METHYL ISOBUTYL KETONE

1. Introduction

Methyl isobutyl ketone (MIBK) (4-methyl-2-pentanone) is an industrially important solvent and chemical intermediate, which, after methyl methacrylate and bisphenol A is the third largest tonnage product obtained from acetone. MIBK occurs naturally in certain fruits and beverages and is not very toxic. It has been commercially produced for more than 60 years. The uses, properties and technologies for the manufacture of MIBK are covered in this article. The information presented is based on the earlier version of the article on ketones (see KETONES) and an additional literature search covering the period through June, 1999.

2. Properties

2.1. Physical Properties. MIBK is a clear colorless liquid with a faint ketonic odor. It is slightly soluble in water but is freely miscible with common organic solvents. Some of the most important physical properties of MIBK are given in Table 1. Some of these properties (1) are temperature dependent, and equations have been published in the literature for the estimation of these properties as a function of temperature. Equations found in the AIChE DIPPR database (2) on MIBK are given for the estimation of the liquid density, viscosity, thermal conductivity, heat capacity, and vapor pressure.

Note that these equations are valid only in the temperature ranges specified. Another important property of MIBK is the formation of azeotropes (3) with a number of compounds including water, and a list of the known azeotropes and non-azeotropes are given in Table 2.

$$\text{Liquid density} = \frac{A}{B^{1+\left(1-\frac{T}{C}\right)^{D}}}\ (\text{kmol/m}^3) \tag{1}$$

$$\text{Liquid viscosity} = \exp\left[A + \frac{B}{T} + C\ \ln(T) + DT^{E}\right]\ (\text{Pa}\cdot\text{s}) \tag{2}$$

$$\text{Liquid thermal conductivity} = A + BT + CT^2 + DT^3 + ET^4\ (\text{W/m/K}) \tag{3}$$

$$\text{Liquid heat capacity} = A + BT + CT^2 + DT^3 + ET^4\ (\text{J/kmol/K}) \tag{4}$$

$$\text{Vapor pressure} = \exp\left[A + B/T + C\ \ln(T) + DT^{E}\right]\ (\text{Pa}) \tag{5}$$

Table 1. **Physical Properties of Methyl Isobutyl Ketone**

Property	Value
molecular weight	100.16 g/mol
boiling point	116°C
freezing point	−84°C
specific gravity at 20°C	0.8020
viscosity at 20°C	0.61 mPa·s (= cP)
surface tension at 20°C	23.6 mN/m (= dyn/cm)
refractive index, n_D^{20}	1.3957
solubility in water at 20°C	1.6 wt%
solubility of water at 20°C	1.9 wt%
liquid specific heat capacity at 20°C	1920 J/(kg·K)
liquid thermal conductivity at 25°C	0.1439 W/(m·°C)
flash point, open cup	23°C
flash Point, closed cup	16°C
flammable limit, lower, in air at 93.3°C	1.2 vol%
flammable limit, upper, in air at 93.3°C	8.0 vol%
autoignition temperature	448°C
enthalpy (net/standard combustion at 25°C)	3.470612E + 07 J/kg
evaporation rate (butyl acetate = 1)	1.6
heat of vaporization	35.60 kJ/mol
vapor pressure at 20°C	14.5 mmHg
vapor thermal conductivity at 25°C	0.01099 W/(m · °C)
vapor density (air = 1)	3.5
critical temperature	301.5°C
critical pressure	3270 kPa
critical compressibility factor	0.253
critical volume	3.684069E-03 m^3/kg

where the coefficients are $A = 0.71687$, $B = 0.26453$, $C = 574.6$, $D = 0.28918$, and $E = 0$ in density equation (valid in the −84 to 301°C temperature range); $A = -11.394$, $B = 1168.7$, $C = -0.007539$, $D = 0$, and $E = 0$ in the viscosity equation (valid in the −84 to 178°C range); $A = 183650$, $B = -79.862$, $C = 0.60769$, $D = 0$, and $E = 0$ in the heat capacity equation (valid in the −84 to 116°C range); $A = 80.503$, $B = -7421.8$, $C = -8.379$, $D = 1.8114^{-17}$, and $E = 6$ in the vapor pressure equation (valid in the −84 to 301°C range). The temperature T is in degree Kelvin in these equations.

2.2. Chemical Properties. MIBK is a very stable compound under ordinary storage and use conditions but undergoes a variety of reactions when mixed with other reagents and subjected to suitable reaction conditions. The reactivity of MIBK originates mainly from the electrophilicity of the carbonyl group and acidity of the α-hydrogens. As a result, MIBK undergoes a number of chemical reactions that are typical of carbonyl-containing compounds, but its chemistry more closely resembles that of other aliphatic ketones. Compared to acetone, the simplest member of the aliphatic ketone family, the reactivity of MIBK is altered by the presence of an additional isopropyl substituent. In general MIBK is less reactive than acetone. The alkyl substituent has both electronic and steric effects on the reaction rate of MIBK and also creates another reactive site, namely, the tertiary C–H bond. Tertiary C–H bonds are more easily

Table 2. **Azeotropes and Non-Azeotropes of Methyl Isobutyl Ketone**

Compound	CAS Registry number	Boiling point, °C	Azeotrope boiling point, °C	MIBK content of azeotrope, wt%
methyl isobutyl ketone	[108-10-1]	115.9		
butyl alcohol	[71-36-3]	117.8	114.4	70
1,3-dimethylcyclohexane	[638-04-0]	120.7	112.0	53
dipropylamine	[142-84-7]	109.2	105.5	<32
epichlorohydrin	[106-89-8]	116.5	115.5	<68
heptane	[142-82-5]	98.4	97.5	13
isobutyl acetate	[110-19-0]	117.4	115.6	NA[a]
isobutyl alcohol	[78-83-1]	108.0	107.9	9
isopropyl sulfide	[625-80-9]	120.5	114.9	72
2-methoxyethanol	[109-86-4]	124.5	114.2	75
methylcyclohexane	[108-87-2]	101.2	<100.1	<20
methyl isovalerate	[556-24-1]	116.5	115.6	55
nitroethane	[79-24-3]	114.2	<113	NA[a]
n-octane	[111-65-9]	125.8	113.4	65
pyridine	[110-86-1]	115.4	114.9	40
tetrachloroethylene	[127-18-4]	121.1	113.9	52
toluene	[108-88-3]	110.8	110.7	3
water		100.0	87.9	75.7
acetic acid	[64-19-7]	118.5	non-azeotrope	
acetone	[67-64-1]	56.2	non-azeotrope	
benzene[b]	[71-43-2]	80.2	non-azeotrope	
2-chloroethanol	[107-07-3]	128.6	non-azeotrope	
chloroform	[67-66-3]	61.2	non-azeotrope	
cyclohexane[b]	[110-82-7]	80.8	non-azeotrope	
diisobutylamine	[110-96-3]	138.5	non-azeotrope	
2,6-dimethyl-4-heptanone	[108-83-8]	169.4	non-azeotrope	
ethanol	[64-17-5]	78.3	non-azeotrope	
2-ethoxyethanol	[110-80-5]	135.3	non-azeotrope	
ethylbenzene	[100-41-4]	136.2	non-azeotrope	
ethyl butyrate	[105-54-4]	121.5	non-azeotrope	
ethyl isobutyrate	[97-62-1]	110.1	non-azeotrope	
isoamyl alcohol	[123-51-3]	131.9	non-azeotrope	
isobutyl ether	[628-55-7]	122.3	non-azeotrope	
isopropyl alcohol	[67-63-0]	82.5	non-azeotrope	
isopropyl propionate	[637-78-5]	110.5	non-azeotrope	
mesityl oxide	[141-79-7]	130.5	non-azeotrope	
methanol	[67-56-1]	64.7	non-azeotrope	
methyl chloroacetate	[96-34-4]	130.0	non-azeotrope	
4-methyl-2-pentyl acetate	[50373-41-6]	146.1	non-azeotrope	
nitromethane	[75-52-5]	101.2	non-azeotrope	
propionic acid	[79-09-4]	140.9	non-azeotrope	

