OLEFINS, HIGHER

1. Introduction

Higher olefins are versatile chemical intermediates for a number of important industrial and consumer products, providing a better standard of living with low environmental impact (qv) in many commercial uses. These uses can be characterized by carbon number and by chemical structure.

The even-numbered carbon alpha olefins (α-olefins) from C_4 through C_{30} are especially useful. For example, the C_4, C_6, and C_8 olefins impart tear resistance and other desirable properties to linear low and high density polyethylene; the C_6, C_8, and C_{10} compounds offer special properties to plasticizers used in flexible poly(vinyl chloride). Linear C_{10} olefins and others provide premium value synthetic lubricants; linear C_{12}, C_{14}, and C_{16} olefins are used in household detergents and sanitizers. In addition, many carbon numbers from C_4 to C_{30+} are

Table 1. **World Producers of Linear α-Olefins**[a]

Company and location	Capacity, 10^3 t	Process
Albemarle Corp.[b]		
Pasadena, Tex., U.S.	472	Albemarle
Feluy, Belgium	204	Albemarle
Chevron Chemical Co., Cedar Bayou, Tex., U.S.	249	Chevron-Gulf
Gujarat-Godrej Innovative Chemicals, Ankleshwar, India	30	Godrej-Lurgi
Idemitsu Petrochemical Co., Ltd., Ichihara, Chiba Prefecture, Japan	50	Idemitsu
Mitsubishi Kasai Corp., Kurashiki, Ikayama Prefecture, Japan	50	Chevron-Gulf
Nizhnekamskneftekhim, Nizhnekamsk, Russia	181	Albemarle
Shell Chemical Co.,		
Geismar, Louisiana, U.S.	590	Shell (SHOP)
Ellesmere Port, Stanlow, United Kingdom	270	Shell (SHOP)
Spolana, Neratovice, Czech Republic	130	Chevron-Gulf
Total	*2226*	

[a] Ref. 3.
[b] Formerly Ethyl Corp.

also utilized in specialty applications such as sizing agents to produce longer-lasting paper. Various uses and production methods of these olefins have been discussed extensively in References 1 and 2. Producers of the even-carbon-number higher olefins are shown in Table 1.

The C_6–C_{11} branched, odd and even, linear and internal olefins are used to produce improved flexible poly(vinyl chloride) plastics. Demand for these branched olefins, which are produced from propylene and butylene, is estimated to be increasing at a rate of 2% per year. However, the growth of the linear α-olefins is expected to slow down to a rate of 5% per year from 1992 to 1997 (3), as opposed to growth rates of 7–10% in the 1980s.

2. Physical Properties

For a listing of selected physical properties of linear alpha olefins, see Tables 2 and 3. Boiling points for this homologous series increase as the carbon number increases; approximately 30°C is added for each $-CH_2-$ group. Thus, 1-butene boils at -6°C and 1-pentene at about 30°C. Melting points, or freezing points, for that matter, do not behave in as regular a fashion, although an increase of about 20°C per $-CH_2-$ group roughly describes the pattern observed for the lighter olefins, and an increase of 10°C per each added carbon for the heavier liquids. For example, the change from 1-butene to 1-pentene is ~20°C, whereas the increase from 1-dodecene to 1-tridecene is about 8°C. Typically, densities for the liquid olefins are in the range of 0.7 g/mL at room temperature.

3. Chemical Properties

The general reactivity of higher α-olefins is similar to that observed for the lower olefins. However, heavier α-olefins have low solubility in polar solvents such as

Table 2. **Properties of C_4 to C_{20} Linear 1-Olefins**

Compound	Mol wt	Density, g/mL 20°C	Viscosity, mm^2/s(=cSt)		Free energy of formation, kJ/mol[a]	CAS Registry number
			20°C	100°C		
1-butene	56.11	0.6012			72.09	[106-98-9]
1-pentene	70.13	0.6402	0.202		78.67	[109-67-1]
1-hexene	84.16	0.67317	0.39		87.61	[592-41-6]
1-heptene	98.19	0.69698	0.50		96.02	[592-76-6]
1-octene	112.2	0.71492	0.656	0.363	104.4	[111-66-0]
1-nonene	126.2	0.72922	0.851	0.427	112.8	[124-11-8]
1-decene	140.3	0.74081	1.09	0.502	121.3	[872-05-9]
1-undecene	154.3	0.75032	1.38	0.587	129.6	[821-95-4]
1-dodecene	168.3	0.75836	1.72	0.678	138.0	[112-41-4]
1-tridecene	182.3	0.7653	2.14	0.782	146.4	[2437-56-1]
1-tetradecene	196.4	0.7713	2.61	0.894	154.8	[1120-36-1]
1-pentadecene	210.4	0.7765	3.19	1.019	163.3	[13360-61-7]
1-hexadecene	224.4	0.78112	3.83	1.152	171.7	[629-73-2]
1-heptadecene	238.4	0.7852	4.60	1.30	180.1	[6765-39-5]
1-octadecene	252.5	0.7888	5.47	1.46	188.5	[112-88-9]
1-nonadecene	266.5	0.7920 f[b]		1.63	196.9	[18435-45-5]
1-eicosene	280.5	0.7950 f[b]		1.82	205.3	[3452-07-1]

[a] To convert kJ/mol to kcal/mol, divide by 4.184.

[b] f = frozen.

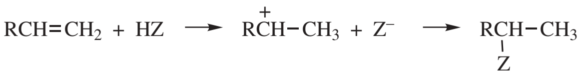
water; consequently, in reaction systems requiring the addition of polar reagents, apparent reactivity and degree of conversion may be adversely affected. Reactions of α-olefins typically involve the carbon–carbon double bond and can be grouped into two classes: (*1*) electrophilic or free-radical additions; and (*2*) substitution reactions.

Table 3. **Safety Factors of C_4 to C_{20} Linear 1-Olefins**

Compound	Flash point, °C	Flammability limit, vol %		Autoignition temperature, °C
		Lower	Upper	
1-butene	na	1.6	9.3	383.8
1-pentene	−18.2	1.5	8.7	272.8
1-hexene	−31.2	1.2	9.2	253.0
1-heptene	−0.1	1.1	8.0	263.0
1-octene	20.8	0.9	7.1	229.9
1-nonene	26.8	0.8	6.4	236.8
1-decene	53.3	0.7	5.9	234.9
1-undecene	71.1	0.7	5.6	236.8
1-dodecene	48.8	0.6	5.4	255.0
1-tridecene	79.4	0.6	5.4	236.8
1-tetradecene	109.9	0.5	5.4	234.9
1-pentadecene	112.8	0.4	5.4	na
1-hexadecene	123.8	0.5	5.4	240.0
1-heptadecene	135.0	0.5	5.4	na
1-octadecene	145.8	0.4	5.4	250.0
1-nonadecene	156.8	0.4	5.4	na
1-eicosene	165.8	0.4	5.4	236.8

