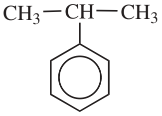
CUMENE

1. Introduction

Cumene [98-82-8] (1-methylethylbenzene, 2-phenylpropane, isopropylbenzene), C_9H_{12}, is an aromatic compound. It is a clear liquid at ambient conditions. High purity cumene is manufactured from propylene and benzene. It is used primarily for the manufacturing of phenol and its coproduct acetone, which are two important petrochemicals with many uses in the chemical and polymer industries. Cumene production in 1998 was estimated to be 3.0 million metric tons in the United States and 7.0 million metric tons in the world (1).



Cumene was first synthesized in large quantities during World War II as an aviation gasoline. It has a high heating value and a high octane number but is not economically competitive as a fuel. Its presence in gasoline now is incidental, being an inevitable minor reaction product of refinery processes such as catalytic reforming and steam cracking. On purpose production of cumene was considered a rather dull business for many years, but has generated considerable excitement recently for two reasons. First, the demand for phenol in the manufacturing of polycarbonates is accelerating, owing to the broadening applications of polycarbonates in the electronic, healthcare, and automobile industries. Second, successful development and commercialization of the zeolite based alkylation technology for the isopropylation of benzene to cumene has rendered obsolete the older processes based on solid phosphoric acid and aluminum chloride. Within a period of just over 2 years during 1996–1998, over one-half of the cumene capacity in the world was converted to the new technology. In many instances, this conversion has more than doubled the nameplate cumene capacity.

2. Properties

Physical, chemical, and thermodynamic properties of cumene are listed in Tables 1 and 2 (2–6). Its transport and other properties of cumene are available in graphical form in the literature (6).

3. Manufacture

Cumene is manufactured by reacting benzene and propylene in the liquid phase over an acidic catalyst:

$$C_6H_6 + CH_2{=}CHCH_3 \rightleftharpoons C_6H_5CH(CH_3)_2$$

The forward reaction, commonly called alkylation, is highly favored thermodynamically. However, actual propylene conversion may be limited by catalyst activity and mass transfer. *n*-Propylbenzene is the isomer more thermodynamically favorable than cumene, but is produced only as a minor by-product because the primary carbon in the propylene molecule is less reactive than the secondary carbon. The secondary carbon is chemisorbed on the acidic site of the catalyst to form a carbonium ion that then reacts with benzene to form cumene. A high selectivity to cumene over *n*-propylbenzene, by a ratio approaching 10,000 : 1, is necessary for a successful commercial process since the isomers cannot be separated economically by distillation or other methods.

Table 1. **Physical Properties of Cumene**

Property	Value
freezing point, °C	−96.03
boiling point, °C	152.39
density, g/cm^3	
0°C	0.8797
20°C	0.8633
40°C	0.8465
refractive index, n_D^{20}	1.4915
thermal conductivity at 25°C, W/(m · K)	0.124
viscosity, mPa · s (= cP)	
0°C	1.073
20°C	0.790
40°C	0.610
surface tension at 20°C, mN/m (= dyn/cm)	28.2
vapor pressure, kPa[a]	
35°C	1
100°C	21
120°C	40
140°C	73
180°C	196
flash point, °C	33
autoignition temperature, °C	425
flammable limits in air, vol %	
lower	0.9
upper	6.5

[a] Calculated from the equation: $\ln P = A - B/(t + C)$; where t = temp, °C; P = vapor pressure, kPa[b]; A = 13.99; B = 3400; and C = 207.78.

[b] To converted kPa to mm Hg, multiply by 7.5.