[a] NA = Not available.

[b] In the 450–760 mm Hg pressure range.

activated than a secondary or primary C–H bond in reactions that involve radical intermediates.

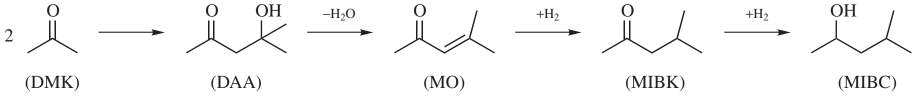
Examples of well-known reactions of aliphatic ketones are the aldol condensation, ketal formation, and carbonyl-to-alcohol reduction reactions. The aldol condensation reaction (4) can be catalyzed by an acid or base catalyst, and the reaction can take place between two molecules of the same ketone (self-aldol), between molecules of two different ketones (cross-aldol), or between a ketone and an aldehyde (cross-aldol). Aldol condensation of acetone is the main chemistry involved in the various processes for the manufacture of MIBK. Aldol condensation of MIBK with acetone is the chemistry used for the manufacture of diisobutyl ketone. Acid-catalyzed condensation of alcohols with ketones produces ketals with the elimination of a molecule of water. The carbonyl-to-alcohol functional group reduction reaction can be carried out by a variety of reagents, but catalytic hydrogenation is the preferred industrial process. Methyl isobutyl carbinol (MIBC) is manufactured by catalytic hydrogenation of MIBK using supported Ni metal catalysts. These reactions are equilibrium controlled, and the equilibrium position will depend on the reaction conditions and structure of the reactants. Numerous other reactions of ketones that have been discussed in advanced textbooks (5,6) are synthetically useful and/or interesting from the mechanistic point of view.

Certain reactions of MIBK, although they may be synthetically unimportant, have some product quality and/or safety implications. Exposure of MIBK to ultraviolet (uv) light, a component of ordinary daylight, will cause it to undergo photochemical reactions. Both the Norrish type I and type II radical fragments can be produced, and these radicals can undergo further reactions to produce a number of decomposition products. Exposure of MIBK to air and heat will cause autoxidation. Hydroperoxides are usually the primary autoxidation products that, owing to their lack of stability, can subsequently decompose to other products. Light and transition metal ion contaminants are known to accelerate the autoxidation reaction. The autoxidation reactions are mechanistically very complex and produce a variety of products in small quantities. Under ordinary storage and use conditions these reactions are slow, and buildup of the decomposition products is negligible over a reasonable period of time. However, prolonged exposure to air and heat should be avoided to minimize the risk of peroxide buildup in MIBK (7–9).

3. Manufacture

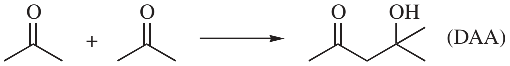
MIBK is produced industrially by four different routes: (*1*) a three-step process using acetone and hydrogen as feeds and proceeding via diacetone alcohol and mesityl oxide intermediates (*2*) a one-step synthesis from acetone and hydrogen (*3*) a one-step mixed-ketone process from isopropyl alcohol and (*4*) a single or multistep mixed-feed process in which other products are coproduced. The three-step process was the conventional technology until the late 1960s. Afterward the simpler one-step synthesis from acetone was commercialized by Veba-Chemie and Deutsche Texaco in Germany, and Tokuyama Soda in Japan. Despite the improvements offered by the direct route, many of the older three-step plants such as the Shell plant in Deer Park, Texas, are still in operation (10). An advantage of the three-step process is the ability to produce other acetone derivatives such as diacetone alcohol and hexylene glycol (2-methyl-2,4-pentanediol) [107-41-5] in the same plant. The one-step process from 2-propanol coproduces di-isobutyl ketone [108-83-8] and acetone, and is practiced in the United States by Union Carbide (11) and in the Netherlands by Shell Chemical Company. The mixed-feed process coproduces products such as methyl *n*-amyl ketone [110-43-0] (12). Eastman is believed to operate a proprietary unpatented mixed-feed process that produces these coproducts (10,11).

3.1. Process Chemistry. The general process chemistry involved in the production of MIBK from acetone, also known as dimethyl ketone (DMK), and hydrogen as feed materials is shown in equation **6** below. The aldol reaction of acetone to diacetone alcohol (DAA), dehydration of DAA to mesityl oxide (MO), and hydrogenation of MO to MIBK/MIBC are the desired chemical reactions that take place in the process. Depending on the process, the DAA and MO intermediates may or may not be isolated. In the conventional three-step process these three reactions are carried out as separate steps and the crude DAA and crude MO intermediates are isolated.



(6)

Several side reactions take place in each of the reaction steps. In the aldol condensation step which uses a base catalyst, DAA from equation 7 can further react with DMK to produce triacetone alcohol (TAA) as a by-product, as shown in equation 8. Partial dehydration of DAA can take place to produce MO (eq. **9**), which can further condense with DMK to produce the trimer shown in equation **10**. The trimer in equation 10 can also be formed by partial dehydration of the unsymmetrical TAA isomer. The trimer can dehydrate to the pyran compounds shown in equation **11**.



