BUTYLENES

1. Introduction

Butylenes are C_4H_8 mono-olefin isomers: 1-butene, *cis*-2-butene, *trans*-2-butene, and isobutylene (2-methylpropene). These isomers are usually coproduced as a mixture and are commonly referred to as the C_4 fraction. These C_4 fractions are usually obtained as by-products from petroleum refinery and petrochemical complexes that crack petroleum fractions and natural gas liquids. Since the C_4 fractions almost always contain butanes, it is also known as the B–B stream. The linear isomers are referred to as butenes.

2. Physical Properties

For any industrial process involving vapors and liquids, the most important physical property is the vapor pressure. Table 1 presents values for the constants for a vapor-pressure equation and the temperature range over which the equation is valid for each butylene.

$$\ln P = A + B/T + C * \ln T + DT * N \tag{1}$$

P is in Pa and T is in K

where P is in Pa and T is in KA screening technique (1) was used to select the experimental data (2) used in the regressions. Large deviations often occur at low temperatures because of the inability of the equation to model the data over the entire temperature range accurately. In order to ensure that the equations are of practical value, the regressions are performed so that emphasis is placed on conditions of industrial importance; ie, data at subatmospheric conditions are weighed much less than those at pressures exceeding 101.3 kPa (1 atm).

Figure 1 presents the ratio of the vapor pressure of a compound to the vapor pressure of *n*-butane at the same temperature. For the chemically similar species included in this figure, this ratio is a first approximation of the relative volatility of the compound to *n*-butane. Whenever the ratios of two compounds approach one another, it becomes increasingly difficult to separate the compounds by simple distillation. Since the butylenes are usually present in mixtures containing the butanes, the butylenes, and the butadienes, Figure 1 shows the ratios for all these species. Figure 1 implies that separating either isobutylene, 1-butene and 1,3-butadiene, or *n*-butane, *trans*-2-butene and *cis*-2-butene, by conventional distillation would be very difficult, if not impossible. In fact, some binary mixtures containing these components form homogeneous azeotropes. The difficulty of these separations greatly influences the design of all industrial processes involving these compounds. If it is necessary to isolate one of these species from the others, it can be expected that the separation process will be expensive.

Table 1. **Vapor-Pressure Equation Constants for the Butanes, Butylenes, and Butadienes**[a]

	A	B	C	D	N	Temperature range, K
n-butane	61.5623	–4259.90	–6.20315	3.07575×10^{-7}	2.5	135–423
isobutane	66.7163	–4237.62	–7.08156	4.00506×10^{-7}	2.5	129–408
1–butene	78.8760	–4713.65	–9.05743	1.28654×10^{-5}	2.0	126–416
cis–2–butene	71.9534	–4681.34	–7.87527	1.00237×10^{-5}	2.0	203–358
trans–2–butene	74.3950	–4648.45	–8.33977	1.20897×10^{-5}	2.0	195–358
isobutylene	83.8683	–4822.95	–9.90214	1.51060×10^{-5}	2.0	194–359
1,2-butadiene	49.5031	–4021.95	–4.28893	5.13547×10^{-6}	2.0	200–284
1,3-butadiene	73.0016	–4547.77	–8.11105	1.14037×10^{-5}	2.0	164–425

[a] See equation 1.

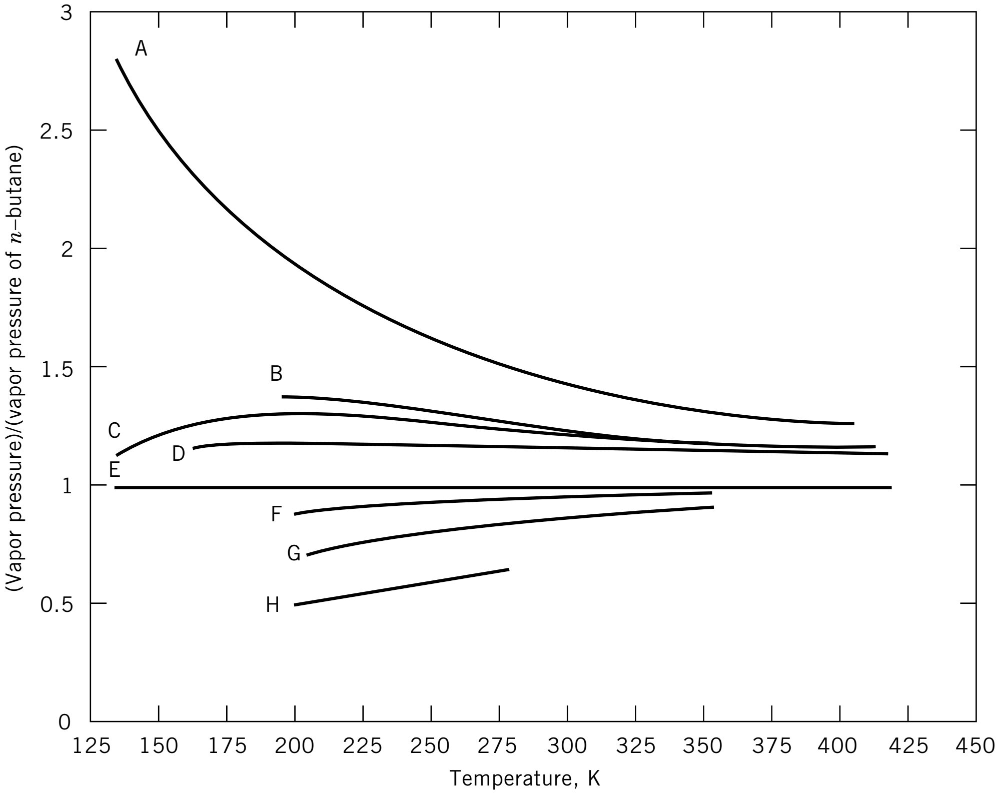


Fig. 1. Vapor-pressure ratios of the C_4 alkanes, alkenes, and dienes with respect to *n*-butane: A, isobutane; B, isobutylene; C, 1-butene; D, 1,3-butadiene; E, *n*-butane; F, *trans*-2-butene, G, *cis*-2-butene; and H, 1,2-butadiene.

Table 2 presents other important physical properties for the butylenes (3). Thermodynamic and transport properties can also be obtained from other sources (4).

3. Chemical Properties

The carbon–carbon double bond is the distinguishing feature of the butylenes and as such, controls their chemistry. This bond is formed by sp^2 orbitals (a sigma bond and a weaker pi bond). The two carbon atoms plus the four atoms in the alpha positions therefore lie in a plane. The pi bond which lies over the plane of the atoms acts as a source of electrons in addition reactions at the double bond. The carbon–carbon bond, acting as a substitute, affects the reactivity of the carbon atoms at the alpha positions through the formation of the allylic resonance structure. This structure can stabilize both positive and negative charges. Thus allylic carbons are more reactive to substitution and addition reactions than alkane carbons (5). Therefore, reactions of butylenes can be

Table 2. **Physical Properties of the Butylenes**

	Values			
Property	1-Butene	*cis*-2-Butene	*trans*-2-Butene	Isobutylene
CAS Registry Number	[106-98-9]	[590-18-1]	[624-64-6]	[115-11-7]
molecular weight	56.11	56.11	56.11	56.11
melting point, K	87.80	134.23	167.62	132.79
boiling point, K	266.89	276.87	274.03	266.25
critical temperature, K	419.60	435.58	428.63	417.91
critical pressure, MPa[a]	4.023	4.205	4.104	4.000
critical volume, L/mol	0.240	0.234	0.238	0.239
critical compressibility factor	0.277	0.272	0.274	0.275
acentric factor	0.1914	0.2018	0.2186	0.1984
Ideal gas properties[b] *at* 298.15 K				
Hf, kJ/mol	–0.126	–6.99	–11.18	–16.91
Gf, kJ/mol	71.34	65.90	63.01	58.11
Cp, J/mol · K	85.8	79.4	88.3	90.2
Hvap, kJ/mol	20.31	22.17	21.37	20.27
Hcomb, kJ/mol	–2719	–2712	–2708	–2724
Saturated vapor at 298.15 K				
viscosity, mPa · s(= cP)	0.00776	0.00782	0.00763	0.00816
thermal conductivity, W/(m · K)	0.0151	0.0135	0.0144	0.0158
Saturated liquid				
density at 298.15 K, mol/L	10.47	11.00	10.69	10.49
surface tension at 298.15 K, mN/m(= dyn /cm)	0.0121	0.0140	0.0132	0.0117
Cp at 266 K, J/mol · K[b]	121.6	118.8	121.8	123.3
viscosity at 266 K, mPa · s(= cP)	0.186	0.214	0.214	0.228
thermal conductivity at 266 K, W/(m · K)	0.120	0.124	0.121	0.117
Flammability limits, vol % in air				
lower limit	1.6	1.6	1.8	1.8
upper limit	9.3	9.7	9.7	8.8
autoignition temperature, K	657	598	597	738

[a] To convert MPa to atm, multiply by 9.869.

[b] To convert kJ to kcal, divide by 4.184.

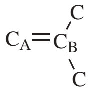
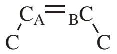
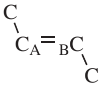
divided into two broad categories: (*1*) those that take place at the double bond itself, destroying the double bond; and (*2*) those that take place at alpha carbons.

Differences in reactivity of the double bond among the four isomers are controlled by substitution pattern and geometry. Inductive effects imply that the carbons labeled B in Table 3 should have less electron density than the A carbons. ^{13}C nmr shift data, a measure of electron density, confirm this.

The electron-rich carbon–carbon double bond reacts with reagents that are deficient in electrons, eg, with electrophilic reagents in electrophilic addition (6,7), free radicals in free-radical addition (8,9), and under acidic conditions with another butylene (cation) in dimerization.

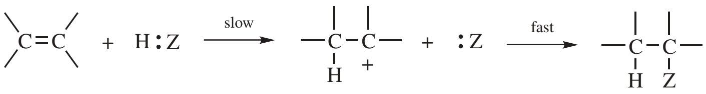
3.1. Electrophile Addition. The addition of electrophilic (acidic) reagents HZ involves two steps: the slow transfer of hydrogen ion from :Z to

Table 3. **^{13}C Nmr Shifts and Hydration Activation Energies for Butylenes**

	^{13}C Nmr^{a} ppm shift at		E_a for hydration, kJ/mol^{b} at	
Butylene	A	B	A	B
$C_A{=}C_B{-}C{-}C$	80.4	53.5	188	145
	82.0^{c}	50.4^{c}	711	108
	69.1	69.1	203	203
	67.7	67.7	203	203

[a] Relative to external CS_2 reference.
[b] To convert kJ to kcal, divide by 4.184.
[c] These values obtained by interpolation.

the butylene to form a carbocation; and, a rapid combination of the carbocation with the base :Z.



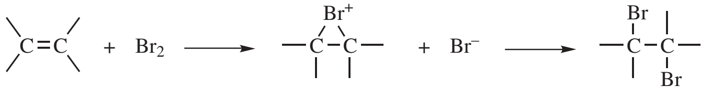
where HZ = HCl, HBr, HI, H_2SO_4, H_3O^+

The rate of addition depends on the concentration of both the butylene and the reagent HZ. The addition requires an acidic reagent and the orientation of the addition is regioselective (Markovnikov). The relative reactivities of the isomers are related to the relative stability of the intermediate carbocation and are isobutylene $\gg$ 1 – butene $>$ 2 – butenes. Addition to the 1-butene is less hindered than to the 2-butenes. For hydrogen bromide addition, the preferred orientation of the addition can be altered from Markovnikov to anti-Markovnikov by the presence of peroxides involving a free-radical mechanism.

Sulfuric acid is about one thousand times more reactive with isobutylene than with the 1- and 2-butenes, and is thereby very useful in separating isobutylene as *tert*-butyl alcohol from the other butenes. The reaction is simply carried out by bubbling or stirring the butylenes into 45–60% H_2SO_4. This results in the formation of *tert*-butyl hydrogen sulfate. Dilution with water followed by heat hydrolyzes the sulfate to form *tert*-butyl alcohol and sulfuric acid. The Markovnikov addition implies that isobutyl alcohol is not formed. The hydration of butylenes is most important for isobutylene, either directly or via the butyl hydrogen sulfate.

