Cumene Production

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INTRODUCTION

The history of the cumene market has been examined in great detail with much discussion regarding product usage, emerging markets, and process economics over the past 10–20 yr.[1] With more than 90% of the world's phenol production technology currently based on the cumene hydroperoxide route, it is the focus of this entry to review the latest technology improvements in cumene processing made over the past 10 yr. Current state-of-the-art processes for the production of cumene as a feedstock for phenol involve zeolitic catalyst technology offerings from UOP, Badger Licensing (formerly ExxonMobil and the Washington Group), and CDTech based on zeolitic catalysis. Much of the improvements in these technologies relate to yield, stability, and operating costs.

CUMENE PRODUCTION

Cumene is produced commercially through the alkylation of benzene with propylene over an acid catalyst. Over the years, many different catalysts have been used for this alkylation reaction, including boron trifluoride, hydrogen fluoride, aluminum chloride, and phosphoric acid. Cumene processes were originally developed between 1939 and 1945 to meet the demand for high-octane aviation gasoline during World War II.[2,3] By 1989, about 95% of cumene demand was used as an intermediate for the production of phenol and acetone. Today, nearly all cumene is used for production of phenol and acetone with only a small percentage being used for the production of α-methylstyrene. The demand for cumene has risen at an average rate of 2–4% per year from 1970 to 2003.[4,5] This trend is expected to continue through at least 2010.

Currently, over 80% of all cumene is produced by using zeolite-based processes. Early processes using zeolite-based catalyst systems were developed in the late 1980s and included Unocal's technology based on a conventional fixed-bed system and CR&L's catalytic distillation system based on an extension of the CR&L MTBE technology.[6–9] At present, the Q-Max™ process offered by UOP and the Badger Cumene Technology developed by ExxonMobil and offered by Badger Licensing represent the state-of-the-art zeolite-based catalyst technologies. A limited number of cumene units remain using the fixed-bed, kieselguhr-supported solid phosphoric acid (SPA) catalyst process developed by UOP and the homogenous $AlCl_3$ and hydrogen chloride catalyst system developed by Monsanto.

Solid Phosphoric Acid Catalyst

Although SPA remains a viable catalyst for cumene synthesis, it has several important limitations: 1) cumene yield is limited to about 95% because of the oligomerization of propylene and the formation of heavy alkylate by-products; 2) the process requires a relatively high benzene/propylene (B/P) molar feed ratio on the order of 7/1 to maintain such a cumene yield; and 3) the catalyst is not regenerable and must be disposed of at the end of each short catalyst cycle. Also, in recent years, producers have been given increasing incentives for better cumene product quality to improve the quality of the phenol, acetone, and especially α-methylstyrene (e.g., cumene requires a low butylbenzene content) produced from the downstream phenol units.

For the UOP SPA catalyst process, propylene feed, fresh benzene feed, and recycle benzene are charged upflow to a fixed-bed reactor, which operates at 3–4 MPa (400–600 psig) and at 200–260°C. The SPA catalyst provides an essentially complete conversion of propylene on a one-pass basis. A typical reactor effluent yield contains 94.8 wt% cumene and 3.1 wt% diisopropylbenzene (DIPB). The remaining 2.1% is primarily heavy aromatics. This high yield of cumene is achieved without transalkylation of DIPB and is a key advantage to the SPA catalyst process. The cumene product is 99.9 wt% pure. The heavy aromatics, which have a research octane number (RON) of about 109, can be either used as high-octane gasoline-blending components or combined with additional benzene and sent to a transalkylation section of the plant where DIPB is converted to cumene. The overall yield of cumene for this process based on benzene and propylene is typically 97–98 wt% if transalkylation is included or 94–96 wt% without transalkylation. Generally, it has been difficult to justify the addition of a transalkylation section to the SPA process based on the relatively low incremental yield improvement that it provides.

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ALCL$_3$ AND HYDROGEN CHLORIDE CATALYST

Historically, $AlCl_3$ processes have been used more extensively for the production of ethylbenzene (EB) than for the production of cumene. In 1976, Monsanto developed an improved cumene process that uses an $AlCl_3$ catalyst, and by the mid-1980s, the technology had been successfully commercialized. The overall yield of cumene for this process can be as high as 99 wt% based on benzene and 98 wt% based on propylene.[10] Detailed process flow information is widely published in the literature for this technology.[11] Dry benzene, both fresh and recycled, and propylene are mixed in an alkylation reaction zone with an $AlCl_3$ and hydrogen chloride catalyst at a temperature of less than 135°C and a pressure of less than 0.4 MPa (50 psig).[11] The effluent from the alkylation zone is combined with recycled polyisopropylbenzene and fed to a transalkylation zone also using $AlCl_3$ catalyst, where polyisopropylbenzenes are transalkylated to cumene. The strongly acidic catalyst is separated from the organic phase by washing the reactor effluent with water and caustic. The distillation section is designed to recover a high-purity cumene product. The unconverted benzene and polyisopropylbenzenes are separated and recycled to the reaction system. Propane in the propylene feed is recovered as liquid petroleum gas (LPG).

ZEOLITE CATALYSTS

In the past decade, beta zeolite (given the universal BEA) has rapidly become the catalyst of choice for commercial production of EB and cumene. Mobil invented the basic beta zeolite composition of matter in 1967.[12] Since that time, catalysts utilizing beta have undergone a series of evolutionary steps leading to the development of the state-of-the-art catalysts such as QZ-2000™ catalyst and QZ-2001™ catalyst for cumene alkylation.

Much of the effort between 1967 and the early 1980s involved characterization of the perplexing structure of beta zeolite. It was quickly recognized that the BEA zeolite structure has a large-pore, three-dimensional structure, and a high acidity capable of catalyzing many reactions. But it was not until early 1988 that scientists at Exxon finally determined the chiral nature of the BEA structure, which is shown in Fig. 1.

While the structure of beta was being investigated, new uses for this zeolite were being discovered. A major breakthrough came in late 1988 when workers at Chevron invented a liquid phase alkylation process using beta zeolite catalyst. Chevron patented the process in 1990.[13] While Chevron had significant commercial experience with the use of Y (FAU) zeolite in liquid phase aromatic alkylation, Chevron quickly recognized the benefits of beta over Y as well and other acidic zeolites used at that time, such as mordenite (MOR) or ZSM-5 (MFI).

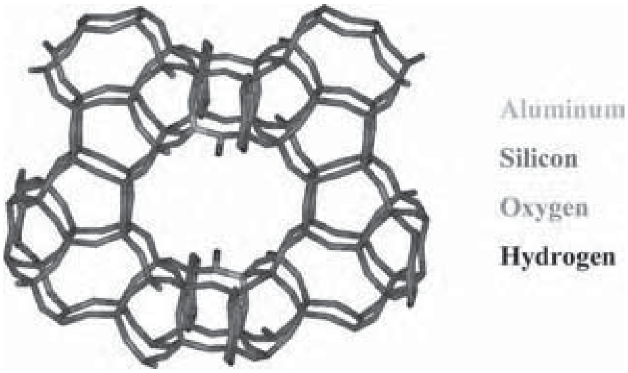

Fig. 1 Beta zeolite. *(View this art in color at www.dekker.com.)*

Fig. 2 shows a comparison of the main channels of these zeolites. Chevron discovered that the open 12-membered ring structure characteristic of beta zeolite coupled with its high acidity made it an excellent catalyst for aromatic alkylation. These properties were key in the production of alkyl aromatics such as EB and cumene in extremely high yields and with product purities approaching 100%. Moreover, Chevron discovered that the combination of high activity and porous structure imparted a high degree of tolerance to many typical feed contaminants.