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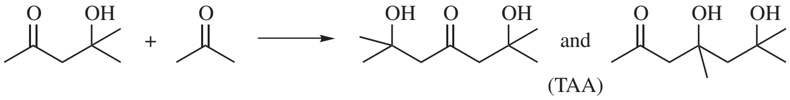

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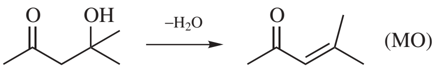

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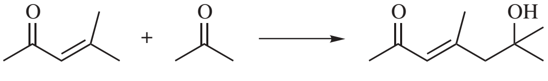

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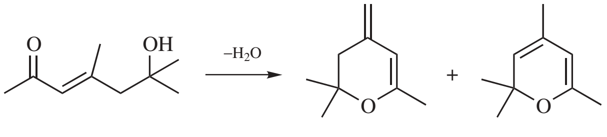
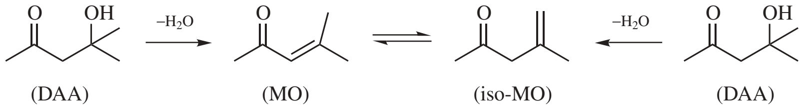


(11)

In the dehydration step, which uses an acid catalyst, DAA dehydrates not only to MO but also to isomesityl oxide (Iso-MO) as a major side reaction (eq. **12**). The trimers produced in the aldol condensation step also undergo dehydration and cyclization reactions as shown in equations (**13–16**).



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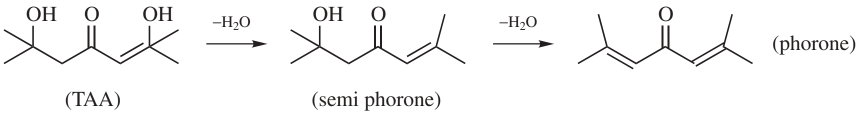

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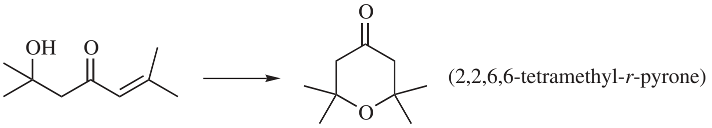

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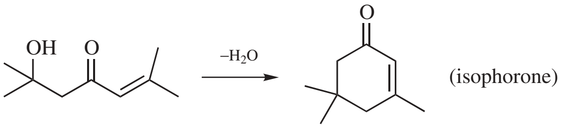

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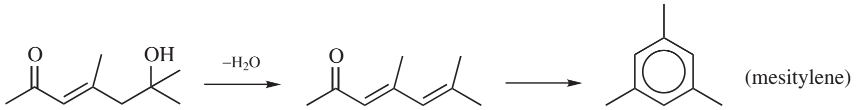
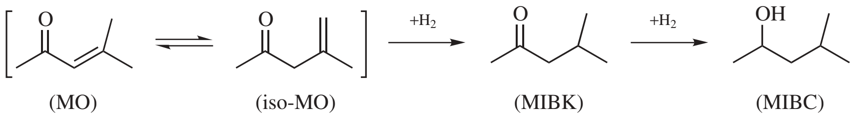


(16)

In the hydrogenation step, depending on the catalyst used, the reaction may not stop at MIBK but proceed to make some MIBC, as shown in equation **17**. The dehydrated trimers (eg, phorone and isophorone) likewise undergo hydrogenation to saturated C9 ketones and alcohols as shown in equations **(18–20)**. Note that equations **(6–20)** represent reversible reactions. More or less the same set of by-products may be produced in the one-step processes as well, but the mechanisms of formation would be expected to be different.



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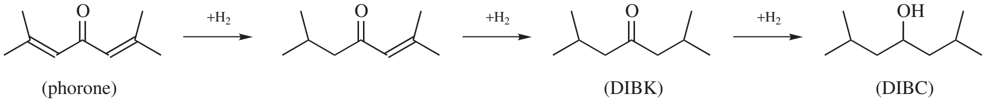
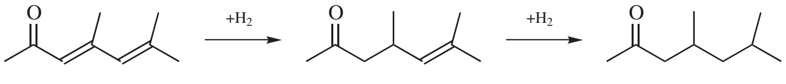
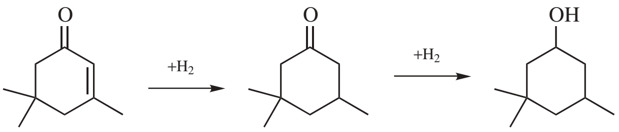


(18)



(iso-DIBK)

(19)



(isophorone)

(20)

3.2. Three-Step Process. *Production of Diacetone Alcohol.* Diacetone alcohol is produced by the low temperature liquid-phase condensation of acetone (13) in the presence of a base catalyst. Base catalysts as solutions in water or water–alcohol solvent mixtures can be employed (14–17), but the catalyst must be completely neutralized (15) with a suitable acid before the crude product is worked up. Solid base catalysts held in a fixed bed are preferred over solution catalysts because of the ready separation of the product from the catalyst. The reaction is exothermic ($\Delta H \sim -5.5$ kcal/mol) and is equilibrium controlled (18–20). The unfavorable effect of increasing temperature on the equilibrium constant has been documented (18). The equilibrium concentration of diacetone alcohol is 23.1 wt% at 0°C, and declines to 9.1 wt% at 30°C (21). Although low temperatures favor diacetone alcohol formation, kinetic considerations require that commercial operation be conducted at 10–20°C. Either single or multistage catalyst beds can be used: single-stage conversion requires lower inlet temperatures, multistage conversion can cascade to progressively lower inlet temperatures (15). Residence times of 20–60 min are typically required. Conversion across the reactors typically ranges from 8 to 15%. As a result of the low conversions, distillation to separate acetone from DAA is employed to allow recycle of unreacted acetone to the reactors. The crude DAA product may contain 85–95% DAA and 5–15% acetone and other impurities. In a catalytic distillation process described in 1998 (22) for the production of DAA, the reaction and the separation are carried out simultaneously in a single unit.

