Kirk-Othmer Encyclopedia of Chemical Technology.

HYDROCARBONS, C_1–C_6

1. Methane, Ethane, and Propane

1.1. 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 (1).

1.2. 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 (see Feedstocks). 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 (3).

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 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

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	1.1×10^{-6}	3.0×10^{-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	4.51×10^{-5}	1.85×10^{-8}
dipole moment	0	0	0
hazards	fire, explosion, asphyxiation[e]	fire, explosion, asphyxiation[e]	fire, explosion, asphyxiation[e]

[a] Ref. 1.
[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.

holes drilled in coal beds and the U.S. Bureau of Mines 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. As much as 11.3×10^9 m^3 (400 trillion (10^{12}) cubic feet or 400 TCF) of methane might be recoverable from U.S. coal beds.

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, Fuels from biomass; Fuels from waste). 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:

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

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. 2.
[b] Components present in trace quantities are not included.

Table 3. World Natural Gas Production,[a] **1993**

Country	Production, 10^9 m^3[b]	Share, %
CIS (former USSR)	761.0	35.0
United States	544.5	25.0
Canada	156.5	7.2
the Netherlands	85.5	3.9
United Kingdom	63.2	2.9
Indonesia	53.3	2.4
Algeria	50.6	2.3
Mexico	37.1	1.7
Saudi Arabia	32.1	1.5
Iran	31.4	1.3
Norway	24.8	1.1
United Arab Emirates	24.3	1.1
Australia	24.0	1.1
next seven	135.2	6.1
all others	156.3	7.2
Total	*2179.8*	*100.0*

[a] Ref. 4.
[b] To convert m^3 to ft^3, multiply by 35.3.

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.

1.3. Production and Shipment

World natural gas reserves and production are shown in Table 3 (see also Fuels, synthetic). The deposits of natural gas are extensive and provide sources of feedstock and fuel.

Table 4. World NGL[a] Production,[b] 1993

Country	Production, 10^3 m^3/d	Share, %
United States	278.4	36.68
Canada	154.9	20.41
Mexico	98.7	13.00
CIS (former USSR)[c]	51.7	6.82
Algeria	23.0	3.03
Indonesia	20.7	2.73
Venezuela	15.9	2.10
Kuwait	13.3	1.75
Australia	13.2	1.74
Egypt	11.1	1.46
all others	78.1	10.29
Total	*759.0*	*100.00*

[a] NGL = natural gas liquid.
[b] Ref. 5.
[c] 1991 data (latest available).

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 Cryogenics). 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 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.

As indicated in Table 4, large-scale recovery of natural gas liquid (NGL) occurs in relatively few countries. This recovery is almost always associated with the production of ethylene (qv) by thermal cracking. Some propane also is used for cracking, but most of it is used as LPG, which usually contains butanes as well. Propane and ethane also are produced in significant amounts as by-products, along with methane, in various refinery processes, eg, catalytic cracking, crude distillation, etc (see Petroleum). They either are burned as refinery fuel or are processed to produce LPG and/or cracking feedstock for ethylene production.

1.4. Uses

1.4.1. 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. In 1993, in fact, acetylene production for chemicals was only about a third of that in 1970 (see Acetylene-derived chemicals). 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_2s) 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 (7).

1.5. Ethane and Propane

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. In the United States, ca 60% of the ethylene is produced by thermal cracking of ethane or ethane/propane mixtures. 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'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.

2. 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).

2.1. Properties

The properties of butane and isobutane have been summarized in Table 5 and include physical, chemical, and thermodynamic constants, and temperature-dependent parameters. Graphs of several physical properties as functions of temperature have been published (17) and thermodynamic properties have been tabulated as functions of temperature (12).