3.1. Electrophilic Addition.

In the following example, an α-olefin reacts with a Lewis acid to form the most stable intermediate carbocation. This species, in turn, reacts with the conjugate base to produce the final product. Thus electrophilic addition follows Markovnikov's rule.



$$\mathrm{RCH{=}CH_2 + HZ \longrightarrow R\overset{+}{C}H{-}CH_3 + Z^- \longrightarrow R\underset{\underset{Z}{|}}{C}H{-}CH_3}$$

3.2. Free-Radical Addition.

A different outcome is expected in free-radical addition. The reaction of an α-olefin with a typical free radical affords the most stable intermediate free radical. This species, in turn, reacts further to form the final product, resulting in the anti-Markownikov mode of addition.

$$\mathrm{RCH{=}CH_2 + Br\cdot \longrightarrow R\dot{C}HCH_2Br}$$

$$\mathrm{R\dot{C}HCH_2Br + H:Br \longrightarrow RCH_2CH_2Br + Br\cdot}$$

3.3. Substitution.

In free-radical substitution, the olefin reacts with a free-radical source to form the allyl free radical, which in turn reacts with available reagent to produce both the final product and a new free radical.

$$\mathrm{RCH_2CH{=}CH_2 + X\cdot \longrightarrow R{-}\dot{C}H{-}CH{=}CH_2 + HX}$$

$$\mathrm{R{-}CH{-}CH{=}CH_2 + X_2 \longrightarrow R{-}\underset{\underset{X}{|}}{C}H{-}CH{=}CH_2 + X^{\cdot}}$$

3.4. Commercial Olefin Reactions.

Some of the more common transformations involving α-olefins in industrial processes include the oxo reaction (hydroformylation), oligomerization and polymerization, alkylation reactions, hydrobromination, sulfation and sulfonation, and oxidation.

Oxo Reaction. Olefins are well known for their ability to form complexes with various transition metals. The resulting coordination compounds have many uses as catalytic species, including hydrogenation, dimerization, oxidation, isomerization, and hydroformylation. The complexes of olefin–Group VIII metals have wide usage in these hydroformylations, or oxo processes. These processes add carbon monoxide and hydrogen to the starting olefin to form, depending on the conditions employed, aldehydes, carboxylic acids, alcohols, or esters. This procedure can be accomplished in single steps or with sequential modifications carried out after the initial hydroformylation step has occurred (see OXO PROCESS).

Oligomerization and Polymerization. Since an allyl radical is stable, linear α-olefins are not readily polymerized by free-radical processes such as those employed in the polymerization of styrene. However, in the presence of Ziegler-Natta catalysts, these α-olefins can be smoothly converted to copolymers of various descriptions. Addition of higher olefins during polymerization of ethylene is commonly practiced to yield finished polymers with improved physical characteristics.

Alkylation. Benzene and phenol feedstocks are readily alkylated under Friedel-Crafts conditions to prepare extensive families of alkylated aromatics. These materials generally are intermediates in the production of surfactants or detergents such as linear alkylbenzenesulfonate (LABS) and alkylphenolethoxylate (APE). Other uses include the production of antioxidants, plasticizers, and lube additives.

Bromination. 1-Bromoalkanes are produced commercially by the anti-Markovnikow free-radical addition of HBr to α-olefins. These are further reacted with dimethyl amine to produce alkyldimethyl amines, which ultimately are converted to amine products for household cleaning and personal care.

Sulfation and Sulfonation. α-Olefin reactions involving the introduction of sulfur-containing functional groups have commercial importance. As with many derivatives of olefins, several of these products have applications in the area of surfactants (qv) and detergents. Typical sulfur reagents utilized in these processes include sulfuric acid, oleum, chlorosulfonic acid, sulfur trioxide, and sodium bisulfite.

Oxidation. Olefins in general can be oxidized by a variety of reagents ranging from oxygen itself to ozone (qv), hydroperoxides, nitric acid (qv), etc. In some sequences, oxidation is carried out to create a stable product such as 1,2-diols or glycols, aldehydes, ketones, or carboxylic acids. In other instances, oxidation results in the formation of intermediates, eg, ozonides, hydroperoxides, or epoxides that can further react without being isolated. Such quality allows the products of this class of reactions to be diverse and versatile with respect to final application.

4. Commercial α-Olefin Manufacture

Most linear α-olefins are produced from ethylene. Ethylene-based capacity in 1993 was 2,196,000 t, compared to only 30,000 t for fatty alcohol-based manufacture.

Linear α-olefins were produced by wax cracking from about 1962 to about 1985, and were first commercially produced from ethylene in 1965. More recent developments have been the recovery of pentene and hexene from gasoline fractions (1994) and a revival of an older technology, the production of higher carbon-number olefins from fatty alcohols.

Ethylene oligomerization can be accomplished in the following commercial processes: (*1*) stoichiometric chain growth on aluminum alkyls followed by displacement (Albemarle); (*2*) catalytic chain growth on aluminum alkyls (Chevron-Gulf); (*3*) catalytic chain growth using a nickel ligand catalyst (Shell); and (*4*) catalytic chain growth using a modified zirconium catalyst (Idemitsu). In the Albemarle (formerly Ethyl) process, stoichiometric quantities of aluminum alkyls are used with subsequent displacement of α-olefins from the aluminum, followed by separation of the α-olefins from the aluminum alkyls. In the Chevron-Gulf process, catalytic amounts of aluminum alkyl are used. The operating temperatures are higher than those in the stoichiometric process, thus favoring displacement reactions after a finite amount of chain growth. In the Shell process, a three-phase system is employed, which gives a high linearity at higher carbon numbers. A nickel ligand catalyst dissolved in a solvent forms one liquid phase, the produced olefins form a second liquid phase, and the ethylene forms a third. Once formed, the olefins usually do not engage in further reactions because most of them are not in contact with the catalyst. Shell practices isomerization and disproportionation to produce a narrow range of internal linear olefins for feed to their oxo-alcohol unit. In the Idemitsu process, a zirconium oligomerization catalyst is modified by adding an aluminum alkyl and a Lewis base or an alcohol in a solvent. Variations in the catalyst mix thus offer a variety of carbon-number distributions, some of which resemble those in the catalytic processes, others approaching those in the stoichiometric process. Although operating at lower pressures than the other ethylene-based oligomerizations, the Idemitsu process still produces high quality linear α-olefins.

Vista has offered for license a stoichiometric process, which has not yet been commercialized, although the related primary alcohol process has been described (see ALCOHOLS, HIGHER ALIPHATIC–SYNTHETIC PROCESSES). Other processes, including developments by Dow and Exxon, have been reported in the literature.

Formation of by-products varies with each process; typical by-products are paraffins, linear internal olefins, and vinylidene (branched) olefins.

