinct molecular profile and, in turn, set of chemical and physical properties. Each class of hydrocarbons, therefore, has historically served different markets. Crude petroleum is composed of four major hydrocarbon groups: paraffins, olefins, naphthenes, and the aromatics.

In addition to the above hydrocarbon groups, crude oil also contains a number of other elements including sulfur, nitrogen, oxygen, metals, and mineral salts. Not all crudes are the same. They differ according to the geographical locations in which they are found.

## 3. Oil Production Patterns: U.S. and International

The United States has remained the dominant oil production region for most of the twentieth century. This production has been critical to the establishment and growth of the U.S. organic petrochemical industry over the last six decades (4,5).

Between the 1860s and the mid-1880s within the United States, most of the petroleum crude came form Pennsylvania, and more particularly, the Pittsburgh area. After 1885, oil production moved into the Midwest, and specifically Ohio and Indiana. Following World War I, the industry began to exploit the midcontinental fields of Oklahoma and Louisiana as well as the fields in New Mexico, Colorado, Wyoming, and California.

The fastest growing area for production of oil was the Gulf of Mexico region: between 1920 and 1941, its share of U.S. oil production had climbed from 6 to 16%. By the 1960s, Texas became the largest single producing state followed by California, Oklahoma, and Louisiana. By the 1980s, the Gulf region controlled 80% of U.S. oil production.

Overall, U.S. oil production continued to climb through the 1960s and 1970s as the Gulf, Mid-Continental, and West Coast fields were more actively exploited and oil production in Alaska accelerated. By the 1980's, U.S. production stood at over three billion barrels per year. In the United States in the late 1990s there are about 165 operating refineries, or about 24% of the number of world refineries, representing an aggregate capacity of between 15 and 16 million barrels per day. In the U.S. in 1998, refinery utilization rates stood at about 94% compared to only 66% in 1982. The major refining states within the United States are Texas, California, and Louisiana. Together, these states account for more than 60% of total U.S. refining capacity.

Although the United States remains the dominant producer, the late 1990s saw a contraction in U.S. oil production, a result, in part, of oil imports from the Middle East and other areas of the world. Indeed, oil production has been expanding outside the U.S. at an accelerating rate. Closely following this growth has been the expansion of petrochemical capacity in these regions.

In 1998, there were over 700 refineries worldwide. In terms of number of refineries, the U.S. led the world with 165. In terms of major regions of the world, North America has 193 refineries (27.5% of the world number), the Far East (including China, India, Japan) has 139 (19.8%), Western Europe has 120 (17.1%), Eastern Europe (including Poland, Romania, and Russia), has 89 (12.7%), Central and South America (including Argentina, Brazil, and Venezuela) has 79 (11.3%), Africa (including Algeria, Egypt, and Nigeria) has 45 (6.4%), and the Middle East (including Iran, Iraq, and Saudi Arabia) has 37 (5.3%).

In terms of distillation capacity, total world capacity is $76.1 \times 10^6$ barrels per day (BPD). North America accounts for $18.8 \times 10^6$ BPD (24.7%) the Far East accounts for $16.3 \times 10^6$ BPD (21.4%), Western Europe, $14.6 \times 10^6$ BPD (19.2%), Eastern Europe, $12.1 \times 10^6$ BPD (15.9), Central/South America, $5.9 \times 10^6$ BPD (7.8%), Middle East, $5.4 \times 10^6$ BPD (7.1%), and Africa, $2.8 \times 10^6$ BPD (3.7%).

It is estimated that total world oil supplies exceeds $2 \times 10^{12}$ barrels or sufficient resources to provide energy lasting to the end of the twenty-first century. There is an increasing effort to find and capture previously unexploited oil reserves. These involve innovative ways of locating oil deposits, including advanced subsurface imaging, new type of marine production facility designs, and advanced drilling technologies, aided by innovative electronics and stronger materials for drilling tools. These technologies have greatly expanded potential oil supplies worldwide. They have allowed access to previously inaccessible oil, especially in deep, off-shore areas, such as Brazil, the Gulf of Mexico, and West Africa. Improved processing of the heavier oils have allowed the efficient use of previously uneconomic fields (eg, possessing heavy oil), such as in parts of South America and Canada.

Both Canada and Mexico have been expanding production. Venezuela remains a leading producer and importer of oil into the United States. New development is taking place here as in other parts of South America. Brazil is becoming an important oil-producing center, as are Argentina and Chile. In Eastern Europe, reserves are being exploited around the Caspian Sea. South East Asia, Indonesia and Malaysia, are extending their petroleum production and processing capabilities. Western Europe is working regions of the North Sea. Other promising oil-producing countries include Australia, India, Pakistan, and parts of the West Coast of Africa.

### 3.1. The Petroleum-Refining Industry

The petroleum-refining industry refines crude oil into fuels, finished nonfuel products, and off-gas raw materials for consumption as intermediates by the chemical industry. Petroleum refining converts crude oil into a vast array of commercial products. Crude oil is the source for over three thousand petroleum-based products for both industrial and consumer applications (5). Price trends for crude oil affect prices for organics, ie, as the price of crude increases, so do the prices of petrochemicals.

The petroleum-refining industry has played a central role in the expansion of energy capacity over the last century. In the late 1990s, petroleum refiners generated products which accounted for approximately 40% of the total energy consumed in the U.S. (in Btus). The industry is characterized by a small number of large, integrated companies with multiple high-capacity refining facilities.

During the last half of the nineteenth century and up to World War I, demand for petroleum revolved around society's need for lamp fuel, kerosene and related heating fuel, solvents, waxes, asphalt products, and mineral oils, industrial greases and lubricants. In the post World War I period, the rise of the automotive industry shifted demand to petroleum as a source of fuel. By the 1930s, the burgeoning aviation industry increasingly tapped petroleum for high-grade gasoline. By this time as well, the chemical industry began purchasing from refineries the large volume of by-product gases generated during cracking and reforming of petroleum as a source of raw materials for synthetic organics.

Since the 1920s, the petroleum refinery has grown larger and more sophisticated. The refinery subsumes three major processes (5).

### 3.2. Separation

The technique of separation (ie, distillation), the first stage processing of petroleum, exploits the different boiling points of the various petroleum fractions. The separation process isolates for use the different portions of the crude. The type and proportions of hydrocarbons present in each fraction depends upon the type of crude oil used and the range of temperatures employed. Distillation involves the following unit operations: heating, vaporization, fractionation, condensation, and cooling of feedstock.

The principal products produced directly from crude oil from such separation processes as distillation include kerosene, lubricants, and waxes. Separation is a physical process only, ie, it does not involve chemical changes.

### 3.3. Conversion

Conversion refers to cracking, reforming, and related processes, which are designed to increase the yields and octane numbers of fuels from petroleum and natural gas.

Conversion is chemical in nature in that it alters the product's molecular structure. Cracking, the most important of the conversion processes, reduces the molecular weight of the molecules composing crude oil and results in higher grade fuels. These processes can be carried out by simple pyrolysis or by catalytic action through the use of chemical reactor technology. Virtually all conversion processes in operation today involve the use of catalysts at some point.

In the early twentieth century, cracking was undertaken under high pressures and temperatures in tubelike stills. This technology was superseded in the late 1930s by fixed-bed catalytic reactors. In these vessels, a stationary catalyst bed cracked incoming oil vapors.

By the 1940s, catalytic cracking was revolutionized by the coming of fluid-bed cracking in which the catalyst itself flowed between and through vessels. This increased significantly the quality of refined products, especially fuels, and led to increased efficiencies of operation (6). Fluid catalytic cracking, which is operated as a totally continuous process, is the dominant method for cracking petroleum today.

In addition, or as a supplement, to cracking, the refinery utilizes other catalytic processes to convert petroleum into high-grade fuels. For example, in the process of isomerization, rearrangement of the molecules occurs, resulting in different chemical configurations (eg, branched as opposed to linear structures) but with the atomic composition remaining constant. Each isomer has a unique set of chemical and physical properties. Polymerization involves the formation of larger molecules (polymers) from smaller ones. Reforming transforms hydrocarbons into other hydrocarbons, often to make aromatics from nonaromatic petroleum constituents (eg, paraffins and naphthenes) which in turn improve fuel performance (2).

