PROPYLENE

1. Introduction

Propylene [115-07-1], $CH_3CH = CH_2$, is perhaps the oldest petrochemical feedstock and is one of the principal light olefins (1) (see Feedstocks). It is used widely as an alkylation (qv) or polymer–gasoline feedstock for octane improvement (see Gasoline and other motor fuels). In addition, large quantities of propylene are used in plastics as polypropylene, and in chemicals, eg, acrylonitrile (qv), propylene oxide (qv), 2-propanol, and cumene (qv) (see Olefin polymers, polypropylene; Propyl alcohols). Propylene is produced primarily as a by-product of petroleum (qv) refining and of ethylene (qv) production by steam pyrolysis.

2. Physical Properties

Physical properties of propylene are listed in Table 1 (1).

Parameters for the van der Waals equation of state per mole of propylene are $a = 6.373$ and $b = -0.08272$ when P is in kPa, V in L, and $R = 8.314$ J/(mol·K); $a = 8.379$ when P is in atm.

$$(P + a/V^2)\ (V - b) = RT$$

Other pressure–volume–temperature (PVT) relationships may be found in the literature; ie, Benedict, Webb, Rubin equations of state (4–7); the Benedict, Webb, Rubin, Starling equation of state (8); the Redlich equation of state (9); and the Redlich-Kwong equation of state (10).

For the virial equation of state (11),

$$PV/RT = 1 + B(T)/V,$$

T, K	$B(T)$
280	-392 ± 5
300	-342 ± 5
320	-297 ± 5
340	-260 ± 5
380	-204 ± 5
420	-162 ± 5
460	-132 ± 5
500	-105 ± 5

the following parameters are valid.

The following relationship exists for liquid density ρ in g/cm^3 on the saturation line when temperature, T, is in K and is valid at 87.85–365.05 K:

$$\rho_1 = AB^{-(1-T/T_a)^{3/7}} \qquad (1)$$

where $A = 0.2252$, $B = 0.2686$, and T_c = critical temperature, 365.05 K (12).

Propylene is usually transported in the Gulf Coast as compressed liquid at pressures in excess of 6.9 MPa (1000 psi) and ambient temperatures. Compressed liquid propylene densities for metering purposes may be found in the *API Technical Data Book* (13). Another method (14–17) predicts densities within 0.25% and has a maximum error on average of only 0.83%.

For the vapor pressure, P_v, of propylene, equations 2 and 3 apply. Equation 2 is the Antoine equation where P_v is in kPa, T is in K, and $A = 5.94327$,

$$\log_{10} P_v = A + \frac{B}{T + C} \tag{2}$$

$B = 784.86$, and $C = 26.15$. If P_v is given in mm Hg, $A = 6.81837$ and B and C remain unchanged. The Antoine equation is valid for $T = 160–240$ K. For temperatures of 123–365 K, equation 3 should be used:

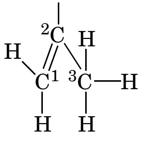
$$\log_{10} P_v = A + \frac{B}{T} + C \log T + DT \tag{3}$$

where P_v is in kPa and T is in K, $A = 34.752$, $B = -1725.5$, $C = -12.057$, and $D = 8.9948 \times 10^{-3}$ (12). If P_v is given in mm Hg, $A = 36.877$.

Ideal gas properties and other useful thermal properties of propylene are reported in Table 2. Experimental solubility data may be found in References 18 and 19. Extensive data on propylene solubility in water are available (20). Vapor–liquid–equilibrium (VLE) data for propylene are given in References (21–35) and correlations of VLE data are discussed in References (36–42). Henry's law constants are given in References (43–46). Equations for the transport properties of propylene are given in Table 3.

3. Chemical Properties

The chemistry of propylene is characterized both by the double bond and by the allylic hydrogen atoms. Propylene is the smallest stable unsaturated hydrocarbon molecule that exhibits low order symmetry, ie, only reflection along the main plane. This loss of symmetry, which implies the possibility of different types of chemical reactions, is also responsible for the existence of the propylene dipole moment of 0.35 D. Carbon atoms 1 and 2 have trigonal planar geometry identical to that of ethylene. Generally, these carbons are not free to rotate, because of the double bond. Carbon atom 3 is tetrahedral, like methane, and is free to rotate. The hydrogen atoms attached to this carbon are allylic.



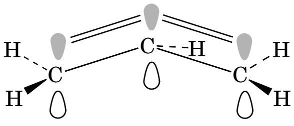
The propylene double bond consists of a σ-bond formed by two overlapping sp^2 orbitals, and a π-bond formed above and below the plane by the side overlap of two *p* orbitals. The π-bond is responsible for many of the reactions that are characteristic of alkenes. It serves as a source of electrons for electrophilic reactions such as addition reactions. Simple examples are the addition of hydrogen or a halogen, eg, chlorine:

$$CH_3CH = CH_2 + H_2 \xrightarrow{\text{catalyst}} CH_3CH_2CH_3 \tag{4}$$

$$CH_3CH = CH_2 + Cl_2 \xrightarrow{\text{catalyst}} CH_3CHClCH_2Cl \tag{5}$$

Reactions of alkenes are described in References 47 and 48 (see also Olefins, higher; Butylenes).

The presence of allylic hydrogens in propylene often serves to distinguish its chemistry from that of ethylene (qv). For example, these hydrogens cause cross-linked, gummy materials to form when propylene polymerizes in the presence of peroxide initiators (49). The effect of the allyl hydrogens on propylene reactions can be explained by the stability of allyl radicals and allyl carbocations. When an allylic hydrogen is abstracted from propylene, the sp^3 hybridized carbon of the methyl group changes to sp^2. The *p*-orbital of this carbon can then overlap with the *p*-orbital involved in the π-bond, forming a new π-bond, where the bonding overlap is over all three carbon atoms. The electrons from the alkene π-bond and the free-radical electron are delocalized over the entire molecule. In molecular-orbital terms, the allyl radical can be represented as stabilized by overlap between the three adjacent atomic *p*-orbitals, forming a molecular orbital that extends over three atoms.



Resonance theory can also account for the stability of the allyl radical. For example, to form an ethylene radical from ethylene requires a bond dissociation energy of 410 kJ/mol (98 kcal/mol), whereas the bond dissociation energy to form an allyl radical from propylene requires 368 kJ/mol (88 kcal/mol). This difference results entirely from resonance stabilization. The electron spin resonance spectrum of the allyl radical shows three, not four, types of hydrogen signals. The infrared spectrum shows one type, not two, of carbon–carbon bonds. These data imply the existence, at least on the time scale probed, of a symmetric molecule. The two equivalent resonance structures for the allyl radical are as follows:

$$\dot{C}H_2 - CH = CH_2 \leftrightarrow CH_2 = CH - \dot{C}H_2$$

The radical is much more stable if both structures exist. Quantum mechanical theory implies that the radical exists in both states separated by a small potential. Moreover, both molecular orbital theory and resonance theory show that the allyl carbocation is relatively stable.

$$\overset{+}{\mathrm{C}}\mathrm{H_2-CH=CH_2} \leftrightarrow \mathrm{CH_2=CH-}\overset{+}{\mathrm{C}}\mathrm{H_2}$$

3.1. Polymerization Reactions. Polymerization addition reactions are commercially the most important class of reactions for the propylene molecule and are covered in detail elsewhere (see Olefin polymers, polypropylene). Many types of gas- or liquid-phase catalysts are used for this purpose. Most recently, metallocene catalysts have been commercially employed. These latter catalysts require higher levels of propylene purity.

3.2. Electrophile Addition Reactions. The addition of electrophilic (acidic) reagents HZ to propylene involves two steps. The first is the slow transfer of the hydrogen ion (proton) from one base to another, ie, from Z^- to the propylene double bond, to form a carbocation. The second is a rapid combination of the carbocation with the base, Z^-. The electrophile is not necessarily limited to a Lowry-Brønsted acid, which has a proton to transfer, but can be any electron-deficient molecule (Lewis acid).