Olefin distribution in the Albemarle stoichiometric process tends to follow the Poisson equation, where X_p is the mole fraction of alkyl groups in which p ethylene units have been added, and n is the average number of ethylene units added for an equal amount of aluminum.

$$X_p = \frac{n^p e^{-n}}{p!} \tag{1}$$

The olefin distribution in the catalytic processes, on the other hand, tends to follow the Schultz-Flory equation, where X_N equals the number of moles of olefins having carbon number N, X_{N-2} equals the moles of olefins having two carbon numbers lower, and Q_N is a constant depending on the reaction conditions; Q_N can range from 0.4–0.9 but usually equals 0.6–0.8.

$$Q_N = \frac{X_N}{X_{N-2}} \tag{2}$$

Typical distributions of four commercial processes are compared in Figure 1.

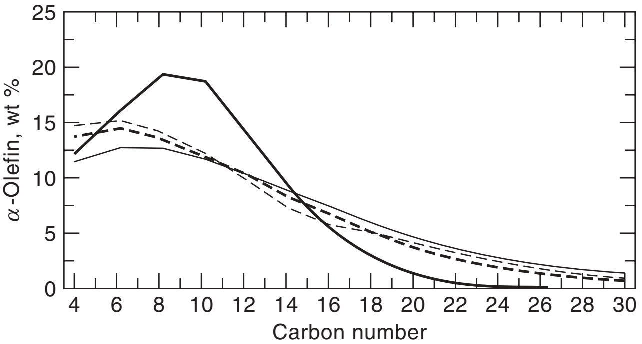


Fig. 1. Typical α-olefin distributions, where (—) represents Albemarle, (- - - -) Chevron, (- - - -) Idemitsu, and (—) Shell.

4.1. Two-Step Ziegler Stoichiometric Process. This commercial two-step process was developed by Albemarle Corporation, which has plants in Pasadena, Texas, and Feluy, Belgium (Fig. 2). A plant in the former USSR is also based on the Albemarle technology. In the first step, incoming ethylene is oligomerized on triethylaluminum in a continuous stoichiometric reactor at 120–150°C and 14–21 MPa (140–210 atm) for about one hour. These longitudinal coil reactors are designed to remove the large heat of reaction; six reactor shells about eight feet in diameter and containing long tubes immersed in boiling water are used at the Pasadena location. Unreacted ethylene is separated in flash drums and recycled after having been compressed and distilled. The aluminum alkyls are then sent to the second step, in which ethylene is used to displace the olefins and regenerate the triethylaluminum for recycle to step one. Displacement conditions are 280–320°C and 1.0 MPa (10 atm) with minimum contact time. The displacement reactors are heat exchangers designed to heat and cool the streams quickly. The resulting olefins are separated from the aluminum alkyls at various stages in the process, as shown in Figure 2. Some olefins are removed before chain growth, and others after. Trace amounts of aluminum alkyls in the olefins are converted to paraffins by caustic hydrolysis. The mixed olefins are separated into commercial carbon numbers by fractional distillation.

Albemarle has the capability to run additional stoichiometric displacement and growth reactions or various aluminum alkyl separation techniques to create the carbon numbers most in demand while suppressing the rest. For example, butene can be used as a displacing agent to create tri(*n*-butyl)aluminum, which, when fed to chain growth, releases higher olefins from C_6 through C_{20+} (Feluy design). Similarly, higher olefins can also be fed to stoichiometric reactors to place them back on the aluminum and to create those needed in the marketplace, such as 1-decene. Albemarle continues to revise its processes to meet market demands; the current facility in Pasadena, for example, is vastly more complicated than its initial process design.

4.2. One-Step Ziegler Process. Gulf Research and Development Corporation developed the one-step Ziegler process shown in Figure 3. This process is now owned by Chevron, which has two plants at Cedar Bayou, Texas. Plants based on licensing the technology are operated by Mitsubishi in Japan and at Neratovice in the Czech Republic (see Table 1). Chevron further improved the process around 1990 by reducing paraffin impurities.

In the one-step Ziegler process, high purity ethylene and a catalytic quantity of triethylaluminum in a solvent are fed to several high pressure continuous reactors. Chevron's original plant, which still operates, had eight reactors, but the new plant has only two (4). The original plant reactors have been described as large horizontal vessels containing a single pipe coil that is immersed in water (5); the new plant reactors are probably similar but much larger. According to the same source (5), α-olefins in the original plant were prepared by polymerizing ethylene at 180–220°C and 14 MPa (140 atm) in a long, narrow reactor that allowed for minimum back mixing and used catalytic amounts of metal alkyls.

At elevated temperatures, the ethylene reacts with the metal alkyl growth products as they are formed, releasing the olefin and the catalyst for further growth reaction. The reaction is exothermic and the temperature can be controlled by regulating the pressure of the steam evolving from the reactor shell.

