ALKYLATION

1. Introduction

The alkylation described in this article is the substitution of a hydrogen atom bonded to the carbon atom of a paraffin or aromatic ring by an alkyl group.

The alkylations of nitrogen, oxygen, and sulfur are described in separate articles (see AMINES; ETHERS).

Significant technological development has been made in the area of alkylation in recent years. Environmental concerns associated with mineral acid catalysts have encouraged process changes and the development of solid-bed alkylation processes. The application of heterogenous catalysts, especially zeolite catalysts, has led to new alkylation technologies. Research efforts to develop environmentally acceptable, economical technologies by applying new materials as alkylation catalysts will continue, and more new technologies are expected to be commercialized in the 1990s.

This article covers important industrial technologies and the direction of future technological development. The description of alkylation chemistry and conventional alkylation technologies covered in the earlier editions of this *Encyclopedia* and other references is minimized (1,2) (see also FRIEDEL-CRAFTS REACTIONS).

2. Nomenclature

Open-chain saturated hydrocarbons have the generic names alkanes and paraffins. In this article, terms such as hexanes, heptanes, and octanes are synonymous with C_6, C_7, and C_8 alkanes, respectively, and do not refer to the straight chains of six carbons, seven carbons, and eight carbons, as defined in the IUPAC system.

The ending *ene* is adopted for straight-chain monounsaturated hydrocarbons. Thus, butenes refer to 1-butene and 2-butene. The ending *ylene* denotes a monounsaturated hydrocarbon that consists of the same number of carbons as expressed by the name; ie, butylenes are 1-butene, 2-butene, and isobutylene (methylpropene). The generic names alkenes and olefins refer to monounsaturated hydrocarbons.

The prefix *iso* is used loosely to denote branched alkanes or alkenes that have one or more methyl groups only as side chains.

3. Alkylation of Paraffinic Hydrocarbons

Paraffin alkylation as discussed here refers to the addition reaction of an isoparaffin and an olefin. The desired product is a higher molecular weight paraffin that exhibits a greater degree of branching than either of the reactants.

The principal industrial application of paraffin alkylation is in the production of premium-quality fuels for spark-ignition engines. Originally developed in the late 1930s to meet the fuel requirements of high performance aviation engines, alkylation is now primarily used to provide a high octane blending component for automotive fuels. Future gasoline specifications will continue to favor the clean-burning characteristics and the low emissions typical of alkylate. These specifications will include reductions in total aromatics, benzene, methyl-*tert*-butyl ether (MTBE), vapor pressure, olefins, sulfur, and distillation endpoint that will reduce the demand for every major gasoline blending component except alkylate (3). Alkylate is an ideal gasoline blend stock because of its high octane and paraffinic nature. Alkylate production capacity as of 2001 reached ~75 million tons per year compared to 58 million tons in 1990 (4) and is expected to grow as worldwide gasoline specifications become more stringent. In addition to this demand for cleaner gasoline, there is a growing demand for gasoline in the United States as well as in many other areas of the world.

3.1. Catalysts and Reactions. Although the alkylation of paraffins can be carried out thermally (5), catalytic alkylation is the basis of all processes in commercial use. Early studies of catalytic alkylation led to the formulation of a proposed mechanism based on a chain of ionic reactions (6–8). The reaction steps include the formation of a light tertiary cation, the addition of the cation to an olefin to form a heavier cation, and the production of a heavier paraffin (alkylate) by a hydride transfer from a light isoparaffin. This last step generates another light tertiary cation to continue the chain.

In practice, the alkylate is a complex mixture of branched paraffins that cannot be explained solely by the chain mechanism. Since the 1960s, studies using more sophisticated experiments and analytical techniques have shown that a complex combination of parallel and sequential ionic reactions must be involved as well (9–13). Oligomerization to C_{12}^{+} cations followed by scission and/or hydride transfer can produce light and heavy ends as well as alkylate of the expected molecular weight. An alternative route to alkylate, especially with isobutylene feeds, is dimerization of feed olefins followed by hydride transfer. Isomerization of the feed olefin prior to alkylation is significant for the *n*-butenes. Hydrogen transfer, or self-alkylation, results in the production of isooctane and a light paraffin from two moles of isobutane and 1 mol of a light olefin. The relative extent of the various reactions depends on the catalyst as well as the feed olefin and operating conditions.

The catalysts used in the industrial alkylation processes are strong liquid acids, either sulfuric acid [7664-93-9] (H_2SO_4) or hydrofluoric acid [7664-39-3] (HF). Other strong acids have been shown to be capable of alkylation in the laboratory but have not been used commercially. Aluminum chloride [7446-70-0] ($AlCl_3$) is suitable for the alkylation of isobutane with ethylene (14). Superacids, such as trifluoromethanesulfonic acid [1493-13-6], also produce alkylate (15). Solid strong acid catalysts, such as Y-type zeolite or BF_3-promoted acidic ion-exchange resin, have also been investigated (16–18). Currently, there is not a commercial operation utilizing a heterogeneous acid catalyst for the production of motor fuel alkylate.

Sulfuric Acid Alkylation. The H_2SO_4 alkylation process was developed during the late 1930s. In the late 1980s, the H_2SO_4 process accounted for ~50% of the motor fuel alkylate produced worldwide.

The modern H_2SO_4 processes are differentiated primarily by the type of reactor system that is used. The reactor must generate a high degree of mixing of the two-phase system (hydrocarbons and H_2SO_4), provide efficient heat removal via refrigeration to keep temperatures in the range of 5–10°C, and provide sufficient time for completion of the reaction. Two reactor systems, the Stratco Contactor (19) and the Kellogg Cascade Reactor (20), account for most of the licensed operating capacity.

A simplified flow diagram of a modern H_2SO_4 alkylation unit is shown in Figure 1. Excess isobutane is supplied as recycle to the reactor section to suppress

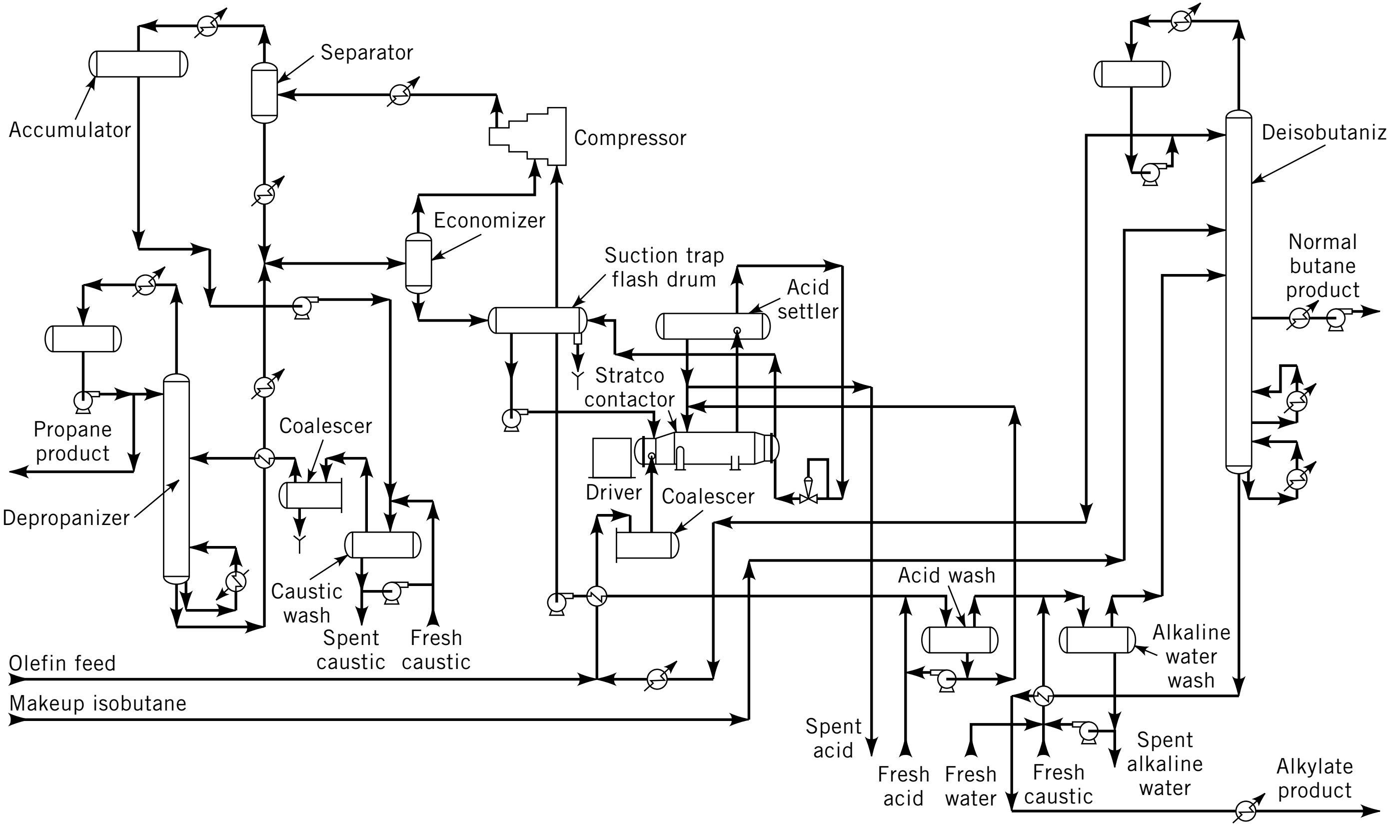


Fig. 1. The H_2SO_4 alkylation unit with effluent refrigeration. Courtesy of Stratco Inc.

polymerization and other undesirable side reactions. The isobutane is supplied both by fractionation and by return of flashed reactor effluent from the refrigeration cycle.

Propane and light ends are rejected by routing a portion of the compressor discharge to the depropanizer column. The reactor effluent is treated prior to debutanization to remove residual esters by means of acid and alkaline water washes. The deisobutanizer is designed to provide a high purity isobutane stream for recycle to the reactor, a sidecut normal butane stream, and a low vapor pressure alkylate product.

The H_2SO_4 concentration is controlled above 90% to provide the optimum activity and selectivity. Purity is maintained by the withdrawal of system acid and replacement with fresh 98% acid. The spent acid is returned to an acid manufacturing plant for reprocessing.

Continuing efforts to reduce residence time and acid level in the acid settler has led to a settler design that incorporates two stages of coalescing for hydrocarbon product separation from the acid phase (21). This new settler design reduces the acid settler size by ~10% as well as reducing residence time and acid level.