Suitable catalysts for the aldol condensation reaction include the hydroxides of alkali metals (14–16,23,24) and oxides or hydroxides of alkaline earth metals (17,23,25–29). Many of the solid base catalysts are susceptible to alkali dissolution by the reaction medium and yield a crude product that contains traces of catalyst. To stabilize DAA against reversion to acetone during the acetone recycle distillation, the solution is first neutralized with phosphoric acid (15,30), carboxylic acid type ion-exchange resin (31), phosphonic acid resin (31), phenolic resin (31), or a dibasic acid such as CO_2 (32). Acetone can then be stripped overhead in a distillation column, preferably under vacuum conditions, and recycled. Commercial catalysts generally have a life of ~1 yr and can be reactivated by washing with hot water and acetone (25,33). It is reported (34) that the addition of 0.2–2 wt% methanol, ethanol, or 2-propanol to a calcium hydroxide catalyst helps prevent catalyst aging. On the other hand, aldehydes are considered to be poisons, and it has been reported that a long catalyst life is obtained by limiting the concentration of aldehydes in the acetone feed (35). The use of more mechanically stable anion-exchange resins as catalysts has been reported (12,22,36–38). The addition of 3–10% weight of C1–C3 alcohols to the acetone feed is beneficial for the reaction over anion-exchange resins (37). Early patents indicated that because water inhibits the aldol condensation mechanism, it was necessary to dry recycle acetone to $<1\%$ water (17,32,39). More recent reports demonstrate DAA production from waste acetone containing 10–50% water (40), and enhanced DAA production over anion-exchange resins using acetone feeds that contain 3–10% water (12,38). Use of alkylene oxide–salt complexes (41) as catalysts for aldol reactions and a cocatalyst (42) for enhancing the rate of base-catalyzed aldol reactions has also been reported. Hydrotalcite-type catalysts have also been shown to be selective for the aldolization of acetone to DAA (43).

Industrially, a selectivity to DAA of between 90 and 95% can be achieved (10). The principal by-products (44) are mesityl oxide and acetone trimers. *sym*-Triacetone dialcohol [3682-91-5] can form by condensation of acetone with diacetone alcohol. Dehydration of *sym*-triacetone dialcohol can yield semiphorone [5857-71-6] (6-hydroxy-2,6-dimethyl-2-hepten-4-one), which may in turn ring close to form 2,2,6,6-tetramethyl-γ-pyrone [1197-66-6], or ultimately dehydrate to phorone [504-20-1] (2,6-dimethyl-2,5-heptadien-4-one) (45). Similarly, an unsymmetrical acetone trimer can also be formed that dehydrates and cyclizes to 2,2,4,6-tetramethylpyran [5526-16-9] (46) or dehydrates to 2,4-dimethyl-2,4-heptadiene-6-one. These impurities complicate the high purity recovery of DAA (47) and are thought to be responsible for a yellow discoloration of DAA. Crude DAA is generally purified by vacuum topping and tailing in a set of distillation columns (48). The use of dibasic acids or nitrogen containing carboxylic or phosphonic acids (49) as stabilizing agents for the refined product has been patented.

Refined DAA is a colorless and mild-smelling liquid that is completely miscible with water and most organic solvents. DAA itself is a good solvent and is used in many applications. Because of its ketone and alcohol functionalities it has special utility in the coatings industry, where it is used to dissolve cellulose acetate to give solutions with high tolerance for water (50). DAA is also used as feed material for the production of hexylene glycol. DAA producers typically finish DAA for sales and feed crude DAA to the dehydration step in which mesityl oxide is produced.

Production of Mesityl Oxide. Mesityl oxide is produced by the liquid-phase dehydration of diacetone alcohol in the presence of acidic catalysts at 100–140°C and atmospheric pressure. The reaction is mildly endothermic ($\sim$5 kcal/mol). As a precursor to MIBK, mesityl oxide is prepared in this manner in a distillation column in which acetone is removed overhead and water-saturated mesityl oxide is produced from a side-draw. Suitable catalysts are phosphoric acid (20,39,51,52) and sulfuric acid (14,39). The kinetics of the reaction over phosphoric acid have been reported (53). Reversion of DAA to acetone is a major side reaction, and the acetone recovered from the dehydration step is recycled to the aldol condensation step. Other than reversion, the dehydration reaction itself is very selective. By-products formed in the dehydration step will depend on the quality of crude DAA feed and also on the reaction conditions employed. The majority of the by-products derived from acetone trimers are shown in the Process Chemistry section. Other by-products are possible (44). Crude mesityl oxide obtained from the dehydration step could be a suitable feed material for the hydrogenation step.

Mesityl oxide can also be produced by the direct condensation of acetone at higher temperatures. This reaction can be operated in the vapor phase over zinc oxide (54–56), zinc oxide–zirconium oxide (57), copper chromite (58), and borate–phosphate (59) or in the liquid phase over cation-exchange resin (60) or zirconium phosphate (61,62). Other catalysts (63–75), such as heat-treated anionic clays (64–66) and magnesium–aluminum complex compound (72,75) catalysts are also known to condense acetone to mesityl oxide. A reactor design for the removal of the heat of reaction has been patented (76).

Mesityl oxide is an oily colorless liquid with an unpleasant odor. It exhibits the versatility and unusual reactivity associated with conjugated α,β-unsaturated carbonyl compounds (77). On standing in air, mesityl oxide slowly forms bis(3,5,5-trimethyl-1,2-dioxolanyl)-3-peroxide (78). Mesityl oxide can contain 5–20% of isomesityl oxide (4-methyl-4-penten-2-one) [141-79-7], the β,γ-unconjugated isomer. At equilibrium, the mixture contains 91% of the α,β-mesityl oxide and 9% of the β,γ-isomer (79–81). Acid or alkali can catalyze the equilibration of the isomers (81). Techniques to isolate the isomers have been reported (79).

Mesityl oxide is more toxic than saturated ketones and is highly irritating to all tissues on vapor or liquid contact. It is absorbed through intact skin, and prolonged exposure can damage liver, kidneys, and lungs. Repeated exposure to vapors can cause anemia and leukopenia (82). However, the odor is so intolerable that long-term exposure is unlikely. Sales of mesityl oxide ceased in the United States in 1986 because of its toxicity. Mesityl oxide is still being produced but is used captively as an intermediate in MIBK and isophorone [78-59-1] production. If desired the MO production step can be bypassed by directly converting DAA to MIBK, and a process for carrying out this conversion has been patented (83).

Production of MIBK. Selective hydrogenation of the olefinic bond in mesityl oxide can be conducted over a fixed-bed catalyst in either the liquid or vapor phase. The catalyst can be present as slurry if a liquid-phase hydrogenation reactor is employed. In the liquid phase the reaction takes place at 150°C and 0.69 MPa; in the vapor phase the reaction can be conducted at atmospheric pressure and temperatures of 150–170°C. Isomesityl oxide reacts at a slower rate than MO. The reaction is highly exothermic and yields ~30 kcal/mol. To prevent temperature runaways and obtain high selectivity, the conversion per pass is limited in the liquid phase, and in the vapor phase inert gases often are used to dilute the reactants (84). The catalysts employed in both vapor- and liquid-phase processes include nickel (85–90), Raney nickel (20,91,92), Ni–Cr (93), palladium (14,94–98), copper–alumina (99), copper–chromium oxide (84), copper–zinc oxide (100), cobalt complexes (101), rhodium (102,103), and rhodium hydride complexes (104–108). Complete conversion of mesityl oxide can be obtained at selectivities of 95–98% (94,100). The kinetics of hydrogenation over $Pd–Al_2O_3$ catalyst has been reported (109).