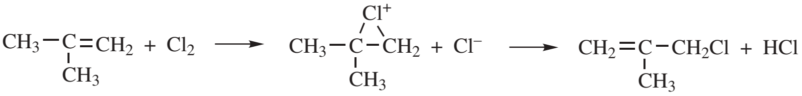
Certain oxidizing agents convert butylenes into 1,2-diols. Of the numerous oxidizing agents that bring about hydroxylation, two of the most commonly used are cold alkaline potassium permanganate, $KMnO_4$, and peroxy acids such as peroxyformic acid, HCO_2OH. Aqueous hydrolysis of the intermediate epoxide is required. $KMnO_4$ gives syn-addition whereas peroxyformic acid gives antiaddition.

Bromine and chlorine convert the 1- and 2-butenes to compounds containing two atoms of halogens attached to adjacent carbons (vicinal dihalides). Iodine fails to react. In this two-step addition mechanism the first step involves the formation of a cation. The halonium ion formed (a three-membered ring) requires antiaddition by the anion.



bromonium ion

Addition to *cis*- and *trans*-2-butene therefore yields different optical isomers (10,11). The failure of chlorine to attack isobutylene is attributed to the high degree of steric hindrance to approach by the anion. The reaction intermediate stabilizes itself by the loss of a proton, resulting in a very rapid reaction even at ambient temperature (12).



$$CH_3{-}\underset{CH_3}{C}{=}CH_2 + Cl_2 \longrightarrow CH_3{-}\underset{CH_3}{\overset{Cl^+}{C{-}}}CH_2 + Cl^- \longrightarrow CH_2{=}\underset{CH_3}{C}{-}CH_2Cl + HCl$$

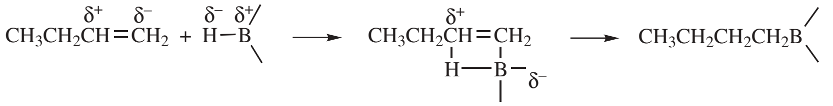
Addition of chlorine or bromine in the presence of water can yield compounds containing halide and hydroxyl on adjacent carbon atoms (haloalcohols or halohydrins). The same products can be obtained in the presence of methanol (13) or acetic acid (14). As expected from the halonium ion intermediate, the addition is anti. As expected from Markovnikov's rule, the positive halogen goes to the same carbon that the hydrogen of a protic reagent would.

Butylenes can be catalytically hydrogenated in the presence of Pt, Pd, or Ni in an exothermic reaction. In the absence of a catalyst, this reaction proceeds at a negligible rate, even at elevated temperatures. Heats of hydrogenation in kJ/mol are as follows: 1-butene, -126.8; isobutylene, -118.8; *cis*-2-butene, -119.7; and *trans*-2-butene, -115.5.

Since a carbocation can add to an alkene to form a larger cation, under acidic conditions isobutylene can dimerize to form 2,4,4-trimethyl-1-pentene [107-39-1] and 2,4,4-trimethyl-2-pentene [107-40-4], which can then be hydrogenated in the presence of nickel to form isooctane [540-84-1]. This reaction is no longer of commercial significance.

Alkylation of isobutylene and isobutane in the presence of an acidic catalyst yields isooctane. This reaction proceeds through the same mechanism as dimerization except that during the last step, a proton is transferred from a surrounding alkane instead of one being abstracted by a base. The cation thus formed bonds with the base. Alkylation of aromatics with butylenes is another addition reaction and follows the same general rules with regard to relative rates and product structure. Thus 1- and 2-butenes yield *sec*-butyl derivatives and isobutylene yields *tert*-butyl derivatives.

Two other reactions of interest are oxymercuration–demercuration and hydroboration–oxidation. Both reactions amount to hydration of the double bond to the alcohol. The former gives Markovnikov addition whereas the latter yields anti-Markovikov addition. In the first reaction the butylene reacts in aqueous mercuric acetate to add $-OH$ and $-HgOOCCH_3$, to the double bond. Then the $—HgOOCCH_3$ is replaced by $—H$ from sodium borohydride. This reaction is very fast and proceeds with 90% yield. A mercurinium ion (in analogy with a halonium ion) is invoked to explain the addition products. In hydroboration, hydrogen and boron from BHR_2 add to the double bond, then the boron is displaced by hydrogen peroxide in alkaline solution. The intermediate here is a four-centered transition state. As boron gains the pi electrons it becomes increasingly willing to release the hydrogen (see HYDROBORATION).



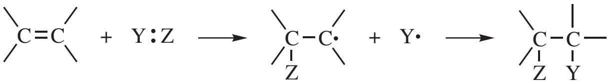
Butylene isomers also can be expected to show significant differences in reaction rates for metallation reactions such as hydroboration and hydroformylation (addition of $HCo(CO)_4$). For example, the rate of addition of di(*sec*-isoamyl)borane to *cis*-2-butene is about six times that for addition to *trans*-2-butene (15). For hydroformylation of typical 1-olefins, 2-olefins, and 2-methyl-1-olefins, specific rate constants are in the ratio 100 : 31 : 1, respectively.

The composition of the products of reactions involving intermediates formed by metallation depends on whether the measured composition results from kinetic control or from thermodynamic control. Thus the addition of diborane to 2-butene initially yields tri-*sec*-butylborane. If heated and allowed to react further, this product isomerizes about 93% to the tributylborane, the product initially obtained from 1-butene (15). Similar effects are observed during hydroformylation reactions; however, interpretation is more complicated because the relative rates of isomerization and of carbonylation of the reaction intermediate depend on temperature and on hydrogen and carbon monoxide pressures (16).

These reactions are also quite sensitive to steric factors, as shown by the fact that if 1-butene reacts with di(*sec*-isoamyl)borane the initially formed product is 99% substituted in the 1-position (15) compared to 93% for unsubstituted borane. Similarly, the product obtained from hydroformylation of isobutylene is about 97% isoamyl alcohol and 3% neopentyl alcohol (17). Reaction of isobutylene with aluminum hydride yields only triisobutylaluminum.

Selectivity among butylene isomers also occurs in vapor-phase heterogeneous catalysis, at least in the case of dehydrogenation of butenes to butadiene, where maximum yields can be obtained by employing slightly different conditions for each isomer (18). In practice, mixtures of isomers are used and an average set of conditions is employed.

3.2. Free-Radical Addition. Free-radical attack on a butylene occurs so that the most stable radical carbon structure forms. Thus, in peroxide-catalyzed addition of hydrogen halides, the addition is anti-Markovnikov.



This reaction proceeds through a chain mechanism. Free-radical additions to 1-butene, as in the case of HBr, RSH, and H_2S to other olefins (19–21), can be expected to yield terminally substituted derivatives. Some polymerization reactions are also free-radical reactions.

3.3. Polymerization. Polymerization reactions, which are addition reactions, are used to produce the principal products formed directly from butylenes: butyl elastomers; polybutylenes; and polyisobutylene (see ELASTOMERS, SYNTHETIC; OLEFIN POLYMERS).

3.4. Substitution Reactions. The chemistry at alpha positions hinges on the fact that an allylic hydrogen is easy to abstract because of the resonance structures that can be established with the neighboring double bond. The allylic proton is easier to abstract than one on a tertiary carbon; these reactions are important in the formation of alkoxybutenes (ethers).

3.5. Isomerization. Isomerization of any of the butylene isomers to increase supply of another isomer is not practiced commercially. However, their isomerization has been studied extensively because: formation and isomerization accompany many refinery processes; maximization of 2-butene content maximizes octane number when isobutane is alkylated with butene streams using HF as catalyst; and isomerization of high concentrations of 1-butene to 2-butene in mixtures with isobutylene could simplify subsequent separations (22). One plant (Phillips) is now being operated for this latter purpose (23,24). The general topic of isomerization has been covered in detail (25–27). Isomer distribution at thermodynamic equilibrium in the range 300–1000 K is summarized in Table 4 (25).

The three isomerizations, *cis*-2-butene $\rightleftharpoons$ *trans*-2-butene, 1-butene $\rightleftharpoons$ 2-butene, and butenes $\rightleftharpoons$ isobutylene, require increasingly severe reaction conditions. When the position of the double bond is shifted, cis-trans isomerization

Table 4. **Equilibrium Butylenes Distribution, Ideal Gas**[a,b]

	Mol %				
Temperature, K	1-Butene	*cis*-2-Butene	*trans*-2-Butene	Total butenes	Isobutylene
300	0.4	3.8	11.8	16.0	84.0
400	1.9	8.3	18.0	28.2	71.8
500	4.5	11.9	21.6	38.0	62.0
600	7.5	14.4	23.4	45.3	54.7
700	10.8	15.8	24.2	50.8	49.2
800	14.0	16.6	24.5	55.1	44.9
900	16.9	17.0	24.6	58.6	41.4
1000	19.6	17.2	24.4	61.2	38.8

[a] At 101.3 kPa = 1 atm.

[b] Ref. 25.

Table 5. **Isomerization of Butylenes**

Catalyst	Temperature, °C	References
cis-2-*Butene* $\rightleftharpoons$ trans-2-*butene*		
^{60}Co γ-rays	ambient	28
Na mordenite and porous Vycor	24.5	28
bis(acetylacetonato)Pd–SiO_2	61.5	29
1-*Butene* $\rightleftharpoons$ -2-*butene*		
Pt–SiO_2–Al_2O_3	–10	30
$RhCl_3$–$SnCl_2$–CH_3OH	ambient	31
$Cl_2[(C_4H_9)_3P]_2Ni$–$(C_2H_5)_2AlCl$–SiO_2	ambient	32
BF_3–Al_2O_3	ambient	33
H_3PO_4, 85%	73	34
Ga_2O_3	190–330	35
iodine	200–250	36
$ZnCrFeO_4$	465	37
Butene $\rightleftharpoons$ *isobutylene*		
Pt–Al_2O_3–SiO_2	475	38
SiO_2	520	39

also occurs, and mixtures of butenes result when the carbon skeleton is rearranged. However, during isomerization of 1-butene to 2-butene, with solid catalysts, the cis isomer is preferentially formed initially even though it is the thermodynamically less favored isomer.

An extremely wide variety of catalysts, Lewis acids, Brønsted acids, metal oxides, molecular sieves, dispersed sodium and potassium, and light, are effective (Table 5). Generally, acidic catalysts are required for skeletal isomerization and reaction is accompanied by polymerization, cracking, and hydrogen transfer, typical of carbenium ion intermediates. Double-bond shift is accomplished with high selectivity by the basic and metallic catalysts.

4. Manufacture

The C_4 isomers are almost always produced commercially as by-products in a petroleum refinery/petrochemical process as shown in Figure 2. Environmental regulations mandated by recent changes in the laws of the United States to reduce the aromatic content in gasoline will have an impact on butylene production in this country. As petroleum refiners search for alternative routes to replace the aromatics in the gasoline pool, oxygenated hydrocarbons will become increasingly attractive, not only for regaining the lost octane value in the gasoline but also for producing a clean burning fuel. Among this class of oxygenates, methyl-*tert*-butyl ether (MTBE) produced from isobutylene appears to be a leading contender (see ETHERS). Free-standing facilities at the gas well head to produce an isobutylene-rich B–B stream cannot be ruled out in the future.

