# HYDROCARBONS

## 1. Introduction

Hydrocarbons, compounds of carbon and hydrogen, are structurally classified as aromatic and aliphatic; the latter includes alkanes (paraffins), alkenes (olefins), alkynes (acetylenes), and cycloparaffins. An example of a low molecular weight paraffin is methane [74-82-8]; of an olefin, ethylene [74-85-1]; of a cycloparaffin, cyclopentane [287-92-3]; and of an aromatic, benzene [71-43-2]. Crude petroleum oils [8002-05-9], which span a range of molecular weights of these compounds, excluding the very reactive olefins, have been classified according to their content as paraffinic, cycloparaffinic (naphthenic), or aromatic. This article focuses on the $C_1$-$C_6$ hydrocarbons.

In the paraffin series, methane, $CH_4$, to *n*-butane, $C_4H_{10}$, are gases at ambient conditions. Propane, $C_3H_8$, and butanes are sometimes considered in a special category because they can be liquefied at reasonable pressures. These compounds are commonly referred to as liquefied petroleum gases (qv) (LPG). The pentanes, $C_5H_{12}$, to pentadecane [629-62-9], $C_{15}H_{32}$, are liquids, commonly called distillates, which include gasoline [8006-61-9], kerosene [8008-20-6], and diesel fuels (see GASOLINE AND OTHER MOTOR FUELS). *n*-Hexadecane [544-76-3], $C_{16}H_{34}$, and higher molecular weight paraffins are solids at ambient conditions and are referred to as waxes (qv). All classes of hydrocarbons are used as energy sources and feedstocks (qv) for petrochemicals.

Hydrocarbons are important sources for energy and chemicals and are directly related to the gross national product. The United States has led the world in developing refining and petrochemical processes for hydrocarbons from crude oil and natural gas [8006-14-2]. In 1861 the United States produced over 99% of the world's output of crude. About 100 years later U.S. production amounted to 35% of the world's production (1). Hydrocarbons from crude oil have become the energy sources of the industrial world, largely replacing wood and even displacing coal. However, in the United States, crude oil production peaked at $1.3 \times 10^6$ t/d ($9.6 \times 10^6$ bbl/d) (conversion factors vary depending on oil source) in 1970, causing increased reliance on foreign oil sources (2). Since the crude oil embargo in 1973, a number of alternative energy sources have been investigated to reduce the U.S. international trade deficit. The fossil-fuel era may turn out to have been a brief interlude between the wood-burning era of the nineteenth century and the renewable energy sources era of the twenty-first century (see FUEL RESOURCES).

Hydrocarbons were first used in the field of medicine by the Romans. Bitumen was used in ancient Mesopotamia as mortar for bricks, as a road construction material, and to waterproof boats. Arabia and Persia have a long history of producing oil.

With the beginning of the industrial revolution around 1800, oil became increasingly important for lubrication and better illumination. Expensive vegetable oils were replaced by sperm whale oil [8002-24-2], which soon became scarce and its price skyrocketed. In 1850 lubrication oil was extracted from coal and oil shale (qv) in England, and ultimately about 130 plants in Great Britain and 64 plants in Pennsylvania, West Virginia, and Kentucky employed this process.

The earliest oil marketed in the United States came from springs at Oil Creek, Pennsylvania, and near Cuba, New York. It was used for medicinal purposes and was an article of trade among the Seneca Indians. At that time, the term Seneca Oil applied to all oil obtained from the earth. The first oil well was drilled in 1859 in Pennsylvania to a depth of 21.2 m for Seneca Oil Co. It produced 280 t (2000 bbl) in that year. This was the beginning of crude oil production.

Because crude oil is a complex mixture of hydrocarbons, early products such as kerosene were not uniform, and with new refining processes a whole new technology was developed. By 1920 the demand for gasoline exceeded that for kerosene and lubricating oils. The development of thermal cracking, followed by catalytic cracking, provided more gasoline and petrochemicals (3) (see CATALYSIS). During World War II the need for higher octane gasoline increased the demand for aromatic hydrocarbons. This led to several refining developments to increase gasoline octane and catalytic hydroforming and reforming to produce aromatics.

Hydrocarbon resources can be classified as organic materials which are either mobile such as crude oil or natural gas, or immobile materials including coal, lignite, oil shales, and tar sands. Most hydrocarbon resources occur as immobile organic materials which have a low hydrogen-to-carbon ratio. However, most hydrocarbon products in demand have a H:C higher than 1.0.

| Products | Molar H:C ratio |
|---|---|
| natural gas | 4.0 |
| LPG | 2.5 |
| gasoline | 2.1 |
| fuel oil | |
| light | 1.8 |
| heavy | 1.3 |
| coal | 0.8 |

Immobile hydrocarbon sources require refining processes involving hydrogenation. Additional hydrogen is also required to eliminate sources of sulfur and nitrogen oxides that would be emitted to the environment. Resources can be classified as mostly consumed, proven but still in the ground, and yet to be discovered. A reasonable estimate for the proven reserves for crude oil is estimated at $140 \times 10^9$ t ($1.0 \times 10^{12}$ bbl) (4). In 1950 the United States proven reserves were 32% of the world's reserve. In 1975 this percentage had decreased to 5%, and by 1993 it was down to 2.5%. Since 1950 the dominance of reserves has been in the eastern hemisphere and in offshore fields. Proved world gas reserves are nearly $4 \times 10^{12}$ trillion metric feet (5) with 31% in the Middle East.

## 2. Survey of Hydrocarbon Use

**2.1. Energy Sources.** Hydrocarbons from petroleum (qv) are still the principal energy source for the United States. About 60% of the world's energy is supplied by gas and oil and about 27% from coal (6–8).

The use of natural gas as a hydrocarbon source depends on transportation. Over long distances and waterways, liquefied natural gas (LNG) is delivered in cryogenic tankers or trucks (see GAS, NATURAL; PIPELINES).

A significant obstacle to increased gas use is the lack of sufficient transportation and distribution systems. Environmental concerns have encouraged reliance on natural gas as a cleaner burning fuel. Combustion of natural gas emits about half the $CO_2$ that coal generates at equivalent heat output.

Natural gas imports have grown more slowly because imports from overseas require governmental licenses and cryogenic liquefaction plants are very expensive. Natural gas imports are chiefly by pipeline from Canada (see GAS, NATURAL).

Gas and oil are the principal energy sources even though the United States has large reserves of coal. Although the use of coal and lignite is being encouraged as an energy source, economic and environmental considerations have kept petroleum consumption high (see also Aviation and Other Gas Turbine Fuels). The use of compressed natural gas (CNG) is expected to grow in response to the Clean Air Act of 1990. Reliance on foreign imports has remained high.

**2.2. Raw Materials.** Petroleum and its lighter congener, natural gas, are the predominant sources of hydrocarbon raw materials, accounting for over 95% of all such materials. Assuring sources of petroleum and natural gas has become a primary goal of national policies all over the world.

*Synthesis Gas Chemicals.* Hydrocarbons are used to generate synthesis gas, a mixture of carbon monoxide and hydrogen, for conversion to other chemicals. The primary chemical made from synthesis gas is methanol, though acetic acid and acetic anhydride are also made by this route. Carbon monoxide (qv) is produced by partial oxidation of hydrocarbons or by the catalytic steam reforming of natural gas. About 96% of synthesis gas is made by steam reforming, followed by the water gas shift reaction to give the desired $H_2/CO$ ratio.

*steam reforming* $$CH_4 + H_2O \longrightarrow CO + 3\,H_2$$

*water gas shift* $$CO + H_2O \longrightarrow CO_2 + H_2$$

*Aliphatic Chemicals.* The primary aliphatic hydrocarbons used in chemical manufacture are ethylene (qv), propylene (qv), butadiene (qv), acetylene, and *n*-paraffins (see ACETYLENE FOR HYDROCARBONS). In order to be useful as an intermediate, a hydrocarbon must have some reactivity. In practice, this means that those paraffins lighter than hexane have little use as intermediates.

*Cyclic Hydrocarbons.* The cyclic hydrocarbon intermediates are derived principally from petroleum and natural gas, though small amounts are derived from coal. Most cyclic intermediates are used in the manufacture of more advanced synthetic organic chemicals and finished products such as dyes, medicinal chemicals, elastomers, pesticides, and plastics and resins. Benzene (qv) is the largest volume aromatic compound used in the chemical industry. It is extracted from catalytic reformates in refineries, and is produced by the dealkylation of toluene (qv) (see also BTX PROCESSING).

### 2.3. End Use Chemicals.

*Lubricants.* Petroleum lubricants continue to be the mainstay for automotive, industrial, and process lubricants. Synthetic oils are used extensively in industry and for jet engines; they, of course, are made from hydrocarbons. Since the viscosity index (a measure of the viscosity behavior of a lubricant with change in temperature) of lube oil fractions from different crudes may vary from +140 to as low as −300, additional refining steps are needed. To improve the viscosity index (VI), lube oil fractions are subjected to solvent extraction, solvent dewaxing, solvent deasphalting, and hydrogenation. Furthermore, automotive lube oils typically contain about 12–14% additives. These additives may be oxidation inhibitors to prevent formation of gum and varnish, corrosion inhibitors, or detergent dispersants, and viscosity index improvers.

Lubricating oils are also used in industrial and process applications such as hydraulic and turbine oils, machine oil and grease, marine and railroad diesel, and metalworking oils. Process oils are used in the manufacture of rubber, textiles, leather, and electrical goods.

Synthetic lubricants are tailored molecules which have a higher viscosity index and a lower volatility for a given viscosity than lube oils from petroleum. Synthetic oils have the following advantages (9): energy conservation, extended drain periods, fuel economy, oil economy, high temperature performance, easier cold starting, cleaner engines, cleaner intake valves, and reduced wear.

Synthetic oils have been classified by ASTM into synthetic hydrocarbons, organic esters, others, and blends. Synthetic oils may contain the following compounds: dialkylbenzenes, poly($\alpha$-olefins); polyisobutylene, cycloaliphatics, dibasic acid esters, polyol esters, phosphate esters, silicate esters, polyglycols, polyphenyl ethers, silicones, chlorofluorocarbon polymers, and perfluoroalkyl polyethers.

