

Aromatics

10.6.1 Aromatics production and use

Introduction

An aromatics complex is a combination of process units that can be used to convert petroleum naphtha and pyrolysis gasoline (pygas) into the basic petrochemical intermediates: Benzene Toluene and Xylenes (BTX). Benzene is a versatile petrochemical building block used in the production of more than 250 different products. Ethylbenzene, cumene, and cyclohexane are the most important benzene derivatives. The xylenes product, also known as mixed xylenes, contains four different aromatic isomers: para-xylene, ortho-xylene, meta-xylene, and ethylbenzene. Small amounts of mixed xylenes are used for solvent applications, but most xylenes are processed further within the complex to produce one or more of the individual isomers. The most important C₈ aromatic isomer is para-xylene, which is used almost exclusively for the production of polyester fibres, resins, and films. In recent years, polyester fibres have shown growth rates of 5 to 6 percent per year and resin has shown growth rates of 10 to 15 percent per year, corresponding to the emergence of PET (polyethylene terephthalate) containers. A small amount of toluene is recovered for use in solvent applications and derivatives, but most toluene is used to produce benzene and xylenes. Toluene is becoming increasingly important for the production of xylenes through toluene disproportionation and transalkylation with C₉ aromatics.

Aromatics complexes can have many different configurations. The simplest complex produces only benzene, toluene, and mixed

xylenes and consists of the following major process units: naphtha hydrotreating for the removal of sulphur and nitrogen contaminants; catalytic reforming for the production of aromatics from naphtha; aromatics extraction for the extraction of BTX.

However, most modern aromatics complexes are designed to maximize the yield of benzene and para-xylene and sometimes ortho-xylene. About one-half of the existing UOP (Universal Oil Products) aromatics complexes are configured for the production of both para-xylene and ortho-xylene. These newer aromatics complexes have not only the major process units mentioned above, but include the following additional major process units: para-xylene extraction for the separation of para-xylene for the other xylene isomers; xylene isomerization for production of an equilibrium mixture of xylene isomers; toluene and C₉ aromatic transalkylation for production of xylenes and benzene.

An aromatics complex may be configured in many different ways, depending on the available feedstocks, the desired products, and the amount of investment capital available. Because of this wide flexibility, the product slate can be varied to match downstream processing requirements.

Feedstock considerations

Any of the following streams may be used as feedstock to an aromatics complex: straight-run naphtha; hydrocracked naphtha; mixed xylenes; pyrolysis gasoline; coke-oven light oil; condensate; Liquid Petroleum Gas (LPG).

Petroleum naphtha is by far the most popular feedstock for aromatics production. Reformatted naphtha, or reformat, accounts for 70% of total

world BTX supply. The pygas by-product from ethylene plants is the next-largest source at 23%. Coal liquids from coke ovens account for the remaining 7%. Pygas and coal liquids are important sources of benzene that may be used only for benzene production or may be combined with reformate and fed to an integrated aromatics complex. Mixed xylenes are also actively traded and can be used to feed a stand-alone Parex-Isomar loop or to provide supplemental feedstock for an integrated complex.

CCR Platforming process

The CCR (Continuous Catalytic Reformer) Platforming process is used throughout the world today in the petroleum and petrochemical industries. It produces aromatics from naphthenes and paraffins, either for use in motor fuel or as a source of specific aromatic compounds. In aromatics applications, the feed naphtha is generally restricted to C_6 through C_9 compounds to maximize the production of benzene, toluene, and xylenes.

The distribution of the hydrocarbon types (paraffins, naphthenes and aromatics) will determine how easily various naphthas can be reformed. Aromatic compounds pass through the Platforming unit relatively unchanged. Naphthenes react rapidly and efficiently to aromatics, while paraffins react slowly and with less selectivity.

Process chemistry

Four major reactions occur in the reactors to produce the desired products: dehydrocyclization of paraffins to 5-membered rings; isomerization of 5-membered to 6-membered rings;

dehydrogenation of 6-membered rings to aromatics; hydrocracking of large hydrocarbons to smaller hydrocarbons. The function of the reformer is to efficiently convert paraffins and naphthenes to aromatics with as little ring opening or cracking as possible.

Process description

Hydrotreated naphtha feed is combined with recycle hydrogen gas and heat exchanged against reactor effluent (**Fig. 1**). The combined feed is then raised to reaction temperature in the charge heater and sent to the reactor section. Typically four adiabatic radial-flow reactors are arranged in a vertical stack. The catalyst flows vertically by gravity down the stack, while the charge flows radially across the annular catalyst beds. The predominant reactions are endothermic, so an interheater is used between each reactor to reheat the charge to reaction temperature. Flue gas from the fired heaters is typically used to generate high pressure steam, but other heat integration options are available.

The effluent from the last reactor is heat exchanged against combined feed, cooled and split into vapour and liquid products in a separator. The vapour phase is rich in hydrogen gas. A portion of the gas is compressed and recycled back to the reactors. The net hydrogen-rich gas is compressed and charged together with the separator liquid phase to the product recovery section. This section can be engineered and optimized to provide the required performance. The liquid product from the recovery section is sent to a stabilizer where light saturates are removed from the aromatics-rich reformate product. Over time, coke builds up on the

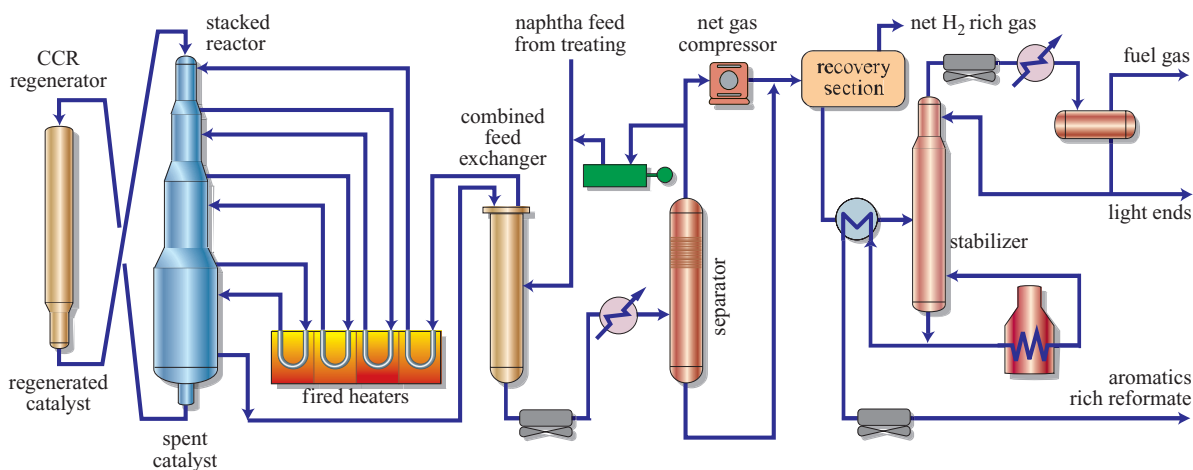


Fig. 1. CCR Platforming process.

Platforming catalyst at reaction conditions. A partially deactivated catalyst is continually withdrawn from the bottom of the reactor stack and transferred to the CCR regenerator. The catalyst flows down through the regenerator where the accumulated carbon is burned off and the moisture and chloride levels are adjusted. Regenerated catalyst is lifted with hydrogen to the top of the reactor stack. Because the reactor and regenerator sections are separate, each can operate at its own optimum conditions. In addition, the regenerator section can be temporarily shut down for maintenance without affecting the operation of the reactor and product recovery sections.

Process performance

An understanding of process chemistry explains the loss of volumetric liquid yield across the reaction zone. Yield loss comes from two sources: natural shrinkage resulting from the higher density of aromatic and cracking reactions that form lower value light products.

The conversion of naphthenes and paraffins to aromatics causes an increase in the density of the reaction material. **Fig. 2** shows the volumetric conversion of typical lean and rich naphthas across the Platforming process. A lean naphtha is one in which the paraffin content of the feed is high, typically above 65%. Rich naphtha has a lower paraffin content and a smaller density shift between feed and reformate. The catalyst system cannot control the volumetric change in yields caused by the density increase to aromatics. However, by decreasing hydrocracking reactions, selective catalyst systems have a tremendous effect on yield loss. Coupling a selective catalyst system with optimized reaction conditions

provides an increase in the catalytic reaction selectivity and the suppression of the hydrocracking reactions. Both of which are key to attaining maximum aromatic and hydrogen yields.

The fact that yields in the reforming reaction system are favoured by low pressure is well known. Great advances have been made over the past two decades in coupling improved catalyst compositions with lower operating pressures. At effective reactor operating pressures of $3.5 \cdot 10^5$ Pa (50 psi), which are typical of UOP's latest designs and recent commercial start-ups, the selectivities of the more difficult reactions are clearly better. Under such conditions, reaction selectivities for heavier paraffin species and heavy 5-membered and 6-membered naphthene ring species range from 80 to 100%. Thus, through pressure reduction and using current catalyst technology, dramatic progress has been achieved towards closing the actual-to-theoretical yield gap.

The lower operating pressures increase the rate of coke formation on the catalyst and can cause an eventual loss of performance. This problem was solved in 1971 with the start-up of the world's first CCR regenerator, which was designed and developed by UOP. In the years since the start-up of this first unit, UOP has continued to improve and expand regeneration capability to keep the CCR regenerator system in balance with the requirements of the reactor section.

Cyclar process

The Cyclar process converts LPG directly into a liquid aromatics product in a single operation. UOP, working jointly with another company, developed the Cyclar process expanding the use of LPG to the production of high-value petrochemical aromatics. LPG consists mainly of the propane and butane fraction recovered from gas and oil fields and petroleum refining operations. The relatively low value and abundance of LPG make it an ideal feedstock for petrochemical applications. Benzene, toluene, and xylenes are produced primarily through the catalytic reforming of petroleum naphtha. However, naphtha is in great demand for gasoline and petrochemical production and the value of naphtha is expected to rise as supplies become tighter. The Cyclar process offers a unique ability to produce petrochemical-grade BTX from a lower-value feedstock, and can be used in production fields

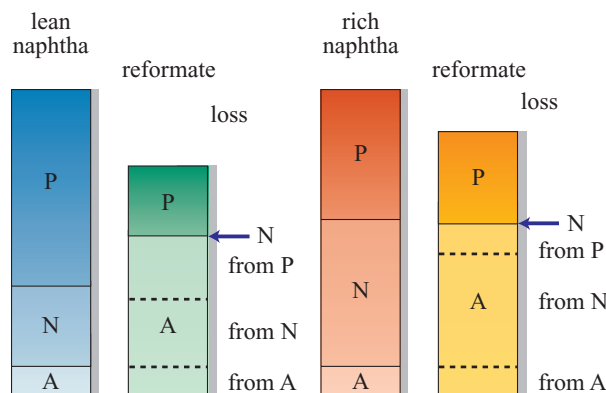


Fig. 2. Platforming process reactions; P, paraffins; N, naphthenes; A, aromatics.

to convert excess LPG into a liquid product for pipeline transport.

Process chemistry

The Cyclar process converts LPG directly to a liquid aromatics product in a single operation. The reaction is best described as dehydrocyclodimerization, and is thermodynamically favoured at temperatures higher than 425°C. The dehydrogenation of light paraffins (propane and butanes) to olefins is the rate limiting step. Once formed, the highly reactive olefins oligomerize to form larger intermediates, which then rapidly cyclize to naphthenes. These reactions, dehydrogenation, oligomerization, and cyclization, are all acid catalyzed.

The final reaction step is the dehydrogenation of the naphthenes to their corresponding aromatics. This reaction is highly favoured at Cyclar process operating conditions, resulting in virtually complete conversion of the naphthenes. The intermediates can also undergo a hydrocracking side reaction to form methane and ethane, resulting in a yield loss. Heavier paraffins such as pentanes can also be included in the feed. Olefins and pentanes are almost completely converted in the Cyclar unit, but the unit must be designed to handle them, since they result in a higher catalyst coking rate than pure butane and propane feedstocks. Although the reaction sequence involves exothermic steps, the preponderance of dehydrogenation reactions result in a highly endothermic overall reaction. This is easily understood from the fact that five moles of hydrogen are produced for every mole of aromatics formed from propane or butane.