MIBC can be a major by-product of MO hydrogenation. It can be separated (110) and used as a solvent or recycled back to the process. Selective hydrogenation by reactive distillation (111) and use of acetic acid in the MO feed to suppress the hydrogenation of MIBK to MIBC has been patented (91). Alkali metal salts have been claimed as promoters for enhancing the activity and selectivity of palladium–catalyzed hydrogenation, and selectivity to MIBK of 99.9% has been claimed (112). Water also enhances the selectivity of Pd catalyzed hydrogenation; selectivities of 89.3 and 99.5% have been measured in the absence and presence of water (113). Hydrogenation of an azeotropic mixture of MO and water has been patented (93).

Hydrogen peroxide treatment of crude MO produced by the sulfuric acid catalyzed dehydration of diacetone alcohol has been claimed (114,115) to offer a long catalyst life, and use of hydrogen peroxide as a promoter for a rhodium complex catalyst has also been disclosed (105). Formic acid (116), *sec*-butyl alcohol (117), and MIBC (118) have been claimed as donors of hydrogen for the hydrogenation of MO. Use of *sec*-butyl alcohol as the hydrogen donor results in the simultaneous production of methyl ethyl ketone and MIBK. The reduction of MO to MIBK can also be accomplished by electrochemical means (119). Other studies on Ni–Cu–Cr (120), palladium complex polymer (121), copper complex (122), polymer-supported Pd (123,124), and Ni–M (125) catalysts have been reported.

Figure 1 illustrates the three-step MIBK process employed by Hibernia Scholven (126,127). This process is designed to permit the intermediate recovery of refined diacetone alcohol and mesityl oxide. In the first step, acetone and dilute sodium hydroxide are fed continuously to a reactor at low temperature and with a reactor residence time of ~1 hour. The product is then stabilized with phosphoric acid and stripped of unreacted acetone to yield a crude diacetone alcohol stream. More phosphoric acid is then added, and the diacetone alcohol dehydrated to mesityl oxide in a distillation column. Mesityl oxide is recovered overhead in this column and fed to a further distillation column where residual acetone is removed and recycled to yield a tails stream containing 98–99% mesityl oxide. The mesityl oxide is then hydrogenated to MIBK in a reactive distillation conducted at atmospheric pressure and 110°C. Simultaneous hydrogenation and rectification are achieved in a column fitted with a palladium catalyst bed, and yields of mesityl oxide to MIBK exceeding 96% are obtained. Other three-step processes have also been described in literature (128).

3.3. One-Step Process from Acetone. The single-step manufacture of MIBK offers lower investment and operating costs, and avoids the low conversion of acetone in the first stage and the reversion of mesityl oxide to acetone in the second stage, which are experienced in the three-step process. Direct synthesis (129) is achieved using a multifunctional catalyst that effects acid aldolization, dehydration, and hydrogenation. Veba-Chemie's patents (130,131) describe a catalyst composed of a cation-exchange resin loaded with 0.05% palladium, over which is passed a 2:1 mol feed ratio of H_2/acetone at ~135°C and 6.1 MPa. At these conditions, a 96% selectivity to MIBK is achieved at 35% acetone conversion. Refined MIBK is then recovered from a four-column refining train in which the first column removes light hydrocarbons and the second recycles unconverted acetone. A decanter is then located upstream of the final two columns and is used to separate an aqueous phase. The third column removes 2-propanol–water mixture, and the final column produces refined MIBK overhead and a heavies (diisobutyl ketone) tails stream. A similar process is operated by

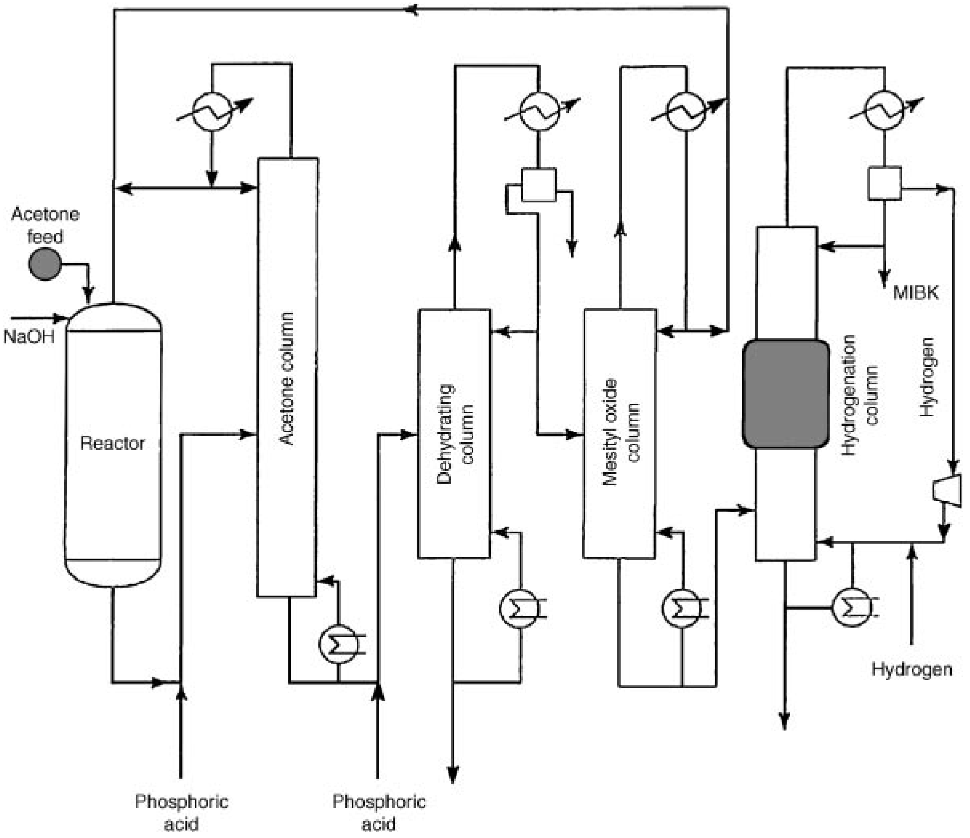


Fig. 1. Three-step MIBK process (126). Courtesy of Chemische Industrie.

