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Mobil-Badger Cumene Technology

C. M. Smith* and T. Sakai**

*ExxonMobil Chemical Company, **Mobil Catalysts Corporation of Japan

The Mobil-Badger Cumene process developed jointly with Raytheon Engineers and Constructors uses a highly selective proprietary ExxonMobil zeolite, MCM-22. This zeolite is exceptionally selective for the alkylation of benzene with propylene over other zeolites allowing it to be used at benzene-to-propylene ratios below 3:1 molar. The use of MCM-22 benefits the cumene producer by allowing production of high-purity cumene at high yields, as well as providing large increases in plant capacity and improved utility consumption. The first commercial operation of the new technology began in May 1996 and currently operated plants supply approximately half of worldwide cumene demand.

Keywords: Cumene, MCM-22, Mobil-Badger

1. Introduction

In 1993 Mobil Technology Company and Raytheon Engineers and Constructors announced a step-out technology for cumene production, based on Mobil's new MCM-22 zeolite. This technology promised to solve virtually all of the deficiencies of the conventional phosphoric acid process used predominantly at the time. Cumene producers and users indicated that they wanted higher purity, higher yields, effective transalkylation to reduce byproduct losses, low capital investment, reduced utilities, and the ability to use refinery-grade feedstocks.

The new process was designed to meet these multiple objectives, and the Mobil-Badger Cumene process was first licensed by Georgia Gulf Corporation of Pasadena, Texas in December 1994. Within 24 months, the Mobil-Badger cumene technology was licensed to 3 more US producers and 3 European producers with combined nameplate

capacity of about 3.1 million metric tonnes per year, —today these seven plants supply approximately half of worldwide cumene demand. Borealis Polymers Oy of Porvoo, Finland started the first plant to operate at a lower 3-to-1 benzene-propylene ratio in October 1997. By 2001 when another 3 plants begin operation, total nameplate capacity for the Mobil-Badger Cumene process will increase to 4.3 million metric tonnes.

2. Process Description

2.1. Key Features

The Mobil-Badger Cumene process employs extremely selective catalysts for the primary alkylation and transalkylation reactions that produce cumene (Fig.1). Side reactions such as oligomerization, olefin cracking and β scission are essentially non-existent in the Mobil-Badger process (Fig.2). Such side reactions, typical of conventional and other nonselective zeolite-based processes, lead to ethylbenzene and butylbenzene byproducts which can contaminate the product cumene, as well as hexylbenzenes and other heavy residues that lower yield.

This highly selective reaction sequence leads

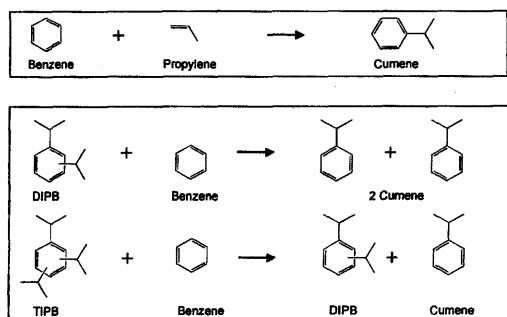


Fig.1 Primary alkylation and transalkylation chemistry for cumene production.

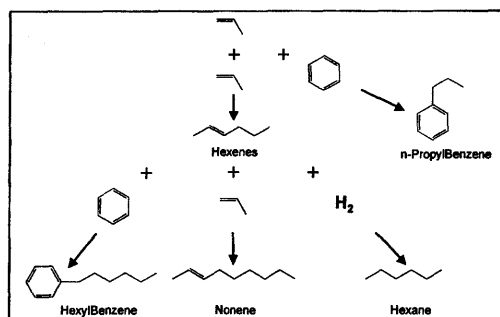


Fig.2 Side reactions typical for the acid catalyzed reaction of benzene with propylene.

to low capital investment in the fractionation section, and reduces coke-forming reactions which shorten catalyst cycle length. A key result of the selective nature of the catalyst is the ability to design the process for exceptionally low benzene-to-propylene ratios (in the range of 2 to 4 molar). This improves utility consumption while providing the potential to substantially increase plant capacity.

The process can be applied to revamp applications of either phosphoric acid or aluminum chloride catalyzed units. In those cases, it may be directly refitted into the existing reactors and plant configuration. However, in a grass-roots design, Fig.3, it uses simple fixed-bed reactors for both alkylation and transalkylation. A portion of the effluent from the alkylation reactors is recirculated through heat exchange directly back to the reactor inlet to control the heat of reaction. Products from the alkylation and transalkylation reactors are then fed to the fractionation system.