Table 5. 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	8
normal bp at 101.3 kPa,[a] K	272.65	261.43	(8, 9)
flammability limits at 293.15 K and 101.3 kPa,[a] vol %			
in air			
lower	1.8	1.8	10
upper	8.4	8.4	10
in oxygen			
lower	1.8	1.8	10
upper	ca 40	ca 40	10
autoignition temperature at 101.3 kPa,[a] K			
in air	693	693	10
in oxygen	558	558	10
flash point, K	199	190	11
heat of combustion, kJ/mol[b]			
gross[c]			
gas	2880	2866	11
liquid	2853	2847	11
net[c]			
gas	2653	2645	11
liquid	2634	2627	11
ΔG°_f, kJ/mol[b]			
ideal gas at 298.15 K	−126.15	−134.51	(9, 12–14)
liquid at 298.15 K	−147.7	−158.4	14
ΔG°_f at 101.3 kPa[a] and 298.15 K, kJ/mol[b]	−17.15	−20.88	(8, 12, 13)
$\log_{10} K_f$ at 298.15 K	3.0035	3.6	8
heat of fusion, kJ/mol[b]	4.660	4.540	10
heat of vaporization at normal bp, kJ/mol[b]	22.39	21.30	(10, 13)
vapor pressure at 310.93 K, kPa[a]	356	498	9
Antoine vapor pressure equationeast.a01-note-0017 [d]			
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)			10
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) $(d\,\text{vol}/dT)_p$, K^{-1}	0.00211	0.00214	11
density, kg/m^3			
gas, at 101.3 kPa[a]	2.5379	2.5285	11
at 288.7 K			
at 298.15 K	2.4553		8
liquid, at saturation pressure and 298.15 K	572.87	551.0	8
critical point			
pressure, MPa[g]	3.797	3.648	8
temperature, K	425.16	408.13	8
density, kg/m^3	228.0	221.0	(8, 10)
volume, cm^3/mol	225	263	8
compressibility factor	0.274	0.283	8
S°, ideal gas at 298.15 K, J/mol·K[b]	309.9	295.4	8

Table 5. ***Continued***

Property	n-Butane	Isobutane	Reference
C_p°, ideal gas, J/mol·K[b]			
at 288.7 K	95.04	94.16	11
at 298.15 K	98.49	96.65	8
C_v°, ideal gas at 288.7, J/mol·K[b]	86.72	85.85	11
C_p°/C_v°, ideal gas at 288.7 K	1.096	1.097	11
C_p°, liquid at 288.7 K and 101.3 kPa,[a] J/mol·K[a]	137.1	138.5	(9, 11)
dT/dp at 101.3 kPa,[a] K/kPa[a]	0.260	0.253	8
dipole moment, C·m[h]	0.0	3.34×10^{-31}	13
surface tension at saturation pressure, mN/m(=dyn/cm)			
at 223.15 K	20.88	18.7	(8, 11)
at 273.15 K	14.84	13.0	(8, 11)
refractive index, n_D^{25}			
liquid at saturation pressure	1.32592	1.3503	10
gas at 101.3 kPa[a]	1.001286		8
stoichiometric combustion flame temperature, K			
in air	2243	2246	10
in oxygen	3118	3118	10
maximum flame speed, m/s			
in air	0.37	0.36	10
in oxygen	3.31	3.3	10

[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. (13, 15), and 16.

[e] $\text{Log}_{10}\ P = A - B/(T + C)$ 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 3.336×10^{-30}.

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.

2.1.1. 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.

2.1.1.1. 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 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.

2.1.1.2. 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).

2.1.1.3. Dehydrogenation. Dehydrogenation of n-butane was once used to make 1,3-butadiene, a precursor for synthetic rubber. There are currently no on-purpose butadiene plants operating in the United States; butadiene is usually obtained as a by-product from catalytic cracking units.

2.1.1.4. 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 (18) (see Hydrocarbon oxidation).

2.1.1.5. 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.

2.1.2. Reactions of Isobutane

2.1.2.1. Alkylation. The addition of isobutane to various C_3–C_4 alkenes is used in the production of high quality gasoline blending stock (19). 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 (20). Licensed commercial processes have been described (21) (see Alkylation; Friedel-crafts reactions).