Deutsche Texaco (132–139) at operating conditions of 130–140°C and 3 MPa. An acetone conversion of 40% and a consumption of 1.4 kg of acetone per kilogram of MIBK are reported (133). A flow sheet of the Deutsche Texaco process (134) is shown in Figure 2. A palladium on ion-exchange resin catalyst (Pd/KU-2) has been reported in a Russian paper (140) to give 94.5% selectivity at an acetone conversion as high as 50% at 120°C reaction temperature.

The Tokuyama Soda single-step catalyst consists of a zirconium phosphate catalyst loaded with 0.1–0.5 wt% palladium (61,62,141–149). Pilot–plant data report (148) that at 140°C, 3 MPa, and a mole ratio of H_2/acetone of 0.2, the MIBK selectivity is 95% at an acetone conversion of 30%. The reactor product does not contain light methyl pentanes, and it allows MIBK recovery in a three-column train with a phase separator between the first and second columns.

Sumitomo Chemical Co. (150–152) and Mitsubishi Kasei Co. (153,154) have patented single-step catalysts containing niobium and palladium. A Sumitomo example reports 93.5% MIBK selectivity at 41.8% acetone conversion and conditions of 160°C and 2 MPa, and a Mitsubishi example reports a 92.5% selectivity at 39.5% conversion at 140°C and 2 MPa. Other significant processes have been patented by such companies as Allied Corporation (155), BASF (156–158), BP

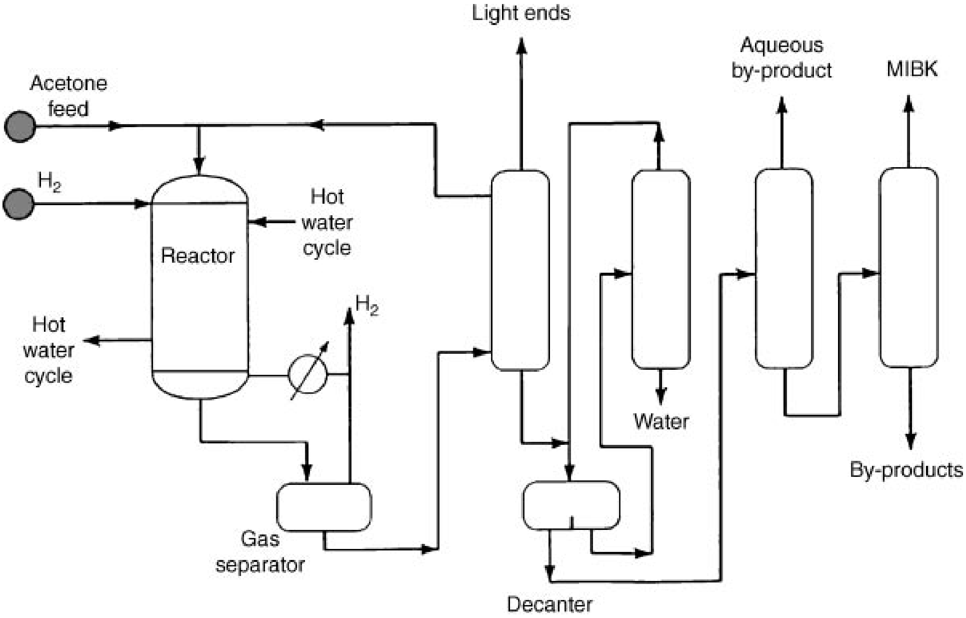


Fig. 2. Deutsche Texaco one-step MIBK process (134).

Chemicals (159), Catalytic Distillation Technology (160), Commercial Solvents Corporation (161), a Czechoslovakian company (162–166), Distillers Co. (167,168), Industrial Technology Research Institute, Taiwan (86,169,170), Japan Bureau of Industrial Technology (171), Sumitomo Chemical Co. (172–174), Mitsubishi (87,175–180), Showa Denko (181), Scholven-Chemie (182,183), Mobil (184), and Union Carbide (185).

In the one-step process, although MIBK is produced selectively, numerous other products are also produced as a result of combining all three steps of the chemical transformation into a single reaction step. The crude liquid product from a pilot plant production of MIBK has been thoroughly analyzed. At least 17 main components comprising >99% of the mass of the crude product have been identified and their quantities reported (186). Mathematical modeling of the reaction over Pd on ion-exchange resin catalyst to predict the optimum reaction conditions (187) and mathematical modeling and optimization of a continuous cascade reactor (188) have been reported. It has been reported that water released during reaction reduces the reaction rate of sulfonic acid resin–Pd catalyst (189). Water may have the same effect on the other single-step catalysts as well. Numerous reports on catalyst preparation (190–203), catalyst testing (146–150,174,204–240), and other process-related studies (241–244) have been published in the journal and patent literature.

3.4. One-Step Coproduction Process from Isopropyl Alcohol. In the one-step process from isopropyl alcohol, the alcohol is first dehydrogenated to acetone and hydrogen in a reversible reaction. The *in situ* produced acetone undergoes aldol condensation and hydrogenation reactions to produce higher ketones. This process, which coproduces acetone and diisobutyl ketone with

MIBK, is practiced in the United States by Union Carbide (11). An early demonstration of this process utilized chromites of zinc, copper, and cadmium at temperatures of 325–350°C to produce higher ketones from secondary alcohols (245). The details of a vapor-phase 2-propanol dehydrogenation and condensation process for the production of acetone, MIBK, and higher ketones have been described (246). The process converts an azeotropic 2-propanol–water feed over a copper-based catalyst at 220°C and produces a product mixture containing 2-propanol (11.4%), acetone (52.4%), MIBK (21.6%), 4-methyl-2-pentanol (2.2%), diisobutyl ketone (DIBK) (6.5%), and isobutyl isoheptyl ketone (IBHK) (1%). The diisobutyl ketone contains ~15% of 4,6-dimethyl-2-heptanone (iso-DIBK), an isomer of DIBK, and the two isomers are not easily separated in commercial scale owing to their similar physical properties. The distribution of products was found to depend largely on reactor temperature and residence time. It has been reported that the product distribution is altered by controlling the average pore diameter of alumina-supported platinum or rhodium catalysts (247–249), and by cofeeding mesityl oxide and/or methyl isobutyl carbinol (250). The combined effects of the nature of the catalyst, reaction temperature, residence time, and feed composition on the product distribution have been reported (251). The one-step route from 2-propanol has been demonstrated over a variety of supported and unsupported metal and metal oxide catalysts (252–262). This process does not require the addition of hydrogen because it has a net production of 1 mol of hydrogen per mole of MIBK produced, as a result of the dehydrogenation of the 2-propanol. In principle, a catalyst used in the one-step process from 2-propanol can also be used in the one-step process for MIBK manufacture from acetone and hydrogen.