There are two important sources for the commercial production of butylenes: catalytic or thermal cracking, and steam cracking. In these two processes, butylenes are always produced as by-products. A catalytic cracking process is

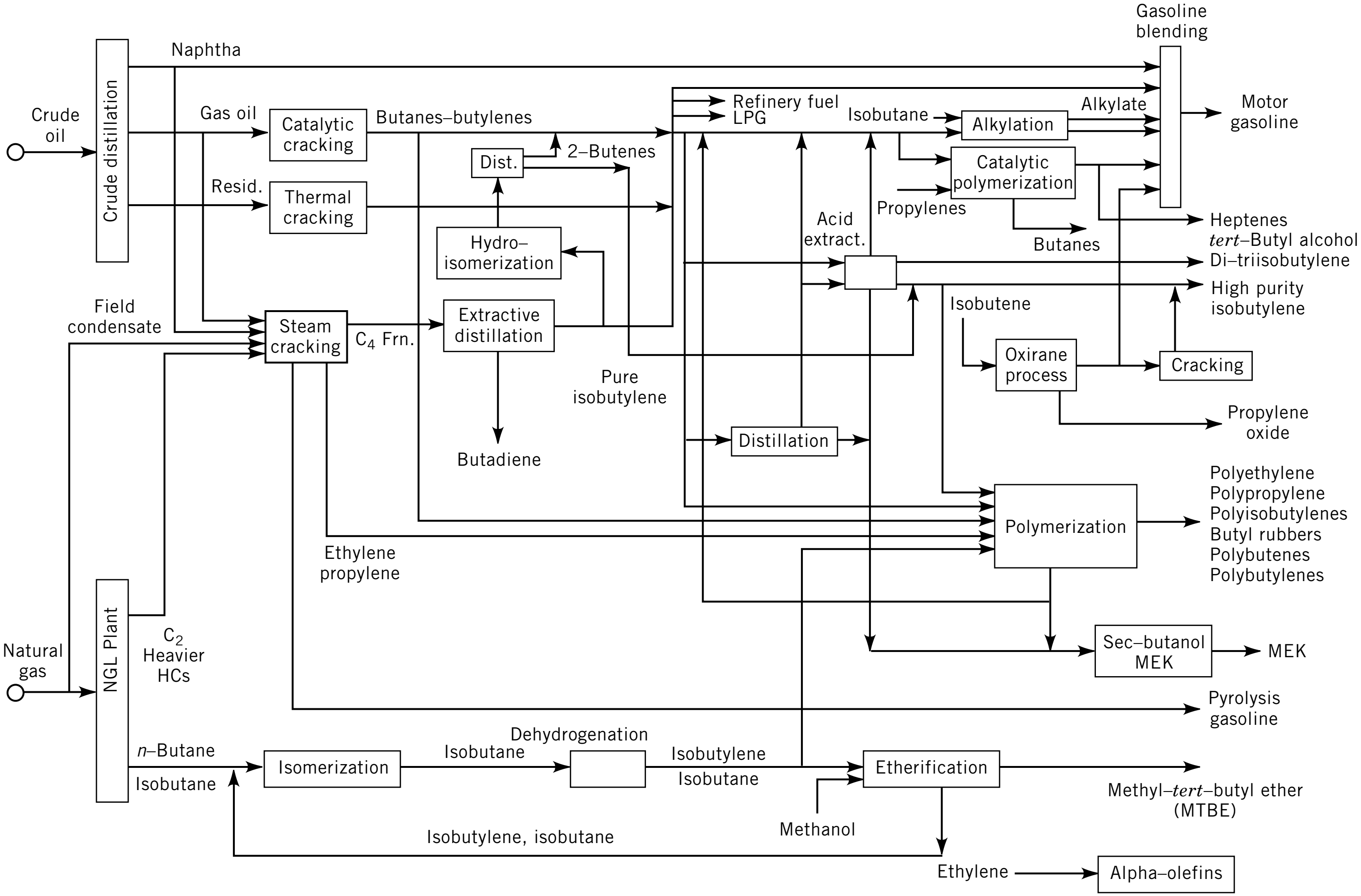


Fig. 2. General U.S. refinery-petrochemical system.

always associated with a petroleum refining complex that upgrades high boiling fractions of hydrocarbons to high octane gasoline. Steam cracking converts a variety of hydrocarbon feedstocks that range from natural gas liquids to heavy petroleum fractions to produce light olefins. As demand for butylenes picks up in the future, a third important source for the commercial production of these products is likely to be the dehydrogenation of butanes.

There are other commercial processes available for the production of butylenes. However, these are site or manufacturer specific, eg, the Oxirane process for the production of propylene oxide; the disproportionation of higher olefins; and the oligomerization of ethylene. Any of these processes can become an important source in the future. More recently, the Coastal Isobutane process began commercialization to produce isobutylene from butanes for meeting the expected demand for methyl-*tert*-butyl ether (40).

Table 6 shows the yield distribution of the C_4 isomers from different feedstocks with specific processing schemes. The largest yield of butylenes comes from the refineries processing middle distillates and from olefins plants cracking naphtha. The refinery product contains 35 to 65% butanes; olefins plants, 3 to 5%. Catalyst type and operating severity determine the selectivity of the C_4 isomer distribution (41) in the refinery process stream. Processes that parallel fluid catalytic cracking to produce butylenes and propylene from heavy crude oil fractions are under development (42).

4.1. Steam Cracking. Steam cracking is a nonselective process that produces many products from a variety of feedstocks by free-radical reactions. An excellent treatise on the fundamentals of manufacturing ethylene has been given (44). Feedstocks range from ethane on the light end to heavy vacuum gas oil on the heavy end. All produce the same product slate but in different amounts depending on the feedstock.

Significant products from a typical steam cracker are ethylene, propylene, butadiene, and pyrolysis gasoline. Typical wt % yields for butylenes from a steam cracker for different feedstocks are ethane, 0.3; propane, 1.2; 50% ethane/50% propane mixture, 0.8; butane, 2.8; full-range naphtha, 7.3; light gas oil, 4.3. A typical steam cracking plant cracks a mixture of feedstocks that results in butylenes yields of about 1% to 4%. These yields can be increased by almost 50% if cracking severity is lowered to maximize propylene production instead of ethylene.

Cracking conditions and feed slate are usually selected to maximize production of light olefins. Selectivity to light olefins depends on the temperature and pressure profiles in the pyrolysis reactor coil, and thus the residence time. These profiles are unique for a given reactor coil, so a great deal of attention goes into the selection of the reactor. Older plants that have a residence time of about 1 s have since been modernized to under 0.4 s by replacing the reactor coil. Newer plants have reactor coil designs that give residence times of 0.1–0.2 s.

Typically, cracking is done at a weight ratio of steam to hydrocarbon that ranges from 0.2 to 1. The high end of this ratio is used for heavy feeds such as vacuum gas oil. Desired cracking severity is achieved at 780–875°C at the reactor coil outlet and at slightly above 130 kPa (19 psi) pressure. Hot furnace effluent from the reactors is quenched rapidly to stop undesirable secondary

Table 6. **Typical Yields and % Compositions of C4 Fractions from Cracking Operations**[a]

	Catalytic cracking			Thermal cracking of residue					
Butylene yield	Gas oil	Residue		Delayed coking		Flexicoking		Steam cracking of naphtha and light gas oil	
wt % on crude	0.5–5	1.5–3	0.1–0.6	0.15–0.8					
wt % on feed	3–10	3–5	1–1.5	1.5–2				0.4–0.5	
C4 composition	Total	Olefin	Total	Total	Olefin	Total	Olefin	Total	Olefin
butane	7–13		7	47		14–23		2–5	
isobutane	28–52		18–14	12		5		1.5–0.6	
isobutylene	26–8	40–23	79	16	40	13	20–18	27.4–22.0	48
1-butene	8–7	12–20	79	13	31	17	26–24	16.0–14.0	30
cis-2-butene	31–20	48–57	75–79	5	12	35–42	54–58	5.5–4.8	10
trans-2-butene	31–20	48–57	70	7	17	35–42	54–58	6.5–5.8	12
1,3-butadiene	0.1–0.5			0.5		7–9		37.0–47.5	

[a] Ref. 43.

reactions. Effluent streams are cooled quickly in heat exchangers to slightly above their dew point, about 120–370°C depending on the feedstock.

Figure 3 shows a typical arrangement of a steam cracker in the United States. Furnace effluent from a steam cracker consists of three phases at ambient temperatures including aqueous liquid, hydrocarbon liquid, and hydrocarbon gas. Effluent from the heat exchangers are further cooled in oil and water wash towers. The oil wash essentially removes the heavy fuel oil fraction and also limits the end point of pyrolysis gasoline in the overhead of this tower. The water wash condenses the dilution steam and the pyrolysis gasoline. The overhead from the water wash tower contains mostly C_4 and lighter fractions. Several fractionation sequences to separate high purity products are available commercially. The choice of sequence depends on the feed slate and economics. Figure 3 shows a front-end demethanizer scheme, which is usually used in steam crackers producing significant amounts of butylenes. Whatever the fractionation scheme used, the C_4 fraction is removed as overhead from the debutanizer. References 45 and 46 give an overview of the ethylene manufacturing process.

The C_4 stream from steam crackers, unlike its counterpart from a refinery, contains about 45% butadiene by weight. Steam crackers that process significant amounts of liquid feedstocks have satellite facilities to recover butadiene from the C_4 stream. Conventional distillation techniques are not feasible because the relative volatility of the chemicals in this stream is very close. Butadiene and butylenes are separated by extractive distillation using polar solvents.

The selection of solvent is dictated by the process used. Strongly dipolar, aprotic solvents alone or mixed with a second solvent to improve separation selectivity are used. The second solvent is usually water, and good solubility in water is an advantage. Toxicity is also an important consideration. Reference 47 is valuable in the selection of solvents. Several extractive distillation technologies are available commercially. Three technologies are used widely including the Nippon-Zein process using dimethylformamide [68-12-2] (48,49), the Shell process using acetonitrile [75-05-8] (50), and the BASF process using *N*-methyl-pyrrolidinone [872-50-4] (51). All these processes produce polymer-grade 1,3-butadiene and a B–B stream. C_4 Acetylenes and 1,2-butadiene in the B–B product are hydrogenated to produce a clean B–B stream.

4.2. Catalytic Cracking. This is a refinery process that produces a mixture of butylenes and butanes with very small amounts of butadiene. The specific composition of the C_4 mixture depends on the catalyst and process conditions. Most catalytic cracking processes employ temperatures about 450–650°C at pressures of about 250–400 kPa (36–58 psi). The two types of catalysts, the amorphous silica–alumina (52) and the crystalline aluminosilicates called molecular sieves or zeolites (53), exhibit strong carbonium ion activity. Although there are natural zeolites, over 100 synthetic zeolites have been synthesized and characterized (54). Many of these synthetic zeolites have replaced alumina with other metal oxides to vary catalyst acidity to effect different type catalytic reactions, for example, isomerization. Zeolite catalysts strongly promote carbonium ion cracking along with isomerization, disproportionation, cyclization, and proton transfer reactions. Because butylene yields depend on the catalyst and process conditions, Table 6 shows only approximations.