2.1.3. Other Reactions

n-Butane or mixtures of *n*-butane and isobutane may be catalytically converted to propane (22) in order to overcome propane shortage, absorb excess butane, reduce worldwide LPG consumption, and satisfy seasonal variations in demand for propane. Dehydrogenation of isobutane to isobutylene has been suggested (23) as a method to increase the quantity of isobutylene feedstock available for methyl *tert*-butyl ether (MTBE) production; MTBE is a high octane gasoline-blending stock (see Gasoline and other motor fuels; Ethers). Aromatics such as xylenes, ethylbenzenes, toluene, and benzene may be made by dehydrocyclodimerization of butanes (24) (see Xylenes and ethylbenzene; Toluene; Benzene; BTXprocessing). Other commercial reactions of butanes include nitration (qv) and halogenation.

2.2. 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 (25). 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 (26).

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 (27); different processing schemes for butane recovery from natural gas have been reviewed (25).

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.

2.3. 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.

2.4. Economic Aspects

The principal sources of butanes are petroleum refining and natural gas liquids. Refinery processes of catalytic reforming and catalytic cracking produce the majority of butanes and hydrocracking, coking, and visbreaking contribute less. Because catalytic cracking and reforming are the most widespread gasoline-producing processes, the supply of butanes is closely associated with gasoline production. Extensive use of butanes by the refineries complicates accurate, quantitative estimates of butane production at the refineries.

2.5. 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 (28). Butanes may be readily detected by gas chromatography. Butanes commonly are stored in caverns (29) or refrigerated tanks.

2.6. Health and Safety

n-Butane and isobutane are colorless, flammable, and nontoxic gases (30). 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%. A threshold limit value (TLV), of 600 ppm for *n*-butane has been recommended (31). 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.

2.7. 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. As recently as the late 1970s butanes accounted for 6–8 vol % of the gasoline sold, and nearly 85% of the total butane consumption. In the early 1990s, the volume of butane in gasoline is falling rapidly, and it is still unclear where the bottom will be.

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 1987 ca 89% of the isobutane consumption in the United States was for motor fuel alkylate (32). 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) (33).

In 1987 nonmotor fuel uses of butanes represented ca 16% of the total consumption. 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 (see Fuels, synthetic). *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.

3. 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).

3.1. Properties

Each isomer has its individual set of physical and chemical properties; however, these properties are similar (Table 6). 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 tertiary hydrogen (37). Other properties available but not listed are given in equations for heat capacity and viscosity (34), and saturated liquid density (36).

Table 6. Properties of Pentanes

Property	*n*-Pentane	Isopentane	Neopentane	Ref.
molecular weight	72.151	72.151	72.151	34
normal freezing point, K	143.429	113.250	256.57	8
normal bp, K	309.224	301.002	282.653	8
water solubility at 25°C, g C_5H_{12}/100 kg H_2O	9.9	13.2		11
spontaneous ignition temperature in air, K	557.0	700.0	729.0	11
flash point, K	233.0	213.0	198.0	35
critical point				
pressure, MPa[a]	3.369	3.381	3.199	8
temperature, K	469.7	460.39	433.75	8
density, kg/m^3	231.9	234.0	237.7	36
volume, m^3/mol	304×10^{-6}	306×10^{-6}	303×10^{-6}	8
compressibility factor	0.262	0.273	0.269	8
heat of combustion, kJ/mol[b] at 298 K				
liquid	3245	3239	3230	8
gas	3272	3264	3253	8
heat of fusion, kJ/mol[b]	8.39	5.15	3.15	8
heat of vaporization, kJ/mol[b]	25.77	24.69	22.75	8
entropy of fusion, kJ/(mol·K)[b]	5.852×10^{-2}	4.548×10^{-2}	1.226×10^{-2}	8
entropy of vaporization, kJ/(mol·K)[b]	8.335×10^{-2}	8.203×10^{-2}	8.050×10^{-2}	8
Antoine vapor pressure equationeast.a01-note-0024 [c]				
A	6.00122	5.91458	5.72918	
B	1075.78	1020.01	883.420	34
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	35
dipole moment, C·m [f]	0.0	3.336×10^{-31}	0.0	34
surface tension, mN/m (=dyn/cm)				
at 20°C	16.00	15.00	12.05	35
at 30°C	14.95	13.93	10.98	35
refractive index, n_D^{25}				
liquid	1.35472	1.35088	1.339	8
gas	1.001585			8
ASTM octane number				
research	61.8	93.0	85.5	11
motor	63.2	89.7	80.2	11

[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. (36, 34), and 36, respectively.