From a technical perspective, the process developed by Chevron was a breakthrough technology in that the high cumene yields and purities were not attainable by the other vapor phase or liquid phase processes of the day. Nevertheless, the manufacturing cost of beta zeolite was still too high for catalyst producers to make a commercially viable catalyst. UOP, however, developed new manufacturing technology to make a beta zeolite based catalyst a commercial reality. In 1991 a new cost-effective synthesis route was invented by Cannan and Hinchey at UOP.[14] The new synthesis route patented the substitution of diethanolamine, a much less expensive templating agent, for a substantial fraction of tetraethylammonium hydroxide, which had been used in the synthesis previously. Moreover, the route further enables the use of tetraethylammonium bromide (instead of the hydroxide) as an additional cost saving approach. Finally, the new synthesis route allows the practical synthesis of beta over a wider range of silica to alumina ratios, a factor that has a profound effect on the catalyst's performance.

Subsequently, UOP sought to develop zeolitic catalysts that would overcome the limitations of SPA including a catalyst that is regenerable, produces higher cumene yield, and decreases the cumene cost of production. More than 100 different catalyst materials were screened, including mordenites, MFIs, Y-zeolites,

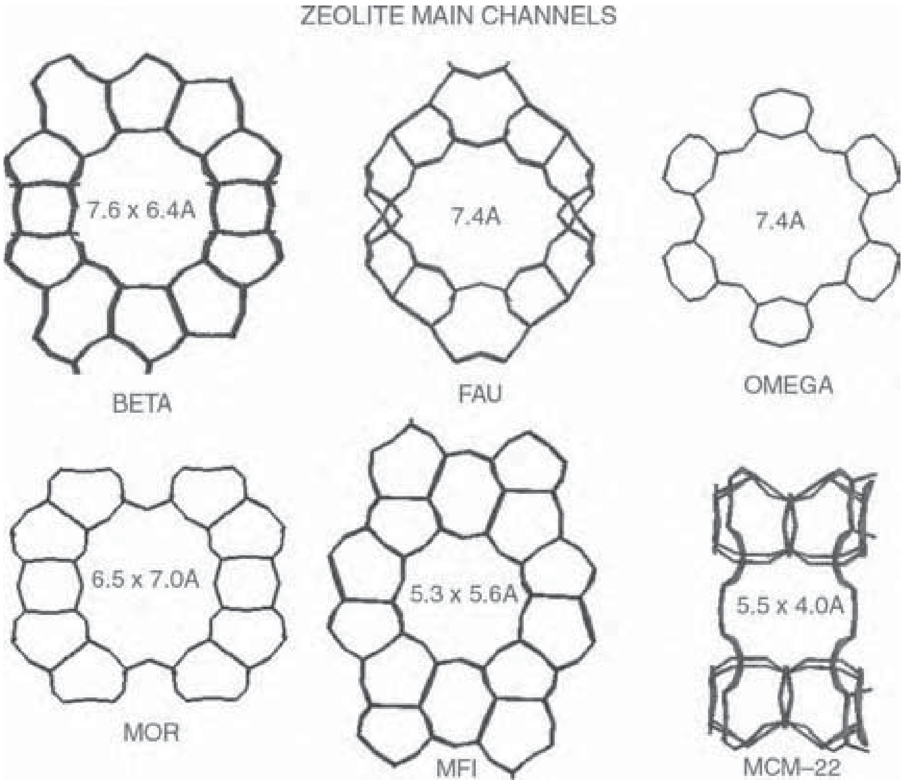

Fig. 2 Comparison of various zeolites. *(View this art in color at www.dekker.com.)*

amorphous silica–aluminas, and beta zeolite. The most promising materials were modified to improve their selectivity and then subjected to more rigorous testing.

On the process side, Unocal developed an early liquid phase fixed-bed reactor system based on a Y-type zeolite catalyst in the 1980s.[15] The higher yields associated with the liquid phase based process were quickly recognized and adapted by the industry with the selectivity to cumene generally falling between 70 and 90 wt% based on converted benzene and propylene dependent on operating conditions. Major side products in the process are primarily polyisopropylbenzenes, which are transalkylated to cumene in a separate reaction zone to give an overall yield of cumene of about 99 wt%. The distillation requirements involve the separation of propane for LPG use, the recycle of excess benzene to the reaction zones, the separation of polyisopropylbenzene for transalkylation to cumene, and the production of a purified cumene product.

By 1992, UOP had selected the most promising catalyst, based on beta zeolite, for cumene production and then began to optimize a liquid phase based process design around this new catalyst. The result of this work led to the commercialization of the UOP Q-Max process and the QZ-2000 catalyst in 1996. More recently in 2001, UOP commercialized a new alkylation catalyst, QZ-2001, which offers improved stability and operation as low as 2 B/P molar feed ratio. The low B/P feed ratio (2) represents the lowest in the industry and affords cumene producers the option to expand capacity and/or revamp existing fractionation equipment with significant cost savings.

The Q-Max process flow scheme based on a liquid phase process is shown in Fig. 3. The alkylation reactor is divided into four catalyst beds contained in a single reactor vessel. Fresh benzene feed is routed through the upper-mid section of the depropanizer column to remove excess water that may be present in the fresh benzene feed. Relatively dry benzene is withdrawn from the depropanizer for routing to the alkylation reactor. Recycle benzene to the alkylation and transalkylation reactors is recovered as a sidedraw from the benzene column. A mixture of fresh and recycle benzene is charged downflow into the alkylation reactor. Propylene feed is divided into portions and injected into the alkylation reactor between the catalyst beds and each portion is essentially completely consumed in each bed. An excess of benzene is used in the alkylation reactor to avoid polyalkylation and to help minimize olefin oligomerization. The alkylation reaction is highly exothermic and the temperature rise in the reactor is controlled by recycling a portion of the alkylation reactor effluent to the reactor inlet to act as a heat sink. In addition, the inlet temperature of each downstream bed is reduced to the same temperature as the first bed inlet by injecting a portion of cooled reactor effluent between beds.

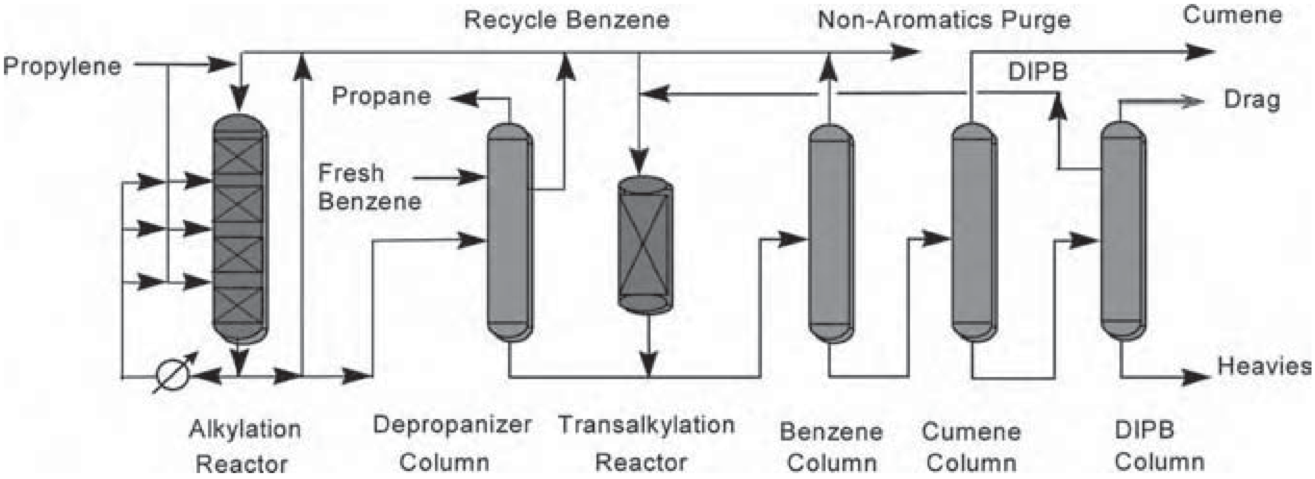

Fig. 3 Q-Max process. *(View this art in color at www.dekker.com.)*

Effluent from the alkylation reactor flows to the depropanizer column, which removes any propane that may have entered with the propylene feed along with excess water that may have entered with the fresh benzene feed. The bottom stream of the depropanizer column goes to the benzene column where excess benzene is collected overhead and recycled. Any trace nonaromatics that may have been in the fresh benzene feed can be purged from the benzene column to avoid an unacceptable accumulation of nonaromatic species in the benzene recycle stream. The benzene column bottom stream goes to the cumene column where the cumene product is recovered overhead. The cumene column bottoms stream, which contains predominantly DIPB, goes to the DIPB column. If the propylene feed contains an excessive amount of butylenes, or if the benzene feed contains an excessive amount of toluene, higher levels of butylbenzenes and/or cymenes can be formed in the alkylation reactor. These compounds are distilled out and purged from the overhead section of the DIPB column. The DIPB stream leaves the DIPB column by a sidedraw and is passed to the transalkylation reactor. The DIPB column bottom stream consists of heavy aromatic by-products, which are normally blended into fuel oil. Steam or hot oil typically provides the heat requirements of the product fractionation section.