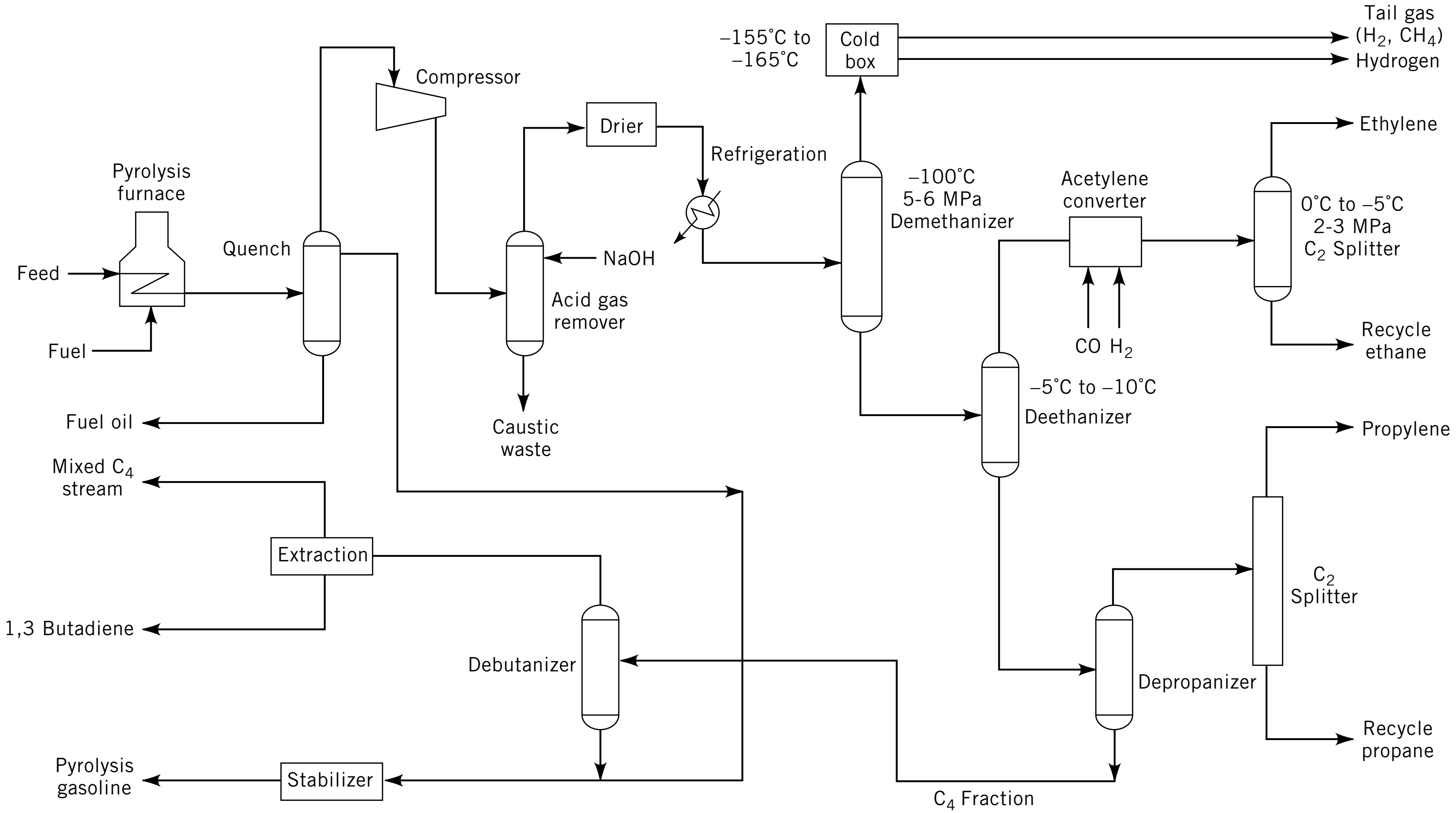


Fig. 3. Steam cracking front-end demethanizer scheme.

Zeolites have largely replaced the silica–alumina catalysts. In addition, the catalytic property is further improved by changing the silica and alumina ratio and by introducing cations such as hydrogen and sodium to impart specific catalytic properties. The most significant advance is in improved selectivity to gasoline range products and not in increased activity. Detailed information on the chemistry of catalytic cracking is available (55).

The most dominant catalytic process in the United States is the fluid catalytic cracking process. In this process, partially vaporized medium-cut petroleum fractions called gas oils are brought in contact with a hot, moving, freshly regenerated catalyst stream for a short period of time at process conditions noted above. Spent catalyst moves continuously into a regenerator where deposited coke on the catalyst is burnt off. The hot, freshly regenerated catalyst moves back to the reactor to contact the hot gas oil (see CATALYSTS, REGENERATION).

4.3. Thermal Cracking. Heavy petroleum fractions such as resid are thermally cracked in delayed cokers or flexicokers (44,56,57). The main products from the process are petroleum coke and off-gas which contain light olefins and butylenes. This stream also contains a considerable amount of butane. Process conditions for the flexicoker are more severe than for the delayed coker, about 550°C versus 450°C. Both are operated at low pressures, around 300–600 kPa (43–87 psi). Flexicokers produce much more linear butenes, particularly 2-butene, than delayed cokers and about half the amount of isobutylene (Table 6). This is attributed to high severity of operation for the flexicoker (43).

4.4. Oxirane Process. In Arco's Oxirane process, *tert*-butyl alcohol is a by-product in the production of propylene oxide from a propylene–isobutane mixture. Polymer-grade isobutylene can be obtained by dehydration of the alcohol. *tert*-Butyl alcohol [75-65-0] competes directly with methyl-*tert*-butyl ether as a gasoline additive, but its potential is limited by its partial miscibility with gasoline.

4.5. Disproportionation of Olefins. Disproportionation or the metathesis reaction offers an opportunity to convert surplus olefins to other desirable olefins. Phillips Petroleum and Institut Français du Petrôle have pioneered this technology for the dimerization of light olefins. The original metathesis reaction of Phillips Petroleum was intended to convert propylene to 2-butene and ethylene (58). The reverse reaction that converts 2-butene in the presence of excess ethylene to propylene has also been demonstrated (59). In this process, ethylene is first dimerized to 2-butene followed by metathesis to yield propylene. Since this is a two-stage process, 2-butene can be produced from the first stage, if needed. In the dimerization step, about 95% purity of 2-butene is achieved at 90% ethylene conversion.

In the Institut Français du Petrôle process (60), ethylene is dimerized into polymer-grade 1-butene (99.5% purity) suitable for the manufacture of linear low density polyethylene. It uses a homogeneous catalyst system that eliminates some of the drawbacks of heterogeneous catalysts. It also inhibits the isomerization of 1-butene to 2-butene, thus eliminating the need for superfractionation of the product (61,62). The process also uses low operating temperatures, 50–60°C, and pressures (63).

Many heterogeneous catalysts have been commercialized to dimerize ethylene to selectively yield 1-butene or 2-butene (64–68). Since ethylene is generally priced higher than butylenes, economics favor the production of butylenes from steam crackers, not from ethylene. An excellent review on metathesis is available (69).

4.6. Oligomerization of Ethylene. 1-Butene is a small by-product in the production of linear alpha-olefins by oligomerization of ethylene. Linear alpha-olefins have one double bond at the terminal position and comprise the homologous series of compounds with carbon atoms between 4 and 19. The primary use of alpha-olefins is in the detergent industry.

4.7. Other Technology. Several technologies are emerging for the production of isobutylene to meet the expected demand for isobutylene: (*1*) deep catalytic cracking; (*2*) superflex catalytic cracking; (*3*) dehydrogenation of butanes; and (*4*) the Coastal process of thermal dehydrogenation of butanes. Of these, both the dehydrogenation technology and the high pressure thermal pyrolysis technology (the Coastal process) have been around for a long time. These technologies were not economical since inexpensive sources of butylenes were available from petroleum refineries and steam crackers. During the 1960s isobutane was in plentiful supply, and the first commercial unit using the Coastal process was built in 1969 at Corpus Christi, Texas, with a capacity of about 150 million t/yr (40). The dehydrogenation technology was also in use where there was a surplus of inexpensive isobutane.A process for producing isobutylene and methanol by the decomposition of methyl-*tert*-butyl ether has been reported (70).

Deep Catalytic Cracking. This process is a variation of fluid catalytic cracking. It uses heavy petroleum fractions, such as heavy vacuum gas oil, to produce propylene- and butylene-rich gaseous products and an aromatic-rich liquid product. The liquid product contains predominantly benzene, toluene, and xylene (see BTX PROCESSING). This process was developed by SINOPEC in China (42,71).

Superflex Catalytic Cracking. A new process called Superflex is being commercialized to produce predominantly propylene and butylenes from low valued hydrocarbon streams from an olefins complex (72). In this process, raffinates (from the aromatics recovery unit and the B–B stream after the recovery of isobutylene) and pyrolysis gasoline (after the removal of the C_6–C_8 aromatics fraction) are catalytically cracked to produce propylene, isobutylene, and a crude C_6–C_8 aromatics fraction. All other by-products are recycled to extinction.

Dehydrogenation of Butanes. These processes are based on the propane dehydrogenation technology commercialized about 35 years ago. Thermodynamics dictate that the operation be carried out at high temperatures and low pressures to improve selectivity. In the dehydrogenation process, conversion of feedstock is equilibrium limited, and thus conversions are low relative to steam cracking. Work has been carried out by Air Products, UOP, Shell, Ashland, ICI, Monsanto, Phillips, and Petrotex. Among these, five distinct technologies are available for converting isobutane to isobutylene. These technologies include Oleflex from UOP (73), Catofin from CDTECH (74), fluidized-bed from Snamprogetti (75), STAR from Phillips Petroleum (76), and Coastal Thermal Cracking from Foster-Wheeler (40,77).

The UOP Oleflex process uses a proprietary platinum catalyst. Dehydrogenation of isobutane to isobutylene is endothermic, and optimum catalyst activity is maintained by supplying the heat of reaction through interheaters. The catalyst system employs UOP's Continuous Catalyst Regeneration (CCR) technology. The bed of catalyst slowly flows concurrently with the reactants and is removed from the last reactor and regenerated in a separate section. The reconditioned catalyst is then returned to the top of the first reactor. The CCR process is usually applied in the reforming of naphtha to aromatics. When supply is limited, n-butane can be isomerized to isobutane using UOP's Butamer process (78). The Butamer process is a fixed-bed, vapor-phase catalytic process that uses organic halides as promoters.

The Catofin process, which was formerly the property of Air Products (Houdry Division), uses a proprietary chromium catalyst in a fixed-bed reactor operating under vacuum. There are actually multiple reactors operating in cyclic fashion. In sequence, these reactors process feed for about nine minutes and are then regenerated for nine minutes. The chromium catalyst is reduced from Cr^{6+} to Cr^{3+} during the regeneration cycle.

The Snamprogetti fluidized-bed process uses a chromium catalyst in equipment that is similar to a refinery catalytic cracker (1960s cat cracker technology). The dehydrogenation reaction takes place in one vessel with active catalyst; deactivated catalyst flows to a second vessel, which is used for regeneration. This process has been commercialized in Russia for over 25 years in the production of butenes, isobutylene, and isopentenes.

The Phillips Steam Active Reforming (STAR) process catalytically converts isobutane to isobutylene. The reaction is carried out with steam in tubes that are packed with catalyst and located in a furnace. The catalyst is a solid, particulate noble metal. The presence of steam diluent reduces the partial pressure of the hydrocarbons and hydrogen present, thus shifting the equilibrium conditions for this system toward greater conversions.

The Coastal process uses steam pyrolysis of isobutane to produce propylene and isobutylene (as well as other cracked products). It has been suggested that the reaction be carried out at high pressure, >1480 kPa (~ 15 atm), to facilitate product separation. This process was commercialized in the late 1960s at Coastal's Corpus Christi refinery.

These processes are all characterized by low isobutane conversion to achieve high isobutylene selectivity. The catalytic processes operate at conversions of 45–55% for isobutane. The Coastal process also operates at 45–55% isobutane conversion to minimize the production of light ends. This results in significant raw material recycle rates and imposing product separation sections.

Dehydrogenation of isobutane to isobutylene is highly endothermic and the reactions are conducted at high temperatures (535–650°C) so the fuel consumption is sizeable. For the catalytic processes, the product separation section requires a compressor to facilitate the separation of hydrogen, methane, and other light hydrocarbons from-the paraffinic raw material and the olefinic product. An excellent overview of butylenes is available (79).

4.8. Separation and Purification of C_4 Isomers. 1-Butene and isobutylene cannot be economically separated into pure components by conventional distillation because they are close boiling isomers (see Table 1 and Fig. 1). 2-Butene can be separated from the other two isomers by simple distillation. There are four types of separation methods available: (*1*) selective removal of isobutylene by polymerization and separation of 1-butene; (*2*) use of addition reactions with alcohol, acids, or water to selectively produce pure isobutylene and 1-butene; (*3*) selective extraction of isobutylene with a liquid solvent, usually an acid; and (*4*) physical separation of isobutylene from 1-butene by absorbents. The first two methods take advantage of the reactivity of isobutylene. For example, isobutylene reacts about 1000 times faster than 1-butene. Some 1-butene also reacts and gets separated with isobutylene, but recovery of high purity is possible. The choice of a particular method depends on the product slate requirements of the manufacturer. In any case, 2-butene is first separated from the other two isomers by simple distillation.

There are currently three important processes for the production of isobutylene: (*1*) the extraction process using an acid to separate isobutylene; (*2*) the dehydration of *tert*-butyl alcohol, formed in the Arco's Oxirane process; and (*3*) the cracking of MTBE. The expected demand for MTBE will preclude the third route for isobutylene production. Since MTBE is likely to replace *tert*-butyl alcohol as a gasoline additive, the second route could become an important source for isobutylene. Nevertheless, its availability will be limited by the demand for propylene oxide, since it is only a coproduct. An alternative process has emerged that consists of catalytically hydroisomerizing 1-butene to 2-butenes (80). In this process, trace quantities of butadienes are also hydrogenated to yield feedstocks rich in isobutylene which can then be easily separated from 2-butenes by simple distillation.