Electrophilic addition requires an acidic reagent. The orientation of the addition is regioselective (Markovnikov) (47). This rule is followed even in the two-step halohydrin (halogen followed by water) formation reaction that goes through the halonium ion intermediate yielding halogen and hydroxyl on adjacent carbon atoms. The Markovnikov rule also explains why hydration of propylene yields isopropyl alcohol rather than *n*-propyl alcohol. The *n*-propyl alcohol is normally obtained through the oxo process (qv), ie, hydroformylation, which goes through an aldehyde intermediate, utilizing a catalyst to add carbon monoxide and hydrogen to ethylene (see Propyl alcohols).

The presence of free radicals can invert this rule, to form anti-Markovnikov products. Free-radical addition in this fashion produces a radical on the central carbon, C-2, which is more stable than the allyl radical. This carbon can then experience further addition. For example, acid-catalyzed addition of hydrogen bromide to propylene yields 2-propylbromide; free-radical, $\mathrm{Br}^\bullet$-catalyzed addition yields 1-propylbromide.

3.3. Substitution Reactions. Substitution reactions can occur on the methyl group by free-radical attack. The abstraction of an allylic hydrogen is the most favored reaction, followed by addition to that position.

Control of addition vs substitution by free radicals can be effected by the reaction conditions, ie, radical concentration, temperature, and phase. Using halogens as propylene reactants, high temperatures and the gas phase favor high radical concentrations and substitution reactions; cold, liquid-phase conditions favor addition reactions.

4. Manufacture

4.1. Steam Cracking. In steam cracking, a mixture of hydrocarbons (qv) and steam (qv) is preheated to ca 870 K in the convective section of a pyrolysis furnace. Then it is further heated in the radiant section to as much as 1170 K (see Ethylene; Petroleum, refinery processes, survey). Steam reduces the hydrocarbon partial pressure in the reactor. The steam-to-hydrocarbon weight ratio is generally a function of the feedstock and ranges from ca 0.2 for ethane to ≥ 2.0 for gas oils (50). The amount of steam used is probably a compromise between yield structure (olefin selectivity), energy consumption, and furnace run length, which is limited by coking. The residence time in the radiant section varies from ca 1 s in older plants to as low as 0.1 s in some newer furnaces. The residence time influences olefin selectivity. Generally, selectivity to ethylene improves as residence time decreases. However, a given furnace is relatively inflexible to gross residence time changes for a specific feedstock because of hydrodynamic and heat-flux limitations.

Chain initiation reactions:	$R\,R' \rightarrow R^\bullet + R'^\bullet$
Hydrogen-abstraction reactions:	$R^\bullet + R'H \rightarrow RH + R'^\bullet$
Radical-decomposition reactions:	$R^\bullet \rightarrow RH + R'^\bullet$
Radical-addition reactions to unsaturated molecules:	$RH + R'^\bullet \rightarrow R''^\bullet$
Chain-termination reactions:	$R^\bullet + R'^\bullet \rightarrow R\,R'$
Molecular reactions:	$RH + R'H \rightarrow R''H + R'''H$
Radical-isomerization reactions:	$R'^\bullet \rightarrow R''^\bullet$

In the radiant section, the hydrocarbon mixture undergoes reactions involving free radicals (51). These mechanisms have been generalized to include the molecular reactions shown below:
The total number of reactions depends on the number of constituents present in the hydrocarbon feedstock. As many as 2000 reactions can occur simultaneously.

The constituents in the furnace effluent are the same for all hydrocarbon feedstocks. These include all hydrocarbons lighter than pentane plus heavier material, eg, gasoline and fuel oil. The proportion of these components in the effluent depends on the feedstock. For example, the furnace effluent of a plant designed for pure ethane cracking contains large amounts of hydrogen (qv), methane, unconverted ethane, and ethylene. Only small amounts of other constituents are produced. Conversely, a furnace cracking gas oil produces large amounts of gasoline and fuel oil in addition to significant quantities of useful olefins, eg, propylene (see Gasoline and other motor fuels).

The separation train of the plant is designed to recover important constituents present in the furnace effluent. The modern olefin plant must be designed to accommodate various feedstocks, ie, it usually is designed for feedstock flexibility in both the pyrolysis furnaces and the separation system (52). For example, a plant may crack feedstocks ranging from ethane to naphtha or naphtha to gas oils.

The yield of propylene produced in a pyrolysis furnace is a function of the feedstock and the operating severity of the pyrolysis. Typical yields of propylene for various feedstock are available (see Ethylene). Under practical operating conditions, ethylene yield increases with increasing severity of feedstock conversion.

Propylene yield passes through a maximum, as shown in Figure 1 (53). The economic optimum effluent composition for a furnace usually is beyond the propylene maximum. The furnace operation usually is dictated by computer optimization, ie, linear programming, of the whole plant, where an economic optimum for the plant is based on feedstock price, yield structures, energy considerations, and market conditions for the multitude of products obtained from the furnace. Thus, propylene produced by steam cracking varies according to economic conditions.

In an olefins plant separation train, propylene is obtained by distillation of a mixed C_3 stream, ie, propane, propylene, and minor components, in a C_3-splitter tower. Propylene is produced as the overhead distillation product, and the bottoms are a propane-rich stream. The size of the C_3-splitter depends on the purity of the propylene product. Two grades of propylene are commonly produced: a chemical grade, which consists of 92–94 wt% propylene, and a >90 wt%, polymer-grade propylene. Specifications for these two grades are listed in Tables 4 and 5 (54,55). A theoretically larger number of distillation trays is required to produce polymer-grade propylene than to produce the chemical grade, because of the close relative volatilities of propane and propylene.

4.2. Refinery Production. Refinery propylene is formed as a by-product of fluid catalytic cracking of gas oils and, to a far lesser extent, of thermal processes, eg, coking. The total amount of propylene produced depends on the mix of these processes and the specific refinery product slate. For example, in the United States, refiners have maximized gasoline production. This results in a higher level of propylene production than in Europe, where proportionally more heating oil is produced.

In fluid catalytic cracking, a partially vaporized gas oil is contacted with zeolite catalyst (see Fluidization). Contact time varies from 5 s–2 min; pressure usually is in the range of 250–400 kPa (2.5–4 atm), depending on the design of the unit; reaction temperatures are 720–850 K (see Butylenes).

Converted feedstock forms gasoline-boiling-range hydrocarbons, C_4 and lighter gas, and coke. Propylene yield varies, depending on reaction conditions, but yields of 2–5% based on feedstock are common (56,57).

Two thermal-cracking processes, ie, delayed coking (58) and Exxon's proprietary process, Flexicoking or fluid coking (59), are used to convert residuum into more valuable products. In delayed coking, residuum and steam are heated in a furnace and then fed into an insulated drum where the free-radical decomposition of the feedstock takes place. Coke eventually fills the drum and must be removed. In fluid coking, a residuum feed is injected into a reactor, where it cracks thermally. Coke formed during the process deposits on other fluidized coke particles and is either removed or gasified. Both fluid and delayed coking occur at 300–600 kPa (3–6 atm). Delayed coking is a lower temperature process (720 vs 820 K) and thus should have lower total olefin yields than fluid coking.

Refinery propylene is recovered at the vapor-recovery unit. Refinery wet gas is passed through an absorber, where it contacts a hydrocarbon liquid, usually a heavy naphtha. The heavier molecular weight dissolves in the liquid, and the lighter material, eg, hydrogen and methane, passes through. The absorbent or rich oil is then passed to a stripper, where dissolved hydrocarbons are removed. The lean oil is recycled to the absorber, and the absorbate is passed to a depropanizer where a propane–propylene stream is taken as the overhead. This refinery-grade stream may require further treatment to remove acid gases, such as hydrogen sulfide, carbonyl sulfide, and carbon dioxide. A chemical- or polymer-grade propylene can be made by further distillation in a propylene concentration unit.

