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PERP PROGRAM

Report Abstract

Benzene/Toluene
PERP06/07-6

January 2009

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INTRODUCTION

Primary sources of aromatics are from refinery catalytic reformers, pyrolysis gasoline from olefins plants, and coal tar processing. Secondary sources include toluene disproportionation (TDP) and toluene hydrodealkylation (THDA) units. THDA units are the swing source and used when benzene supply is tight and prices get high enough to justify the economics of those plants.

About 70 percent of the global production of benzene is by extraction from either reformate or pyrolysis gasoline (pygas). The former is produced in the catalytic reforming of naphtha, a technology primarily directed at the production of high octane gasoline components. The latter is a liquid byproduct formed in the production of olefins by steam cracking liquid feeds, such as naphtha or gas oil. Ethylene plants typically operate near full capacity, but the feedstock slate may vary depending on market conditions. Extraction from reformate and pygas are the most economical sources of benzene.

The composition of BTX (benzene, toluene and xylenes) depends on the source. The table below compares BTX from pygas and reformate. Pygas is typically rich in benzene, whereas xylenes and toluene are the main components of reformate.

Typical BTX Composition from Pygas and Reformate
(Weight percent)

	Pygas ¹		Reformate		Typical Demand Split
	Standard Severity	Medium Severity	CCR ²	SR ³	
BTX content	58	42	51	42	49
Benzene	48	44	17	14	49
Toluene	3	31	39	39	23
Xylenes	19	25	44	47	28

¹ Based on cracking full range naphtha

² Continuous catalytic regenerative reformer

³ Semi-regenerative reformer

The table also very roughly shows the global demand for BTX products. In general, benzene is present in the main feedstocks in proportions lower than market demand, whereas toluene is in considerable excess. To some extent this imbalance is corrected by their relative values as gasoline components because refiners have the option of extracting BTX as chemical products or blending them in fuel. Xylenes and toluene are more valuable as blendstocks than benzene as the benzene content in gasoline is restricted for environmental reasons.

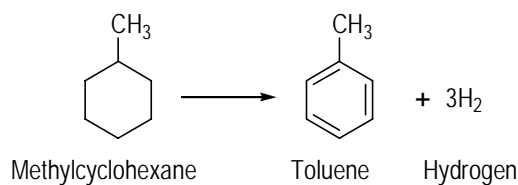
CURRENT COMMERCIAL TECHNOLOGY

In this section, technologies based on extraction and dealkylation are described, along with a discussion of each major feedstock and estimates of reformat and benzene production costs. A discussion of non-conventional routes to BTX is also included. The emphasis of the economic analysis is placed on benzene because of its importance as a chemical product.

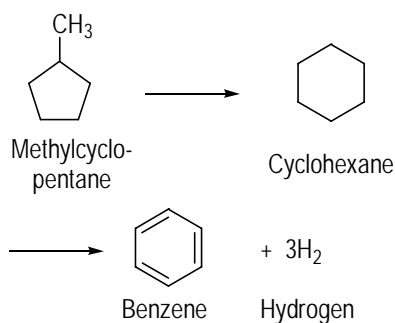
Catalytic Reforming

Modern catalytic reforming using platinum was first commercialized in 1949 by UOP for use by the petroleum industry; The term "reforming" is used to designate a process by which the molecular structure of naphtha is changed, with the intent of lessening the knocking tendency (i.e. raising the octane number) of naphtha intended for use in internal combustion engines.

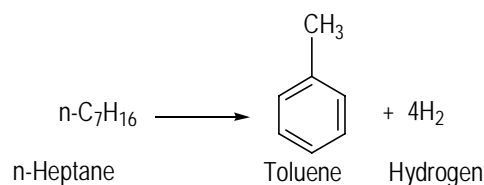
It is important to note the simultaneous production of hydrogen when aromatics are manufactured by catalytic reforming, as exemplified in the reactions shown below (the dehydrogenation of cyclohexanes to aromatics, dehydroisomerization of alkylcyclopentanes to aromatics and dehydrocyclization of paraffins to aromatics). This hydrogen by-product is an important source of hydrogen within the refinery.



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The maximum potential yields of aromatics that could be obtained from naphthenes and paraffins if hydrocracking could be suppressed are determined by the thermodynamic equilibria for aromatization reactions. These data show, first, that corresponding aromatic yields from the various classes of compounds follow the order (from highest to lowest) alkylcyclohexanes, alkylcyclopentanes, paraffins. Second, aromatic yields increase with the number of carbon atoms per molecule; benzene from C₆ paraffin has a lower yield than toluene from C₇ paraffin. Third, for a given reactant, the potential aromatics yield increases as the hydrogen partial pressure is decreased.

As the catalyst ages, it is necessary to change the process operating conditions to maintain the reaction severity and to suppress undesired reactions.

