

THE PRODUCTION OF CUMENE USING Zeolite CATALYST Aspen Model Documentation

Index

- Process Summary
- About This Process
- Process Definition
- Process Conditions
- Physical Property Models and Data
- Chemistry/Kinetics
- Key Parameters
- Selected Simulation Results:
 - Blocks
 - Streams
- References

Process Summary

This Aspen Plus model simulates the production of cumene by the alkylation of Benzene using Propylene and Zeolite catalyst.

The plant is designed to have a capacity of 595 million lb/yr (270,000 t/yr) of cumene at a 0.9 stream factor. This capacity is sufficient to supply cumene to a world-scale phenol plant of about 200,000 t/yr (440 million lb/yr).

About This Process

Essentially all cumene produced worldwide is used as a feedstock in phenol plants, which convert it to phenol and acetone by cumene peroxidation. Therefore, the cumene and phenol markets are strongly tied. From 1993 to 1998, world cumene demand grew at a rate of 4.7%/yr, increasing from 5.6 million to 7.1 million t/yr. Through 2003, in accordance with announced phenol additions, demand is forecast to grow at 4.2%/yr in North America and 5.1%/yr worldwide. Worldwide cumene capacity was estimated at 9.5 million t/yr in 1998 and is projected to reach 10.4 million t/yr by year-end 2003. Starting in 1996, several cumene producers have completed plant revamps using the new zeolite catalyst technology. Because these expansions were introduced ahead of the corresponding phenol additions, the operating rate of the world cumene industry declined from 82% in 1995 to about 74% in 1998. The operating rate is expected to recover after the planned start-up of major phenol expansions in 1999 and 2000.

The main end uses for cumene, as a phenol intermediate, are bisphenol A, phenolic resins, and caprolactam. Bisphenol A is produced from phenol and acetone, with end-use applications in polycarbonate and epoxy resins. A shift in the phenol derivatives market has taken place in recent years, with bisphenol A overtaking phenolic resins as the major driver for phenol growth. Consequently, pressure has increased for product improvements in both phenol and acetone, in turn creating demand for higher quality cumene produced upstream.

In addition to bisphenol A, the main drivers for acetone demand are methyl methacrylate and solvent applications. The growth expected in these markets is lower than that of phenol, which has led to increasing concern over future acetone oversupply. Competitive routes for phenol production, without coproduction of acetone, are still being pursued. Recently, Solutia announced a one-step process for making phenol from benzene, which bypasses the cumene intermediate [see PEP Review 97-6, One-Step Phenol from Benzene by the AlphOx Process (December 1998)]. These alternative phenol processes are not expected to pose a serious threat to the cumene industry in the near future.

TECHNICAL ASPECTS

The only chemical route to cumene in current commercial practice is the alkylation of benzene with propylene over an acid catalyst. This report evaluates three processes for cumene production, which are respectively based on the following catalysts: solid phosphoric acid (SPA), aluminum chloride (AlCl₃), and zeolites. Brief descriptions of the technologies, along with a discussion of their advantages and limitations, are provided below.

The Solid Phosphoric Acid-Based Process

UOP developed the cumene process using SPA catalyst in the 1940s. It was basically adapted from a refinery process that converted light olefins into gasoline components. Until the early 1990s, the SPA process was the dominant technology for cumene production, with more than 40 plants licensed worldwide.

The SPA catalyst is a composite of phosphoric acid and a solid binder material, such as kieselguhr or diatomaceous earth. Benzene alkylation with propylene is carried out in fixed bed reactors, at 180–240°C (360–464°F). Propylene conversion is nearly total, and selectivity of benzene to cumene is about 95%. The main reaction by-products are polyisopropylbenzenes (PIPB) such as di- and tri-isopropylbenzene.

In the product recovery section, a two-stage rectified flash system recovers part of the unconverted benzene and removes the propane contained in the propylene feedstock. The enriched cumene stream is then separated in two distillation columns: a benzene fractionator and a cumene purification column. The latter column separates overhead cumene product from a stream containing the heavy polyalkylates.

The main limitations of the SPA technology are related to product purity and yield, as well as operational and environmental issues. Phosphoric acid is not sufficiently active to promote the transalkylation of PIPB back to cumene. PIPB and other heavy components must be removed in the bottoms of the last distillation column, resulting in yield losses. To minimize the formation of PIPB, as well as of propylene oligomers, the process typically employs a high benzene/propylene (B/P) feed ratio of in the reaction system.

Because of the high operating temperatures in the SPA-based reactor, the catalyst is subject to dehydration and requires the controlled addition of water for proper performance. If excessive water is introduced, the SPA pellets tend to agglomerate, resulting in shorter catalyst life and difficulties in unloading the reactor. The catalyst is not regenerable and must be disposed of after 6 to 18 months of continuous operation.