4.3. Advanced Cracking Techniques. Technologies were developed to pyrolyze whole crude oil or various heavy petroleum fractions. These methods have in common very high temperatures, ultrashort residence times in the reactor zone, and rapid quench of the reaction products to minimize undesirable by-products.

Synthetic Fuels. Hydrocarbon liquids made from nonpetroleum sources can be used in steam crackers to produce olefins. Fischer-Tropsch liquids, oil-shale liquids, and coal-liquefaction products are examples (60) (see Fuels, synthetic). Work using Fischer-Tropsch catalysts indicates that olefins can be made directly from synthesis gas–carbon monoxide and hydrogen (61,62). Shape-selective molecular sieves (qv) also are being evaluated (63).

Catalytic Processes. Commercial interest in propane dehydrogenation has been increasing and numerous plants are being built outside the United States. Several plants are being operated for various strategic reasons. There are four technologies that can be licensed for propane dehydrogenation. These are CATOFIN from ABB Lummus, OLEFLEX from UOP, Fluidized Bed Dehydrogenation (FBD) from Snamprogetti, and Steam Active Reforming (STAR) from Phillips Petroleum. These routes differ primarily in the type of catalyst, the reactor design, and the methods used to increase the conversion, eg, the operating pressure, use of diluents, and reaction temperatures.

The CATOFIN process uses a relatively inexpensive and durable chromium oxide–alumina as catalyst. This catalyst can be easily and rapidly regenerated under severe conditions without loss in activity. To improve propylene selectivity and to increase the propane conversion, this technology uses a vacuum. Dehydrogenation is carried out in the gas phase over fixed beds. Because the catalyst cokes up rapidly, five reactors are typically used. Two are on-stream, while two are being regenerated and one is being purged. The reactors are cycled between the reaction and the reheat/regeneration modes, and the thermal inertia of the catalyst controls the cycle time, which is typically less than 10 minutes (64). This technology was first commercialized in 1986 for the production of isobutylene. The first plant to use this technology for propylene production having a capacity of 245,000 metric tons was built at Antwerp by North Sea Petrochemicals, a joint venture between Himont and Statoil (65,66). Pemex built a 340,000-t/yr plant in Morelos, Mexico (67,68).

The OLEFLEX process uses multiple side-by-side, radial flow, moving-bed reactors connected in series. The heat of reaction is supplied by preheated feed and interstage heaters. The gas-phase reaction is carried out over a catalyst, platinum supported over alumina, under very near isothermal conditions. The first commercial installation of this technology, having an annual capacity of 100,000 t, was made in 1990 by the National Petrochemical Corporation in Thailand. A second unit, at 245,000 t capacity, has been built in South Korea by the ISU Chemical Company (69).

Fluidized bed dehydrogenation technology is more prevalent in the former Soviet Union. A continuous fluidized-bed reactor system is used with a chromium on alumina catalyst. The catalyst is recirculated from the reactor to the regeneration section on a 30–60-min cycle. This process resembles conventional fluidized catalytic cracking technology used in the oil industry. The process operates under low pressure and has a low pressure drop and uniform temperature profile (69).

Steam-activated reforming technology uses a noble metal-promoted zinc aluminate spinel catalyst in a fixed-bed reactor. The reaction is carried out in the gas phase and uses multiple fired tube reactors in parallel operating under isothermal conditions and at pressures of 344–415 kPa (50–60 psig). Steam is added to the hydrocarbon feed to provide heat to the endothermic reaction, to suppress coke formation, and to increase the equilibrium conversion by lowering partial pressures of hydrogen and propane.

Because propane dehydrogenation is equilibrium-limited and per-pass propylene yield is low, the effluent compression and product purification sections account for nearly 85% of total capital required. Therefore, improvements in the separation section represent the greatest potential for cost reduction. Research efforts are being directed at developing a low cost route to olefins–paraffins separation (70). Concurrent research is being carried out to remove hydrogen *in situ* in a permeable ceramic reactor. Efforts are also directed at developing high temperature catalytic membrane reactors containing palladium and its alloys in the pores (71,72).

5. Economic Aspects

Propylene is consumed in both chemical and fuel applications. The manufacture of propylene accounts for more than half of the world's consumption of propylene for chemical use. Polypropylene demand remains high. It is used as a substitute for polyethylene and ABS resins. Growth is strong in the automotive industry where polypropylene is used as a replacement for metal allowing improved performance and reduced weight (73).

The bulk of propylene production and consumption is concentrated in North America, Western Europe, and Japan. (See Table 6 for U.S. production of propylene in 2002/2003). Demand in these regions was down in 2002, but demand in other regions has shown dramatic growth. World consumption is expected to grow at the rate of 5%/year through 2006. The highest growth in consumption is expected in the Middle East (20%/yr), Africa (10%/yr), and Central and South America (8%/yr). Growth in the established regions is expected to be about 3.5%/yr in North America, 2.9%/yr in Western Europe, and 1.8%/yr in Japan (74).

In 2002, worldwide production for chemical use amounted to 60×10^6 t and was valued at roughtly $\$25 \times 10^9$. Consumption is outpacing production. The supply-side shortage in the United States has been accommodated by increased imported materials. Dedicated units may be needed to fill demand. There are no stand-alone production units in the United States at present.

6. Storage and Handling

Precautions must be taken to avoid health and fire hazards wherever propylene is handled (75). Equipment capable of causing ignition should be shut down while connecting, disconnecting, loading, and unloading equipment (76). Electrical installations in unloading areas should be classified under Division II requirements of the National Electrical Code (77). No part of any cylinder containing propylene should be subjected to temperatures above 325 K.

Propylene is very volatile and is usually stored as a liquid under pressure. However, it can be stored safely at ambient temperature in approved containers. Storage tanks should be of welded-steel construction in accordance with the ASME Code for Unfired Pressure Vessels (78). All piping and related equipment should be steel and conform to the piping codes of ANSI (79). Waste mixtures containing propylene should not be allowed to enter drains or sewers where the danger of vapor ignition exists. Commercial quantities of propylene are shipped by tanker or pipeline and are stored aboveground in pressure vessels or underground in brine caverns.

7. Health and Safety Factors

Propylene is a colorless gas under normal conditions, has anesthetic properties at high concentrations, and can cause asphyxiation. It does not irritate the eyes and its odor is characteristic of olefins. Propylene is a flammable gas under normal atmospheric conditions. Vapor-cloud formation from liquid or vapor leaks is the main hazard that can lead to explosion. The autoignition temperature is 731 K in air and 696 K in oxygen (80). Evaporation of liquid propylene can cause skin burns. Propylene also reacts vigorously with oxidizing materials. Under unusual conditions, eg, 96.8 MPa (995 atm) and 600 K, it explodes. It reacts violently with NO_2, N_2O_4, and N_2O (81). Explosions have been reported when liquid propylene contacts water at 315–348 K (82). Table 7 shows the ratio T_w/T_{sl}, where T_w is the initial water temperature, and T_{sl} is the superheat limit temperature of the hydrocarbon.

8. Uses

Propylene has many commercial and potential uses. The actual utilization of a particular propylene supply depends not only on the relative economics of the petrochemicals and the value of propylene in various uses, but also on the location of the supply and the form in which the propylene is available. For example, economics dictate that recovery of high purity propylene for polymerization from a small-volume, dilute off-gas stream is not feasible, whereas polymer-grade propylene is routinely recovered from large refineries and olefins steam crackers. A synthetic fuels project located in the western United States might use propylene as fuel rather than recover it for petrochemical use; a plant on the Gulf Coast would recover it (see Fuels, synthetic).