Very high VI (120–145) lubestocks made by hydrocracking and wax isomerization are also becoming important at lower cost than the synthetics. These are primarily isoparaffins or mononaphthenes with long isoparaffin side chains. New technology will be developed for additives and synthetic oils (see LUBRICATION AND LUBRICANTS; HYDRAULIC FLUIDS).

To conserve hydrocarbons, certain reclaiming technologies have been developed, involving re-refining used lubricating oils and reclaiming rubber. Refining oil had been curtailed because of environmental problems with acid sludge. New technology for re-refining oils without creating the acid sludge disposal problems is being marketed.

*Agriculture/Food. Traditional Uses.* Large quantities of hydrocarbons are used in agriculture, particularly as energy sources. Although solar energy is a cheap alternative, the convenience and reproducibility of drying with LPG has made hydrocarbon-derived energy the drying method of choice for such diverse applications as curing tobacco and drying peanuts, corn, and soybeans. In addition to these uses, hydrocarbons are used as the feedstock for a large variety of pesticides (see INSECTICIDES).

In addition to these uses related to crop production, hydrocarbons are used extensively in packaging, particularly in plastic films and to coat boxes with plastic and (to a much lesser extent) wax. Polymeric resins derived from hydrocarbons are also used to make trays and cases for delivery of packaged foodstuffs (see FILM AND SHEETING MATERIALS; PACKAGING, CONTAINERS FOR INDUSTRIAL MATERIALS; PAPER).

Highly pure *n*-hexane is used to extract oils from oilseeds such as soybeans, peanuts, sunflower seed, cottonseed, and rapeseed. There has been some use of hydrocarbons and hydrocarbon-derived solvents such as methylene chloride to extract caffeine from coffee beans, though this use was rapidly supplanted by supercritical water and/or carbon dioxide, which are natural and therefore more acceptable to the public.

*Feedstock for Protein.* Certain microorganisms, such as some bacteria, fungi, molds, and yeasts can metabolize hydrocarbons and hydrocarbon-derived materials. Because single-cell proteins (SCPs) are about 50% protein by weight, it was believed early in the development phase that the economics of SCP production would be favorable. That belief has proven essentially correct, but acceptance of SCPs as a primary source of food protein has been very slow. Except for limited uses as flavor enhancers and similar additive, SCPs have not made a significant impact on the markets for proteins. The future for hydrocarbons as a feedstock for SCPs is not bright, as the original *n*-paraffin feeds have been largely supplanted by alcohols derivable from nonpetroleum sources.

*Surfactants.* Surfactants (qv) are chemicals, natural or synthetic, that reduce the surface tension of water or other solvents, and are used chiefly as soaps, detergents, dispersing agents, emulsifiers, foaming agents, and wetting agents. Surfactants may be produced from natural fats and oils, from silvichemicals such as lignin, rosin, and tall oil, and from chemical intermediates derived from coal and petroleum.

The greatest amount of surfactant consumption is in packaged soaps and detergents for household and industrial use. The remainder is used in processing textiles and leather, in ore flotation and oil-drilling operations, and in the manufacture of agricultural sprays, cosmetics, elastomers, food, lubricants, paint, pharmaceuticals, and a host of other products.

*Coatings.* Protective and decorative coatings (qv) for homes, vehicles, and a variety of industrial uses provide a large market for hydrocarbons. At one time, most paints, varnishes, and other coatings utilized organic chemical solvents. However, due to environmental concerns and solvent cost, approximately 40% of all coatings are waterborne, or even dispense with the solvent altogether (powder coating).

Vinyl, alkyd, and styrene–butadiene latexes are used as film formers in most architectural coatings. Because alkyd resins (qv) require organic solvents, their use has decreased substantially for architectural coatings, but is still holding up in industrial applications, where their greater durability justifies the added expense (see LATEX TECHNOLOGY).

*Polymers.* Hydrocarbons from petroleum and natural gas serve as the raw material for virtually all polymeric materials commonly found in commerce, with the notable exception of rayon which is derived from cellulose extracted from wood pulp. Even with rayon, however, the cellulose is treated with acetic acid (qv), much of which is manufactured from ethylene (see FIBERS, REGENERATED CELLULOSE).

*Synthetic Fibers.* Virtually all synthetic fibers are produced from hydrocarbons, as follows:

| Fiber | Hydrocarbon precursor |
|---|---|
| nylon | cyclohexane |
| cellulose acetate | ethylene, methane |
| acrylics | propylene |
| polyesters | *p*-xylene, ethylene |
| polyolefins | propylene, ethylene |
| carbon fibers | pitch |

*Elastomers.* Elastomers are polymers or copolymers of hydrocarbons (see ELASTOMERS, SYNTHETIC, SURVEY; RUBBER, NATURAL). Natural rubber is essentially polyisoprene, whereas the most common synthetic rubber is a styrene–butadiene copolymer. Moreover, nearly all synthetic rubber is reinforced with carbon black, itself produced by partial oxidation of heavy hydrocarbons. The two most important elastomers, styrene–butadiene rubber (qv) and polybutadiene rubber, are used primarily in automobile tires.

*Plastics and Resins.* Plastics and resin materials are high molecular weight polymers which at some stage in their manufacture can be shaped or otherwise processed by application of heat and pressure. Some 40–50 basic types of plastics and resins are available commercially, but literally thousands of different mixtures (compounds) are made by the addition of plasticizers, fillers, extenders, stabilizers, coloring agents, etc.

The two primary types of plastics, thermosets and thermoplastics, are made almost exclusively from hydrocarbon feedstocks. Thermosetting materials are those that harden during processing (usually during heating, as the name implies) such that in their final state they are substantially infusible and insoluble. Thermoplastics may be softened repeatedly by heat, and hardened again by cooling.

## 3. Methane, Ethane, and Propane

### 3.1. Physical Properties.

Methane, ethane, and propane are the first three members of the alkane hydrocarbon series having the composition, $C_nH_{2n+2}$. Selected properties of these alkanes are summarized in Table 1 (10).

Table 1. **Selected Properties of Methane, Ethane, and Propane**[a]

| Property | Methane | Ethane | Propane |
|---|---|---|---|
| CAS registry number | [74-82-8] | [74-84-0] | [74-98-6] |
| molecular formula | $CH_4$ | $C_2H_6$ | $C_3H_8$ |
| molecular weight | 16.04 | 30.07 | 44.09 |
| mp, K | 90.7 | 90.4 | 85.5 |
| bp, K | 111 | 185 | 231 |
| explosivity limits, vol% | 5.3–14.0 | 3.0–12.5 | 2.3–9.5 |
| autoignition temperature, K | 811 | 788 | 741 |
| flash point, K | 85 | 138 | 169 |
| heat of combustion, kJ/mol[b] | 882.0 | 1541.4 | 2202.0 |
| heat of formation, kJ/mol[b] | 84.9 | 106.7 | 127.2 |
| heat of vaporization, kJ/mol[b] | 8.22 | 14.68 | 18.83 |
| vapor pressure at 273 K, MPa[c] | | 2.379 | 0.475 |
| specific heat, J/(mol · K)[b] | | | |
| at 293 K | 37.53 | 54.13 | 73.63 |
| at 373 K | 40.26 | 62.85 | 84.65 |
| density, kg/m$^3$[d] | | | |
| at 293 K | 0.722 | 1.353 | 1.984 |
| at 373 K | 0.513 | 0.992 | 1.455 |
| critical point | | | |
| pressure, MPa[c] | 4.60 | 4.87 | 4.24 |
| temperature, K | 190.6 | 305.3 | 369.8 |
| density, kg/m$^3$[d] | 160.4 | 204.5 | 220.5 |
| triple point | | | |
| pressure, MPa[c] | 0.012 | $1.1 \times 10^{-6}$ | $3.0 \times 10^{-10}$ |
| temperature, K | 90.7 | 90.3 | 85.5 |
| liquid density, kg/m$^3$[d] | 450.7 | 652.5 | 731.9 |
| vapor density, kg/m$^3$[d] | 0.257 | $4.51 \times 10^{-5}$ | $1.85 \times 10^{-8}$ |
| dipole moment | 0 | 0 | 0 |
| hazards | fire, explosion, asphyxiation[e] | fire, explosion, asphyxiation[e] | fire, explosion, asphyxiation[e] |

[a] Ref. 10.

[b] To convert J to cal, divide by 4.184.

[c] To convert MPa to atm, divide by 0.101.

[d] To convert kg/m$^3$ to lb/ft$^3$, divide by 16.0.

[e] No significant toxic effects.

### 3.2. Manufacturing and Processing.

The main commercial source of methane, ethane, and propane is natural gas, which is found in many areas of the world in porous reservoirs; they are associated either with crude oil (associated gas) or in gas reservoirs in which no oil is present (nonassociated gas). These gases are basic raw materials for the organic chemical industry as well as sources of energy. The composition of natural gas varies widely but the principal hydrocarbon usually is methane (see GAS, NATURAL). Compositions of typical natural gases are listed in Table 2.

Gas is classified as dry or wet depending on the amount of condensable hydrocarbons contained in it. A dry gas that is low in hydrogen sulfide and carbon dioxide needs little or no treatment prior to its use as a fuel or chemical feedstock; however, if these acidic contaminants are present, they must be removed. Processes using regenerable bases frequently are used for such purposes, ie, the weak acidity of carbon dioxide and hydrogen sulfide allows them to be separated from natural gas or other gaseous feeds by adsorption in aqueous bases. There are numerous proprietary processes which isolate the acid gases, typically by absorption in aqueous solution of mono- or diethanolamines (MEA and DEA) or their heavier analogues. The processes differ in the amines used, the plant configuration, and the presence and identity of cosolvents (12).