Process description

The Cyclar process is divided into three major sections (**Fig. 3**). The reactor section includes a radial-flow reactor stack, combined feed exchanger, charge heater, and interheaters.

The CCR regenerator section includes a regenerator stack and catalyst transfer system. The product recovery section includes product separators, compressors, stripper, and gas recovery equipment. The flow scheme is similar to that of the CCR Platforming process, which is used widely throughout the world for reforming petroleum naphtha. Fresh feed and recycle are combined and heat exchanged against reactor effluent. The combined feed is then raised to reaction temperature in the charge heater and sent to the reactor section. Four adiabatic,

radial-flow reactors are arranged in one or more vertical stacks. Catalyst flows by gravity down the stack, while the charge flows radially across the annular catalyst beds. Between each reactor, the charge is reheated to reaction temperature in an interheater. The effluent from the last reactor is split into vapour and liquid products in a separator. The liquid is sent to a stripper where light saturates are removed from the C₆₊ aromatic product. Vapour from the separator is compressed and sent to a gas recovery section, typically a cryogenic unit, for separation into a 95% pure hydrogen product stream, a fuel gas stream of light saturates, and a recycle stream of unconverted LPG.

Over time, coke builds up on the Cyclar catalyst at reaction conditions. The partially deactivated catalyst is continually withdrawn from the bottom of the reactor stack and transferred to the CCR regenerator for regeneration. The catalyst flows down through the regenerator where the accumulated carbon is burned off. Regenerated catalyst is lifted with hydrogen to the top of the reactor stack. Because the reactor and regenerator sections are separate, each can operate at its own optimum conditions. In addition, the regenerator section can be temporarily shut down for maintenance without affecting the operation of the reactor and product recovery sections.

The principal Cyclar operating variables are temperature, space velocity, pressure, and feedstock composition. The temperature must be high enough to ensure nearly complete conversion of reaction intermediates in order to produce a liquid product that is essentially free of non-aromatic impurities, but low enough to minimize nonselective thermal reactions. Space velocity is optimized against conversion within this temperature range to obtain high product yields with minimum operating costs. Reaction pressure has a big impact on process performance. UOP currently offers two alternative Cyclar process designs. The low pressure design is recommended where maximum aromatic yield is desired. The high-pressure design requires only half the catalyst and is attractive where minimum investment and operating costs are the overriding considerations.

Product quality and yields

The major liquid products from the Cyclar process are benzene, toluene, xylenes, and heavier aromatics. In general, the aromatics yield increases with the carbon number of the

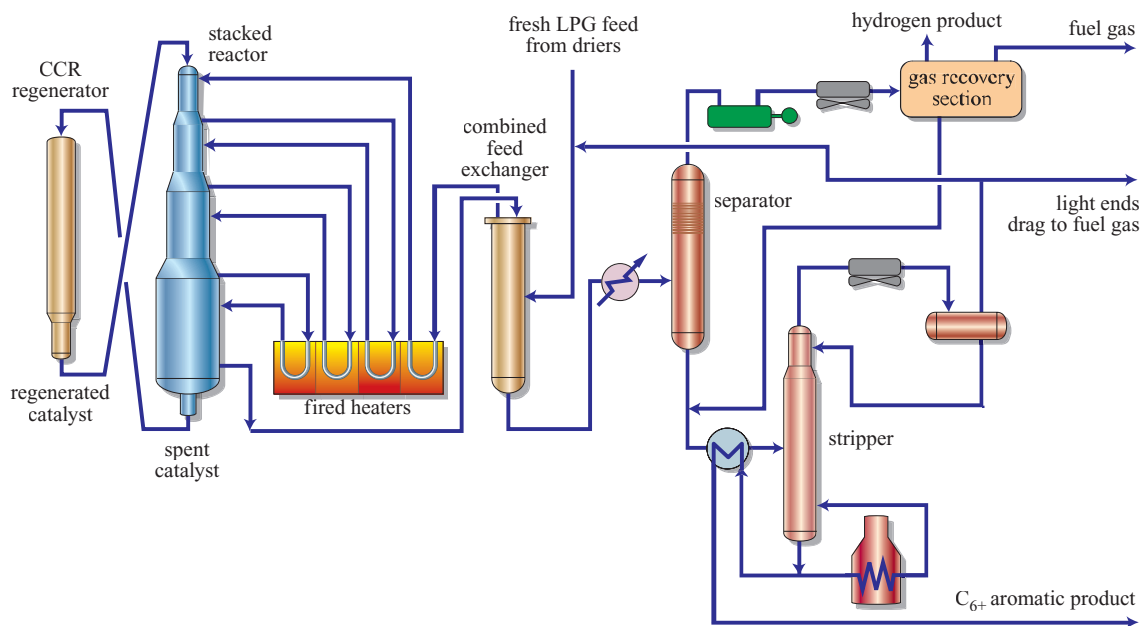


Fig. 3. Cyclar process.

feedstock. In a low-pressure operation, the overall aromatics yield increases from 61 wt% of fresh feed with an all-propane feedstock to 66% with an all-butane feed, with a corresponding decrease in fuel gas production. These yield figures can be interpolated linearly for mixed propane and butane feedstocks. The distribution of butane species in the feed has no effect on yields. The distribution of aromatic species in the liquid product is also unaffected by feedstock composition. Butane feedstocks produce a product that is leaner in benzene and richer in xylenes than that produced from propane. With either propane or butane feeds, the liquid product contains about 91% BTX and 9% heavier aromatics.

The Cyclar process produces high-quality aromatic products. Petrochemical grade toluene and xylenes can be obtained by fractionation alone, without the need for subsequent extraction. The by-product light ends contain substantial amounts of hydrogen, which may be recovered in several different ways, depending on the purity desired. An absorber/stripper system produces a 65 mol% hydrogen product stream; a cold box produces 95 mol% hydrogen; an absorber-stripper system combined with a Pressure Swing Adsorption (PSA) unit produces 99 mol% hydrogen; and a cold box combined with a PSA unit can produce 99 + mol% hydrogen, if desired.

RZ Platforming process

RZ Platforming process is a fixed bed system that is well suited for use in aromatics production facilities, particularly for those producers who require large amounts of benzene. The RZ Platforming process uses the RZ-100 catalyst. By virtue of its ability to convert the most difficult feed components (C_6 and C_7 paraffins) to aromatics, the RZ-100 catalyst represents a major step beyond conventional reforming catalyst technology.

The RZ Platforming process is primarily used for situations where higher yields of BT (Benzene Toluene) aromatics and hydrogen are desired. Benzene production especially benefits from RZ-100's catalyst selectivity performance. The superior ability of the RZ Platforming process to handle light, paraffinic feeds and its flexibility in processing straight-run naphtha fractions provide many options for improving aromatics production and supplying needed hydrogen, either in new units or in existing aromatics facilities.

Process chemistry

The Platforming process is designed to efficiently convert paraffins and naphthenes to aromatics with as little ring opening or cracking as possible.

Although RZ-100 catalyst is similar in many ways to conventional reforming catalysts, it

differs greatly in the production of light aromatics – benzene and toluene. The selectivity of conventional reforming catalysts for benzene and toluene is significantly lower than for the C_8 aromatics. By comparison, the selectivity of the RZ-100 catalyst for light aromatics is vastly improved.

Process description

The RZ Platforming unit configuration is similar to other fixed bed platforming units (**Fig. 4**). Treated naphtha feed is combined with recycle hydrogen gas and heat exchanged against reactor effluent. The combined feed is then raised to reaction temperature in the charge heater and sent to the reactor section. Radial-flow reactors are arranged in a conventional side-by-side pattern. The predominant reactions are endothermic, so an interheater is used between each reactor to reheat the charge to reaction temperature.

Flue gas from the fired heaters is typically used to generate high pressure steam, but other heat integration options are available. The effluent from the last reactor is heat exchanged against combined feed, cooled and split into vapour and liquid products in a separator. The vapour phase is rich in hydrogen gas and a portion of the gas is compressed and recycled back to the reactors. The net hydrogen-rich gas is compressed and charged together with the separator liquid phase to the product recovery section. This section can be engineered and optimized to provide location-specific required performance. The liquid product from the recovery section is sent to a stabilizer where light saturates are removed from the C_{6+} aromatic

product. Catalysts deactivate over time at reaction conditions. Typical cycle lengths are eight to twelve months. Efficient *ex situ* regeneration facilities for rejuvenation of RZ-100 catalysts are available.

Process performance

Although the CCR Platforming process is the most efficient means possible for producing xylenes from heavier naphtha fractions, its conversion of C_6 and C_7 paraffins to aromatics is normally below 50%, even at low pressure. The RZ Platforming process offers constant aromatics selectivity, in the range of 80% or higher, even when processing the most difficult C_6 and C_7 paraffin feed components.

Feedstock to the RZ Platforming unit can range from extraction-unit raffinate to BTX naphtha. A very effective application for the RZ-100 catalyst is the production of aromatics and hydrogen from light, paraffinic feeds, such as a BT raffinate. The RZ-100 catalyst can also be used in parallel with a conventional reforming unit to optimize the production of the desired aromatics by processing different fractions of the hydrotreated feed. In such cases, the conventional reformer can be dedicated to process the heavier feed fraction, taking advantage of its superior ability to produce xylenes. The light naphtha, which is rich in C_6 and C_7 components, can be routed to the RZ Platforming unit, where selectivity for converting light paraffins to benzene and toluene is greatest.

Parex process

The Parex process is an innovative, adsorptive separation method for the recovery of

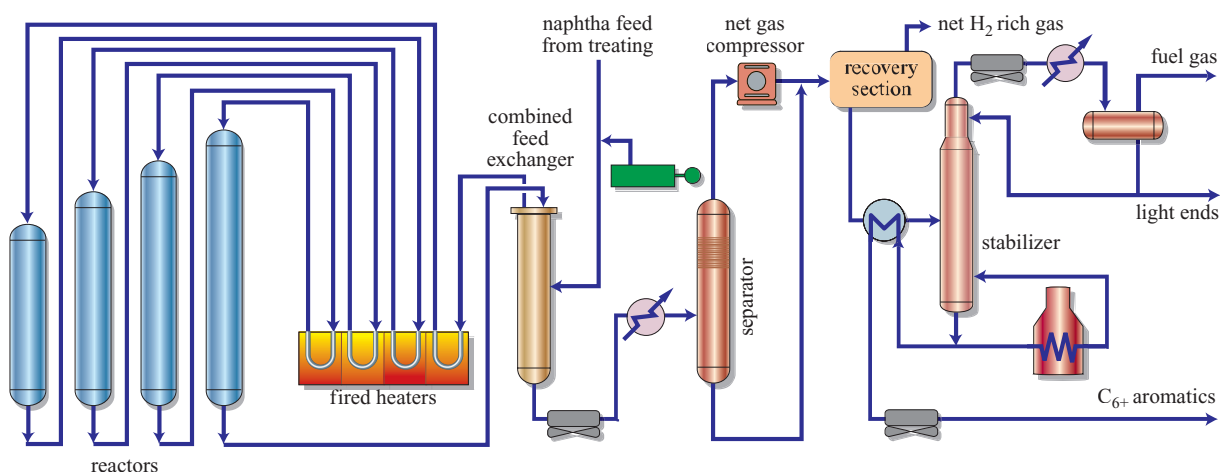


Fig. 4. RZ Platforming process.

para-xylene from mixed xylenes that offers high product purity, high product recovery, high on-stream efficiency, and extended adsorbent life. 'Mixed xylenes' refers to a mixture of C₈ aromatic isomers that includes ethylbenzene, para-xylene, meta-xylene, and ortho-xylene. These isomers boil so closely together that separating them by conventional distillation is not practical. The Parex process provides an efficient means of recovering para-xylene using a solid zeolitic adsorbent which is selective for para-xylene. Unlike conventional batch chromatography, the Parex process simulates a moving bed of adsorbent with continuous counter-current flow of a liquid feed over the adsorbent. Feed and products enter and leave the adsorbent bed continuously, at nearly constant compositions. This technique is called simulating-moving-bed separation.