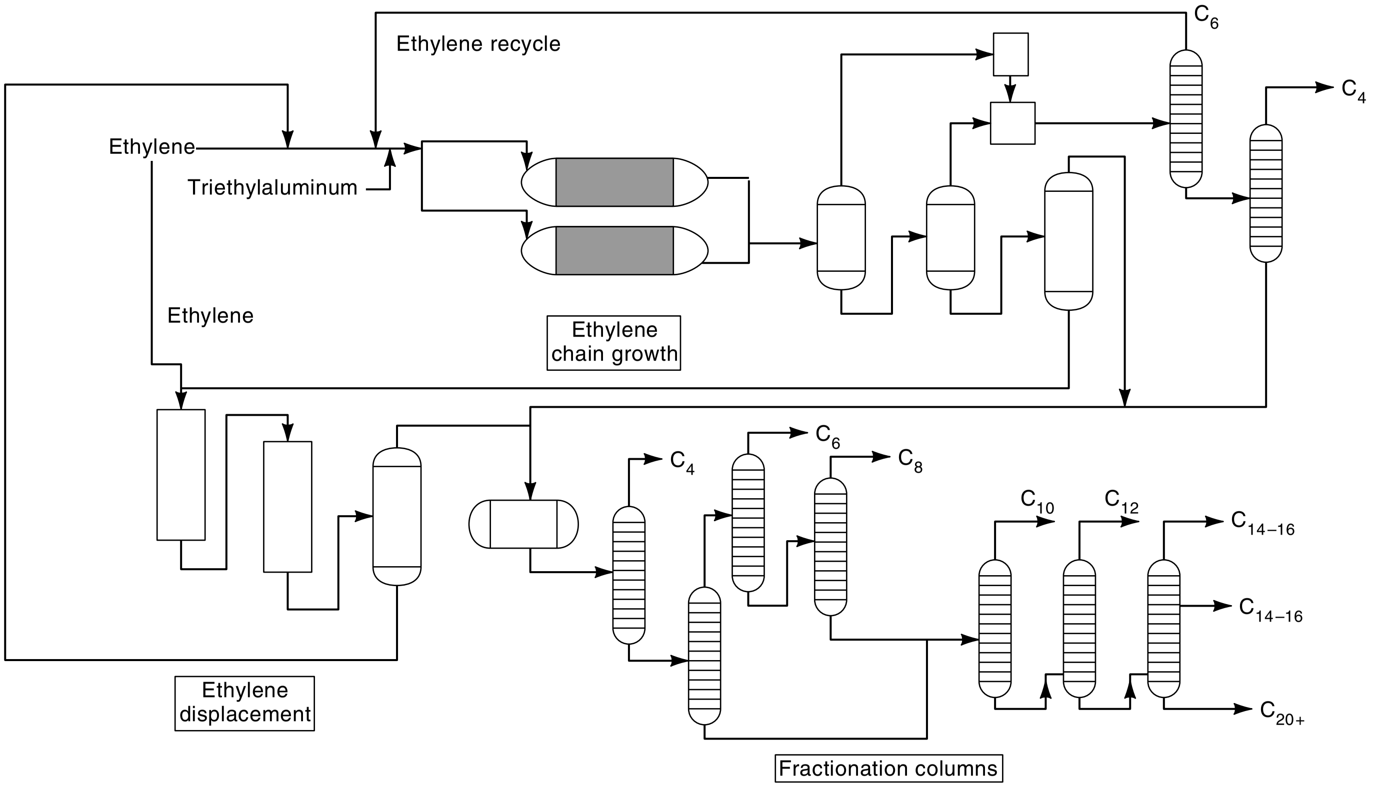


Fig. 2. Albemarle α-olefin schematic (Pasadena, Tex., and Feluy, Belgium; Belgium location includes butene recycle to exhaustion).

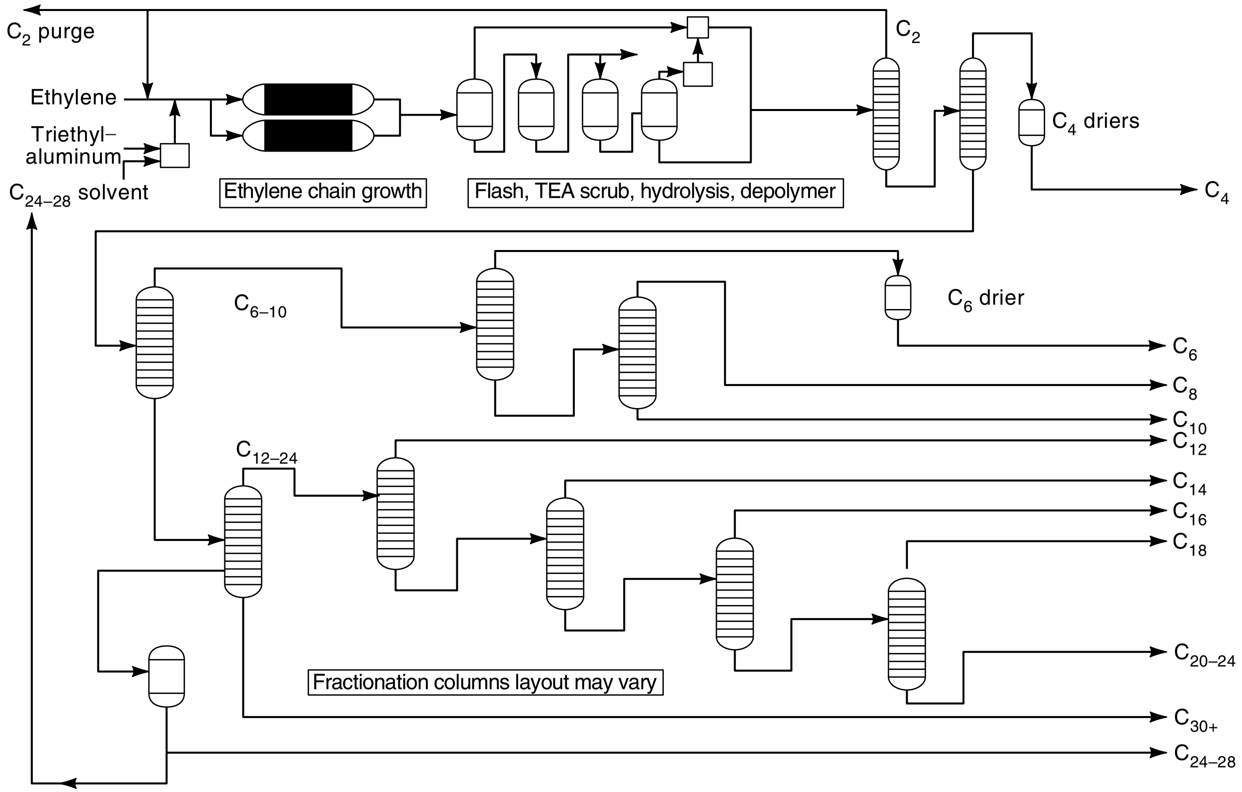


Fig. 3. Chevron α-olefin schematic where TEA = triethylaluminum (Cedar Bayou, Tex.; also Mitsubishi, Japan, and Spolana, Czech Republic). The layout of the fractionation columns may vary.

Depending on olefin product quality requirements, ethylene conversion per pass can vary from 30–90 wt%, taking at least 5 minutes of reactor residence time; olefin product distribution can also be varied by controlling the reaction temperature. Since the reactor coils must be cleaned periodically to remove waxy polymer for good temperature control and stable operations, the provision of backup reactors is necessary.

The solvent is C_{24-28} α-olefins recycled from the fractionation section. Effluent from the reactors includes product α-olefins, unreacted ethylene, aluminum alkyls of the same carbon number distribution as the product olefins, and polymer. The effluent is flashed to remove ethylene, filtered to remove polyethylene, and treated to reduce the aluminum alkyls in the stream. In the original plant operation, these aluminum alkyls were not removed, resulting in the formation of paraffins (~1.4%) when the reactor effluent was treated with caustic to kill the catalyst. In the new plant, however, it is likely that these aluminum alkyls are transalkylated with ethylene by adding a catalyst such as 60 ppm of a nickel compound, eg, nickel octanoate (6). The new plant contains a caustic wash section and the product olefins still contain some paraffins (~0.5%). After treatment with caustic, crude olefins are sent to a water wash to remove sodium and aluminum salts.

Ethylene is recycled, some of which is purged, to eliminate the accumulation of ethane. The olefins are distilled into even-carbon-number fractions from 4 through 18 and blends of C_{20-22}, C_{24-28}, and C_{30+}. Various blends of the C_6–C_{18} carbon numbers are also available. 1-Butene and 1-hexene are dried to remove moisture; 1-butene is stored in a sphere and the other products are placed in dome-roof rundown and product storage tanks. The 1-octene and higher carbon-number storage tanks have an interconnected nitrogen system that protects quality and reduces emissions. Auxiliary systems include a cooling tower, hot oil heaters, and a reactor-wash solvent system utilizing a xylene mixture. With time, the reactors build up a polymer coat that must be removed with a hot oil wash system.