The Aluminum Chloride-Based Process

AlCl_3 has long been used as a catalyst in liquid-phase alkylation processes, particularly in the production of ethylbenzene from benzene and ethylene. In the 1970s, Monsanto and Lummus introduced a modified version of the technology, using small concentrations of AlCl_3 in a homogeneous liquid-phase reactor. During the 1980s, three cumene producers in the United States, France, and Finland retrofitted their SPA-based plants into single-phase AlCl_3 -based processes. This technology, currently licensed by Kellogg, was also employed in a grassroots cumene plant in Taiwan that came onstream in 1995.

In the Monsanto-Kellogg process, the catalyst is a mixture of anhydrous AlCl_3 and hydrogen chloride, which is completely dissolved in the liquid hydrocarbon phase. Benzene alkylation takes place below 135°C (275°F), and at sufficient pressure to keep the reactants in the liquid phase. The alkylation effluent is mixed with recycle PIPB and fed to a transalkylation zone, where PIPB is converted back to cumene in an equilibrium reaction. A three-stage wash system, with water and caustic solution, removes the AlCl_3 catalyst from the reaction product. Next, a series of four distillation columns is used for overhead separation of propane (contained in the fresh propylene), unconverted benzene, cumene product, and PIPB. A small stream of high boiling compounds is separated in the bottoms of the last column.

Because PIPB can be recycled to extinction in the reaction system, the Monsanto-Kellogg process achieves an overall selectivity of benzene to cumene of about 99%. Product purity is also improved over the SPA-based process, because the AlCl_3 catalyst reduces propylene oligomerization and suppresses the formation of t-butylbenzene (a final product impurity). High-quality cumene can be obtained with a relatively low B/P feed ratio (between 2 and 3, on a molar basis). Another feature of the homogeneous catalyst system is that AlCl_3 is

used on a once-through basis. From an operational perspective, this feature is an advantage because changes in catalyst activity can be compensated for by simply adjusting the catalyst feed rate. However, the spent catalyst solution creates a waste disposal problem. In some cases, a 25% AlCl_3 solution can be recovered as a flocculating agent for water treatment applications. Nevertheless, these applications usually require tight control of contamination by hydrocarbons, particularly by benzene.

An additional drawback of the use of AlCl_3 and hydrogen chloride is that they are highly corrosive. Special materials of construction must be used in the reaction and catalyst separation systems.

The Zeolite-Based Process

Zeolite catalysts have been commercially employed in ethylbenzene processes since 1980. Their use for cumene production, however, required additional years of research. In 1992, Dow added a zeolite transalkylation reactor to its SPA-based cumene plant at Terneuzen, the Netherlands. In the next few years, cumene processes based completely on zeolite technology started to be offered for license. Examples include the processes developed by Mobil-Badger, UOP, and CDTech (a partnership between ABB Lummus Global and Chemical Research & Licensing).

Between 1996 and 1998, several cumene expansions employing zeolite technology were completed worldwide. In the United States, 7 cumene plants were retrofitted from SPA to zeolite technology, with 4 using the Mobil-Badger process and 3 using UOP technology. The CDTech process will be used in a grassroots plant planned for construction in Taiwan by 2000. EniChem also developed its own zeolite technology, which was employed to revamp its SPA-based facilities at Porto Torres, Italy.

Except for the CDTech process, which combines catalytic reaction and distillation in a single column, all zeolite-based processes consist of essentially the same flowsheet configuration. The alkylation reaction is carried out in fixed-bed reactors at temperatures below those used in SPA-based processes. When refinery-grade propylene is used as a feedstock, the effluent from alkylation is sent to a depropanizer column that removes propane overhead. A separate transalkylation reactor converts recycled PIPB and benzene to additional cumene. The bottoms of the depropanizer are then mixed with the transalkylation reactor effluent and fed to a series of three distillation columns. Benzene, product cumene, and PIPB are respectively separated in the overhead of each column, with PIPB and benzene recycled to the reaction system. A small stream of heavy aromatics is separated in the bottoms of the PIPB column.

Like the AlCl_3 catalyst, zeolites are sufficiently active to transalkylate PIPB back to cumene. Overall selectivity of benzene to cumene is quite high, varying from 99.7% to almost stoichiometric, depending on the nature of the zeolite employed. Product purities as high as 99.97% can be obtained, with B/P feed ratios between 3 and 5.

A particular advantage of the zeolite catalysts is that they are regenerable and can be used for several cycles. Therefore, the waste disposal problems associated with SPA and AlCl_3 catalysts are greatly reduced. In addition, carbon steel can be used as the material of construction throughout the plant because of the mild operating conditions and the absence of highly corrosive compounds.

One limitation of the zeolite technology is potential poisoning of the catalyst by contaminants in the feed. Depending on feedstock quality, guard beds or additional feed pretreatment may thus be required. If refinery-grade propylene is used, for example, its sulfur content must be closely controlled.