The acid extraction process uses strong mineral acids, such as sulfuric, hydrochloric, and phosphoric. These acids selectively remove isobutylene from mixed butylenes. The Exxon, BASF, and the Compagnie Française de Raffinage (CFR) processes have been commercialized. The Nippon Petrochemical extraction process uses hydrochloric acid along with a heavy-metal catalyst. Reportedly, the selectivity to isobutylene hydration is significantly higher than in the sulfuric acid process. However, because of corrosion problems of stainless steel, this process requires titanium and palladium alloys.

The CRF, Exxon, and BASF processes use sulfuric acid as the extraction medium. The BASF process is the dominant process in Europe. It uses the dilutest acid of any commercial process. This permits selective reaction even in the presence of butadiene. The BASF process uses vapor–liquid extraction unlike the Exxon and CRF processes which are of the liquid–liquid type.

The desired extraction process is the exothermic proton-catalyzed hydrolysis of isobutylene to *tert*-butyl alcohol. This alcohol is further dehydrated to yield pure isobutylene. At low concentrations the hydrolysis reaction is favored:

$$(CH_3)_2C{=}CH_2 + H_2O \xrightarrow{H^+} (CH_3)_3COH$$

At high concentrations, there is a tendency to form an organic hydrosulfate:

$$(CH_3)_2C{=}CH_2 + H_2SO_4 \longrightarrow (CH_3)_3CHSO_4$$

The main differences between these processes are the acid concentration and the extraction temperature to effect selective removal of isobutylene. The acid concentration range is 45–65%. Figure 4 shows a simplified flow diagram of the CFR process.

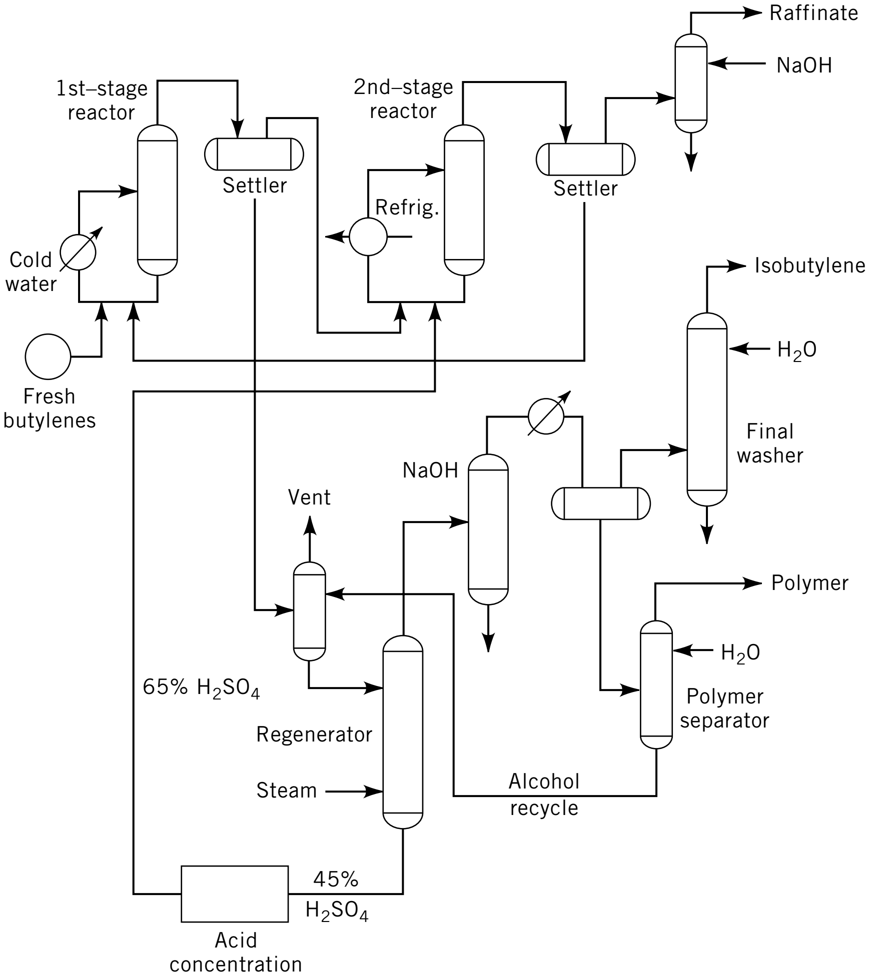


Fig. 4. Isobutylene extraction process.

In the physical separation process, a molecular sieve adsorbent is used as in the Union Carbide Olefins Siv process (81–83). Linear butenes are selectively adsorbed, and the isobutylene effluent is distilled to obtain a polymer-grade product. The adsorbent is a synthetic zeolite, Type 5A in the calcium cation exchanged form (84). UOP also offers an adsorption process, the Sorbutene process (85). The UOP process utilizes a liquid B–B stream, and uses a proprietary rotary valve containing multiple ports, which direct the flow of liquid to various sections of the adsorber (86,87). The cis- and trans-isomers are alkylated and used in the gasoline blending pool.

1-Butene can be separated from 2-butenes by simple distillation. If the B–B streams contain dienes, these must be hydrogenated prior to the separation of the linear butenes. If not hydrogenated, these contaminants tend to divide themselves between the purified isomers. Trace quantities of acetylinic compounds and butadiene are hydrogenated selectively using a noble metal catalyst.

Hydrogenation after separation is not desirable as the catalyst used for hydrogenation isomerizes butenes, which affects product purity. If butanes are also present, as they are in the refinery streams, they also distribute themselves in the purified products. If pure isomers are required, butanes can be separated by extractive distillation, and the residual C_4 isomers can be isomerized. These all increase the cost of the separation process. There is a balance between the purity sought and the cost associated in achieving it.

5. Shipment and Handling

5.1. Storage and Transportation. Handling requirements are similar to liquefied petroleum gas (LPG). Storage conditions are much milder. Butylenes are stored as liquids at temperatures ranging from 0 to 40°C and at pressures from 100 to 400 kPa (1–4 atm). These conditions are much lower than those required for LPG. Their transportation is also similar to LPG; they are shipped in tank cars, transported in pipelines, or barged.

6. Economic Aspects

The United States, Western Europe, and Japan account for 90% of the butylenes market. In 2001, 32×10^6 t of butylenes were consumed in these three regions (88).

Fuel markets comprise 90% of the total use of butylenes. The fuel market includes the manufacture of gasoline, blending of components, gasoline alkylates, polymer gasoline, and dimersol. Isobutylene is a raw material for oxygenate, methyl-*tert*-butyl ether, and ethyl-*tert*-butyl ether. Butylenes are directly blended into gasoline for volatility control. Another market is with propane and butane as liquefied petroleum gas.

The other 10% of the market consists of *n*-butenes as precursors for *sec*-butyl alcohols, butadiene, and 1-butene. Chemical markets worldwide are growing slowly. Isobutylene has grown slowly in the U.S., Western Europe, and Japan, especially in the U.S. Other isobutylene derivatives, such as butyl rubber and polybutylenes are mature markets.

7. Analytical Methods

Butenes are best characterized by their property of decolorizing both a solution of bromine in carbon tetrachloride and a cold, dilute, neutral permanganate solution (the Baeyer test). A solution of bromine in carbon tetrachloride is red; the dihalide, like the butenes, are colorless. Decoloration of the bromine solution is rapid. In the Baeyer test, a purple color is replaced by brown manganese oxide (a precipitate) and a colorless diol. These tests apply to all alkenes.

Identification of C_4 isomers is now routinely performed by gas chromatography. Advances in column technology permit rapid analysis with good accuracy in capillary columns (89). Pure isomers require quantification of contaminants, usually in parts per million. Gas–liquid chromatography and mass spectroscopy are the most commonly used analytical tools. ASTM standards are excellent sources of analytical procedures for hydrocarbon mixtures. Al_2O_3–KCl PLOT capillary gas chromatographic columns provide very good and fast separation in the following elution order: *trans*-2-butene, 1-butene, isobutylene, and *cis*-2-butene.

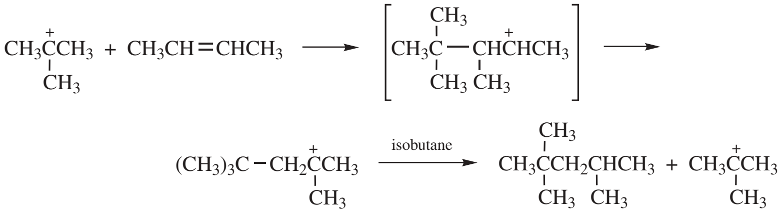
8. Health and Safety Factors

The effect of long-term exposure is not known, hence, they should be handled with care. Reference 90 lists air and water pollution factors and biological effects. They are volatile and asphyxiants. 1-Butene, *cis* 2-butene, and *trans* 2-butene are very dangerous fire hazards when exposed to heat or flame. *cis* 2-Butene and *trans*-2-butene are very likely to explode. 1-Butene is moderately explosive. 2-Butene emits acrid smoke and irritating vapors when heated to decomposition (91). Care should be taken to avoid spills because they are extremely flammable. Physical handling requires adequate ventilation to prevent high concentrations of butylenes in the air. Explosive limits in air are 1.6 to 9.7% of butylenes. Their flash points range from −80 to −73°C. Their autoignition is around 324 to 465°C (Table 2). Water and carbon dioxide extinguishers can be used in case of fire.

9. Uses

Among the butylenes, isobutylene has become one of the important starting materials for the manufacture of polymers and chemicals. There are many patents that describe the use of isobutylene or its derivatives to produce insecticides, antioxidants, elastomers, additives for lubricating oils, adhesives, sealants, and caulking compounds.

9.1. Fuels. *Alkylate.* Alkylation means the chemical combination of isobutane with any one or a combination of propylene, butylenes, and amylenes to produce a mixture of highly branched paraffins that have high antiknock properties with good stability. These reactions are catalyzed by strong acids such as sulfuric or hydrofluoric acid and have been studied extensively (45,92–96). In the United States mostly butylenes and propylene are used as the olefins. The alkylate contains a mixture of isoparaffins, ranging from pentanes to decanes and higher, regardless of the olefins used. The dominant paraffin in the product is 2,2,4-trimethylpentane, also called isooctane. The reaction involves methide-ion transfer and carbenium-ion chain reaction, which is catalyzed by strong acid.



$$\mathrm{CH_3}\underset{\mathrm{CH_3}}{\overset{+}{\mathrm{C}}}\mathrm{CH_3} + \mathrm{CH_3CH{=}CHCH_3} \longrightarrow \left[\mathrm{CH_3}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\underset{\mathrm{CH_3}}{\mathrm{CH}}\overset{+}{\mathrm{C}}\mathrm{HCH_3}\right] \longrightarrow$$

$$\mathrm{(CH_3)_3C-CH_2}\underset{\mathrm{CH_3}}{\overset{+}{\mathrm{C}}}\mathrm{CH_3} \xrightarrow{\text{isobutane}} \mathrm{CH_3}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{CH_2}\underset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{HCH_3} + \mathrm{CH_3}\underset{\mathrm{CH_3}}{\overset{+}{\mathrm{C}}}\mathrm{CH_3}$$

The C_7 and C_8 paraffins comprise about 90% of the alkylate; C_8 accounts for over 60%. Over 70% of the commercial alkylation processes employ sulfuric acid as the catalyst. Among the butylenes, 2-butene is superior to 1-butene. The C_3–C_4 fraction from the catalytic crackers is considered to be a superior feedstock to the alkylation unit.

Polymer Gasoline. Refinery trends tend to favor alkylation over polymerization. Unlike the alkylation process, polymerization does not require isobutane. The catalyst is usually phosphoric acid impregnated on kieselghur pellets. Polymerization of butylenes is not an attractive alternative to alkylation unless isobutane is unavailable. The motor octane number of polymer gasoline is also low, and there is considerable shrinkage in product volume. The only commercial unit to be built in recent years is at Sasol in South Africa. The commercial process was developed by UOP in the 1940s (97).

Gasoline Blending and LPG. Direct blending of butylenes into gasoline has the highest value since there is no shrinkage in product volume or conversion cost. The amount of butylenes that can be blended is limited by vapor-pressure specifications, amounting to only 8 to 10% of the gasoline pool. More butylenes could be used in winter to increase volatility for easy starting. In warm seasons, the butylenes have to be reduced to prevent vapor lock in the motor carburetor. Environmental concern in recent years has reduced the amount of butylenes, which could be blended into gasoline.