Table 2. **Chemical and Thermodynamic Properties of Cumene**

Property	Value
relative molar mass	120.2
critical temperature, °C	358.0°C
critical pressure, kPa[a]	3220
critical density, g/cm^3	0.280
heat of vaporization at bp, J/g[b]	312
heat of vaporization at 25°C, J/g[b]	367
heat of formation (liquid) at 25°C, J/mol[b]	−44, 150
free energy (vapor) at 25°C, J/mol[b]	137,000
heat of combustion at constant pressure and 25°C, J/g[b]	
gross (product water as liquid)	43,370
net (product water as vapor)	41,170
heat capacity (liquid) at 25°C, J/(mol · K)[b]	197
heat capacity (ideal vapor) at 25°C, J/(mol · K)[b]	153
characteristic odor	aromatic
odor threshold, ppmv	1.2
threshold limit value, ppmv	50

[a] To convert kPa to atm, divide by 101.3.

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

Part of the cumene formed from the above reaction is further alkylated to diisopropylbenzenes:

$$C_6H_5CH(CH_3)_2 + CH_2{=\!=}CHCH_3 \rightleftharpoons (CH_3)_2CHC_6H_4CH(CH_3)_2$$

which in turn may be alkylated to triisopropylbenzenes and tetraisopropylbenzenes. The diisopropylbenzenes, triisopropylbenzenes, and tetraisopropylbenzenes are collectively called polyiospropylbenzenes (PIPB), and can be reverted to cumene by reaction with benzene:

$$(CH_3)_2CHC_6H_4CH(CH_3)_2 + C_6H_6 \rightleftharpoons 2\ C_6H_5CH(CH_3)_2$$

This reaction is called transalkylation. Alkylation is an exothermic reaction but transalkylation is essentially isothermal.

Excess benzene is used in alkylation to moderate the temperature rise caused by the heat of reaction, to hinder the formation of polyisopropylbenzens, and to suppress oligomerization of propylene. A high ratio of benzene to propylene is advantageous for a high selectivity to cumene, but the recovery of a large excess benzene, by distillation, carries an economic penalty in investment and energy consumption. The ability to suppress oligomerization without large excess benzene is key to any new cumene process because oligomers and their derivatives are responsible for most of the yield losses and most of the impurities in the product, including saturated and unsaturated non-aromatics, ethylbenzene, butylbenzenes, and α-methylstyrene.

Until 1996, all of the commercial cumene processes used either solid phosphoric acid (phosphoric acid supported on alumina) or an aluminum chloride complex as the catalyst (7,8) (see ALKYLATION). In 1995, $>80\%$ of the cumene in the world was produced by the solid phosphoric acid (SPA) process licensed by UOP. The SPA process is illustrated in Figure 1. Liquid propylene, typically a mixture of propylene and propane, is mixed with fresh and recycled benzene. About 500 ppm of water is also added to maintain the activity of the catalyst. The mixture is preheated to a temperature in the 180–200°C range and enters a fixed bed reactor at a pressure of ~550 psig. The quantity of the alkylation catalyst is large, approximately 1 kg for each metric ton of annual cumene capacity. For a world scale plant of 300,000 metric tons per year, two alkylation reactors in parallel are typically required. Each reactor is subdivided into three or four beds with internal structures to support the catalyst. Early use of this technology incorporated a benzene/propylene molar feed ratio of typically 8:1. Subsequent improvement with interbed injection of propylene reduced the feed molar ratio to 5:1. The reactors operate adiabatically with part of the heat of reaction absorbed by the vaporization of propane that is recycled with the benzene.

The reactor effluent is sent to a depropanizer/rectifier to recover the propane that enters the process with the propylene feedstock as Liquefied Petroleum Gas (LPG), to recycle some propane to the reactor, to recover part of the unreacted benzene, and to preheat the fresh benzene. The remaining unreacted benzene is recovered in the benzene recycle column (RC). The C_6 nonaromatics that were contained in the benzene feedstock, and that were made from oligomerization of propylene, are also rejected in this column by purging, often called