In an aromatics complex, the Parex unit is located downstream of the xylenes column and is integrated with an Isomar unit. The feed to the xylenes column consists of the C₈₊ aromatics product from a CCR Platforming unit and the xylenes produced in a Tatoray unit. The C₈ fraction from the overhead of the xylenes column is fed to the Parex unit, where high purity para-xylene is recovered in the extract. The Parex unit raffinate is sent to the Isomar unit, where the other C₈ aromatic isomers are converted into additional para-xylene and recycled back to the xylene column. The Parex process is designed to recover more than 97 wt% of the para-xylene from the feed in a single pass while delivering product purity of 99.9 wt% or better.

The high purity para-xylene recovered in the Parex process is used for the production of polyester fibres, resins, and films. Para-xylene is converted to terephthalic acid (TPA) or dimethyl terephthalate (DMT), which are then reacted with ethylene glycol to form polyethylene terephthalate (PET) which is the raw material for most polyesters.

Process description

The separation takes place in the adsorbent chambers. Each adsorbent chamber is divided into a number of adsorbent beds. Each bed of adsorbent is supported from below by specialized internals or grids, that are designed to produce highly efficient flow distribution. Each internals assembly is connected to the rotary valve by a bed line. The internals between each adsorbent bed are used to inject or withdraw liquid from the chamber while simultaneously collecting liquid

from the bed above and redistributing the liquid over the bed below. A typical Parex unit has 24 adsorbent beds with 26 sets of chamber internals, and 24 bed lines connecting the beds to the rotary valve. Due to practical construction considerations, most Parex units consist of two adsorption chambers in series with 12 beds each. In the Parex process, there are four major streams that are distributed to the adsorbent chamber by the rotary valve. These 'net' streams include: a) feed in (mixed xylenes feed); b) dilute extract out (para-xylene product diluted with desorbent); c) dilute raffinate out (ethylbenzene, meta- and ortho-xylene diluted with desorbent); d) desorbent in (recycle desorbent from the fractionation section).

At any given time, only four of the bed lines are active, carrying the net streams into and out of the adsorbent chamber. The rotary valve is used to periodically switch the positions of the liquid feed and withdrawal points as the composition profile moves down the chamber. A pump provides the liquid circulation from the bottom of the first adsorbent chamber to the top of the second. A second pump provides circulation from the bottom of the second adsorbent chamber to the top of the first. In this way, the two adsorbent chambers function as a single continuous loop of adsorbent beds. The dilute extract is sent to the extract column for separation of the extract from the desorbent. The overhead from the extract column is sent to a finishing column where the highly pure para-xylene product is separated from any toluene which may have been present in the feed.

The dilute raffinate from the rotary valve is sent to the raffinate column for separation of the raffinate from the desorbent. The overhead from the raffinate column contains unextracted C₈ aromatic components: ethylbenzene, meta-xylene, ortho-xylene, and any non-aromatics which may have been present in the feed. The raffinate product is then sent to the Isomar unit where additional para-xylene is formed and then recycled back to the Parex unit.

The desorbent from the bottom of both the extract and raffinate columns is recycled back to the adsorbent chambers through the rotary valve. In order to prevent this accumulation, provision is made to take a slipstream of the recycle desorbent to a small desorbent rerun column where any heavy contaminants are rejected. During normal operation, mixed xylenes are stripped, clay-treated, and rerun prior to being sent to the Parex unit. Therefore, the amount of

heavy contaminants to be removed from the bottom of the desorbent rerun column is not significant.

Isomar process

The Isomar process is used to maximize the recovery of a particular xylene isomer from a mixture of C₈ aromatic isomers. The Isomar process is most often applied to para-xylene recovery, but it can also be used to maximize the recovery of ortho-xylene or meta-xylene. In the case of para-xylene recovery, a mixed xylenes feed is charged to a Parex process unit where the para-xylene isomer is preferentially extracted. The raffinate from the Parex unit, almost entirely depleted of para-xylene, is then sent to the Isomar unit. The Isomar unit re-establishes an equilibrium distribution of xylene isomers, essentially creating additional para-xylene from the remaining ortho- and meta-xylenes. Effluent from the Isomar unit is then recycled back to the Parex unit for recovery of additional para-xylene. In this way, the ortho- and meta-xylenes and ethylbenzene are recycled to extinction. Depending on the type of catalyst, ethylbenzene is converted into xylenes or benzene.

Process chemistry

There are two broad categories of xylene isomerization catalysts: ethylbenzene (EB) isomerization catalysts, which convert ethylbenzene into additional mixed xylenes, and ethylbenzene dealkylation catalysts, which convert ethylbenzene to a valuable benzene co-product.

UOP currently offers I-400 EB isomerization catalyst and I-300 EB dealkylation catalyst. The selection of the isomerization catalyst depends on the configuration of the aromatics complex, the composition of the feedstocks, and the desired product slate. The I-400 catalyst is typically chosen when the primary goal of the complex is to maximize production of para-xylene. Alternatively, I-300 catalyst can be used to de-bottleneck an existing Parex unit or crystallizer by converting more EB per pass through the isomerization unit and eliminating the requirement for naphthene intermediate circulation around the Parex-Isomar recycle loop. The EB isomerization reaction presents a thermodynamic limit, insofar as the EB conversion to equilibrium is equal to about 30 wt% per pass. The EB dealkylation reaction is not thermodynamic limited, allowing for up to 70

wt% or greater EB conversion per pass. The reduction in the size of the Parex-Isomar loop with an I-300 reload comes at the expense of lower paraxylene yields, since all the EB in the feed is being converted to benzene rather than additional para-xylene. All xylene isomerization catalysts cause some loss of aromatic rings to by-products across the reactor. A large portion of the total feed from the Isomar unit goes to the xylene column. A typical Parex-Isomar loop exhibits a combined feed ratio of about 3.5. Therefore, a small reduction in the per-pass by-product formation across the Isomar unit translates to a large yield advantage. The Isomar process exhibits minimal by-product formation, with the precise level being a function of feed composition, catalyst type and operating severity. For EB isomerization catalysts, the by-product formation is based on the per-pass losses of C₈ cyclics (EB, xylenes and C₈ naphthenes). For the I-400 catalyst, the ring loss per pass will be in the range of 1.5-2 mol% per pass. The C₈ ring loss for the I-9 catalyst ranges from 3 to 5 mol% per pass. For EB dealkylation catalysts, the by-product formation is based on the per-pass losses of xylenes. For I-300 catalyst, this is in the range of 1-2 wt%. The EB is converted to benzene with a selectivity that is typically more than 90 mol%. Overall aromatic ring conservation is very high – more than 99 mol% for EB dealkylation catalysts. Most of the by-products from Isomar (except for the benzene from I-300) catalyst can be re-converted to xylenes when a Tatory transalkylation unit is part of the flow-scheme.

I-300 catalyst offers the simplicity of a single catalyst system. The Isomar process requires about half as much I-300 catalyst as the previous generation of catalysts, and its use eliminates multiple beds of different catalysts with complicated loadings and distributors. Unlike some ethylbenzene dealkylation catalysts, the I-300 catalyst does not require continuous addition of ammonia to achieve desired activity and selectivity.

Process description

An Isomar unit is always combined with a recovery unit for one or more of the xylene isomers. Usually it is combined with a Parex unit for recovery of para-xylene. In the Parex-Isomar flow scheme (**Fig. 5**), fresh mixed xylenes are fed to the xylene column, which can be designed either to recover ortho-xylene in the bottoms or simply reject C₉₊ aromatic components in order

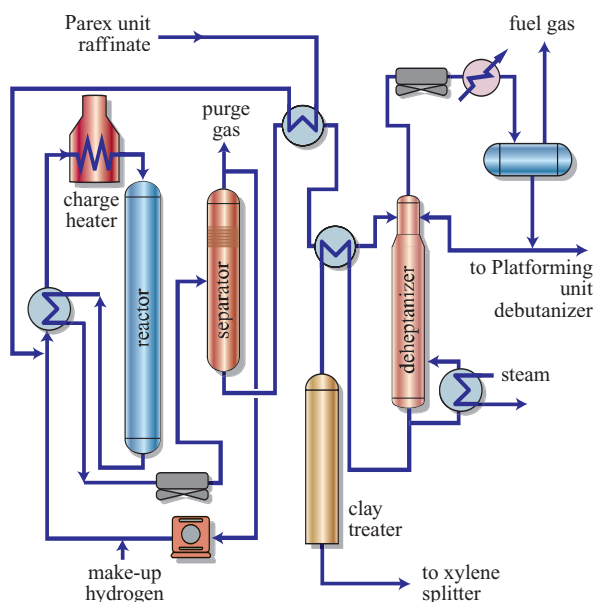


Fig. 5. Isomar process.

to meet feed specifications to the Parex unit. The xylene column overhead is then directed to the Parex unit where 99.9 wt% para-xylene is produced. The raffinate from the Parex unit, containing less than 1 wt% para-xylene, is sent to the Isomar unit.

Process performance

The best way to compare xylene isomerization catalysts is to measure the overall para-xylene yield from the Parex-Isomar loop. The para-xylene yield, based on fresh mixed xylenes fed to the Parex-Isomar loop, is characterized by the following considerations.

The basis for the comparison is the Parex-Isomar yield flow scheme, processing a fresh mixed xylenes feed consisting of 17 wt% ethylbenzene, 18 wt% para-xylene, 40 wt% meta-xylene, and 25 wt% ortho-xylene. The operating severity for the I-9 and I-400 catalyst is 22.1 wt% para-xylene of the total xylenes from the Isomar unit. The operating severity for I-300 catalyst is 65 wt% conversion of ethylbenzene per pass. With the I-9 catalyst, the overall yield of para-xylene is 84 wt% of the fresh mixed xylenes feed. Since it has very high overall aromatic ring retention, but converts ethylbenzene to benzene, the I-300 catalyst exhibits a higher overall yield of benzene plus para-xylene, but the yield of para-xylene is only 76.5 wt%. This means that more mixed xylenes are required to produce a target amount

of para-xylene with I-300 catalyst. I-400 catalyst relies on the same reaction chemistry as I-9 catalysts, but is more selective and exhibits lower ring loss. With I-400 catalyst, the overall yield of para-xylene is 7 wt% higher than with I-9 catalysts, at 91 wt% of fresh mixed xylenes feed.

Tatoray process

The Tatoray process is used to selectively convert toluene and C_9 aromatics (A_9) into benzene and xylenes. In a modern aromatics complex, this process is integrated between the aromatics extraction and xylene recovery sections of the plant. Extracted toluene is fed to the Tatoray process unit rather than being blended into the gasoline pool or sold for solvent applications.

To maximize the production of para-xylene from the complex, the A_9 by-product can also be fed to the Tatoray process unit. This shifts the chemical equilibrium from benzene production to xylenes production. In recent years, the demand for para-xylene has outstripped the supply of mixed xylenes. The Tatoray process provides an ideal way to produce additional mixed xylenes from toluene and heavy aromatics. Incorporating a Tatoray process unit into an aromatics complex can more than double the yield of para-xylene from a given naphtha feedstock.

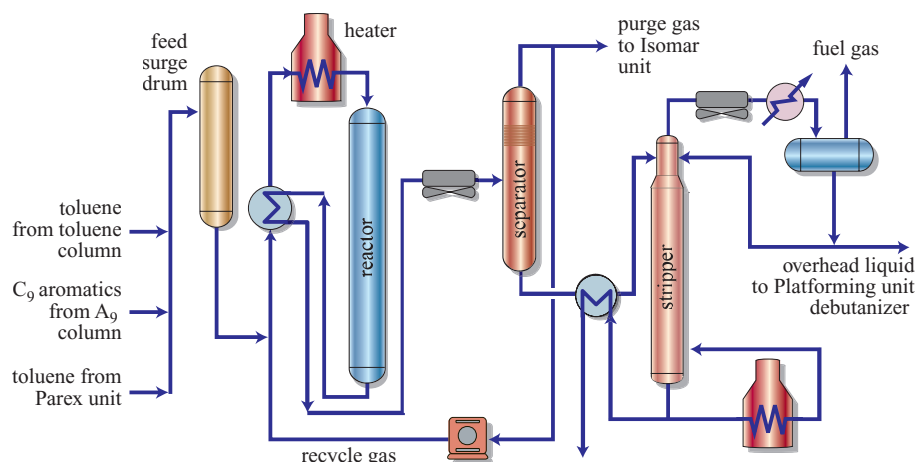
Process chemistry

The two major reactions in the Tatoray process are disproportionation and transalkylation. The conversion of toluene into benzene and xylenes is called toluene disproportionation. Transalkylation is the conversion of a mixture of toluene and A_9 into xylenes.