3.5. Mixed-Feed Coproduction Process. MIBK can be coproduced with other ketones such as methyl *n*-amyl ketone (MNAK) either in a single-step process, or by the conventional three-step process. Eastman is believed to operate a single-step process, but no details are available (10, 11). BASF (263), Union Carbide (264), and Shell (12) have patented processes for coproducing other ketones with MIBK. The Shell patent describes the coproduction of MNAK and MIBK from acetone and *n*-butyraldehyde by a three-step process, whereas the BASF and Union Carbide patents describe single-step processes. Other patents (32,265–268) describe methods for cross-condensing an aldehyde and a ketone to make higher ketones.

3.6. Miscellaneous Methods of Preparing MIBK. MIBK has been prepared by reaction between acetaldehyde and isobutene in the presence of an organic peroxide (269) and acetone and propylene in the presence of an aldehyde initiator (270). A noncatalytic vapor-phase production from acetone and propylene (271) and a catalytic process in which two different aldehydes are decarbonylatively coupled (272) to make MIBK have also been claimed.

4. Economics Aspects

The producers of MIBK in the United States, Europe, East Asia, and South and Central America and their annual production capacities are shown in Table 3. Historical U.S. MIBK annual production and price are listed in Table 4. Overall,

Table 3. **U.S., European, East Asian, and Central and South American MIBK Production**[a]

Producer	Plant location	1999 Capacity, million lb/yr
	U.S.	
Eastman Chemical Company	Kingsport, Tenne.	20
Shell Chemical Company	Deer Park, Tex.	100
Union Carbide Corporation	Institute, W. Va.	75
U.S. total		*195*
	Europe	
Elf Atochem SA	Maurienne, Savoie, France	31
Shell Chimie SA	Berre-l'Etang, Bouches du Rhône, France	55
Società Italiana Serie Acetica Sintetica SpA	Pioltello, Lombardia, Italy	55
Shell Nederland Chemie BV	Rotterdam-Pernis, Netherlands	99
Europe total		*240*
	East Asia	
Kyowa Yuka Company, Ltd.	Yokkaichi, Mie, Japan	33
Mitsubishi Chemical Corporation	Kurashiki, Okayama, Japan	44
Mitsui Chemical, Inc.	Kuga-gun, Yamaguchi, Japan	49
Kumho P&B Chemicals, Inc.	Yoechon, Chollanam-do, South Korea	26
Lee Chang Yung Chemical Industry Corp.	Linyuan City, Kaohsiung Hsien, Taiwan	44
East Asia total		*196*
	South and Central America	
Sol Petroleo SA - Carboclor Division	Campana, Buenos Aires, Argentina	15
Rhodia SA	Paulínia, São Paulo, Brazil	26
South and Central America total		*41*
All regions total		*672*

[a] Courtesy of SRI International, 1999 Directory of Chemical Producers.

the average annual growth rate for MIBK is expected to be 0% during 1998–2003. During the same time period, growth of 2.4 and 1.9% is expected for MIBK used in the manufacture of rubber antiozonants and acetylenic surfactants, respectively, while a decline in consumption of 0.6 and 2.1% is expected for MIBK used in surface coating and solvent/extraction applications, respectively (11). MIBK is listed as a hazardous air pollutant (HAP). EPA is considering a petition to delist MIBK. If delisting occurs MIBK consumption may increase significantly.

5. Specifications

MIBK is sold according to international standard quality specifications written by organizations such as American Chemical Society (ACS), ASTM (American Society of Testing and Materials), BSI (British Standards Institution), and DIN (Deutsches Institut für Normalisierung). As examples of these standard

Table 4. **U.S. Production and Price[a] of MIBK[b]**

Year	Production, $\times 10^6$ lb	Price, ¢/lb
1965	168.9	13
1970	199.0	14
1975	150.2	23
1980	168.3	39
1985	130.9	49
1986	142.6	35
1987	151.2	38
1988	155.0	45
1989	170.8	45
1990	180.0	45
1991	170.0	47
1992	164.2	51
1993	150.0	51
1994	170.0	52
1995	170.0	63
1996	175.0	63
1997	178.0	63
1998	178.0	63

[a] Prices are midyear list, fob, freight paid, tank trucks delivered.
[b] Ref. 11. Courtesy of SRI International.

specifications, ACS and ASTM D1153-94 specifications (273) are given in Table 5. The major impurities present in commercial MIBK are MIBC and water. Smaller amounts of impurities such as acetone, isopropyl alcohol, and C6−C9 hydrocarbons, including mesitylene, mesityl oxide, and diisobutyl ketone, can also be present. The actual impurities and the levels will depend on the manufacturing process. Special quality requirements (SQR) with respect to the concentration of certain impurities may be specified depending on the end use of the product.

Table 5. **Specifications of MIBK**

Property	ACS specification	ASTM D1153-94 specification
appearance	clear	
purity, min	98.5 wt%	99.0 wt%
color (Pt-Co scale), max	15	15
apparent specific gravity:		
20/20°C		0.800−0.803
25/25°C		0.796−0.799
water, max	0.1 wt%	0.1 wt%
acidity as acetic acid, max	0.002 mequiv/g	0.01 wt%
odor		nonresidual
nonvolatile matter, max	0.005 wt%	5 mg/100 mL
distillation:		
initial boiling point, min		114.0°C
dry point, max		117.0°C
MIBC impurity, max		0.3 wt%

6. Health, Safety, and Environmental Issues

MIBK is generally considered to exhibit low mammalian toxicity and at levels to which the general human population is exposed is unlikely to present any hazard (274). The relatively high volatility, rapid atmospheric phototransformation, and ready biodegradability of MIBK indicate that adverse environmental and human health effects are likely to occur only after accidental spills or owing to uncontrolled industrial effluents, as well as during occupational exposure (274).

The principal route of MIBK exposure is by inhalation of its vapors, but it can also be absorbed by ingestion or through the skin. Studies on humans have reported a low odor threshold of 0.4 ppm (275). Exposure at a concentration of 100 ppm resulted in headache and nausea or in respiratory irritation (276). Exposure at 200 ppm resulted in eye irritation (277), and exposure to high concentration (>1000 ppm) can produce central nervous system depression and narcosis (278). The low odor threshold and irritating properties provide warning of high concentrations. Ingestion of MIBK may result in aspiration into the lungs, causing a chemical pneumonitis (279). Prolonged and repeated contact to the skin may cause dermatitis. Chronic occupational exposure to MIBK has been observed to cause nausea, headache, burning in the eyes, weakness, insomnia, intestinal pain, and slight enlargement of the liver in humans. No information is available on the reproductive, developmental, or carcinogenic effects of MIBK in humans (280). In the United States, occupational exposure to MIBK is regulated by OSHA, which has set a permissible exposure limit (PEL) of 50 ppm as an 8-h time-weighted average (TWA) and a short-term exposure limit (STEL) of 75 ppm. The American Conference of Governmental Industrial Hygienists (ACGIH) recommends a threshold limit value (TLV) of 50 ppm and a STEL of 75 ppm (281). The EPA has evaluated MIBK for chronic toxicity and has given it a composite score of 4 (scores range from 1 to 100, with 100 being the most toxic) (282). Acute exposure animal tests, such as the LC_{50} and LD_{50} tests in rats, mice, rabbits, and guinea pigs, have demonstrated MIBK to have low acute toxicity by inhalation or dermal exposure and moderate acute toxicity by ingestion (283).