Beyond generating organic fuels from petroleum, conversion processes are important for organic chemical manufacture because they produce byproduct gases containing a mixture of aliphatic and aromatic chemicals. These gases, which in the early years of refining, were simply allowed to escape into the atmosphere as wastes, along with natural gas, became the critical raw materials and intemediates for the burgeoning petrochemical complexes. These complexe were increasingly located near to the refineries. This is because the gases contained critical intermediates for a wide range of organic syntheses. By the start of World War II, the refiners themselves began capturing and recycling the gases for the synthesis of commercially useful organics on-site.

### 3.4. Upgrading

Upgrading refers to improving the quality of a product. Upgrading operations can be physical or chemical in nature. An important form of upgrading is the use of additives, such as tetraethyl lead, to improve the performance of gasoline.

Generally in refineries, these three processes are operated in tandem. For example, separation processes may be integrated with cracking units to isolate the various products resulting from the cracking operation.

## 4. The Petroleum Refining Plant

The location of organic petrochemical facilities depends on a number of closely interacting factors. No factor is more critical than the locational distribution of refining facilities. Petrochemical plants generally are sited close to petroleum refining centers (7). This is an important economic consideration since the refiners must supply large volumes of feedstocks, often their by-products, in gaseous or liquid form, as well as energy units, to organic chemical plants.

The refineries, in turn, are likely to be located near to crude petroleum sources. Refineries may also be located in the more heavily industrialized regions, such as the East and West Coasts of the United States, to be near the markets for their finished products.

The typical petroleum refinery operation has become larger, more international in character, and more closely integrated with petrochemical facilities. The smaller refinery accounts for less of the fuel market than previously. Thus, between 1982 and 1997, the total number of operating U.S. refineries had declined from 300 to 164. This contraction was due for the most part to the closing down of the smaller refining operations [ie, refineries with less than 50,000 barrels of crude oil per day (BPD) capacity)]. Although in 1997 the smaller refineries still accounted for up to one-half of all U.S. facilities, in aggregate they control barely 14% of total U.S. crude refining capacity (5).

The center of the large-scale petroleum refining plant is the fluid catalytic cracking unit. By the mid-1990s, the technology was virtually the only catalytic cracking process in operation in the major refineries. By 1997, there were approximately 350 fluid cracking facilites in operation worldwide, with most located within the U.S. Between 8 to 9% of the fluid units existing worldwide (25–30 units) are owned and operated by Exxon, the original innovator of fluid cracking. Fluid catalytic cracking accounts for over 95% of all high-octane fuel within the U.S. (5).

In the late 1990s, the growth of fluid cracking as a major petroleum refining process was about 2% per year. Total world fresh feed capacity for the fluid process now stands at more than $11 \times 10^6$ barrels/day. Worldwide, fluid catalytic units generate $80 \times 10^9$ gallons of high-grade gasoline annually. This represents nearly half of the total world gasoline production (5).

A major development for fluid catalytic technology through the 1990s has been its closer integration with the large petrochemical complex. Essential petrochemical activity has been relying more on fluid technology and less on thermal units for their intermediate olefin and aromatic feedstock.

## 5. The Rise of Petrochemicals

The organic petrochemicals industry began in earnest in the United States in the years following World War I. Over the following three decades, petroleum competed with coal and grain as feedstocks for the manufacture of synthetic organic chemicals (2,3). (See also Petroleum)

In the 1920s and 1930s, most attention of the industry was focused on new process technologies involving the olefins: ethylene, butylene, and propylene. Petroleum refiners participated in organic chemical manufacture to only a limited extent prior to World War II. Most notably, in the early 1920s, Standard Oil of New Jersey (Exxon) developed a process for synthesizing isopropyl alcohol on a mass production basis. Additionally, in the 1930s, Shell produced synthetic ammonia from natural gas as well as selected organics using the off-gases of their refining operations as raw materials.

For the most part, early petrochemical manufacture was carried out by chemical producers proper. By the late 1920s, Union Carbide, through its division, Carbide and Carbon Chemicals Company, produced ethylene and its derivatives from natural gas found in West Virginia. Ethylene was obtained by the direct cracking of natural gas and liquid petroleum fractions. Propylene and the butenes were derived either as a byproduct of ethylene production or from refinery operations. Important synthetics developed at this time by Carbide included ethylene glycol, which was used as one of the first synthetic antifreeze materials for automotive radiator systems, as well as ethylene oxide, acetone, and the vinyl plastics. The glycol ethers were also produced and were used in new surface coatings for automobiles.

In the 1930s as well, Dow Chemical began the mass production of petrochemicals using locally occurring petroleum and natural gas. One of its principal achievements prior to World War II was the development of a process for the manufacture of styrene; a critical intermediate in the making of synthetic rubber and polystyrene resins. Another petrochemical achievement by the chemical industry was the synthesis of methanol and formaldehyde from natural gas.

World War II proved to be a watershed time for petroleum-based synthetic organics. Whereas World War I utilized the inorganics sector for making large quantities of advanced explosives, World War II consumed different sorts of materials for new applications. Tanks, trucks, and aircraft required volume production of high-octane fuel. Also consumed were new synthetic materials for tires, parachutes, communications equipment, and the like. It was during World War II that the petroleum refiners actively converted their petroleum processing capability to the making of strategically vital petrochemicals, most notably synthetic rubber and fibers.

In the post World War II period, petrochemicals expanded in a number of ways. Geographically, Europe and Asia increasingly adopted petroleum-based processing technology, much of it adapted from U.S. technology. In the United States as well, petrochemical production took root across a wider geographical area. By the late 1990s, important organic chemical centers were located in Texas, Louisiana, Oklahoma as well as Illinois, Ohio, Michigan and West Virginia.

In addition, more products, previously manufactured from coal or grain, began to be derived from the more economical petroleum-based processes. Moreover, established petrochemicals, such as ethylene and ammonia, were produced in larger and technically more advanced plants.

By the 1960s, over 70% of all synthetic organics manufactured globally was derived from petroleum or natural gas. By the 1970s, there were approximately 3,000 distinct chemicals commercially produced from fossil fuels. In the late 1990s, over 90% of all organics production was based on either petroleum or natural gas. These raw materials generated in excess of 6,000 specific commercial organic compounds (5).

Through the 1990s, the United States has remained the world's main petrochemical center. In 1997, looking at total petrochemical manufacture, there were 54 petrochemical establishments in the U.S. employing a total of nearly 11,000 people with an aggregate value of shipments $20.5 billion. Texas is the country's largest petrochemical manufacturer with 21 establishments. Louisiana follows with seven and Illinois with three. The value of petrochemical shipments for the three states are $\$16.6 \times 10^9$, $\$1.5 \times 10^9$, and $\$109.3 \times 10^6$, respectively (8).

## 6. Catalysts and Petrochemicals

Catalysts have played a dominant role in synthetic organic chemicals manufacture since the early part of the twentieth century. Catalysts are generally composed of one or more metals and metal compounds. Through the action of promoters mixed into the catalyst mass, they accelerate and often help direct industrial chemical transformations. Their commercial function is to accelerate reactions to the point that they become economically feasible.

The early commercial catalysts, which were either iron or platinum-based, were developed in Germany, most notably for the mass manufacture of the inorganic heavy chemical, sulfuric acid. By World War I, catalytic production of ammonia, phthalic anhydride, and methanol took center stage, first in Germany and then in the United States. In the 1930s, the first catalytic cracking technology, introduced by the U.S. refiner, Sun Oil, went on line commercially followed in the next ten years by larger and more advanced catalytic cracking and reforming technologies. These designs culminated in the 1940s with two landmark catalytic petroleum processing technologies: fluid cracking (Jersey Standard) and platforming (Universal Oil Products) (2).