This process is designed to function at a much higher level of conversion per pass than other toluene disproportionation processes. With a typical 50:50 feedstock ratio of toluene and C_9 aromatics, the overall conversion is approximately 50% per pass. This high conversion level minimizes the amount of unconverted material that must be recycled back through the BT fractionation section of the complex. A smaller recycle stream minimizes the size of the benzene and toluene columns, the size of the Tatoray process unit, and the utility consumption of all of these units.

The Tatoray process reactions are conducted in a hydrogen atmosphere to minimize coke formation on the catalyst. Because there is

Fig. 6.
Tatoray process.



negligible ring destruction in the Tatoray process, there is very little hydrogen consumption. The methyl groups are highly stable at reaction conditions and are therefore essentially conserved in the reaction. Most of the hydrogen consumption can be attributed to the cracking of the non-aromatic impurities in the feed to the Tatoray unit.

Process description

The Tatoray process uses a very simple flow scheme consisting of a fixed bed reactor and a product separation section (**Fig. 6**). The fresh feed to the Tatoray unit is combined with hydrogen-rich recycle gas, preheated by exchange with the hot reactor effluent, and vapourized in a fired heater where it is raised to reaction temperature. The hot feed vapour goes to the reactor, where it is sent down-flow over a fixed bed of catalyst.

The reactor effluent is cooled by exchange with the combined feed, mixed with make-up gas to replace the small amount of hydrogen consumed in the reactor, and then sent to a product separator. Hydrogen-rich gas is taken off the top of the separator and recycled back to the reactor. A small portion of the recycle gas is purged to remove accumulated light ends from the recycle gas loop. Liquid from the bottom of the separator is sent to a stripper column.

The C_5 overhead from the stripper is cooled and separated into gas and liquid products. The stripper overhead gas is exported to the fuel gas system. The overhead liquid is recycled back to the Platforming unit debutanizer column so that any benzene in this stream may be recovered in the sulpholane (extraction) unit. The benzene and xylene products, together with the unreacted

toluene and A_9 , are taken from the bottom of the stripper and recycled back to the BT fractionation section of the aromatics complex.

Process performance

A Tatoray process unit is capable of processing feedstocks ranging from 100 wt% toluene to 100 wt% A_{9+} . The optimal concentration of A_{9+} in the feed is typically 40-60 wt%. The ability to process A_{9+} makes more feedstock available for xylenes production and dramatically shifts the selectivity of the unit away from benzene. Feeds may contain up to 10% C_{10} aromatics.

An aromatics complex without a Tatoray unit can produce approximately 200,000 MTA (Metric Tons per Annum) of para-xylene from 25,000 BPSD (Barrels Per Stream Day) of Light Arabian naphtha (160-300°F cut). If an A_7 Tatoray process unit (toluene feed only) is added to the complex, the same amount of naphtha can produce 280,000 MTA of para-xylene, a 40% increase. When an A_7/A_{9+} Tatoray process unit is added to the complex, the endpoint of the naphtha is increased from 300 to 340°F in order to maximize the amount of A_{9+} precursors in the feed. The heavier naphtha will produce approximately 420,000 MTA para-xylene – an increase of 110% over the base complex.

The Tatoray process produces petrochemical grade benzene and xylenes products. Benzene purity with 100% toluene feed easily meets the ASTM specifications for Refined 545 grade benzene. With a feed of 50% toluene and 50% C_9 aromatics, the benzene product purity meets the specifications for Refined 535 grade benzene. The xylene product from a Tatoray unit contains

an equilibrium distribution of xylene isomers and is very low in ethylbenzene. This low ethylbenzene concentration makes the xylenes produced by the Tatoray process valuable as feedstock to either a Parex unit or a para-xylene crystallization unit.

PX-Plus process

The PX-Plus process selectively disproportionates toluene to benzene and xylenes. The process is para selective, with the product having a para-xylene concentration in the xylene fraction of about 90%, significantly above the equilibrium value of 25% that is achieved by toluene and C₉ aromatic transalkylation technologies, such as the Tatoray process. The PX-Plus process provides an economical way to expand existing para-xylene facilities.

Increasing the para-xylene concentration in aromatics complex streams by adding a PX-Plus unit has significant benefits. Recoveries from a single stage crystallizer can be increased from 65% to more than 80% when the feed para-xylene concentration increases. Due to the similarity of operating temperature and pressure to that of many refining and petrochemical reactor systems, existing idle equipment can often be considered for re-use in the PX-Plus unit. The PX-Plus process can also be used for large-scale grassroots facilities where sufficient toluene is available and where significant quantities of benzene are desired along with para-xylene.

Process chemistry

The disproportionation of toluene to benzene and xylenes proceeds via a bimolecular

intermediate. Once the bimolecular intermediate cleaves to benzene and xylene, some amount of shifting of methyl groups can occur on the xylene molecule. The catalyst pore structure allows benzene and para-xylene to escape while inhibiting the diffusion of ortho-xylene and meta-xylene.

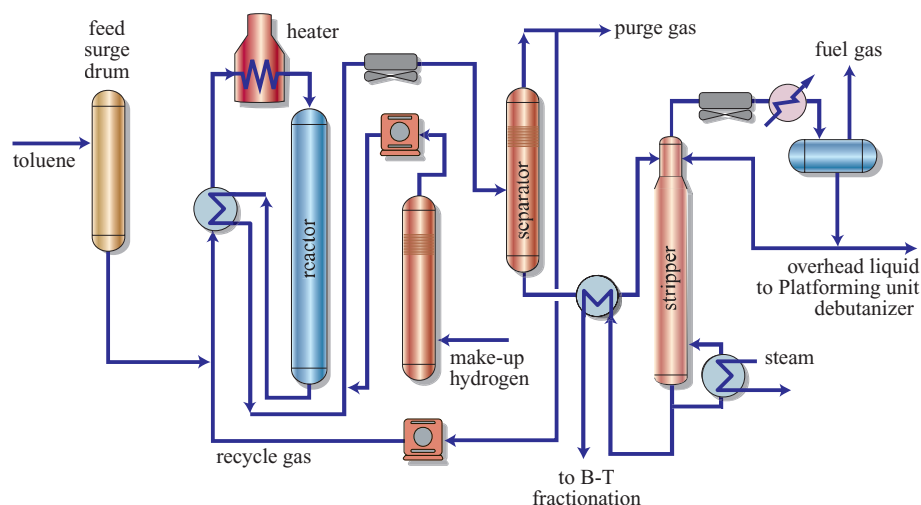
Process description

In the PX-Plus unit (**Fig. 7**), fresh toluene feed is first combined with hydrogen-rich recycle gas, preheated by exchange with the hot reactor effluent, and then vapourized and raised to the reaction temperature in a fired heater. Depending on the size of the unit, the reactor may be downflow or radial flow. The effluent from the reactor flows through the feed-effluent exchanger, is condensed, and sent to the product (gas-liquid) separator, where recycle hydrogen is removed. The separator liquid is sent to the stripper column, where light by-products are removed overhead. The stripper bottoms stream is then sent to benzene-toluene fractionation. High purity benzene is recovered overhead, and the recycle toluene is recovered and sent back to the reactor. The para-xylene concentrate may then be fed directly to a single stage crystallizer, or it may be sent to the Parex unit via the xylene rerun column along with the fresh feed mixed xylenes and the recycle isomers.

Process performance

For a typical PX-Plus process unit, para-xylene concentration in the product xylenes is 90%, toluene conversion per pass is 30%, benzene/xylenes mole ratio is 1.32 and benzene

Fig. 7.
PX-Plus process.



quality is high. At 30% toluene conversion, the PX-Plus process produces less than 2 wt% light by-products per pass. The para-xylene yield based on toluene converted is around 41 wt% and the benzene yield is 46 wt%.

TAC9 process

The TAC9 process is used to selectively convert C_9 - C_{10} aromatics into mixed xylenes. In a modern aromatics complex, the transalkylation technologies, such as the Tatoray and TAC9 processes, are integrated between the aromatics extraction or fractionation and the xylene recovery sections of the plant. Fractionated heavy aromatics can be fed to the TAC9 unit rather than being blended into the gasoline pool or sold for solvent applications.

Incorporating transalkylation technology into an aromatics complex for the processing of toluene and C_9 - C_{10} aromatics can more than double the yield of para-xylene from a given naphtha feedstock. The TAC9 process provides a more efficient means of obtaining additional mixed xylenes from the heaviest portion of the aromatics. Processors of heavy aromatics can produce higher value products by upgrading by-product streams.

Process chemistry

The TAC9 process involves several types of reactions of C_9 - C_{10} aromatics. Included are disproportionation (re-arrangement of alkyl groups between two identical molecules, such as toluene), transalkylation (transfer of groups between different molecules), and dealkylation (complete or partial removal of an alkyl group). In the TAC9 process, the dealkylation of the alkyl groups occurs in such a way that the methyl groups are retained.

The compounds involved are primarily alkyl substituted aromatic compounds or alkylbenzenes. For example, the ethyl groups involved in the reactions would be those of aromatics having at least one ethyl substitute, such as diethylbenzene, methyl-ethylbenzene (ethyl toluene), or dimethyl ethylbenzene (ethyl xylene). Moreover, the methyl groups involved would be those of compounds, which are aromatics having only methyl substitutes, such as toluene, xylene, or trimethylbenzene. The highly active TAC9 catalyst converts almost all ethyl, propyl, and butyl groups on aromatic rings to light ends by dealkylation. The methyl groups react via disproportionation and transalkylation. By controlling the feed composition, a methyl balance for xylene production is achieved.

The xylene yield achieved is a function of both the methyl to phenyl (aromatic) ratio as well as the ratio of ethyl groups to methyl groups in the fresh

feed. Higher ratios of methyl to ethyl groups result in higher xylene yields. In some instances, a small benzene drag to an extraction unit may be required to optimize the yields. Mixed xylenes with very low ethylbenzene concentrations can be achieved. This low concentration is beneficial to operation of the Isomar and Parex units of an integrated complex.

The typical feedstock is a combination of C_9 and C_{10+} aromatics derived either from reformates or hydrotreated pyrolysis gasoline (an aromatic-rich by-product of ethylene crackers). The distribution of alkyl groups and the C_9 to C_{10} ratio of the feeds will vary with the source as well as with the upstream pre-fractionation.

Conventional transalkylation technologies are limited in their ability to process C_{10+} material primarily due to the adverse impact that they have on catalyst life. Higher levels result in shorter cycles between catalyst regenerations, thus reducing the unit on-stream efficiencies. However, the highly active TAC9 catalyst converts these heavies efficiently to higher valued products while maintaining an economical catalyst life.

The TAC9 reactions are conducted in a hydrogen atmosphere in order to minimize coke formation on the catalyst. There is very low aromatic loss in the TAC9 process. Methyl groups are highly stable at reaction conditions and are therefore essentially conserved in the reaction. Most of the hydrogen consumption can be attributed to the dealkylation reactions and to the cracking of the non-aromatic impurities in the feed to the TAC9 unit.

Toray Industries introduced the current generation of TAC9 catalyst in 1996. Commercial experience has demonstrated the ability to operate for several years without regeneration. Cycle lengths of more than five years have been observed. The catalyst is regenerated using a simple carbon burn procedure.

Process description

The TAC9 process uses a very simple flow scheme, identical to the flow scheme for the Tatoray process. It consists of a fixed bed reactor and a product separation section. The fresh feed is mixed with recycle material then charged to the TAC9 unit. Feed material is first combined with hydrogen-rich recycle gas, preheated by exchange with the hot reactor effluent, and then vapourized in a fired heater where it is raised to reaction temperature. The hot feed vapour then flows to the reactor, where it flows down-flow over a fixed bed of catalyst.