A tube insert technology is currently being implemented to provide a cost effective incremental increase in alkylation capacity (22). The inserts are placed in the Contact Reactor and optimize the overall heat transfer coefficient of the bundle by ~20% and minimize corrosion. Other process benefits include lower reaction temperature, higher alkylate octane, lower acid consumption, and increased Contact Reactor capacity.

HF Alkylation. The HF alkylation process was developed in the late 1930s and commercialized in the 1940s. Initially, the growth rate of capacity was lower than for H_2SO_4, but by the 1980s, the capacity was approximately equivalent.

The modern HF alkylation processes are also differentiated primarily by the reactor system that is used. The Phillips process employs a gravity acid circulation system and a riser reactor (23). The UOP process uses a pumped acid circulation system and an exchanger reactor (24).

A simplified flow diagram of a modern HF alkylation unit is shown in Figure 2. Olefin feed and recycle isobutane are combined prior to contacting the acid catalyst in the reactor. Cooling water maintains the reactor temperature in the range of 20–40°C. Acid is settled from the reactor effluent and is returned to the reactor. The hydrocarbon phase is routed to the isostripper for fractionation into an isobutane recycle stream, a sidecut normal butane product, and an alkylate bottoms product. Propane is removed from the system by routing an overhead stream from the isostripper to the HF stripper. If the unit processes any significant quantity of propylene, a depropanizer is included to produce a high purity propane product.

Before leaving the unit, the products are treated with potassium hydroxide to remove any trace acidity. In addition, any product streams that are used for liquefied petroleum gas (LPG) are processed over alumina at elevated temperatures to remove residual organic fluorides.

The HF concentration of the acid catalyst is maintained in the range of 85–95% by regeneration within the unit's fractionation facilities. A separate acid regeneration column (not shown in Fig. 2) is also included to provide a

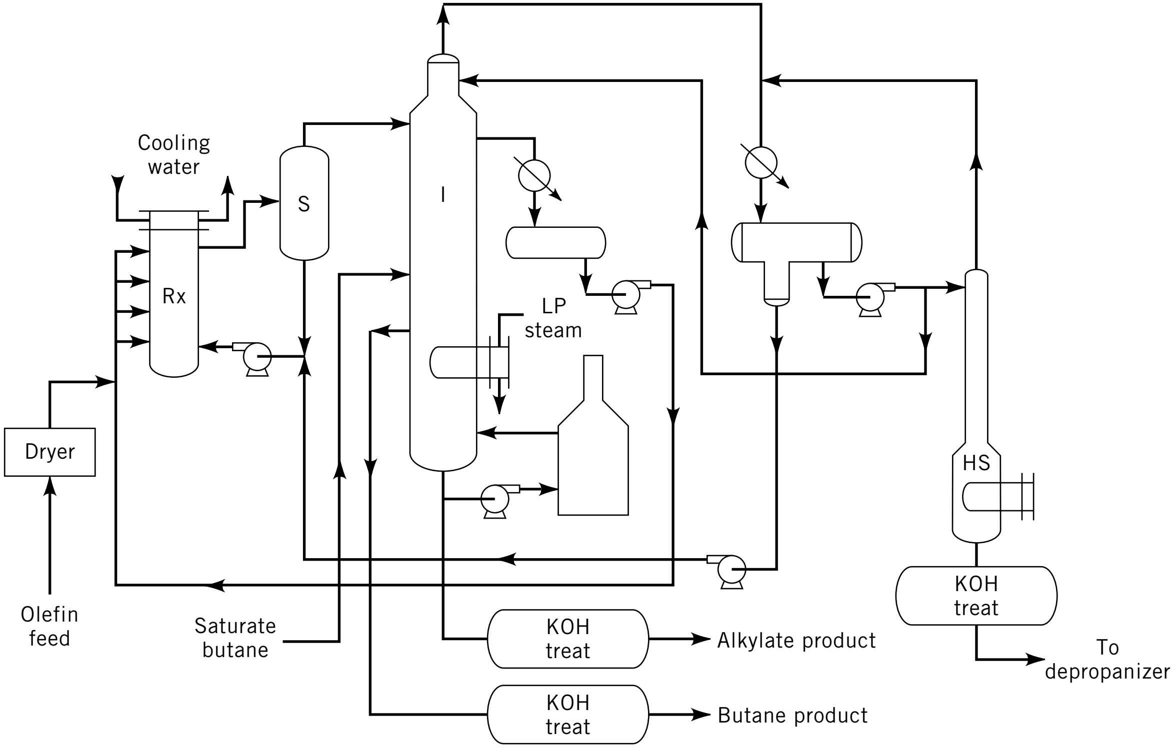


Fig. 2. The UOP HF alkylation process with butylene feed: Rx = reactor; S = settler; I = isostripper; HS = HF stripper.

means to remove excess acid-soluble oils and water. The regeneration of acid in the unit accounts for the low consumption of fresh acid by the HF process.

New and existing unit modifications have been developed and incorporated over the years to increase operational safety to reduce risk of HF acid release or dramatically minimize its impact if an accidental release occurs. Some of these risk reduction features include HF detectors, water sprays, isolation valves, reactor acid compartmentalization, rapid gravity acid transfer, and reduced acid inventory requirements (25,26). Quantitative risk analyses have been conducted and have shown dramatic decreases in risk with the addition of these mechanical modifications to both new and existing operating units.

A further advancement in the HF alkylation technology in the 1990s included the development of additives to reduce the volatility of the HF acid. Two separate but parallel HF additive technologies were developed. Chevron Texaco–UOP introduced the Alkad Process (27) and Phillips–Mobil developed the ReVap Process (25,28). In both of these technologies, the additive is handled as a “drop in” to the existing equipment. The reactor section and HF acid and hydrocarbon fractionation towers are utilized normally. In both cases, however, additional equipment is required to recover and recirculate the proprietary additives. The additive in the ReVap Process is recovered from both the acid phase as well as from the hydrocarbon phase. In this case, the additive is only recovered from the acid phase in an additional additive stripper column. In both cases, additive can be recovered with essentially no loss.

The additive technologies have demonstrated several advantages. A significant aerosol reduction is expected with both additives. Large-scale test releases of these modified acids were conducted at the Quest Consultants test site in Oklahoma. The results showed a 60–83% reduction in aerosol with the Alkad additive samples and 60–90% reduction for the ReVap additive depending on additive level and release conditions. This reduction in aerosol indicates that these additives may also be used in the transport of HF to minimize hazards upon accidental release. Additional additive could be added upon transport in order to achieve ~100% aerosol reduction and adjusted to appropriate level upon delivery. Materials of construction used in conventional HF processes are acceptable, alkylate can be produced over a wide range of processing and feedstock conditions, and alkylate quality is similar or slightly better with the additives.

3.2. Feedstock and Products. *Isobutane.* Although other isoparaffins can be alkylated, isobutane [75-28-5] is the only paraffin commonly used as a commercial feedstock. The hydrocarbon cracking operations that generate feed olefins generally do not produce sufficient isobutane to satisfy the reaction requirements. Additional isobutane must be recovered from crude oil, natural gas liquids, or generated by other refinery operations. A growing quantity of isobutane is produced by the isomerization of *n*-butane [106-97-8].

Butylenes. Butylenes are the primary olefin feedstock to alkylation and produce a product high in trimethylpentanes. The research octane number, which is typically in the range of 94–98, depends on isomer distribution, catalyst, and operating conditions.

The effect of butene isomer distribution on alkylate composition produced with HF catalyst (29) is shown in Table 1. The alkylate product octane is highest

Table 1. **HF Alkylation Products from Pure Butene Isomers**[a]

	Feed isomer			
Alkylate product	1-Butene [106-98-9]	*trans*-2-butene [590-18-1]	*cis*-2-butene [624-64-6]	Isobutylene [115-11-7]
carbon number distribution, wt%				
C_5	3.3	1.9	1.8	5.5
C_6	1.7	1.5	1.5	3.1
C_7	2.4	2.3	2.1	3.7
C_8	85.0	91.4	91.8	80.1
C_{9+}	7.6	2.9	2.8	7.6
total	*100.0*	*100.0*	*100.0*	*100.0*
C_8H_{18} structural distribution, wt%				
trimethylpentanes	77.5	92.1	91.4	89.0
dimethylhexanes	22.1	7.9	7.8	11.0
methylheptanes	0.4		0.8	
estimated octane				
research—clear	94.4	97.8	97.6	95.4
motor—clear	91.6	94.6	94.4	93.4

[a] Ref. 30.

for 2-butene feedstock and lowest for 1-butene; isobutylene is intermediate. The fact that the major product from 1-butene is trimethylpentane and not the expected primary product dimethylhexane indicates that significant isomerization of 1-butene has occurred before alkylation.

The H_2SO_4 catalyst produces a high octane product of similar composition from either 2-butene or 1-butene. This fact suggests that the isomerization of 1-butene to 2-butene is more complete than in the HF system. Isobutylene produces a slightly lower product octane than do the n-butenes. The location of a MTBE [1634-04-4] process upstream of the H_2SO_4 alkylation unit has a favorable effect on performance because isobutylene is selectively removed from the alkylation feed.

Propylene. Propylene alkylation produces a product that is rich in dimethylpentane and has a research octane typically in the range of 89–92. The HF catalyst tends to produce somewhat higher octane alkylate than the H_2SO_4 catalyst because of the hydrogen-transfer reaction, which consumes additional isobutane and results in the production of trimethylpentane and propane.

Amylenes. Amylenes (C_5 monoolefins) produce alkylates with a research octane in the range of 90–93. In the past, amylenes have not been used widely as an industrial alkylation charge, although in specific instances, alkylation with amylenes has been practiced (31). In the future, alkylation with amylenes will become more important as limits are placed on the vapor pressure and light olefin content of gasolines. J. Peterson and his collegues in a recent paper have shown economics and product quality of alkylate obtained from amylenes (32).

3.3. Future Technology Trends.

As previously discussed, the future technology developments in paraffin alkylation will be greatly influenced by environmental considerations. The demand for alkylate product will continue to increase because alkylate is one of the most desirable components in modern low-emission gasoline formulations. Increased attention will be focused on improving process safety, reducing waste disposal requirements, and limiting the environmental consequences of any process emissions.