Condensable hydrocarbons are removed from natural gas by cooling the gas to a low temperature and then by washing it with a cold hydrocarbon liquid to absorb the condensables. The uncondensed gas (mainly methane with a small amount of ethane) is classified as natural gas. The condensable hydrocarbons (ethane and heavier hydrocarbons) are stripped from the solvent and are separated into two streams. The heavier stream, which largely contains propane with some ethane and butane, can be liquefied and is marketed as liquefied petroleum

Table 2. **Composition of Typical Natural Gases**[a]

| | Location | | | | |
|---|---|---|---|---|---|
| | United States | | | | |
| Component, vol% | Salt Lake, Utah | Webb, Texas | Klifside, Texas | Sussex, England | Lacq, France |
| methane | 95.0 | 89.4 | 65.8 | 93.2 | 70.0 |
| ethane | 0.8 | 6.0 | 3.8 | 2.9 | 3.0 |
| propane | 0.2 | 2.2 | 1.7 | | 1.4 |
| butanes | | 1.0 | 0.8 | | 0.6 |
| pentanes and heavier hydrocarbons | | 0.7 | 0.5 | | |
| hydrogen sulfide | | | | 1.0 | 15.0 |
| carbon dioxide | 3.6 | 0.6 | | | |
| helium, nitrogen | 0.4 | 0.1 | 25.6 | | |
| helium | | | 1.8 | | |
| *Total* | *100* | *100* | *100* | *97.1*[b] | *90*[b] |

[a] Ref. 11.

[b] Components present in trace quantities are not included.

gas (LPG) (qv). The heavier fractions, which consist of $C_5$ and heavier hydrocarbons, are added to gasoline to control volatility (see GASOLINE AND OTHER MOTOR FUELS).

Relatively small amounts of methane, ethane, and propane also are produced as by-products from petroleum processes, but these usually are consumed as process or chemical feedstock fuel within the refineries. Some propane is recovered and marketed as LPG.

There are, however, a variety of other sources of methane that have been considered for fuel supply. For example, methane present in coal (qv) deposits and formed during mining operations can form explosive mixtures known as fire damp. In Western Europe, some methane has been recovered by suction from bore holes drilled in coal beds and the U.S. Geological Survey has tested the economic practicality of such a system. Removal of methane prior to mining the coal would reduce explosion hazards associated with coal removal.

Methane also is commonly produced by the decomposition of organic matter by a variety of bacterial processes, and the gas is used as a fuel in sewage plants (see WATER, SEWAGE). Methane also is called marsh gas because it is produced during the decay of vegetation in stagnant water.

There has been considerable research into the production of substitute natural gas (SNG) from fractions of crude oil, coal, or biomass (see FUELS, SYNTHETIC, GASEOUS FUELS; BIOMASS ENERGY; FUYEL RESOURCES). The process involves partial oxidation of the feedstock to produce a synthesis gas containing carbon monoxide and hydrogen. After removal of acid gases ($CO_2$ and $H_2S$) and water gas shift ($CO + H_2O \longrightarrow CO_2 + H_2$) to produce the necessary ratio of $H_2$ to CO, methane is produced by the following reaction:

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

A commercial-scale SNG plant, the Great Plains Plant in North Dakota, was actually built and operated for several years using a scheme based on coal. However, upon termination of the government subsidy, the plant's owner, ANR Inc., found it uneconomical to continue plant operation and shut down the plant in the late 1980s.

**3.3. Production and Shipment.** World natural gas reserves are shown in Table 3. The deposits of natural gas are extensive and provide sources of feedstock and fuel.

The large-scale use of natural gas requires a sophisticated and extensive pipeline system (see PIPELINES). In many underdeveloped areas, large quantities of natural gas are being flared because they must be produced with crude oil. However, the opportunity for utilizing the streams or for bringing the gas to industrial markets is being developed. Several large-scale ammonia plants have been built in developing countries (Pakistan, Saudi Arabia, Iran, etc). In some cases, pipeline delivery is feasible, namely from Algeria to France and from Libya to Italy. A third possibility is liquefaction of the methane and shipment in specially designed refrigerated tanker ships (see CRYOGENIC TECHNOLOGY). The process for liquefying, transporting, and revaporizing the natural gas requires advanced technology and particular attention to safety. Liquefaction of natural gas requires removal of its sensible and latent heats either by an

Table 3. **World Natural Gas Reserves by Country as of January 1, 2003**[a]

| Country | Reserves (trillion cubic feet)[b] | Percent of world total |
|---|---|---|
| World | 5,501 | 100.0 |
| Top 20 countries | 4,879 | 88.7 |
| Russia | 1,680 | 30.5 |
| Iran | 812 | 14.8 |
| Qatar | 509 | 9.2 |
| Saudi Arabia | 224 | 4.1 |
| United Arab Emirates | 212 | 3.9 |
| United States | 183 | 3.3 |
| Algeria | 160 | 2.9 |
| Venezuela | 148 | 2.7 |
| Nigeria | 124 | 2.3 |
| Iraq | 110 | 2.0 |
| Indonesia | 93 | 1.7 |
| Australia | 90 | 1.6 |
| Norway | 77 | 1.4 |
| Malaysia | 75 | 1.4 |
| Turkmenistan | 71 | 1.3 |
| Uzbekistan | 66 | 1.2 |
| Kazakhstan | 65 | 1.2 |
| Netherlands | 62 | 1.1 |
| Canada | 60 | 1.1 |
| Egypt | 59 | 1.1 |
| Rest of world | 622 | 11.3 |

[a] Ref. 13.

[b] To convert $ft^3$ to $m^3$, multiply by $2.832 \times 10^{-2}$.

adiabatic expansion process or by multistage mechanical refrigeration (qv). In the expanding cycle, the pressure of the gas is the energy source. The efficiency of the expansion process is low but capital and operating costs are lower than those of the multistage refrigeration process.

Liquefied natural gas (LNG) also plays a large role in both the transportation and storage of natural gas. At a pressure of 101.3 kPa (1 atm), methane can be liquefied by reducing the temperature to about −161°C. When in the liquid form, methane occupies approximately 1/600 of the space occupied by gaseous methane at normal temperature and pressure. In spit of the very low temperature of the liquid, LNG offers advantages for both shipping and storing natural gas.

**3.4. Economic Aspects.** Ethane is primarily extracted from natural gas and then consumed as a feedstock in the production of industrial fuel. The U.S. and Canada have long been the dominant producers and consumers of ethane. Consumption has increased in the Middle East. Western Europe consumes smaller amounts and Japan has no market for ethane.

In 2000, 14.8 million metric tons were consumed for ethylene manufacture in the United States. The annual growth rate for ethylene is expected to be 5% through 2005. Natural gas prices hit unprecedented highs in 2000 and profit margins decreased. Natural gas is expected to be cheaper in the future and, thus, the U.S. ethylene-based petrochemical industry should remain competitive (14).

Western Europe uses naphtha as its main feedstock for ethylene.

The Middle East might become a major supplier of petrochemical products The region's vast reserve of oil and gas has prompted investment in ethane to ethylene production. The region is expected to add 9 million metric tons capacity by 2010. This would represent 22% of additional global capacity by 2010.

**3.5. Health and Safety Factors.** Methane is on the Environmental Protection Agency Toxic Substances Control Act (U.S. EPA TSCA) Chemical Inventory and the Test Submission Data Base. The ACGIH recommends that methane be called a simple asphyxiant, that is, an "inert" gas or vapor that acts primarily as a simple asphyxiant without other physiological effects when present at high concentration in air. For simple asphyxiants, a time-weighted average (TWA) of 1000 ppm is suggested by the ACGIH (15).

Ethane is on the EPA TSCA Chemical Inventory and the Test Submission Data Base. Industrially, ethane is handled similarly to methane, and an occupational exposure limit of 1000 ppm is recommended by the ACGIH. A TLV is not recommended for each simple asphyxiant (15).

Propane is on the EPA TSCA Chemical Inventory and Test Submission Data Base. The immediately dangerous to life or health (IDLH) concentration established by NIOSH is 2100 ppm, based on 10% of the lower explosion limit for safety considerations, even though the relevent toxicological data indicate that irreversible health effects or impairment of escape exist only at higher concentrations. The exposure limits for propane in the United States are OSHA PEL, 1000 ppm, NIOSH exposure limit, 1000 ppm, ACGIH TLV, 2500 ppm (15).

**3.6. Uses.** *Methane.* The largest use of methane is for synthesis gas, a mixture of hydrogen and carbon monoxide. Synthesis gas, in turn, is the primary feed for the production of ammonia (qv) and methanol (qv). Synthesis gas is produced by steam reforming of methane over a nickel catalyst.

Methane is also used for the production of several halogenated products, principally the chloromethanes. Due to environmental pressures, this outlet for methane is decreasing rapidly.

At one time, methane was widely used to produce acetylene (qv), by processes involving either electric arcs or partial oxidation. The so-called Reppe chemicals (ie, 1,4-butanediol and derivatives), once made solely from acetylene, can now be made from butane; the outlook for continued acetylene demand from methane is poor. Much interest has been shown in direct conversion of methane to higher hydrocarbons, notably ethylene. Development of such a process would allow utilization of natural gas from remote wells. Much gas is currently flared (burned) from such wells because the pipeline gathering systems needed for such gas tend to be prohibitively expensive. If the gas could be converted on-site to a condensable gas or pumpable liquid, bringing those hydrocarbons to market would be facilitated. In the early 1990s, partial oxidative coupling of methane to higher hydrocarbons (chiefly $C_2$s) achieved by passing methane and an oxygen-containing gas over a basic oxide catalyst at high temperatures (600–700°C) and low pressures ($<1$ atm) has been the method of choice. However, despite enormous efforts, $C_2$ yields higher than about 30% have not yet been realized. Direct methane conversion to other materials, such as methanol, has similarly not yielded commercially interesting results, mainly due to the extreme temperatures and very low throughput required for high selectivity to the desired products (16).

*Ethane.* The most important commercial use of ethane and propane is in the production of ethylene (qv) by way of high temperature (ca 1000 K) thermal cracking. Large ethylene plants have been built in Saudi Arabia, Iran, and England based on ethane recovery from natural gas in these locations. Ethane cracking units have been installed in Australia, Qatar, Romania, and France, among others.

Ethane has been investigated as a feedstock for production of vinyl chloride, at scales up to a large pilot plant, but nearly all vinyl chloride is still produced from ethylene.

