

PERP Program - Xylenes

New Report Alert

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Nexant's *ChemSystems* Process Evaluation/Research Planning program has published a report, **Xylenes (05/06-8)**. To view the table of contents or order this report, please click on the link below: http://www.nexant.com/products/csreports/index.asp?body=http://www.chemsystems.com/reports/show_cat.cfm?catID=2

Introduction

The xylene isomers, *meta*-xylene, *ortho*-xylene and in particular *para*-xylene, are important chemical intermediates. *ortho*-Xylene is oxidized to make phthalic anhydride which is used to make phthalate plasticizers among other things. *meta*-Xylene is oxidized to make isophthalic acid, which is used in unsaturated polyester resins (UPR). However, *para*-xylene has by far the largest market of the three isomers. The largest use of *para*-xylene is in its oxidation to make terephthalic acid. Terephthalic acid is used in turn to make polymers such as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT). PET is one of the largest volume polymers in the world. As such the demand for *para*-xylene is several times that for *meta*- and *ortho*-xylene.

Configuration Options for Xylenes Production

There are numerous variations for the configuration of an aromatics plant. The yields from an aromatics facility are heavily dependent on the composition of the naphtha feed to the reformer (specifically the paraffin, olefin, naphthene and aromatic (PONA) content) and the cut point.

The simplest design takes the xylenes rich stream from the bottom of the reformer splitter and sends them to a xylenes column. Here the heavier aromatics (C₉₊) are removed from the bottom of the column and the C₈ aromatics contained in the overhead stream are sent to the recovery section. The latter can be either an adsorption system, such as UOP's Parex or Axens' Eluxyl, or a crystallization unit. Here the *para*-xylene is recovered and the remaining xylenes are sent to an isomerization unit.

Within the isomerization unit the xylenes mixture is re-equilibrated. Ethylbenzene can either be isomerized or dealkylated depending on the catalyst used and the product required. The main products are benzene, toluene and *para*-xylene.

If *ortho*-xylene is to be recovered, the xylenes column is designed to allow for some *ortho*-xylene to be removed with the heavier aromatics. This bottom stream is sent to an *ortho*-xylene column, where the *ortho*-xylene is removed in the overhead stream as a product. Recovery of *ortho*-xylene has an immediate, negative impact on *para*-xylene production.

The second option for the production of xylenes and recovery of *para*-xylene is to add a toluene disproportionation (TDP) unit to the complex. This can be either a conventional TDP or a selective

TDP (STDP). In this scenario all the toluene is recycled to extinction and no toluene is produced as a product. The benzene and *para*-xylene output is increased significantly using this configuration.

Still other configurations include a transalkylation unit. Some technologies (e.g., UOP's Tatoray) include the disproportionation of toluene and the transalkylation of C₉ and C₁₀ aromatics within the same unit. In this case toluene is either recovered as a product along with benzene and *para*-xylene or reacted with the C₉/C₁₀ aromatics in the transalkylation unit. In either case, only C₁₁₊ heavy aromatics are produced.

There are synergies that exist between a refinery, a steam cracker and an aromatics plant that should reduce the capital investment. Common utilities between the three plants will provide economy of scale savings, but in addition excess steam from a refinery can be consumed in the aromatics plant. Raffinate from the aromatics plant is an excellent feed for a steam cracker since it is very paraffinic and essentially equivalent to light naphtha. Pyrolysis gasoline from the steam cracker provides an additional source of BTX for the aromatics plant. Hydrogen from both the steam cracker and aromatics plant can be consumed in the refinery, which is almost always deficient in hydrogen. Light ends from the aromatics plant can be sent to the fuel facilities within the refinery.