Hydrofluoric acid has long been recognized as a hazardous material that must be handled with care. However, in recent years concerns have increased over the possible consequences of an accidental release of HF. The results of a 1986 spill test showed that a large portion of the released HF can form a vapor cloud (33). In response to this information, the refining industry has acted to further tighten the already rigorous operating and design standards for HF plants. Periodic hazard reviews are being conducted for all operating units to ensure that the proper systems and procedures are in place (34,35).

Improved feedstock pretreatment is important to minimize catalyst consumption and reduce subsequent spent-catalyst handling requirements. Selective hydrogenation of dienes can be used to reduce acid consumption, both in HF and H_2SO_4 alkylation (36). More effective adsorptive treating systems have been applied to remove oxygen-containing contaminants that are frequently introduced in upstream processing steps.

Because solid acid catalyst systems offer advantages with respect to their handling and noncorrosive nature, research on the development of a commercially practical solid acid system to replace the liquid acids will continue. A major hurdle for solid systems is the relatively rapid catalyst deactivation caused by fouling of the acid sites by heavy reaction intermediates and by-products. At this time there are two technologies which are being offered for commercialization, but have not yet been demonstrated on a large scale. These technologies are the ABB Lummus Global ALKYCLEAN technology (37) and the UOP Alkylene technology (38). Both of these technologies require frequent catalyst regeneration, which is accomplished via hydrogen stripping. A moving bed process design is used in the UOP Alkylene technology, while a number of fixed bed reactors operating in a cyclical regeneration mode is used in the ABB Lummus Global ALKYCLEAN process design.

4. Alkylation of Aromatic Hydrocarbons

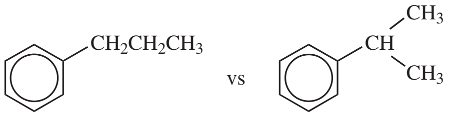
Most of the industrially important alkyl aromatics used for petrochemical intermediates are produced by alkylating benzene [71-43-2] with monoolefins. The most important monoolefins for the production of ethylbenzene, cumene, and detergent alkylate are ethylene, propylene, and olefins with 10–18 carbons, respectively. This section focuses primarily on these alkylation technologies.

4.1. Acid Catalysts and Reaction Mechanism. Acid catalysts promote the addition of alkyl groups to aromatic rings. Olefins, alcohols, ethers, halides, and other olefin-producing compounds can be used as alkylating reagents. In addition to traditional protonic acid catalysts (H_2SO_4, HF, phosphoric acid) and Friedel-Crafts-type catalysts ($AlCl_3$, boron fluoride), any solid acid catalyst having a comparable acid strength is effective for aromatic alkylation. Typical solid acid catalysts are amorphous and crystalline alumino-silicates, clays, ion-exchange resins, mixed oxides, and supported acids (39). Among these solid acid catalysts, ZSM-5, Y-type zeolites, and more recently MCM-22 (40) and beta-zeolite (41) have become the new commercial catalysts for aromatic alkylation. A new catalytic function, shape selectivity, was found in the application of zeolite catalysts as represented by selective formation of *p*-xylene in toluene alkylation with methanol over a ZSM-5 catalyst (42). The specific catalysts used in the commercial alkylation processes are described in discussions of specific products, eg, for ethylbenzene production.

The first step in the catalytic alkylation of aromatics is the conversion of an olefin or olefin-producing reagent into a carbonium ion or polarized complex. Then, this carbonium ion or complex, which is a powerful electrophile, attacks the aromatic ring (43).

A tertiary carbonium ion is more stable than a secondary carbonium ion, which is in turn more stable than a primary carbonium ion. Therefore, the alkylation of benzene with isobutylene is much easier than is alkylation with ethylene. The reactivity of substituted aromatics for electrophilic substitution is affected by the inductive and resonance effects of a substituent. An electron-donating group, such as the hydroxyl and methyl groups, activates the alkylation; and an electron-withdrawing group, such as chloride, deactivates it.

The rearrangement of carbonium ions that readily occurs according to the thermodynamic stability of cations sometimes limits synthetic utility of aromatic alkylation. For example, the alkylation of benzene with *n*-propyl bromide gives mostly isopropylbenzene (cumene) C_9H_{12} and much less *n*-propylbenzene. However, the selectivity to *n*-propylbenzene [103-65-1] versus isopropylbenzene [98-82-8] changes depending on alkylating reagents, conditions, and catalysts; eg, the alkylation of benzene with *n*-propyl chloride at room temperature gives mostly *n*-propylbenzene (44).



4.2. Base Catalysts and Reaction Mechanism. Alkali metals and their derivatives can catalyze the alkylation of aromatics with olefins (45). In contrast to acid-catalyzed alkylation, in which the aromatic ring is alkylated, an olefin is added to the alkyl group of aromatics over a base catalyst through a carbanion intermediate. The carbanion intermediate is produced from an aromatic compound by the abstraction of benzylic hydrogen as a proton by a base. The carbanion reacts with an olefin to grow the side chain of the aromatic compound (46).

The side-chain alkylation of toluene with methanol to produce a mixture of styrene and ethylbenzene can be catalyzed by alkali-cation-exchanged X- and Y-type zeolites (47), magnesium oxide [1309-48-4] (MgO), titanium oxide [13463-67-7] (TiO_2), and mixtures of MgO and TiO_2 and calcium oxide [1305-78-8] (CaO) and TiO_2 (48). Toluene is activated on a basic site and reacts with formaldehyde, which is produced from methanol. The coexistence of weak acid sites promotes the reaction (49). The conversion of relatively low cost toluene into more valuable ethylbenzene and styrene is attractive. However, the ethylbenzene or styrene process based on side-chain alkylation has not been developed for commercial applications.

4.3. Industrial Application. *Ethylbenzene.* This alkylbenzene is almost exclusively used as an intermediate for the manufacture of styrene monomer [100-42-5]. A small amount (<1%) is used as a solvent and as an intermediate in dye manufacture (1,50,51). The ethylbenzene growth rate projections for 1990–1995 range from 3.0 to 3.5% per year (50).

Ethylbenzene [100-41-4] is primarily produced by the alkylation of benzene with ethylene [74-85-1], although a small percentage of the world's ethylbenzene capacity is based on the superfractionation of ethylbenzene from mixed xylene streams (52). A wide variety of different alkylation processes have been developed and commercialized since the 1940s. These processes can generally be divided into liquid- and vapor-phase processes.

Liquid-Phase Processes. Prior to 1980, commercial liquid-phase processes were based primarily on an $AlCl_3$ catalyst. $AlCl_3$ systems have been developed since the 1930s by a number of companies, including Dow, BASF, Shell Chemical, Monsanto, Société Chimique des Charbonnages, and Union Carbide–Badger. These processes generally involve ethyl chloride or occasionally hydrogen chloride as a catalyst promoter. Recycled alkylated benzenes are combined with the $AlCl_3$ and ethyl chloride to form a separate catalyst–complex phase that is heavier than the hydrocarbon phase and can be separated and recycled.

In 1974, Monsanto brought on-stream an improved liquid-phase $AlCl_3$ alkylation process that significantly reduced the $AlCl_3$ catalyst used by operating the reactor at a higher temperature (53–55). In this process, the separate heavy catalyst–complex phase previously mentioned was eliminated. Eliminating the catalyst–complex phase increases selectivities and overall yields in addition to lessening the problem of waste catalyst disposal. The ethylbenzene yields exceed 99%.

In the 1980s, environmental pressures associated with the problem of disposal of the waste $AlCl_3$ catalyst led to the development of two new liquid-phase processes based on zeolite catalysts, which are considered environmentally inert. The first of these processes is a conventional fixed-bed catalyst system (Fig. 3). The catalyst was developed by Unocal, and the process is jointly licensed by ABB Lummus Global and UOP. The operating conditions with regard to temperature and pressure are mild, and carbon steel can be used throughout the process. The technology has no corrosive elements, and the ethylbenzene yields exceed 99% (56–58). The first commercial unit successfully started in Japan in August, 1990.

The second new zeolite-based liquid-phase process was developed by Chemical Research & Licensing Company (CR&L). The process is based on the concept of catalytic distillation, ie, reaction and separation in the same vessel. The concept has been applied commercially for the production of MTBE (59–62) and for the production of ethylbenzene.

Current state-of-the-art technology from the mid-1990s to present involves the use of liquid phase technologies offered by the partnerships of ABB Lummus Global/UOP based on a proprietary beta-zeolite catalyst and ExxonMobil/Washington Group International, Inc. process based on MCM-22 catalyst.