By the late 1940s, catalysts were used in the making of intermediates for such critical organic synthetics as advanced fuels, and in the polymerization production of vinyl plastics, nylon, polyethylene, synthetic rubber, and the methacrylates. In the late 1960s and early 1970s, catalysts entered the environmental arena as the central component in catalytic converters for the control of automotive emissions (2).

By the late 1990s, catalysts accounted for well over 60% of organic production and 90% of current organic chemical processes. In 1999, catalyst manufacture represented in excess of $\$10 \times 10^9$ in four large market segments: refining, polymerization, chemicals, and environmental remediation. In that year, more than 100 firms were engaged in the manufacture of catalysts internationally. More than half of these were based in the United States (9).

The catalysis industry remains highly fragmented. Catalyst manufacturers range from large multinationals to small, locally based companies. These firms compete by providing high value added. No single firm dominates any individual market segment for catalysts. Catalyst manufacturing firms tend to specialize in specific types of catalysts for particular petrochemical processes (9).

Recent developments in the industry involve improved large-scale manufacture of catalysts. This is crucial in reducing catalyst costs. As important, catalysts are being designed with more specific and precise site architectures, and in turn, greater reaction selectivity. Catalyst research has focused on the aluminum silicate-based zeolites and organic-based ion-exchange resins. These catalysts are used in a growing array of organic reactions as well as in advanced fluid cracking technology. Most recently, the chemical industry has been developing a series of catalysts designed to polymerize a new generation of linear, low-density polyolefins. By 2005, these so called metallocene catalysts are expected to capture 18% and 5.5% of the production of linear low-density polyethylene and polypropylene production, respectively (10).

## 7. The Petrochemical Plant

Within the synthetic organic chemicals industry, a few large-scale production facilities account for the bulk of total production. Within the United States and internationally, organic chemical facilities tend to be located close to petroleum refineries. Location of plants depends as well on access to transportation networks. This is important both for shipping raw materials into the plant and transporting chemical intermediates and final products out.

Most synthetic organic plants are multiproduct and multiprocess production units. Processes are designed so that the level of output of interrelated products can be varied over a wide range of operating conditions. This allows the synthetic organic production unit to respond to different types of feedstock and product price schedules (7).

## 8. Environmental Trends

Environmental concerns first emerged in the petrochemicals industry at the end of World War II. In 1945, the petrochemicals industry began recovering sulfur from the hydrogen sulfide present in natural and refinery gas. This was done because of the problem of air pollution and world sulfur shortages in the late 1940s and early 1950s. This recovery technology was based on novel and more efficient absorbents.

In more recent years, organic chemical companies have been investing billions of dollars in environmental technology to meet rapidly growing regulatory requirements. Companies are going beyond this and attempting to integrate environmentally beneficial technologies into their processes and to incorporate greater degree of recyclability into their production designs. In part this is to avert potential future and costly environmental regulation. By these measures, they hope to convince the regulatory authorities that the industry can regulate itself.

There are also commercial considerations. The growing role of international standards through such bodies as the International Standards Organization (ISO) means that companies who are not environmentally compliant to the ISO 14,000 standards will be at a competitive disadvantage: customers will avoid doing business with them in favor of environmentally cleaner companies. The industry also understands that there is a direct correlation between environmental compliance and increased manufacturing productivity, a vitally important concern for organic chemical companies.

Important groups of organic chemicals that have come under regulatory control since the 1970s, and in particular with respect to clean air, include the methyl-based fuel additives and the halogen hydrocarbons in the form of the chlorofluorocarbons (CFCs).

### 8.1. Methyl-T-butyl Ether (MTBE)

Methyl-*t*-butyl ether (MTBE) has been an especially important additive. It was first used as a fuel additive in the 1940s. MTBE began replacing tetraethyl lead in this country to enhance octane number. In the late 1980s, California was the first state to promulgate its use as an oxygenate for cleaner burning fuel. The consumption of MTBE in the U.S. increased rapidly between 1990 and 1995 with the passage of the Clean Air Act and a few years later the implementation of the Federal reformulated gasoline program (see Gasoline and other motor fuels).

In 1998, MTBE was produced at over 50 U.S. plants located in 14 states. In 1998, over $3 \times 10^9$ gallons of MTBE, requiring $1.3 \times 10^9$ gallons of methanol feedstock, were added to reformulated gasoline.

In the late 1990s, MTBE has come under serious attack. MTBE has been linked to possible serious disease. The probable occurrence of cancerous tumors in laboratory rats injected with MTBE alerted federal agencies as to the possible health hazard of the substance (11). Also, MTBE has been linked to the contamination of ground water. In 1999, EPA reversed itself, recommending the phasing out of MTBE as an additive to gasoline.

This restriction will close off an important market for methanol in the U.S. Ethanol will most likely replace MTBE as an effective oxygenate additive. The finding on MTBE also is refocusing attention on alternative fuel sources. Both methanol and ethanol are likely to play important roles in this market.

### 8.2. Chlorofluorocarbons (CFCs)

The chlorofluorocarbons (CFCs), which are neither toxic nor flammable, had found wide application in aerosol sprays and as solvents and refrigerants (in the form of freon). In the late 1950s, freon was used in air conditioners in automobiles, homes, and office buildings (12).

In the 1970s and 1980s, scientists observed that CFCs that entered the atmosphere decomposed by exposure to ultraviolet (uv) radiation. The result was the formation of inorganic chlorine. This released chlorine was shown to react with and eat away at the earth's stratospheric ozone layer, a protective shield against radiation from space. As a result, the use of CFCs in air conditioners, spray cans, and other applications have been severely restricted by regulatory fiat.

In the 1990s, the Clean Air Act restricted the emissions into the atmosphere of a wide range of organics, including the furans, dioxins, and their derivatives. Other regulatory initiatives involved restrictions of selected organics in factory effluents (clean water) and as wastes which can be sent to landfills (solid wastes). In addition to the U.S. Environmental Protection Agency (EPA), the U.S. Department of Transportation (DOT) regulates the interstate transport of hazardous organic materials. The United Nations has been regulating the international transportation of hazardous organics by air, sea, and land.

## 9. Economic Patterns: U.S. and International

### 9.1. General Trends

In the late 1960s and early 1970s the world organic chemical industry was reasonably profitable. Although the market place remained competitive, companies found market niches using new products or variations of older products. In this way, each company, which remained strongly linked to domestic demand, carved out a viable market territory for itself.

Over the last 30 years, the chemical industry has become truly global. Globalization has opened up new markets for organic chemicals. In 1970, chemical exports from all countries had a dollar value of $\$20 \times 10^9$. By 1998, this figure had grown 25-fold to $\$500 \times 10^9$ (7).

Organic chemical companies are pursuing much more diverse competitive strategies compared to thirty years ago. Some companies, including Exxon Mobil, BP, and Shell, focus primarily on basic chemical intermediates and polymers. Other companies, including ICI and Ciba, concentrate on chemical specialties. Still other firms, such as Monsanto and Hoechst, have emphasized biotechnology as opposed to chemical production. Some companies, including Dow, DuPont, and Union Carbide, take a more balanced strategy poised between economically cyclical commodities and the higher value added specialty products (7).

Between 1983 and 1993, the production of industrial organic chemicals has increased an average 3% annually. Petrochemicals enjoyed rapid growth and good profits in the early 1990s. At that time, the industry committed funds to expansion. By 1997, with the Asian economic crisis, prices fell for basic petrochemicals. Overcapacity is a continual threat to the industry as producers tend to act independently (ie, without reference to other manufacturers). In the face of fluctuating demand. Overcapacity resulted in canceled projects and the closing of plants (13,14). Industry specialists felt that the bottom of the cycle hit in 1999 (15).

**Table 1. Market Trends For Chemicals and Organics, × $10^9$ \$[a]**

| | year | | | | | |
|---|---|---|---|---|---|---|
| area | 1998 | 1999 | 2000 | 2001 | 2002 | 2003 |
| world[b] | 1,600 | 1,648 | 1,697 | 1,816 | 1,943 | 2,079 |
| United States[c] | 72.3 | 77.2 | 82.3 | 86.7 | 89.8 | 92.5 |

[a] Refs 5, 8, 13–15.
[b] Includes all chemicals.
[c] Includes synthetic organics only.