The catalytic reforming process is used in the production of gasoline of desired octane number, aromatics (benzene, toluene, mixed xylenes including ethyl benzene) and hydrogen for plant use (e.g., hydrotreating of the naphtha feed). The only difference in operations for aromatics production and motor fuel production is in the choice of operating parameters to maximize the yields of benzene, toluene and mixed xylenes (BTX). The process involves rearranging the molecular structure of naphthenic and paraffinic compounds. Aromatic hydrocarbons and heavily branched paraffins have the highest octane. Catalytic reforming results in an increased yield of aromatics. Three basic reactions take place during the catalytic reforming process:

- Hydrogen abstraction (during the dehydrogenation of the naphthenes and dehydrocyclization of the paraffins to aromatics)
- Hydrocracking (the splitting of heavy molecules into lighter fractions by hydrogen addition)
- Isomerization (the rearranging of hydrocarbon molecules into more compact shapes without changing their molecular weight)

A current objective of many aromatics complexes is to increase the yield of xylenes and to deemphasize the production of benzene. Demand is growing faster for xylene derivatives than for benzene derivatives. Refinery modifications are being effected to reduce the benzene content of gasoline in industrialized countries that will increase the supply of benzene available to meet demand. Benzene produced from disproportionation processes often is not sufficiently pure to be competitive in the market. A higher yield of xylenes at the expense of benzene thus is a favorable objective, and processes to transalkylate C₉ and C₁₀ aromatics along with toluene have been commercialized to obtain high xylene yields.

When xylenes are required, toluene disproportionation (TDP) is one route (re-arrangement of the alkyl group between two identical toluene molecules). In some cases, the processes can also accept C₉ and C₁₀ aromatic feedstocks. The reaction for C₉ feedstocks is transalkylation, the transfer of the alkyl group between different molecules such as benzene and trimethyl benzene, and the reaction for C₉/C₁₀/C₁₁ feedstocks is dealkylation, complete or partial removal of an alkyl group.

The products slate can be shifted dramatically by choice of fresh feed and recycle streams. For example, a net product of benzene and mixed xylenes can be achieved by recycling toluene with C₉₊ aromatics. Recycling benzene with C₉₊ aromatics yields a net product of toluene and mixed xylenes. Operation with feed and recycle of only C₉₊ aromatics will yield a BTX product high in xylenes.

Selective toluene disproportionation processes use shape-selective catalysis to produce a xylenes stream rich in *para*-xylene. The rich *para*-xylene stream produced in the selective toluene disproportionation (STDP) process can be sent to a single stage of crystallization or a small Parex unit for recovery of a high purity *para*-xylene product, but a reject mixed xylenes stream is also produced from this complex. In addition, a large amount of benzene is produced (ratio of benzene and xylenes close to 1.0 on a weight basis).

Xylenes Separation

The recovered aromatics stream from extraction of reformat consists of benzene, toluene, mixed xylenes, and C₉₊ materials. Each of these can be separated by conventional distillation, although it is difficult to separate the individual xylenes isomers due to the closeness of their boiling points. It is possible, however, to separate ethylbenzene and *ortho*-xylene from the mixed xylenes feed by conventional distillation.

A xylenes splitter, which ordinarily would separate the C₉₊ aromatics from the xylenes, can be redesigned to remove *ortho*-xylene as well. An *ortho*-xylene column containing 100-150 trays and operating at a reflux ratio of 5/1 to 8/1 separates the lighter *ortho*-xylene from the C₉₊ aromatics. This option, although increasing investment costs (for the same *para*-xylene production), is practiced by about 60 percent of U.S. xylenes producers.

The typical composition of a mixed xylenes feed to separation is about 19 percent ethylbenzene, 44 percent *meta*-xylene, 20 percent *ortho*-xylene, and 17 percent *para*-xylene. The usual objective of such a process scheme is to maximize the production of *para*-xylene, which is in high demand for the production of terephthalic acid. *ortho*-Xylene is also recovered for use as feedstock to phthalic anhydride production. *meta*-Xylene may optionally be recovered to feed an isophthalic acid plant. In an alternative arrangement mixed xylenes are fed to the xylenes splitter; however, this results in the feed to *meta*-xylene recovery being devoid of ethylbenzene.