4.3. Shell Higher Olefins Process (SHOP). In the Shell ethylene oligomerization process (7), a nickel ligand catalyst is dissolved in a solvent such as 1,4-butanediol (Fig. 4). Ethylene is oligomerized on the catalyst to form α-olefins. Because α-olefins have low solubility in the solvent, they form a second liquid phase. Once formed, olefins can have little further reaction because most of them are no longer in contact with the catalyst. Three continuously stirred reactors operate at ca 120°C and ca 14 MPa (140 atm). Reactor conditions and catalyst addition rates allow Shell to vary the carbon distribution.

The chain-growth catalyst is prepared by dissolving two moles of nickel chloride per mole of bidentate ligand (BDL) (diphenylphosphinobenzoic acid in 1,4-butanediol). The mixture is pressurized with ethylene to 8.8 MPa (87 atm) at 40°C. Boron hydride, probably in the form of sodium borohydride, is added at a molar ratio of two borohydrides per one atom of nickel. The nickel concentration is 0.001–0.005%. The 1,4-butanediol is used to solvent-extract the nickel catalyst after the reaction.

The reactor outlet is flashed to remove ethylene which is then compressed and recycled; α-olefins are separated from the solvent that contains the catalyst, treated to remove catalyst, and then distilled into commercial fractions. Most of

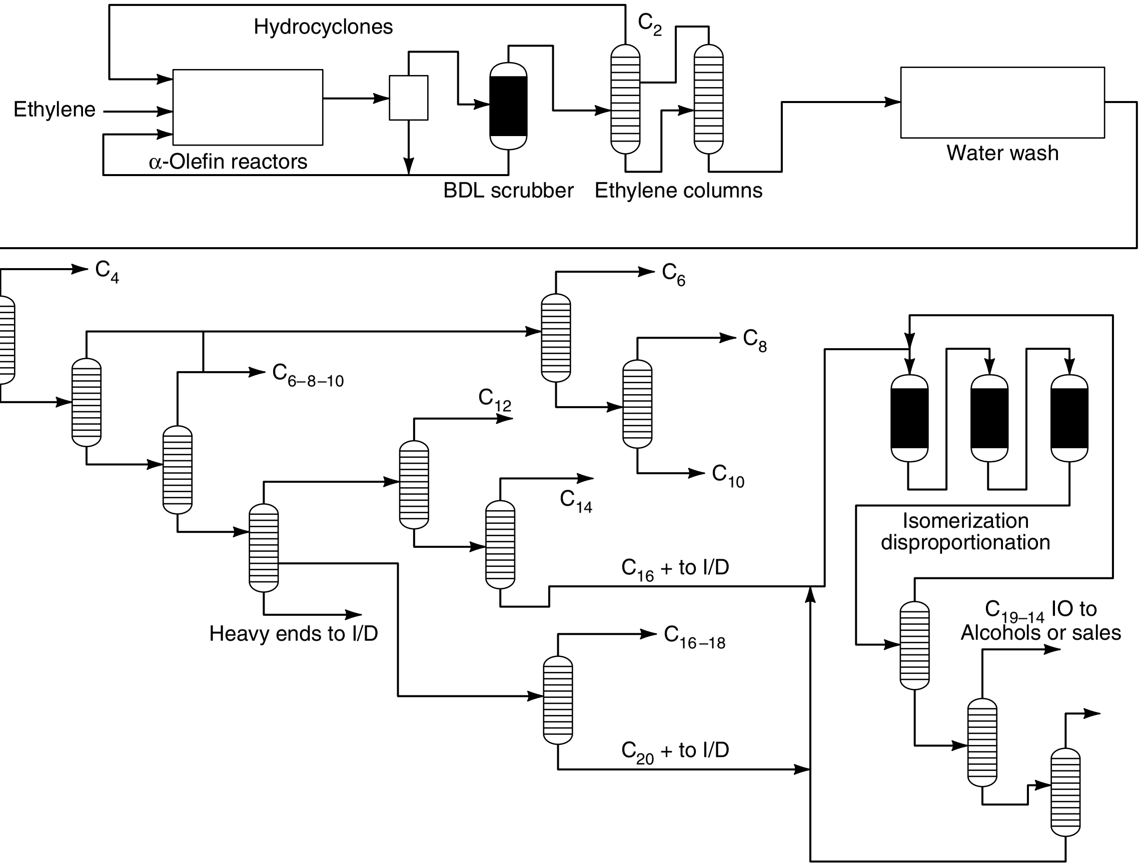


Fig. 4. Shell α-olefin and internal olefins schematic (Geismar, La. and Stanlow, United Kingdom).

the catalyst in the solvent is recycled but a portion is purged. The catalyst in the purge stream is recovered by reducing the oxidized nickel with boron hydride.

A key portion of the SHOP process is the isomerization–disproportionation (I/D) process in which excess light (C_4–C_{10}) and heavy olefins (C_{16+}) are converted to detergent range (C_{11}–C_{15}) odd and even linear internal olefins. For each pass through this system, only 10–15% of the olefins fed are converted to the desired range; consequently, this equipment must be large and feature two distillation columns that are probably >6 m in diameter. In the I/D unit the adsorber bed is probably composed of two molecular sieves (qv), one operating and the other regenerating. The isomerization catalyst is probably a heterogeneous magnesium oxide at 0.4–2.1 MPa (4–21 atm) and 80–140°C, with two beds operating and one regenerating. The disproportionation catalyst is probably rhenium oxide on alumina operating at about 120°C and 1.5 MPa (15 atm), with two operating and one regenerating.

These detergent range (C_{11}–C_{15}) odd and even linear internal olefins are fed to oxo-alcohol plants to produce C_{12}–C_{16} semilinear alcohols. Most of the alcohols are ethoxylated and sold into detergent markets (8). Shell balances carbon numbers by a combination of the ethylene oligomerization extent, I/D unit operation, and alcohol carbon-number composition.

4.4. Idemitsu Process. Idemitsu built a $50\ \mathrm{t} \times 10^3$ per year plant at Chiba, Japan, which was commissioned in February of 1989. In the Idemitsu process, ethylene is oligomerized at 120°C and 3.3 MPa (33 atm) for about one hour in the presence of a large amount of cyclohexane and a three-component catalyst. The cyclohexane comprises about 120% of the product olefin. The catalyst includes zirconium tetrachloride, an aluminum alkyl such as a mixture of ethylaluminumsesquichloride and triethylaluminum, and a Lewis base such as thiophene or an alcohol such as methanol (qv). This catalyst combination appears to produce more polymer (~2%) than catalysts used in other α-olefin processes. The catalyst content of the crude product is about 0.1 wt%. The catalyst is killed by using weak ammonium hydroxide followed by a water wash. Ethylene and cyclohexane are recycled. Idemitsu's basic α-olefin process patent (9) indicates that linear α-olefin levels are as high as 96% at C_{18} and close to 100% at C_6 and C_8. This is somewhat higher than those produced by other processes.