The reactor effluent is cooled by exchange with the combined feed, cooled in a product condenser, and then collected in the product separator.

Hydrogen-rich gas taken off the top of the separator is combined with make-up hydrogen and then recycled back to the reactor. A small portion of the recycle gas is purged from the recycle gas loop. Liquid from the bottom of the separator is sent to a stabilizer column. The C_5 overhead from the stabilizer is cooled and separated into gas and liquid products. The stabilizer overhead gas is exported to the fuel gas system. The stabilized TAC9 product is sent to product fractionation.

The process operating conditions (temperatures and pressure) are similar to those of the Tatoray process. The overall conversion is close to 50%. This can be tailored for the re-use of equipment in a revamp situation.

Sulpholane process

The sulpholane process combines liquid-liquid extraction with extractive distillation to recover high purity aromatics from hydrocarbon mixtures, such as reformed petroleum naphtha (reformate), pyrolysis gasoline, or Coke Oven Light Oil (COLO). Contaminants that are the most difficult to eliminate in the extraction section are easiest to eliminate in the extractive distillation section and vice versa. This hybrid combination of techniques allows sulpholane units to process feedstocks of much broader boiling range than would be possible by either technique alone. A single sulpholane unit can be used for simultaneous recovery of high-purity C_6 - C_9 aromatics, with individual aromatic components recovered downstream by simple fractionation. Typically, when just benzene or toluene is produced, the sulpholane unit can be built as an Extractive Distillation (ED) unit only and the extractor can be eliminated, thereby simplifying the design.

The sulpholane process takes its name from the solvent used: tetrahydrothiophene 1, 1-dioxide, or 'sulpholane'. Sulpholane is the most efficient solvent available for the recovery of aromatics. Most extraction units can be made to operate at high purity and recovery by circulating more and more solvent. Because the sulpholane solvent exhibits higher selectivity and capacity for aromatics than any other commercial extraction solvent, sulpholane units operate at the lowest available solvent-to-feed ratio for any given reformate feedstock. Therefore, for reformate applications, a sulpholane unit is less expensive to build and operate than any other type of extraction unit.

A sulpholane unit is usually incorporated within an aromatics complex to recover high-purity benzene and toluene products from reformate. In a modern, fully integrated aromatics complex, the sulpholane

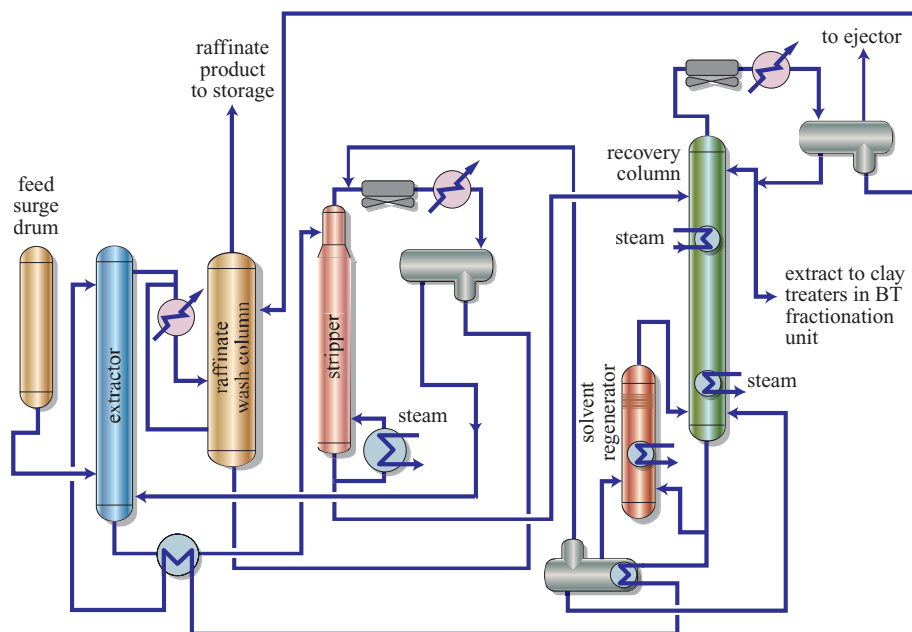
unit is located downstream of the reformate splitter column. The C_6 - C_7 fraction from the overhead of the reformate splitter is fed to the sulpholane unit. The aromatic extract from the sulpholane unit is clay treated to remove trace olefins, and individual benzene and toluene products are recovered by simple fractionation. The raffinate from the sulpholane unit is usually blended into the gasoline pool or used in aliphatic solvents. Benzene must always be recovered by extraction or extractive distillation in order to meet purity specifications for petrochemical applications. Toluene must be extracted for direct use in petrochemical applications and is usually extracted before being fed to a dealkylation or disproportionation unit for production of additional benzene and xylenes. Modern CCR Platforming units operate at such high severity that the C_8+ fraction of the reformate does not contain any significant amount of non-aromatic impurities and may be sent directly to the xylenes recovery section of the plant without extraction. However, the C_8+ fraction of pygas and COLO streams contains significant amounts of non-aromatic impurities and, therefore, must be extracted before either being recovered as marketable mixed xylenes or sent to xylene recovery.

Process description

As shown in **Fig. 8**, fresh feed enters the extractor and flows upward, countercurrent to a stream of lean solvent. As the feed flows through the extractor, aromatics are selectively dissolved in the solvent. A raffinate stream, very low in aromatics content, is withdrawn from the top of the extractor. The rich solvent, loaded with aromatics, exits the bottom of the extractor and enters the stripper. The non-aromatic components having volatilities higher than that of benzene are completely separated from the solvent by extractive distillation and removed overhead along with a small quantity of aromatics. This overhead stream is recycled to the extractor where the light non-aromatics displace the heavy non-aromatics from the solvent phase leaving the bottom of the extractor. The bottoms stream from the stripper, substantially free of non-aromatic impurities, is sent to the recovery column, where the aromatic product is separated from the solvent.

Because of the large difference in boiling point between the sulpholane solvent and the heaviest aromatic component, this separation is accomplished easily, with minimal energy input. To minimize solvent temperatures, the recovery column is operated under vacuum. Lean solvent from the bottom of the recovery column is

Fig. 8. Sulpholane process.



returned to the extractor. The extract is recovered overhead and sent on to distillation columns downstream for recovery of the individual benzene and toluene products. The raffinate stream exits the top of the extractor and is directed to the raffinate wash column. In the wash column, the raffinate is contacted with water to remove dissolved solvent. The solvent-rich water is vapourized in the water stripper by exchange with hot circulating solvent and then used as stripping steam in the recovery column. Accumulated solvent from the bottom of the water stripper is pumped back to the recovery column. The raffinate product exits the top of the raffinate wash column. The amount of sulpholane solvent retained in the raffinate is negligible. The raffinate product is commonly used for gasoline blending or aliphatic solvent applications. Under normal operating conditions, the sulpholane solvent undergoes only minor oxidative degradation. A small solvent regenerator is included in the design of the unit as a safeguard against the possibility of air leaking into the unit. During normal operation, a small slip-stream of circulating solvent is directed to the solvent regenerator for removal of oxidized solvent.

The extract product from a sulpholane unit may contain trace amounts of olefins and other impurities which would adversely affect the acid wash colour tests of the final benzene and toluene products. To eliminate these trace impurities, the extract is clay-treated prior to

fractionation. Clay treating is done at very mild conditions and clay consumption is minimal.

The treated extract is directed to the aromatics fractionation section where high-purity benzene, toluene, and sometimes mixed xylenes are recovered. The design of the aromatics fractionation section varies depending on the particular processing requirements of the customer.

Process performance

The performance of the sulpholane process has been well demonstrated in more than 130 operating units. The recovery of benzene exceeds 99.9 wt%, and recovery of toluene is typically 99.8 wt%. The sulpholane process is also efficient at recovery of heavier aromatics if necessary. Typical recovery of xylenes exceeds 98 wt%, and 99 wt% recovery has been demonstrated commercially with rich feedstocks.

Sulpholane units routinely produce a benzene product with a 5.5°C solidification point or better, and many commercial units produce benzene containing less than 100 ppm non-aromatic impurities. The toluene and C₈ aromatics products from a sulpholane unit are also of extremely high purity, easily exceeding nitration grade specifications. In fact, the ultimate purity of all of the aromatic products is usually more dependent on the design and proper operation of the downstream fractionation section than on the extraction efficiency of the sulpholane unit itself. The purity and recovery performance of an aromatics extraction unit is largely a function of energy consumption.

In general, higher solvent circulation rates result in better performance, but at the expense of higher energy consumption. The sulpholane process demonstrates the lowest energy consumption of any commercial aromatics extraction technology. A typical sulpholane unit consumes 275-300 kcal of energy per kilogram of extract produced, even when operating at 99.99 wt% benzene purity and 99.95 wt% recovery. Sulpholane units are also designed to efficiently recover solvent for recycle within the unit. Expected solution losses of sulpholane solvent are less than 5 ppm of the fresh feed rate to the unit.

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10.6.2 Aromatic intermediates in petrochemical industry

Introduction

The alkylation reaction of aromatic compounds is widely used in the chemical industry for the production of important intermediates such as ethyl benzene and cumene. **Fig. 1** shows the main alkylations employed in industry for the transformation of benzene, toluene and xylene, by reaction with olefins, into isopropyl benzene (cumene), diisopropyl benzene, ethyl benzene, diethyl benzene, C₁₀-C₁₄ Linear Alkyl Benzenes (LAB), cymene, isobutyl benzene, and *o*-tolyl pentene. In **Fig. 1** the principal derivatives of these intermediates are also indicated. The alkylations shown are of two types: the alkylation of the aromatic ring catalysed by acids and that of the side chain, catalysed by bases.

From the point of view of production volumes, the acid-catalysed alkylations of benzene are the most important: in 2004 about 75% of the benzene produced in the world (36.5 million tons) was alkylated with olefins, 71% of which was to produce ethyl benzene and cumene (**Table 1**).

Alkylation of aromatic hydrocarbons with olefins

The alkylation reaction of aromatic hydrocarbons can be performed using various alkylating agents:

alkyl halides, alcohols, alkyl sulphates, and olefins.

Olefins are the most extensively used alkylating agents in the petrochemical industry. The alkylation reaction of the aromatic ring with olefins is an exothermic reaction and thus is favoured, from the thermodynamic point of view, at low temperatures. In fact the equilibrium constant diminishes with increasing temperature, as illustrated in **Fig. 2** for the alkylation of benzene with ethylene and propylene. The enthalpy of reaction at 25°C in the gaseous state is -105.51 and -99.65 kJ/mol, for the formation of ethyl benzene and cumene respectively. Thus the formation of these alkyl aromatics is accompanied by a release of energy, in the form of heat, which needs to be taken into account in the design of production plants.

Acid catalysis

Different types of acids are used as catalysts for the alkylation of aromatic hydrocarbons: *a*) metal halides, such as aluminium and gallium chloride and borium fluoride; *b*) mixed oxides and zeolites; *c*) protonic acids such as sulphuric acid, hydrofluoric acid and phosphoric acid; and *d*) sulphonc resins. The most active ones are the Brönsted acids, which contain an acidic proton. The metal halides, which are Lewis acids, are not very active alkylation catalysts if used as such and must be activated by means of adding small quantities of a

Fig. 1. Main aromatic hydrocarbon alkylations with olefins of industrial interest.