*Propane.* Propane's largest use outside of steam cracking is as fuel, since propane is the chief constituent of NGL. Historically, NGLs have been used for homes and businesses located away from natural gas systems. Recently, environmental concerns coupled with the clean-burning nature of NGL (since virtually all of the sulfur and other pollutants are removed during processing of the natural gas) have stimulated research on and field trials of propane as a fuel source for internal combustion engines in cars, buses, and so on. Several oil companies have even established fueling stations on interstate highways. Propane's main competition in the replacement fuel market is compressed natural gas (CNG). Compared to CNG, NGLs have better driveability, longer range, and more simple conversion from gasoline.

## 4. Butanes

Butanes are naturally occurring alkane hydrocarbons that are produced primarily in association with natural gas processing and certain refinery operations such as catalytic cracking and catalytic reforming. The term butanes includes the two structural isomers, $n$-butane [106-97-8], $CH_3CH_2CH_2CH_3$, and isobutane [75-28-5], $(CH_3)_2CHCH_3$ (2-methylpropane).

### 4.1. Properties.

The properties of butane and isobutane have been summarized in Table 4 and include physical, chemical, and thermodynamic constants, and temperature-dependent parameters. Graphs of several physical properties as functions of temperature have been published (26) and thermodynamic properties have been tabulated as functions of temperature (21).

The alkanes have low reactivities as compared to other hydrocarbons. Much alkane chemistry involves free-radical chain reactions that occur under vigorous conditions, eg, combustion and pyrolysis. Isobutane exhibits a different chemical behavior than $n$-butane, owing in part to the presence of a tertiary carbon atom and to the stability of the associated free radical.

*Reactions of n-Butane.* The most important industrial reactions of $n$-butane are vapor-phase oxidation to form maleic anhydride (qv), thermal cracking to produce ethylene (qv), liquid-phase oxidation to produce acetic acid (qv) and oxygenated by-products, and isomerization to form isobutane.

*Maleic Anhydride.* The largest chemical use for $n$-butane is as feedstock for maleic anhydride. A dilute air–butane mixture is passed over a vanadium–phosphorus catalyst 400–500°C to produce maleic anhydride [108-31-6] in good

Table 4. **Properties of Butane**

| Property | $n$-Butane | Isobutane | Reference |
|---|---|---|---|
| molecular weight | 58.124 | 58.124 | |
| normal fp in air at 101.3 kPa,[a] K | 134.79 | 113.55 | 17 |
| normal bp at 101.3 kPa,[a] K | 272.65 | 261.43 | 17, 18 |
| flammability limits at 293.15 K and 101.3 kPa,[a] vol % | | | |
| in air | | | |
| lower | 1.8 | 1.8 | 19 |
| upper | 8.4 | 8.4 | 19 |
| in oxygen | | | |
| lower | 1.8 | 1.8 | 19 |
| upper | ca 40 | ca 40 | 19 |
| autoignition temperature at 101.3 kPa,[a] K | | | |
| in air | 693 | 693 | 19 |
| in oxygen | 558 | 558 | 19 |
| flash point, K | 199 | 190 | 20 |
| heat of combustion, kJ/mol[b] | | | |
| gross[c] | | | |
| gas | 2880 | 2866 | 20 |
| liquid | 2853 | 2847 | 20 |
| net[c] | | | |
| gas | 2653 | 2645 | 20 |
| liquid | 2634 | 2627 | 20 |
| $\Delta G_f^\circ$, kJ/mol[b] | | | |
| ideal gas at 298.15 K | −126.15 | −134.51 | 18, 21–23 |
| liquid at 298.15 K | −147.7 | −158.4 | 23 |
| $\Delta G_f^\circ$ at 101.3 kPa[a] and 298.15 K, kJ/mol[b] | −17.15 | −20.88 | 7, 21, 22 |
| $\log_{10} K_f$ at 298.15 K | 3.0035 | 3.6 | 17 |
| heat of fusion, kJ/mol[b] | 4.660 | 4.540 | 19 |
| heat of vaporization at normal bp, kJ/mol[b] | 22.39 | 21.30 | 19, 22 |
| vapor pressure at 310.93 K, kPa[b] | 356 | 498 | 18 |
| Antoine vapor pressure equation[d, e] | | | |
| $A$ | 5.9340 | 5.8731 | |
| $B$ | 935.86 | 882.80 | |
| $C$ | −34.42 | −33.15 | |
| $T$ max | 290 | 280 | |
| $T$ min | 195 | 187 | |
| thermal conductivity at 101.3 kPa,[a] W/(m·K) | | | 19 |
| at 273.15 K | 0.0136 | 0.0140 | |
| at 323.15 K | 0.0182 | 0.0185 | |
| at 373.15 K | 0.0234 | 0.0242 | |
| coefficient of thermal expansion for air saturated liquid at 288.7 K, saturation pressure, (1/vol) $(d\ \mathrm{vol}/dT)_p$, $\mathrm{K}^{-1}$ | 0.00211 | 0.00214 | 20 |
| density, kg/m$^3$ | | | |
| gas, at 101.3 kPa[a] | 2.5379 | 2.5285 | 20 |
| at 288.7 K | | | |
| at 298.15 K | 2.4553 | | 17 |
| liquid, at saturation pressure and 298.15 K | 572.87 | 551.0 | 17 |
| critical point | | | |
| pressure, MPa[g] | 3.797 | 3.648 | 17 |
| temperature, K | 425.16 | 408.13 | 17 |
| density, kg/m$^3$ | 228.0 | 221.0 | 17, 19 |
| volume, cm$^3$/mol | 225 | 263 | 17 |
| compressibility factor | 0.274 | 0.283 | 17 |

Table 4 (*Continued*)

| Property | $n$-Butane | Isobutane | Reference |
|---|---|---|---|
| $S°$, ideal gas at 298.15 K, J/mol · K[b] | 309.9 | 295.4 | 17 |
| $C_p°$, ideal gas, J/mol · K[b] | | | |
| at 288.7 K | 95.04 | 94.16 | 20 |
| at 298.15 K | 98.49 | 96.65 | 17 |
| $C_v°$, ideal gas at 288.7, J/mol · K[b] | 86.72 | 85.85 | 20 |
| $C_p°/C_v°$, ideal gas at 288.7 K | 1.096 | 1.097 | 20 |
| $C_p°$, liquid at 288.7 K and 101.3 kPa,[a] J/mol · K[a] | 137.1 | 138.5 | 18, 20 |
| $dT/dp$ at 101.3 kPa,[a] K/kPa[a] | 0.260 | 0.253 | 17 |
| dipole moment, C · m[h] | 0.0 | $3.34 \times 10^{-31}$ | 22 |
| surface tension at saturation pressure, mN/m(=dyn/cm) | | | |
| at 223.15 K | 20.88 | 18.7 | 17, 20 |
| at 273.15 K | 14.84 | 13.0 | 17, 20 |
| refractive index, $n_D^{25}$ | | | |
| liquid at saturation pressure | 1.32592 | 1.3503 | 19 |
| gas at 101.3 kPa[a] | 1.001286 | | 17 |
| stoichiometric combustion flame temperature, K | | | |
| in air | 2243 | 2246 | 19 |
| in oxygen | 3118 | 3118 | 19 |
| maximum flame speed, m/s | | | |
| in air | 0.37 | 0.36 | 19 |
| in oxygen | 3.31 | 3.3 | 19 |

[a] To convert kPa to atm, divide by 101.3

[b] To convert J to cal, divide by 4.184.

[c] Real gas at 101.3 kPa[a] and 288.7 K; liquid at saturation pressure and 298.15 K.

[d] Equations for vapor pressure, liquid volume, saturated liquid density, liquid viscosity, heat capacity, and saturated liquid surface tension are described in Refs. 23–25.

[e] $\log_{10} P = A - B/(T + C)$ where $P$ = vapor pressure, kPa[f]; $T$ = temperature, K; $A$, $B$, and $C$ = constants.

[f] To convert kPa to mm Hg, multiply by 7.5.

[g] To convert MPa to atm, divide by 0.1013.

[h] To convert C · m to debye, divide by $3.336 \times 10^{-30}$.

yield. Formerly benzene was used as feedstock, but in the last few years nearly all maleic anhydride in the United States, and an increasing proportion worldwide, is made from butane.

*Thermal Cracking.* $n$-Butane is used in steam crackers as a part of the mainly ethane–propane feedstream. Roughly 0.333–0.4 kg ethylene is produced per kilogram $n$-butane. Primary by-products include propylene (50–57 kg/100 kg ethylene), butadiene (7–8.5 kg/100 kg), butylenes (5–20 kg/100 kg), and aromatics (6 kg/100 kg).

*Liquid-Phase Oxidation.* Liquid-phase catalytic oxidation of $n$-butane is a minor production route for acetic acid manufacture. Formic acid (qv) also is produced commercially by liquid-phase oxidation of $n$-butane (27).

*Isomerization.* Structural isomerization of $n$-butane to isobutane is commercially useful when additional isobutane feedstock is needed for alkylation (qv). The catalysts permit low reaction temperatures which favor high proportions of isobutane in the product. The Butamer process also is well known for isomerization of $n$-butane.

*Reactions of Isobutane. Alkylation.* The addition of isobutane to various $C_3$–$C_4$ alkenes is used in the production of high quality gasoline blending stock (28). The highly branched $C_7$–$C_8$ hydrocarbons that are produced have high octane ratings; eg, the significant quantities of trimethylpentanes that are produced are 100–109.6 research octane number-clear (see GASOLINE AND OTHER MOTOR FUELS). The alkylation reaction is promoted by acidic systems such as $AlCl_3$–HCl, $H_2SO_4$, and HF. A complicated series of reactions occurs by a carbonium ion mechanism. As many as 40 products are produced in concentrations of 100 ppm or more (29). Licensed commercial processes have been described (30) (see ALKYLATION; FRIEDEL-CRAFTS REACTIONS).