Fractionation requirements are largely dictated by the quality of the feedstocks. Base product fractionation requires only three columns for (1) benzene which is recycled in the process, (2) the cumene product, and (3) diisopropylbenzenes (DIPB), which are fed with benzene back to the transalkylator to produce additional cumene. If refinery grade propylene is used, the addition of a small depropanizer tower may be needed to recover LPG. Other fractionation requirements are set by

the presence of feedstock impurities, e.g. significant amounts of ethylene or butenes in the propylene feedstock or toluene in the benzene feedstock. The process does not make significant amounts of either ethylbenzene (EB) or butylbenzenes (BB), and therefore the cumene recovery tower can normally be designed for the easy fractionation of cumene from diisopropylbenzenes. If there are significant levels of ethylene or butylene in the feed, removing these contaminants by using an optional propylene pre-fractionator can be more efficient than removing their resulting by-products, EB and BB from the cumene. Toluene in the feed will produce cymenes – if these impurities are present, the fractionation system can be designed to remove them in a purge from the DIPB tower overhead.

2.2. MCM-22 Catalyst for Alkylation

MCM-22 is well recognized as the best alkylation catalyst for cumene and EB synthesis. Although many acid catalysts can promote these alkylation reactions, medium pore zeolites (e.g. ZSM-5) are not large enough to show good overall reaction rates in the liquid phase and are unselective in the vapor phase. In both cases, the size of the molecules and the use of lower temperature liquid-phase conditions leads to the choice of large pore zeolites (e.g. MCM-22, Mordenite, β and Y) to overcome diffusion constraints. The similarities end there, however since the choice of catalyst to produce cumene and EB are strongly influenced by different

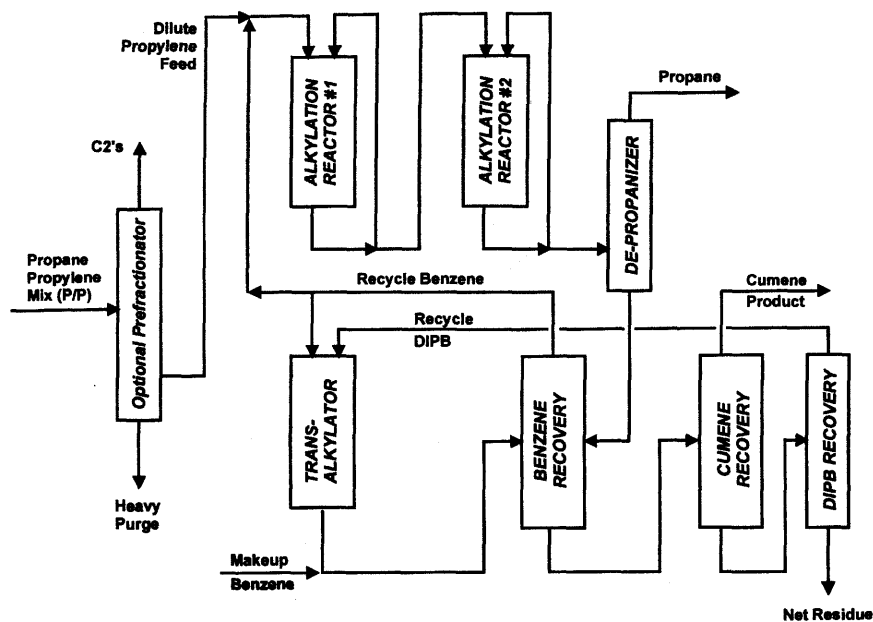


Fig.3 Grassroots Mobil-Badger cumene plant.

factors. Selectivity to the monoalkylated product is of importance in EB whereas ethylene oligomerization is a secondary factor.

Propylene oligomerization is of primary importance in cumene synthesis because propylene reacts 2 to 3 orders of magnitude faster than ethylene over Bronsted acid catalysts. This unselective chemistry occurs readily over conventional solid phosphoric acid (SPA) catalysts and large pore zeolites, forcing a process design that reduces the impact of oligomerization on byproduct formation and catalyst aging. The usual approach maximizes aromatics-to-olefin ratio in the bulk phase surrounding the catalyst via complex catalytic distillation technology or utility-intensive high benzene recycle levels.