### 9.2. Regional Patterns

Since the world chemical industry is dominated by synthetic organic chemicals, the latter closely shadows the economic performance of the chemical industry as a whole.

The global chemicals industry is a \$1.6 × $10^{12}$ business. The world petrochemical industry is expected to grow at an average annual rate of 3% between 2000 and 2005 (13–15). By 2005, the market for chemicals globally will reach over \$2 × $10^{12}$ (see table 1).

In North American, in 1997, U.S. production of chemicals and allied products was valued at \$392 × $10^9$, or about 25% of world chemical production. In 1999, the United States produced 28% of all the chemicals manufactured worldwide. In the United States, until 1997, U.S. production of organic chemicals has been growing between 2% and 4% annually. Total shipments declined by 0.8% from 1997 to 1998, to \$72.3 × $10^9$. By 2003, the U.S. Commerce department forecasts organic shipments will total \$92.5 × $10^9$, an increase of 7% per year.

In the late 1990s, organic chemicals represented the largest part of U.S. chemical exports. More than one-half of all chemical shipments exported abroad were synthetic organics, either intermediates or final products. In 1997, the U.S. exported \$15.8 × $10^9$ of organic chemicals and imported \$14.5 × $10^9$. By 2003, the Department of Commerce forecasts that exports of organics will rise to \$24.1 × $10^9$ while imports will increase to \$21.5 × $10^9$.

In 1999, the European Union (EU) produced 30% of the world's total chemical production. Germany remains the single most important chemical producer in Europe followed by France, UK, and Italy. Together, these four countries produced 67% of EU chemical output. The EU has exhibited the highest rate of chemical growth internationally. Between 1990 and 1998, the EU had an average annual growth of 2.8% compared with 2.2% for the United States and 1.6% for Japan (16–18).

Japan's chemical production accounts for 13% of the world's total chemical production. About 30% of Japan's petrochemical products are exported, mostly to other parts of Asia. The trend in Japan is towards mergers of local firms into a half-dozen or so companies centered on ethylene. These are forming around the large ethylene centers: Chiba, Kawasaki, and Mizushima.

Other parts of the world are making important gains as centers of organics production. Between 2000 and 2005, it is expected that the share of total organic production represented by the United States, Western Europe, and Japan will drop from 71 to 63%. More competition in organic chemical production is expected from the Pacific rim, China and Korea as well as from India and the Middle East (19–21).

Asia as a whole (not counting Japan) currently represents 14% of the world's total chemical production. For petrochemicals production in Asia, the annual growth will average 6.5% in the 2002 to 2010 period. The Asia-Pacific region's buildup in petrochemicals will raise its share of global production to 30% or about the same as North America by 2003 (19–21).

In the Middle East, petroleum and chemical companies are seeking new markets for value-added petroleum derivatives. The larger, international corporations will acquire or build integrated refinery-petrochemical complexes in partnership with local firms.

## 10. Product Segments

### 10.1. Methanol: The Methyl Compounds, Formaldehyde, Acetic Acid, and the Methacrylates

#### *10.1.1. History and Process Technology*

Methanol was one of the first organic chemicals produced in the twentieth century. It was first manufactured in bulk in Germany in the mid-1920s, and imported in tonnage amounts into the U.S. in 1927. Soon thereafter, DuPont began producing methanol from coal as part of its ammonia production operations at Belle, West Virginia. In these processes, methanol was synthesized through the high pressure catalytic hydrogenation of carbon monoxide gases. Within a few years, the United State became the dominant producer of methanol in the world resulting in a sharp drop of German imports (2)

Eventually, chemical producers within the United States developed technology to produce methanol directly from natural gas which is a more efficient route than the coal-based processes. The process involved the partial catalytic oxidation of natural gas hydrocarbons. Following World War II, production of methanol expanded internationally. Methanol (qv) is produced today almost solely from petroleum and natural gas (2).

#### *10.1.2. Consumption Patterns*

The first big use for methanol was as an antifreeze for automotive radiators. Over the years, other organic materials have supplemented or replaced methanol in this market. Methanol remains an important intermediate in the manufacture of formaldehyde, as well as acetic acid, methyl *tert*-butyl ether (MTBE), and methyl methacryate (7). (see Methanol)

In the 1990s, the manufacture of formaldehyde (qv) represented the largest single market for methanol. Over the next few years, the production of MTBE as an additive to gasoline competed with formaldehyde as a consumer of methanol. In 1998, approximately 35% of total methanol consumed went into the manufacture of formaldehyde, 30% into the production of MTBE, and 10% into acetic acid. Other outlets for methanol include the methylamines, the methyl halides, and dimethyl terephthalate (7).

In 1998, formaldehyde consumed $9.2 \times 10^6$ t of methanol globally. By 2005, this consumption is expected to reach $11.2 \times 10^6$ t. World MTBE consumption of methanol equaled $7 \times 10^6$ t in 1998. Some estimates forecast that world consumption of MTBE will reach $8.2 \times 10^6$ t in 2005. However, an expected phasing out of MTBE in the U.S. and internationally may result in a sharp reduction in total consumption. Acetic acid production used $2.3 \times 10^6$ t of methanol in 1998, a figure which will rise to $3.5 \times 10^6$ t in 2005. Methyl methacrylate manufacture consumed 728, 000 t of methanol in 1998 and is projected to use 974, 000 t in 2005. As for the solvent group as a whole, $1.1 \times 10^6$ t of methanol were consumed in 1998, and consumption is expected to grow to $1.3 \times 10^6$ t in 2005. In 1998, between $5 \times 10^6$ and $6 \times 10^6$ metric tons of methanol was consumed in a variety of other applications (22–24).

#### *10.1.3. Global Supply and Demand*

Global methanol production was about $26 \times 10^6$ metric tons in 1998. By 2005, production is expected to reach $32.5 \times 10^6$ t. In the late 1990s, the industry faced chronic over capacity. Worldwide, there is expected to be an excess capacity in methanol. Between 1999 and 2002, it is anticipated that more than $2.5 \times 10^6$ t of capacity will come on line. New methanol plants are beginning operations in the Middle East and Asia (eg, South Korea). But in this period global demand will increase by only $1.1 \times 10^6$ t, leaving an excess of methanol of $1.4 \times 10^6$ t. Global methanol operating rates are not expected to go above 75% for the period. As a consequence, the contract price for methanol on the whole has been on the decline. In 1997, the average annual contract price for methanol stood at 57.0 cents per gallon. By 1998, the price was 42.0 cents per gallon and by 1999 only 27.0 cents per gallon. The average annual contract price increased a bit in 2000 to 30 cents per gallon (22–24).

The movement to ban MTBE in the United States and internationally will result in even less demand for methanol. In 1998, the demand for methanol in Asia began to decline. Moreover, MTBE use as a gasoline

**Table 2. Global Consumption of Methanol, by Principal Market Segment, $\times 10^6$ t**[a]

| | Year | |
|---|---|---|
| Market | 1998 | 2005 |
| formaldehyde | 9.2 | 11.2 |
| MTBE | 7.0 | 8.2 |
| acetic acid | 2.3 | 3.5 |
| methyl methacrylate | 0.728 | 0.974 |
| solvents | 1.1 | 1.3 |

[a] Refs. 7, 22–24.

**Table 3. U.S. Methanol Trends, $\times 10^6$ t**[a]

| | year | | |
|---|---|---|---|
| Supply | 1998 | 1999 | 2000 |
| production | 5.9 | 5.2 | 4.5 |
| imports | 2.6 | 3.0 | 4.2 |
| available supply<br>production + imports | 8.5 | 8.2 | 8.7 |
| imports, %, available supply | 30.6 | 36.6 | 48.3 |

[a] Refs. 22–25.

additive has leveled off in the United States, in part because of health concerns and in part because of the introduction of alternative additives. The use of MTBE has not expanded much in other countries. Methanol demand as a fuel in Brazil has also contracted (11).