This Section discusses many aspects of Catalytic Reforming, such as the:

- Chemistry of reforming processes including dehydrogenation reactions, isomerization of paraffins and naphthenes, hydrocracking and miscellaneous others.
- Catalysts used in these reforming processes.
- Process Variables including pressure, temperature, feedstock quality, feed boiling range, naphtha quality (naphthenic versus paraffinic), impurities, space velocity, hydrogen to hydrocarbon ratio.
- Reformer Types including semi-regenerative, continuous catalyst regeneration (ccr), cyclic.
- Feed Preparation.
- Reformer Operation including Gasoline Mode, BTX Operation.
- Yields and Utilities.
- Commercial Technology.

In addition to Catalytic Reforming, other current commercial technologies discussed in this Process Evaluation/Research Program (PERP) report include:

- **Production from Pyrolysis Gasoline**
 - Pyrolysis gasoline (pygas), a byproduct of olefins production by steam cracking naphtha of gas oil feedstocks, contains a high proportion of aromatics, primarily benzene and toluene, and a smaller amount of C₈ aromatics that contain up to 40 percent ethylbenzene.
- **Aromatics Extraction**
 - It is necessary to use a solvent extraction technique to recover BTX products of commercial quality, since aromatics and non-aromatics may have similar boiling points and form azeotropes. After extraction, the BTX products can be separated, if necessary, by distillation. There are three basic types of solvent extraction systems: Azeotropic, Extractive, liquid/Liquid solvent).

- **Dealkylation Processes**
 - The market demand for benzene, as a proportion of total BTX, is higher than the proportion of benzene in typical BTX products. Conversion of toluene and, to a lesser extent, xylenes, is practiced by two basic techniques: (1) Hydrodealkylation which involves stripping the methyl groups from toluene or xylenes to produce benzene and methane e.g. Detol, Litol and Pyrotol processes); and (2) Toluene disproportionation - although not purely dealkylation - is also included under this heading as a discretionary method of producing benzene. The toluene is converted to benzene and xylenes in this process.
- **Production from Coke Oven Light Oil**
 - Light oil arises as a byproduct in the coking of coal, largely to provide a carbon source in steel making. To make coke, coal is pyrolyzed at around 1,000°C; temperatures vary widely in practice. About 70 percent of the product is solid coke, consisting primarily of carbon. The remainder is volatilized, and leaves through the top of the coke ovens. This gaseous stream is fractionated, and its cuts are used in various ways.
- **Production of Aromatics via Nonconventional Routes**
 - There exist several nonconventional routes to convert low value refinery byproducts to benzene, toluene, and xylenes. These have been developed and commercialized by various companies over the past several years and include Asahi Chemical's Alpha Process, BP/UOP's Cyclar™ Process, CP Chem's Aromax® Process, and UOP's RZ Platforming™ Process.

DEVELOPING TECHNOLOGIES

Since the last PERP report on this subject there have been numerous patents and patent applications dealing with the production of aromatics. A majority of these have been awarded to the two major licensors of aromatics technology, namely UOP and IFP (Axens). Nexant has reviewed the recent developments for the production of benzene and toluene. The more interesting developments are discussed in this section:

- A novel catalyst combination that converts methanol (MeOH) to aromatics (MTA) and especially xylenes.
- Direct catalytic conversion of methane to higher hydrocarbons and specifically to aromatics (e.g., such as benzene).
- Axens is licensing a new technology developed and patented by SK Corp. for upgrading pyrolysis gasoline.
- Chevron Chemical Company (now Chevron Phillips Chemical Company) has been awarded a patent in which reforming/aromatization of hydrocarbons occurs in two parallel reformers in order to maximize the benzene and *para*-xylene production.
- China Petroleum and Chemical Corporation (CPCC) and Sinopec have developed a new composite solvent for extractive distillation (ED) of aromatics.

- ExxonMobil proposes a bound zeolite catalyst for use in alkylation, transalkylation or isomerization of aromatic hydrocarbons.
- Fina has been awarded a number of patents dealing with toluene disproportionation and transalkylation of heavy aromatics.
- IFP has discovered, among other things, a catalyst with substantially improved properties with respect to previous reforming catalyst.
- With respect to the Cyclar™ process, SABIC has made several improvements to the process and catalyst.
- UOP has developed a new family of zeolites that can be used in alkylation of aromatics, transalkylation of aromatics, isomerization of aromatics and alkylation of isoparaffins.

ECONOMIC ANALYSIS

The costs of production for the various technologies for producing reformat have been developed at a world scale plant capacity. Of the five types of technologies reviewed - see below - we have shown that the economics can vary widely. This range of economic performance is clearly seen where all five processes are viewed on a side-by-side basis.

- CCR™ Reforming
- RZ Platforming™
- Cyclar™
- Aromax®
- Alpha Process

The costs of production of benzene from various sources employing different technologies – see below - have been developed.