Mobil adopted a very severe catalyst screening test early in its program to develop a new cumene process technology. A single-pass single-stage fixed bed alkylation experiment was set up at low-temperature liquid-phase conditions and at a 3-to-1 benzene-to-propylene mole ratio. In this test, conventional large pore zeolites aged at accelerated rates and produced a poor-quality cumene product.

Only MCM-22 exhibited stable activity and produced a high quality product in this accelerated test. Other catalysts that showed limited potential for cumene production in this test were zeolites β and ZSM-12 although both these catalysts aged rapidly. Today, the only zeolite catalysts used for commercial cumene production are based on MCM-22 and zeolite β .

The very facile propylene oligomerization reaction causes coke formation and catalyst deactivation via bandwise aging through the catalyst bed. It leads to increased impurities in the cumene product through associated side reactions. It reduces cumene yield since propylene is not selectively converted to alkylated product, and it leads to increased utilities and capital in the plant design to compensate for these deficiencies. The selectivity of MCM-22 allows for stable operation and makes these compromises unnecessary.

The first plots in Fig.4 illustrate the reaction extent (measured as temperature since this is an exothermic reaction) versus bed depth. The second pair of plots illustrate how the reaction profile changes with increasing time. In the case of MCM-22 the curve flattens slightly showing a

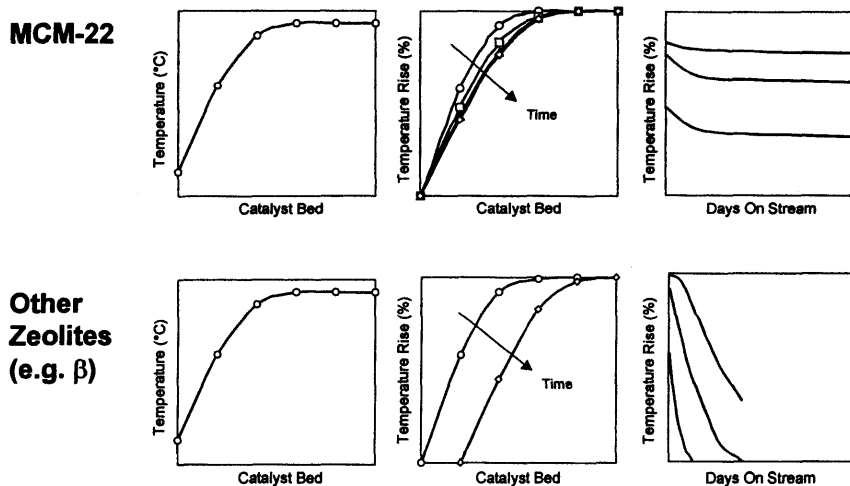


Fig.4 MCM-22 reaches steady state activity compared to other zeolites which show rapid bandwise aging.

uniform aging pattern; in the case of other zeolites, a reaction front moves down the bed leaving a "dead" zone behind it – this is bandwise aging. The last pair of figures shows that performance can easily be tracked by measuring the percent temperature rise at fixed points in the catalyst bed. Whereas the figure shows stable operation with MCM-22, all other solid acid catalysts will require cyclic operation. Increasing temperature during the cycle and/or using a cyclic catalyst reactivation procedure are common methods of dealing with this type of rapid aging. Although increased operational severity that results at the end-of-cycle will help restore activity, it can also degrade product purity since it promotes byproduct reactions.

Zeolite β ages much more rapidly than MCM-22 under the test conditions, and consequently, propylene conversion is changing with time in the test using zeolite β . Propylene conversion is about 94% in the material balance shown below compared with MCM-22 at a higher level of 98%. Even though this conversion difference is not reflected in the total product selectivity, the cumene selectivity is still more than 5% lower with β than it is with MCM-22. In addition, zeolite β produces more than

Table 1 Propylene conversion and selectivities of MCM-22 and zeolite β .

	MCM-22	Zeolite β
Propylene Conversion*	98.0	94.4
Benzene: C ₃ =, Mole Ratio	3	3
Total Product Selectivity, wt%		
C ₃ = Oligomers	1.7	9.2
Cumene	84.9	79.1
PIPBs	13.4	11.7
PIPB/Cumene (m/m) %	11.3	10.8
C ₃ = Balance, Liquid Product, wt%		
C ₃ = Oligomers	4.7	21.4
Σ Alkylated Product	95.3	78.6

*Propylene conversion is not complete since this is a once-through test at high space velocity.