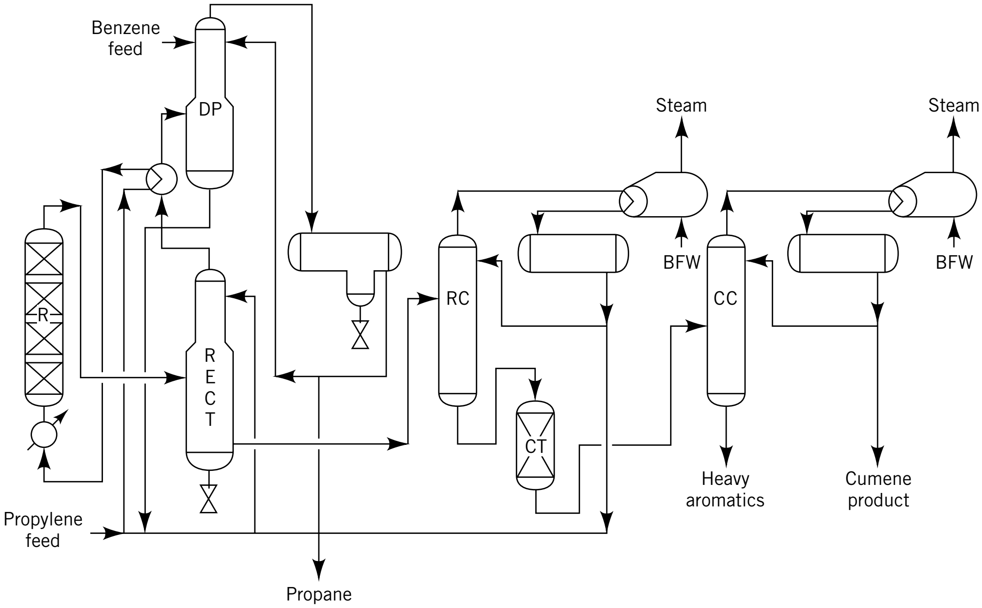


Fig. 1. UOP catalytic condensation process for cumene synthesis. R = reactor; RECT = rectifier; DP = depropanizer; RC = recycle column; CT = clay treater; CC = cumene column; and BFW = boiler feed water. Courtesy of UOP Research Center, Des Plainis, Ill.

the "benzene drag". Benzene drag can be reduced by concentrating the nonaromatics in a separate column or in the benzene column with a special design to take the bulk of the benzene as a side stream. The benzene column bottoms are distilled in the cumene column (CC) to recover purified cumene in the overhead. A plant based on this process may also include one or more clay treaters (CT), which remove oligomers by converting them to heavier material, which can be easily separated by distillation.

The cumene column bottoms, called heavy aromatics, consists of polyisopylbenzenes, hexylbenzenes, other higher alkylbenzenes, heavy nonaromatics, and diphenyl compounds. It has a high octane number and is often used for gasoline blending. However, the future of this application is in doubt in view of proposed regulations to limit high boilers in gasoline (known as T190). This stream represents a yield loss of $\sim$5%. Efforts were made to develop technologies to recover the diisopropylbenzene and to convert it to cumene by transalkylation. However, commercialization was unsuccessful mainly because the heavy aromatics contain high concentrations of impurities, particularly hexylbenzenes, that are in the boiling range of diisopropylbenzenes.

In spite of the low yield and marginal product quality, the SPA process was widely accepted because it requires a smaller investment and has greater raw material flexibility than the aluminum chloride process. These advantages are particularly significant when a cumene unit is treated as part of a refinery. It conveniently uses the heavy aromatics for gasoline blending, which was the key reason for many cumene production units being part of refineries, particularly in the United States. Refineries also have raw material cost advantages because the SPA process can accept refinery grade propylene and low purity benzene as the feedstocks. The nonaromatics contained in benzene feedstock and made from propylene oligomerization can be purged by sending a benzene stream from the recycle column to the refinery. The heavy aromatic stream serves as a sink for by-products such as *n*-propylbenzene, α-methylstyrene, cymenes, and butylbenzenes.