The sidedraw from the DIPB column containing mainly DIPB combines with a portion of the recycle benzene and is charged downflow into the transalkylation reactor. In the transalkylation reactor, DIPB and benzene are converted to additional cumene. The effluent from the transalkylation reactor is then sent to the benzene column.

QZ-2000 or the newer QZ-2001 catalyst can be utilized in the alkylation reactor while QZ-2000 catalyst remains the catalyst of choice for the transalkylation reactor. The expected catalyst cycle length is 2–4 yr, and the catalyst should not need replacement for at least three cycles with proper care. At the end of each cycle, the catalyst is typically regenerated ex situ via a simple carbon burn by a certified regeneration contractor. However, the unit can also be designed for in situ regeneration. Mild operating conditions and a corrosion-free process environment permit the use of carbon–steel construction and conventional process equipment.

An alternative zeolite process was developed by CR&L and licensed by CDTech and is based on the concept of catalytic distillation, which is a combination of catalytic reaction and distillation in a single column.[6–9] Catalytic distillation uses the heat of reaction directly to supply heat for distillation of the reaction mixture. This concept has been applied commercially for producing not only cumene but also EB and methyl *tert*-butyl ether (MTBE). The use of a single column that performs both the reaction and the distillation functions has the potential of realizing substantial savings in capital cost by essentially eliminating the need for a separate reactor section. Unfortunately, many available zeolite catalysts that are ordinarily very effective in promoting alkylation in a fixed-bed environment are much less effective when used in the environment of the catalytic distillation column. Also, a separate fixed-bed finishing reactor may be required to ensure that complete conversion (100%) of the olefin occurs to avoid yield losses of propylene to the LPG product stream. As such, the amount of catalyst and physical size of the distillation column may be substantially larger than the benzene column used in the conventional fixed-bed process. Thus, the savings realized by the elimination of the reactor section may be more than offset by the increased catalytic distillation column size, catalyst cost, and addition of a finishing reactor. Depending on the relative values and trade-off of these considerations including utility values, catalytic distillation may still be an appropriate option for producers in certain circumstances, although market interest in this process option for cumene production has been low in recent years.

Zeolitic Alkylation Chemistry

The production of cumene proceeds by a modified Friedel–Crafts alkylation of benzene with propylene. This reaction can be promoted with varying degrees of effectiveness using many different acid catalysts. The basic alkylation chemistry and reaction mechanism are shown in Fig. 4. The olefin forms a carbonium ion intermediate, which attacks the benzene ring in an electrophilic substitution. The addition of propylene to the benzene ring is at the middle carbon of C3 olefin double bond, in accordance with Markovnikov's rule. The presence of the isopropyl group on the benzene ring weakly activates the ring toward further alkylation, producing DIPB and heavier polyalkylate by-products.

Because new high-activity beta zeolite catalysts such as QZ-2000 catalyst are such strong acids, they can be used at lower reaction temperatures than SPA catalyst or other relatively lower-activity zeolites such as MCM-22 catalyst.[16,17] The lower reaction temperature in turn reduces the olefin oligomerization reaction rate, which is relatively high for SPA catalyst. The result is that beta zeolite catalysts tend to have higher selectivity to cumene and lower selectivity to both nonaromatics that distill with cumene (such as olefins, which are analyzed as Bromine Index, and saturates) and heavy by-products. For example, although butylbenzene is typically produced from traces of butylene in the propylene feed, there is always the potential also for butylbenzene to form through the oligomerization of propylene to nonene, followed by cracking and alkylation to produce butylbenzenes and amylbenzenes. As a result of having relatively high activity and operating at relatively low temperature, beta zeolite catalyst systems tend to eliminate oligomerization. This results in essentially no butylbenzene formation other than that formed from the butylenes in the propylene feed. The cumene product from a beta zeolite based process such as the Q-Max process unit fed with a butylene-free propylene feedstock typically contains less than 15 wt ppm butylbenzenes.

The Q-Max process typically produces near-equilibrium levels of cumene (between 85 and 95 mol%) and DIPB (between 5 and 15 mol%). The DIPB is fractionated from the cumene and reacted with recycle benzene at transalkylation conditions to produce additional cumene. The transalkylation reaction is believed to occur by the acid catalyzed transfer of one isopropyl group from DIPB to a benzene molecule to form two molecules of cumene, as shown in Fig. 5

Beta zeolite catalyst is also an extremely effective catalyst for the transalkylation of DIPB to produce cumene. Because of the high activity of beta zeolite, transalkylation promoted by beta zeolite can take place at very low temperature to achieve high conversion and minimum side products such as heavy aromatics and additional *n*-propylbenzene as highlighted in Fig. 6. Virtually no tri-isopropyl benzene is produced in the beta system owing to the shape selectivity of the three-dimensional beta zeolite structure, which inhibits compounds heavier than DIPB from forming.

As a result of the high activity and selectivity properties of beta zeolite, a beta zeolite based catalyst