The zeolite technology was introduced for the commercial production of cumene in the early 1990s. The first installation of a completely zeolite-based cumene process, which uses Mobil-Badger technology, went on stream at Georgia Gulf's plant in 1996. In addition to Mobil-Badger, UOP and CDTech offer zeolite-based processes for licensing. The technology has been extensively used by cumene producers to retrofit existing solid phosphoric acid (SPA) based plants, allowing significant gains in production capacity and product purity. Several grassroots cumene plants employing zeolites have also been announced.

This section presents conceptual designs and economics for two versions of the zeolite-based process—one employing refinery-grade and the other using chemical-grade propylene as feedstock. The designs are intended to resemble the processes using conventional fixed-bed alkylation reactors, as in the technologies of Mobil-Badger, UOP, and Dow-Kellogg. PEP Review 92-3-4, *Cumene by a Catalytic Distillation Process* (1994), evaluated the cumene process using a catalytic distillation reactor (licensed by CDTech).

REVIEW OF TECHNICAL DEVELOPMENTS

Zeolites are porous crystalline materials composed of a three-dimensional framework of SiO_4 and AlO_4 tetrahedra, each with a silicon or aluminum atom in the center. These tetrahedra are cross-linked by the sharing of adjacent oxygen atoms, forming ring structures that are characteristic of each type of zeolitic material. The number of tetrahedra in the rings determines the size of the pores and channels within the zeolite framework. High reaction selectivities can be obtained with zeolite catalysts, partly because of the molecular sieving effect of the zeolites. PEP Report 153A, *Catalysts* (1996), provides a more detailed discussion of zeolite properties, preparation, and applications.

Medium-pore zeolites (such as Mobil's ZSM-5) are well-known alkylation catalysts, particularly in the vapor-phase production of ethylbenzene. These catalysts normally require the use of high reaction temperatures to achieve acceptable rates of benzene diffusion. For cumene production, however, high temperatures lead to excessive formation of n-propylbenzene (NPB) and propylene oligomers, as well as fast catalyst deactivation (435305). Thus, most recent research has focused on the use of wide-pore zeolites, such as zeolite Y (faujasite-type), modernite, and zeolite beta. The main challenge has been to develop a zeolite combining high activity, selectivity, and stability for cumene production (639092, 639132, 639136, 639139).

The Dow-Kellogg process is based on a highly dealuminated modernite catalyst, coded 3 DDM, with a two- or three-dimensional channel system (639005, 639007, 639092, 639136). UOP has filed two patents on cumene production with zeolite beta (639022, 639109) and holds the rights to patents assigned to Unocal using steam-stabilized zeolite Y (330773, 517045, 639015, 639081, 639110). Patents describing the catalytic distillation process (licensed by CDTech) mention the use of zeolites Y, beta, or omega (592940, 639105, 639107). Finally, the Mobil-Badger process is based on the MCM-22 zeolite developed by Mobil (560563, 639093, 639130, 639131). Unlike typical wide-pore zeolites (with 12-ring pores), MCM-22 contains 10-ring medium pores and large 12-ring supercages. Other zeolites with diffraction patterns similar to that of MCM-22 have been recently disclosed by Mobil (639008, 639010, 639070, 639087) and by Chevron (482696).

Zeolites are frequently prepared in a sodium form and subsequently treated by ion exchange with acids or ammonium salts. In the case of the ammonium-exchanged zeolite, the acidic form is normally obtained by an additional heating step that releases ammonia. Rare earths, alkaline metals, or other metal components can also be added to the zeolite by ion exchange or impregnation (408681, 639012, 639111, 639114, 639125). To increase the physical strength and attrition resistance of the catalyst, the zeolite crystals are often mixed with a binder material such as clay, silica, or a metal oxide.

Important factors to be controlled in a zeolite include surface area, pore size distribution, crystal size, and Si/Al molar ratio. Many patents mention the use of zeolite dealumination as a way of improving catalyst selectivity and stability (502283, 517045, 517085, 639005, 639022, 639074). By increasing the Si/Al ratio of the zeolite, its acidic activity is reduced because fewer sites are available for protonation. In addition, dealumination may significantly change the pore size distribution of the zeolite, leading to better catalyst performance. Typical methods for dealumination include mineral acid treatment, anhydrous calcination, and hydrothermal (steam) treatment. Some patents claim that additional acid treatment is required after calcination to completely remove nonframework (amorphous) aluminum from the catalyst (517085, 639005, 639022).

The zeolite-based alkylation reaction is typically carried out at 120–180°C (248–356°F) and 300–600 psig, with an overall range for the benzene/propylene (B/P) molar ratio between 3 and 5 and a WHSV of 0.5–50 h⁻¹. As in the AlCl₃-based process, the reaction pressure should be sufficient to keep essentially all propylene in the liquid phase. Therefore, the required pressure varies according to the amount of propane contained in the propylene feedstock.