The uses of propylene may be loosely categorized as refinery or chemical purpose. In the refinery, propylene occurs in varying concentrations in fuel-gas streams. As a refinery feedstock, propylene is alkylated by isobutane or dimerized to produce polymer gasoline for gasoline blending. Commercial chemical derivatives include polypropylene, acrylonitrile, propylene oxide, isopropyl alcohol, and others. In 2002, ca 60% of the world propylene supplies were consumed in the production of polypropylene (74). Polypropylene has been the largest consumer of propylene since the early 1970s and is likely to dominate propylene utilization for some time.

8.1. Refinery *Fuel.* Propylene has a net heating value of 45.8 MJ/kg (19,700 Btu/lb) and is often contained in refinery fuel-gas streams. However, propylene is diverted from streams for refinery fuel use in large quantities only when economics for other uses are unfavorable, or equipment for propylene recovery does not exist or is limited in capacity. Propylene is also contained in liquid petroleum gas (LPG), but is limited to a maximum concentration of 5 vol % in certain grades (83) (see Liquefied petroleum gas).

Alkylate. In petroleum refining, alkylation (qv) is the reaction of light olefins with isoparaffins, principally isobutane, to produce isoparaffins of higher molecular weight for gasoline blending. Alkylation produces material of higher octane rating than polymerization does, and alkylation predominated as gasoline-pool octane requirements increased after World War II. Although butenes are the preferred olefins for alkylation, propylene is also used, depending on the availability of butenes and alkylate demand. The basic alkylation reactions are acid-catalyzed (84). Propylene alkylation requires higher temperatures and acid strengths than alkylation of butenes, and butenes are good promoters of propylene alkylation (85). The principal isomer of propylene alkylation by isobutane is 2,3-dimethylpentane as compared to the higher octane quality 2,2,4-, 2,3,3-, and 2,3,4-trimethylpentanes obtained from butenes (see Alkylation). Commercial alkylation units are described in Reference 86.

Polymer Gasoline. Polymerization of butenes and propylene in the refinery, first through thermal, ie, free-radical, reactions and later by acid-catalyzed mechanisms, was the first successful process for upgrading light olefinic gases, which are coproduced in petroleum-cracking processes. Although alkylation gained in importance as gasoline-pool octane requirements increased, polymerization has been the subject of new interest as isobutane supplies have decreased (87) (see Gasoline and other motor fuels).

One of the forms of polymerization for gasoline is the Dimersol process (72). Refinery propylene, ie, 67 wt% propylene–33 wt% propane, reacts in the liquid phase with a nickel coordination complex and aluminum alkyl catalyst at ca 330 K and 1725 kPa (250 psi) (88). Propylene conversions are 90–97%. The heat of reaction is removed by circulation through an external cooler. Ammonia and water are injected into the reactor effluent to neutralize the catalyst, hydrocarbon and aqueous phases are separated, and the hydrocarbon is fractionated to produce LPG, which contains unreacted propane and propylene, as well as dimerization products consisting mainly of isohexenes. The process can also be based on butane–butene feeds. As a gasoline blending component, the Dimersol product may have clear octane ratings of 89, which is somewhat higher than that of traditional propylene polymer gasoline, ie, 87 (83,84).

8.2. Chemical. *Propylene Oligomers.* Through acid-catalyzed Friedel-Crafts processes similar to those in refinery alkylation and polymerization, propylene forms oligomers, eg, nonenes, dodecenes, and higher molecular weight olefins and viscous polypropenes (89) (see Friedel-crafts reactions). These materials are used in the production of alkyl–aryl sulfonate detergents and motor oil additives (90,91).

Polypropylene. One of the most important applications of propylene is as a monomer for the production of polypropylene. Propylene is polymerized by Ziegler-Natta coordination catalysts (92,93). Polymerization is carried out either in the liquid phase where the polymer forms a slurry of particles, or in the gas phase where the polymer forms dry solid particles. Propylene polymerization is an exothermic reaction (94).

$$n\ C_3H_6\ (g) \longrightarrow (C_3H_6)_n \quad \Delta H_{298} = -104\text{KJ/mol} \quad (-24.89\text{kcal/mol}) \tag{6}$$

$$n\ C_3H_6\ (l) \longrightarrow (C_3H_6)_n \quad \Delta H_{298} = -98.1\text{KJ/mol} \quad (-21.30\text{kcal/mol}) \tag{7}$$

The focus of commercial research since the mid-1990s is on catalysts that give desired and tailored polymer properties for improved processing. Development of metallocene catalyst systems is an example.

Most commercial processes produce polypropylene by a liquid-phase slurry process. Hexane or heptane are the most commonly used diluents. However, there are a few examples in which liquid propylene is used as the diluent.

Polypropylene is used in battery cases and in the replacement of metal parts in automobiles. Growth is particularly strong in the automotive sector (74). It is also widely used in consumer products, eg, kitchen wares, trays, toys, packaging materials, continued growth in the fibers and filaments markets, especially for continued growth in carpet backing and carpet face yarns is expected. Film, both oriented and unoriented, is also a significant growth market for polypropylene.

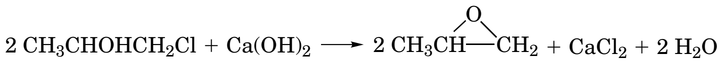
Acrylonitrile. Catalytic oxidation of propylene in the presence of ammonia (qv) yields acrylonitrile (95).

$$CH_2 = CHCH_3 + NH_3 + \frac{3}{2}O_2 \longrightarrow CH_2 = CHCN + 3H_2O \tag{8}$$

Yields based on propylene are 50–75%, and the main by-products are acetonitrile and hydrogen cyanide (96).

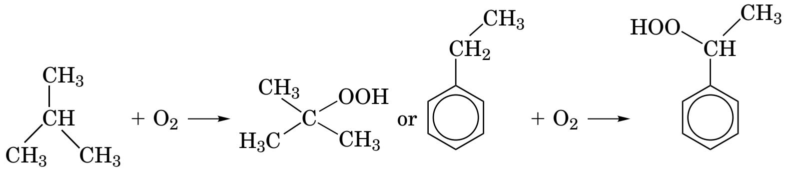
Propylene Oxide. Propylene oxide is produced from propylene by two main processes. The first is chlorohydrination of propylene at ca 310 K, followed by epoxidation of the chlorohydrin by calcium hydroxide.

$$CH_3CH = CH_2 + HOCl \longrightarrow CH_3CHOHCH_2Cl \tag{9}$$



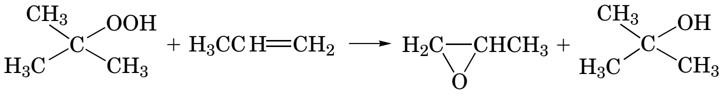
$$\mathrm{2\,CH_3CHOHCH_2Cl + Ca(OH)_2 \longrightarrow 2\,CH_3\underset{\diagdown O \diagup}{CH{-}CH_2} + CaCl_2 + 2\,H_2O} \tag{10}$$

The second process involves reaction of propylene with peroxides, as in the Oxirane process (97), in which either isobutane or ethylbenzene is oxidized to form a hydroperoxide.

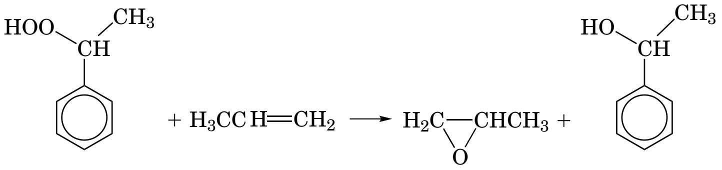


(11)

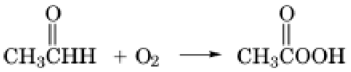
The hydroperoxide reacts with propylene, forming propylene oxide and an alcohol.