The aluminum chloride process is capable of transalkylating PIPBs back to cumene, thus giving a higher yield, which can be the decisive consideration to a producer who cannot use the heavy aromatics profitably. In this process, alkylation is carried out at a temperature below 100°C and at low pressure. The propylene feedstock must be either chemical grade (95%) or preferrably polymer grade. The benzene feed is dehydrated to maintain the activity of the catalyst and to minimize its corrosivity. The reaction section is expensive because it requires Hastelloy, glass-lined, or brick-lined construction, and the reactor effluent must be thoroughly washed to remove the aluminum chloride before it enters the distillation section. The disposal of the spent catalyst solution has also become an environmental issue. The ability to transalkylate PIPB allows this alkylation to be carried out with a low benzene/propylene ratio of ~2:1, which makes the benzene recycle column relatively small. The cumene column is similar to that in the SPA process. An additional column is used to separate PIPBs from the residue. The residue, ~1% of the cumene yield, is used as a fuel. The recovered PIPB is reacted with benzene in a transalkylator to form additional cumene. The aluminum chloride process is available for licensing from Kellogg based on a process developed by Monsanto.

Since 1996, there have been extensive conversions and expansions of existing cumene plants from the earlier SPA or aluminum chloride technologies to zeolite-based processes (9–11). As of 1999, over one-half of the worldwide demand of cumene can be met from plants using zeolite-based technologies.

For >25 years, the cumene industry had been searching for a technology that would eliminate corrosion and waste disposal problems and give high yield and high product purity while reducing the capital investment and energy consumption. The demand for high-purity cumene increased as more cumene was consumed for the production of polycarbonates via phenol and bisphenol A. One process that meets these criteria is the Mobil/Badger cumene process, available for licensing from Badger Technology Center of Washington Group International. Other zeolite-based cumene processes include those developed by CDTech, Dow/Kellogg, and UOP.

The Mobil/Badger zeolite-based cumene process is illustrated in Figure 2. The process is based on ExxonMobil's proprietary MCM-22 catalyst and was jointly developed by the ExxonMobil and the Washington Group. The process includes a fixed bed alkylation reactor, a fixed bed transalkylation reactor, and a distillation section. Propylene and benzene are premixed and fed to the alkylation reactor where propylene is completely reacted in the liquid phase. The alkylator effluent flows to the depropanizer where nonreactive propane is recovered as LPG. The depropanizer bottoms flows to the recycle column where excess benzene is recovered and recycled to the reactors. The crude cumene from the benzene column bottoms flows to the cumene column where high purity cumene

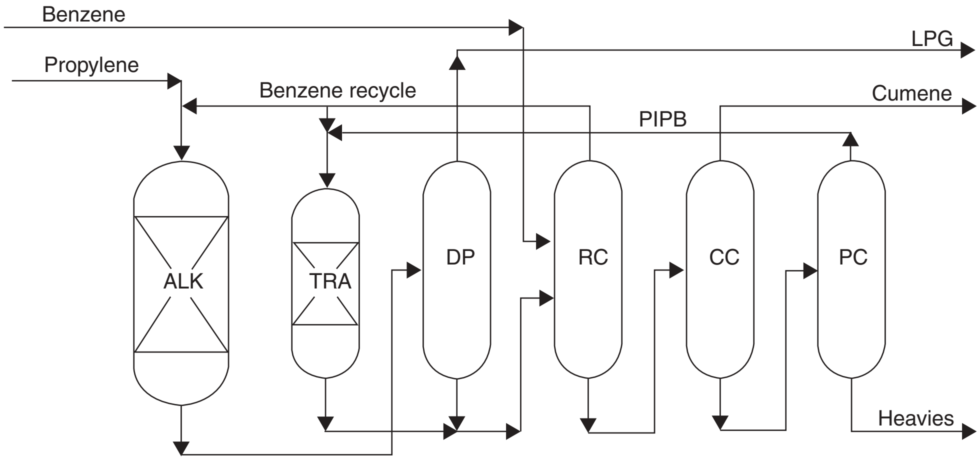


Fig. 2. Mobil/Badger cumene process. ALK = alkylationreactor; TRA = transalkylation reactor; DP = depropanizer; RC = recyclecolumn; CC = cumene column; and PC = PIPB column. Courtesy of Washington Group International.