Since the heating values are similar to LPG, butylenes may be blended with LPG for bottle gas (98,99). In Europe, because LPG is unavailable, it is common to use butylenes as fuel. In the United States, butylenes have a higher value as an alkylate feed. LPG, which is readily available, is used as fuel instead.

9.2. Chemicals. Although the amount of butylenes produced in the United States is roughly equal to the amounts of ethylene and propylene produced, the amount consumed for chemical use is considerably less. The utilization of either ethylene or propylene for each of at least five principal chemical derivatives is about the same or greater than the utilization of butenes for butadiene, their main use. This production is only about one-third of the total; the two-thirds is derived directly from butane. The underlying reasons are poorer price–performance compared to derivatives of ethylene and propylene and the lack of applications of butylene derivatives. Some of the C_4 products are more easily derived from 1-, 2-, and 3-carbon atom species, eg, butanol, 1,4-butanediol, and isobutyl alcohol (see ACETYLENE-DERIVED CHEMICALS; BUTYL ALCOHOLS).

$$2\ CH_2{=}CH_2 \xrightarrow{[O]} CH_3CHO \longrightarrow CH_3CH{=}CHCHO \xrightarrow{H_2} CH_3CH_2CH_2CH_2OH$$

$$HC{\equiv}CH + 2\ CH_2O \xrightarrow{H_2} HOCH_2CH_2CH_2CH_2OH$$

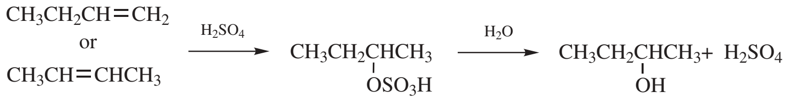
$$CH_3CH{=}CH_2 \xrightarrow[H_2]{CO} CH_3CH_2CH_2CH_2OH + (CH_3)_2CHCH_2OH$$

The price of butanes and butylenes fluctuates seasonally depending on the demand for gasoline in the United States. Since much chemical-product usage is determined by price–performance basis, a shift to development of butylene-based technology may occur. Among the butylenes, demand for isobutylene is likely to increase (and so its price) as more derivatives such as methyl methacrylate and methacrylic acid are produced from isobutylene instead of the conventional acetone cyanohydrin process.

Butadiene. Most butadiene [106-99-0] is produced by extraction of C_4 streams from olefins units. Only about 10% of butadiene was produced from butenes in the United States (100). In Western Europe and Japan hardly any butenes are used to produce butadiene. Butadiene requirements in these countries are entirely met by the extraction units, since they crack only naphthas and heavier hydrocarbon feedstocks. The recent trend in the United States is to rely on the extraction units for its requirements (see Butadiene).

sec-Butyl Alcohol. *sec*-Butyl alcohol [78-92-2] is produced entirely from butenes using indirect hydration with sulfuric acid. Nearly all of the *sec*-butyl alcohol is converted to methyl ethyl ketone (MEK) [78-93-3] by catalytic dehydrogenation. MEK is an outstanding solvent for a wide variety of coating resins. *sec*-Butyl alcohol growth rate is closely tied in with the demand for MEK.

A typical feed to a commercial process is a refinery stream or a steam cracker B–B stream (a stream from which butadiene has been removed by extraction and isobutylene by chemical reaction). The B–B stream is a mixture of 1-butene, 2-butene, butane, and isobutane. This feed is extracted with 75–85% sulfuric acid at 35–50°C to yield butyl hydrogen sulfate. This ester is diluted with water and stripped with steam to yield the alcohol. Both 1-butene and 2-butene give *sec*-butyl alcohol. The sulfuric acid is generally concentrated and recycled (101) (see Butyl alcohols).



$$\begin{array}{c} CH_3CH_2CH{=}CH_2 \\ \text{or} \\ CH_3CH{=}CHCH_3 \end{array} \xrightarrow{H_2SO_4} CH_3CH_2\underset{\underset{\displaystyle OSO_3H}{|}}{C}HCH_3 \xrightarrow{H_2O} CH_3CH_2\underset{\underset{\displaystyle OH}{|}}{C}HCH_3 + H_2SO_4$$

Di- and Triisobutylenes. Diisobutylene [18923-87-0] and triisobutylenes are prepared by heating the sulfuric acid extract of isobutylene from a separation process to about 90°C. A 90% yield containing 80% dimers and 20% trimers results. Use centers on the dimer, C_8H_{16}, a mixture of 2,4,4-trimethylpentene-1 and -2. Most of the dimer-trimer mixture is added to the gasoline pool as an octane improver. The balance is used for alkylation of phenols to yield octylphenol, which in turn is ethoxylated or condensed with formaldehyde. The water-soluble ethoxylated phenols are used as surface-active agents in textiles, paints, caulks, and sealants (see Alkylphenols).

$$C_8H_{16} + C_6H_5OH \longrightarrow (C_8H_{17})C_6H_4OH \xrightarrow{n-C_2H_4O}$$

$$(C_8H_{17})\text{—}C_6H_4\text{—}(OCH_2CH_2)_nOH$$

The octylphenol condensate is used as an additive to lubricating oils and surface-active agents. Other uses of dimer are amination to octylamine and octyldiphenylamine, used in rubber processing; hydroformylation to nonyl alcohol for phthalate production; and carboxylation via Koch synthesis to yield acids in formulating paint driers (see Drying).

Butylated Phenols and Cresols. Butylated phenols and cresols, used primarily as oxidation inhibitors and chain terminators, are manufactured by direct alkylation of the phenol using a wide variety of conditions and acid catalysts, including sulfuric acid, *p*-toluenesulfonic acid, and sulfonic acid ion-exchange resins (102,103). By use of a small amount of catalyst and short residence times, the first-formed, ortho-alkylated products can be made to predominate. For the preparation of the 2,6-substituted products, aluminum phenoxides generated *in situ* from the phenol being alkylated are used as catalyst. Reaction conditions are controlled to minimize formation of the thermodynamically favored 4-substituted products (see ALKYLPHENOLS). The most commonly used is *p*-*tert*-butylphenol [98-54-4] for manufacture of phenolic resins. The *tert*-butyl group leaves only two rather than three active sites for condensation with formaldehyde and thus modifies the characteristics of the resin.

2,6-Di-*tert*-butyl-4-methylphenol [25377-21-3] (di-*tert*-butyl-*p*-cresol) or butylated hydroxytoluene (BHT)) is most commonly used as an antioxidant in plastics and rubber. Use in food is decreasing because of legislation and it is being replaced by butylated hydroxy anisole (BHA) (see ANTIOXIDANTS; FOOD ADDITIVES).

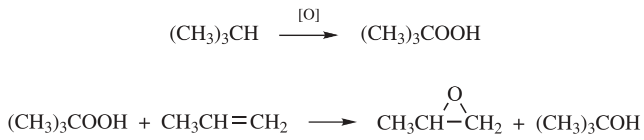
Heptenes. Heptenes, C_7H_{14}, are used for the preparation of isooctyl alcohol [26952-21-6] by hydroformylation (see OXO PROCESS). The heptenes are prepared by very carefully controlled fractionation of polymer gasoline. Specifications generally call for >99.9% C_7 content (including some paraffin that is also formed) to simplify processing.

tert-Butylamine. *tert*-Butylamine [75-64-9] is used as an intermediate in the manufacture of lubricating oil additives and miscellaneous chemicals. It is manufactured using the Ritter reaction. Isobutylene first reacts with sulfuric acid and then HCN to yield *tert*-butylamine.

$$(CH_3)_2C{=}CH_2 \xrightarrow{H_2SO_4} (CH_3)_3COSO_3H \xrightarrow{HCN} (CH_3)_3CN{=}CHOSO_3H \xrightarrow{H_2O}$$

$$(CH_3)_3CNHCHO \xrightarrow{OH^-} (CH_3)_3CNH_2$$

tert-Butyl Alcohol. *tert*-Butyl alcohol [75-65-0] is an intermediate in the separation of isobutylene from a mixed butane–butylene stream. It is manufactured by the hydrolysis of the acid extract in the isobutylene separation process. A small amount is used as a solvent. It is also a significant coproduct in Arco's (now BP) Oxirane process (104) which produces propylene oxide [75-56-9]. *tert*-Butyl alcohol is derived from isobutane, which is the oxygen carrier for the process:



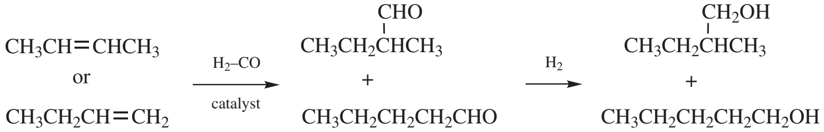
$$(CH_3)_3CH \xrightarrow{[O]} (CH_3)_3COOH$$

$$(CH_3)_3COOH + CH_3CH{=}CH_2 \longrightarrow CH_3\overset{O}{CH{-}CH_2} + (CH_3)_3COH$$

It competes directly with MTBE as an octane enhancer in the gasoline pool. Since MTBE is more desirable than *tert*-butyl alcohol because of its total miscibility with gasoline, *tert*-butyl alcohol will be an important source of isobutylene used in the manufacture of MTBE. High purity isobutylene, C_4H_8, can be obtained by dehydration of *tert*-butyl alcohol, $C_4H_{10}O$.

tert-Butyl Mercaptan. *tert*-Butyl mercaptan [75-66-1] is used primarily as an odorant at <30 ppm for natural gas so that leaks can be easily detected. It is manufactured by the reaction of isobutylene and hydrogen sulfide in the presence of acid catalysts (105).

Primary Amyl Alcohols. Primary amyl alcohols (qv) are manufactured by hydroformylation of mixed butenes, followed by dehydrogenation (106). Both 1-butene and 2-butene yield the same product though in slightly different ratios depending on the catalyst and conditions. Some catalyst and conditions produce the alcohols in a single step. By modifying the catalyst, typically a cobalt carbonyl, with phosphorus derivatives, such as tri(*n*-butyl)phosphine, the linear alcohol can be the principal product from 1-butene.



$$\begin{array}{c} CH_3CH{=}CHCH_3 \\ \text{or} \\ CH_3CH_2CH{=}CH_2 \end{array} \xrightarrow[\text{catalyst}]{H_2\text{–}CO} \begin{array}{c} CH_3CH_2\overset{\overset{CHO}{|}}{C}HCH_3 \\ + \\ CH_3CH_2CH_2CH_2CHO \end{array} \xrightarrow{H_2} \begin{array}{c} CH_3CH_2\overset{\overset{CH_2OH}{|}}{C}HCH_3 \\ + \\ CH_3CH_2CH_2CH_2CH_2OH \end{array}$$

The main use of the amyl alcohols is as esters such as acetates for solvents.

Di- and Triisobutylaluminums. Triisobutylaluminum [100-99-2] is prepared by reaction of isobutylene with aluminum at 80°C and 20.3 MPa (200 atm) of hydrogen (107). It is used as a catalyst for ethylene oligomerization to prepare even numbered, linear 1-olefins. Use of stochiometric quantities of triisobutylaluminum followed by oxidation of the resulting mixture of long-chain aluminum alkyls yields even numbered, terminal primary alcohols in the plasticizer and detergent range (108). Oxychem uses this process in the United States to manufacture plasticizer (C_6–C_{10}) and detergent (C_{16}–C_{22}) range alcohols (see ALCOHOLS, HIGHER ALIPHATIC).

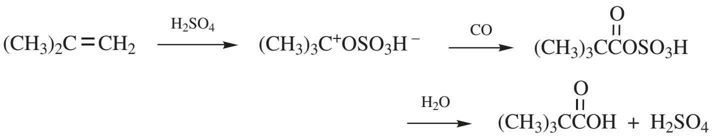
Triisobutylaluminum is converted to diisobutylaluminum chloride [1779-25-5] and diisobutylaluminum hydroxide [1191-15-7], which are used as cocatalysts for Ziegler polymerization systems. Corresponding ethyl compounds are prepared via the reaction of triisobutylaluminum with ethylene.