*Other Reactions.* *n*-Butane or mixtures of *n*-butane and isobutane may be catalytically converted to propane (31) in order to overcome propane shortage, absorb excess butane, reduce worldwide LPG consumption, and satisfy seasonal variations in demand for propane. Aromatics such as xylenes, ethylbenzenes, toluene, and benzene may be made by dehy drocyclodimerization of butanes (32) (see XYLENES AND ETHYLBENZENE; TOLUENE; BENZENE; BTX PROCESSING). Other commercial reactions of butanes include nitration (qv) and halogenation.

**4.2. Manufacture and Processing.** Butanes are recovered from raw natural gas and from petroleum refinery streams that result from catalytic cracking, catalytic reforming, and other refinery operations. The most common separation techniques are based on a vapor–liquid, two-phase system by which liquid butane is recovered from the feed gas.

Although raw natural gas is an important source of butanes, the concentrations therein are relatively small, eg, 0.30 mol% *n*-butane and 0.35 mol% isobutane (33). The primary method of recovery is absorption (qv) of the propane, butanes, and heavier hydrocarbons in a refrigerated absorption oil that is composed of natural gasoline components which have been recovered from the gas. The natural-gas feed is contacted with the absorption oil at 5.52–8.27 MPa (54.5–81.6 atm) and 233–255 K. The oil from the absorber contains propane, butanes, natural gasoline, and dissolved ethane and methane, and flows to a de-ethanizing absorber that operates at lower pressure. Methane and ethane are taken overhead and the bottom product, which contains propane and butane, enters a debutanizer where propane and butane are separated from the gasoline absorption oil. Some of the gasoline is removed as a product and the rest is cooled and returned to the absorbers. The propane–butane stream undergoes final product separation in a depropanizer column (34).

Refrigeration (qv), adsorption, expansion, compression, fractionation, and cryogenic processes are used to recover products from natural gas. Advantages of the turbo expanders in cryogenic processes are high thermodynamic efficiencies and simplicity. Chilled feed gas, containing butanes, is fed to the expander side of an expander–compressor. The pressure is lowered by near isentropic expansion to the demethanizer operating pressure resulting in efficient further cooling of the feed gas to the demethanizer temperature. The expanding gas delivers shaft work to the compressor side of the expander–compressor which partially recompresses the residue gas. Details of a recovery process based on a turbo expander have been described (35); different processing schemes for butane recovery from natural gas have been reviewed (33).

The butane-containing streams in petroleum refineries come from a variety of different process units; consequently, varying amounts of butanes in mixtures containing other light alkanes and alkenes are obtained. The most common recovery techniques for these streams are lean oil absorption and fractionation. A typical scheme involves feeding the light hydrocarbon stream to an absorber-stripper where methane is separated from the other hydrocarbons. The heavier fraction is then debutanized, depropanized, and de-ethanized by distillation to produce $C_4$, $C_3$, and $C_2$ streams, respectively. Most often the $C_4$ stream contains butylenes and other unsaturates which must be removed by additional separation techniques if pure butanes are desired.

**4.3. Shipment.** Butanes are shipped by pipeline, rail car, sea tanker, barge, tank truck, and metal bottle throughout the world. All U.S. container shipments must meet Department of Transportation regulations. Domestic water shipments are regulated by the U.S. Coast Guard.

**4.4. Economic Aspects.** The world butane business is operated by the oil and gas industries. Usually butane data are included as part of the liquefied petroleum gas stream and separate data are not always available.

In 2001, North America consumed 55 thousand metric tons of butanes. Increases in butane's market share,especially as an ethylene feedstock, will be affected by its relative price competitiveness against liquid natural gas, naphtha, and gas oil. In the Middle East, there is a trend for the LPG production to be used domestically. Capacities in Africa and Latin America are expected to increase. Asian demand should keep butane prices competitive (36).

In Western Europe, future butane production will increase from natural gas sources rather than refineries. It is expected that Eastern Europe, mainly Russia, will see improved economies and butane production and consumption should rise dramatically. Japan's use of butanes should remain flat during the next few years (36).

**4.5. Specifications, Standards, Quality Control, and Storage.** Large quantities of butane are shipped under contract standards rather than under national or worldwide specifications. Most of the petrochemical feedstock materials are sold at purity specifications of 95–99.5 mol%. Butane and butane–petroleum mixtures intended for fuel use are sold worldwide under specifications defined by the Gas Processors Association, and the specifications and test methods have been published (37). Butanes may be readily detected by gas chromatography. Butanes commonly are stored in caverns (38) or refrigerated tanks.

**4.6. Health and Safety Factors.** *n*-Butane and isobutane are colorless, flammable, and nontoxic gases (39). They are simple asphyxiants, irritants, and anesthetics at high concentrations. Isobutane causes drowsiness in a short time in concentrations of 1 vol%; however, there are no apparent injuries from either hydrocarbon after 2 h exposures at concentrations of up to 5%. Occupational exposure limits for butane for NIOSH is 800 ppm and the ACGIH TLV is 800 ppm also (40). The extreme flammability of these hydrocarbons necessitates handling and storage precautions. Storage in well-ventilated areas away from heat and ignition sources is recommended. Because they are heavier than air, they should not be used near sparking motors or other nonexplosion-proof equipment. Contact of the liquid form of the hydrocarbons with the skin can cause frostbite. Both butane and isobutane form solid hydrates with water at low temperatures. Hydrate formation in liquefied light petroleum product pipelines and certain processing equipment can lead to pluggage and associated safety problems. Isobutane hydrate forms more readily than *n*-butane hydrates.

**4.7. Uses.** Butanes are used as gasoline blending components, liquefied gas fuel, and in the manufacture of chemicals. *n*-Butane and small amounts of isobutane are blended directly into motor fuel to control the fuel's volatility. Larger amounts of butanes are used in the winter, particularly in cold climates, to make engine starting easier. Recent environmental regulations in the United States have limited the permitted vapor pressure of gasolines, particularly in the summer months. Strictly speaking, the regulations apply only to areas which cannot meet air quality standards (nonattainment areas) but gasolines are usually blended to meet the strictest requirements in their sales areas.

Although *n*-butane is used directly in motor gasoline, isobutane is alkylated with $C_3$–$C_4$ olefins to produce highly branched $C_7$–$C_8$ hydrocarbons having high octane ratings. High octane blend stocks, eg, alkylates and reformates, are useful for raising the octane rating of the total refinery gasoline pool. In addition to its use as a motor fuel alkylate, isobutane is a reactant in the production of propylene oxide (qv) by peroxidation of propylene (qv) (41).

Liquid petroleum gas (LPG) is a mixture of butane and propane, typically in a ratio of 60:40 butane–propane; however, the butane content can vary from 100 to 50% and less (see LIQUEFIED PETROLEUM GAS). LPG is consumed as fuel in engines and in home, commercial, and industrial applications. Increasing amounts of LPG and butanes are used as feedstocks for substitute natural gas (SNG) plants. *n*-Butane, propane, and isobutane are used alone or in mixture as hydrocarbon propellents in aerosols (qv).

Production of maleic anhydride by oxidation of *n*-butane represents one of butane's largest markets. Butane and LPG are also used as feedstocks for ethylene production by thermal cracking. A relatively new use for butane of growing importance is isomerization to isobutane, followed by dehydrogenation to isobutylene for use in MTBE synthesis. Smaller chemical uses include production of acetic acid and by-products. Methyl ethyl ketone (MEK) is the principal by-product, though small amounts of formic, propionic, and butyric acid are also produced. *n*-Butane is also used as a solvent in liquid–liquid extraction of heavy oils in a deasphalting process.

## 5. Pentanes

There are three isomeric pentanes, ie, saturated aliphatic hydrocarbons of molecular formula $C_5H_{12}$. They are commonly called *n*-pentane [109-66-0], isopentane [78-78-4] (2-methylbutane), and neopentane [463-82-1] (2,2-dimethylpropane).

**5.1. Properties.** Each isomer has its individual set of physical and chemical properties; however, these properties are similar (Table 5). The fundamental chemical reactions for pentanes are sulfonation to form sulfonic acids, chlorination to form chlorides, nitration to form nitropentanes, oxidation to form various compounds, and cracking to form free radicals. Many of these reactions are used to produce intermediates for the manufacture of industrial chemicals. Generally the reactivity increases from a primary to a secondary to a

Table 5. **Properties of Pentanes**

| Property | *n*-Pentane | Isopentane | Neopentane | Ref. |
|---|---|---|---|---|
| molecular weight | 72.151 | 72.151 | 72.151 | 42 |
| normal freezing point, K | 143.429 | 113.250 | 256.57 | 17 |
| normal bp, K | 309.224 | 301.002 | 282.653 | 17 |
| water solubility at 25°C, g $C_5H_{12}$/100 kg $H_2O$ | 9.9 | 13.2 | | 20 |
| spontaneous ignition temperature in air, K | 557.0 | 700.0 | 729.0 | 20 |
| flash point, K | 233.0 | 213.0 | 198.0 | 43 |
| critical point | | | | |
| pressure, MPa$^a$ | 3.369 | 3.381 | 3.199 | 17 |
| temperature, K | 469.7 | 460.39 | 433.75 | 17 |
| density, kg/m$^3$ | 231.9 | 234.0 | 237.7 | 44 |
| volume, m$^3$/mol | $304 \times 10^{-6}$ | $306 \times 10^{-6}$ | $303 \times 10^{-6}$ | 17 |
| compressibility factor | 0.262 | 0.273 | 0.269 | 17 |
| heat of combustion, kJ/mol$^b$ at 298 K | | | | |
| liquid | 3245 | 3239 | 3230 | 17 |
| gas | 3272 | 3264 | 3253 | 17 |
| heat of fusion, kJ/mol$^b$ | 8.39 | 5.15 | 3.15 | 17 |
| heat of vaporization, kJ/mol$^b$ | 25.77 | 24.69 | 22.75 | 17 |
| entropy of fusion, kJ/(mol · K)$^b$ | $5.852 \times 10^{-2}$ | $4.548 \times 10^{-2}$ | $1.226 \times 10^{-2}$ | 17 |
| entropy of vaporization, kJ/(mol · K)$^b$ | $8.335 \times 10^{-2}$ | $8.203 \times 10^{-2}$ | $8.050 \times 10^{-2}$ | 17 |
| Antoine vapor pressure equation$^{c,d}$ | | | | |
| *A* | 6.00122 | 5.91458 | 5.72918 | 42 |
| *B* | 1075.78 | 1020.01 | 883.420 | |
| *C* | −39.94 | −40.05 | −45.37 | |
| *T*, max | 330 | 322 | 305 | |
| *T*, min | 220 | 216 | 260 | |
| dielectric constant | 1.843 | 1.843 | 1.801 | 43 |
| dipole moment, C · m$^f$ | 0.0 | $3.336 \times 10^{-31}$ | 0.0 | 42 |
| surface tension, mN/m (=dyn/cm) | | | | |
| at 20°C | 16.00 | 15.00 | 12.05 | 43 |
| at 30°C | 14.95 | 13.93 | 10.98 | 43 |
| refractive index, $n_D{}^{25}$ | | | | |
| liquid | 1.35472 | 1.35088 | 1.339 | 17 |
| gas | 1.001585 | | | 17 |
| ASTM octane number | | | | |
| research | 61.8 | 93.0 | 85.5 | 20 |
| motor | 63.2 | 89.7 | 80.2 | 20 |

[a] To convert MPa to atm, divide by 0.101.