product is recovered overhead. The cumene column bottoms is sent to the PIPB column where PIPB is recovered and sent to the transalkylator. In the transalkylator, PIPB reacts with benzene to form additional cumene. The transalkylator effluent joins the depropanizer bottoms and flows to the recycle column.

The main features of the Mobil/Badger cumene process include a low benzene/propylene ratio, clean reactions in simple and small reactors, simple distillation, nearly stoichiometrical yield, maximum feedstock flexibility, and minimal environmental impact. These features lead to low capital and operating costs and high product purity. Most existing SPA and aluminum chloride cumene plants can be converted to the Mobil/Badger process with a capacity expansion of 30 to >100% with minimal capital investment. As of 1999, seven licensed plants are in operation with a combined capacity equivalent to >45% of the world cumene demand. Five more plants with a combined capacity equivalent to another 20% of the worldwide cumene demand are in the design and construction stage.

4. Economic Aspects

Cumene production follows the demand for phenol and its derivatives. In 1998, the U.S. domestic cumene production was estimated at 3.0 million metric tons and the consumption was ~2.7 million metric tons (1). The balance was exported. Based on a trend from 1989 on, the demand is projected to increase at ~3% per year through 2003 (12).

Exact costs per metric ton for cumene are difficult to assess because nearly one-half of the cumene is made captively; that is, the cumene is produced at a site, then further processed to phenol at the same site. Therefore, the “price” for the cumene depends on internal transfer prices for the benzene and propylene

Table 3. **Cost of Cumene Production per Metric Ton Cumene**

Factor	Consumption, t	Typical cost, $	Manufacturing cost, %
benzene charge	(0.651)	226	53
propylene charge, 95% purity	0.351	167	39
by-product (credit at $250/t)	(0.002)	(1)	(10)
utilities			
heat and electricity	1600 MJ[a]	5	1
steam credit	(1.1)	(6)	(1)
catalyst and chemicals		3	1
labor, insurance, maintenance, etc		4	1
interest and depreciation at 30% of capital		32	7
Total		*430*	

[a] To convert MJ/t cumene to Btu/lb, divide by 2.324.

feedstocks, as well as other internal costs. This information is closely held by individual producers.

From 1985 through 1998, the cumene list price fluctuated between $375 and $465 per metric ton, ending up at $465 per metric ton in the first half of 1998 (1,13). In August of 1998, the United States list price for bulk quantities of cumene dropped to $320 per metric ton. This weakening in the price of cumene was partly due to phenol capacity addition lagging the cumene expansion projects, which are mostly complete between 1996 and 1998 (12). A compilation of prices from then until April 2001 shows cumene prices improved significantly to $450 per metric ton in late 1999 and improved further to $560 per metric ton in early 2001 (13).

In a modern cumene plant, the cost of production is made up of the factors shown in Table 3. The feedstocks accounts for ~90% of the cost. Other operating costs, such as utilities, labor, and capital charges, make up the difference.

5. Specifications and Analytical Methods

Cumene sold as merchant grade for chemical purposes is usually produced to the specifications listed in Table 4. Captively manufactured cumene typically is not held to such strict values, although 99.9% purity is common.