The Idemitsu process flow diagram is shown in Figure 5. Ethylene, cyclohexane, and a three-component catalyst are fed to a reactor. The ethylene is flashed and recycled, the catalyst is deactivated and removed, and the cyclohexane is distilled between the hexene and octene and then recycled. Catalyst usage is small, amounting to less than 0.1% of production capacity. Key parts of the process and components include catalyst preparation, oligomerization reactor, compressors to recycle ethylene, polymer removal, catalyst deactivation and washing, cyclohexane column and recycle storage, distillation columns for single cuts, cooling water system, refrigeration for ethylene column, steam system, and hot oil supply for distillation reboilers. Because of the large amount of solvent recycle and the production of single cuts generated by the Idemitsu process, its utilities are significant.

4.5. IFP Process for 1-Butene from Ethylene. 1-Butene is widely used as a comonomer in the production of polyethylene, accounting for over

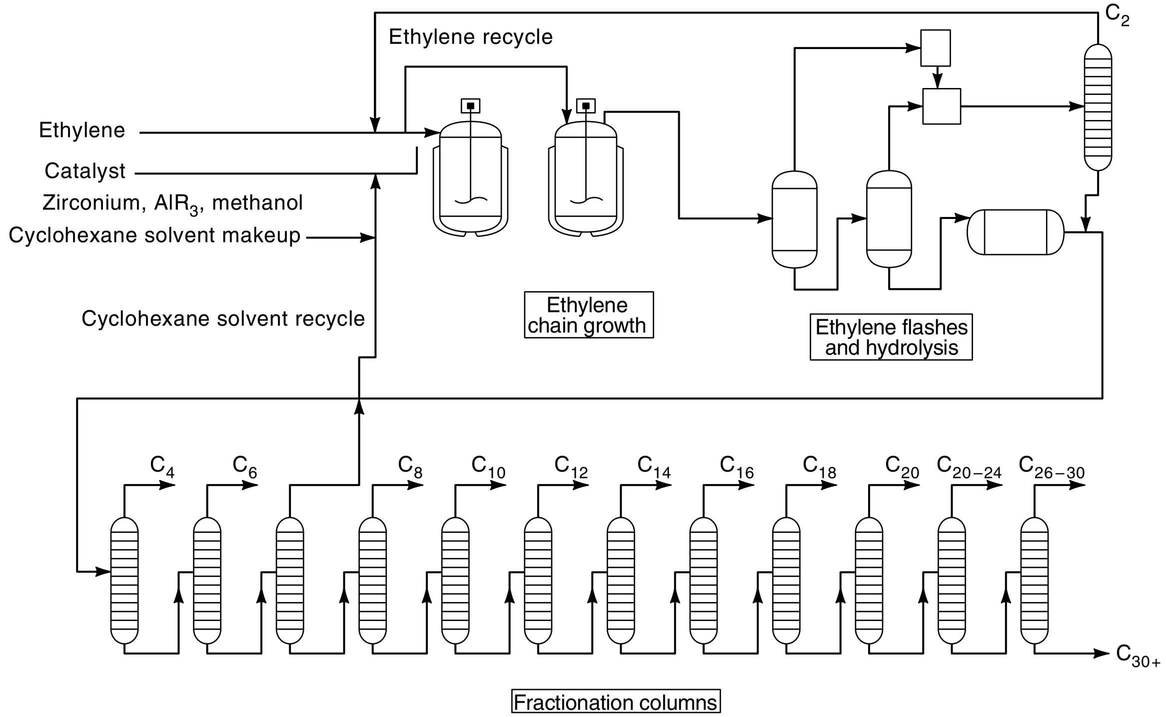


Fig. 5. Idemitsu α-olefin schematic (Japan).

107,000 t in 1992 and 40% of the total comonomer used. About 60% of the 1-butene produced comes from steam cracking and fluid catalytic cracker effluents (10). This 1-butene is typically produced from by-product raffinate from methyl *tert*-butyl ether production. The recovery of 1-butene from these streams is typically expensive and requires the use of large plants to be economical. Institut Francais du Petrole (IFP) has developed and patented the Alphabutol process which produces 1-butene by selectively dimerizing ethylene.

Similar to IFP's Dimersol process, the Alphabutol process uses a Ziegler-Natta type soluble catalyst based on a titanium complex, with triethylaluminum as a co-catalyst. This soluble catalyst system avoids the isomerization of 1-butene to 2-butene and thus eliminates the need for removing the isomers from the 1-butene. The process is composed of four sections: reaction, co-catalyst injection, catalyst removal, and distillation. Reaction takes place at 50–55°C and 2.4–2.8 MPa (350–400 psig) for 5–6 h. The catalyst is continuously fed to the reactor; ethylene conversion is about 80–85% per pass with a selectivity to 1-butene of 93%. The catalyst is removed by vaporizing liquid withdrawn from the reactor in two steps: classical exchanger and thin-film evaporator. The purity of the butene produced with this technology is 99.90%. IFP has licensed this technology in areas where there is no local supply of 1-butene from other sources, such as Saudi Arabia and the Far East.

4.6. SASOL. SASOL, South Africa, has constructed a plant to recover 50,000 tons each of 1-pentene and 1-hexene by extractive distillation from Fischer-Tropsch hydrocarbons produced from coal-based synthesis gas. The company is marketing both products primarily as comonomers for LLDPE and HDPE (see OLEFIN POLYMERS). Although there is still no developed market for 1-pentene in the mid-1990s, the 1-hexene market is well established. The Fischer-Tropsch technology produces a geometric carbon-number distribution of various odd and even, linear, branched, and alpha and internal olefins; however, with additional investment, other odd and even carbon numbers can also be recovered. The Fischer-Tropsch plants were originally constructed to produce gasoline and other hydrocarbon fuels to fill the lack of petroleum resources in South Africa.

4.7. Godrej-Lurgi. Gujarat-Godrej Innovative Chemicals Co. began the production of α-olefins in 1992 in a plant of 30,000 t/yr capacity at Ankleshwar, India, utilizing the Godrej-Lurgi process (11). This is a revival of an old process for producing α-olefins from fatty alcohols, last practiced commercially by Archer-Daniels-Midland in 1966 in the United States. Since fatty alcohols are usually more expensive than α-olefins, this process is usually not economical; α-olefins from this plant are used to produce α-olefin sulfonate for the Indian surfactant market.

In the Godrej-Lurgi process, olefins are produced by dehydration of fatty alcohols on alumina in a continuous vapor-phase process. The reaction is carried out in a specially designed isothermal multitube reactor at a temperature of approximately 300°C and a pressure of 5–10 kPa (0.05–0.10 atm). As the reaction is endothermic, temperature is maintained by circulating externally heated molten salt solution around the reactor tubes. The reaction is sensitive to temperature fluctuations and gradients, hence the need to maintain an isothermal reaction regime.