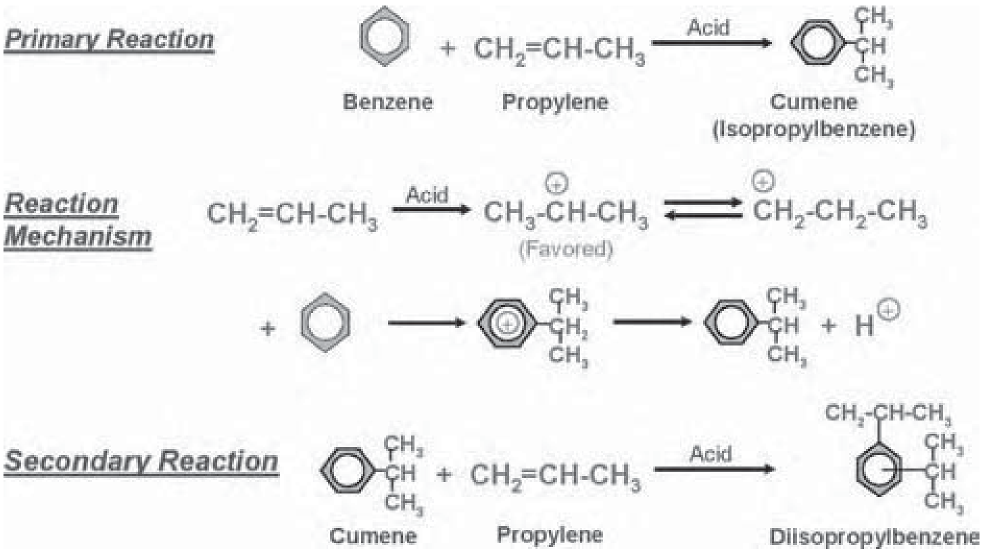

Fig. 4 Alkylation chemistry. *(View this art in color at www.dekker.com.)*

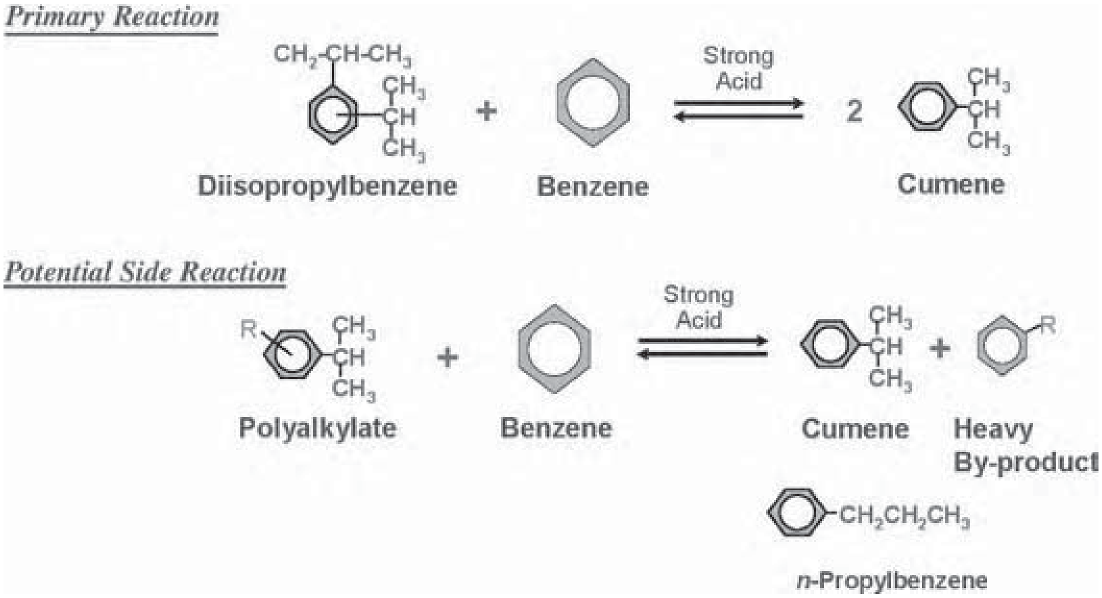

Fig. 5 Transalkylation chemistry. *(View this art in color at www.dekker.com.)*

(e.g., QZ-2001 catalyst or QZ-2000 catalyst) is specified for both the alkylation and the transalkylation sections of the Q-Max process.

With both alkylation and transalkylation reactors working together to take full advantage of the QZ-2001/QZ-2000 catalyst system, the overall yield of cumene based on benzene and propylene feed in the Q-Max process can be at least 99.7 wt% or higher. Because the Q-Max process uses small, fixed-bed reactors and carbon–steel construction, the erected cost is relatively low. Also, because the QZ-2001/QZ-2000 catalyst system is more tolerant of feedstock impurities (such as water, *p*-dioxane, sulfur, etc.) compared to other catalysts available, the Q-Max process requires

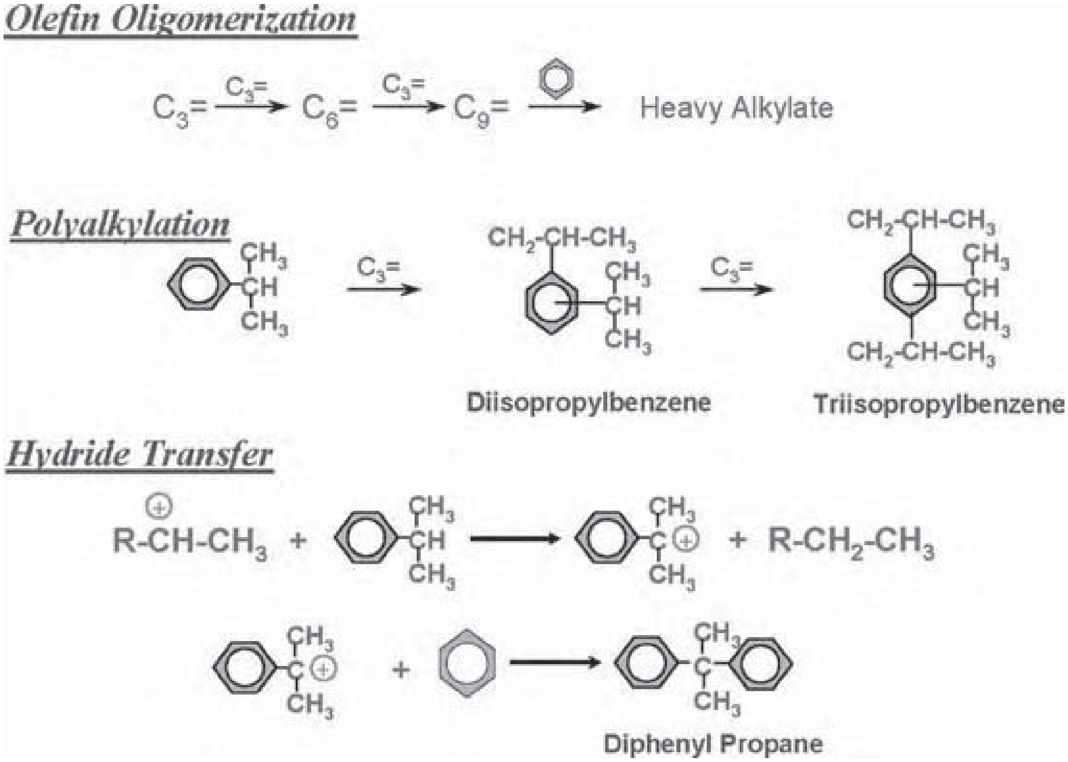

Fig. 6 Possible alkylation side reactions. *(View this art in color at www.dekker.com.)*

minimal pretreatment of the feeds, which further minimizes the capital costs.

This is in distinct contrast to other technologies based on zeolites other than beta where extensive feed contaminant guard beds are required to protect the catalyst from rapid and precipitous deactivation and loss of conversion when exposed to trace amounts of sulfur, water, oxygenates, and nitrogen.

Cumene Product Impurities

Beta zeolite catalyst can be optimized to nearly eliminate all undesirable side reactions in the production of cumene. The improvement in beta zeolite catalyst quality has occurred to the point that any significant impurities in the cumene product are governed largely by trace impurities in the feeds. The selectivity of the catalyst typically reduces by-products to a level resulting in production of ultrahigh cumene product purities up to 99.97 wt%. At this level, the only significant by-product is *n*-propylbenzene with the catalyst producing essentially no EB, butylbenzene, or cymene beyond precursors in the feed. Fig. 7 shows the reactions of some common feedstock impurities that produce these cumene impurities.

Beta Catalyst Resistance to Feed Contaminants

Beta zeolite is a large pore zeolite with optimized acid site densities that exhibits:

- Good mass transfer properties.
- Significant reduction in undesirable polymerization and by-product side reactions.
- High tolerance to feedstock impurities and poisons.

The resistance of new zeolitic catalysts to temporary and permanent catalyst poisons is essential to the economic and commercial success of a zeolitic based cumene process. The following commercial data obtained using beta zeolite as a catalyst illustrates the outstanding ability of beta zeolite to cope with a wide range of feedstock contaminants:

Cyclopropane

n-Propylbenzene (nPB) is formed by alkylation of benzene with cyclopropane or *n*-propanol, and by anti-Markovnikov alkylation of benzene with propylene. Cyclopropane is a common impurity in propylene feed and approximately half of this species is converted to nPB in the alkylation reactor. Essentially, all alkylation catalysts produce some nPB by anti-Markovnikov alkylation of propylene. The tendency to form nPB rather than cumene decreases as the reaction temperature is lowered, making it possible to compensate for cyclopropane in the feed to some extent. As the operating temperature of zeolitic alkylation catalyst is decreased, the deactivation rate increases. However, because of the exceptional stability of the beta zeolite catalyst system, a unit operating with beta zeolite catalyst can be operated for extended cycle lengths and still maintain an acceptable level of nPB in the cumene product. For example, with FCC-grade propylene feed containing typical amounts of cyclopropane,