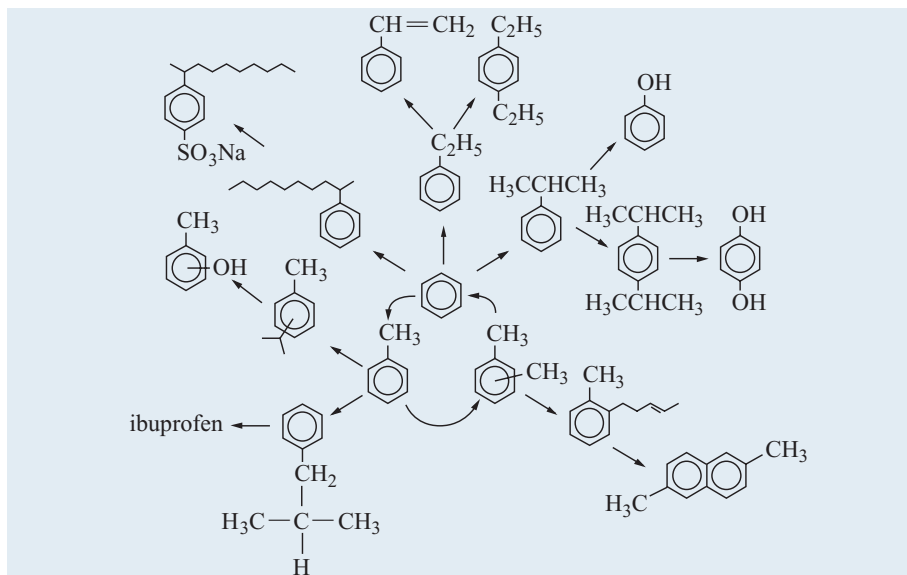
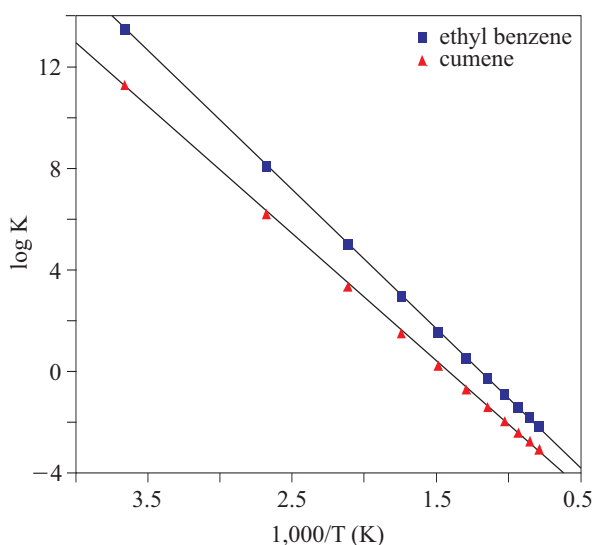


Table 1. Breakdown of benzene use in the chemical industry

DERIVATIVE	MILLIONS TONS OF BENZENE	%
Ethyl benzene	19.5	53.4
Cumene	6.3	17.3
LAB	1.3	3.5
Cyclohexane	5.0	13.8
Nitrobenzene	2.3	6.3
Other	2.1	5.7
TOTAL	36.5	100

co-catalyst, such as a hydrohalic acid. The co-catalyst reacts with the Lewis acid thus generating a Brønsted acid. These catalysts are also known as Friedel-Crafts catalysts and are still extensively used in alkylation, even if the new processes use solid acid catalysts. The Friedel-Crafts catalysts and mineral acids in general are toxic and highly corrosive and therefore difficult to handle and store, as they corrode the containers, the pipes, and apparatus in which they are used. At the end of the reaction they are mixed with the product and must be separated by means of operations which are expensive and energy consuming. It is often necessary to neutralize them with bases and the salts obtained in this way are then separated by washing with water. In this manner the acid catalyst is not recovered and the salt water produced must be disposed of, resulting in

**Fig. 2.** Dependence of the equilibrium constants of the alkylation reactions of benzene with ethylene and propylene to produce ethyl benzene and cumene.

problems related to the environmental impact. For all of these reasons the solid acid catalysts, and in particular the zeolites, are preferred in the new generation of technologies (Perego and Ingallina, 2004).

Zeolites are high porosity crystalline aluminium silicates, exhibiting regular pores with diameters ranging from 0.3 to 1 nm. Depending on the atomic structure of any given zeolite, up to 50% of its volume can be formed by porous cavities. The fundamental unit of the zeolitic structure is the tetrahedron formed by Si^{+4} and Al^{+3} attached to four atoms of oxygen. The tetrahedra are connected together by sharing an oxygen atom to form polymer chains. The formation of the three dimensional structure is due to the fact that all four atoms of oxygen in each tetrahedron are shared with other tetrahedra. On the basis of the number of tetrahedra that make up the opening of the zeolitic channels, the zeolites are classified in the following way: small pores (8 tetrahedra), medium pores (10 tetrahedra), large pores (12 tetrahedra) and extra large pores (>12 tetrahedra). Another characteristic of the zeolitic porosity is the presence of interconnections between the networks of channels, which can be one-dimensional, two-dimensional or three-dimensional. The presence of aluminium in tetrahedral coordination generates negative charges that are locally neutralized by the cations present in the zeolitic channels; by exchanging these cations with the proton a zeolitic acid is obtained.

Zeolitic catalysis is characterized by shape selectivity (Csicsery, 1995). This principle is quite simple: the system of pores of a zeolite can regulate the entrance of the molecules of the reagents and determine the dimensions of the intermediates and the products. The zeolites of interest for the alkylation of aromatics are predominantly of medium and large pore size, as shown in **Table 2**, together with the most important structural characteristics.

Reaction mechanism. The alkylation mechanism first involves the formation of an electrophile E^+ by means of the interaction between the olefin and the acid; followed by electrophilic attack on the aromatic ring ($\text{Ar}-\text{H}$), with the formation of an intermediate $[\text{E}-\text{Ar}-\text{H}]^+$, known also as the Wheland intermediate or arenium ion. From this intermediate, an alkyl aromatic is formed by elimination of H^+ , i.e. of a proton. In the case of alkylation of benzene with ethylene, catalysed by a HA acid, the reaction sequence:

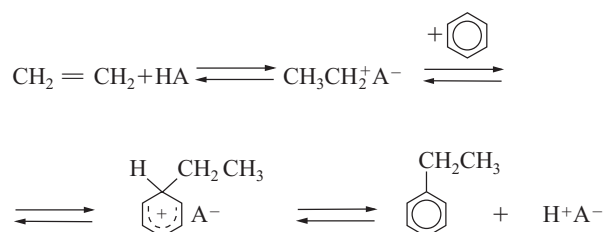


Table 2. Relevant zeolites in catalytic alkylation

ZEOLITE	IZA CODE (INTERNATIONAL ZEOLITE ASSOCIATION)	DIMENSIONAL STRUCTURE OF CHANNELS	PORES	DIMENSIONS OF PORES (nm)
Beta	BEA	3D	large	0.66×0.67 0.56×0.56
Mordenite	MOR	1D	large	0.65×0.70
Y	FAU	3D	large	0.74×0.74
MCM-22	MWW	3D	medium	0.55×0.40 0.51×0.41
ZSM-5	MFI	3D	medium	0.53×0.56 0.51×0.55

The activated species $\text{CH}_3 - \text{CH}_2^+ \text{A}^-$ is often represented as a free carbocation $\text{CH}_3 - \text{CH}_2^+$. This is, however, a qualitative representation, and in fact the completely free carbocation is never obtained: the protonation of ethylene produces a single primary carbocation. In the case of higher olefins the protonation can form two carbocations; for example from propylene the secondary carbocation (*i*-propyl, $\text{CH}_3\text{CH}^+\text{CH}_3$) and the primary one, (*n*-propyl, $\text{CH}_3\text{CH}_2\text{CH}_2^+$), may be generated. The relative stability of the carbocations increases in the order primary<secondary<tertiary and influences the rate and selectivity of the alkylation reaction.

Kinetics. The effect of the nature of the alkyl group on the reaction rate is shown in **Table 3**. The isopropylation of toluene is approximately 1,460 times faster than its ethylation, using GaBr_3 as the catalyst and the alkyl bromide as the alkylating agent. Similar data were reported for the alkylation of benzene with olefins, with a zeolite catalyst (REY, rare earth exchanged Y zeolite): at 100°C propylation is about 300 times faster than ethylation (Beck and Haag, 1997).

These data agree with the protonic affinity (Vogel, 1985), i.e. the tendency of an olefin to be protonated thus creating the corresponding carbocation:

ethylene to ethyl	672 kJ/mol
propylene to <i>i</i> -propyl	755 kJ/mol
<i>i</i> -butene to <i>t</i> -butyl	810 kJ/mol

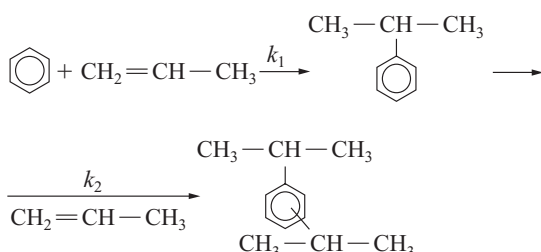
Selectivity. The products of alkylations using acid catalysts are those derived from the most stable carbocations. For example, in the case of the alkylation with propylene, the *i*-propyl benzene (cumene) is practically the only product of mono-alkylation, because the formation of the *i*-propyl carbocation is favoured with respect to the *n*-propyl carbocation: the difference in the enthalpies of formation between the two carbocations in the gas phase is 67 kJ/mol. In addition to the alkylation of the aromatic ring, the olefin can also follow other reaction paths: it can react with itself forming higher oligomers, as in the case of the production of cumene accompanied by the formation of propylene oligomers (for example nonene), or it can isomerize forming other olefins that, in their turn, can produce other alkylation products, such as in the case of the alkylation of benzene with 1-dodecene where, together with 2-phenyl dodecane, other isomers are also formed (3-,4-,5-,6-phenyl dodecane).

Oligomerization and isomerization are parallel reactions to alkylation and reduce its selectivity. Both are reactions which are catalysed by acids and can be limited through the use of very selective alkylation catalysts or by means of suitable operating conditions. The selectivity is also affected by consecutive reactions. After the first alkylation the aromatic substrate can undergo successive alkylations, forming polyalkylated by-products. The presence of alkyl substituents on the aromatic ring increases its reactivity, due to their ability to favour the delocalization of the positive charge on the Wheland intermediate. In fact, the presence of alkyl substituents such as ethyl or *i*-propyl on the aromatic ring increases the rate of Friedel-Crafts alkylation by a factor of 1.4 to 3.2 with respect to unsubstituted benzene

Table 3. Relative rate of the alkylation of toluene (Allen and Yats, 1961)

ALKYL GROUP	RELATIVE RATE
Methyl	1.0
Ethyl	13.7
<i>i</i> -propyl	20,000

(Olah, 1973). Various methods are employed in order to maximize the yield of the monoalkylate. The most obvious is to operate with a large molar excess, or with a high aromatic/olefin ratio. This also makes it possible to limit the sub-production of oligomers (Norris Shreve and Albright, 1958). The disadvantage is constituted by the necessity of separating the aromatic excess and recycling it, with elevated energy costs. Another stratagem involves the use of very selective catalysts such as zeolites, capable of reducing the formation of the bigger polyalkylates and to favour the formation of the monoalkylates. For example, in the alkylation of benzene with propylene catalysed by Beta zeolite:



the ratio between the rate constants for the formation of the products di- and mono-alkylates is equal to 0.54 (Perego *et al.*, 1999).

Alkylation of benzene

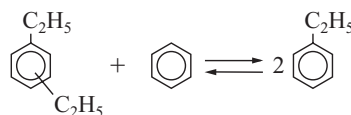
Ethyl benzene

In 2004 the world production of Ethyl Benzene (EB) was about 26 million tons, with demand growing

on average at a rate of 4-5% per year. Almost all EB is used for the production of styrene, a raw material for thermoplastic polymers and elastomers.