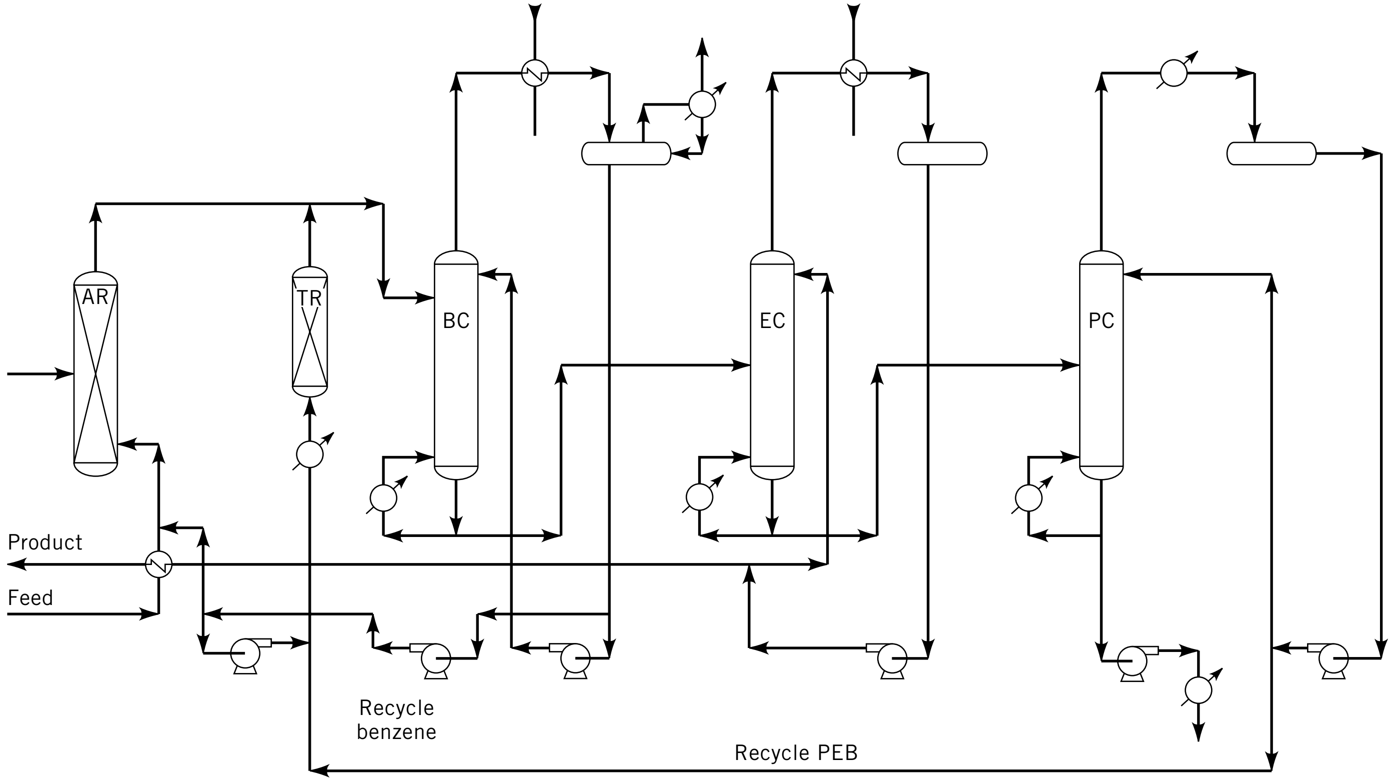


Fig. 3. Unocal–Lummus–UOP ethylbenzene process: AR = alkylation reactor; TR = transalkylation reactor; BC = benzene column; EC = ethylbenzene column; PC = polyethylbenzene (PEB) column.

Beta-zeolite is quickly becoming the catalyst of choice for commercial production of ethylbenzene and cumene. Mobil invented the basic beta-zeolite composition of matter in 1967 (63). Since that time, catalysts utilizing beta-zeolite have undergone a series of evolutionary steps leading to the development of state-of-the-art catalysts such as the UOP EBZ-500 and QZ-2000 for ethylbenzene and cumene alkylation service, respectively.

Much of the effort between 1967 and the early 1980s involved characterization of beta's perplexing structure. It was quickly recognized that beta (BEA) had a large three dimensional pore structure and had a high acidity capable of catalyzing many reactions. It wasn't until early 1988, however, that scientists at Exxon finally solved the chiral nature of the BEA structure.

At the same time that the structure of beta was being investigated, extensive research was being conducted to identify new uses for this zeolite. A major breakthrough came in late 1988 with the invention by workers at Chevron of a liquid phase alkylation process using beta-zeolite catalyst. While Chevron had significant commercial experience with the use of Y (FAU) zeolite in liquid phase aromatic alkylation service, they were quick to recognize the benefits of BEA over Y as well as the other acidic zeolites used at the time, such as mordenite (MOR) or ZSM-5 (MFI). Chevron discovered that the open 12-membered ring structure characteristic of beta coupled with the high acidity of the material made it an ideal catalyst for aromatic alkylation. These properties were shown to be key in the production of aromatic derivative products such as ethylbenzene and cumene with extremely high yields and product purities approaching 100%. Moreover, the combination of high activity and porous structure imparted a high degree of tolerance to many of the contaminants ordinarily found in the feedstocks to these processes. A liquid-phase process was developed by Chevron in 1990 and the rights were acquired by UOP in 1995 as a basis for the Lummus/UOP EB*One* process for ethylbenzene and Q-Max process for cumene production.

The superior performance of the new liquid-phase process, however, provided the incentive for the development of a new manufacturing technology to make this catalyst a commercial reality. In 1991, a new cost-effective synthesis route invented by UOP paved the way for the successful commercialization of the process. The new synthesis route involved the substitution of alkanolamines as a low cost replacement for the tetraethylammonium hydroxide that had to be used heretofore as the templating agent. Finally, the new synthesis route enabled the practical synthesis of beta-zeolite over a wider range of silica to alumina ratios, a factor that has a profound effect on the catalyst's performance.

In contrast to UOP, ExxonMobil uses MCM-22 catalyst in its EBMax liquid phase EB process (43). MCM-22 consists of two nonintersecting 10- and 12-ring pore systems. It is believed that the primary alkylation reactions take place in the 12-ring "pockets" giving rise to somewhat higher EB selectivity. However, there remains some debate in the literature as to how much of an effect this structure has on enhancing selectivity. Separate studies conducted at Enichem (64) show very little difference in monoalkylate selectivity for MCM-22 catalyst vs. well-optimized low Si/Al2 beta-zeolite catalyst.

Vapor-Phase Processes. Although vapor-phase alkylation has been practiced since the early 1940s, it could not compete with liquid-phase processes until the 1970s when the Mobil-Badger vapor-phase ethylbenzene process was introduced (Fig. 4). The process is based on Mobil's ZSM-5 zeolite catalyst (49,65,66). The nonpolluting and noncorrosive nature of the process is one of its major advantages over the $AlCl_3$ liquid-phase system. Unlike the liquid-phase system, the reactors operate at high temperature (400–450°C) and low pressure (2–3 MPa). The high temperature allows the net process heat input and exothermic heat of reaction to be recovered as steam. However, the high temperature vapor-phase operation causes catalytic deactivation by fouling as a result of the deposition of carbonaceous materials, and so the catalyst requires periodic regeneration. Two reactors are required so that processing and regeneration can proceed alternately without interrupting production. Ethylbenzene yields are ~98%.

A modified ZSM-5 catalyst has a unique shape-selective property for producing *p*-ethyltoluene [622-96-8] selectively by the alkylation of toluene [108-88-3] with ethylene (67). *p* -Ethyltoluene is an intermediate in the production of poly (*p*-methylstyrene) [24936-41-2] (PPMS), which is reported to have physical advantages, such as higher flash point and glass-transition temperatures and lower specific gravity, over polystyrene (68,69).

Cumene. Cumene processes were originally developed between 1939 and 1945 to meet the demand for high octane aviation gasoline during World War II (1,2). In 1989, ~95% of cumene demand was as an intermediate for the production of phenol [108-95-2] and acetone [67-64-1]. A small percentage is used for the production of α-methylstyrene. The demand for cumene [98-82-8] has risen at an average rate of 2–3% per year since 1970 (70,71), and this trend continued throughout the 1990s.

Currently, almost all cumene is produced commercially by two processes: (*1*) a fixed-bed, kieselguhr-supported phosphoric acid catalyst system developed by UOP and (*2*) a homogeneous $AlCl_3$ and hydrogen chloride catalyst system developed by Monsanto.

Two new processes using zeolite-based catalyst systems were developed in the late 1980s. Unocal's technology is based on a conventional fixed-bed system. CR&L has developed a catalytic distillation system based on an extension of the CR&L MTBE technology (59–62).

SPA Catalyst. The solid phosphoric acid (SPA) catalyst process has been the dominant source of cumene since the 1930s. This process accounts for >90% of cumene operating capacity (72). A simplified process flow diagram is given in Figure 5.

Propylene feed, fresh benzene feed, and recycle benzene are charged to the upflow reactor, which operates at 3–4 MPa and at 200–260°C. The SPA catalyst provides an essentially complete conversion of propylene [115-07-1] on a one-pass basis. A typical reactor effluent yield contains 94.8 wt% cumene and 3.1 wt% diisopropylbenzene [25321-09-9] (DIPB). The remaining 2.1% is primarily heavy aromatics. This high yield of cumene is achieved without transalkylation of DIPB and is unique to the SPA catalyst process.

The cumene product is 99.9 wt% pure, and the heavy aromatics, which have a research octane number (RON) of 109, can either be 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

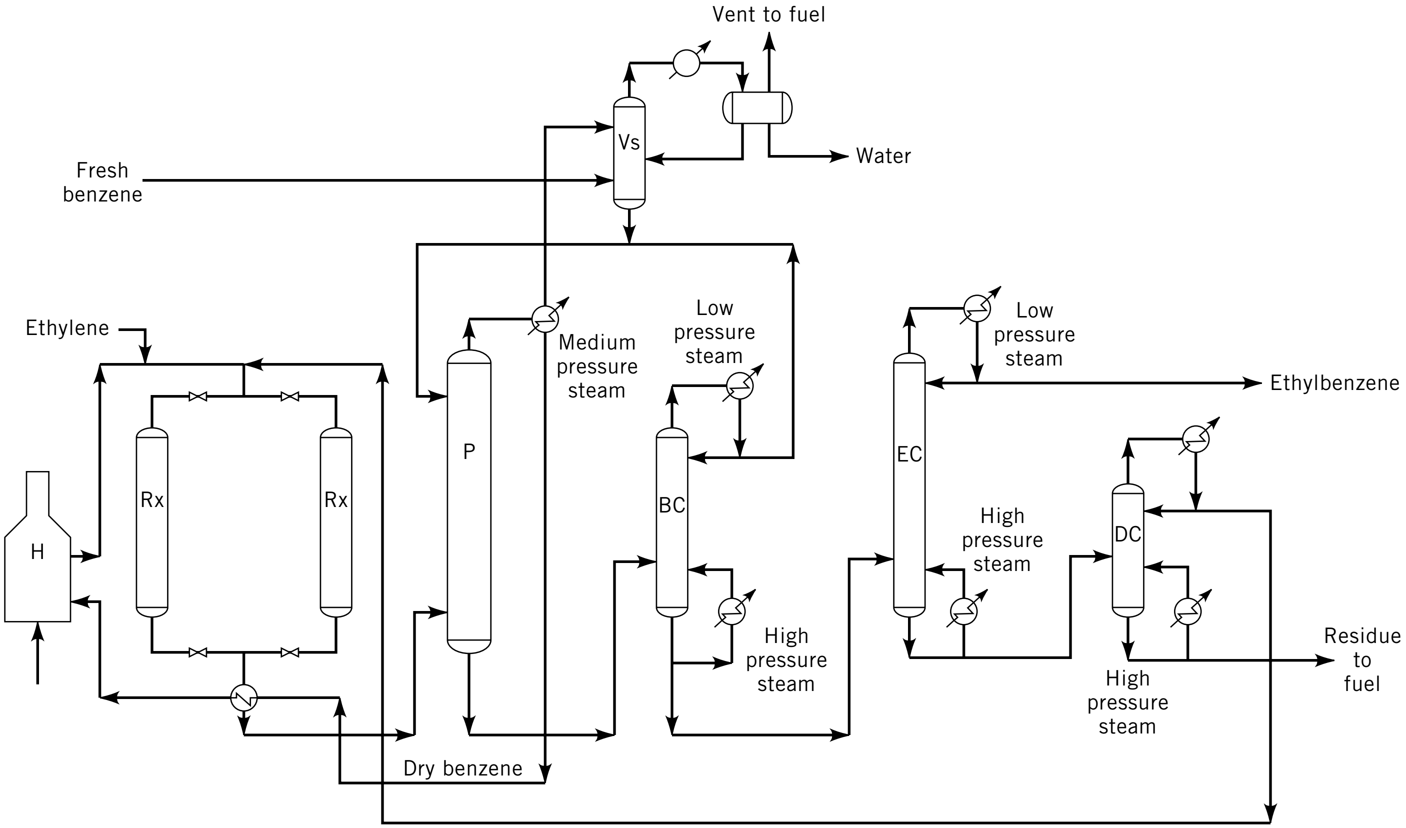


Fig. 4. Mobil-Badger process for ethylbenzene production: H = heater; Rx = reactor; P = prefractionator; BC = benzene recovery column; VS = vent gas scrubber; EC = ethylbenzene recovery column; DC = diethylbenzene recovery column; Courtesy of VCH Publishers, Inc.