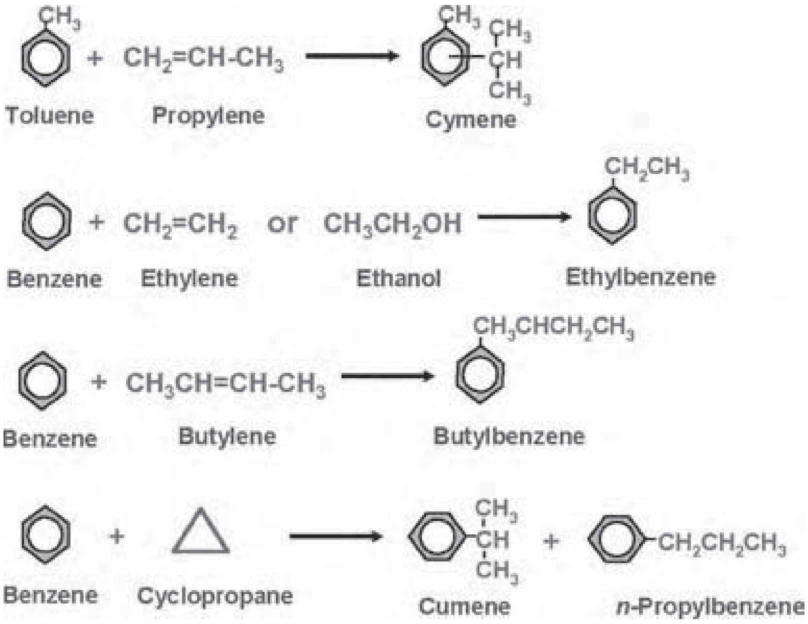

Fig. 7 Reactions of feed impurities. *(View this art in color at www.dekker.com.)*

a beta zeolite based process can produce an overall cumene product containing 250–300 wt ppm nPB while achieving an acceptable catalyst cycle length.

Water

Water can act in this environment as a Bronsted base to neutralize some of the weaker zeolite acid sites. This effect is not harmful to any appreciable extent to the beta zeolite catalyst at typical feed stock moisture levels and under normal alkylation and transalkylation conditions. This includes processing of feedstocks up to the normal water saturation condition (typically 500–1000 ppm) resulting in 10–150 ppm water in the feed to the alkylation reactor dependent on feed and/or recycle stream fractionation efficiency.

Oxygenates

Small quantities of methanol and ethanol are sometimes added to the C_3s in pipelines to protect against freezing because of hydrate formation. Although the beta zeolite catalyst is tolerant of these alcohols, removing them from the feed by a water wash may still be desirable to achieve the lowest possible levels of EB or cymene in the cumene product. Cymene is formed by the alkylation of toluene with propylene. The toluene may already be present as an impurity in the benzene feed, or it may be formed in the alkylation reactor from methanol and benzene. Ethylbenzene is primarily formed from ethylene impurities in the propylene feed. However, similar to cymene, EB can also be formed from ethanol.

p-Dioxane is sometimes present in benzene from extraction units that use ethylene glycol based solvents. It is reported to cause deactivation in some zeolitic alkylation catalysts even at very low ppm levels. However, beta zeolite catalyst appears to be tolerant to *p*-dioxane at levels typically found in benzene extraction processes and does not require costly removal of this impurity.

Sulfur

Sulfur has no significant effect on beta zeolite catalyst at the levels normally present in olefin and benzene feeds considered for cumene production. However, even though the beta zeolite catalyst is sulfur tolerant, trace sulfur that makes its way into the finished cumene unit product may be a feed quality concern for downstream phenol processors where the typical sulfur specification is <1 ppm. The majority of sulfur compounds associated with propylene (mercaptans) and those associated with benzene (thiophenes) are converted to by-products outside the boiling range of cumene. Because some sulfur compounds form by-products that boil within the boiling range of cumene, the sulfur content of the cumene product depends on the sulfur content of the propylene and especially benzene feeds to a certain extent. Sulfur at the levels usually present in propylene and benzene feeds considered for cumene production will normally result in cumene product sulfur content that is within specifications.

Unsaturates

Use of beta zeolite catalyst does not require the benzene feed to be clay treated prior to use in alkylation service. Some of the unsaturated material in the benzene can lead to the formation in the alkylation reactors of polycyclic-aromatic material which will get preferentially trapped in some zeolites having relatively small-sized pores. This can lead to increased deactivation rates in such small-pore zeolites. Beta zeolite's large pore structure makes it possible to more easily handle this polycyclic-aromatic material and as a result does not require further treatment of the benzene feed to remove unsaturated material. In addition, alpha-methylstyrene (AMS) is produced by alkylation of benzene with methylacetylene or propadiene. Some of the AMS alkylates with benzene, forming diphenylpropane, a heavy aromatic that leaves the unit with the DIPB column bottoms.

Nitrogen, Metal Cations, and Arsine

The presence of trace amounts of organic nitrogen compounds and metal cations in the benzene feed or arsine in the olefin feed has been known to neutralize the acid sites of any zeolite catalyst. Good feedstock treating practice or proven guard-bed technology easily handles these potential poisons. For example, basic nitrogen, which can sometimes be present in the benzene fresh feed, is easily removed using very low-cost UOP guard-bed technology. To facilitate monitoring of feeds for potential nitrogen based contaminants, UOP has developed improved analytical techniques to help in the evaluation. These methods include UOP 971 (''Trace Nitrogen in Light Aromatic Hydrocarbons'' by Chemiluminescence) used to detect total nitrogen down to 30 ppb and UOP 974 (''Nitrogen Compounds in Light Aromatic Hydrocarbons'' by GC) used to detect individual nitrogen species down to about 100 ppb.

CURRENT STATE-OF-THE-ART CUMENE TECHNOLOGY

Currently, the major processes for cumene production are liquid phase technologies offered by UOP and

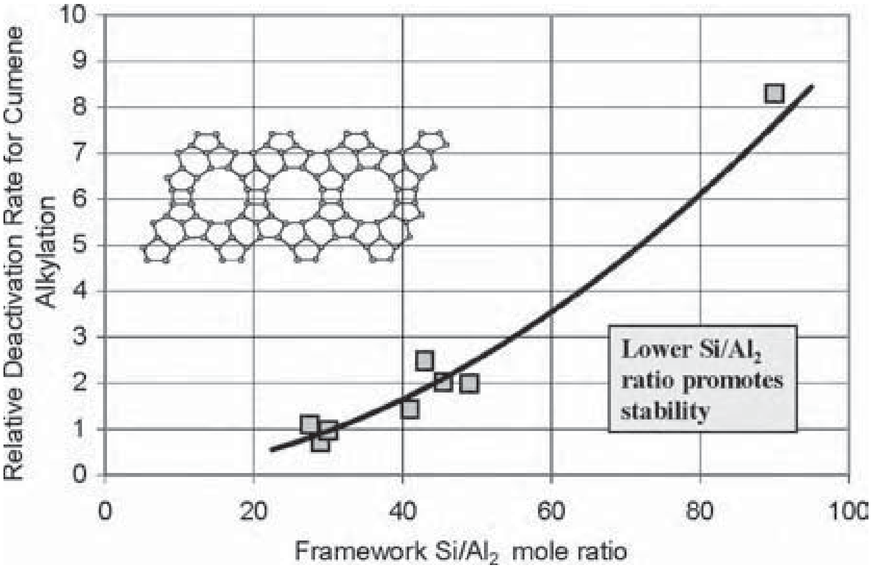

Fig. 8 Effect of framework Al on beta catalyst stability. *(View this art in color at www.dekker.com.)*

Badger Licensing (ExxonMobil technology) based on beta zeolite (such as QZ-2001 and QZ-2000 catalysts) and MCM-22 catalyst, respectively. Over the past decade, great progress has been made in improving and optimizing catalyst formulations for use in applications to produce cumene from benzene alkylation. For example, the ability to synthesize beta zeolite in a wide range of Si/Al_2 ratios has given catalyst designers the ability to tailor the zeolite into a form that optimizes activity and selectivity. A parametric study on the effects of Si/Al_2 ratio on activity and selectivity was published by Bellusi.[18] In this work, it was found that as the silica to alumina ratio was increased from 28 to 70, there was a decrease in both activity and selectivity toward isopropylbenzene-type compounds. Additionally, the less active catalysts had a greater tendency toward oligomerization and were more prone toward coking.