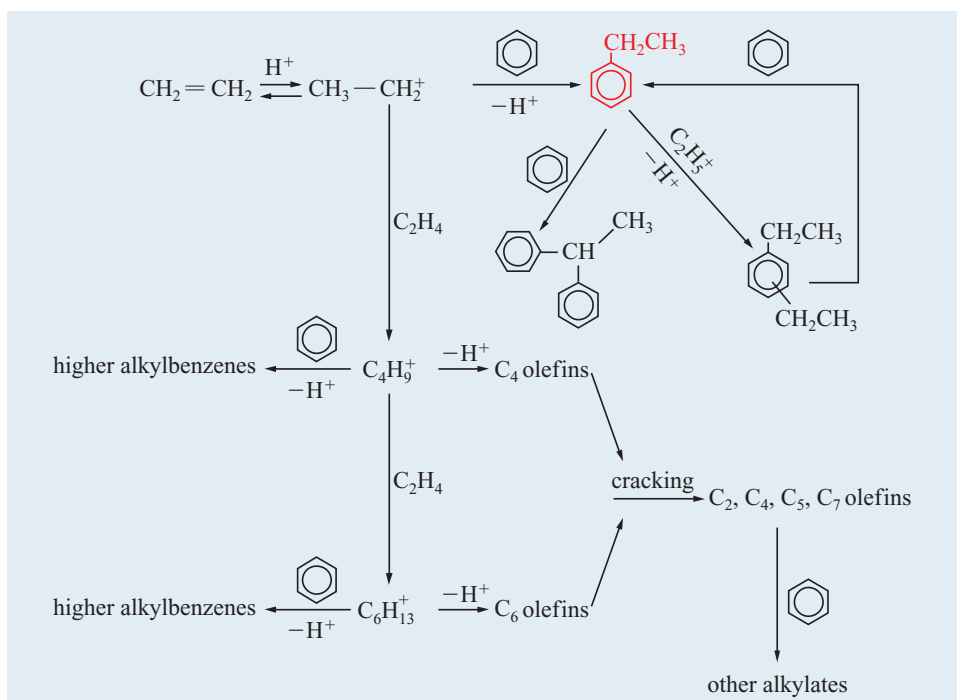
Alkylation of benzene to EB. The main reactions that take place during the alkylation of benzene with ethylene, catalysed by acids, are summarized in **Fig. 3**.

The first stage is represented by the formation of the ethyl carbocation, which then follows one of two principal reaction paths. Either it reacts with benzene to give EB, following which, by successive alkylations, forms Di-Ethyl and Tri-Ethyl Benzene (DEB and TEB), or it reacts with an other molecule of ethylene to form a C₄ carbocation that can then successively undergo alkylation, oligomerization, isomerization and cracking giving other alkyl benzenes and olefins. To a very limited extent EB can alkylate benzene to 1,1-diphenyl ethane. It is important to emphasize that DEB and TEB can react with benzene to give EB. This reaction, known as transalkylation, is an equilibrium reaction:



and under suitable conditions can already take place during alkylation. The traditional process for the production of EB was developed around 1930. The catalyst used was AlCl₃-HCl and all the operations were carried out in an agitated reactor, under somewhat gentle conditions: 170°C and 0.7 MPa. On leaving the reactor, after separation, the polyethyl

Fig. 3. Main reactions during the alkylation of benzene with ethylene.



benzenes (mainly DEB and TEB) were recycled in the alkylation reactor where they were converted, in the presence of an excess of benzene, by transalkylation, reaching a conversion near to the thermodynamic equilibrium. The equilibrium composition is a function of the ratio of ethylene/benzene; this ratio is typically in the range between 0.35 and 0.55 (Franck and Stadelhofer, 1988).

In order to overcome the problems connected with the use of AlCl_3 , starting in the mid 1960s, various zeolitic catalysts were tested for this reaction. In 1976 Mobil-Badger started up the first industrial plant for the production of EB in the gas phase, with a fixed-bed reactor, loaded with a catalyst based on ZSM-5. The reactor operated under high temperature (390–450°C) and pressure (1.5–2 MPa) conditions. As in the process with AlCl_3 , after separation, the polyalkylates were recycled to the reactor for transalkylation. Due to the deactivation related to the deposition of carbon residues (coke) in the zeolitic pores, the catalyst had to be regenerated every 40–60 days. The regeneration was performed *in situ*, by blowing in air to allow the combustion of the coke. The high frequency of this operation made it necessary to have two reactors, one for the regeneration and one for the reaction, in order to guarantee continuous production. This process, used commercially from 1980 onwards, was successively improved by the addition of a reactor dedicated to the transalkylation of the polyethyl benzenes, thus obtaining an improvement both in the yield and in the catalyst life (Wang, 1993).

A considerable improvement came later, obtained by UOP/Lummus/Unocal with the development of a process in the liquid phase. The advantage of the liquid phase is represented by better thermal control that is reflected in an extension of the catalyst life. In this way the regenerations are less frequent and can be conducted on the catalyst which is discharged from the reactor and put into dedicated ovens. Due to problems related to diffusion control, medium pore zeolites such as ZSM-5, were not suitable for use in the liquid phase. For this reason, in the new process a large-pore zeolite, called Y zeolite, was used. The process was commercially used for the first time in Japan in 1990 (Narsolis *et al.*, 1997).

Other large-pore zeolites have been shown to be suitable for liquid phase alkylation of benzene with ethylene (for example, L, Omega, ZSM-12, Beta). In particular the zeolite Beta has turned out to be more selective than an Ultra-Stabilised Y zeolite (USY), with a global selectivity (EB+DEB+TEB) of 99.3% against 91.1% for zeolite Y. Both zeolites have a three-dimensional system of channels, but

the presence of large cavities (1.2 nm in diameter) at the intersections of the channels (in zeolite Y) is probably the cause of the formation of a large amount of by-products that, apart from reducing the selectivity, produce a faster deactivation of the catalyst (Bellussi *et al.*, 1995).

Very interesting results have also been obtained with MCM-22, a zeolite of medium pore size, characterized by two systems of channels independent of each other, one of which containing large cavities open to the exterior on the external surface, with openings formed by 12 tetrahedra and with dimensions of 0.71×0.71 nm. Thanks to this peculiarity, MCM-22 demonstrates a catalytic activity comparable to USY, but inferior to that of Beta. However, the selectivity is higher, both with respect to USY and to Beta, in as much that the formation of DEB and TEB, is particularly reduced (Cheng *et al.*, 1999). MCM-22 was applied to a liquid phase process called EBMax which has been commercialized by Exxon/Mobil since 1995.

The zeolite Beta is the process catalyst developed by Polimeri Europa for the production of EB. After some years of evaluation in a pilot plant, the catalyst was evaluated in an industrial reactor of an existing EB plant, starting in 2001. The catalyst, based on zeolite Beta, demonstrated exceptional performance both from the point of view of the consumption of raw materials and of the quality of the EB produced. The flow diagram of the Polimeri Europa process is shown in **Fig. 4** (Girotti *et al.*, 2004). The catalyst is distributed in the reactor on more beds and the supply of ethylene is directed over these in such a way as to create a much higher local ratio of benzene/ethylene with respect to the global ratio, for the reasons described above. This is a stratagem which is used in all alkylation processes using reactors with catalytic beds.

Since 1990 UOP/Lummus has improved its own liquid phase process (Narsolis *et al.*, 1997), which now is used commercially under the name *EBOne*. The catalyst, originally a zeolite Y, now consists of a modified zeolite Beta. The improvements made to the catalyst have also been extended to the process developed by CDTECH (a consortium between ABB Lummus and Chemical Research and Licensing), based on catalytic distillation that combines the reaction and distillation into a single operation. The catalyst, packaged in 'bales', is positioned on the plates of the distillation column (**Fig. 5**). On each individual plate the ratio of benzene/ethylene proves to be very high ($>1,000$), due to the resistance to mass transfer and to the liquid-vapour equilibrium, with the resulting

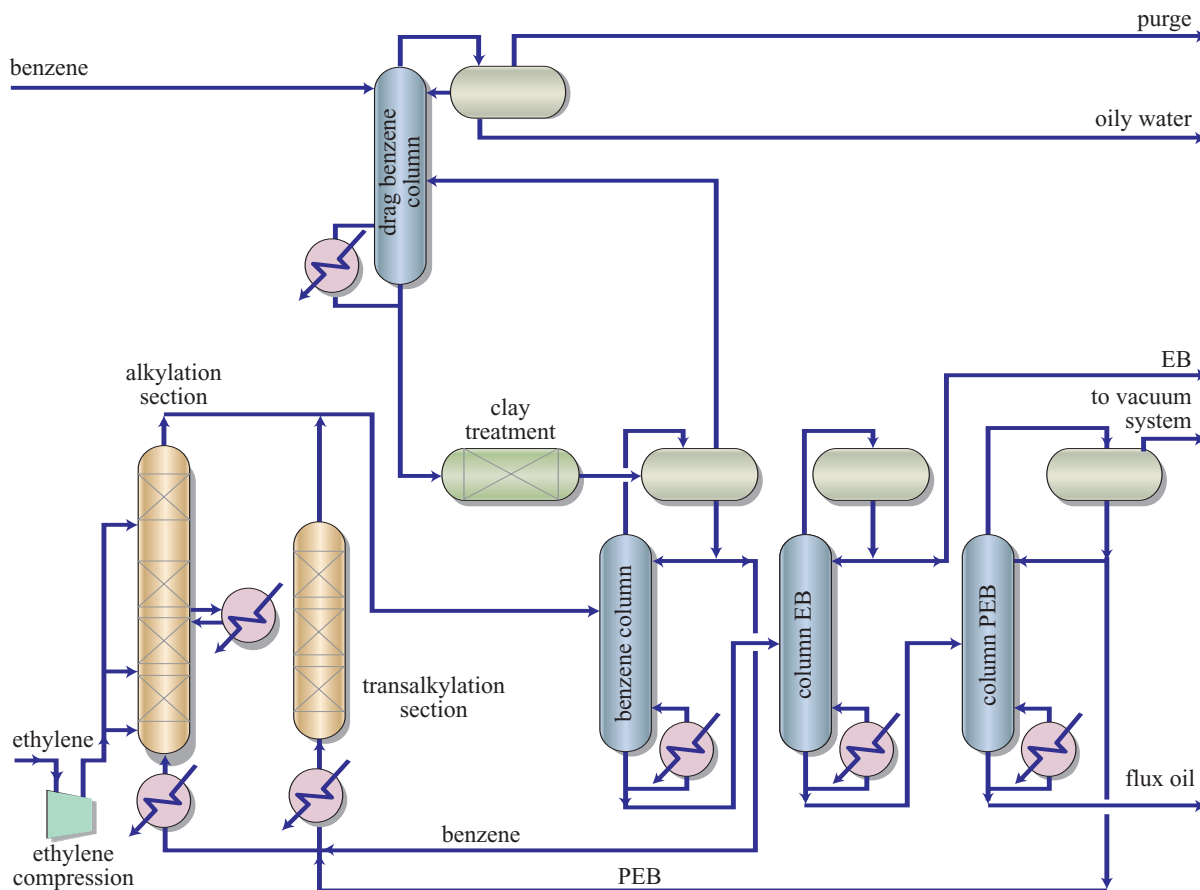


Fig. 4. Flow scheme for the liquid phase process for the production of EB.

advantages in terms of selectivity. In addition, the heat of reaction is exploited to distil the benzene, thus making an energy saving. This process, known as CDTECH EB, is particularly suitable for diluted flows of ethylene (Cho and Zhu, 2003). Of over 70 industrial EB plants in the world, in 2002, only 24% still used $\text{AlCl}_3\text{-HCl}$ as the catalyst; the others were using zeolitic catalysts: 40% in gas phase and 36% in the liquid phase (Perego and Ingallina, 2002).

Isopropyl benzene (cumene)

World production of cumene in 2004 was 9.5 million tons; it is almost exclusively used for the production of acetone and phenol, and a growth of 5% per year is predicted for the consumption of phenol.

Alkylation of benzene with propylene. The alkylation reaction of benzene with propylene is very similar to that with ethylene (Fig. 6).

The *i*-propyl carbocation reacts with benzene to give cumene and by successive alkylations to give di- and tri-isopropyl benzene. Di- and tri-isopropyl benzene can transalkylate to cumene in the presence of an excess of benzene. The carbocation

can, in addition, react with propylene producing C_6 carbocations which evolve by means of oligomerization, cracking and alkylation, to give higher oligomers and other alkyl benzenes. Small quantities of *n*-propyl benzene are also obtained by isomerization of cumene. This represents a very critical aspect, as *n*-propyl benzene cannot be separated by simple distillation and thus its formation affects the final quality of the cumene.

