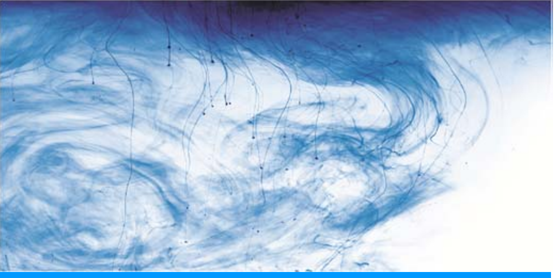

CHEMSYSTEMS
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Benzene/Toluene

PERP 2011-1

Report Abstract
October 2011

Nexant

Benzene/Toluene

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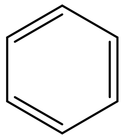
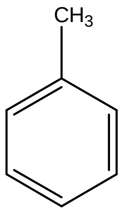
INTRODUCTION

Benzene is a colorless liquid (bp 80 °C) with a sweet, aromatic odor, highly flammable and toxic (a known carcinogen). Toluene is also a colorless liquid (bp 110 °C) with a sweet aromatic smell, and highly flammable. The chemical structures of benzene and toluene may be represented as shown below:



Benzene



Toluene

COMMERCIAL TECHNOLOGY

About 70 percent of the global production of benzene is by extraction from either reformate or pyrolysis gasoline, these being the most economical sources of benzene.

Reformate is formed in the catalytic reforming of naphtha, a technology primarily directed at the production of high octane gasoline components. Essentially, all of the benzene, toluene and mixed xylenes (BTX) recovered in an oil refinery is produced in the catalytic reforming unit (both continuous catalytic regenerative and semi-regenerative types). The catalytic reforming process is used in the production of gasoline of desired octane number and aromatics (benzene, toluene, and mixed xylenes including ethyl benzene). Hydrogen is co-produced and is invariably employed for plant use (e.g., hydrotreating of the naphtha feed). The only difference in reforming operations for aromatics production as opposed to motor fuel production is in the choice of operating parameters (especially feedstock selection) to maximize the yields of BTX.

Pyrolysis gasoline or pygas is a liquid byproduct formed in the production of olefins (alkenes) by steam cracking liquid feeds, such as naphtha or gas oil. Pygas contains a high proportion of aromatics, primarily benzene and toluene, and a smaller amount of mixed xylenes which themselves can contain up to 40 percent ethylbenzene. Yields of pygas are determined by the severity of the steam cracking operation, and the composition of the feedstocks.

The composition of BTX depends on the source. Table 1 compares BTX from pygas and reformate. Pygas is typically rich in benzene, whereas xylenes and toluene are the main components of reformate.

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 blend stocks than benzene. In addition, benzene content in gasoline is restricted for environmental reasons.

Table 1 Typical BTX Composition from Pygas and Reformate
(Weight percent)

	Pygas[1]		Reformate	
	Standard Severity	Medium Severity	CCR[2]	SR[3]
BTX content	58	42	51	42
Benzene	48	44	17	14
Toluene	33	31	39	39
Xylenes	19	25	44	47

A third source of BTX is coke oven light oil (or COLO) also known as “benzole”, light oil produced during the coking of coal. Coke ovens are operated primarily for the coke product. The production of by-products coke oven gas, light oil, and coal tar is simply a consequence of the high temperature baking of coal. The coke product is fuel for the furnaces used in separating iron from its ores. Although this was once the only source of aromatics, it is now a minor contributor to the total supply amounting to only four percent of the global capacity (mostly in the Former Soviet Union, China and Eastern Europe). Clean Air Act emission regulations restrict output from this source.

Conversion of toluene and, to a lesser extent, xylenes, into benzene, is practiced by two basic techniques: Hydrodealkylation and disproportionation. Hydrodealkylation involves stripping the methyl groups from toluene or xylenes to produce benzene and methane. All the commercial processes involve the same basic chemistry. For toluene, the fundamental reaction may be represented as:

$$C_6H_5CH_3 + H_2 \longrightarrow C_6H_6 + CH_4$$

Similar reactions occur with higher alkylated benzenes. Xylenes dealkylate in two steps, whereas ethylbenzene dealkylates directly to benzene and ethane. Side reactions result in the formation of diphenyls or polymers.