In addition to excess supply, which leads to lower prices, producers of methanol must contend with fluctuating and unpredictable natural gas prices. Accordingly, a rationalization in the methanol market is expected to take place over the next few years. This will settle the market and avoid the highs and lows traditionally seen in the methanol market. In 1999, methanol production already has been cut in Canada, the United States, and Eastern Europe. However, more high cost producers will need to exit before the market stabilizes.

The global markets for methanol will still be growing across the board, although not necessarily at the rate at which supplies are increasing (see Table 2).

### *10.1.4. The United States*

Methanol production in the U.S., which for most of the 1990s grew between 2 and 5% annually, began contracting in 1998, in large part because of the Asian financial crisis. Production continued to decline through 2000 as U.S. producers faced growing imports from abroad and over capacity at home. In the period 1998 to 2000, U.S. methanol production contracted 23.7%, from $5.9 \times 10^6$ t to $4.5 \times 10^6$ t. In the same period, imports into the U.S. grew 61.5%, from $2.6 \times 10^6$ t to $4.2 \times 10^6$ t. The available supply of methanol in the U.S., which is the sum of production and imports, expanded 2.4%, from $8.5 \times 10^6$ t to $8.7 \times 10^6$ t. In the late 1990s, the percentage of total methanol supply represented by imports grew significantly from 30.6% in 1998 to 48.3% in 2000. This means that methanol imports controlled an increasing portion of total supply vis-a-vis domestic production (see Table 3) (22–25).

## 10.2. Ethylene: Polyethylenes, Vinyls, Styrenes, and Glycols

### *10.2.1. History and Process Technology*

Ethylene began commercial production in the mid-1920s at the West Virginia Plant of Union Carbide (Carbide and Carbon Chemicals Corporation). At that time, Carbide Developed a thermal process to convert ethane contained in natural gas into ethylene for the purpose of manufacturing a variety of ethylene-based chemicals (2,3). The process for making ethylene did not involve use of a catalyst (see Ethylene). Since that time, the technology has expanded and been refined to allow greater efficiencies and volume of production. Capacity extension is generally effected by retrofitting new designs and equipment onto an existing plant rather than constructing entirely new facilities from the ground up (7).

Globally, napththa obtained from petroleum or natural gas is used as feedstock for 51% of all ethylene produced. Ethane from natural gas is the second most prevalent ethylene source (28%). By 2005, it is expected that naphtha's share of the ethylene market will grow to 55% while ethane's share will drop a bit to 26%.

From the environmental perspective, ethylene itself is not considered a threat. However, certain of its derivatives, such as ethylene oxide and vinyl chloride, are believed to be carcinogenic.

### *10.2.2. Consumption Patterns*

The main use for ethylene is in the production of polyethylene plastics. About 57% of total ethylene consumed goes into the synthesis of polyethylene in one form or another. This figure is expected to rise to over 60% by 2005. In addition to the conventional low-density polyethylene (LDPE), which first came on the market in the late 1940s, ethylene is consumed in the manufacture of more recent variations including linear low-density polyethylene (LLDPE), and high-density polyethylene (HDPE). LDPE, LLDPE, and HDPE have properties which allow polyethylene to be used in a wide range of high performance applications. The three different types of polyethylenes are synthesized under different operating conditions and using distinct catalyst systems (see Olefen polymers, polyethylene (7).

In the late 1990s, the conventional, low-density forms of polyethylene consumed 20.5% of all ethylene produced, HDPE took in 24.5% of total ethylene, and LLDPE captured 12.1% of ethylene. Of the various types of polyethylene, LLDPE is growing the fastest with an annual rate of growth of 8.5%. HDPE ranks second, with an annual growth rate of 5.4%. The conventional low-density form of polyethylene is growing at a 1.5% annual rate (26). Conventional LDPE is losing market share to both LLDPE and HDPE in commodity applications but retains a niche market in areas such as ethylene–vinyl acetate resins.

In addition to the polyethylenes, important derivatives of ethylene include ethylene dichloride, ethylene oxide, and ethylbenzene. Ethylene dichloride, which ranks second as a market for ethylene, is a critical intermediate in the manufacture of vinyl chloride (which in turn is polymerized). More than 98% of ethylene dichloride goes to make vinyl chloride monomer (7).

Ethylene dichloride is made at normal pressures and at 60°C. Iron, aluminum, copper, or antimony chlorides are used as catalysts. Approximately 16% of ethylene consumed is dedicated to the synthesis of ethylene dichloride. The market for ethylene dichloride is growing at a rate of 5.2% annually (7).

Vinyl chloride, derived from ethylene dichloride, is one of the most important commodity, large-volume chemicals. The main market for vinyl chloride is in the synthesis of vinyl polymers. Vinyl chloride also serves as the source of vinyl-based ethers, esters, and halogen products. These various reactions take place at normal temperatures and pressures (see Vinyl polymers, vinyl chloride polymers). Reactions to make poly(vinyl chloride) resins are polymerizations and use peroxide-based catalysts. The reactions to make the vinyl acetates, esters, and ethers are substitution reactions and employ a palladium catalyst (7). PVC grew by 5.5% per year between 1993–1997 but declined by 1% in 1998 because of the Asian crisis. PVC forecast demand will return to 4.9% per year for 2000–2003 (7,27).

About 13% of ethylene consumed is used in making ethylene oxide which, in turn, is consumed in the synthesis of ethylene glycol, the premier automotive antifreeze and intermediate for the synthesis of the

**Table 4. Global Ethylene Trends, × $10^6$ t[a]**

| | year | | | | | |
|---|---|---|---|---|---|---|
| | 1985 | 1990 | 1995 | 1999 | 2000 | 20 |
| capacity | 50 | 63 | 79 | 94.7 | 104 | 11 |
| demand | 44 | 56 | 69 | 82.4 | 88 | 10 |
| surplus | 6 | 7 | 10 | 12.3 | 16 | 10 |

[a] Refs. 25, 28–30

polyesters. Ethylene oxide is also an essential intermediate in the synthesis of a large number of ethylene-based compounds of commercial use, including the rapidly growing polyethylene terphthalate (PET) resins. Ethylene oxide is synthesized under pressure and at 250 to 300°C. The ethylene oxide process uses a silver catalyst. Approximately 60% of ethylene oxide is converted to the glycol using an acid catalyst. Ethylene oxide demand is increasing at a rate of 7.3% annually (7).

Following ethylene oxide in importance as a market for ethylene is ethylbenzene, which is the main ingredient in the synthesis of styrene, one of the two monomeric components in synthetic rubber (the other is butadiene). It is estimated that 7% of ethylene consumed goes into making ethyle benzene. Ethylbenzene is made under normal temperatures and pressures and with the use of catalysts made of aluminum, iron, and boron chlorides. The market for ethylbenzene for use in styrene resins has been growing, but the latter market has seen increased competition from the polypropylenes.

The remaining portion of ethylene consumed (7%) is dedicated to making such disparate products as the linear olefins and olefin-based alcohols (3%), vinyl acetate (2%), ethanol (1%), and other, miscellaneous chemicals (1%), including acetaldehyde, ethyl chloride, and propionaldehyde (7).

### *10.2.3. Global Supply and Demand*

Ethylene (qv) represents the largest segment of the world petrochemicals market in terms of both revenue and volume. In 1994, ethylene accounted for 24.2% of revenues and 35.4% in volume of total petrochemicals produced.

The market for polyethylene, in particular, is significant and growing. The world demand for polyethylene materials is in excess of 45 × $10^6$ t per year. Demand is expected to reach 64 × $10^6$ t annually over the next few years. See Table 4 for global ethylene trends.

The world demand for ethylene has been growing since the mid-1980s, but not as rapidly as capacity. In 1985, the global market for ethylene stood at 44 × $10^6$ t. By 1990, demand had grown to 56 × $10^6$ t tons and by 1995, 69 × $10^6$ t. In 1998, world ethylene demand was 80 × $10^6$ t. Demand for ethylene in 2000 is estimated at 88 × $10^6$ t tons and in 2003 is projected at 104.4 × $10^6$ t. Overall, world ethylene demand through 2005 is forecast to grow at an annual rate of between 5% and 6%.