[b] To convert J to cal, divide by 4.184.

[c] Equations for four-parameter vapor pressure, Harlacher vapor pressure, and liquid volume can be found in Refs. 42 and 44, respectively.

[d] $\mathrm{Log}_{10} P = A - B/(T + C)$ where $P$ = vapor pressure, kPa[e]; $T$ = temperature, K; *A, B,* and *C* = constants. To convert Antoine equation to mm Hg, add 0.8751 to *A*.

[e] To convert kPa to atm, divide by 101.3

[f] To convert C · m to debye, divide by $3.336 \times 10^{-30}$.

Table 6. **Estimated Concentration of Pentanes, %**

| Stream | Pentane | Isopentane |
|---|---|---|
| straight-run gasoline | 6.8 | 6.3 |
| natural gasoline | 6.8 | 6.3 |
| catalytic cracker naphtha | 1 | 5 |

tertiary hydrogen (45). Other properties available but not listed are given in equations for heat capacity and viscosity (42), and saturated liquid density (44).

### 5.2. Occurrence and Recovery.

Pentanes occur chiefly in straight-run gasoline, natural gasoline, and in certain refinery streams. Straight-run gasoline is the gasoline boiling range material recovered from crude oil by distillation (ie, before any other processing). Natural gasoline is the $C_5$+ fraction of the liquids recovered from natural gas. Appreciable quantities of pentanes are produced in catalytic cracking, while smaller amounts come from hydrocracking and catalytic reforming. Table 6 shows typical pentane concentration in these streams.

Most of the gasoline range material from refinery units is added to the gasoline pool. Natural and straight-run gasolines, however, are often depentanized by distillation, and the resulting pentane fraction processed through a splitting column or molecular sieve unit to separate the normal and isopentane. The isopentane (research octane = 93) is added to the gasoline pool, while the *n*-pentane (research octane = 61.8) is isomerized over fixed-bed platinum catalysts.

### 5.3. Health and Safety Factors.

Pentanes are only slightly toxic. Because of their high volatilities and, consequently, their low flash points, they are highly flammable. Pentanes are classified as nonreactive, ie, they do not react with fire-fighting agents. The fire hazard properties for pentanes are listed in Table 7 (46).

The threshold limit value for the time-weighted average (8-h) exposure to pentanes is 600 ppm or 1770 mg/m$^3$ (51 mg/SCF); the short-term exposure limit (15 min) is 750 ppm or 2250 mg/m$^3$ (64 mg/SCF) (47). Pentanes are classified as simple asphyxiants and anesthetics (qv).

The ICC classifies all three pentanes as flammable liquids and requires that they be affixed with a red label for shipping. Because of their high vapor pressures, *n*- and isopentane are transported in heavy-walled drums and neopentanes are transported in cylinders (see PACKAGING, CONTAINERS FOR INDUSTRIAL MATERIALS).

Table 7. **Pentane Fire Hazard Properties**

| Pentane | Bp, °C | Flash point, °C | Ignition temperature, °C | Flammability limits, vol % | |
|---|---|---|---|---|---|
| | | | | Lower | Upper |
| isopentane | 27.8 | <−51 | 420 | 1.4 | 7.6 |
| *n*-pentane | 36.1 | <−40 | 260 | 1.5 | 7.8 |
| neopentane | 9.5 | gas | 450 | 1.4 | 7.5 |

**5.4. Uses.** The main use for pentanes has been in motor fuel, though regulations limiting fuel vapor pressure are decreasing the amount of pentanes, particularly isopentane, present in gasoline during warm parts of the year. At one time, significant quantities of pentane were used as feedstock for ethylene units. However, most U.S. ethylene capacity is now based on ethane–propane feedstock; only limited amounts of heavier material can be tolerated without overloading the downstream purification train.

Isopentane can be alkylated with light olefins to give gasoline material; however, the resulting alkylate is lower quality (research octane = 74–80) than that produced from isobutane (research octane clear = 90–98). The demand for higher gasoline-pool octane discourages isopentane alkylation. Nevertheless, some outlet has to be found for the increasing amount of pentane displaced from gasoline by vapor pressure regulation, and it is likely that much of that pentane will find its way into alkylation streams.

## 6. Hexanes

**6.1. Properties.** Properties of the principal hydrocarbons found in commercial hexane are shown in Table 8. The flash point of *n*-hexane is −21.7°C and the autoignition temperature is 225°C. The explosive limits of hexane vapor in air are 1.1–7.5%. Above 2°C the equilibrium mixture of hexane and air above the liquid is too rich to fall within these limits (50).

**6.2. Manufacture.** Commercial hexanes are manufactured by two-tower distillation of a suitable charge stock, eg, straight-run gasolines that have been distilled from crude oil or natural gas liquids that have been stripped from natural gas. Product composition is a function of the charge stock used and the degree of separation achieved in the fractionators. Because benzene forms minimum boiling azeotropes with *n*-hexane, methylcyclopentane, and cyclohexane, it cannot be eliminated by fractionation. Another source of hexanes is the BTX raffinate which remains after the removal of aromatics from catalytic reformates (see BTX PROCESSING). Catalytic reformates are the products obtained from reforming naphthas for the conversion of cycloparaffins to aromatics. Raffinates are low in cycloparaffins and aromatics, and hexanes that have been obtained from them are highly paraffinic.

Highly pure *n*-hexane can be produced by adsorption on molecular sieves (qv) (see ADSORPTION, LIQUID SEPARATION) (51). The pores admit normal paraffins but exclude isoparaffins, cycloparaffins, and aromatics. The normal paraffins are recovered by changing the temperature and/or pressure of the system or by elution with a liquid that can be easily separated from *n*-hexane by distillation. Other than benzene, commercial hexanes also may contain small concentrations of olefins (qv) and compounds of sulfur, oxygen, and chlorine. These compounds cannot be tolerated in some chemical and solvent applications. In such cases, the commercial hexanes must be purified by hydrogenation.

The composition and properties of and the range of hydrocarbon distributions and impurities encountered in three commercial hexanes are listed in

Table 8. **Properties of Hydrocarbons Found in Commercial Hexanes**

| Hydrocarbon | CAS Registry number | Freezing point, °C | Normal bp, °C | Liquid density, kg/m$^3$ at 20°C | Liquid refractive index, $n_D^{20}$ | Antoine vapor pressure equation[b,c,d] | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $A$ | $B$ | $C$ | range, K |
| 2-methylbutane | [78-78-4] | −159.900 | 27.852 | 619.67 | 1.35373 | | | | |
| $n$-pentane | [109-66-0] | −129.730 | 36.065 | 626.20 | 1.35748 | | | | |
| cyclopentane | [287-92-3] | −93.866 | 49.262 | 745.38 | 1.40645 | | | | |
| 2,2-dimethylbutane | [75-83-2] | −99.870 | 49.741 | 649.16 | 1.36876 | 5.8797 | 1081.2 | −43.81 | 230−350 |
| 2,3-dimethylbutane | [79-29-8] | −128.538 | 57.988 | 661.64 | 1.37495 | 5.9347 | 1127.2 | −44.25 | 235−354 |
| 2-methylpentane | [107-83-5] | −153.660 | 60.271 | 653.15 | 1.37145 | 5.9640 | 1135.4 | −46.58 | 240−370 |
| 3-methylpentane | [96-14-0] | | 63.282 | 664.31 | 1.37652 | 5.9738 | 1152.4 | −46.02 | 240−365 |
| $n$-hexane | [110-54-3] | −95.322 | 68.736 | 659.33 | 1.37486 | 6.0027 | 1171.6 | −48.78 | 245−370 |
| methylcyclopentane | [96-37-7] | −142.455 | 71.812 | 748.64 | 1.40970 | 5.9878 | 1186.1 | −47.11 | 250−375 |
| benzene | [71-43-2] | 5.533 | 80.100 | 879.01 | 1.50112 | 6.0305 | 1211.0 | −52.36 | 280−377 |
| cyclohexane | [110-82-7] | 6.554 | 80.738 | 778.55 | 1.42623 | 5.9662 | 1201.5 | −50.50 | 280−380 |
| 2,2-dimethylpentane | [590-35-2] | −123.811 | 79.197 | 673.85 | 1.38215 | | | | |
| 2,4-dimethylpentane | [108-08-7] | −119.242 | 80.500 | 672.70 | 1.38145 | | | | |
| 1,1-dimethylcyclopentane | [1638-26-2] | −69.795 | 87.846 | 754.48 | 1.41356 | | | | |

[a] Ref. 48.

[b] Ref. 42.

[c] Equations for Harlacher vapor pressure, vapor heat capacity, saturated liquid volume, and liquid viscosity can be found in Refs. 42 and 50.

[d] $\text{Log}_{10}\, P = A - B/(T + C)$ where $P$ = vapor pressure, kPa[e]; $T$ = temperature, K; $A$, $B$, and $C$ = constants.

[e] To convert $P$ (kPa) to $P$ (mm Hg), add 0.875 to $A$; to convert kPa to mm Hg, multiply by 7.5.