Crystallization requires low temperatures and is typically accomplished in two stages, the first at -60°C to -70°C and the second at 0°C (32°F). Although considered older technology, crystallization

is still being used and has found a niche with the recovery from relatively pure *para*-xylene streams such as produced in STDP units. Most new plants use selective adsorption separation processes.

The adsorption process for *para*-xylene recovery uses a molecular sieve adsorbent that has a strong affinity for *para*-xylene and a weaker affinity for the other isomers. Per pass recovery of *para*-xylene is 97 percent compared to 65 percent for crystallization. The adsorption process has the additional advantage of being able to accept a feed with substantial quantities of ethylbenzene and other diluents and still maintain this recovery.

The raffinate from the *para*-xylene recovery operation is typically sent to an isomerization unit to convert its largely *meta*-xylene content into an equilibrium mixture containing *para*-xylene and *ortho*-xylene as well. This serves to increase the production of these isomers, at the expense of *meta*-xylene production, from a given quantity of mixed xylenes feed.

Isomerization is a fixed bed, catalytic process operating at moderate temperature and pressure. Any ethylbenzene present is converted to either benzene or xylenes depending on the catalyst employed. The interconversion of the three xylene isomers is catalyzed by acidic catalysts. The equilibrium concentration is affected slightly by temperature; isomerization at lower temperatures produces more *para*-xylene. The initial concentration of each isomer also has a minor effect as can the shape-selectivity of the pores in acidic zeolite catalysts. The isomerization proceeds as if the methyl group moves in a sequence of steps (i.e. there is no direct conversion between *ortho*-xylene and *para*-xylene).

The report discusses in detail the recovery of the three xylene individual isomers by a variety of different processes used commercially.

Economics

Cost of production estimates have been prepared of the production of *para*-xylene at a capacity of 600 thousand metric tons per year (1,323 million pounds per year) in a single train on the USGC during the fourth quarter of 2005. The following *para*-xylene cost of production estimates are provided:

- Feedstock – mixed xylenes; technologies – adsorption/isomerization (EB isomerization)
- Feedstock – mixed xylenes; technologies – adsorption/isomerization (EB dealkylation)
- Feedstock – mixed xylenes; technologies – crystallization/isomerization (EB dealkylation)
- Feedstock – mixed xylenes; technologies – adsorption/isomerization (EB isomerization) w/*ortho*-xylene byproduct
- Feedstock – toluene; technologies – STDP followed by one-stage crystallization
- Feedstock – toluene; technologies – PxMax followed by melt static crystallization
- Feedstock – toluene; technologies – TDP followed by adsorption/isomerization

- Feedstock – toluene and C₉₊ aromatics; technologies – TDP followed by adsorption/isomerization
- Feedstock – C₉ aromatics; technologies – C₉ transalkylation followed by adsorption/isomerization

Commercial

Total xylenes demand may be split the same way as mixed xylenes and individual isomer demand. The largest consumption is as a mixed xylenes stream used as one component of gasoline. In this application the xylenes are not normally separated from the catalytic reformat in which they are produced. *para*-Xylene is used almost exclusively in the production of the polyester intermediates PTA (purified terephthalic acid) and DMT (dimethyl terephthalate).

This report is concerned with the xylenes that are extracted for use whose main applications are the following:

- Mixed Xylenes - used in solvent production
- *para*-Xylene - PTA and DMT used in polyester production
- *ortho*-Xylene - phthalic anhydride used in plasticizer production
- *meta*-Xylene - isophthalic acid used in specialty polyester production

para-Xylene is used almost exclusively in the production of the polyester intermediates PTA (purified terephthalic acid) and DMT (dimethyl terephthalate). More than 90 percent of *para*-xylene is consumed in the production of PTA.

The report includes global consumption, capacity, and supply/demand/trade data, broken out by regions (including the Americas, Europe, Middle East, and Asia Pacific) for *para*-xylene.

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