[d] 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 3.336×10^{-30}.

3.2. 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

Table 7. 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

Table 8. Pentane Fire Hazard Properties

Pentane	Bp, °C	Flash point, °C	Ignition temperature, °C	Flammability limits, vol % Lower	Flammability limits, vol % 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

quantities of pentanes are produced in catalytic cracking, while smaller amounts come from hydrocracking and catalytic reforming. Table 7 shows typical pentane concentration in these streams.

Most pentanes are still blended into motor fuel, though increasingly strict vapor pressure regulations may end this practice in the United States by the year 2000. 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.

3.3. Health and Safety

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 8 (38).

The threshold limit value for the time-weighted average (8-h) exposure to pentanes is 600 ppm or $1800\ \mathrm{mg/m^3}$ (51 mg/SCF); the short-term exposure limit (15 min) is 750 ppm or $2250\ \mathrm{mg/m^3}$ (64 mg/SCF) (39). 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 neo-pentanes are transported in cylinders (see Packaging containers and industrial materials).

3.4. 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.

Some isopentane is dehydrogenated to isoamylene and converted, by processes analogous to those which produce methyl *t*-butyl ether [1634-04-4] (MTBE) to *t*-amyl methyl ether [994-05-8] (TAME), which is used as a fuel octane enhancer like MTBE. The amount of TAME which the market can absorb depends mostly on its price relative to MTBE, ethyl *t*-butyl ether [637-92-3] (ETBE), and ethanol, the other important oxygenated fuel additives.

4. Hexanes

Hexane refers to the straight-chain hydrocarbon, C_6H_{14}; branched hydrocarbons of the same formula are isohexanes. Hexanes include the branched compounds, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane, and the straight-chain compound, *n*-hexane. Commercial hexane is a narrow-boiling mixture of these compounds with methylcyclopentane, cyclohexane, and benzene (qv); minor amounts of C_5 and C_7 hydrocarbons also may be present. Hydrocarbons in commercial hexane are found chiefly in straight-run gasoline which is produced from crude oil and natural gas liquids (see Gasoline and other motor fuels; Gas, natural). Smaller volumes occur in certain petroleum refinery streams.

4.1. Properties

Properties of the principal hydrocarbons found in commercial hexane are shown in Table 9. The flash point of *n*-hexane is $-21.7\ ^{\circ}C$ 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 (42).

4.2. 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) (43). 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 10. 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

Table 9. Properties of Hydrocarbons Found in Commercial Hexanes[a]

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 equationeast.a01-note-0029 cceast.a01-note-0030 [b]			
						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. 40.

[b] Ref. 34.

[c] Equations for Harlacher vapor pressure, vapor heat capacity, saturated liquid volume, and liquid viscosity can be found in Refs. 34 and 41.

[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.

hydrogenation. Hence its benzene, sulfur, and olefin contents are low. Hexane C is typical of a stream that meets specifications for polymerization-grade material.

4.3. Health and Safety

Hexane is classified as a flammable liquid by the ICC, and normal handling precautions for this type of material should be observed. According to the ACGIH, the maximum concentration of hexane vapor in air to which a worker may be exposed without danger of adverse health effects is 125 ppm; benzene is rated at 10 ppm.

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 (44).

4.4. 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

Table 10. 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.

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.

5. 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 (45). Cyclohexane was produced first by hydrogenation of benzene in 1898 (46).

5.1. Properties

Properties of cyclohexane are given in Table 11, and a number of binary azeotropes that are formed with cyclohexane are listed in Table 12.

Table 11. 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 kPaeast.a01-note-0037 [b]	
$\log_{10}P = 5.965 - 2766.63/(T - 50.50)$	
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. 47.
[d] Equations for saturated liquid density, liquid heat capacity, vapor heat capacity, and liquid viscosity can be found in Ref. 34.
[e] To convert $\log P_{(\mathrm{kPa})}$ to $\log P_{(\mathrm{mmHg})}$, add 0.875 to 5.965.
[f] To convert $\log P_{(\mathrm{kPa})}$ to $\log P_{(\mathrm{mmHg})}$, 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 (48, 49).

5.1.1. 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.