- Benzene from Reformate Extraction (Sulfolane) including BTX Distillation
- Benzene Recovery from Pygas:
 - Solvent Extraction (LLE) of Pygas
 - Extractive Distillation (ED) of Pygas
 - Bulk Dealkylation of Pygas
- Benzene via the Litol Process
- Benzene via Toluene Hydrodealkylation (THDA)
- Benzene via Toluene Disproportionation (TDP)
- Benzene via Selective Toluene Disproportionation (STDP)

It is important to note that the economics presented herein are in essence a “snapshot” in time. Nexant have tried to mitigate this by carrying out sensitivity analysis using five-year historical averages for feed and product prices. The results of this sensitivity for the reformat cases and for the benzene cases studied in this report are discussed.

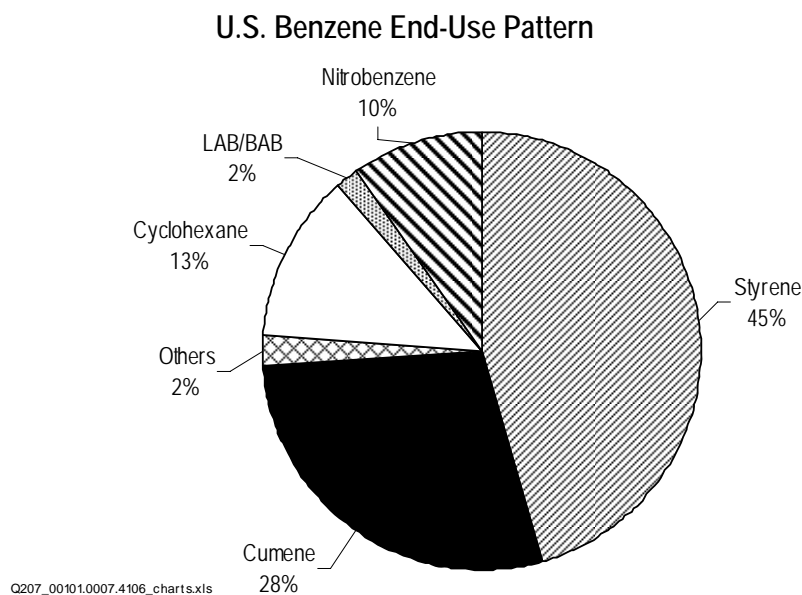
The sensitivity of the costs of production to feed price for the costs of production of reformate and for the costs of production of benzene, for the cases studied are also discussed.

Nexant's view with respect to some of the strategic issues (Access to feedstock, Outlet for by-products, Investment requirements, Revamp and integration potential or strategy, Feedstock/product price fluctuations/forecasts, Technology availability/licensing terms, Technology risk, Security of supply/strategic importance) for the reformate processes considered is given.

MARKET ANALYSIS

Benzene has many uses, and demand continues to grow despite increasing restrictions and environmental regulations. These uses - including, Styrene/Ethylbenzene, Cumene/Phenol, Cyclohexane, Nitrobenzene, Chlorobenzene, Alkylbenzene, Maleic Anhydride and others - are discussed in this section.

Regional benzene consumption for the United States is shown in the figure below. Just under half of the benzene in the United States is consumed in the production of ethylbenzene for styrene. Its growth is modest due to low polystyrene production growth and a projected reduction in styrene exports. Cumene is the next largest benzene derivative in this region and makes up just over one-quarter of the total consumption. Cyclohexane, nitrobenzene and LAB consume most of the rest of the benzene within the region. .

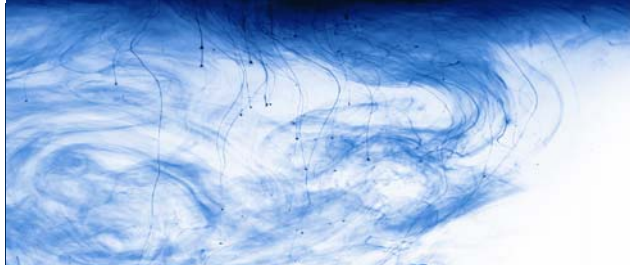


Toluene is primarily used as a component in gasoline, and is extracted from reformate or other sources. Controls on the total aromatics content in gasoline will be less stringent than those relating to benzene; the blending value of toluene is around 10 percent higher than benzene's.

Of the toluene extracted or otherwise produced, the largest single use is for the production of benzene by dealkylation or the production of both benzene and xylenes by disproportionation. The other toluene applications are outlined.

Consumption, Supply/Demand and Trade data for the USA, Western Europe, and Asia Pacific is discussed. This includes:

An extensive listing of Benzene and Toluene plant capacity for each of the three regions: Details of **company, plant site, Benzene and Toluene capacity at the specified plant, the process used and the country where the plant is located** are given.



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