In a typical configuration, the alkylation reactor consists of a series of fixed catalyst beds with upflow or downflow of liquid reactants. Alternative configurations include moving bed reactors (502880, 517033), which allow continuous regeneration of spent catalyst; and slurry reactors (502944, 639124). In the fixed-bed alkylator, the temperature is usually controlled by the staged injection of propylene feed and by interstage cooling (482696, 517045, 517088, 639005, 639068, 639077, 639113), which allows better control of local temperatures and propylene concentrations along the bed and results in lower by-product formation. Heat exchangers or the staged addition of the benzene feed can be used for interstage cooling. UOP has also disclosed a reactor employing indirect cooling through an internal set of corrugated plates (639023, 639024, 639025).

The catalytic distillation process CDTech uses (435304) allows simultaneous reaction and fractionation of the organic mixture in a single vessel. An essentially benzene-free alkylation effluent is recovered as a bottom product. The upper part of the reactor/column is packed with special bales of fiberglass fabric and steel mesh containing a zeolite catalyst. Fresh benzene is added to the column reflux, whereas propylene is injected below the catalyst bed. PEP Review 92-3-4 provides further details about the CDTech process. CDTech has also disclosed that the propylene conversion in the distillation reactor is limited to about 90%, which requires the use of an additional fixed-bed polishing reactor (639107, 639108).

Acidic zeolites are sufficiently active to transalkylate polyisopropylbenzenes (PIPB) back to cumene. Transalkylation is typically carried out at 130–220°C (266–428°F) and 300–600 psi, with a benzene/PIPB molar ratio range of 4 to 10. Although alkylation and transalkylation can occur simultaneously (639076, 639077, 639125), two separate fixed-bed reactors are normally employed. Some patents also describe using one zeolite catalyst for alkylation and another for transalkylation (482696, 639074).

In a typical zeolite-based process, the separation section includes a depropanizer, a recycle benzene column, a cumene rectifier, and a column for separating recyclable PIPB from small amounts of heavy residue. A portion of the benzene recycle stream is mixed with PIPB and sent to the transalkylation reactor. An additional reactor can also be used to convert diphenylalkanes into lighter aromatics (517088, 639101). In the catalytic distillation process, the alkylation effluent stream is essentially free from benzene, and a separate benzene recycle column is not needed. However, CDTech has disclosed the use of a depropanizer for further fractionation of the distillation reactor overhead (639107).

Compared with alkylation catalyzed by SPA, the zeolite-based alkylation generates a higher amount of diisopropylbenzene (DIPB). However, these by-products can be recycled to extinction in a separate transalkylation reactor, where they are converted to additional cumene. Because only small amounts of heavy compounds are generated, the zeolite-based process can achieve overall cumene yields above 99.5% and product purities as high as 99.97%. In UOP's process, product impurities are claimed to derive primarily from impurities in the feedstocks (639126). A particular advantage of the zeolite catalysts is their regenerability, which allows use for several cycles and results in significantly less waste disposal than required with SPA and AlCl₃ catalysts. Zeolite regeneration can be carried out by thermal treatment in a controlled oxygen atmosphere (517033) or by contacting the catalyst with a stream of hydrogen and benzene (639079).

THE ZEOLITE-BASED PROCESS USING REFINERY-GRADE PROPYLENE

Several cumene producers, especially those in the United States, use captive benzene and propylene feedstocks from integrated refinery facilities. As a result, propylene streams containing relatively large amounts of propane (20–50%) are frequently employed. Below, we present PEP's conceptual design for a zeolite-based plant using refinery-grade propylene (with 30 mol% propane) as feedstock. The plant capacity is 595 million lb/yr (270,000 t/yr) of cumene at a 0.9 stream factor, which is sufficient to supply feedstock to a world-scale phenol plant of about 440 million lb/yr (200,000 t/yr).

Process Definition

Table 1 provides the design bases and assumptions. The process consists of two sections:

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- Section 100—Alkylation
- Section 200—Cumene Recovery.

Section 100—Alkylation

In the alkylation section, benzene is contacted with propylene in a series of two reactors R-101A&B, each of which contains two beds of zeolite catalyst. The aromatic feed is charged into the top of the first reactor at 125°C (257°F), whereas the fresh propylene stream is split between the four catalyst beds. Alkylation takes place at 490 psig, with total conversion of propylene and about 90 mol% of benzene-to-cumene selectivity. The main reaction by-product is DIPB, which is subsequently separated and converted to cumene by transalkylation. Other by-products include small amounts of heavy aromatics and impurities in the cumene product. The adiabatic temperature rise in the catalyst beds is limited to 25°C (45°F) by recycling part of the reaction effluent through cooler E-102. Interstage cooler E-101 is also placed between the two alkylation reactors. Low-pressure (20 psig) steam is generated in both E-101 and E-102. The zeolite catalyst beds have a cycle length of 2 years and are completely regenerable.