Butylene Oxide. Butylene oxides are prepared on a small scale by Dow by chlorohydrin technology. There appears to be no technical reason why they could not be prepared by the propylene oxide Oxirane process (see CHLOROHYDRINS).

A significant use of butylene oxide [26249-20-7] is as an acid scavenger for chlorine-containing materials such as trichloroethylene. Inclusion of about 0.25–0.5% of butylene oxide, based on the solvent weight, during preparation of vinyl chloride and copolymer resin solutions minimizes container corrosion which may be detrimental to resin color and properties.

p-tert-Butyltoluene. *p*-*tert*-Butyltoluene [98-51-1], prepared by acid catalyzed alkylation of toluene with isobutylene under mild conditions (109,110), is an intermediate in the production of *p*-*tert*-butylbenzoic acid [98-73-7]. This acid is used as a chain-length control agent in the preparation of unsaturated polyester resins. Solubility characteristics offer some advantage over benzoic acid.

Neopentanoic (Pivalic) Acid. Neopentanoic acid [75-98-9] is prepared using the Koch technology in which isobutylene reacts with carbon monoxide in the presence of strong acids such as H_2SO_4, HF, and $BF_3{\cdot}H_2O$ (111–114). General reaction conditions are 2–10 MPa (about 20–100 atm) of CO and 40–150°C.

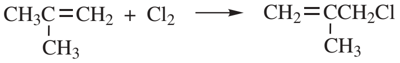


$$(CH_3)_2C{=}CH_2 \xrightarrow{H_2SO_4} (CH_3)_3C^+OSO_3H^- \xrightarrow{CO} (CH_3)_3C\overset{O}{\overset{\|}{C}}OSO_3H$$

$$\xrightarrow{H_2O} (CH_3)_3C\overset{O}{\overset{\|}{C}}OH + H_2SO_4$$

The acids are converted to peroxy esters for use as polymerization initiators. The metal salts are used as driers in paint formulations (see Carboxylic acids, trialkylacetic acids).

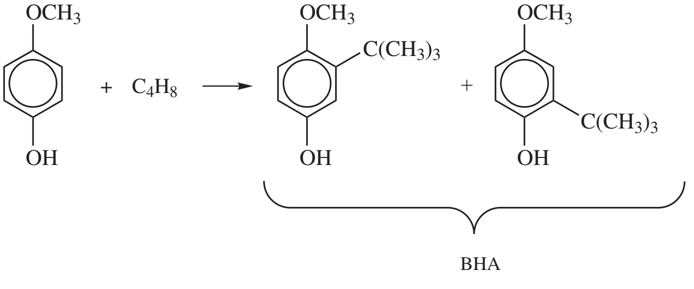
Methylallyl Chloride. Methallyl chloride [563-47-3] is the principal product when isobutylene and chlorine react over a wide range of temperatures (115). Very little addition takes place.



$$CH_3\underset{CH_3}{\underset{|}{C}}{=}CH_2 + Cl_2 \longrightarrow CH_2{=}\underset{CH_3}{\underset{|}{C}}CH_2Cl$$

This allylic chloride is a chemical intermediate for various specialty products, but it has no single significant commercial use (see Chlorocarbons and chlorohydrocarbons, allyl chloride).

Butylated Hydroxy Anisole (BHA). This material is an oxidation inhibitor and has been accepted for use in foods where the use of butylated hydroxytoluene (BHT) is restricted (see Food additives). It is manufactured by the alkylation of 4-hydroxyanisole [150-76-5] with isobutylene that yields a mixture of 2- and 3-*tert*-butyl isomers as products (116).



Methyl Methacrylate and Methacrylic Acid. The traditional production of methyl methacrylate [80-62-6] and methacrylic acid [79-41-4] involves the reaction of acetone with HCN and subsequent conversion to methyl ester and byproduct ammonium bisulfate.

The handling of toxic materials and disposal of ammonium bisulfate have led to the development of alternative methods to produce this acid and the methyl ester. There are two technologies for production from isobutylene now available: ammoxidation to methyl methacrylate (the Sohio process), which is then solvolyzed, similar to acetone cyanohydrin, to methyl methacrylate; and direct oxidation of isobutylene in two stages via methacrolein [78-85-3] to methacrylic acid, which is then esterified (117). Since direct oxidation avoids the need for HCN and NH_3, and thus toxic wastes, all new plants have elected to use this technology.

Methyl tert-Butyl Ether (MTBE). Methyl *tert*-butyl ether [1634-04-4] is made by the etherification of isobutylane with methanol, and there are six commercially proven technologies available. These technologies have been developed by Arco, IFP, CDTECH, Phillips, Snamprogetti, and Hüls (licensed jointly with UOP). The catalyst in all cases is an acidic ion-exchange resin. The United States has been showing considerable interest in this product. Western Europe has been manufacturing it since 1973 (ANIC in Italy and Hüls in Germany). Production of MTBE in the U.S. was reported recently at 2 59,190 barrels/day (118).

The etherification reaction is equilibrium limited, requiring an excess of methanol to drive the reaction. Conversion is favored by low temperature whereas the reaction kinetics are favored by high temperature. A compromise on temperature must be made in order to obtain an economic design. The etherification reaction is exothermic, and these technologies differ primarily in the type of reactor employed and the method for removing heat of reaction. In these processes, the reaction is carried out in two reactors connected in series to facilitate heat removal and also for economic reactor design. Typically, isobutylene conversion is about 95%, with most of the conversion taking place in the first reactor. Units can also be designed to obtain greater than 99% conversion.

The first reactor in series in the Arco, IFP, and Phillips processes is adiabatic (vessel filled with catalyst). The exothermic heat of reaction is removed in a pump-around loop where a portion of the reactor contents are taken from the reactor, pumped through an external exchanger, cooled, and returned to the reactor.

The Snamprogetti process utilizes a tubular isothermal reactor (tubes filled with catalyst) for the first reactor with cooling water on the shell side to control temperature. The Hüls process uses either an adiabatic or isothermal reactor for the first reactor.

In the CDTECH process (formerly CR&L technology), the first reactor is adiabatic. The heat of reaction is removed partly by vaporization of the reaction mix. The operating temperature is controlled by adjusting the operating pressure.

The reactor combinations for the two reactors in series consist of two fixed-beds for the Arco process; an expanded bed followed by a catalytic distillation reactor for IFP; a fixed-bed followed by a catalytic distillation reactor for CDTECH; and two fixed-beds for Phillips. The Hüls process uses an adiabatic reactor for the second reactor.

The various sources of isobutylene are C_4 streams from fluid catalytic crackers, olefin steam crackers, isobutane dehydrogenation units, and isobutylene produced by Arco as a coproduct with propylene oxide. Isobutylene concentrations (weight basis) are 12 to 15% from fluid catalytic crackers, 45% from olefin steam crackers, 45 to 55% from isobutane dehydrogenation, and high purity isobutylene coproduced with propylene oxide. The etherification unit should be designed for the specific C_4 feedstock that will be processed.

Polymers. Polymers account for about 3–4% of the total butylene consumption and about 30% of nonfuels use. Homopolymerization of butylene isomers is relatively unimportant commercially. Only stereoregular poly (1-butene) [9003-29-6] and a small volume of polyisobutylene [25038-49-7] are produced in this manner. High molecular weight polyisobutylenes have found limited use because they cannot be vulcanized. To overcome this deficiency a butyl rubber copolymer of isobutylene with isoprene has been developed. Low molecular weight viscous liquid polymers of isobutylene are not manufactured because of the high price of purified isobutylene. Copolymerization from relatively inexpensive refinery butane–butylene fractions containing all the butylene isomers yields a range of viscous polymers that satisfy most commercial needs (see OLEFIN POLYMERS; ELASTOMERS, SYNTHETIC-BUTYL RUBBER).

BIBLIOGRAPHY

"Butylenes" in *ECT* 2nd ed., Vol. 3, pp. 830–865, by C. E. Morrell, Esso Research and Engineering Company; in *ECT* 3rd ed., Vol. 4, pp. 346–375, by M. C. Hoff, UK Im, W. F. Hauschildt, and I. Puskas, Amoco Chemicals Company; in *ECT* 4th ed., Vol. 4, pp. 701–735, by N. Calamur, M. E. Carrera, and R. A. Wilsak, Amoco Chemical Company; "Butylenes" in *ECT* (online), posting date: December 4, 2000, by Narasimhan Calamur, Martin E. Carrera, and Richard A. Wilsak, Amoco Chemical Company.

CITED PUBLICATIONS

1. R. A. Wilsak and G. Thodos, *Ind. Eng. Chem. Fundam.* **23**, 75 (1984).
2. *DIPPR, Project 801, Data Compilation* (July 1990) and earlier references cited therein; R. D. Goodwin, *NBSIR 79-1621*, Thermophysical Properties Division, National Engineering Laboratory, National Bureau of Standards, Boulder, Colo. 1979; G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.* **57**, 876 (1935); *ibid.* **58**, 146 (1936); P. B. Ayscough, K. J. Ivin, and J. H. O'Donnell, *Trans. Faraday Soc.* **61**, 1601 (1965); J. B. Garner, *Petrol. Refiner* **24** (2), 99 (1945); J. G. Aston and G. J. Szasz, *J. Am. Chem. Soc.* **69**, 3108 (1947); D. G. Laird and C. S. Howat, *Fluid Phase Equilibria* **60**, 173 (1990).
3. B. D. Smith and R. Srivastava, *Thermodynamic Data for Pure Compounds*, Part A, Elsevier Science Publishers, Amsterdam, The Netherlands, 1986; *DIPPR, Project 801, Data Compilation* (July 1990); R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill Book Co., New York, 1987; *Beilstein Online*, Beilstein Institute for Organic Chemistry, Springer-Verlag, Heidelberg, F. R. Germany, 1990.
4. *American Petroleum Institute Research Project 44*, Thermodynamics Research Center, Texas Engineering Experiment Station, Texas A & M University, College Station, Tex., 1976; *Technical Data Book—Petroleum Refining*, Refining Department, 4th ed., American Petroleum Institute, 1983; *Physical Property Data for the Design Engineer*, C. F. Beaton and G. F. Hewitt, eds., Hemisphere Publishing Corp., New York, 1989; E. W. Flick, ed., *Industrial Solvents Handbook*, 3rd ed., Noyes Data Corp., Park Ridge, N.J., 1985.
5. R. T. Morrison and R. N. Boyd, *Organic Chemistry*, 4th ed., Allyn and Bacon, Boston, Mass., 1983; D. E. Dorman, M. Jantelot, and J. D. Roberts, *J. Org. Chem.* **36**, 2157 1971; I. Hirana, O. Kikuchi, and K. Suzuki, *Bull. Chem. Soc. Jpn.* **49**, 3321 (1976).