Table 9. **Compositions of Typical Commercial Hexanes**

| Property | Hexane A | Hexane B | Hexane C |
|---|---|---|---|
| *Hydrocarbon analysis, liquid vol%* | | | |
| 2,3-dimethylbutane | 0.05 | 0.16 | |
| 2-methylpentane | 3.48 | 1.49 | 0.30 |
| 3-methylpentane | 9.38 | 5.40 | 3.27 |
| *n*-hexane | 63.91 | 81.23 | 88.19 |
| methylcyclopentane | 19.43 | 11.71 | 8.23 |
| cyclohexane | 0.78 | | |
| benzene | 2.81 | 0.004 | 0.01 |
| dimethylpentanes | 0.16 | | |
| *Physical and chemical properties* | | | |
| distillation (ASTM D1078) initial bp, °C | 68.3 | 68.2 | 67.1 |
| dry point | 71.0 | 69.0 | 67.3 |
| flash point, °C | | −23 | |
| aniline point, °C (ASTM D611) | | 65.3 | 66.1 |
| Reid vapor pressure, kPa,[a] at 37.8°C | 33.8 | 35.9 | 35.2 |
| specific gravity (°API) | 0.689 (73.9) | 0.674 (78.4) | 0.672 (79.0) |
| bromine number | | 0.0001 | 0.0016 |
| peroxides (as $H_2O_2$), ppm | | <1 | <1 |
| carbonyls (as acetone), ppm | | <1 | 3.8 |
| acidity | | nil | |
| sulfur, ppm (ASTM D1266 app. I) | 25 | <1 | 0.4 |
| phenols, ppm (ASTM D52-R) | | | <1.0 |
| water, ppm | | | 54 |
| color (ASTM D156) | | +30 | +30 |

[a] To convert kPa to psi, multiply by 0.145.

Table 9. Hexane A is derived from fractionation of natural gas liquids. Because there is not an available effective treatment to remove impurities, the benzene and sulfur contents in hexane A are high. Hexane B is highly pure relative to A and is recovered in a refinery operation that involves hydrogenation. Hence its benzene, sulfur, and olefin contents are low. Hexane C is typical of a stream that meets specifications for polymerization-grade material.

**6.3. Health and Safety Factors.** Hexane is classified as a flammable liquid by the ICC, and normal handling precautions for this type of material should be observed. The ACGIH TLV the maximum concentration of hexane vapor in air to which a worker may be exposed without danger of adverse health effects is 150 ppm; the NIOSH PEL is 50 ppm; the OSHA PEL is 500 ppm (52).

*n*-Hexane can be grouped with the general anesthetics (qv) in the class of central nervous system depressants. Hexane vapors are mildly irritating to mucous membranes. Exposure to concentrations in excess of 1% hexane may cause dizziness, unconsciousness, prostration, and death. Prolonged skin contact with hexane results in irritation and dermatitis. Direct contact with lung tissue can result in chemical pneumonitis, pulmonary edema, and hemorrhage (53).

**6.4. Uses.** Other than fuel, the largest volume application for hexane is in extraction of oil from seeds, eg, soybeans, cottonseed, safflower seed, peanuts, rapeseed, etc. Hexane has been found ideal for these applications because of its high solvency for oil, low boiling point, and low cost. Its narrow boiling range minimizes losses, and its low benzene content minimizes toxicity. These same properties also make hexane a desirable solvent and reaction medium in the manufacture of polyolefins, synthetic rubbers, and some pharmaceuticals. The solvent serves as catalyst carrier and, in some systems, assists in molecular weight regulation by precipitation of the polymer as it reaches a certain molecular size. However, most solution polymerization processes are fairly old; it is likely that those processes will be replaced by more efficient nonsolvent processes in time.

## 7. Cyclohexane

Cyclohexane [110-82-7], $C_6H_{12}$, is a clear, essentially water-insoluble, noncorrosive liquid that has a pungent odor. It is easily vaporized, readily flammable, and less toxic than benzene. Structurally, it is a cycloparaffin. Cyclohexane was synthesized by Baeyer in 1893 and it was discovered by Markovnikov in Caucasian petroleum fractions shortly thereafter. Its presence in United States crude oils was established in 1931 (54). Cyclohexane was produced first by hydrogenation of benzene in 1898 (55).

**7.1. Properties.** Properties of cyclohexane are given in Table 10, and a number of binary azeotropes that are formed with cyclohexane are listed in Table 11.

*Stereochemistry.* Cyclohexane can exist in two molecular conformations: the chair and boat forms. Conversion from one conformation to the other involves rotations about carbon–carbon single bonds. Energy barriers associated with this type of rotation are low and transition from one form to the other is rapid. The predominant stereochemistry of cyclohexane has no influence in its use as a raw material for nylon manufacture or as a solvent.

*Reactions.* The most important commercial reaction of cyclohexane is its oxidation (in liquid phase) with air in the presence of soluble cobalt catalyst or boric acid to produce cyclohexanol and cyclohexanone (see HYDROCARBON OXIDATION; CYCLOHEXANOL AND CYCLOHEXANONE). Cyclohexanol is dehydrogenated with zinc or copper catalysts to cyclohexanone which is used to manufacture caprolactam (qv).

Cyclohexane is dehydrogenated easily to benzene over platinum or palladium catalysts on charcoal or alumina at 300–320°C (59,60). Dehydrogenation of cyclohexane over palladium or platinum begins at 170°C and is a reversible reaction; below 200°C, the equilibrium favors cyclohexane formation. Dehydrogenation occurs smoothly without ring scission (61). In contrast, nickel on charcoal gives appreciable quantities of methane. The activity of nickel is moderated by using alumina as a support and, at 300–310°C, dehydrogenation occurs without ring scission (62).

Isomerization of cyclohexane in the presence of aluminum trichloride catalyst with continuous removal of the lower boiling methylcyclopentane by distillation results in a 96% yield of the latter (63). The activity of $AlCl_3$–HCl catalyst has been determined at several temperatures. At 100°C, the molar ratio of methylcyclopentane to cyclohexane is 0.51 (64).

Table 10. **Properties of Cyclohexane**

| Property | Value |
|---|---|
| mol wt | 84.156 |
| fp, °C | 6.554 |
| molal fp lowering, °C | 20.3 |
| bp, °C | 80.738 |
| flammability limits (in air), vol% | 1.3–8.4 |
| flash point (closed up), °C | −17 |
| heat of transition, kJ/kg[a] | 80.08 |
| heat of fusion, kJ/kg[a] | 31.807 |
| heat of vaporization, kJ/kg[a] | |
| at 25°C | 392.50 |
| at 80.7°C | 357.44 |
| vapor pressure, kPa[b] | |
| at 30°C | 16.212[c] |
| at 40°C | 24.613[c] |
| at 50°C | 36.237[c] |
| at 60°C | 51.901[c] |
| at 70°C | 72.521[c] |
| at 80°C | 99.095[c] |
| Antoine equation[d] | |
| at 1.333–199.95 kPa[b,e] | |
| $\log_{10}P = 5.965 - 2766.63/(T - 50.50)$ | |
| at 1.333 kPa[b] to $P_c$[f] | |
| $\log_{10}P = 22.373 + 5562.12/T - 2.303/\log_{10}T + 4.22P/T^2$ | |
| transition point, °C | −87.05 |
| critical pressure, kPa[b] | 4110.00[c] |
| critical temperature, °C | 281.0 |
| critical density, g/cm$^3$ | 0.2718 |
| surface tension at 20°C, N/m[g] | 0.0253 ± 0.3 |
| $n_D^{20}$[h] | 1.4623 |
| $d_4^{20}$[h] | 0.77855 |
| dielectric constant at $10^5$ Hz and 25°C | 2.023 |
| kinematic viscosity at 20°C, mm$^2$/s(= cSt) | 1.259 |
| dynamic viscosity at 20°C, mPa · s(= cP) | 0.980 |
| specific heat relative to water at 25.9°C | 0.440 |
| cryoscopic constant $(A)$[i], mole fraction, °C | 0.00411 |

[a] To convert J to cal, divide by 4.184.

[b] To convert kPa to atm, divide by 101.3.

[c] Ref. 56.

[d] Equations for saturated liquid density, liquid heat capacity, vapor heat capacity, and liquid viscosity can be found in Ref. 42.

[e] To convert $\log P_{(\mathrm{kPa})}$ to $\log P_{(\mathrm{mm\ Hg})}$, add 0.875 to 5.965.

[f] To convert $\log P_{(\mathrm{kPa})}$ to $\log P_{(\mathrm{mm\ Hg})}$, add 0.875 to 22.373.

[g] To convert N/m to dyn/cm, divide by 0.001.

[h] For air-saturated liquid at 101.3 kPa.

[i] For use in calculating mol % purity, $p$, by using the equation $\log p = 2.00000 - (A/2.30259)(T' - T)$ where $T'$ is the freezing point of a given sample (57,58).

**7.2. Occurrence.** Cyclohexane is present in all crude oils in concentrations of 0.1–1.0%. The cycloparaffinic crude oils, such as those from Nigeria and Venezuela, have high cyclohexane concentrations, and the highly paraffinic crude oils, such as those from Indonesia. Saudi Arabia, and Pennsylvania,

Table 11. **Binary Azeotropes by Cyclohexane**

| Second component | Cyclohexane, wt% | Bp, °C |
|---|---|---|
| water | 91.6 | 69.0 |
| benzene | 45 | 77.5 |
| methanol | 39 | 54.2 |
| ethyl alcohol | 70 | 64.9 |
| *n*-propyl alcohol | 80 | 74.3 |
| isopropyl alcohol | 67 | 68.6 |
| *n*-butyl alcohol | 96 | 79.8 |
| isobutyl alcohol | 86 | 78.1 |

have low concentrations; and concentrations of cycloparaffins in crude oils from Texas, Oklahoma, and Louisiana tend to fall in between (see NOMENCLATURE IN THE PETROLEUM INDUSTRY).