Transalkylation of DIPB into additional cumene occurs in a separate reactor, R-102, which contains a zeolite catalyst similar to the one used for alkylation. A DIPB stream from the cumene recovery section is mixed with recycle benzene and heated to 170°C (338°F) in E-103. The reaction is carried out at 250 psig with nearly isothermal conditions and a DIPB conversion of 50%.

Section 200—Cumene Recovery

The liquid effluent from the alkylation reactor is fed to depropanizer C-201, which also serves to dry the fresh benzene stream from T-151. The overhead product is separated into a propane phase, credited as liquefied petroleum gas (LPG), and a small stream of wastewater. From the bottom of C-201, the aromatic stream is mixed with the transalkylation reactor effluent and sent to benzene fractionator C-202, where essentially all benzene is recovered overhead. A small purge stream is removed from the benzene distillate to prevent the buildup of nonaromatic impurities. From intermediate storage in T-201, the benzene stream is heated to 125°C (257°F) in E-205 and recycled to the alkylation and transalkylation reactors.

Cumene is obtained as the overhead product from column C-203. After being cooled in E-208, the product is stored in rundown tanks T-202A&B. The bottom stream from the cumene fractionator is fed to column C-204, which operates under vacuum to recover DIPB overhead. Residue from the bottom of C-204 is cooled in E-211 and sent to disposal as fuel. The DIPB stream, after intermediate storage in T-203, is recycled to the transalkylation reactor.

Hot oil is used in the reboilers of all distillation columns and in transalkylation feed heater E-103. Cumene condensation in E-206 generates low-pressure steam (60 psig), most of which is used to heat the benzene recycle in E-205. A slop tank, not shown in Figure 7.1, is provided for temporary storage of out-of-specification product.

Process Conditions

Table 1 provides the design bases and assumptions for the process:

Table 1
CUMENE PROCESS USING ZEOLITE CATALYST
AND REFINERY-GRADE PROPYLENE

DESIGN BASES AND ASSUMPTIONS

References	560563, 639022, 639068, 639126
Capacity, lb/yr (t/yr)	595 million (270,000)
Stream factor	0.9
Alkylation reactor	Two reactors, each with two catalyst beds, an intercooler between the reactors, and cold propylene feed to each catalyst bed
Catalyst	Zeolite
Catalyst regeneration frequency, years	2
Catalyst life, years	6
Temperature, °C (°F)	125–150 (257–302)
Pressure, psig	440
WHSV, lb of feed/lb of catalyst/hr	6.0
B/P feed ratio, mole/mole	4.0
Conversion, %	
Propylene	100
Benzene	22.7
Selectivity of benzene to cumene, %	89.9
Selectivity of propylene to cumene, %	81.7
Transalkylation reactor	Single catalyst bed
Catalyst	Zeolite
Catalyst life, years	6
Temperature, °C (°F)	170 (338)
Pressure, psig	250
WHSV, lb of feed/lb of catalyst/hr	4.0
Benzene/DIPB feed ratio, mole/mole	5.0
Conversion of DIPB, %	50
Overall yields, mol%	
Cumene on benzene	99.6
Cumene on propylene	99.9

Physical Property Methods and Data

The Aspen Plus simulation uses the Peng Robinson physical property method.

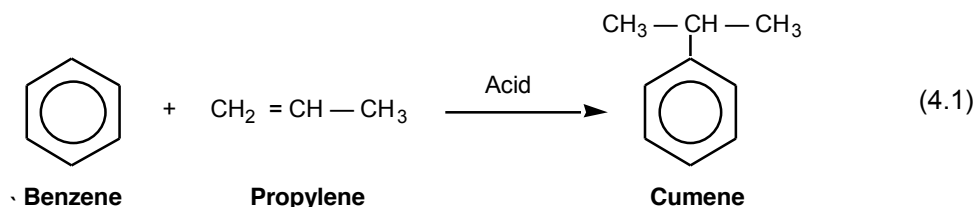
Chemistry/Kinetics

Reactors

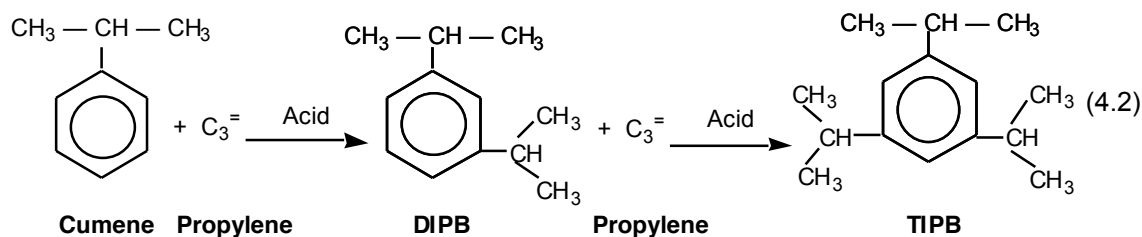
As a chemical intermediate, cumene (or isopropylbenzene) is obtained in a manner very similar to the manufacture of ethylbenzene. All commercial cumene is produced by alkylating benzene with propylene in the presence of an acidic catalyst. This section presents the main chemical reactions involved in cumene synthesis, along with a discussion of final product impurities and quality specifications.