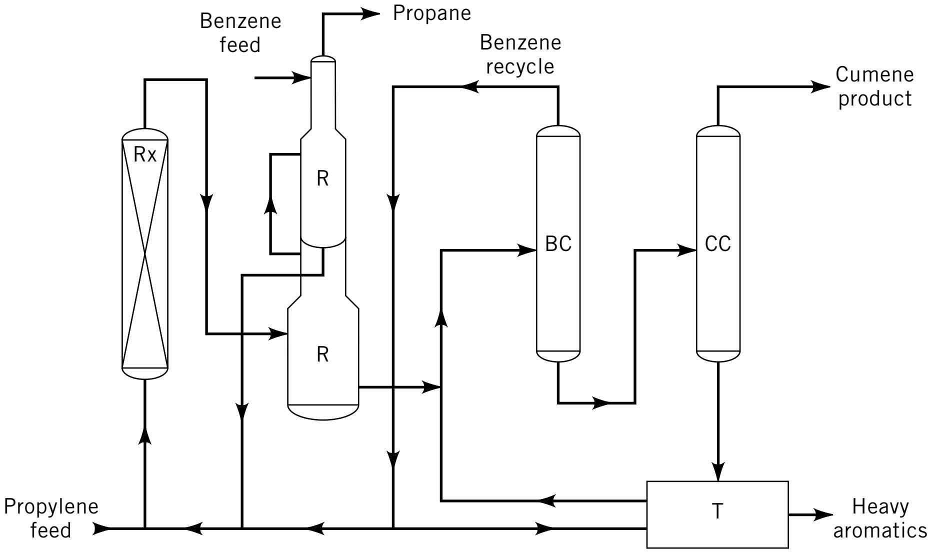


Fig. 5. UOP Cumene process: Rx = reactor; R = rectifier; BC = benzene column; CC = cumene column; T = transalkylation.

overall yields of cumene for this process are typically 97–98 wt% with transalkylation and 94–96 wt% without transalkylation.

$AlCl_3$ and Hydrogen Chloride Catalyst. Historically, $AlCl_3$ processes have been used more extensively for the production of ethylbenzene 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 yields of cumene for this process can be as high as 99 wt% based on benzene and 98 wt% based on propylene (73).

A simplified process flow diagram is shown in Figure 6 (74). Dry benzene, fresh and recycle, and propylene are mixed in the alkylation reaction zone with the $AlCl_3$ and hydrogen chloride catalyst at a temperature of $<135°C$ and a pressure of <0.4 MPa (74). The effluent from the alkylation zone is combined with recycle polyisopropylbenzene and fed to the transalkylation zone, 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 system 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. Unocal introduced a fixed-bed liquid-phase reactor system based on a Y-type zeolite catalyst (75) in the early 1980s. The selectivity to cumene is generally between 70 and 90 wt%. The remaining components are primarily polyisopropylbenzenes, which are transalkylated to cumene in a separate reaction zone to give an overall yield of cumene of $\sim$99 wt%. The distillation requirements involve the separation of propane for LPG use, the recycle of excess

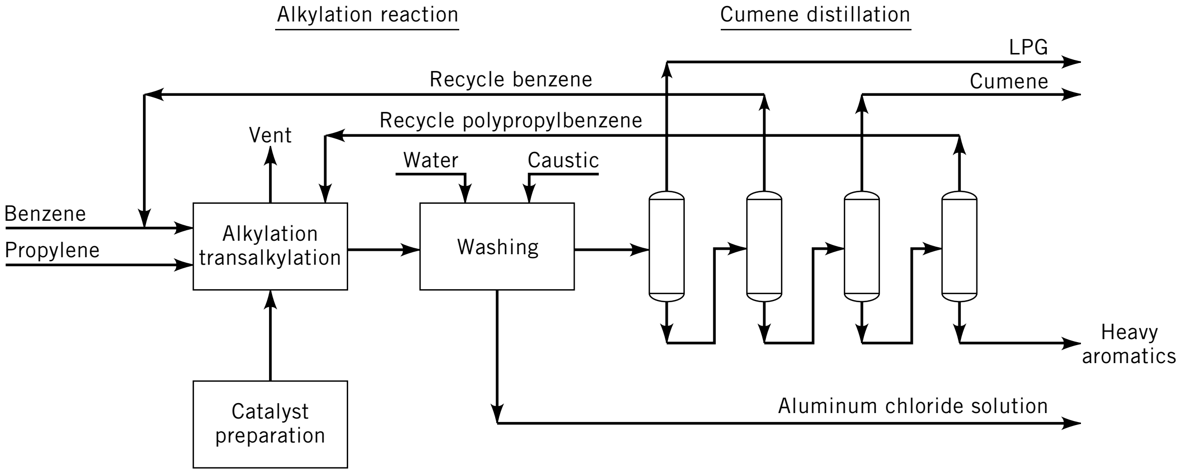


Fig. 6. Monsanto–Lummus Crest cumene process.

benzene to the reaction zones, the separation of polyisopropylbenzene for transalkylation to cumene, and the production of a purified cumene product.

The second zeolite process was developed by CR&L and is based on the concept of catalytic distillation (59–62), which is a combination of catalytic reaction and distillation in a single column. The basic principle is to use the heat of reaction directly to supply heat for fractionation. This concept has been applied commercially for the production of MTBE and cumene.

Current state-of-the-art processes for cumene are similar to ethylbenzene and consist of liquid-phase technologies offered by UOP and ExxonMobil based on beta-zeolite and MCM-22 catalysts, respectively. Over the past decade, great progress has been made in improving and optimizing catalyst formulations for use in both the EB and cumene alkylation applications. 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 (76). 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 IPBs. Additionally, the less active catalysts had a greater tendency toward oligomerization and were more prone toward coking. An analogous trend was observed for ethylene, as well.

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 down to 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 (eg, diisopropylbenzene equilibrium) and, at the same time, minimizes 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 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.

The feature of complete regenerability is another attribute that distinguishes beta-zeolite catalysts from other commercially practiced technology, where selectivity can be lost upon regeneration (77).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 optimal performance when compared to

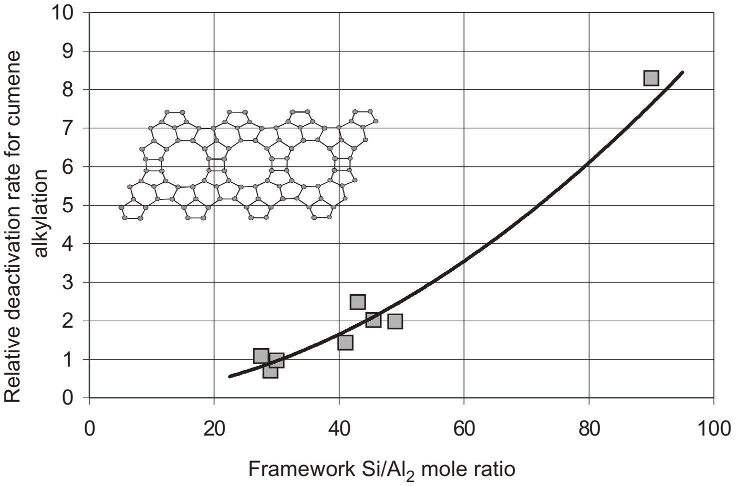


Fig. 7. Relative stability of beta-zeolite as a function the Si/Al ratio.

today's state-of-the-art formulation. Figure 7 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. Stabilizing the zeolitic structure through careful process and chemical means results 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 finds that beta-zeolite is the most effective catalyst for cumene alkylation among others tested including Y, mordenite and an isostructural synthesis of MCM-22.

The principles described above also led to the development of a new generation cumene alkylation catalyst, QZ-2001. In Figure 8, results from accelerated stability testing of QZ-2000 and QZ-2001 catalyst demonstrates the superior stability of the latest catalyst version.

Since new high activity beta-zeolite catalysts such as QZ-2000 are such strong acids, they can be used at lower temperatures than SPA catalyst or competing lower activity zeolites such as MCM-22 (43,78). The lower reaction temperature reduces the rate of competing olefin oligomerization reactions that is particularly high in SPA based processes. The result is higher selectivity to cumene and lower production of non-aromatics that distill with cumene (including olefins, which are analyzed as Bromine Index, and saturates) as well as lower heavy by-products production. For example, although butylbenzene is typically produced from traces of butylene in the propylene feed, there is always the potential for butylbenzene formation through the oligomerization of propylene to nonene, followed by cracking and alkylation to produce butylbenzenes and amylbenzenes. As a result of the high-activity and low-operating temperature of the beta-zeolite catalyst system, the Q-Max process essentially eliminates oligomerization. This results in almost no butylbenzene formation beyond that from butylenes in the feed. The cumene product from a Q-Max unit processing a butylene-free propylene feedstock typically contains <15 wt-ppm butylbenzenes.