Throughout most of this period, world ethylene (qv) capacity exceeded demand and by increasing margins. During late 1980s, soaring demand for olefins in general, and ethylene in particular, resulted in new expansions. Global capacity jumped nearly 20% between 1989 and 1991.

In 1985, world ethylene capacity was 50 × $10^6$ t and in 1990, 63 × $10^6$ t. By 1995, capacity stood at 79 × $10^6$ t and in 1999 at 94.7 × $10^6$ t. In 2000, world ethylene capacity is estimated at 104 × $10^6$ t and by 2003, 114.7 × $10^6$ t.

Between 1990 and 2000, capacity grew 65.1% compared to demand, which in the same period increased only 57.1%. This means that through the period capacity exceeded demand by a growing amount. From 1990 to 2000, this surplus grew 128.6%, from 7 × $10^6$ t to 16 × $10^6$ t. If demand and capacity projections hold, the surplus will remain at least until 2003, but will decline to 10.3 × $10^6$ t. These surplus trends will affect operating rates. Whereas world ethylene operating rates were at a peak of 91% in 1997, operating rates are expected to hit low of 86% in 2001.

As with methanol, a decline in average annual contract price for ethylene is observed, followed by expected declining profits for producers. Whereas in 1997 and 1998, the ethylene contract price was about 24 cents/lb (11 cents/kg), in 1999 the price dipped to 22 cents/lb (10 cents/kg) (25).

Despite expected growth in global ethylene demand, the market for ethylene worldwide may be blunted by problems arising in the ethylene glycol and ethylene dichloride industries. Global capacity for both these chemicals are increasing at a rate exceeding demand. This is particularly true of the ethylene glycol industry. By 2001, glycol capacity worldwide will reach $15.3 \times 10^6$ tons compared to a projected demand of just $11 \times 10^6$ tons. By 2003, ethylene dichloride will achieve a capacity of over $53 \times 10^6$ tons compared to a demand of only $47.6 \times 10^6$ tons. This over expansion is likely to lead to declining prices for these two commodities and reduced profit margins. Low margins will depress reinvestment in new plants over the next several years, thus reducing the demand for ethylene as raw material.

### *10.2.4. Regional Trends*

Western Europe is a principal production center for ethylene. In 1998, European ethylene production rose 2%, to $18.9 \times 10^6$ t. Western Europe produces about 20% of the world's ethylene supplies. It is expected that, between 1998 and 2005, Western Europe's ethylene capacity will increase 20%, from $17.5 \times 10^6$ t to $21 \times 10^6$ t. Western Europe consumption of ethylene has remained slightly less than its capacity. Eastern Europe as well has been increasing its ethylene capacity. The following countries possess at least 200,000 tons of capacity: Austria, the Czech Republic, Germany, Hungary, Poland, Slovakia, and the Ukraine. Overall, Eastern Europe possess in excess of $2.2 \times 10^6$ t of ethylene capacity.

Asia represents another emerging region for ethylene. A particularly important ethylene consuming sector is ethylene glycol. Asia consumes more than 50% of the world's ethylene glycol, mostly in the manufacture of polyester resins. Until 1998, the market for ethylene in Asia grew at a rate between 10% and 25% annually. By the first half of 1998, demand for ethylene fell dramatically along with prices. Nevertheless, anticipating a resurging demand, Asia and the Middle East are bringing on line new ethylene capacity. East Asia and Asia Pacific in particular are becoming self-sufficient in ethylene. This is affecting imports of ethylene from North America and Western Europe (20,31,32).

In 1999, Japanese ethylene production rose 9%, to a record $7.48 \times 10^6$ t. China also has demonstrated a rapidly growing ethylene capacity. Between 1996–2000, Chinese ethylene capacity rose from $3.7 \times 10^6$ t/yr to $4.7 \times 10^6$ t/yr. South Korea, with a capacity of over $3.5 \times 10^6$ t/yr, is another important Asian ethylene center. China is South Korea's most important market for the latter's ethylene exports.

In addition to these countries, India's ethylene market has been growing, along with the chemicals industries in general. In 1997, India produced $1.2 \times 10^6$ t of ethylene. The demand for ethylene in India is growing faster than production. India's consumption for ethylene exceeds $6 \times 10^6$ t, the bulk of which is supplied by imports (33).

Overall, in 1996, Asia accounted for 14% of global ethylene demand. It is expected that this figure will increase to 22% by 2005. Asia's ethylene capacity is increasing at a rate of $3.9 \times 10^6$ t/yr. Demand is growing at the rate of $7 \times 10^6$ t/yr.

### *10.2.5. The United States*

Ethylene ranks fourth in terms of production volume for all organics in the U.S. In 1997, there were 24 producers of ethylene in the U.S. In that year, domestic capacity stood at $56.5 \times 10^9$ lb ($25.6 \times 10^9$ kg)

Since 1984, the growth rate in the demand for ethylene within the United States has been 4.4% annually. This rate of growth is significantly higher than the 2.9% annual growth averages for the previous ten-year period. In 1997, the United States accounted for 29% of global ethylene demand. Although a surplus in ethylene

**Table 5. U.S. Ethylene Trends, × $10^9$ kg**[a]

| | year | | |
|---|---|---|---|
| | 1997 | 1998 | 2002 |
| demand | 23 | 25 | 26.9 |
| capacity | 25.6 | 28.4 | 29.6 |
| surplus | 2.5 | 3.3 | 2.6 |

[a] Ref. 25, 28–30, 34.

capacity has been increasing in the U.S., it is expected that supply and demand will become more balanced after 2000. By 2002, surplus in capacity will be close to 1997 levels. See Table 5 for ethylene trends in the United States.

A major market in the U.S., in additional to the polyethylenes, is poly(vinyl chloride). The bulk (70%) of the consumption of poly(vinyl chloride) in the U.S. goes into construction applications (7). In the late 1990s, demand for poly(vinyl chloride) has been increasing at 3.6% annually. In 2000, it is estimated that U.S. demand for poly(vinyl chloride) will reach 14 × $10^9$ pounds. Between 1997 and 2000, U.S. capacity for poly(vinyl chloride) was growing at 2.3 × $10^9$ pounds per year (27).

### 10.3. The Higher Olefins: Propylene and Butylene

#### *10.3.1. History and Process Technology*

The higher olefins appeared later than ethylene as commercially important chemicals. Whereas ethylene first found its markets in the 1920s, butylene and propylene did not become commercially significant until the 1940s.

Butylene was a particularly critical input in the making of both synthetic rubber and aviation fuel during World War II. With respect to the former, it served as the basis for butadiene, via steam reforming technology, which in turn combined with styrene (qv) in the synthesis of rubber. The development of fluid catalytic cracking was a particularly important landmark in the history of the butylenes and of synthetic rubber. The fluid process generated large volumes of butylene-rich off-gases which permitted the viability of the butadiene-styrene rubber technology as a full-scale enterprise, (See Propylene; Butylenes) (2,3).

Currently, the butylenes are produced either from fluid cracking operations or as a co-product with ethylene in steam-cracking facilities. Butadiene continues to be made from butylene by applying catalytic dehydrogenation technology. Steam reforming of the butylene also is a route to butadiene.

The United States remains a major supplier of butadiene from the butylenes. In 1996, total U.S. capacity amounted to 2.0 × $10^9$ kg 4.5 × $10^9$ lb. In the latter half of the 1990s, the U.S. demand for butylene-derived butadiene grew at a rate of between 2 and 4% annually.

Since the 1960s, the higher olefins have become more completely dominated by the propylenes. New process technology has allowed the efficient extraction of larger volumes of propylene from the by product gases produced by cracking operations. Improved processes have also made propylene-based resins available in large quantities and at reduced prices. Propylene enjoys a broader range of applications than the butylenes. Accordingly, the remainder of the discussion on the higher olefins focus is on propylene and its compounds.

Propylene is co-produced with ethylene in steam crackers. About one-third of a pound of propylene is produced for every pound of ethylene in these operations. By the late 1990s, about 70% of propylene was being derived as a by-product of steam cracking of feedstock composed of ethane, propane, butane, and napthas.