5 times the propylene oligomers produced when using MCM-22. From the propylene balance on the liquid product, zeolite β directs over 20% of propylene fed to the test unit into propylene oligomers. Thus, using zeolite β results in a substantially reduced selectivity to alkylated products, 78% down from 95% for MCM-22. The slightly lower polyisopropylbenzene (PIPB) selectivity with zeolite β probably reflects some size exclusion selectivity from the pore system. Table 1 summarizes propylene conversion and selectivities of MCM-22

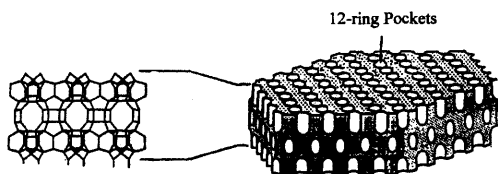


Fig.5 Schematic illustration of a single layer hexagonal crystallite of MCM-22 showing surface pockets.

and zeolite β .

The much lower selectivity for propylene oligomerization over MCM-22 compared to all other conventional zeolites is a result of its unusual structure. Fig.5 shows schematic illustration of a single-layer hexagonal crystallite of MCM-22 having surface pockets. The pockets in MCM-22 show an exceptionally strong affinity for aromatic hydrocarbons over olefins, and these pockets are also the sites of the alkylation reaction. In conventional zeolites, shape selectivity is the result of molecular interactions with a constrained pore system by (1) size exclusion, (2) reduced diffusivity, or (3) restricted transition states. A completely different mechanism based on understanding the effect catalyst structure has on adsorption-desorption equilibria must be considered to explain the selectivity of MCM-22. Computational modeling has confirmed that the pockets in MCM-22 are 3 times more likely to contain benzene than the pores of zeolite β . Therefore, the catalytic sites of MCM-22 are preferentially occupied by aromatics even when the benzene-to-propylene ratio in the bulk phase is quite low. This is why propylene oligomerization is suppressed, and explains why MCM-22 is so uniquely effective for the alkylation of benzene to produce cumene.

3. Pilot Plant Operation

Extensive pilot plant data has been obtained to verify the performance characteristics of the Mobil-Badger process. Since the commercial process is highly integrated, all aspects of the process were incorporated into the pilot plant including

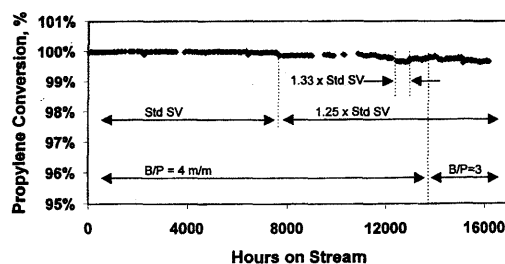


Fig.6 Pilot plant results demonstrate exceptional alkylation stability even at low benzene-to-propylene ratio.

alkylation, transalkylation, and on-line fractionation. With this type of highly integrated experimental design, minor byproducts will accumulate in the same way they do in commercial operation. As a result, their impact on catalyst aging and product purity can be determined.

The alkylation catalyst has been tested on refinery-grade, chemical-grade and polymer-grade propylene with refinery grade benzene from a variety of sources. For single stage operation, Fig.6 shows that propylene conversion has changed little at constant reaction temperature; dropping from essentially complete conversion to 99.9% after 16,000 hours on stream. Conversion remained stable even though space velocity (SV) was increased at about 8000 hours and Benzene-to-Propylene mole (B/P) ratio was reduced from 4 to 3. Additional work has shown that MCM-22 can operate stably at B/P ratios of 2 and below.

During parametric studies, a temporary lowering of alkylation activity due to the presence of water in the feed was observed. Water lowers activity by competitive adsorption on catalytic sites; alkylation activity is fully recovered after water is removed from the feed. Other feed contaminants, notably basic nitrogen, act as irreversible poisons where the activity could only be recovered after catalyst regeneration. Such behavior is typical of all zeolites.

The transalkylation catalyst has undergone aging tests using diisopropylbenzene and benzene feedstocks derived from the alkylation section of

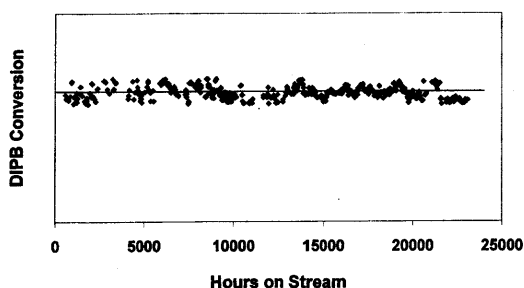


Fig.7 Pilot plant results demonstrate transalkylator-stability.