MIBK is a flammable liquid. It has a closed-cup flash point of 16°C, and autoignition temperature of 448°C; it forms explosive mixtures with air with lower and upper explosive limits of 1.2 and 8.0%, respectively. MIBK may form explosive peroxides when exposed to air and can react vigorously with reducing materials (281). MIBK should be stored in tightly closed containers under an inert atmosphere in well ventilated areas.

MIBK is a volatile organic compound that is subject to air pollution control regulations. The purpose of these regulations is to limit the atmospheric release of materials that either could be toxic or could be precursors of ozone and other species associated with photochemical smog. Legislation has become progressively more stringent as the long-term effects of atmospheric pollution have become evident. In the United States, most states have developed their own programs to govern the release of toxic air pollutants (TAPs). Pertinent federal statutes under which MIBK is regulated include the 1986 Superfund Amendments and Reauthorization Act (SARA), Title III (Section 313); the 1990 Clean Air Act Amendments; and the voluntary agreement between the EPA and the Chemical

Manufacturers Association (CMA) termed the 33/50 project. The packaging, handling, and hazard communication requirements related to the transport of hazardous materials, which includes MIBK, is regulated by the Department of Transportation (DOT) (284).

The 1990 Clean Air Act Amendments list 189 hazardous air pollutants (HAPs) (285) that the EPA must regulate to enforce maximum achievable control technology (MACT) to standards which were set by the year 2000. The emission of VOCs in areas of the United States that do not meet national standards for ground level ozone (ozone nonattainment areas) is also regulated under the 1990 Clean Air Act Amendments. The 33/50 project calls for reduction of emissions of 17 specified solvents to predetermined levels by 1995. SARA provides a mechanism by which the community can be informed of the existence, quantities, and releases of toxic chemicals, and requires that anyone releasing specific toxic chemicals above a threshold level to annually submit a toxic chemical release form to the EPA.

The impact of these regulations is to require users and producers of MIBK to limit release by either reformulating to new solvent systems, installing environmental control systems that recover and/or recycle MIBK, or reducing emissions with carbon absorption beds or incineration equipment.

In the United States MIBK is regulated as hazardous waste under the Resource Conservation and Recovery Act (RCRA), which gives the EPA authority to control hazardous waste from “cradle to grave.” This includes the generation, transportation, treatment, storage, and disposal of hazardous waste. The goal of RCRA are to protect human health and the environment from the hazards posed by waste disposal, to conserve energy and natural resources through waste recycling and recovery, to reduce or eliminate the amount of waste generated, and to ensure that wastes are managed in a manner that is protective of human health and the environment. According to the Toxic Release Inventory (TRI), 156 million lb of waste MIBK were managed in 1997. Of this, 77 million lb were recycled, 48 million lb were used in fuel blending for energy recovery, and 15 million lb were treated and disposed of by other methods. Additionally 16 million lb were released on and off-site (286).

MIBK is not likely to persist in the environment (274). MIBK will volatilize from soil and water and is subsequently degraded by reaction with hydroxyl radicals (reaction half-life, 16–17 h) or direct photolysis in the atmosphere (reaction half-life, 15 h) (287). Photolysis from soil and water surfaces can occur (287). Aerobic biodegradation occurs in soils, fresh water, and saltwater. MIBK is not expected to be bound to sediment or suspended organic matter and is expected to be mobile in soil and subject to leaching from landfills (287). MIBK is not expected to bioconcentrate in fish or other aquatic organisms (287), and its toxicity for microorganisms, fish, algae, and aquatic invertebrates is low (274).

7. Uses

The principal end uses for MIBK in the United States are given in Table 6 (11).

The majority of MIBK consumed in the United States is used as a solvent for surface coatings. MIBK is classified as a medium boiler and is used

Table 6. **Uses for MIBK in United States**[a]

	U.S. MIBK consumption, × 10^6 lb					
	Solvent applications					
Year	Surface coatings	Solvent / extraction	Other	Rubber antiozonant	Specialty surfactants	Total
1988	100	10	13	25	3	151
1989	110	10	12	26	4	162
1990	105	8	10	20	3	146
1991	100	8	11	21	3	143
1992	100	8	11	21	4	144
1993	94	8	7	21	5	135
1994	104	9	7	22	7	149
1995	102	9	8	23	9	151
1996	105	11	8	23	10	157
1997	104	10	8	23	10	155
1998	103	10	8	24	10	155

[a] Ref. 11. Courtesy of SRI International.

extensively in nitrocellulose lacquers, epoxy, acrylic, alkyd, and vinyl resin based coating systems, as well as in polyurethane paints. Although MIBK is classified as a volatile organic compound (VOC), demand continues to be high, particularly for use in high solids coatings, where the superior solvent properties of oxygenates such as MIBK are required.

MIBK is used in a variety on nonsurface-coating solvent applications. It is used as a solvent in adhesives, ink and dye formulations, and in textile and leather finishing. It is used in the purification and extraction of antibiotics and other pharmaceuticals, and in the manufacture of agricultural chemicals. MIBK is an effective extraction/separation agent for metals, and is used to separate plutonium from uranium, niobium from tantalum (274), and zirconium from hafnium (289,290). As a versatile extracting agent, it is also used to dewax mineral oils (291), refine tall oil, and purify stearic acid, butanol, and ethanol.

As a raw material, MIBK is used in the manufacture of rubber antiozonants, such as *N*-(1,3-dimethylbutyl)-*N′*-phenyl-*p*-phenylenediamine. Reaction of MIBK with acetylene yields acetylenic surfactant glycols used in ink, paint, and pesticide formulations. MIBK is also used in the manufacture of MIBC, which is primarily used as a lube oil additive and as a frother in treating copper ores and coal. Other applications of MIBK include use as an ethanol denaturant, as a synthetic flavoring adjuvant, in food contact packaging materials, and in dry cleaning preparations.

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