Alkylation REACTIONs

The alkylation of aromatic hydrocarbons belongs to a general class of electrophilic reactions known as Friedel-Crafts reactions (639059). Common Friedel-Crafts catalysts include Lewis acids (AlCl_3 , BF_3), Brønsted acids (H_2SO_4 , H_3PO_4 , HF), and acidic zeolites. In cumene production, propylene acts as the alkylating agent as shown in equation (4.1):



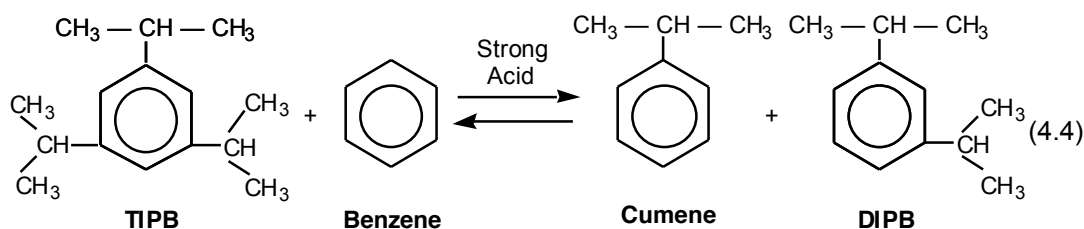
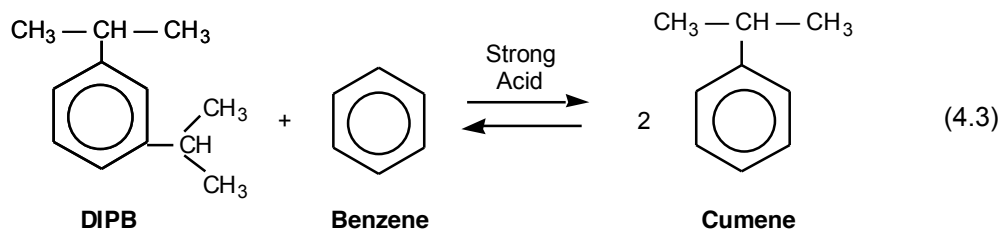
The reaction is exothermic (-23.4 kcal/mole at 250°C), rapid, and irreversible. It can take place with any of the catalysts mentioned above, although AlCl_3 , H_3PO_4 , and zeolites are preferred commercially. Propylene conversions near 100% are usually obtained. During alkylation, a small portion of cumene reacts further with propylene to form higher alkylated products as shown in equation (4.2):



The proportion of *ortho*, *meta*, and *para* configurations of diisopropylbenzene (DIPB) is affected by the type of catalyst used. The *ortho* substitution is usually formed in smaller amounts because of steric hindrance effects. Although DIPB is the dominant by-product, its further alkylation also leads to significant amounts of triisopropylbenzene (TIPB).

Transalkylation reactions

In the presence of a strong acid, DIPB and TIPB can be converted back to cumene. The so-called transalkylation reactions involve the transfer of isopropyl groups between different species, as shown in equations (4.3) and (4.4):



The transalkylation reactions are equilibrium-limited, essentially neutral in terms of heat released, and slower than the alkylation reactions. Processes based on AlCl_3 or zeolite catalysts use transalkylation to improve overall cumene yield by separating DIPB and TIPB from the alkylation reactor effluent and recycling them to extinction in a transalkylation reactor. Solid phosphoric acid, however, has a relatively low acid strength and is not as effective as a transalkylation catalyst.

OTHER side reactions

In addition to DIPB and TIPB, several minor by-products are involved in the chemistry of cumene synthesis. Figure 4.1 shows a diagram of the main side reactions and corresponding by-products that affect the yield and purity of the cumene product. The rate and extent of each individual reaction are influenced by process conditions and by the nature of the acid catalyst employed.

Propylene can oligomerize to form hexenes, nonenes, or even heavier olefins. These by-products affect the Bromine Index, which is a measurement of olefins content in the final product. In addition, the olefin oligomers tend to react with aromatics to form heavier alkylbenzenes, such as hexyl- and nonyl-benzene. Propylene oligomerization can be minimized by increasing the molar ratio of benzene to propylene in the reactor feed. However, larger amounts of benzene in the reaction system result in increased downstream separation costs.