(12)

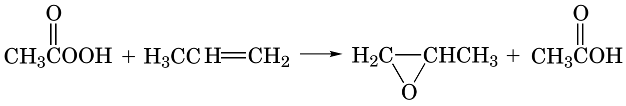


tert-Butyl alcohol can be dehydrated to form isobutylene, and methylphenyl carbinol can be dehydrated to form styrene (qv). Thus, in either reaction sequence a by-product of significant value is obtained. Hydroperoxide formation occurs under mild conditions (400 K, 400–3500 kPa (4.3–34.5 atm)) to minimize decomposition to the alcohol (98). Epoxidation of the propylene occurs in the liquid phase under similar conditions in the presence of a catalyst containing Mo, V, or Ti. Conversions are ca 10–20% for propylene and greater than 95% for the hydroperoxide. Both Shell Netherlands and Atlantic Richfield/Halcon have proprietary technology for this process. One other commercialized process involving hydroperoxides is the Daicel process (99). Peracetic acid is produced by oxidation of acetaldehyde in solution in the presence of metal ion catalyst at 300–320 K and 2.53–4.05 MPa (25–40 atm) (see Peroxides and peroxide compounds, organic).



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}HH + O_2 \longrightarrow CH_3\overset{\overset{O}{\|}}{C}OOH} \tag{13}$$

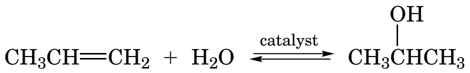
Peracetic acid then reacts with propylene at 320–350 K and 1.00–1.34 MPa (10–13.2 atm), forming propylene oxide and acetic acid.



(14)

Propylene oxide (qv) uses include manufacture of polyurethanes, unsaturated polyester, propylene glycols (qv) and polyethers, and propanolamines (see Alkanolamines; Glycols; Polyethers; Polyesters, unsaturated; Urethane polymers).

Isopropyl Alcohol. Propylene may be easily hydrolyzed to isopropyl alcohol. Early commercial processes involved the use of sulfuric acid in an indirect process (100). The disadvantage was the need to reconcentrate the sulfuric acid after hydrolysis. Direct catalytic hydration of propylene to 2-propanol followed commercialization of the sulfuric acid process and eliminated the need for acid reconcentration, thus reducing corrosion problems, energy use, and air pollution by SO_2 and organic sulfur compounds. Gas-phase hydration takes place over supported oxides of tungsten at 540 K and 25 MPa (247 atm) or over supported phosphoric acid at 450–540 K and 2.5–6.5 MPa (25–64 atm) (100).



$$CH_3CH{=}CH_2 + H_2O \xrightleftharpoons{\text{catalyst}} CH_3\overset{\overset{OH}{|}}{C}HCH_3 \tag{15}$$

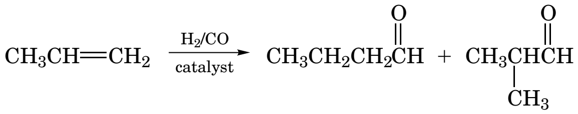
At conditions of high temperature and low pressure, for sufficient catalyst activity and acceptable reaction rates, equilibrium conversions may be as low as 5%, necessitating recycle of large amounts of unreacted propylene (101).

Conversions of ca 75% are obtained for propylene hydration over cation-exchange resins in a trickle-bed reactor (102). Excess liquid water and gaseous propylene are fed concurrently into a downflow, fixed-bed reactor at 400 K and 3.0–10.0 MPa (30–100 atm). Selectivity to isopropanol is ca 92%, and the product alcohol is recovered by azeotropic distillation with benzene.

A third catalytic route to isopropyl alcohol from propylene involves the use of polytungsten compounds in solution in a liquid-phase reactor (101). Propylene is hydrated at ca 540 K under pressure. Conversions are 60–70% and selectivity to 2-propanol is 99%.

Cumene. Cumene (qv) is produced by Friedel-Crafts alkylation of benzene by propylene (103,104). The main application of cumene is the production of phenol (qv) and by-product acetone (qv). Minor amounts are used in gasoline blending (105).

Butyraldehydes. Normal and isobutyraldehydes are produced from propylene by the oxo or hydroformylation process (see Oxo process).



$$CH_3CH{=}CH_2 \xrightarrow[\text{catalyst}]{H_2/CO} CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}H + CH_3\underset{\underset{CH_3}{|}}{C}H\overset{\overset{O}{\|}}{C}H \tag{16}$$

The two main industrial processes that are employed are described in Reference 106. Normal butyraldehyde (qv) is the product of primary interest (103,107).

8.3. Other. Ethylene can be produced by steam cocracking of propylene with ethane and propane. Ethylene and butenes can also be produced by catalytic disproportionation of propylene (108).

$$2CH_2 = CHCH_3 \rightleftarrows CH_2 = CH_2 + CH_3CH = CHCH_3 \qquad (17)$$

2-Butene is the main C-4 olefin isomer.

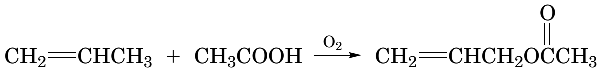
Acrolein can be obtained by propylene oxidation in a process similar to ammoxidation (109) (see Acrolein and derivatives).

$$CH_2 = CHCH_3 \xrightarrow{O_2} CH_2 = CHCHO + H_2O \qquad (18)$$

High temperature chlorination of propylene yields allyl chloride, which is used in glycerol (qv) production (110):

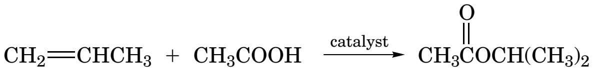
$$CH_2 = CHCH_3 + Cl_2 \xrightarrow{770K} CH_2 = CHCH_2Cl + HCl \qquad (19)$$

Allyl acetate can be obtained by the vapor-phase reaction of propylene and acetic acid over a supported Pd catalyst (eq. 20) (110). Reaction of acrylic acid and propylene yields isopropyl acrylate (eq. 21), and catalytic reaction with acetic acid produces isopropyl acetate (eq. 22) (110).



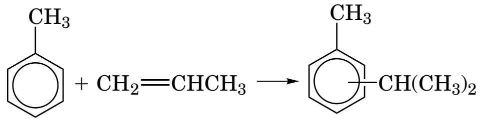
$$CH_2{=}CHCH_3 + CH_3COOH \xrightarrow{O_2} CH_2{=}CHCH_2O\overset{O}{\overset{\|}{C}}CH_3 \qquad (20)$$

$$CH_2{=}CHCH_3 + CH_2{=}CHCOOH \xrightarrow{H^+} CH_2{=}CH\overset{O}{\overset{\|}{C}}OCH(CH_3)_2 \qquad (21)$$



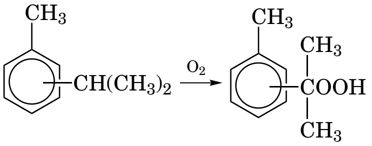
$$CH_2{=}CHCH_3 + CH_3COOH \xrightarrow{\text{catalyst}} CH_3\overset{O}{\overset{\|}{C}}OCH(CH_3)_2 \qquad (22)$$

Cresols can be made from propylene by reaction with toluene to produce cumene (111).

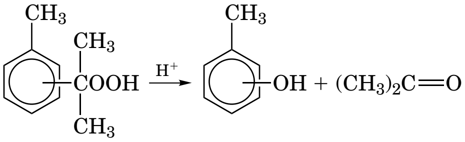


(23)

The cumene is oxidized to cymene hydroperoxide, which decomposes to cresols and acetone. The process is similar to phenol (qv) production from cumene.



(24)



(25)

Bibliography

"Propylene" in *ECT* 1st ed., Vol. 11, pp. 193–197, by J. Happel and W. H. Kapfer, New York University; in*ECT* 2nd ed., Vol. 16, pp. 579–584, by W. H. Davis, Texas National Bank of Commerce, and L. K. Beach, Enjay Chemical Laboratory; in *ECT* 3rd ed., Vol. 19, pp. 228–246, by M. R. Schoenberg, J. W. Blieszner, and C. G. Papadopoulos, Amoco Chemicals Corp.; in *ECT* 4th ed., Vol. 20, pp. 249–271, N. Calamur and M. Carrera, Amoco Corp; "Propylene" in *ECT* (online), posting date: December 4, 2000 by N. Calamur and M. Carrera, Amoco Corp.