6. Health and Safety Factors

Cumene is a significant fire hazard when exposed to flame or sparks and is in the class of liquids that can be ignited under almost all normal temperature conditions (5). Cumene has an autoignition temperature of 425°C and a flash point of 33°C (14). The lower and upper flammable limit of cumene is 0.9 and 6.5% by volume, respectively. Outside or detached storage is preferred. Inside storage should be in a standard flammable liquid storage warehouse, room, or cabinet, separate from oxidizing material, nitric acid, and sulfuric acid. In fighting

Table 4. **Frequently Used Specifications for Cumene**

Property	Test	Value
specific gravity, 15.5°C/15.5°C	ASTM D891	0.864 min/0.867 max
bromine index	ASTM D1492	5 max
color	ASTM D1209	10 max
sulfur compounds, as ppmw S	ASTM D4045	1 max
product assay		
cumene, wt%	ASTM D3760	99.9 min
ethylbenzene, ppm	ASTM D3760	50 max
n-propylbenzene, ppm	ASTM D3760	300 max
butylbenzenes, ppm	ASTM D3760	50 max

cumene fires, use water, dry chemical, foam, or carbon dioxide (14). Use water spray to keep fire-exposed containers cool. Water may be ineffective in controlling or extinguishing cumene fires (15).

Cumene is a primary skin and eye irritant. Exposure may result in significant narcosis, headache, and nausea. Because the depressant action has a slow induction period and a long elimination period, possible cumulative effects need to be considered. The recommended threshold limit value (TLV) is 50 ppm (245 mg/m^3), which is an 8-h time-weighted average for exposure to cumene (16). A skin notation included in earlier issues was removed in 1998 (16). The permissible exposure limit for cumene, which is an 8-h time-weighted average given by the Occupational Safety and Health Administration (OSHA), is also 50 ppm (245 mg/m^3), with a skin designation (17).

Cumene is expected to exist almost entirely in the vapor phase in the atmosphere (18). In water, mixed cultures of microorganisms collected from various locations and depths in the Atlantic Ocean were all found capable of degrading cumene (19). A number of studies have examined the aerobic degradation of cumene in seawater and groundwater (20,21). The results indicate that cumene would normally be naturally degraded to below detectable limits within 1 week to 10 days. The solubility of cumene in water is ~50 mg/L at 20°C (22). Cumene is tightly adsorbed and is not significantly mobile in soil (23).

7. Uses

Virtually all the cumene produced is used as feedstock for the production of phenol (qv) and its coproduct acetone (qv). The cumene oxidation process for phenol synthesis has been growing in popularity since the 1960s and is prominent today. The first step of this process is the formation of cumene hydroperoxide [80-15-9]. The hydroperoxide is then selectively cleaved to phenol [108-95-2] and acetone [67-64-1] in an acidic environment (24).

Phenol, in its various purity grades, is used for bisphenol-A employed in making epoxy resins (qv) and polycarbonates (qv) (33% of the phenol produced), for phenolic resins to bond construction materials like plywood and composition board (30%), and for caprolactam (qv), the starting material for nylon-6 (14%). Minor amounts are used for alkylphenols (qv) and others (24).

Acetone supply is strongly influenced by the production of phenol, and so the small difference between total demand and the acetone supplied by the cumene oxidation process is made up from other sources (25). The largest domestic use for acetone is methyl methacrylate [80-62-6] (45% of the acetone production), followed by bisphenol A [80-05-7] (20%), and solvent (17%). Methyl methacrylate is expected to continue growing at a modest rate through the early years of the next decade (26). In solvent uses, acetone has benefited from its removal from the U.S. government's Volatile Organic Compounds (VOC) list.

α-Methylstyrene [98-83-9] is produced in controlled quantities from the cleavage of cumene hydroperoxide, or it can be made directly by the dehydrogenation of cumene. In 1998, about 2% of the cumene produced went to α-Methylstyrene (27). α-Methylstyrene is used for acrylonitrile–butadiene–styrene resins (ABS, 34% of production), for *p*-cumyl phenol (PCP, 22%), and others.

Cumene in minor amounts is used as a thinner for paints, enamels, and lacquers. It is also used to produce acetophenone, dicumylperoxide, and DIPB and is a good solvent for fats and resins. As such, cumene has been suggested as a replacement for benzene in many of its industrial applications (28).

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