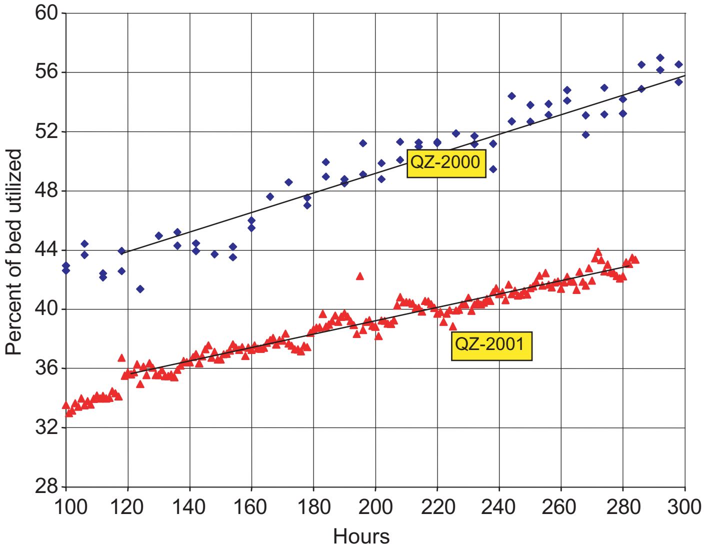


Fig. 8. Comparison of QZ-2000 and QZ-2001 catalyst stability.

The Q-Max process typically produces 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 optimal conditions for transalkylation to produce additional cumene. Beta-zeolite catalyst is also an extremely effective catalyst for the transalkylation of DIPB to produce cumene. Due to the high activity of beta-zeolite, transalkylation in the Q-Max process can be accomplished at very low temperatures to achieve high conversion and minimum side products such as heavy aromatics and additional *n*-propylbenzene. As a result of the high activity and selectivity properties of beta-zeolite, the same catalyst (eg, QZ-2000) is specified for both the alkylation and transalkylation sections of the process. With both of these reactors working together to take full advantage of the QZ-2000 catalyst, the overall yield of cumene is increased to at least 99.7 wt%.

The improvement in beta-zeolite catalyst quality has progressed 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 ultra-high cumene product purities of up to 99.97 wt%. At this level, the only significant by-product is *n*-propylbenzene with the catalyst producing essentially no ethylbenzene, butylbenzene, or cymene beyond precursors in the feed.

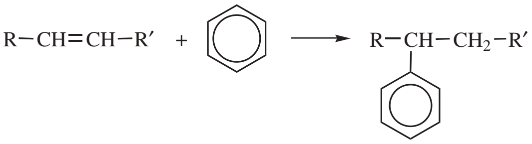
Cymene. Methylisopropylbenzene [25155-15-1] can be produced over a number of different acid catalysts by alkylation of toluene with propylene (79–82). Although the demand for cymene is much lower than for cumene, one commercial plant was started up in 1987 at the Yan Shan Petrochemical Company in the People's Republic of China. The operation of this plant is based on SPA technology offered by UOP for cumene. The cymene is an intermediate for the production of *m*-cresol (3-methylphenol) [108-39-4].

Detergent Alkylate. In the 1940s, sodium dodecylbenzene sulfonate (DDBS) [25155-30-0] produced by the alkylation of benzene with propylene tetramer ($C_{12}H_{24}$) [6842-15-5] followed by sulfonation with oleum [8014-95-7] (H_2SO_4 mixture with sulfur trioxide) or sulfur trioxide and then neutralization was found to have detergent characteristics superior to those of natural soaps. Because of its price stability and effectiveness, DDBS became the standard synthetic surfactant in the industry. By 1955, these efficient surfactants were also leading to environmental problems, such as buildup of foam in downstream discharge sites. This buildup was attributed to the poor biodegradability of the highly branched structure of the propylene tetramer side chain (83–85).

During the early 1960s, linear alkylbenzene sulfonates (LABS), prepared by the sulfonation of linear alkylbenzenes (LAB), began to replace DDBS in industrialized countries due to its superior biodegradability. LAB is produced by the alkylation of benzene with linear aliphatic olefins; such as alpha olefins produced via ethylene oligomerization or linear internal olefins produced via catalytic dehydrogenation of linear paraffins. In the 1970s, LABS capacity increased rapidly with facilities being installed around the world. Except in a few parts of the world, the use of DDBS was phased out by 1980.

The synthetic detergent industry has become one of the largest chemical process industries. The worldwide annual production of LAB has increased from 1.1 million tons in 1980 to 1.8 million tons in 1990 and 2.4 million tons in 2000 (87). Paraffin dehydrogenation followed by alkylation accounts for ~88% of the current world production.

Industrial Processes. A variety of acid catalysts have been used for the production of alkylbenzenes by the alkylation of benzene with higher olefins (C_{10}–C_{15} detergent-range olefins). HF and $AlCl_3$ have been used since the 1960s and H_2SO_4 was used in some earlier units. In 1995, the first detergent alkylation unit, using a solid acid catalyst developed by UOP and CEPSA, was started-up. The Detal process offers superior LAB product quality and lower capital costs due to simplified catalyst handling and downstream product clean up compared with either HF or $AlCl_3$. The main reaction in detergent alkylation is the alkylation of benzene with the straight-chain olefins to yield a linear alkylbenzene:



At the conditions used, some side reactions, such as the formation of dialkylbenzenes, take place:

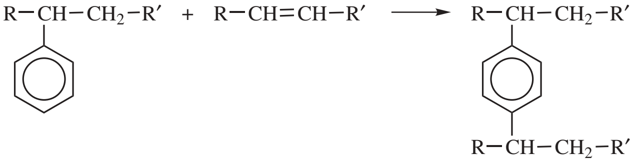
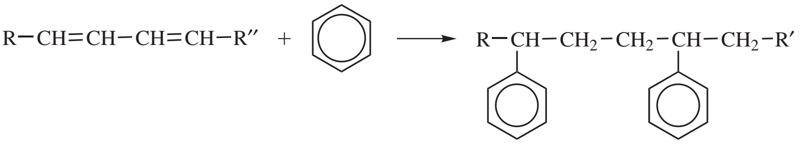


Table 2. **Isomer Distribution, wt%, of Dodecylbenzene from 1-Dodecene and Benzene**

	Catalyst system		
Phenyl position	HF	$AlCl_3$	H_2SO_4
1	0	0	0
2	20	32	41
3	17	22	20
4	16	16	13
5	23	15	13
6	24	15	13

Any diolefins present in the olefin stream can also react to form diphenylalkanes:



Some heavier compounds are also formed by a combination of these reactions. In addition to the alkylation activity, all of these acid catalysts possess, in varying degrees, activity to shift the olefinic double bond along the chain. Thus, regardless of the position of the double bond in the olefin feed, the position of the phenyl group in the final product, as shown in Table 2 for the reaction of 1-dodecene [112-41-4] with benzene, is specific to the catalyst system used (87,88).

$AlCl_3$ Alkylation Process. The first step in the $AlCl_3$ process is the chlorination of *n*-paraffins to form primary monochloroparaffins. Then in the second step, the monochloroparaffin is alkylated with benzene in the presence of $AlCl_3$ catalyst (89,90). Considerable amounts of indane (2,3-dihydro-1H-indene [496-11-7]) and tetralin (1,2,3,4-tetrahydronaphthalene [119-64-2]) derivatives are formed as by-products because of the dichlorination of paraffins in the first step (91). Only a few industrial plants built during the early 1960s use this technology to produce LAB from linear paraffins. The $C_{10}-C_{15}$ alpha olefins also can be alkylated with benzene using this catalyst system.

HF Alkylation Process. The most widely used technology today is based on the HF catalyst system (92). During the mid-1960s, commercial processes were developed to selectively dehydrogenate linear paraffins to linear internal olefins (93–95). Although these linear internal olefins are of lower purity than are alpha olefins, they are more cost-effective because of their lower cost of production. Furthermore, with improvement over the years in dehydrogenation catalysts and processes, such as selective hydrogenation of diolefins to monoolefins (96,99), the quality of linear internal olefins has improved.

A simplified flow diagram for a typical UOP Detergent Alkylate Process is shown in Figure 9. A necessary feature of the reaction section of early alkylation units was the use of two reactors: the first-stage reactor completes the major part

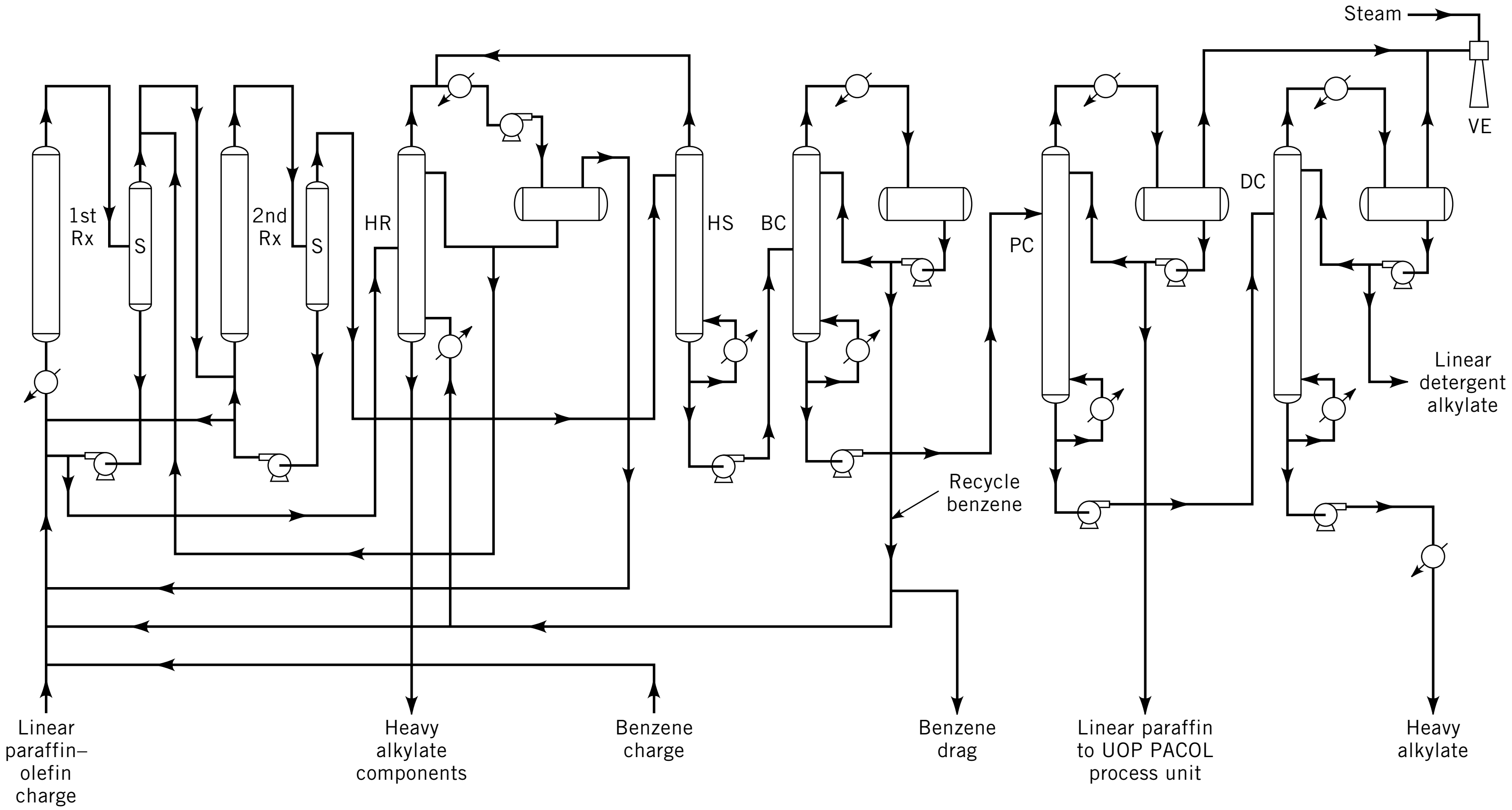


Fig. 9. UOP Detergent alkylate process: Rx = reactor; S = settler; HR=HF regenerator; HS=HF stripper; BC = benzene column; PC = paraffin column; DC = detergent alkylate column; VE = vacuum ejector.