Cited Publications?

1. D. S. Sanders, D. M. Allen, and W. T. Sappenfield, *Chem. Eng. Prog.* **73**(7), 40 (1977).
2. R. C. Reid, T. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, 3rd ed., McGraw-Hill Book Co., Inc., New York, 1977.
3. Technical data, NASA Technical Department R-132, Lewis Research Center, Cleveland, Ohio, 1962.
4. M. Benedict, G. B. Webb, and L. C. Rubin, *Chem. Eng. Prog.* **17**(8), 419 (1951).
5. H. W. Cooper and T. C. Goldfrank, *Hydrocarbon Process.* **46**(12), 141 (1967).
6. S. K. Sood and G. A. Haselden, *AIChE J.* **16**, 891 (1970).
7. E. Bender, *Cryogenics* **15**, 667 (Nov. 1975).
8. I. E. Starling and Y. C. Kwok, *Hydrocarbon Process.* **50**(10), 90 (1971).
9. Otto Redlich, *Ind. Eng. Chem. Fundam.* **14**(3), 257 (1975).
10. B. D. Djordjevic and co-workers, *Chem. Eng.* **32**, 1103 (1977).
11. J. H. Dymond and E. B. Smith, *The Virial Coefficients of Gasses, A Critical Compilation*, Clarendon Press, London, 1969, p. 72.
12. C. L. Yaws, *Physical Properties*, McGraw-Hill Book Co., Inc., New York, 1977, pp. 167, 197, and 217.
13. *API Technical Data Book—Petroleum Refining*, Vol. **I**, American Petroleum Institute.
14. J. R. Tomlinson, *Technical Publication TP-1*, Natural Gas Processors Association, Tulsa, Okla., 1971.

15. R. W. Hankinson and G. H. Thomson, *AIChE J.* **25**, 653 (1979).
16. G. H. Tomson, K. R. Brobst, and R. W. Hankinson, *AIChE J.* **28**, 671 (1982).
17. R. W. Hankinson, T. A. Coker, and G. H. Thomson, *Hydrocarbon Process.* **82**(4), 207 (Apr. 1982).
18. R. Battino, *Chem. Rev.* **66**, 395 (1966).
19. E. Wilhelan, R. Battino, and R. T. Wilcock, *Chem. Rev.* **77**(2), 219 (1977).
20. A. Azarnoosh and J. J. Ketta, *J. Chem. Eng. Data* **4**, 211 (1957).
21. I. Wichterle, J. Linek, and E. Hale, *Vapor–Liquid Equilibrium Data Biography*, Elsevier Science, Inc., New York, 1973, p. 221; Suppl., 1977.
22. H. H. Reamer and B. H. Sage, *Ind. Eng. Chem.* **43**, 1628 (1951).
23. K. Ishii, S. Hayami, T. Shirai, and K. Ishida, *J. Chem. Eng. Data* **11**(3), 288 (1966).
24. D. D. Li and J. J. McKetta, *J. Chem. Eng. Data* **8**, 271 (1963).
25. R. B. Williams and D. L. Katz, *Ind. Eng. Chem.* **46**, 2512 (1954).
26. S. L. McCurdy and D. L. Katz, *Oil Gas J.* **43**(45), 102 (1945).
27. W. G. Schneider and O. Maass, *Can. J. Res.* **19**(10), 231 (1941).
28. G. G. Haselden, F. A. Holland, M. B. King, and R. F. Strickland-Constable, *Proc. Roy. Soc. London Ser. A* **240**, 1 (1957).
29. H. Lee, D. M. Newitt and M. Rubemann, *Proc. Roy. Soc. London Ser. A* **178**, 506 (1941).
30. R. A. McKay, H. H. Reamer, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.* **43**, 2112 (1951).
31. G. H. Hanson and co-workers, *Ind. Eng. Chem.* **42**, 735 (1950).
32. A. N. Mann and co-workers, *J. Chem. Eng. Data* **8**(4), 499 (1963).
33. D. B. Manley and G. W. Swift, *J. Chem. Eng. Data* **16**(3), 301 (1971).
34. D. R. Laurence and G. W. Swift, *J. Chem. Eng. Data* **17**(3), 333 (1972).
35. G. H. Goff and co-workers, *Ind. Eng. Chem.* 42, 735 (1950).
36. M. Hirata, S. Ohe, and K. Nagahama, *Computer Aided Data Book of Vapor–Liquid Equilibria*, Kadausha Ltd., Elsevier, Tokyo, Japan, 1975.
37. M. Sagara, Y. Arai, and S. Saito, *J. Chem. Eng. Jpn.* **5**(4), 418 (1972).
38. H. K. Bae, K. Nagahama, and M. Hirata, *J. Jpn. Petrol. Inst.* **21**(4), 249 (1978).
39. M. L. McWilliams, *Chem. Eng.* **80**(25), 138 (Oct. 29, 1973).
40. C. S. Howat and G. W. Swift, *Ind. Eng. Chem. Process Des. Develop.* **19**, 318 (1980).
41. E. W. Funk and J. M. Prausnitz, *AIChE J.* **17**(1), 254 (1971).
42. S. E. M. Haman, W. K. Chung, I. M. Epshayal, and B. C. Y. Lu, *Ind. Eng. Chem. Process Des. Develop.* **16**(1), 1977.
43. J. Y. Lenior and co-workers, *J. Chem. Eng. Data* **17**(3), 340 (1971).
44. S. Ng, H. G. Harris, and J. M. Prausnitz, *J. Chem. Eng. Data* **17**(4), 482 (1969).
45. H. Sayara and co-workers, *J. Chem. Eng. Jpn.* **8**(2), 98 (1975).
46. G. T. Preston and J. M. Prausnitz, *Ind. Eng. Chem. Fundam.* **10**(3), 384 (1971).
47. R. T. Morrison and R. N. Boyd, *Organic Chemistry*, 3rd ed., Allyn and Bacon, Inc., Boston, Mass., 1977, p. 143.
48. T. G. W. Solomons, *Organic Chemistry*, John Wiley & Sons, Inc., New York, 1977.
49. H. Wittcoff, *J. Chem. Educ.* **57**, 707 (1980).
50. S. B. Zdonik, E. J. Green, and L. P. Hallee, *Manufacturing Ethylene*, The Petroleum Publishing Co., Tulsa, Okla., 1970.
51. A. G. Goosens, M. Dente, and E. Ranzi, *Hydrocarbon Process.* **57**(9), 227 (1978).
52. S. B. Zdonik, E. J. Bassler, and L. P. Hallee, *Hydrocarbon Process.* **53**(2), 73 (Feb. 1974).
53. L. E. Chambers and W. S. Potter, *Hydrocarbon Process.* **53**(1), 121 (1974).
54. Amoco Chemicals Manufacturing Specifications, Chicago, Ill., 1975.
55. A. Hahn, A. Chaptal, and J. Sialelli, *Hydrocarbon Process.* **54**, 1989 (1975).