This study parallels work performed at UOP, where, through the use of nonconventional synthesis techniques, samples have also been prepared with Si/Al_2 ratios as low as 10. Through this work it has been found that with a Si/Al_2 ratio of 25, the catalyst maintains sufficient activity to achieve polyalkylate equilibrium (e.g., DIPB equilibrium) and, at the same time, minimizes the formation of heavier diphenyl compounds (and hence maximizes yield) in cumene service.

Perhaps the most critical understanding was developed with regard to the need to minimize the Lewis acidity of the catalyst and at the same time maintain high Brønsted acidity. Studies at UOP demonstrated that olefin oligomerization was directly related to the

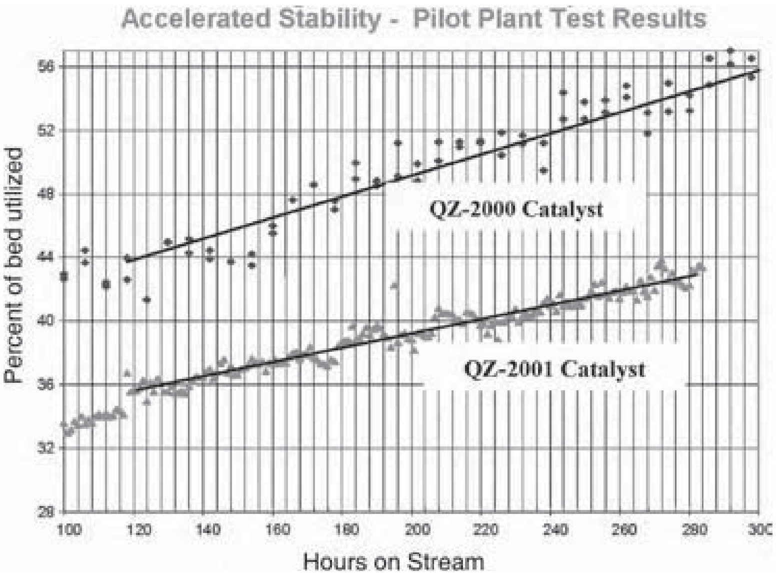

Fig. 9 Stability of QZ-2001 catalyst vs. QZ-2000 catalyst. *(View this art in color at www.dekker.com.)*

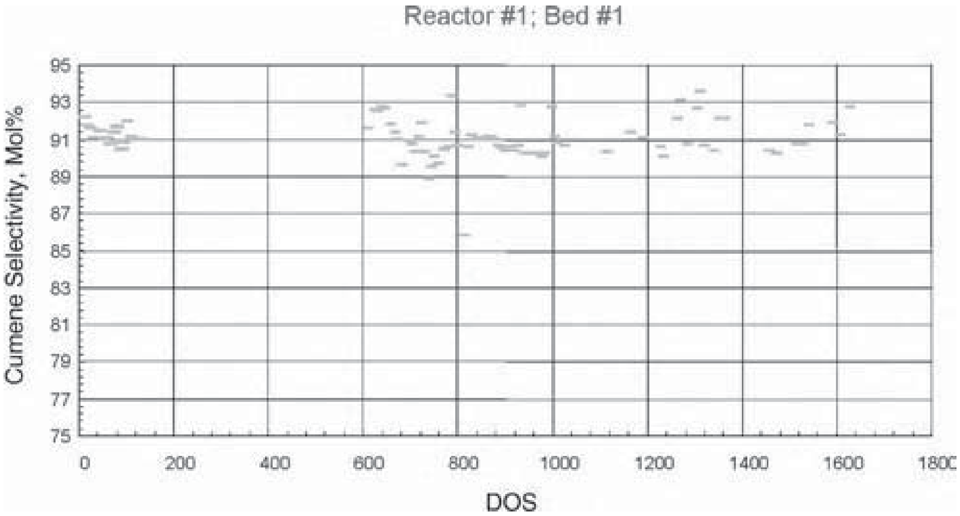

Fig. 10 JLM commercial data on catalyst stability. *(View this art in color at www.dekker.com.)*

Lewis acid function of the catalyst. Olefin oligomerization reactions can lead to the formation of heavy compounds (coke type precursors), which have a negative effect on catalyst stability. Thus, minimization of the Lewis character of the beta leads to a catalyst with high stability. Generally, Lewis acidity in beta zeolite has been attributed to the existence of nonframework aluminum atoms. The most common mechanism for the formation of nonframework alumina is through steam dealumination during the catalyst calcination step of the manufacturing process. By careful control of the temperature, time, and steam levels during the manufacturing process, it is possible to produce a catalyst that is extremely stable at typical alkylation conditions.

From a commercial standpoint this knowledge has had the additional benefit of developing a regeneration protocol that is extremely robust. It has been demonstrated in commercial in situ and ex situ procedures that the beta zeolite catalyst can be regenerated with excellent results providing complete restoration of fresh catalyst performance. The feature of complete regenerability is another attribute that distinguishes beta zeolite catalysts from other commercially available zeolite catalysts such as MCM-22 catalyst, where significant activity and selectivity can be lost upon regeneration.[19] The ability to regenerate catalyst is essential in a commercial environment to provide additional flexibility to cope with a wide range of feedstock sources, feedstock contaminants, and potential operational upsets.

The historical development of beta zeolite showed that early versions of beta catalyst demonstrated less than optimum performance when compared to today's state-of-the-art formulation. Fig. 8 is a plot of the relative stability of beta zeolite as a function of the Si/Al_2 ratio of the beta zeolite structure in which the dominating influence of this parameter is evident. Uop has learned to stabilize the zeolite structure through careful process and chemical means. This has resulted in a catalyst system that is extremely robust, highly regenerable, and tolerant of most common feedstock impurities.

Additional studies of beta zeolite have come to similar conclusions. For example, Enichem has found that beta zeolite is the most effective catalyst for cumene alkylation

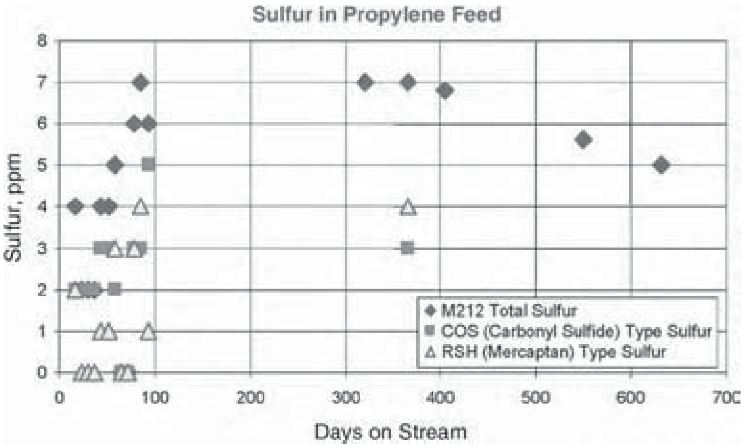

Fig. 11 JLM commercial data on sulfur in propylene feed. *(View this art in color at www.dekker.com.)*

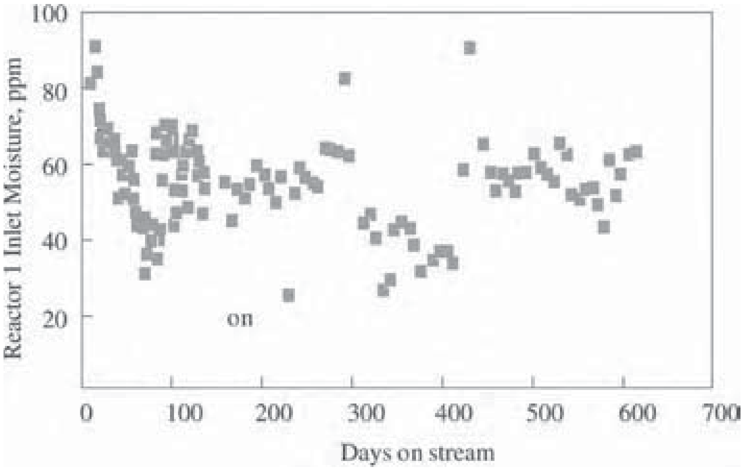

Fig. 12 JLM commercial data on alkylation reactor moisture content. *(View this art in color at www.dekker.com.)*

among other zeolites tested including Y, mordenite, and an isostructural synthesis of MCM-22 catalyst.[20]

The principles described above also led to the development of the new-generation QZ-2001 alkylation catalyst.[21] In Fig. 9, results from accelerated stability testing of QZ-2000 and QZ-2001 catalysts demonstrate the superior stability of the latest catalyst system. QZ-2001 catalyst exhibits as much as twice the stability when compared to QZ-2000 catalyst. The benefit afforded by QZ-2001 catalyst can be utilized by cumene producers in several ways. It can be taken directly through reduction of the catalyst loading for a specific run length, or alternatively as a convenient way to increase run length, or to increase throughput through the cumene unit, by allowing operation at a lower B/P feed ratio.