Propylene is also extracted from the off gases generated in fluid cracking units. About 30% of propylene is produced as a by-product of fluid catalytic processing of gasoline.

**Table 6. Global Propylene Trends, × $10^6$ t[a]**

| | year | | | | |
|---|---|---|---|---|---|
| | 1997 | 1998 | 1999 | 2000 | 2001 |
| capacity | 38 | 40.5 | 43.0 | 46.0 | 49.0 |
| demand | 50 | 53.5 | 55.0 | 57.0 | 59.0 |
| surplus Demand (i.e., capacity Deficiency) | 12 | 13 | 12 | 11 | 10 |

[a] Refs. 25, 29.

The obtaining of propylene from cracking operations, whether through steam or fluid cracking, is an economically favorable activity for refiners since propylene is more valuable on a per unit basis as a petrochemical than as a fuel. Another source of propylene is through the dehydrogenation of propane, obtained from natural gas. Universal Oil Products "Oleflex" process is a notable propane-based route to propylene.

Environmentally, as with ethylene, the higher olefins are not generally considered a threat to human health. However, certain of propylene's derivatives, including acrylonitrile and propylene oxide, are believed to be carcinogenic and are regulated as such.

#### *10.3.2. Consumption Patterns*

The primary use for propylene is as an intermediate in the making of the polymer, polypropylene. The principal markets for polypropylene are as a fiber and in film production, packaging and as a material for molded parts. Approximately 36% of all propylene produced goes into the synthesis of polypropylene. Polypropylene is made under normal temperatures and pressures through the polymerization reaction using aluminum alkyls and titanium oxide catalysts (7).

Acrylonitrile, which is the critical material in the making of acrylics, accounts for 16% of propylene use. Acrylonitrile is synthesized through the oxidation process at normal pressures and 400°C using phosphomolybdate catalysts (7).

About 11% of propylene goes into the making of propylene oxide. Propylene oxide, like ethylene oxide, is an important organic intermediate. It is manufactured at elevated pressures and at a temperature of 37°C using a tungsten catalyst (7).

The remaining 37% of propylene use goes into the synthesis of such chemicals as cumene (9%), the butyraldehydes (7%), various oligomers (6%), isopropyl alcohol (6%), and other diverse organics (9%).

#### *10.3.3. Global Supply and Demand*

Between 1997 and 2000, global propylene demand grew about 18%, from $50 \times 10^6$ t to $59 \times 10^6$ t. This translates into an average annual demand growth of between 3 and 4%. While propylene capacity has also been increasing, the propylene industry has not experienced the same reduction in prices and in turn contraction in profit margins as has the ethylene producers. For propylene, demand has traditionally exceeded capacity resulting in an overall capacity deficiency. However, between 1998 and 2001, the rate of growth of capacity is expected to more than double the rate of growth of demand (21.0% vs 10.3%). As a result, during this period, the capacity deficiency will contract.

Price trends reflect this supply–demand balance. Between 1997 and 1999, the average annual price for propylene has hovered around 16.0 cents lb (7.3 cents/kg), a figure significantly lower than noted for ethylene anytime during this same period (25).

Global demand for propylene is expected to increase at a rate of between 5% and 6% annually after 2001. This growth will be led by an expected 5.5% annual growth rate for polypropylene. See Table 6 for global propylene trends.

**Table 7. U.S. Polypropylene Capacity, × $10^9$ kg[a]**

| Year | Capacity |
|---|---|
| 1996 | 5.67 |
| 1997 | 6.08 |
| 1998 | 6.58 |
| 1999 | 7.89 |
| 2000 | 8.30 |
| 2001 | 8.71 |
| 2002 | 9.16 |

[a] Refs. 25, 29.

#### 10.3.4. Regional Trends and the United States

Regionally, until 1998, the market for propylene in Asia grew at a rate between 10 and 25% annually. East Asia and the Middle East are in the process of bringing on line greater propylene capacity.

In the United States, in 1997, there were 33 producers of propylene with combined capacity of 31 × $^9$ lb/yr (14.0 kg/yr). In the United States, propylene from fluid cracking units accounted for nearly 50% of demand in 1997. Over 50% of U.S. propylene is consumed by polypropylene plants. In the late 1990s, Polypropylene capacity in the U.S. increased rapidly since 1996. By 2002 it is expected that U.S. polypropylene capacity will reach over $9 \times 10^9$kg ($20 \times 10^9$ lb) (see Table 7).

The United States is one of the largest propylene exporting countries and so is heavily dependent on foreign markets. In the late 1990s, between 40% and 50% of U.S. propylene exports went to Asia. These exports are expected to decline over the next few years as Asia expands its own propylene capacity. (see Olefin polymers, polypropylene).

### 10.4. The Aromatics: Benzene, Toluene, and the Xylenes

#### 10.4.1. History and Process Technology

The olefins are characterized by linear (and branched) molecular structures; the aromatics are composed of cyclic or ring-like structures. The aromatics are capable of being formed into products not accessible from olefins.

Between the mid-nineteenth to the mid-twentieth century, the aromatics industry was dominated by the Germans using their advanced coal tar technology. With benzene (qv), toluene (qv), and xylene (BTX) (see Xylenes and ethylbenzene) as intermediates, they synthesized a wide range of dyes, medicinals, and resins which were exported throughout the world. The industrialized countries, including the United States, were dependent upon these materials to supply a broad range of their industries.

Since World War II and up to today, the United States assumed leadership of the aromatics as petroleum and natural gas became the major source of the BTXs. Catalytic cracking technology, culminating in fluid catalytic cracking, produced off gases containing a significant portion of BTX materials. These gases were captured and stripped of these intermediates for use in chemical synthesis

A major technical achievement in the field was the development by Universal Oil Products (UOP) in 1950 of the reforming-based technology known as the platforming process. Employing a platinum-based catalyst, high pressures, and multiple reactors in series, the process generated large quantities of BTX intermediates from petroleum for use by the organic chemicals industry. (see Btx processing) Today, fluid catalytic cracking and platforming still represent two of the major sources for BTX intermediates for use in chemical processing (2,3).

Such reformate-based technology is an especially important source for the mixed xylenes. In 2000, the technology accounted for 82% of mixed xylene production worldwide. Extraction technology is then used to separate the main components: *para*-, *meta*-, and *ortho*-xylene isomers. An alternative route to the xylenes is being increasingly employed. The procedure, known as toluene disproportionation, involves converting toluene to benzene and a mixed xylene stream. UOP and ExxonMobil have developed toluene disproportionation technology.

### *10.4.2. Consumption Patterns*

The aromatics in general have a wide variety of applications including use as solvents, feedstock for a number of cyclic organic derivatives, and as components in the blending of gasoline. Toluene also has been a central feed in the making of explosives for decades.

Focusing on benzene, its major use is in the synthesis of ethylbenzene, a critical intermediate in the making of styrene (qv). Approximately 52% of benzene that is consumed is dedicated to the synthesis of ethyl benzene. Ethyl benzene is made in one of two types of alkylation processes. One process uses only moderate pressures and temperatures and uses an aluminum chloride catalyst. The second process is performed under more rigorous operating conditions and employs a zeolite-based catalyst (7).

The ethyl benzene produced is, in turn, converted into styrene by an oxidation process with an iron oxide catalyst at relatively low pressures and temperatures near 600 degrees centigrade (7). Two thirds of the demand for styrene is for polystyrene, which has numerous uses as a packaging material as well as a material used in molded parts for appliances, furniture, and toys. Between 7 and 10% annually of styrene continues to be used as one of the principal components in synthetic rubber.