Although not purely dealkylation, the topic of toluene disproportionation (TDP) is also included under this heading as a discretionary method of producing benzene. TDP is one route (re-arrangement of the alkyl group between two identical toluene molecules) to produce both benzene and xylenes. In some cases, the processes which are normally fed with toluene can also accept C_9 and C_{10} aromatic feedstocks. The reactions are:

- for toluene feedstocks - disproportionation
- for C_9 feedstocks - transalkylation, the transfer of group between different molecules such as benzene and trimethyl benzene
- for C_9/C_{10}/C_{11} feedstocks dealkylation, complete or partial removal of an alkyl group

The transalkylation (TA) and disproportionation reactions are equilibrium constrained while the dealkylation reactions are kinetically constrained. The products slate can be shifted dramatically by choice of fresh feed and recycle streams.

In addition there exist several nonconventional routes to convert low value refinery by-products to BTX. 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 Chevron Phillips Chemical's Aromax® Process, UOP's RZ Platforming™, and UOP's combination of Unicracking™.

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: A**zeotropic distillation**, which uses a low boiling point solvent with an affinity for non-aromatics; **Extractive distillation (ED)**, which employs a high boiling point solvent with an affinity for aromatics; and **Liquid/liquid solvent extraction (LLE)**, which uses solvents that form a separate liquid phase.

LLE is usually employed where recovery of benzene and toluene are important with respect to yield and quality. ED is usually employed where the key product is benzene and/or the yield is not so critical. Within each type, there are a number of solvents available. However, for a given process design the solvent type is not replaceable.

BIOTECHNOLOGY

Anellotech, Inc. (Anellotech) is a biofuel start-up company founded by University of Massachusetts chemical engineering professor, George Huber. Anellotech has developed technology based on pyrolysis of sawdust or other finely divided waste lignocellulosic or cellulosic biomass in a fluid-bed of zeolite to produce a stream of BTX, naphthalenes, olefins, and lights. They claim that the types of aromatics (and olefins) produced can be adjusted according to the market demand using several approaches.

Virent Energy Systems, Inc. (Virent) claims that their BioForming® platform can convert a wide range of biomass-derived feedstocks to fuels and chemicals. Although Virent's technology is claimed to have the flexibility and capability to produce a wide range of final end products, Virent has stated that the main focus of their ongoing research has been to produce liquid biofuels.

PROCESS ECONOMICS

The costs of production for the various technologies for producing reformate have been developed at various world scale plant capacities ranging from 300 to 1 000 kta.

Cost estimates for benzene production via the following processes have been evaluated:

- Benzene recovery from reformate or pygas via solvent extraction
- Benzene recovery from pygas via extractive distillation

- Benzene via bulk dealkylation of pygas
- Benzene from coke oven light oil via the litol process
- Benzene via hydrodealkylation
- Benzene via toluene disproportionation and selective toluene disproportionation
- Benzene via C7/C9 transalkylation

The above cost estimates highlight the different process performances as they are all compared at world scale capacity on the USGC. However, other regions reflect to a greater extent the developing industry based on planned new projects. Therefore, Nexant has also developed and compared the economics for the production of benzene via extraction from pygas for the following regions as well: Western Europe, Southeast Asia, China, Japan, South Korea and the Middle East

All cost tables given in this report include a breakdown of the cost of production in terms of raw materials, utilities direct and allocated fixed costs, by unit consumption and per metric ton and annually, as well as contribution of depreciation to arrive at a cost estimate (a simple nominal return on capital is also included)

COMMERCIAL ANALYSIS

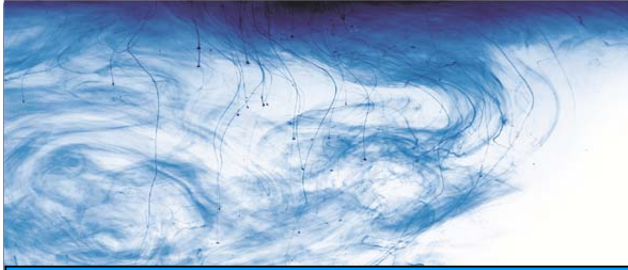
One of the major uses of benzene is as a gasoline component. It is contained within streams that contribute to the gasoline pool, primarily catalytic reformate. This market analysis contained in the report is concerned only with the non-fuel uses of benzene.

Benzene has many uses, and demand continues to grow despite increasing restrictions and environmental regulations. Creation of styrene monomer is the largest use of benzene, followed by cumene/phenol, cyclohexane, and nitrobenzene. Those derivatives are used to produce a wide range of plastics, fibers, resins and films. Benzene is also an excellent solvent for waxes, resins, rubber and various other organic materials, but toxicological properties greatly limit use.

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.

- Benzene global supply, demand and trade data is given and discussed
- In addition, supply, demand and trade data for benzene is given and discussed according to key regions (i.e., United States, Western Europe, and Asia Pacific)
- A list of plants producing benzene and toluene in each of the key regions above is given showing specific plant capacities, owning company, location and annual tonnage produced



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