6. J. Hine, *Physical Organic Chemistry*, McGraw-Hill Book Co., New York, 1962, Chapt. 9.
7. P. B. D. de la Mare and R. Bolton, *Electrophilic Addition to Unsaturated Systems*, Elsevier Science Publishing Co., New York, 1966.
8. D. C. Nonhebel, J. M. Tedder, and J. C. Walton, *Radicals*, Cambridge University Press, 1979.
9. W. A. Pryer, *Introduction to Free Radical Chemistry*, Prentice-Hall, Englewood Cliffs, N.J., 1965.
10. J. B. Hendrickson, O. J. Cram, and G. S. Hammond, *Organic Chemistry*, McGraw-Hill Book Co., New York, 1970, p. 614.
11. M. C. Hoff, K. W. Greenlee, and C. E. Boord, *J. Am. Chem. Soc.* **73**, 3329 (1951).
12. J. Burgin and co-workers, *Ind. Eng. Chem.* **13**, 1413 (1939).
13. J. Chetron, M. Henant, and G. Marinier, *Bull. Chim. Soc. Fr.*, 1966 (1969).
14. J. H. Polstar and K. Yates, *J. Am. Chem. Soc.* **91**, 1469 (1969).
15. H. C. Brown, *Hydroboration*, W. A. Benjamin Inc., New York, 1962, pp. 114, 192, 200.
16. I. Wender and co-workers, *J. Am. Chem. Soc.* **78**, 5401 (1956).
17. *Ibid*, **77**, 5760 (1955).
18. U.S. Pat. 2,555,054 (May 22, 1951), J. Owen (to Phillips Petroleum Co.).
19. L. F. Fieser and M. Fieser, *Advanced Organic Chemistry*, Reinhold Publishing Co., New York, 1961, p. 162.
20. U.S. Pat. 2,392,294 (Jan. 1, 1946), W. E. Vaughn and F. W. Rust (to Shell Development Co.).
21. U.S. Pat. 2,925,443 (Feb. 1, 1960), W. L. Wash (to Gulf Research and Development Co.).
22. V. J. Guerico, *Oil Gas J.*, 68 (Feb. 21, 1977).
23. *Chem. Eng.*, 62 (Feb. 13, 1978).
24. *Chem. Week*, 49 (Nov. 16, 1977).
25. J. E. Germain, *Catalytic Conversion of Hydrocarbons*, Academic Press, Inc., New York, 1969.
26. T. Brooks and co-workers, *The Chemistry of Petroleum Hydrocarbons*, Reinhold Publishing Corp., New York, 1955.
27. G. Egloff, G. Hulla, and V. I. Komarewski, *Isomerization of Pure Hydrocarbons*, Reinhold Publishing Corp., New York, 1942; D. R. Stuhl, E. F. Westrum, and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, John Wiley & Sons, Inc., New York, 1969.
28. W. G. Burns and co-workers, *Trans. Faraday Soc.* **64**, 129 (1968); K. Otsuka and A. Morikawa, *Chem. Commun.* (6),218 (1975).
29. Y. Misono, Y. Saito, and Y. Yoneda, *J. Catal.* **10**(2), 200 (1968).
30. R. Nicolova and co-workers, *C. R. Acad. Sci. Ser. C* **265**(8), 468 (1967).
31. K. Tanaka, *Sci. Pap. Inst. Phys. Chem. Res. Jpn.* **69**(2), 50 (1975).
32. U.S. Pat. 3,641,184 (Feb. 8, 1972), C. E. Smith and B. J. White (to Phillips Petroleum Co.).
33. K. Matsura, A. Suzuki, and M. Itoh, *J. Catal.* **23**, 396 (1971).
34. W. B. Smith and W. Y. Watson, *J. Am. Chem. Soc.* **84**, 3174 (1962).
35. T. A. Gilmore and J. J. Rooney, *Chem. Commun.*, 219 (1975).
36. K. W. Egger and S. W. Benson, *J. Am. Chem. Soc.* **88**, 236 (1966).
37. U.S. Pat. 3,527,834 (Sept. 8, 1970), W. L. Kehl, R. J. Rennard, and H. E. Swift (to Gulf Research and Development Co.).
38. J. Dubien, L. DeMourgues, and Y. Trambouze, *Bull. Soc. Chem. Fr.* (1), 108 (1967).
39. U.S. Pat. 3,479,415 (Nov. 18, 1969), E. Shull (to Air Products and Chemicals, Inc.).
40. M. J. McGrath and M. Soudek, *1990 Summer National Meeting, AIChE,* San Diego, Calif., Aug. 19–22, 1990.

41. E. G. Wollaston and co-workers, *Hydrocarbon Process.* **54**(9), 93 (1975).
42. Eur. Pat. 305,720 A2 (July 22, 1988), L. Zelting, L. Shunhua, and G. Xingpin (to Research Institute of Petroleum Processing, China).
43. D. F. Blaser, in J. J. McKetta, ed., *Encyclopedia of Chemical Processing and Design,* Vol. 10, Marcel Dekker, Inc., New York, 1979, p. 13.
44. S. B. Zodnik, E. J. Green, and L. P. Halle, *Manufacturing Ethylene*, The Petroleum Publishing Co., Tulsa, Okla., 1972.
45. D. M. Considine, ed., *Chemical and Process Technology Encyclopedia*, McGraw-Hill Book Co., Inc., New York, 1974, p. 429.
46. R. E. Haney, *High. Polm.* **24**(2), 577 (1971).
47. C. Marsden, *Solvent Guide,* 2nd ed., Interscience Publishers, New York, 1963.
48. S. Tukao, *Hydrocarbon Process.* **45**(11), 151 (1966).
49. U.S. Pat. 3,001,608 (Sept. 26, 1961), L. Lorenz, and co-workers (to BASF).
50. H. D. Evans and D. H. Sarno, *Seventh World Pet. Congr.* **5**, 259 (1967).
51. H. Klein and H. M. Weitz, *Hydrocarbon Process.* **47**(11), 135 (1968).
52. L. B. Ryland, M. W. Tamele, and J. N. Wilson, in P. H. Emmett, ed., *Catalysis,* Vol. VI, Reinhold Publishing Corp., New York, 1968, p. 1.
53. R. M. Barrer, *Chem. Ind. London*, 1203 (1968).
54. D. W. Breck, *Zeolite Molecular Sieves*, John Wiley & Sons, Inc., New York, 1974.
55. B. C. Gates, J. R. Katzer, and G. C. Schuit, *Chemistry of Catalytic Process*, McGraw-Hill Book Co., Inc., New York, 1979, p. 112–180.
56. *Oil Gas J.* **73**, 53 (Mar. 10, 1975).
57. Ref. 45, p. 1089.
58. R. L. Banks and G. C. Bailey, *Ind. Eng. Chem., Prod. Res. Dev.* **3**, 170 (1964).
59. R. L. Banks, *J. Mol. Catal.* **8**, 269 (1980).
60. J. F. Boucher and co-workers *Oil Gas J.* (Mar. 1982).
61. Y. Chauvin, J. Gillard, B. Juguin, L. Leonard, and M. Derrien, *1987 Spring National Meeting*, AIChE, Houston, Tex., Apr. 1987.
62. *Hydrocarbon Process.*, 73–75 (Mar. 1990).
63. *Hydrocarbon Process.*, 18–120 (Nov. 1984); 26 (Nov. 1985).
64. U.S. Pat. 3,341,620 (Sept. 12, 1967), (to Phillips Petroleum Co.).
65. Brit. Pat. 1,064,829 (Apr. 12, 1967), (to British Petroleum Co.).
66. U.S. Pat. 3,915,897 (Oct. 28, 1975), (to Phillips Petroleum Co.).
67. U.S. Pat. 4,242,531 (Dec. 30, 1980), (to Phillips Petroleum Co.).
68. U.S. Pat. 4,487,847 (Dec. 11, 1984), (to Phillips Petroleum Co.).
69. E. D. Cooper and R. L. Banks, *1985 Spring National Meeting*, AIChE, Houston, Tex., 1985.
70. U.S. Pat. Appl. 20030013933 (Jan. 16, 2003), M. Yamase and Y. Suguki (to Sumitomo Chemical Co., Ltd.).
71. L. Ziating, J. Fukang, and M. Enze, paper presented at the *1990 Annual Meeting of National Petroleum Refiners Association*, San Antonio, Tex., Mar. 25–27, 1990, paper no. AM-90-40.
72. *Chem. Eng. News* **68**(41) 12 (Oct. 8, 1990).
73. F. P. Wilcher, B. V. Vora, and P. R. Pujado, *Dewitt 1990 Petrochemical Review,* paper S-1, Houston, Tex., Mar. 27–29, 1990.
74. R. G. Craig, T. J. Delaney, and J. M. Dufallo, in Ref. 75, paper T-1.
75. G. Fusco, D. Sanflippo, and F. Buonomo, in Ref. 75, paper W-1.
76. R. O. Dunn, in Ref. 75, paper U-1.
77. J. J. Lacatena, in Ref. 75, paper V-1.
78. *Hydrocarbon Process.*, 104 (Apr. 1986).
79. J. P. Kennedy and I. Kirshenbaum, *High Polym.* **24**(2), 691 (1971); Ref. 65, p. 677.

80. Y. Chauvin and co-workers, "Dimersol B: A Key to Olefin Interconversion," *1987 Spring Meeting AIChE, Apr. 1, 1987, Session 70, Paper No. 70; Hydrocarbon Process.*, 106 (Apr. 1986).
81. J. R. Barber, J. J. Collins, and T. C. Sayer, paper presented at *68th National Meeting*, AIChE, Houston, Tex., Feb. 1971.
82. *Hydrocarbon Process.* **55**(9), 226, (1976).
83. M. S. Adler and co-workers, paper presented at the *85th National Meeting*, AIChE, June 1978.
84. U.S. Pat. 3,721,064 (Mar. 20, 1973), (to Union Carbide Corp.).
85. A. J. DeRosset and co-workers, paper presented at the *Symposium on Recent Advances in the Production and Utilization of Light Olefins*, American Chemical Society, Anaheim, Calif., Mar. 12–17, 1978; ACS Preprint **23**(2) 766–774 (1978).
86. U.S. Pat. 2,985,589 (May 23, 1961) (to UOP).
87. *Chem. Eng. News*, 48 (May 12, 1978).
88. T. Lacson, T. Kaelin, and T. Sasano, *Chemical Economics Handbook*, SRI, Menlo Park, Calif., April 2002.
89. H. M. McNair and E. J. Bonelli, *Basic Gas Chromatography*, Varian Instrument Division, Calif., Mar. 1969.
90. K. Verscheren, ed., *Handbook of Environmental Data on Organic Chemicals*, Van Nostrand Reinhold Co., New York, 1983, pp. 304, 317.
91. R. J. Lewis, *Sax's Dangerous Properties of Industrial Materials*, 10th ed., Vol. 2, John Wiley & Sons, Inc., New York, 2000.
92. C. R. Cupit, J. E. Gwyn, and E. C. Jernigan, *Petr. Manage.* **33**(12), 203 (Dec. 1961); **34**(1), 207 (Jan. 1962).
93. I. H. Gary and G. E. Handwerk, *Petroleum Refining*, Marcel Dekker, Inc., New York, 1975, p. 142.
94. J. P. Kennedy and I. Kirshenbaum, *High. Polym.* **24**(2), 701 (1971).
95. Ref. 55, p. 15.
96. C. L. Thomas and E. J. McNeils, *Seventh World Pet. Congr.*, Review Paper **12** (Apr. 1967).
97. P. C. Weinert and G. Egolff, *Pet. Process.* **3**, 585 (1948).
98. Ref. 93, p. 7.
99. G. D. Hobson and W. Pohl, *Modern Petroleum Technology,* 5th ed., John Wiley & Sons, Inc., New York, 1984, p. 517.
100. "Butadiene Chemical Profile", *Chemical Market Reporter*, March 25, 2002.
101. A. L. Waddams, *Chemicals from Petroleum,* 3rd ed., John Murray, London, England, 1973.
102. G. A. Olah, *Friedel-Crafts and Related Reactions,* Vol. II, Part 1, Interscience Publishers, New York, 1964.
103. P. Wiseman, *Industrial Organic Chemistry*, Wiley-Interscience, New York, 1970, p. 169.
104. *Ibid.*, p. 93.
105. A. V. Hahn, *The Petroleum Industry*, McGraw-Hill Book Co., Inc., New York, 1975, p. 591.
106. Ref. 111, p. 219.
107. C. E. Coates, M. L. H. Green, and K. Wade, *Organometallic Compounds,* Vol. I, Mathew & Co., Ltd., London, 1968, p. 299.
108. Ref. 111, p. 245.
109. Ref. 111, p. 153.
110. Ref. 113, p. 526.
111. *Chem. Eng. News*, 46 (Aug. 1963).
112. U.S. Pat. 3,296,286 (1967), (to Esso Research and Engineering).

113. Brit. Pat. 1,174,209 (Dec. 17, 1969), A. Kiwantes and B. Stouthamer (to Shekk Internationale Research Maalschppij N.V.).
114. Jpn. Pat. 73 23, 413 (July 13, 1973), Y. Komatsu, T. Tamura, and H. Okayama (to Maruzen Oil Co.).
115. J. Burgin and co-workers, *Ind. Eng. Chem.* **31**, 1413 (1939).
116. Ref. 102, p. 93.
117. Y. Oda and co-workers, *Hydrocarbon Process.* (10), 115 (1975).
118. MTBE, Chemical Profile, *Chemical Market Reporter*, Jan. 6, 2003.

NARASIMHAN CALAMUR
MARTIN E. CARRERA
RICHARD A. WILSAK
Amoco Chemical Company