of the alkylation reaction, and the second-stage reactor the last traces of unsaturated hydrocarbons react, and a sizable portion of the soluble polyaromatics is removed. Modern units with lower diene-containing feeds employ a single alkylation reactor (93).

High-purity olefin feed or an olefin–paraffin mixture from a dehydrogenation unit is combined with makeup and recycle benzene and cooled prior to mixing with HF acid. The reaction section consists of a mixer reactor and an acid settler. Because of dilution by excess benzene and paraffin, the temperature rise resulting from the exothermic reaction is relatively small. A portion of the HF phase from the settler is sent to the HF regenerator, where heavy byproducts are removed to maintain the required purity of the HF acid. The hydrocarbon phase from the acid settler proceeds to the fractionation section, where the remaining HF catalyst, excess benzene, unreacted *n*-paraffins, heavy alkylate, and the LAB product are separated by means of sequential fractionation columns. The HF acid and benzene are recycled to the alkylation reactor. The unreacted *n*-paraffins are passed through an alumina treater to remove combined fluorides and are then recycled back to the dehydrogenation unit. Not shown in Figure 9 is the HF acid handling and neutralization section. This section is not basic to the process but is required for the safe operation of the unit (98).

Detal Process. The most recent advance in detergent alkylation is the development of a solid catalyst system. UOP and Compania Espanola de Petroleos SA (CEPSA) have jointly developed the Detal process, which uses a fixed-bed heterogeneous aromatic alkylation catalyst system for the production of LAB (99). Petresa, a subsidiary of CEPSA, started up the first unit utilizing this process in Quebec, Canada in 1995 (100). Two additional Detal units are currently in operation. In contrast to HF and $AlCl_3$, the Detal catalyst is non-corrosive and eliminates problems associated with the handling and disposal of the previous catalysts. A variety of other solid acid catalysts for detergent alkylation have been described in the literature (101–109), but none have been used commercially at the present time.

The flow scheme of the UOP/CEPSA Detal process is presented in Figure 10. The process is operated in conjunction with UOPs dehydrogenation technology to produce linear olefins. The olefin feed and recycle benzene are combined with make up benzene before introduction to the fixed-bed reactor containing the solid acid catalyst. The reaction occurs in the liquid phase under mild conditions to achieve optimal product quality. The reactor effluent flows directly to the fractionation system that is identical to that for the hydrofluoric acid process. The hydrofluoric acid stripper column, settlers, other hydrofluoric acid related piping and equipment as well as the product alumina treater are eliminated. Carbon steel metallurgy can now be used due to the elimination of the liquid acid. In order to improve product yield and quality, there are two additional process units included in the overall Detal process scheme. First, a DeFine unit selectively hydrogenates diolefins to monoolefins (same as in hydrofluoric acid technology) to increase alkylate yield. Second, a PEP Process is added to eliminate aromatics from the olefin feed stream. These aromatics would alkylate in the Detal unit leading to faster catalyst deactivation and lower quality product.

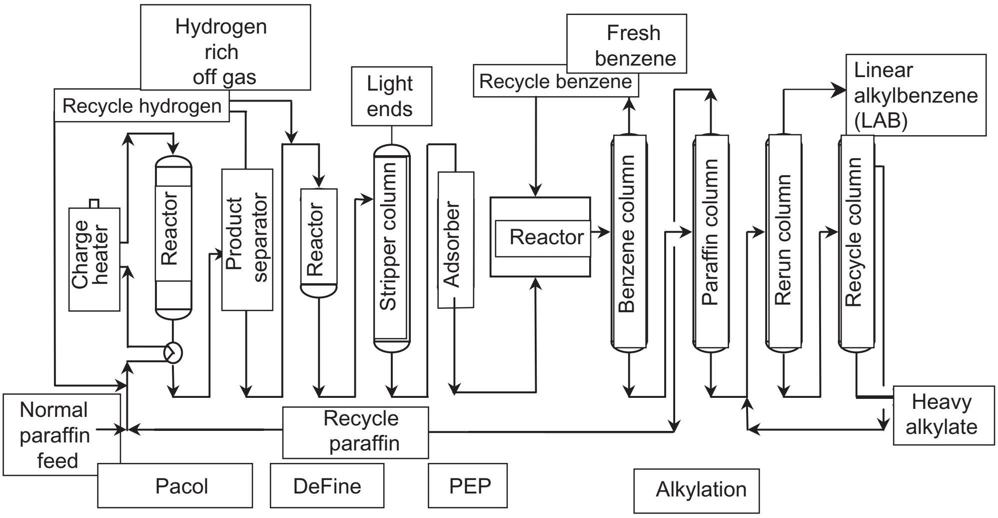


Fig. 10. UOP/Cepsa detal process for the production of LAB.

Table 3 compares linear alkylbenzene product properties for the HF and Detal catalyst systems. Bromine index and sulfonatability are key measures of product quality because they affect final product cost. High bromine index product also produces a highly colored sulfonate that requires further treatment. Recently, reduction in non-alkylbenzene components, in particular reduction of tetralins, and improved linearity has also become important. Both of these parameters are related to the rate of biodegradation of the ultimate LAS product. (105).

As can be seen in Table 3, the Detal linear alkylbenzene product is made in higher yield, with higher linearity, improved sulfonate color, and less tetralin by-product compared to the HF alkylation process. It also has higher 2-phenylalkane content that gives improved solubility in many detergent formulations. For example, the cloud point of a liquid detergent formulation prepared with LABs

Table 3. **Typical LAB Product Properties**

Property	$AlCl_3$ alkylate	HF alkylate	Detal alkylate
specific gravity	0.860	0.860	0.860
bromine number	0.015	0.015	0.015
Saybolt color	+30	+30	+30
Doctur test	negative	negative	negative
water, wt%	0.01	0.01	0.01
sulfonation, wt%	98.5	98.5	98.5
biodegradability, wt%	95	95	95
paraffins, wt%	0.3	0.3	0.3
indanes or tetralins, wt%	5–15	1–3	1–3
2-phenylalkanes, wt.%	30	15	25
n-alkylbenzene, wt%	90	94	94
average molecular weight	235–260	235–260	235–260

derived from Detal LAB is lower than that of the same formulation produced from HF LAB over a wide range of surfactant concentrations (106). All of these properties demonstrate that the current Detal technology produces a superior product than the hydrofluoric acid technology. Due to the higher tetralin content from aluminum chloride based alkylation process it is being phased out.

Economics of the current Detal and hydrofluoric acid technologies have been summarized in detail (106). For an 80,000 MTA linear alkylbenzene unit, the estimated erected costs for the Detal and HF systems are $67 and 72 million, respectively. Thus, fixed plant investment has been reduced by $\sim$15% by the use of a solid acid catalyst. The absence of the hydrofluoric liquid acid and required neutralization facilities for the acid wastes is also reflected in lower operating costs.

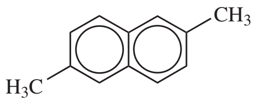
Xylenes. The main application of xylene isomers, primarily *p*- and *o*-xylenes, is in the manufacture of polyester fibers, films, resins and plasticizers. Demands for xylene isomers and other aromatics such as benzene have steadily been increasing over the last two decades. Food packaging applications, which use polyester blends derived from *m*-xylene, have been increasing 10–15% per year during the 1990s. This has led to a singificant increase in the capacity for the *m*-xylene isomer. The major source of xylenes is catalytic reforming of naphtha and pyrolysis of naphtha and gas oils. A significant amount of toluene and C_9+ aromatics, which have lower petrochemical value, is also produced by these processes. More valuable pure xylene isomers can be manufactured from these low value aromatics by transalkylation, eg, the UOP Tatoray process (109), the Toray TAC9 process. (110) and the ExxonMobil TransPlus technology (111).

It is also possible to produce *p*-xylene in concentrations that are significantly above equilibrium by selective toluene disproportionation processes such as the UOP PX-Plus (112) process and the ExxonMobil MSTDP or MTPX technologies (113). These latter coproduce a significant amount of benzene from the toluene feed. The Xylene isomers are recovered by technologies such as the UOP Parex process (114) for *p*-xylene and the UOP MX Sorbex process (115) for *m*-xylene. The *o*-xylene isomer can be recovered by fractionation. The “raffinate” product from the recovery processes is sent to an isomerization unit, which reestablishes the equilibrium among the C_8 aromatics. Typical technologies are the UOP Isomar process (116–118) and ExxonMobil Xymax process (119–120). The Tatoray process can be applied to the production of xylenes and benzene from feedstock that consists typically of toluene [108-88-3], either alone or blended with C_9 aromatics (particularly trimethylbenzenes and ethyl-toluenes) and C_{10} alkyl aromatics. The main reactions are transalkylation (or disproportionation) of toluene to xylene and benzene or of toluene and trimethylbenzenes to xylenes in the vapor phase over a highly selective fixed-bed catalyst in a hydrogen atmosphere at 350–500°C and 1–5 MPa. Ethyl groups are dealkylated or transalkylated (121,122). The TAC9 process, developed by Toray and licensed by UOP, converts C_9+ aromatics primarily to xylenes, at conditions that are similar to those of the Tatoray process.