5.1.2. 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 (50, 51). 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 (52). 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 (53).

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 (54). 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 (55).

5.2. 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, have low concentrations; and concentrations of cycloparaffins in crude oils from Texas, Oklahoma, and Louisiana tend to fall in between (see Petroleum).

5.3. 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 (56). 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 **??**.

Some processes use only one reactor (57) or a combination of liquid- and vapor-phase reactors (58). 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 level, a catalyst life

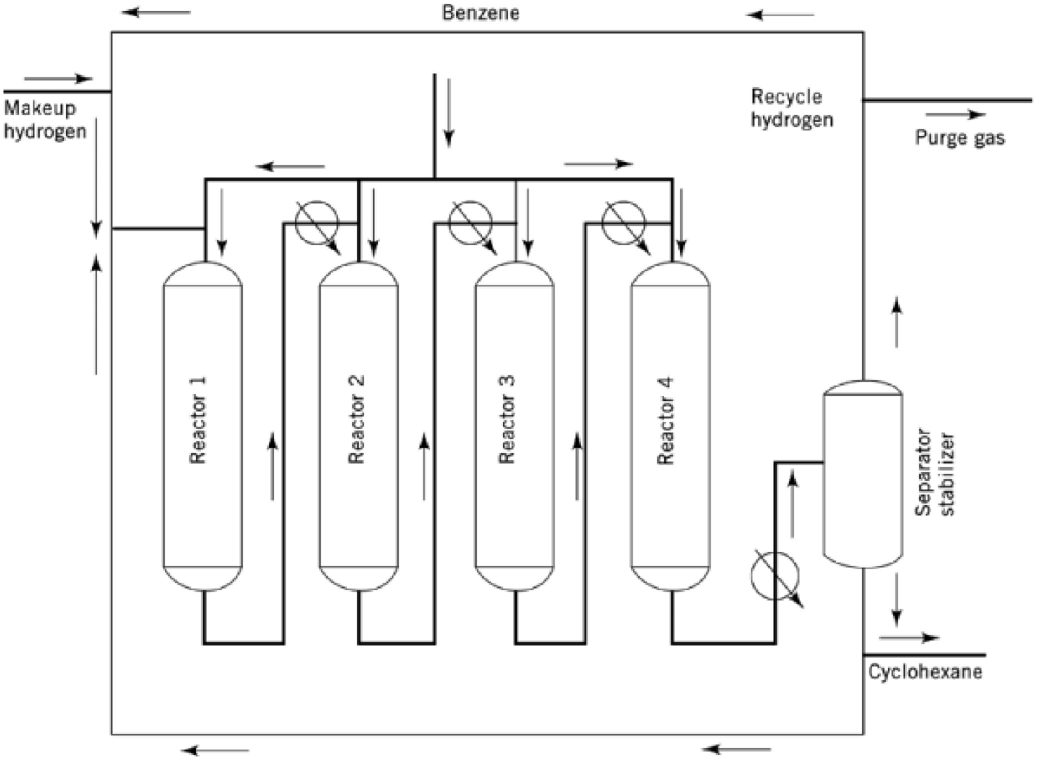

Fig. 1. Hydrogenation of benzene to cyclohexane.

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.

5.4. 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 (57, 58). 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).

The United States accounts for about a third of the world's consumption of cyclohexane, or 3.785×10^6 m^3/yr (about 1 billion gallons per year). U.S. producers and their 1990 capacities are listed in Table 13. Texaco has announced that it is leaving the cyclohexane business, but the timing is not yet certain. 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).

Table 12. 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

Table 13. U.S. Cyclohexane Producers,[a] 1993

Producer	Capacity, 10^3 m^3/yr[b]
Phillips Petroleum	852
Texaco	284
Chevron	144
CITGO	114
Total	1394

[a] Ref. 59

[b] To convert m^3/yr to gal/yr, multiply by 264.

5.5. 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 (see Table 11). 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.

5.6. Analysis

Hydrocarbon mixtures containing cyclohexane can be analyzed using gas chromatography. Specific retention volumes for several stationary phases have been determined (60). 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 61. 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.

5.7. Health and Safety

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.

5.8. 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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