Long-Term Stability of Beta Zeolite Catalyst

Commercial operation with a wide variety of olefin feedstocks from different sources has demonstrated the flexibility of beta zeolite in the Q-Max process. Refinery grade, chemical grade, or polymer grade propylene feedstocks have been successfully used to make high-quality cumene product in the Q-Max process.

A good example of the ruggedness of the beta zeolite catalyst can be found in the case of JLM's Blue Island (Illinois) Q-Max operation. The operation started in August 1996 as the first Q-Max process operation with UOP beta zeolite catalyst. Initial operating results were reported in 1997.[22] The unit has continued to operate with stable performance for more than 7 yr without catalyst regeneration in spite of the presence of significant levels of feed contaminants.

Excellent monoalkylation selectivity has also been observed over many years of service in the JLM operation as shown in Fig. 10. Under the normal operating conditions of the unit, an equilibrium cumene selectivity of about 91 mol% is predicted. Thus, results clearly show that the beta zeolite catalyst is active enough to achieve near-equilibrium selectivity. This is an important feature of the catalyst as the amount of dialkylate that must be processed in the transalkylator and the subsequent cost of processing this material are minimized.

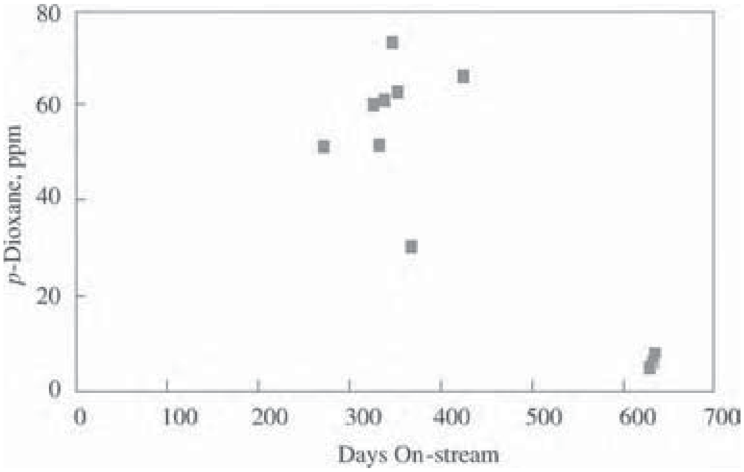

Fig. 13 JLM commercial data on benzene feed *p*-dioxane content. *(View this art in color at www.dekker.com.)*

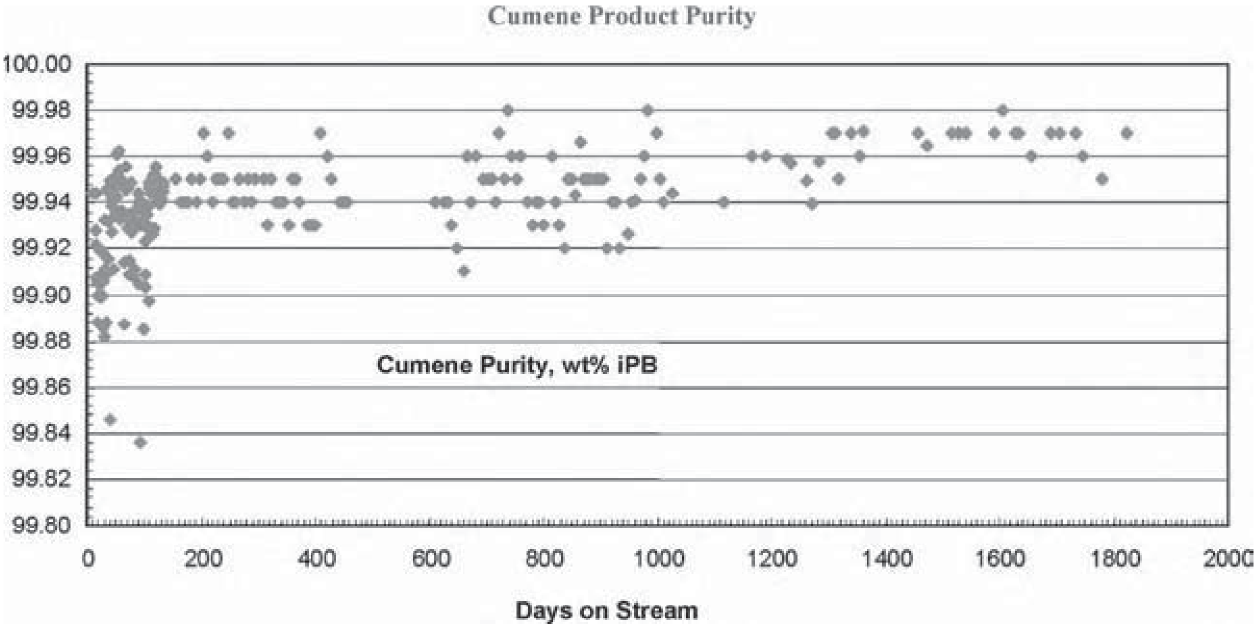

Fig. 14 JLM commercial data on cumene product purity. *(View this art in color at www.dekker.com.)*

Feed contaminants such as sulfur, water, and *p*-dioxane were monitored very closely during the first 2 yr onstream as shown in Figs. 11–13.

The impact of these impurities on cumene product quality was negligible during this period. The customer was able to maintain extremely high-quality cumene throughout the life of the beta catalyst, as shown in Fig. 14.

Another important observation is that sulfur levels from 3 to 7 ppm, moisture levels of 30–70 ppm, and even *p*-dioxane excursions up to 70 ppm had virtually no impact on catalyst stability or performance, as seen in Figs. 10 and 15. Note that the alkylation catalyst selectivity and catalyst bed inlet temperature and weight average bed temperature remain virtually unchanged after years of operation.

Beta Zeolite Catalyst Regeneration

As a result of beta's high activity and robustness, catalyst requirements are minimized. At the end of