Cracking reactions lead to the formation of ethylbenzene, butylbenzenes, and diphenyl compounds. These reactions may involve either the cracking of a higher alkylbenzene or the cracking of a propylene oligomer followed by benzene alkylation with the lower molecular weight olefins. Some α -methylstyrene may also be produced by cumene dehydrogenation.

The mechanism of cumene synthesis involves the protonation of propylene to form an isopropyl carbocation, which attacks the benzene ring by electrophilic substitution. An undesirable side reaction, known as "hydride transfer," occurs when carbocation abstracts an hydride ion (H) from the side chain of an alkylated aromatic (639014). Cumene, for instance, may be attacked by the isopropyl carbocation to form a cumyl carbonium ion. This intermediate may then react with a molecule of benzene and generate diphenylpropane. A variety of bi-aromatic compounds can be formed, depending on which alkylated aromatic and which specific carbon is attacked by the carbocation. The hydride transfer reactions also lead to the coproduction of alkanes, such as propane and isomers of hexane.

Another important side reaction is the isomerization of cumene to form n-propylbenzene (NPB). This reaction is reversible, with NPB being slightly favored over cumene at equilibrium conditions (639131). In addition, the rate of NPB generation is strongly temperature-dependent. Thus, isomerization must be kinetically controlled by the proper selection of reaction conditions (temperature, catalyst properties). An alternative route for NPB formation is the nonselective reaction of benzene with propylene.

Impurities in the benzene and propylene feedstocks can also lead to the formation of a number of by-products. Propane is the main impurity in the propylene feed, with concentrations typically in the range of 4–8% for chemical grade and 30–50% for refinery-grade propylene. However, propane is inert during alkylation and is usually recovered in the cumene process as fuel or liquefied petroleum gas. Minor propylene impurities include ethylene, butylene, and cyclopropane, which by benzene alkylation may form ethylbenzene, butylbenzenes, and n-propylbenzene, respectively.

Small amounts of methanol and ethanol are occasionally added to the propylene feed to prevent hydrate freezing in pipelines (639126). During alkylation, these contaminants may respectively form toluene and ethylbenzene. Toluene, which is also an impurity in the benzene feed, can lead to the formation of cymenes (isopropyltoluenes). Finally, commercial benzene may contain sulfur compounds like thiophene, which can be readily alkylated to isopropylthiophene (639120).

quality SPECIFICATIONS and product impurities

A shift in the phenol derivatives market has taken place over the last years, with bisphenol A overtaking phenolic resins as the major driver for phenol growth. Consequently, pressure has increased for product quality improvements in both phenol and acetone, and is reflected in higher quality demands for the cumene produced upstream. With the introduction of zeolite technology for cumene production, product purities exceeding 99.95% have become feasible. Therefore, new quality standards for cumene have been established in the merchant market.

Table 4.1 shows typical specifications of merchant-grade cumene, according to the type of catalyst used in the process. Cumene produced for captive consumption may have less stringent specifications, although a minimum purity of 99.9% is usually adopted (639121). A Bromine Index of 50 corresponds to about 400 ppm of olefinic compounds.

The main impurities included in typical cumene specifications are ethylbenzene, NPB and butylbenzenes. However, the final product usually contains small amounts of other impurities,

which can also affect the quality of the phenol produced downstream. Table 4.2 lists important cumene impurities and their corresponding impact on the cumene peroxidation process.

Table 4.1
TYPICAL CUMENE SPECIFICATIONS

	SPA-Based Process	Homogeneous AlCl₃-Based Process	Zeolite-Based Process
Bromine Index	50 max.	5 max.	5 max.
Color	10 max.	10 max.	10 max.
Sulfur Compounds, ppmw of S	1 max.	1 max.	1 max.
Product Purity			
Cumene, wt%	99.9 min.	99.9 min.	99.95 min.
Ethylbenzene, ppm	200 max.	200 max.	50 max.
NPB, ppm	300 max.	150 max.	250 max.
Butylbenzenes, ppm	200 max.	100 max.	50 max.

Source: 639121, 639131, 639135

Table 4.2
CUMENE IMPURITIES

Impurity	By-products Formed by Cumene Peroxidation	Impact on Downstream Phenol Plant
Nonaromatics	Organic acids and others	Yield loss
Ethylbenzene	Acetaldehyde	Acetone contaminant
NPB	Propionaldehyde	Acetone contaminant
Butylbenzenes	—	α -Methylstyrene contaminant
Cymenes	Cresols	Phenol contaminant
Polyalkylates	Alkylphenols	Yield loss
Sulfur compounds	—	Oxidation inhibitors