The PX-Plus, MSTDP and MTPX processes produce *p*-xylene [106-42-3] (*p*-dimethylbenzene) over a pretreated modified MFI catalyst at concentrations in the xylene products that range from 80 to 93% depending on catalyst pretreatment and operating conditions. A *p*-xylene concentration higher than an equilibrium concentration of 24% results from the much greater diffusivity of *p*-xylene in the selectivated MFI pore structure than that of ortho and meta isomers. Further isomerization of the *p*-xylene is minimized by the passivation of active sites on the exterior surface of the MFI. Toluene conversions of 25–32 wt% are achieved at 2–6 h^{-1} weight hourly space velocity, 400–420°C, 2.3–3.5 MPa and 1–4 H_2 to hydrocarbon molar feed ratio. The selective alkylation of toluene with methanol to produce *p*-xylene as a predominant isomer can be achieved over shape-selective catalysts (123–125). With a modified MFI zeolite catalyst, >99% *p*-xylene in xylene isomers can be produced at 550°C. This *p*-xylene concentration exceeds the equilibrium concentration of 23% (123). The primary by-product is water, making this technology economical only under very particular circumstances.

Polynuclear Aromatics. The alkylation of polynuclear aromatics with olefins and olefin-producing reagents is effected by acid catalysts. The alkylated products are more complicated than are those produced by the alkylation of benzene because polynuclear aromatics have more than one position for substitution. For example, the alkylation of naphthalene [91-20-3] with methanol over mordenite and Y-type zeolites at 400–450°C produces 1-methylnaphthalene [90-12-0] and 2-methylnaphthalene at a two to one ratio of ~1.8. The selectivity to 2-methylnaphthalene [91-57-6] is increased by applying a ZSM-5 catalyst to give a 2:1 ratio of ~8 (126).

2,6-Dimethylnaphthalene [581-42-0] (2,6-DMN) can be a precursor for 2,6-naphthalenedicarboxylic acid [1141-38-4], which is a starting material for high performance polyesters (polyethylene naphthalate or PEN) as well as polyamides.



2,6-DMN can be produced by alkylating naphthalene or 2-methylnaphthalene at 250–450°C over zeolite catalysts (126,127). However, no commercial technology by this synthetic route had been developed as of 1991, primarily because of low catalytic selectivity. A multistep synthetic route to 2,6-DMN starting with butadiene and *o*-xylene has been used on a commercial scale. However, the market growth for PEN has been very slow due to its relatively high cost.

4.4. Future Technology Trends. Over the years, improvements in aromatic alkylation technology have come in the form of both improved catalysts and improved processes. This trend is expected to continue into the future.

Catalysts. Nearly all of the industrially significant aromatic alkylation processes of the past have been carried out in the liquid phase with unsupported acid catalysts. For example, $AlCl_3$ and HF have been used commercially for at least one of the benzene alkylation processes to produce ethylbenzene (128,129), cumene (130), and detergent alkylates (92–95). Exceptions to this historical trend have been the use of a supported boron trifluoride for the production of ethylbenzene and of a solid phosphoric acid (SPA) catalyst for the production of cumene (72,131).

Since 1976, these forms of acids have become a significant environmental concern from both a physical handling and disposal perspective. This concern has fueled much development work toward solid acid catalysts, including zeolites, silica–aluminas, and clays (132,133).

A liquid-phase ethylbenzene process jointly licensed by ABB Lummus and UOP initially used a Y-type zeolite catalyst developed by Unocal. During the 1990s, significant advances took place with numerous new zeoletic and other solid acid catalysts that were introduced for the production of ethylbenzene (43,63), cumene (75–77) and detergent alkylate (99). Because of their initial commercial success and the industry's growing awareness of environmental issues, solid acid catalysts are expected to ultimately replace liquid acid catalysts (134).

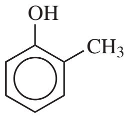
Process. As solid acid catalysts have replaced liquid acid catalysts, they have typically been placed in conventional fixed-bed reactors. An extension of fixed-bed reactor technology is the concept of catalytic distillation being offered by CR&L (59). In catalytic distillation, the catalytic reaction and separation of products occurs in the same vessel. The concept has been applied commercially for the production of MTBE and is also being offered for the production of ethylbenzene and cumene.

A new alkylation process, the Alkymax process was introduced by UOP in 1990. This process was developed in response to proposed legislation requiring the reduction of benzene (a known carcinogen) in gasoline (135). Refinery propylene, typically from a fluid catalytic cracker, is used to alkylate the benzene in light reformate (136). In addition to lowering the benzene content, the alkylate formed has a high octane value and can typically boost the octane of the gasoline pool by 0.5 RON.

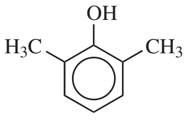
5. Other Alkylations

Alkylation of Phenol. The hydroxyl group activates the alkylation of the benzene ring because it is a strong electron-donating group; therefore, the alkylation of phenol [108-95-2] can be achieved with olefins and olefin-producing reagents under milder conditions than the alkylation of aromatic hydrocarbons. The alkylation of phenol with olefins and other alkylating reagents is discussed in other publications (137 and 138) (see also ALKYLPHENOLS).

Alkylated phenol derivatives are used as raw materials for the production of resins, novolaks (alcohol-soluble resins of the phenol–formaldehyde type), herbicides, insecticides, antioxidants, and other chemicals. The synthesis of 2,6-xylenol [576-26-1] has become commercially important since PPO resin, poly (2,6-dimethyl phenylene oxide), an engineering thermoplastic, was developed (139,140). The demand for *o*-cresol and 2,6-xylenol (2,6-dimethylphenol) increased further in the 1980s along with the growing use of epoxy cresol novolak (ECN) in the electronics industries and poly(phenylene ether) resin in the automobile industries. The ECN is derived from *o*-cresol, and poly(phenylene ether) resin is derived from 2,6-xylenol.



o-cresol



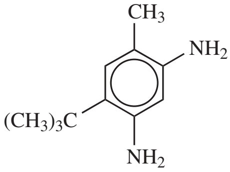
2,6-xylenol

Cresol and xylenol can be prepared by the methylation of phenol with methanol over both acid and base catalysts. It is postulated that phenol methylation on acid catalysts proceeds through the initial formation of anisole (methoxybenzene [100-66-3]) followed by intramolecular rearrangement of the methyl group to form *o*-cresol. The methyl group in the ortho position can further undergo isomerization to form meta and para isomers. The formation of *m*- and *p*-cresols is accelerated at higher temperatures and with stronger acid catalysts (141,142). Xylenol isomers are produced by the consecutive methylation of cresol isomers. The methylation of phenol is more selective to *o*-cresol with base catalysts than with acid catalysts. On base catalysts, phenol adsorbs dissociatively on a pair of basic and acidic sites to form a protonic site and an adsorbed phenolate species, respectively. This proton site activates methanol to produce a carbonium ion, which reacts with the benzene ring of an adjacently adsorbed phenolate species at the ortho position (138).

The commercial process for the selective synthesis of *o*-cresol [95-48-7] and 2,6-xylenol by the alkylation of phenol with methanol in a fixed-bed reactor was developed by the General Electric Company. The high selectivity is effected by using a magnesium oxide catalyst at high temperatures (475–600°C). The alkylation occurs at the positions ortho to the hydroxyl group. Because the catalyst does not have isomerization activity, the products are *o*-cresol, 2,6-xylenol, and minor amounts of 2,4,6-trimethylphenol [527-60-6] and anisole [100-66-3] (143). Similar commercial processes using a fixed-bed reactor system have been commercialized by BASF, Groda, and Mitsubishi Gas Chemicals (118). A new phenol methylation process technology for the production of *o*-cresol and 2,6-xylenol has recently been developed by Asashi Chemical Industry (144). This new process uses a new catalyst and a fluidized-bed reactor. The catalyst is a silica-supported iron–vanadium mixed oxide modified by metal promoters. This catalyst is active at 300–350°C and is selective for *o*-cresol and 2,6-xylenol formation. The catalyst-bed temperature can be maintained uniformly at relatively low temperatures because of the high heat-transfer efficiency of the fluidized-bed reactor system; therefore, side reactions caused at high temperatures are eliminated and the catalyst life becomes long. Because no significant amount of meta and para isomers is produced in this process, high purity *o*-cresol (99.95%) and 2,6-xylenol (99.85%) can be produced.

Alkylation of Aromatic Amines and Pyridines. Commercially important aromatic amines are aniline [62-53-3], toluidine [26915-12-8], phenylenediamines [25265-76-3], and toluenediamines [25376-45-8] (see AMINES, AROMATIC). The ortho alkylation of these aromatic amines with olefins, alcohols, and dienes to produce more valuable derivatives can be achieved with solid acid catalysts. For example, 5-*tert*-butyl-2,4-toluenediamine ($C_{11}H_{18}N_2$), which is used for performance polymer applications, is produced at 85% selectivity and 84%

2,4-toluenediamine [95-80-7] (2,4-TDA) conversion by alkylation of 2,4-TDA with isobutylene over a Y-type zeolite catalyst at 180–200°C (145).



The alkylation of pyridine [110-86-1] takes place through nucleophilic or homolytic substitution because the π-electron-deficient pyridine nucleus does not allow electrophilic substitution, eg, Friedel-Crafts alkylation. Nucleophilic substitution, which occurs with alkali or alkaline metal compounds, and free-radical processes are not attractive for commercial applications. Commercially, catalytic alkylation processes via homolytic substitution of pyridine rings are important. The catalysts effective for this reaction include boron phosphate, alumina, silica–alumina, and Raney nickel (146).

6. Health and Safety Factors

Generally, specific health and safety factors relating to feedstock and products must be addressed for each particular industrial alkylation process. The reader is referred to the sections of the *Encyclopedia* that describe specific chemical compounds. In addition, the properties of the catalyst systems employed in alkylation must be considered. The hazardous properties of the homogeneous acid catalysts, HF, H_2SO_4, and $AlCl_3$, are documented in other sections of this encyclopedia (see ALUMINUM COMPOUNDS; FLUORINE COMPOUNDS, INORGANIC; SULFURIC ACID AND SULFUR TRIOXIDE). In industrial applications, specialized procedures are required to ensure the safe handling of these materials. Replacing these materials with solid acid catalysts will become more important in the future. The solid acid catalysts themselves present a disposal problem that favors the development of regenerable catalysts or the implementation of recycling procedures.

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