Cumene, which is also produced from propylene, is the second most important product derived from benzene. Cumene is used to make such critical organic intermediates as acetone and phenol. Approximately 22% of benzene use is dedicated to the synthesis of cumene by the process of alkylation. In this process, only moderate pressures and temperatures are applied. The catalysts used are composed of phosphoric acid and silicate compounds. Cumene can then be oxidized with a catalyst to make phenol (7). The phenol, in turn, has a number of uses, including an intermediate in the synthesis of the polycarbonate resins. The resins are used, among other things, as a material of construction in automotive bodies and windows

Cyclohexane accounts for 14% of benzene use. Cyclohexane is an intermediate on the route to adipic acid which, in turn, is made into such polymers as nylon. In the commercial process, cyclohexane from benzene is produced by hydrogenation using nickel catalysts.

The nitrobenzenes, produced via nitration without catalysts and at relatively low pressures and temperatures (60°C), account for about 5% of total benzene use. The nitrobenzenes, when combined with hydrogen in the presence of a copper catalyst, are used to make aniline, an essential component of synthetic dyes.

The chlorobenzenes, produced via chlorination at low pressures and temperatures (30–40°C), account for about 2% of benzene use. Detergent alkylates and surfactants represent about 2% of benzene use. These are made by the process of sulfonation at low temperatures and pressures. The remaining 3% of benzene produced globally is used to make a number of diverse products including maleic anhydride, xylenol, cyclohexanol, cyclohexanone, aniline, and biphenols (7).

Mixed xylenes are composed of three isomeric components: orthoxylene, paraxylene, and metaxylene. Orthoxylene is used to make phthalic anhydride, *para*-xylene is consumed in the production of polyethylene terephthalate (PET), and *meta*-xylene is made into a gasoline additive and is a component in the manufacture of the organic intermediate, isophthalic acid. Overall, the manufacture of industrial solvents consumes about $2 \times 10^6$ t, or about 8.2% of total demand, of mixed xylenes worldwide.

### *10.4.3. Global Supply and Demand*

The rate of growth of demand for the various aromatics depends on the demand schedules for the different end markets. Demand for benzene depends in the aggregate on market growth for the various benzene-derived materials, such as styrene, cumeme, and cyclohexane.

**Table 8. Global Mixed Xylene Trends, × $10^6$ t[a]**

| | year | | | | |
|---|---|---|---|---|---|
| | 1999 | 2000 | 2001 | 2002 | 2003 |
| capacity | 34.6 | 36.3 | 38.1 | 40.0 | 42.0 |
| demand | 24.4 | 25.9 | 27.5 | 29.1 | 30.8 |
| surplus capacity | 10.2 | 10.4 | 10.6 | 10.9 | 11.2 |

[a] Refs. 25, 29.

The rate of growth of styrene demand globally has been about 3.1% per year and is expected to remain at this rate through 2003. (Between 1998 and 2003, the global consumption of synthetic rubber is expected to increase 12.5% to 12.1 × $10^6$ t.) The rate of growth of cumene and cyclohexane is growing at 4.5% and 4% per year, respectively. Phenol demand, driven strongly by polycarbonate resin production, is expected to be between 4% and 5% annually (25,35).

In the late 1990s, the demand for benzene worldwide has been growing between 3% and 4% annually. In 1996, global benzene demand was 26 × $10^6$ t. It is expected that by 2001, benzene demand will reach 32 × $10^6$ t. Benzene capacity worldwide is also increasing. Between 1999 and 2001, the industry expects an additional 5.6 × $10^6$ t annually of benzene capacity (25,36).

This added production capability will depress average operating rates from 76% (1998) to 72% (2001). Prices are also being affected. The price index for the aromatics as a group declined from 84 to 78 from 1995 to 1999 (1989 = 100). This is shown particularly for benzene. Between 1995 to 2000, the price for benzene dropped from $1.00 per gallon to 72 cents per gallon. In this same period, the price for toluene dropped from $1.00 to 87 cents and xylenes from $1.10 to 86 cents (25).

Examining the xylenes, in mid-2000, mixed xylene prices were on the rise because of the higher prices from crude oil and gasolines. Prices have climbed despite weakening demand for the isomers. Global operating rates for the mixed xylenes are at about 85%. P-Xylene is responsible for about 79% of the 24.4 × $10^6$ metric tons total mixed xylenes in demand worldwide (1999). *o*-Xylene represents about 13% of total consumption with the remaining 8% of world consumption accounted for by *m*-xylene.

Globally, the demand for the para-xylenes is expected to grow 6% to 8% annually and *o*-xylenes 3% to 5% annually from 1999 to 2003. Overall, the world demand for the mixed xylenes will increase between 5% to 7% annually.

Between 1999 and 2003, the global demand for mixed xylenes will grow about 26.2%, from 24.4 × $10^6$ t to 30.8 × $10^6$ t. During the same period, mixed xylene capacity will increase 21.4%, from 34.6 × $10^6$ t to 42.0 × $10^6$ t. And, in turn, surplus capacity will expand 9.8%, from 10.2 × $10^6$ t to 11.2 × $10^6$ t (see Table 8).

#### *10.4.4. Regional Trends*

Until World War II, Europe had been the center of aromatics production based on coal tar. Indeed, the German firm BASF remains Europe's biggest merchant consumer of benzene.

Growth in aromatics markets are most dramatic outside Europe. Asia is seeing a 6.8% annual increase in demand for benzene. The Middle East and to a lesser extent North Africa, which are becoming important sources of benzene, are helping to supply Asia.

Malaysia is expected to become a significant exporter of benzene after 2000 (37). Malaysia is exploiting oil and natural gas opportunities by building large petrochemical complexes with high benzene output capability. It is predicted that Malaysia will export between 90,000 and 135,000 tons of benzene annually over the next few years. The benzene will be exported to Asia, Europe, and North America (38). Mexico also is becoming a large importer of benzene as it has been reducing its capacity in the manufacture of this chemical.

**Table 9. U.S. Mixed Xylene Capacity, $\times 10^6$ t[a]**

| Year | Capacity |
|---|---|
| 1999 | 8.4 |
| 2000 | 8.8 |
| 2001 | 9.2 |
| 2002 | 9.7 |
| 2003 | 10.2 |

[a] Refs. 25, 29.

The xylenes also have become a significant international commodity. Asia is the most important producing region for the xylenes, accounting for 48% of global capacity (2000). Japan and South Korea dominate the xylene market in Asia. North America ranks second with 27%, followed by Western Europe (11%), Eastern Europe (7%), the Mideast and Africa (5%), and South America (2%).

### *10.4.5. The United States*

In 1997, the U.S. aromatics industry employed nearly 3,000 persons and shipped aromatic products worth $\$3.6 \times 10^9$ (8).

In 1998, North America accounted for 32% of global demand for benzene. Of total North American demand, 90% originated in the United States. This demand is being driven for the most part by the market for benzene-derived styrene. In the United States in 1997 there were 14 domestic producers of styrene with total capacity of $7 \times 10^9$ pounds annually. The U.S. demand for styrene stood at $9.3 \times 10^9$ pounds in 1997. U.S. styrene demand is growing at around 3% annually (8,25,39,40).

However, relatively little growth in U.S. benzene capacity is expected in the U.S. during the 1999–2002 period. The U.S. is relying more than previously on imports to meet demand requirements. Asian producers, in particular, have been importing increasing amounts of benzene into the U.S. In 1998, Korea, importing 400,000 tons of benzene, was a primary source of foreign benzene into the U.S. (25,31).

Finally, looking at the other major aromatic intermediates in 1997, toluene demand in the United States increased 4.5% to $930 \times 10^6$ gallons. In that same year, there were 23 producers (refinery and nonrefinery) of toluene in the United States with a total capacity of $1.6 \times 10^9$ gal ($6.1 \times 10^9$ L). If demand trends hold, U.S. demand for toluene in 2002 will stand at nearly $1.2 \times 10^9$ gal ($4.5 \times 10^9$ L) (25,41).

The United States is also a major producer of mixed xylenes. In 1999, there were 15 xylene producers. In that year, the U.S. had a capacity of approximately $8.4 \times 10^6$ t of the xylenes. In 1999, The top three producers were ExxonMobil, BP Amoco, and Chevron Phillips. By 2003, U.S. mixed xylene capacity is expected to reach $10.2 \times 10^6$ t. During these years, the portion of total world xylene capacity represented by the U.S. will increase (see Table 9).

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