The demand for cumene as a high-octane additive for military aeroplanes in the Second World War led to the development of the first process based on the use of sulphuric acid. The problems related to the use of a free acid were overcome in the 1940s, with the introduction, by UOP, of a catalyst based on Supported Phosphoric Acid (SPA). This technology is still widely used today: the catalyst is loaded in a fixed-bed reactor operating in the liquid phase (180-240°C; 3-4 MPa). The formation of polyalkylates, that are not transalkylated by SPA, and the oligomers of propylene, is minimized by operating with a high ratio of benzene/propylene (from 5 to 10). Also in this case, the ratio is further increased by subdividing the supply

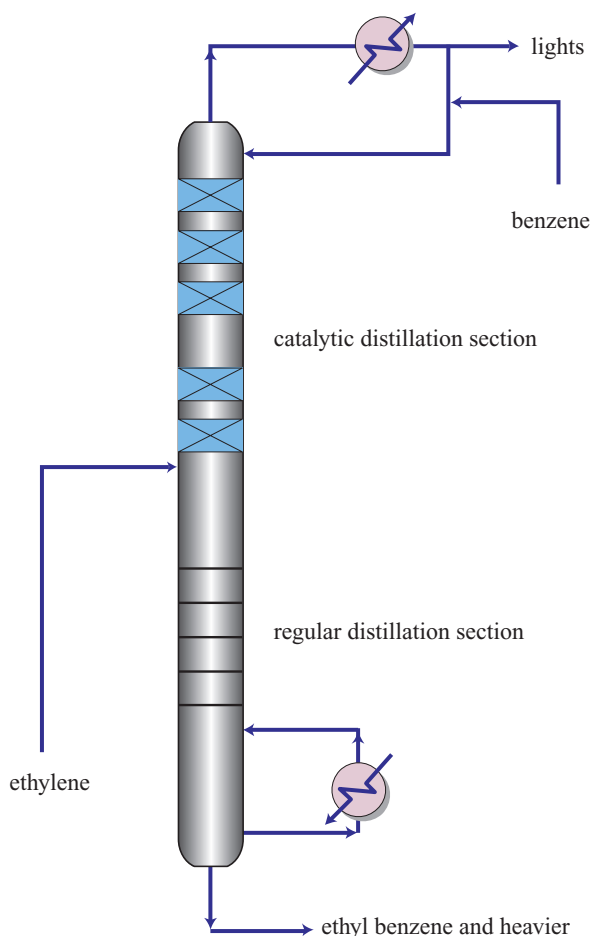


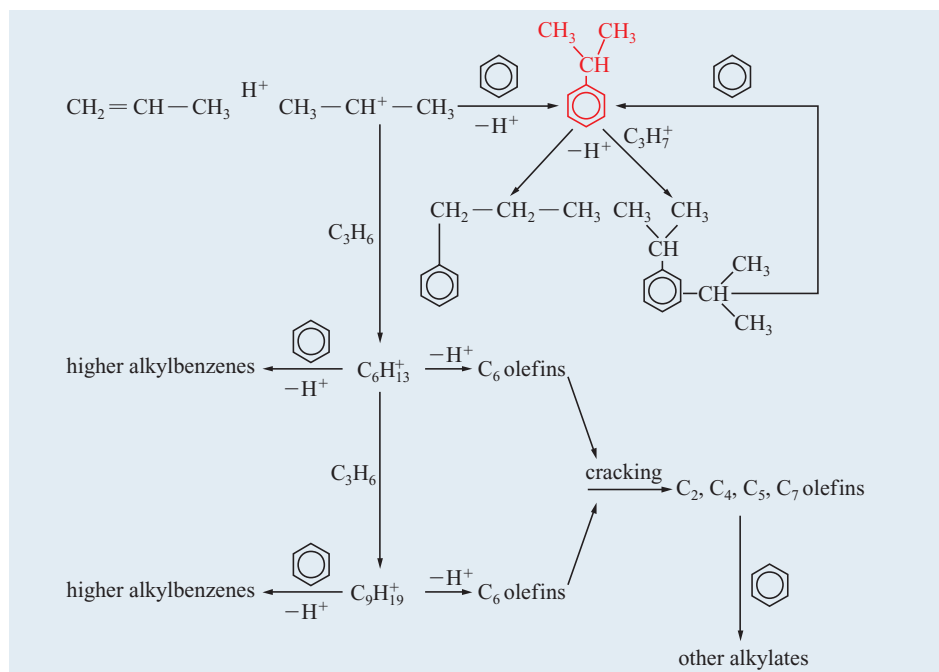
Fig. 5. Catalytic distillation concept for the production of EB.

of propylene to individual catalytic beds. The SPA catalyst, even though supported, nevertheless generates problems of corrosion, due to a release of free acid; in addition, at the end of its life cycle it can not be regenerated.

In the 1970s, Monsanto-Lummus introduced a new technology based on the use of $\text{AlCl}_3\text{-HCl}$, very similar to that used for EB. The advantage of AlCl_3 resides in its ability to catalyse the transalkylation of the polyalkylates, that can then be recycled to the alkylation reactor, in contrast to the SPA catalyst. However, only a few plants have been implemented with this technology.

The search for zeolitic catalysts for the production of cumene has been in many ways similar to that for EB, even if many more years were necessary to arrive at a significant result, than with EB. This is due mainly to the fact that the zeolite ZSM-5, the catalyst for Mobil's EB process, demonstrated a major limitation in the cumene reaction, represented by the elevated level of co-production of *n*-propyl benzene. On the other hand, ZSM-5, being of medium pore size, is not sufficiently active in the liquid phase (Bellussi *et al.*, 1995). Also for cumene, a noticeable improvement was thus obtained by operating in the liquid phase with large pore zeolites. With catalysts based on these zeolites, around the middle of the 1990s new processes were publicised and the first industrial demonstrations developed by Dow-Kellogg, Mobil-Raytheon, CDTech, EniChem and UOP. In all cases, it was a matter of improvements made in existing plants, through the substitution of SPA with a zeolitic catalyst.

Fig. 6. The alkylation reaction of benzene with propylene.



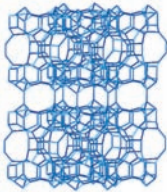
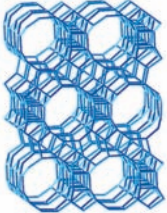
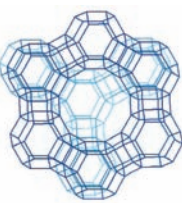
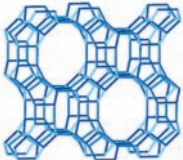
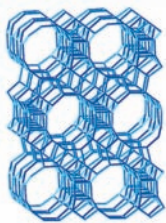
company	ExxonMobil	UOP	CD-tech	Dow-Kellog	Polimeri Europa
process		Q-max	CDCumene	3-DDM	
zeolite	MCM-22	Beta	Y	Mordenite	Beta
					
reactor	recycled fixed bed	fixed bed	catalytic distillation	fixed bed	fixed bed

Fig. 7. Processes for the production of cumene with zeolitic catalysts.

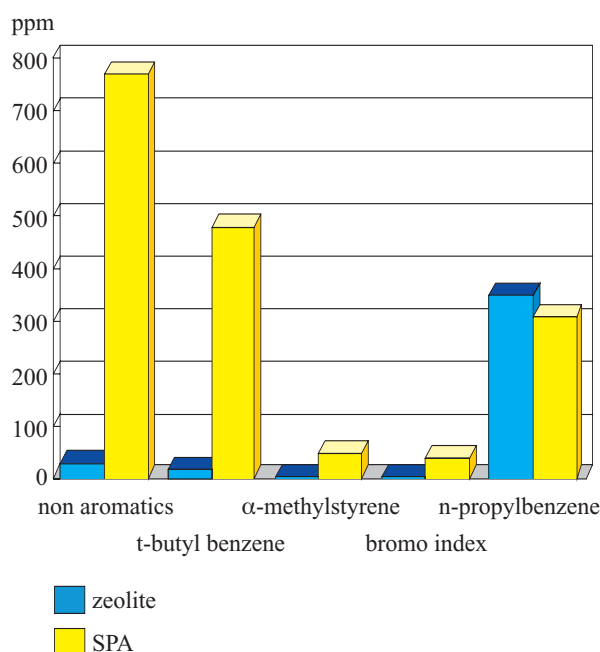


Fig. 8. Comparison of catalyst performance between a zeolite Beta catalyst and an SPA catalyst.

In **Fig. 7** the type of reactor and the zeolites used in these processes are shown.

Starting in March 1996, Enichem (now Polimeri Europa) evaluated a new catalyst based on zeolite Beta on a reactor of the plant for cumene production at

Porto Torres. The results were very positive both with regard to the specific consumption of raw materials and to the quality of the cumene. **Fig. 8** compares the quality of cumene obtained with a zeolite catalyst and with an SPA catalyst, in terms of the concentration of impurities. On the basis of these results the whole plant was converted to zeolite Beta. After years of operation the new catalyst has shown a high level of stability, reaching a production of more than 30,000 tons of cumene per ton of catalyst, compared with the 1,500 tons obtained per ton of SPA. The flow diagram of the Polimeri Europa cumene production process is shown in **Fig. 9** (Girotti *et al.*, 2004). In 2001, out of around 40 cumene plants existing in the world, 14 were already operating with a zeolitic catalyst (Degnan *et al.*, 2001).

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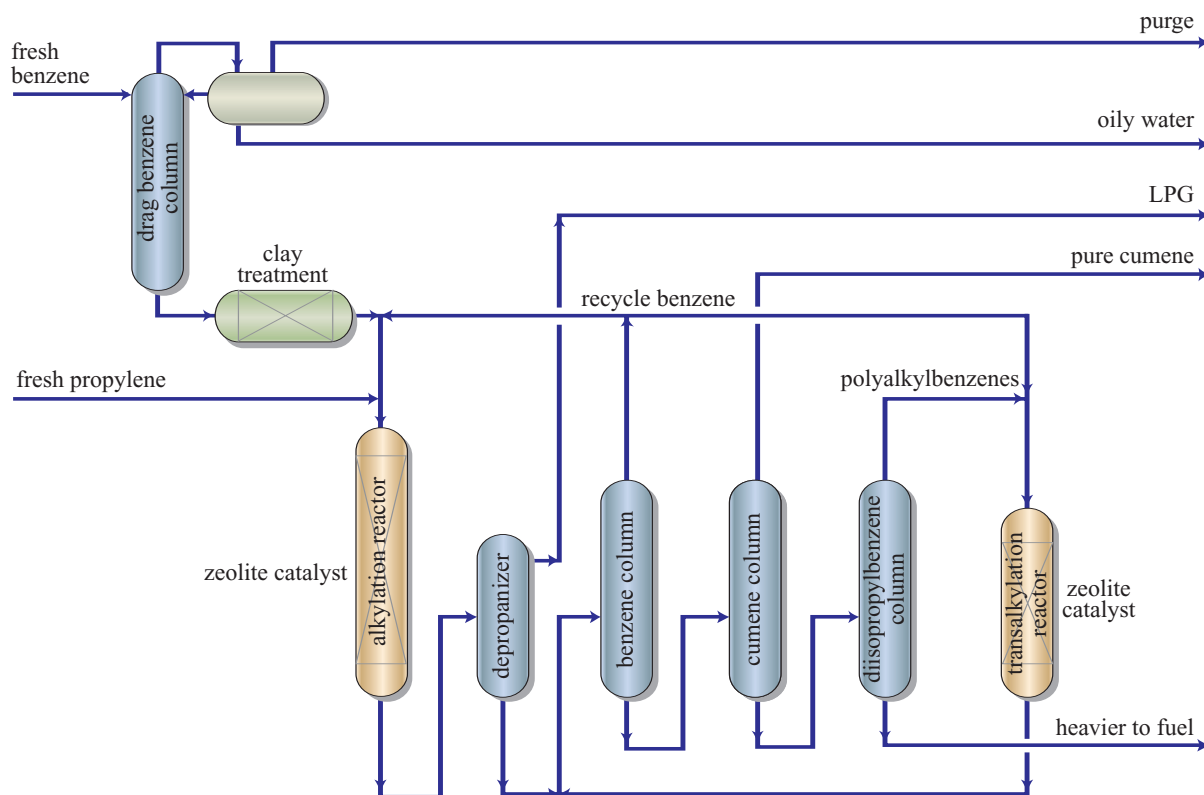


Fig. 9. Flow scheme of the liquid phase process for the production of cumene.

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