Table 2 Cumene purity level in the absence of feedstock contaminants.

MCM-22	
Cumene Purity, wt%	99.98
Impurities, wt ppm	
<i>n</i> -Propylbenzene	170
Ethylbenzene	20
Butylbenzene	20
Cymenes	None Detected

the pilot plant. Conversion varies above and below the target conversion shown in Fig.7; this is due to minor parametric changes in operating conditions. However, at fixed conditions, there is no measurable aging over the course of the 20,000 hours of accumulated stream data.

In addition to the excellent stability shown by MCM-22, work with chemical grade propylene demonstrates the very high overall selectivity of the Mobil-Badger process for alkylation and transalkylation compared to those reactions that lead to byproduct formation. In the absence of benzene and propylene feed impurities, Table 2 shows that the expected cumene purity levels are exceptionally high, 99.98 wt%. The Bromine Index, a measure of the presence of olefins, is always <5 indicating the absence of these impurities.

4. Commercial Experience and Licensing Status

The first commercial operation was refitted

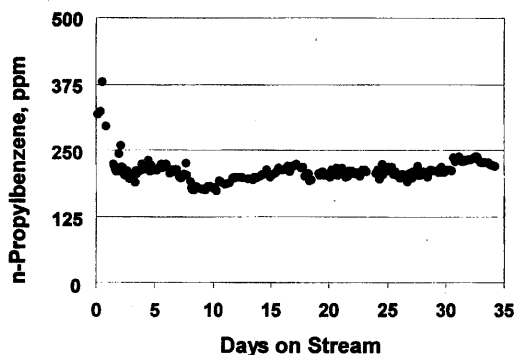


Fig.8 Commercial operation shows production capability at NPB levels below 250 ppm.

into a plant that previously used solid phosphoric acid technology. This plant, operated by Georgia Gulf in Pasadena, Texas was recommissioned with the new Mobil-Badger technology in May 1996 at a design capacity of 1.5 billion pounds per year and a benzene-to-propylene ratio of 4 m/m. The MCM-22 catalyst has performed well at Georgia Gulf on pipeline grade propylene available in the U.S. Gulf Coast; over 30 months of continuous alkylation service has been achieved without catalyst reactivation or regeneration. Transalkylation catalyst has been in continuous service since startup in 1996.

After initial startup, Georgia Gulf demonstrated that NPB could be controlled to levels below 250 ppm (Fig.8) when producing cumene from refinery grade feedstocks. There are several sources of *n*-propylbenzene (NPB) impurities in the cumene product. It is produced in both the direct alkylation of benzene with propylene and in the transalkylation of DIPB with benzene to produce cumene. In addition, about half of the cyclopropane, a reactive component present in propylene feedstocks is converted to NPB; the rest is converted to cumene. Although the conversion selectivity of cyclopropane cannot be controlled, NPB in the Mobil-Badger process can be controlled by keeping alkylation and transalkylation temperatures low. The exceptional stability of the MCM-22 catalyst is a major factor in maintaining low NPB levels throughout long

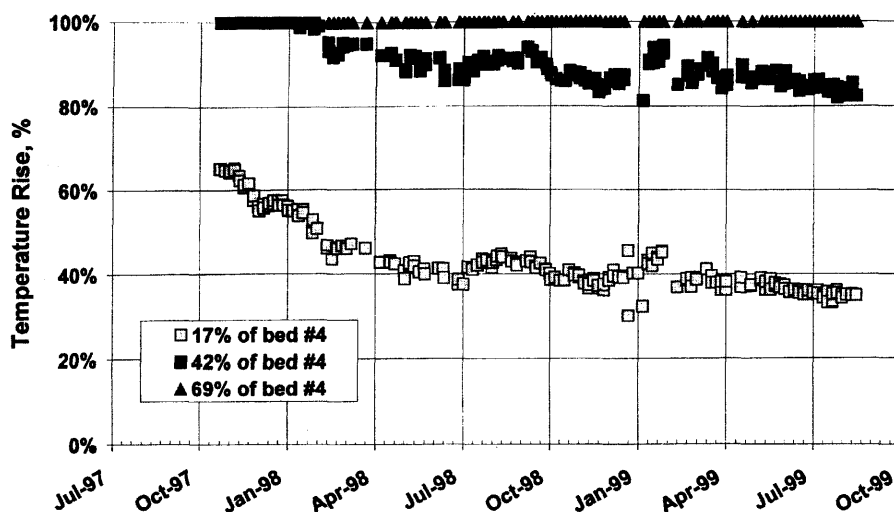


Fig.9 Borealis alkylator performance is stable for 2 years at 3:1 m/m benzene-to-propylene ratio.