56. E. G. Wollaston, W. J. Haflin, and W. D. Ford, *Hydrocarbon Process.* **54**(9), 93 (Sept. 1975).
57. R. B. Ewell and G. Gadmer, *Hydrocarbon Process.* **57**(4), 125 (1978).
58. J. H. Gary and G. E. Handwerk, *Petroleum Refining*, Marcel Dekker, Inc., New York, 1975, p. 52.
59. *Oil Gas J.*, 53 (Mar. 10, 1975).
60. H. J. Glidden and C. F. King, *Chem. Eng. Prog.* **76**(12), 47 (1980).
61. V. U. S. Rao and R. J. Gormley, *Hydrocarbon Process.* **59**(11), 139 (1980).
62. B. Bussemeir, C. D. Frohning, and B. Cornils, *Hydrocarbon Process.* **55**(11), 105 (1976).
63. P. D. Caesar, J. A. Brennan, W. E. Garwood, and J. Cirik, *J. Catal.* **56**, 274 (1979).
64. S. Gussow, D. C. Spence, and E. A. White, *Oil Gas J.* (Dec. 8, 1980).
65. *Chem. Week*, 5 (Sept. 2, 1992).
66. *Chem. Week*, 15 (Nov. 4, 1992).
67. *Chem. Week*, 8 (Jan. 1993).
68. *Chem. Mktg. Reporter*, **240**(15), 3, 14, 15 (1991).
69. E. Chang, *Alkane Dehydrogenation and Aromatization*, Process Economics Program, Report No. 203, SRI International, Menlo Park, Calif., 1992.
70. *Facilitated Transport Process for Low-Cost Olefin–Paraffin Separation*, Advanced Technology Program No. 70NANB4H1528 National Institute of Science and Technology, 1994.
71. Z. D. Ziaka, R. G. Minet, and T. T. Tsotsis, *AIChE J.* **39**(3), 526 (1993).
72. J. Shu, B. P. A. Grandjean, A. Van Nete, and S. Kaliaguine, *Can. J. Chem. Eng.* **69**, 1036 (1991).
73. *Chemical Economics Handbook*, SRI Consulting, Menlo Park, Calif., March. 2004.
74. “Propylene, Chemical Profile,” *Chem. Market Reporter* (Oct. 6, 2003).
75. *Chemical Safety Data Sheet SD-59, Propylene*, Manufacturing Chemists Association, Washington, D.C., rev. 1974.
76. Standards for Storage Handling of Liquefied Petroleum Gases, *National Fire Code*, Sect. 5, No. 58, National Fire Protection Assn., Boston, Mass., 1977.
77. *National Electric Code*, No. 70, National Fire Protection Assn., Boston, Mass., 1971.
78. *ASME Boiler and Pressure-Vessel Code*, Section 8, American Society of Mechanical Engineers, New York, 1980.
79. *ANSI B31 Series*, B31.3., American Society of Mechanical Engineers, New York, 1980.
80. H. F. Coward and co-workers, *Limits of Flammability of Gases and Vapors*, Bulletin 503, U.S. Bureau of Mines, Washington, D.C., 1952.
81. R. J. Lewis, Sr., ed., *Sax’s Dangerous Properties of Industrial Materials*, 11th ed., Wiley, Hoboken, N.J., 2004.
82. W. M. Porteous and R. C. Reid, *Chem. Eng. Prog.* **72**, 93 (1976).
83. J. W. Andrews, P. Bonnifay, B. Cha, D. Douillet, and J. Raimbault, paper presented at *The NPRA Annual Meeting*, AM-76-25, San Antonio, Tex., Mar. 28, 1976.
84. R. J. Hengstebeck, *Petroleum Processing, Principles and Applications*, McGraw-Hill Book Co., Inc., New York, 1959.
85. W. S. Knoble and F. E. Herbert, *Petr. Refiner*, 101 (Dec. 1959).
86. C. R. Cupit, J. E. Cwyu, and E. C. Jernigan, *Petro/Chem. Eng.*, 203 (Dec. 1961); *Petro/Chem. Eng.*, 207 (Jan. 1962).
87. G. E. Weisingntel, *Chem. Eng.*, 77 (June 16, 1980).
88. P. M. Kohn, *Chem. Eng.*, 114 (May 23, 1977).
89. E. K. Jones, *Adv. Catal.* **8**, 219 (1956).
90. A. Schrieshein and I. Kirschenbaum, *Chemtech.*, 310 (May 1978).

91. C. M. Fontana, R. J. Herold, E. J. Kinney, and R. C. Miller, *Ind. Eng. Chem.* **44**, 2944 (1952).
92. P. Pin and R. Mulhempt, *Angew. Chem. Int. Ed. Engl.* **19**, 857 (1980).
93. J. Boor, Jr., *Ziegler-Natta Catalysts and Polymerizations*, Academic Press, Inc., New York, 1979.
94. G. S. Parks and H. P. Mosher, *J. Polym. Sci. Part A* **1**, 1979 (1963).
95. D. J. Hadley, R. E. Saunders, and P. T. Mapp, in E. G. Hancock, ed., *Propylene and its Industrial Derivatives*, Earnest Benn Ltd., London, 1973, pp. 416 ff.
96. P. R. Pujado, B. V. Vora, and A. P. Krueding, *Hydrocarbon Process.* **56**(5), 169 (1977).
97. R. Landau, G. A. Sullican, and D. Brown, *Chemtech.*, 602 (Oct. 1979).
98. K. Weissermel and H. J. Arpe, *Industrial Organic Chemistry*, Verlag-Chemie, Weinheim, Austria, 1978, p. 239.
99. 1979 Petrochemical Handbook, *Hydrocarbon Process.* **59**(11), 240 (1979).
100. Ref. (19), p. 175.
101. Y. Onove, Y. Mizutani, S. Akiyama, and Y. Izumi, *Chemtech.*, 432 (July 1978).
102. W. Nier and J. Woellner, *Hydrocarbon Process.* **51**(11), 113 (1972).
103. W. C. Fernelius, H. Wittcoff, and R. E. Varneria, *J. Chem. Educ.* **57**, 707 (1980).
104. J. C. Fielding, in Ref. 95, pp. 244 ff.
105. R. A. Persale, E. L. Pollitzer, D. J. Ward, and P. R. Pujado, *Chem. Econ. Eng. Rev.* **10**(7), 25 (1978).
106. R. Fowler, H. Conner, and R. A. Gaehl, *Hydrocarbon Process.* **55**(9), 247 (1976).
107. H. Weber, W. Demmeling, and A. M. Desia, *Hydrocarbon Process.* **55**(4), 129 (1976).
108. Ref. 19, pp. 77–80.
109. G. E. Schaal, *Hydrocarbon Process.* **52**(9), 218 (1973).
110. L. F. Hatch and S. Matar, *Hydrocarbon Process.* **57**(6), 149 (1978).
111. K. Sto, *Hydrocarbon Process.* **52**(8), 89 (1973).

NARASIMHAN CALAMUR
MARTIN CARRERA
Amoco Corporation

Table 1. **Propylene Physical Properties**[a]

Property	Value
mol wt	42.081
freezing temperature, K	87.9
bp, K	225.4
critical temperature, K	365.0
critical pressure, MPa[b]	4.6
critical volume, cm^3/mol	181.0
critical compressibility	0.275
Pitzer's acentric factor	0.148
liquid density, at 223 K, g/cm^3	0.612
dipole moment, 10^{-30} C·m[c]	1.3
standard enthalpy of formation, kJ/mol[d]	20.42
standard Gibbs energy of formation for ideal gas, at 101.3 kPa (=1 atm), kJ/mol[d]	62.72
heat of vaporization at bp, kJ/mol[d]	18.41
Lennard-Jones potential[e]	
T, nm	0.4678
ϵ_0/K, K	298.9
solubility, at 20°C, 101.3 kPa (1 atm), mL gas/100 mL solvent	
in water	44.6
in ethanol	1250
in acetic acid	524.5
refractive index, n_D	1.3567

[a] Ref. 2, unless otherwise noted.

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

[c] To convert C·m to debye, divide by 3.336×10^{-30}.

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

[e] Ref. 3.