The acidic alumina catalyst is very active when fresh; this leads to extensive α-olefin isomerization to internal olefins in the first 100 hours of operation with new catalyst. Thereafter, the desired alpha selectivity of the catalyst bed (ca 93%) is achieved. During prolonged operation, the catalyst tends to lose efficacy due to poisoning. The catalyst bed can be regenerated by increasing the temperature and circulating a nitrogen–oxygen mixture through it to oxidize impurities. The endothermic nature of the reaction can lead to radial temperature gradients as well as capillary condensation of feedstock and products on catalysts at the center of the tubes; consequently, the selection of tube diameter is particularly important in the design of this reactor.

The conversion of fatty alcohols is approximately 99%. The reaction product is then condensed and sent to a distillation column to remove water and high boilers. Typically, α-olefin carbon-number distribution is controlled by the alcohol composition of the reactor feed. The process is currently used to produce C_{16-18} α-olefins from C_{16-18} fatty alcohols. A typical product composition is C_{14} at <5%, C_{16} at 50–70%, C_{18} at 30–50%, C_{20} at <2%, *n*-α-olefins at >93.0%, total internals at <7.0%, branched olefins (mainly vinylidenes) at <0.5%, fatty alcohols at <1.5%, dienes at <0.1%, and paraffins at <1.0%; aromatics, however, have not been detected.

4.8. Wax Cracking.

One or more wax-cracked α-olefin plants were operated from 1962 to 1985; Chevron had two such plants at Richmond, California, and Shell had three in Europe. The wax-cracked olefins were of limited commercial value because they contained internal olefins, branched olefins, diolefins, aromatics, and paraffins. These were satisfactory for feed to alkyl benzene plants and for certain markets, but unsatisfactory for polyethylene comonomers and several other markets. Typical distributions were C_{6-9}, 33%; C_{10}, 7%; C_{11-14}, 25%; and C_{15-20}, 35%. Since both odd and even carbon-number olefins were produced, the cost of separations was also increased.

4.9. Chlorination and Chlorination–Dehydrochlorination of Paraffins.

Linear internal olefins were produced by Shell at Geismar from 1968 to 1988, using the dehydrochlorination of chlorinated linear paraffins, a process that also yields hydrogen chloride as a by-product. To avoid the production of dichloroparaffins, which are converted to diolefins by dehydrochlorination, chlorination of paraffins is typically limited to 10% conversion.

Vista, Huntsman, and other linear alkylbenzene (LAB) producers feed chlorinated paraffins to an alkylation reactor to produce detergent alkylate without prior separation of the unreacted paraffins. Large amounts of paraffins must be recycled in these processes.

4.10. Catalytic Dehydrogenation of Normal Paraffins.

Huntsman, Vista, and other linear alkylbenzene producers also use partial dehydrogenation of normal paraffins to produce linear internal olefins for alkylation with benzene. The resulting olefins are highly linear, containing 96 wt% of linear random olefins. Typically, the olefin carbon numbers are limited to the C_{11-14} range. No more than four consecutive carbon numbers may be used or separations become economically impossible. With about 10% conversion per pass, large amounts of paraffins are recycled. Overall yields are in the 85 to 90% range.

A few companies, eg, Enichem in Italy, Mitsubishi in Japan, and a plant under construction at Fushun in China, separate the olefins from the paraffins to recover high purity (95–96%) linear internal olefins (LIO) for use in the production of oxo-alcohols and, in one case, in the production of polylinear internal olefins (PIO) for use in synthetic lubricants (syn lubes). In contrast, the UOP Olex process is used for the separation of olefins from paraffins in the liquid phase over a wide carbon range.

UOP Inc. is the key source of technology in this area, having numerous patents and over 70 units operating worldwide (12). The dehydrogenation catalyst is usually a noble metal such as platinum. For a typical conversion, the operating temperature is 300–500°C at 100 kPa (1 atm) (13); hydrogen-to-paraffin feed mole ratio is 5:1.

4.11. Branched Olefins. Solid phosphoric acid polymerization is the commonly used process for the polymerization of propylene to the corresponding trimer and tetramer, and of propylene–butylene mixtures to heptenes (14). In the UOP process, light olefins are fed to a multibed reactor containing solid phosphoric acid, which is made from a pelletized and calcined mixture of phosphoric acid on kieselguhr. Operating conditions are 175–225°C and >2.8 MPa (>27 atm) (15). In the production of heptenes, some 30 to 40 wt % of the C_3–C_4 olefin feed is converted to useful heptenes; the remainder, which consists of hexenes, octenes, and heavier cuts, are blended into motor gasoline. In either operation, heat removal is achieved by injecting cold reactor effluent between the catalyst beds. Because of the large yields of undesirable olefins, these operations usually are associated with petroleum refining to ensure economical disposal of the by-products.

Dimersol is a commercial process for the dimerization of propylene, butylenes, or a mixture of both, to C_6 and C_8 olefins; this process produces a more linear olefin than the phosphoric acid process. The reaction is conducted at ambient temperature, using a water-soluble catalyst complex (16).

5. Uses

The principal outlets for higher olefins are in the polymer, surfactant, and detergent industries (1,3) (see also ALCOHOLS, HIGHER ALIPHATIC–SYNTHETIC PROCESSES). Generally, higher olefins are seldom incorporated directly into a product as an ingredient; rather, they are processed through at least one chemical reaction step before appearing in a finished product.

5.1. Polymers. The manufacture of alcohols from higher olefins via the oxo process for use in plasticizers is a significant outlet for both linear α-olefins and branched olefins such as heptenes, nonenes, and dodecenes. These olefins are converted into alcohols containing one more carbon number than the original olefin. The alcohols then react with dibasic anhydrides or acids to form PVC plasticizers. The plasticizers produced from the linear olefins have superior volatility and cold-weather flexibility characteristics, making them an ideal product to use in flexible PVC for automobile interiors.

α-Olefins in comonomers in linear low density polyethylene (LLDPE) and high density polyethylene (HDPE) have grown at a high rate since the 1980s. Butene, hexene, and octene are the principal comonomers used, although BP also uses 4-methyl-1-pentene as a LLDPE comonomer. Because 1-butene and

1-hexene are interchangeable in several LLDPE processes, the choice of comonomer by a particular producer is a function of both economics and desired final properties. In the mid-1990s, SRI estimated the 1992–1997 comonomer growth rates at 11.0% for 1-hexene and 8.3% for 1-octene.

The introduction of metallocene and single-site polyethylene catalyst systems may eventually change the demand for higher olefins used as comonomers. Some sources indicate that their use will increase the demand for comonomers, but others feel that they will reduce comonomer use. At any rate, it is not expected that their introduction will have a significant effect on comonomer growth rates for the period 1992–1996 (see OLEFIN POLYMERS).

5.2. Detergents. The detergent industry consumes a large quantity of α-olefins through a variety of processes. Higher olefins used to produce detergent actives typically contain 10–16 carbon atoms because they have the desired hydrophobic and hydrophilic properties.