Table 3 Georgia Gulf test run.

Georgia Gulf Test Run*	
Cumene Purity, wt%	99.97
Impurities, wt ppm	
<i>n</i> -Propylbenzene	200
Ethylbenzene	25
Butylbenzene	15
Bromine Index	<5

*June 1996.

operating cycles.

Ethylbenzene (EB) and butylbenzenes (BB) are also important contaminants that are controlled in the manufacture of cumene. These byproducts, produced by acid catalyzed propylene oligomerization followed by oligomer cracking and aromatics alkylation, are largely suppressed over MCM-22. MCM-22's very high affinity for aromatics limits propylene adsorption on catalyst's surface. Therefore, the Mobil catalyst shows very high alkylation selectivity even at low aromatics to olefins ratios in the reaction mixture. This has been demonstrated in the commercial data in which EB typically tracks to about 30 ppm and BB typically tracks to about 10 ppm.

A 72 hour performance test was conducted at Georgia Gulf in mid-June 1996. Table 3 shows the result of the test run at about 105% of guaranteed design capacity. The seven original plants, all now operating, have exceeded their guarantees; greater than expected cumene purity levels have been achieved at greater than design throughput in every case.

Borealis was the first plant to begin operating at a benzene-to-propylene ratio of 3 m/m using the Mobil-Badger process. This unit was originally constructed using conventional SPA technology, and later converted to AlCl_3 to increase capacity. The conversion to the Mobil-Badger process used the original multistage SPA reactor to provide Borealis with additional capacity without increasing benzene circulation. Both the alkylation and transalkylation catalysts have now been operated continuously for 24 months, since October of 1997, with no apparent activity loss after the initial break-in period. Fig.9 shows the percent temperature rise at three points through Bed #4 of the Borealis reactor (refer to Fig.4 which describes the expected pattern with MCM-22 versus other acid catalysts).

During the first six months of operation, a steady state activity level was achieved in which

Table 4 Commercial status of Mobil-Badger cumene technology.

	Location	Benzene/ Propylene	Months Onstream	Capacity MTA
Georgia Gulf	USA	4:1	40	680
Koch	USA	4:1	26	630
Borealis	Finland	3:1	23	190
Citgo	USA	4:1	22	540
Caproleuna	Germany	4:1	17	270
Ertisa (CEPSA)	Spain	3.2:1	16	430
Sun	USA	4:1	13	385
Undisclosed	Asia	3:1	2001*	-
Undisclosed	Asia	3:1	2001*	-
Undisclosed	USA	2.5:1	2001*	-

*Expected Startup Date.

about 90% conversion occurs at 42% bed depth; this level remains steady thereafter. Although small variations in activity did occur in 1998, catalyst activity recovers, — this is most likely the result of intermittently high water levels in the feedstock. The Borealis data vividly demonstrates the unique capacity of MCM-22 to prevent the propylene oligomerization chemistry that leads to bandwise aging (see Fig.4) over all other solid acid and zeolite catalysts.

Table 4 lists licensed plants currently operating and expected to startup by 2001 using the Mobil-Badger cumene process. Today, these plants represent more than 10 years of combined commercial operating experience. Catalyst life cycle performance has been proven, with commercial operation at benzene-to-propylene (B/P) ratios as low as 3 m/m. Mobil continues to develop next generation catalysts that will extend cumene performance to

B/P ratios at and below 2 m/m, — saving utilities and providing low cost incremental capacity to licensees of the Mobil-Badger technology. In addition, MCM-22 and the new family of the alkylation catalysts are also used as a substitute for AlCl_3 in EB synthesis as well as for the production of linear alkylbenzenes, an area that has traditionally employed aluminum chloride and HF catalysts.

Acknowledgement

The authors would like to thank Borealis Polymers Oy of Porvoo, Finland for use of their commercial operation data.

Reference

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