Table 2. **Thermal Properties of Propylene**[a]

Property	Equation[b]	Value of constants			
		A	*B*	*C*	*D*
	Ideal gas				
heat capacity,[c]	$C_p = A + BT + CT^2 + DT^3$	2.85	0.238	-1.2×10^{-4}	2.3×10^{-8}
heat of formation,[c] kJ/mol[d]	$H_f = A + BT + CT^2$	35.3	-5.77×10^{-2}	2.22×10^{-5}	
free energy of formation,[c] kJ/mol[d]	$G_f = A + BT$	75.3	1.75		
	Liquid				
heat of vaporization,[e] kJ/kg[d]	$H_v = H_{vi}((T_c - T)/(T_c - T_i))^n$	437.6[f]	225.45[g]	365.06[h]	0.38[i]
heat capacity,[j] J/(kg·K)[d]	$C_p = A + BT + CT^2 + DT^3$	1969	7.04	-7.04×10^{-2}	1.84×10^{-4}

[a] Ref. 12.

[b] Temperature in K.

[c] Equation valid for range 298–1500 K.

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

[e] Valid for range 87.85–365.05 K.[f]

[f] Value is for H_{vi} in kJ/kg. To convert J to cal, divide by 4.184.

[g] Value is for T_i in K.

[h] Value is for T_c in K.

[i] Value is for n.

[j] Valid for range 88–373 K.

Table 3. **Transport Properties of Propylene**[a]

			Value of constants			
Property	Equation	Value at 25°C	*A*	*B*	*C*	*D*
		Gas, from −100 *to 1000*°C				
thermal conductivity, W/(m·K)[b]	$k_G = A + BT = CT^2 + DT^3$	1.84×10^{-2}	-7.577×10^{-3}	6.096	9.96×10^{8}	3.94×10^{-11}
viscosity, $P_{a \cdot 5}$[c]	$_G = A + BT + CT^2$	8.39×10^{-6}	-5.601×10^{-7}	31.88×10^{-9}	-62.91×10^{-13}	
		Liquid				
thermal conductivity,[d] W/(m·K)[b]	$k_L = A + BT + CT$	0.115[e]	2.9×10^{5}	-6.05×10^{-2}	1.26×10^{-2}	
viscosity, mPa·s[c] (=cP)	$\log_L = A + B/T + CT + DT^2$					
from −185.3 to 160°C			−27.8	1.096	2602	−863.5
from −160 to 91.9°C			−5.009	413.2	1.771	−30.92
surface tension,[f] mN/m (=dyn/cm)	$= n \cdot {}_1((T_c T)/(T_c - T_1))$		19.98[g]	203[h]	365.05[i]	1.1797[j]

---

[a] Ref. 1.

[b] To convert W/(m·K)to cal/(s·cm·K), divide by 418.4.

[c] To convert Pa·s to centipoise, multiply by 10^3.

[d] Range, −185 to 70°C.

[e] At 20°C.

[f] Range, −185.3 to 91.9°C.

[g] Value is for $_1$ in mN/m.

[h] Value is for T_l in K.

[i] Value is for T_c in K.

[j] Value is for n.

Table 4. **Product Specification for Chemical-Grade Propylene**

Component	Specification, wt%	ASTM Test method
Constituents		
propylene	92–94	D2163
ethane and lighter	<0.4	D2163
ethylene	<0.02	D2723
hydrocarbons		
C_4 and above	<0.2	D2712
C_5 and above	<0.005	D2162
propane	<8.0	D2163
Impurities[a]		
acetylene + methyl acetylene + propadiene	<100	D2712
total H_2, O_2, CO, CO_2, and N_2	<100	D2504
sulfur	<10	D3120
water	<50	D2713
halides	<10	
alcohols	<50	
amines	<5	
butadiene	<20	D2712
butenes	<125	
dimethyl formamide	<0.3	

[a] Values are in ppm wt.

Table 5. **Product Specifications for Polymer-Grade Propylene**

Component, ppm wt	Specification	ASTM Test method
propylene	99.5[a]	D2163
ethane	<1000	D2163
total acetylenes, dienes, and other unsaturates	<10	D2712
hydrogen	<	D2504
oxygen	<8	D2504
carbon monoxide	<4	D2504
water	<10	
sulfur	<5	D3120
total nitrogen, aldehydes, ketones, and alcohols	<10	D2504

[a] Value is wt%.

Table 6. **U.S. Producers of Propylene and Their Capacities, $\times 10^3$ t[a]**

Producer	Capacity
Alon USA Bio Spring Tex	36
Atofina Petrochemicals, Port Arthur, Tex.	118
BASF/Fina, Port Arthur, Tex.	544
Baton Rouge Propylene Concentrator, Port Allen, La.	680
BP Chemicals, Chocolate Bayou, Tex.	1361
Lima, Ohio, Texas City, Tex., Whiting, Ind.	
Chevron Phillips Chemical, Cedar, Bayou, Tex., Port Arthur, Tex, Sweeny, Tex.	1452
Chevron Texaco, El Segundo, Calif., Richmond, Calif.	141
Citgo, Corpus Christi, Tex., Lake Charles La.	308
ConocoPhillips, Linden, N.J., Wood River, Ill.	295
Dow Chemical, Freeport, Tex., Plaguemine, La., Taft, La.	1134
DuPont, Orange, Tex.	50
Enterprise Products, Mont Belvieu, Tex.	499
Equistar, Channelview, Tex., Chocolate Bayou, Tex., Cinton, Iowa, Corpus Christi, Tex., La. Porte, Tex., Lake Charles, La., Morris, Ill.	2576
ExxonMobil, Baton Rouge, La., Baytown, Tex., Beaumont, Tex., Houston	2068
Flint Hills Resources, Corpus Christi, Tex.	204
Formosa, Point Comfort, Tex.	272
Frontier Oil, El Dorado, Kan.	27
Huntsman Odessa, Tex., Port Arthur, Tex.	581
Javelina Company, Corpus Christi, Tex.	45
Koch Hydrocarbon Southwest Mont Belvieu, Tex.	1360
Los Angeles Refining, Wilmington, Calif.	64
Marathon Ashland, Catlettsburg, Ky., Detroit, Mich., Garyville, La., Texas City, Tex.	644
Motiva Enterprises, Delaware City, Del, Port Arthur, Tex.	349
Murphy Oil, Meraux, La.	91
Shell, Deer Park, Tex., Norco, La.	1225
Sunoco, Brandenburg, Ky., Marcus Hook, Pa., Philadelphia, Toledo, Ohio, Westville, N.J.	544
Tesoro Petroleum, Anacortes, Wash.	36
Texas Eastman, Longview, Tex.	318
Valero Energy, Corpus Christi, Tex., Houston, Krotz Springs, La., Texas City, Tex.	474
Westlake CA&O, Calvert City, Ky.	159
Williams Olefins, Gelsmar, La.	45
Williams Refining, Memphis, Tenn.	136
Total	*17,836*

Table 7. **T_w/T_{sl} Ratios for Liquid Propylene Spills in Water**[a]

Initial water temperature, T_w, K	T_w/T_{sl}[b]	Result
311–314	0.95–0.96	ice formation
315–348	0.97–1.07	explosion
353–358	1.08–1.10	rapid pops

[a] Ref. 82.

[b] T_{s1} = superheat limit temperature of propylene.

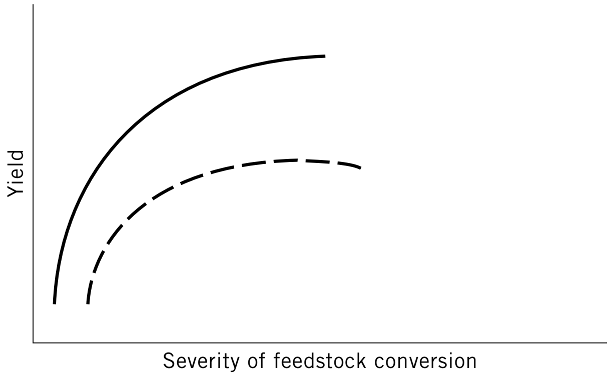


Fig. 1. Ethylene (—) and propylene (–) yields.