The oxo process is employed to produce higher alcohols from linear and branched higher olefins. Using a catalyst that is highly selective for hydroformylation of linear olefins at the terminal carbon atom, Shell converts olefins from the Shell higher olefin process (SHOP) to alcohols. This results in a product that is up to 75–85% linear when a linear feedstock is employed. Other oxo processes, such as those employed by ICI, Exxon, and BASF (all in Europe), produce C_{13-15} oxo-alcohols from α-olefin feedstocks; such alcohols have a linearity of about 60%. Enichem, on the other hand, produces oxo-alcohols in Italy from internal olefins and their products have a somewhat lower linearity. These oxo-alcohols are then ethoxylated and/or sulfated to produce nonionic and anionic surfactants for use in consumer and industrial products.

Nonene, or propylene tetramer, is used to alkylate phenol, which is subsequently ethoxylated to produce nonylphenol ethoxylate, an efficient, reliable industrial surfactant.

Linear alkylbenzene (LAB) is produced from C_{10-14} α-olefins and C_{11-15} internal linear olefins. Branched olefins such as propylene tetramer are used to produce branched alkylbenzene (BAB). Higher olefin streams are used to enrich the circulating olefin–paraffin stream in conventional paraffin-based LAB plants in order to boost capacity or to tailor the carbon-number distribution. Linear α- and internal olefins are also used as a direct substitute for propylene tetramer to convert hard alkylate (BAB) plants to linear alkylbenzene with no additional capital investment. As such, they offer the BAB producer an opportunity to convert quickly to LAB for biodegradable surfactants. LAB is converted to an anionic surfactant by sulfonation. The sulfonated product of branched alkylbenzene is not biodegradable and is declining in use worldwide; it is being replaced by anionic surfactants either based on LAB or on other hydrophobes, such as fatty alcohols.

In addition, C_{14-16} and $_{16-18}$ α-olefins can be directly sulfonated to produce α-olefin sulfonate (AOS). AOS was formerly used as an efficient, reliable surfactant in consumer products in the United States and Japan. However, it has been phased out in the United States and is being replaced in Japan by products based on the methyl esters of palm oil which are deemed more natural than the petrochemically derived α-olefin hydrophobe. An excellent emulsifier, AOS has been tested in a number of enhanced oil-recovery applications. Most of this work, however, is dormant as the 1994 price of oil did not make most enhanced oil-recovery projects profitable. Should the price of oil increase, some of this work would likely be reactivated.

Lighter C_6–C_8 α-olefins and C_8 branched olefins are converted by the oxo process into fatty acids containing one carbon number greater than the starting α-olefin. These fatty acids are then used to produce alkenylbenzenesulfonic acid products which are used in the United States and in Europe as perborate bleach activators in heavy-duty laundry detergents.

Finally, α-olefins find their way into the surfactant and disinfectant market through conversion, first to alkyl dimethylamine, then to benzyl chloride quats (BADMAC) and amine oxides. The former are used broadly as disinfectants, often in combination with cleaning products. The latter is a direct active in consumer and industrial cleaning products.

5.3. Lubricants. Lubricants represent a significant and growing outlet for higher olefins. Both basestocks and lube additives are produced from higher olefins by a variety of processes (see LUBRICATION AND LUBRICANTS).

Decene can be oligomerized to produce a variety of high quality synthetic lube basestocks, often called polyalphaolefin oligomer (PAO). The principal component of these basestocks is decene trimer. However, other oligomers such as dimer, tetramer, and pentamer are also present in the various poly-α-olefin oligomer blends. Decene oligomer is typically offered in 2,4,6,8, and 10 $mm^2/s(= cSt)$ blends. Higher viscosity grades (40 and 100 $mm^2/s(= cSt)$) are produced by a different process, also from decene.

It appears that decene oligomer is growing at approximately 15% per year. At this growth rate, some forecasters fear that the decene demand could ultimately exceed the available supply. However, α-olefin producers, especially Albemarle Corporation, can modify their processes to produce additional decene. Since decene oligomer has shown itself to be a versatile basestock, further growth is expected in automatic transmission fluids, gear oils, both hydraulic and industrial lubricants, as well as in the very large crankcase market. In addition, Enichem (Italy) produces an oligomerized internal olefin that has been qualified by AGIP for use in some of their synthetic products.

Hindered esters are also produced from C_6 and C_8 α-olefins. These olefins are converted into C_7–C_9 fatty acids by the oxo process; the acids are then treated with polyols such as pentaerythritol and trimethylol propane to produce hindered esters, which find use in lubricants for jet engines and other high performance applications.

Benzene is alkylated with C_{16-18} and C_{20+} olefins and subsequently sulfonated and neutralized with a dibasic salt such as calcium, magnesium, or barium. These so-called overbased sulfonates are used in crankcase additive packages.

5.4. Other Uses. A small but growing outlet for C_{16} and higher linear olefins is the production of alkenylsuccinic anhydride (ASA) for the paper industry. ASA is an effective alkaline sizing agent and competes with alkylketene dimer (AKD) in this application.

Additional uses for higher olefins include the production of epoxides for subsequent conversion into surface-active agents, alkylation of benzene to produce drag-flow reducers, alkylation of phenol to produce antioxidants, oligomerization to produce synthetic waxes (qv), and the production of linear mercaptans for use in agricultural chemicals and polymer stabilizers. Aluminum alkyls can be produced from α-olefins either by direct hydroalumination or by transalkylation. In addition, a number of heavy olefin streams and olefin or paraffin streams have been sulfated or sulfonated and used in the leather (qv) industry.

6. Health and Safety Factors

6.1. Toxicological Information. The toxicity of the higher olefins is considered to be virtually the same as that of the homologous paraffin compounds. Based on this analogy, the suggested maximum allowable concentration in air is 500 ppm. Animal toxicity studies for hexene, octene, decene, and dodecene have shown little or no toxic effect except under severe inhalation conditions. The inhalation LD_{50} for 1-hexene is 33,400 ppm; for these olefins both LD_{50} (oral) and LD_{50} (dermal) are >10 g/kg.

6.2. Handling. The main hazard associated with these olefins, especially the lighter homologues, is their low flash point. Table 3 shows flammability limits, autoignition temperatures, and flash points for the series. Although no special precautions are necessary with regard to fire extinguishing, these olefin products should be stored and shipped under an inert atmosphere to maintain product purity. Many applications for α-olefins are adversely impacted by low concentrations of moisture, peroxides, and oxygenates in general. Inhibition with antioxidants (qv) such as hindered phenols and amines should be considered if end uses are compatible with trace amounts of these materials. Finally, special attention should be given to the light olefins ($<C_8$), because the peroxides formed by inadequate handling or storage methods may be concentrated in the heavy residues during distillation. If required, α-olefin manufacturers can provide methods of peroxide removal in olefins.

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