References

- 319470 McAllister, S.H., et al., "Production of Cumene by Vapor- and Liquid-Phase Alkylation Processes," Chem. Eng. Prog., 43, 4 (April 1947), 189-196
- 319845 Pujado, P.R., et al., "Air vs. Oxygen. Cheapest Route to Phenol," Hydrocarbon Processing, 55, 3 (March 1976), 91-96
- 319940 Ward, D.J. (to UOP), "Cumene Production," US 4,008,290 (February 15, 1977)
- 330754 Ward, D.J. (to UOP), "Solid Phosphoric Acid Catalyzed Alkylation of Aromatic Hydrocarbons," US 4,051,191 (September 27, 1977)
- 435248 Gerwatowski, S. A. (to UOP), "Aromatic Hydrocarbon Alkylation Process," US 4,108,914 (August 22, 1978)
- 435255 Calcagno, B., et al. (to Euteco Impianti), "Process for the Production of Cumene," US 4,341,913 (July 27, 1982)
- 435256 Sartorio, E., et al. (to Euteco Impianti), "Process for the Production of Cumene," US 4,343,957 (August 10, 1982)
- 435265 De Graff, R.R. (to UOP), "Process for Alkylation of Hydrocarbons," US 4,695,665 (September 22, 1987)
- 501859 Ward, D.J. (to UOP), "Integrated Fractionation in the Recovery of Alkylaromatic Hydrocarbons," US 4,555,311 (November 26, 1985)
- 501860 De Graff, R.R. (to UOP), "Aromatic Hydrocarbon Alkylation Process Product Recovery Method," US 4,587,370 (May 6, 1986)
- 502285 Barger, P.T., et al. (to UOP), "Alkylation/Transalkylation Process," US 4,857,666 (August 15, 1989)
- 639059 Olah, G. A., et al., "Friedel-Crafts Alkylations," in Comprehensive Organic Synthesis, Vol. 3 (1991), G. Pattenden, ed., Pergamon Press
- 639027 Ward, D.J. (to UOP), "Hydrocarbon Conversion Process," US 5,177,283 (January 5, 1993)
- 639061 Stine, L.O., et al. (to UOP), "Simultaneous Moving Bed Reaction Process," US 4,072,729 (February 7, 1978)
- 639064 Chao, T.H., et al. (to UOP), "Catalytic Condensation Process," US 5,059,737 (October 22, 1991)
- 639065 Wilcher, F.P., et al. (to UOP), "Solid Phosphoric Acid Catalyst," US 5,081,086 (January 14, 1992)
- 639066 Ferck, D.L., et al. (to UOP), "Effluent Separation Method for Aromatic Hydrocarbon Alkylation Process," US 5,105,041 (April 14, 1992)
- 639102 Imai, T., et al. (to UOP), "Shaped Catalyst Particles Utilizable for the Conversion of Organic Compounds," US 5,043,509 (August 27, 1991)
- 639104 Burton, V.P., et al. (to UOP), "Catalyst Regeneration Method," US 4,062,801 (December 13, 1977)
- 639115 Bishkin, D.B. (to Monsanto), "Alkylation Process Improvement," US 4,291,189 (September 22, 1981)
- 3, 4, 5 639120 Brayford, D.J., "Cumene," in Encyclopedia of Chemical Processing and Design, 14 (1982), 33-52

Reports

Cesar, M., *One-Step Phenol from Benzene by the Alphox Process*, PEP Review 97-6, Process Economics Program, SRI Consulting, Menlo Park, California (December 1998)

Fong, W., *Cumene by a Catalytic Distillation Process*, PEP Review 92-3-4, Process Economics Program, SRI International, Menlo Park, California (May 1994)

Guerra, M., *Phenol*, PEP Report 22C, Supplement C, Process Economics Program, SRI International, Menlo Park, California (March 1991)

Scheeline, H. W., et al., *Styrene*, PEP Report 33, Supplement B, Process Economics Program, SRI International, Menlo Park, California (December 1977)

Smith, R. M., *Catalysts*, PEP Report 153A, Supplement A, Process Economics Program, SRI Consulting, Menlo Park, California (February 1996)

Wang, S. H., ed., *1998 PEP Yearbook International*, Process Economics Program, SRI Consulting, Menlo Park, California (1998)

Wang, S. H., *Styrene*, PEP Report 33, Supplement C, Process Economics Program, SRI International, Menlo Park, California (March 1993)

Yen, Y.-C., *Phenol*, PEP Report 22, Supplement A, Process Economics Program, SRI International, Menlo Park, California (September 1972)

Yen, Y.-C., *Phenol*, PEP Report 22, Supplement B, Process Economics Program, SRI International, Menlo Park, California (December 1977)

Yen, Y.-C., et al., *Styrene*, PEP Report 33, Process Economics Program, Stanford Research Institute, Menlo Park, California (October 1967)

Yen, Y.-C., et al., *Styrene*, PEP Report 33, Supplement A, Process Economics Program, SRI International, Menlo Park, California (March 1973)

Chemical Economics Handbook, SRI Consulting, Menlo Park, California

World Petrochemicals Program, SRI Consulting, Menlo Park, California

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