**7.3. Manufacture and Shipment.** Essentially all high purity cyclohexane is made by hydrogenation of benzene (qv). A small amount of cyclohexane of lower purity is produced by fractional distillation from crude oil and from catalytic reformer effluent (65). Hydrogenation of benzene to cyclohexane can be carried out in either the liquid or vapor phase in the presence of hydrogen. Various processes have been developed for producing cyclohexane and all are catalytic and involve nickel, palladium, or platinum as the catalysts. Generally, the metal is put on a support although Raney nickel is used in one process. Because of the equilibrium relationship between cyclohexane and benzene, temperature control of the reaction is critical; however, this is complicated because hydrogenation is exothermic. Consequently, most commercial cyclohexane processes involve multistage reactors in which recycling of cyclohexane, staged injection of benzene feed, and inter-reactor cooling to absorb the heat of hydrogenation occur. A generalized flow scheme for a vapor-phase multistage process is shown in Figure 1.

Some processes use only one reactor (66) or a combination of liquid- and vapor-phase reactors (67). The goal of these schemes is to reduce energy consumption and capital cost. Hydrogenation normally is carried out at 2–3 MPa (20–30 atm). Temperature is maintained at 300–350°C to meet a typical specification of less than 500 ppm benzene in the product; at higher temperatures, thermodynamic equilibrium shifts to favor benzene and the benzene specification is impossible to attain. Also, at higher temperatures, isomerization of cyclohexane to methylcyclopentane occurs; typically there is a 200 ppm specification limit on methylcyclopentane content.

Carbon monoxide and sulfur compounds are catalyst deactivators. Small amounts of carbon monoxide can be present in the hydrogen from catalytic reformers and ethylene units (which are the typical sources) even after cryogenic concentration of the hydrogen. Therefore the hydrogen that is fed to the unit usually is passed through a methanator before being introduced into the hydrogenation reactors. The methanator converts the carbon monoxide to methane and water. In most instances, there is no sulfur in the hydrogen: the content of sulfur compounds in benzene usually is specified to be less than 1 ppm as sulfur. At this

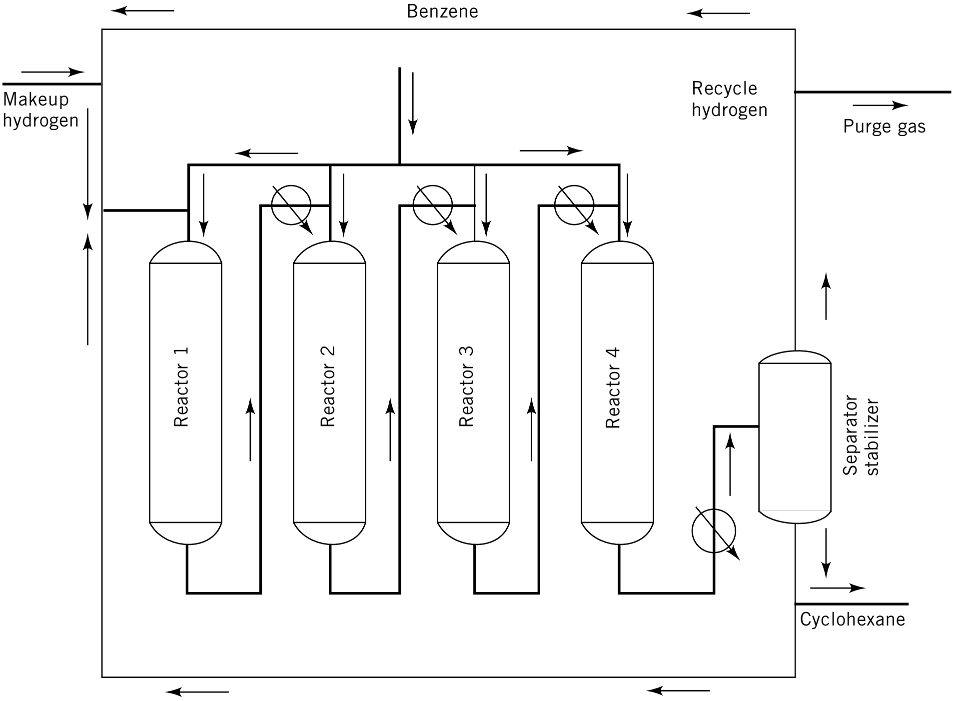

**Fig. 1.** Hydrogenation of benzene to cyclohexane.

level, a catalyst life of several years can be achieved. The majority of cyclohexane that is produced is shipped in bulk by tank car, tank truck, barge, or tanker.

**7.4. Economic Aspects.** In a well-designed multistage hydrogenation unit, operating costs are small as a result of recovery of the heat of hydrogenation between reactor stages by steam generation or integration with other process units, or by more efficient one- and two-stage processes (66,67). Consequently, the principal costs in cyclohexane manufacture are maintenance expenses, interest and return charges on the plant and working capital, and the cost of benzene and high purity hydrogen. The cost of hydrogen recovery from the gases produced from catalytic reforming of naphtha or from ethylene manufacture is included in the manufacturing cost. The price of cyclohexane is dependent on the price of benzene (qv). Virtually all cyclohexane goes to the production of nylon (see POLYAMIDES, GENERAL).

The U.S. producers and their 2000 capacities are listed in Table 12. Over 90% of all cyclohexane goes to the production of nylon through either adipic acid (qv) or caprolactam (qv). The balance is used to produce 1,6-hexamethylenediamine [124-09-4] (HMDA) and for various solvent uses (see DIAMINES AND HIGHER AMINES, ALIPHATIC; POLYAMIDES, GENERAL).

In 2001, world demand for cyclohexane was about 4.4 metric tons. The cyclohexane market is considered mature, but demand for nylon fiber is expected to grow, especially is China and Taiwan. China uses cyclohexane for preparation of nylon fiber and as a raw material for polyester-based shoe adhesives. The

Table 12. **U.S. Cyclohexane Producers,**[a] **2000**

| Producer | Capacity, $10^6$gal/yr[b] |
|---|---|
| Chevron Phillips | 340 |
| CITGO | 40 |
| Exxon Mobile | 65 |
| Huntsman | 90 |
| Koch | 25 |
| Sun Refining | 35 |
| *Total* | 595 |

[a] Ref. 68.

[b] To convert to $m^3$/yr, divide by 264.

Republic of Korea is also expected to increase usage. The annual growth rate through 2006 is expected at 3% (69).

The biggest use for cyclohexane is in the preparation of cyclohexanol and cyclohexanone, the precursors for adipic acid and caprolactam. Cyclohexane is used also as a solvent.

**7.5. Specifications.** For nylon manufacture, a typical purity specification of cyclohexane is 99.8%. The principal contaminants are unconverted benzene, aliphatic hydrocarbons that have boiling points near benzene and that are in the benzene that is fed to the hydrogenation unit, and methylcyclohexane which is formed by hydrogenation of the small amount of toluene in the benzene. Freezing point and specific gravity are used as determinants of purity. Also, a distillation range for the product of 1°C with 80.7°C included in the range usually is specified. However, gas chromatography generally is used for production and quality control as it is a more exact analytical method. A sulfur level of less than 1 ppm also is specified for high purity cyclohexane and is measured by ASTM method D3120.

**7.6. Analytical Methods.** Hydrocarbon mixtures containing cyclohexane can be analyzed using gas chromatography. Specific retention volumes for several stationary phases have been determined (70). Cyclohexane may be distinguished from other cycloparaffins and most aliphatic hydrocarbons, such as methylcyclopentane and hexane, respectively, by boiling point difference. Cyclohexane is differentiated from benzene (bp, 80.1°C) and 2,4-dimethylpentane (bp, 80.5°C) by chemical means, eg, by dehydrogenation over platinum. Cyclohexane also is distinguished from benzene by determining its inertness to fuming sulfuric acid unless exposed for prolonged periods of time.

Quantitative estimation of cyclohexane in the presence of benzene and aliphatic hydrocarbons may be accomplished by a nitration-dehydrogenation method described in Reference 71. The mixture is nitrated with mixed acid and under conditions that induce formation of the soluble mononitroaromatic derivative. The original mixture of hydrocarbons then is dehydrogenated over a platinum catalyst and is nitrated again. The mononitro compounds of the original benzene and the benzene formed by dehydrogenation of the cyclohexane dissolve in the mixed acid. The aliphatic compound remains unattacked and undissolved. This reaction may be carried out on a micro scale.

**7.7. Health and Safety Factors.** The threshold limit value (TLV) for cyclohexane is 300 ppm (1050 mg/m$^3$). With prolonged exposure at 300 ppm and greater, cyclohexane may cause irritation to eyes, mucous membranes, and skin. At high concentrations, it is an anesthetic and narcosis may occur. Because of its relatively low chemical reactivity, toxicological research has not been concentrated on cyclohexane.

**7.8. Uses.** Almost all of the cyclohexane that is produced in concentrated form is used as a raw material in the first step of nylon-6 and nylon-6,6 manufacture. Cyclohexane also is an excellent solvent for cellulose ethers, resins, waxes (qv), fats, oils, bitumen, and rubber (see CELLULOSE ETHERS; RESINS, NATURAL; FATS AND FATTY OILS; RUBBER, NATURAL). When used as a solvent, it usually is in admixture with other hydrocarbons. However, a small amount is used as a reaction diluent in polymer processes.

The cyclohexane in crude oil has three primary dispositions. Some of it is included in a light fraction (35–75°C) that is distilled from crude oil and is blended with other materials into motor gasoline (see GASOLINE AND OTHER MOTOR FUELS). Alternatively, this fraction is used as a feed to ethylene manufacture, particularly in Europe. The third, and most important disposition, is as a feed to a catalytic reformer where the naturally occurring cyclohexane is converted to benzene by dehydrogenation (see BTX PROCESSING). The cyclohexane used in this fashion often is reconverted by hydrogenation for use in nylon manufacture after recovery of high purity benzene by solvent extraction of the liquid product from the catalytic reformer. Direct recovery of cyclohexane from crude oil for chemical applications is practiced to a limited extent because of the small volumes of cyclohexane needed and the difficulty in fractionally distilling it from the many hydrocarbons in crude oil that boil at similar temperatures.

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