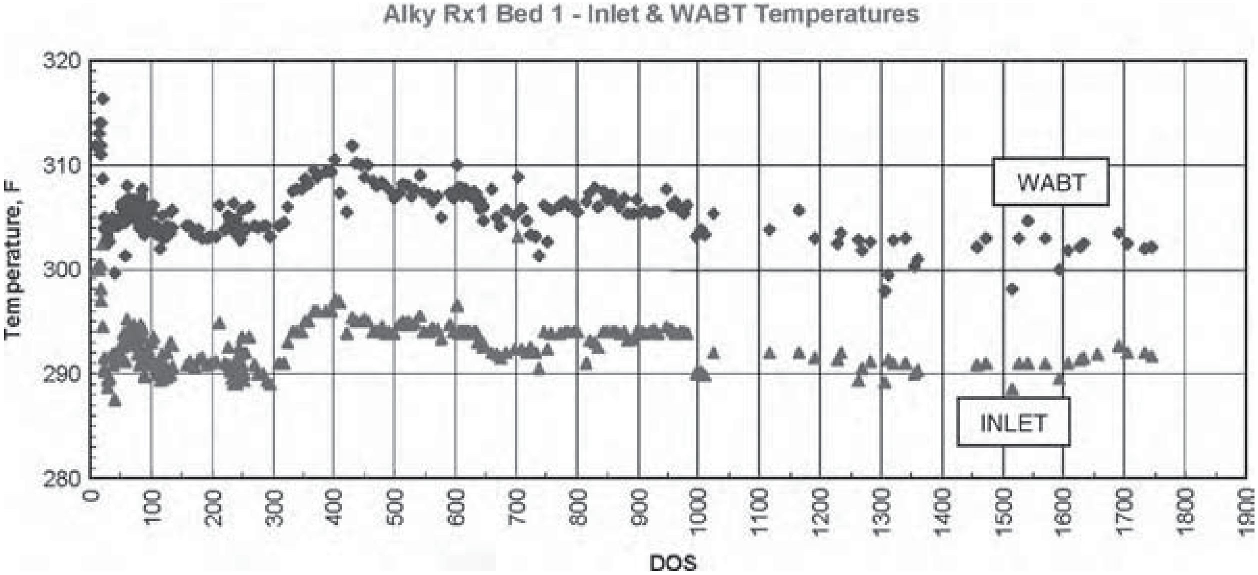

Fig. 15 JLM commercial data. *(View this art in color at www.dekker.com.)*

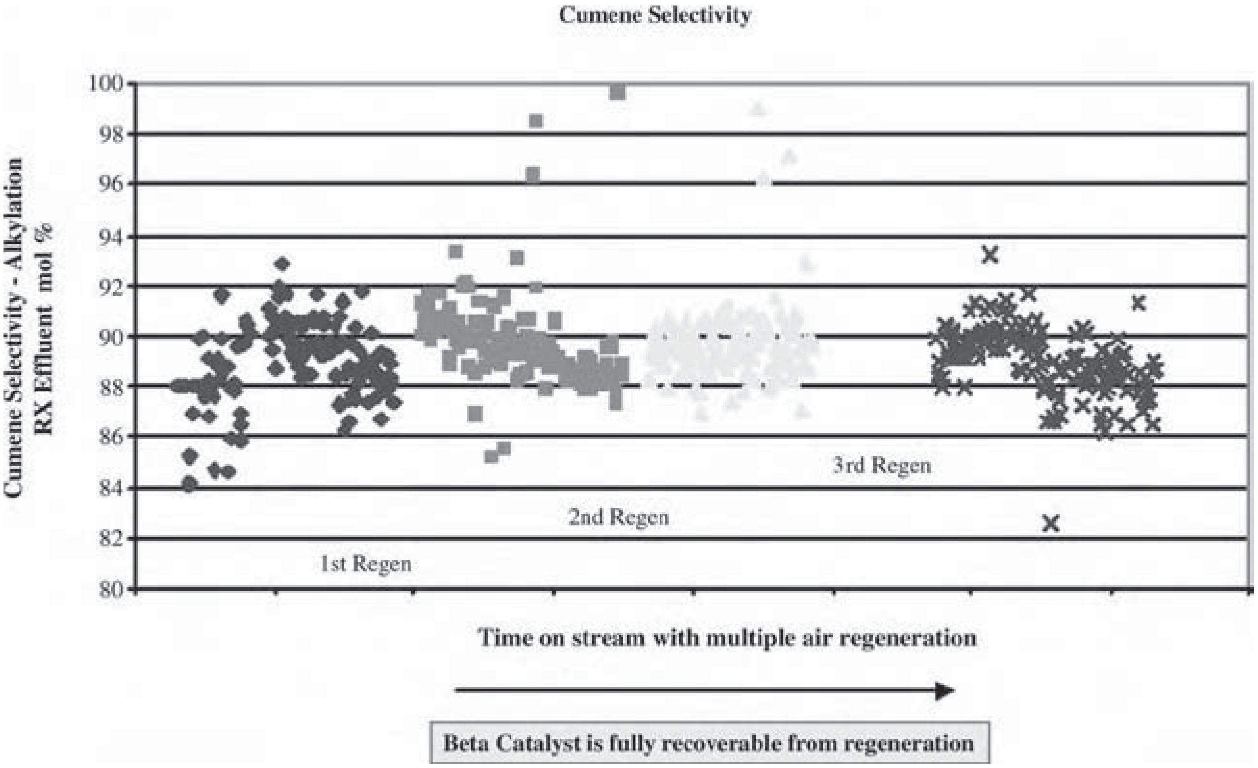

Fig. 16 Commercial Q-Max process data. Effect of in situ QZ-2000 catalyst regeneration on cumene selectivity. *(View this art in color at www.dekker.com.)*

each cycle, the catalyst can be regenerated ex situ by a certified regeneration contractor. The regenerability of beta zeolite catalyst provides an ultimate life of three cycles or more if appropriate processing and regeneration guidelines are followed. If desired, the Q-Max process unit can be designed to accommodate in situ catalyst regeneration. Both options have been successfully demonstrated in commercial operation.

Figs. 16 and 17 show an example of the performance of QZ-2000 catalyst after multiple in situ

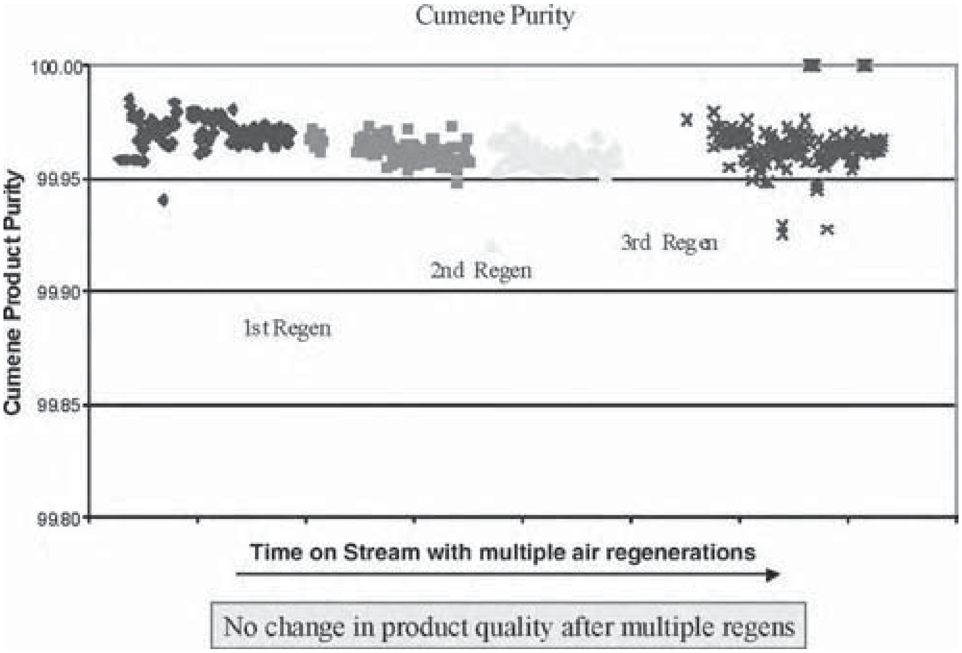

Fig. 17 Commercial Q-Max process data. Effect of in situ QZ-2000 catalyst regeneration on cumene purity. *(View this art in color at www.dekker.com.)*

regenerations in a commercial cumene unit. The cumene unit experienced premature deactivation because of excessive basic nitrogen levels in the feed as well as unsatisfactory plant operation.

Taking advantage of the in situ regeneration capability, the customer opted to regenerate the catalyst three times during this period. The results show the remarkable resilience of the beta zeolite catalyst to the stresses of regeneration with virtually no loss in monoalkylate selectivity or cumene product quality as a result of repeated regenerations.

CONCLUSIONS

Fixed-bed zeolitic cumene technology is the process of choice for the cumene/phenol industry. Most of the previously installed cumene capacity based on older $AlCl_3$ and SPA technologies has now been replaced with the newer zeolitic technology over the past 10 yr. The result is greatly improved yields and reduced operating and capital costs. UOP's Q-Max process based on beta zeolite has emerged as the leader for cumene technology. This is primarily due to the high activity, robustness, and lower operating costs associated with operating a beta zeolite based catalyst system.

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