Lecture 8
Aromatics Product Profile,
Ethyl Benzene & Styrene,
Cumene & Phenol, Bisphenol,
Aniline
LECTURE 8

AROMATICs PRODUCT PROFILE, ETHYL BENZENE & STYRENE, CUMENE AND PHENOL, BISPHENOL, ANILINE

Aromatics are backbone of organic chemical industries. Aromatic hydrocarbons especially benzene, toluene, xylene (BTX), and ethyl benzene are major feedstock for large number of intermediates which are used in the production of synthetic fibers, resins, synthetic rubber, explosives, pesticides, detergent, dyes, intermediates, etc. Styrene, linear alkyl benzene, and cumene are the major consumer of benzene. Product profile of aromatics is shown in Figure M-VII 8.1.

Global production and consumption of benzene in 2009 were between 36.4 and 36.6 million metric tons. Average global capacity utilization was 69.2 percent in 2009, lower than in 2008. Global benzene consumption is estimated to have decreased by 3.8 percent in 2009; however, it is expected to average growth of 4.7 percent per year from 2009 to 2014, and 2.6 percent per year from 2014 to 2019 [Petrochemical overview, SRI consulting]. Ethyl benzene/styrene monomer and cumene/phenol with demand shares of 52.6 percent and 18.3 percent respectively of the global benzene market respectively are the leading end-use segments for benzene in 2010. Other uses such as cyclohexane, nitrobenzene and LAB collectively consumed less than 15 percent of global benzene demand in 2010 [Styrene market & Asian demand to drive global benzene markets” Chemical weekly November 22, 2011, p.205].

Global production and consumption of toluene in 2009 were each almost 18.4 million metric tons. Global capacity utilization was 64 percent in 2009. Toluene consumption estimated to have decreased by almost 2 percent in 2009. Demand is expected to grow on average 3.6 percent per year from 2009 to 2014, and 2.2 percent per year from 2014 to 2019 [Petrochemical overview, SRI consulting].

Global production and consumption of mixed xylenes in 2009 were each approximately 41 million metric tons. Global capacity utilization was around 74 percent in 2009. Xylenes consumption in 2009 is estimated to have increased by around 4.6 percent from 2008; it is
expected to average growth of 5.2 percent per year from 2009 to 2014, and 3.3 percent per year from 2014 to 2019. Operating rates are expected to drop in 2010 but gradually increase afterward [Petrochemical overview, SRI consulting]. Product profiles of major aromatics-BTX are given in Table M-VII 8.1.

Table M-VII 8.1: World Aromatic Petrochemicals Scenario

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>33,278</td>
<td>3.5</td>
<td>4.2</td>
<td>2.8</td>
<td>43,945</td>
<td>4,443</td>
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<tr>
<td>Toluene</td>
<td>16,688</td>
<td>1.9</td>
<td>3.5</td>
<td>2.4</td>
<td>24,642</td>
<td>1,184</td>
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<tr>
<td>Ethyl benzene</td>
<td>25,130</td>
<td>4.2</td>
<td>3.5</td>
<td>2.7</td>
<td>27,536</td>
<td>5,948</td>
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<tr>
<td>Styrene</td>
<td>22,188</td>
<td>3.9</td>
<td>3.5</td>
<td>2.7</td>
<td>23,742</td>
<td>6,087</td>
</tr>
<tr>
<td>Mixed Xylenes</td>
<td>29,187</td>
<td>5.7</td>
<td>5.1</td>
<td>4.1</td>
<td>36,784</td>
<td>6,640</td>
</tr>
<tr>
<td>Xylene</td>
<td>3,050</td>
<td>3.4</td>
<td>4.5</td>
<td>2.7</td>
<td>3,948</td>
<td>498</td>
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<tr>
<td>p-Xylene</td>
<td>18,701</td>
<td>6.2</td>
<td>5.8</td>
<td>4.6</td>
<td>20,605</td>
<td>7,359</td>
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<tr>
<td>Cumene</td>
<td>9,214</td>
<td>5.8</td>
<td>4.7</td>
<td>2.6</td>
<td>10,612</td>
<td>505</td>
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<tr>
<td>Phenol</td>
<td>7,166</td>
<td>5.2</td>
<td>4.4</td>
<td>1.7</td>
<td>7,843</td>
<td>1,262</td>
</tr>
<tr>
<td>Caprolactam</td>
<td>3,746</td>
<td>6.1</td>
<td>3.1</td>
<td>3.3</td>
<td>4,566</td>
<td>448</td>
</tr>
<tr>
<td>Terephthalic Acid</td>
<td>24,822</td>
<td>8.2</td>
<td>5.9</td>
<td>5.0</td>
<td>26,168</td>
<td>8,038</td>
</tr>
<tr>
<td>Phthalic Anhydride</td>
<td>3,488</td>
<td>3.5</td>
<td>4.1</td>
<td>2.5</td>
<td>4,374</td>
<td>358</td>
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<tr>
<td>Dimethyl Terephthalate</td>
<td>3,747</td>
<td>-3.7</td>
<td>1.5</td>
<td>0.5</td>
<td>4,710</td>
<td>53</td>
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<tr>
<td>TDI</td>
<td>1,383</td>
<td>3.9</td>
<td>4.1</td>
<td>3.7</td>
<td>1,809</td>
<td>932</td>
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</tbody>
</table>

Source: Chemistry Industry News, March 2004
Figure M-VII 8.1: Product Profile of Aromatics

Benzene
- Naphthalene
- Cumene
- Linear alkyl benzene
- Cyclohexane
- Ethyl benzene
- Maleic Anhydride
- Chloro benzene
- Nitrobenzene
- BHC

Toluene
- Gasoline
- Nitrotoluene
- Trinitrotoluene
- Benzoic acid
- Solvents
- p-cresol

Xylenes
- m-xylene
- o-xylene
- p-xylene

Phthalic anhydride, insecticides, \(\beta\)-naphthol, moth balls, surface active agent, synthetic tanning agents, dyes, rubber chemicals, solvents, agricultural uses: Adipic acid, aniline, Bisphenol-A, caprolactam, phenolic resin, pesticides, dyes, rubber chemical Methyl isobutyl ketone, methyl methacrylate, solvent methyl isobutyl carbinitol.

Detergent
- Nylon 6, nylon 66, adipic acid.

Polystyrene, SBR, ABS and SAN resins, styrenat polyester, acrylonitrile butadienes, styrene plastic protective coatings. Acids (fumaric, malic); lubricating oil additives; copolymers; agricultural chemicals, unsaturated polyester resin; 1,4-butylanediol (Resins, polyurethane solvent, pharmaceuticals).

Aniline, phenol, DDT, chloronitrobenzene, biphen

Dyes and intermediates, rubber chemicals, drugs and pharmaceuticals, photographic chemicals, isocyanate.

Pesticides
- Motor gasoline

Polyurethane (Rigid foam, flexible foam, surface coatings)

Explosives

Caprolactam, pharmaceuticals and flavors, phthalates, terephthalic acid.

Phenol, sodium benzoate - food preservatives.

Di-tert-butyl-p-cresol (antioxidants)

Resins, unsaturated polyesters, plasticizers, other esters.

Plasticizers, polyester resins, alkyl resins, dyes and pigments, herbicides, isatoic anhydride, polyester polyols, phthalimide-fungicides.

Polyester fibers, films, polyethylene, terephthalate
Global production and consumption of p-xylene in 2009 were each approximately 27.6 million metric tons. Global capacity utilization was 83 percent in 2009, unchanged from 2008. p-Xylene consumption is estimated to have increased by approximately 4.7 percent in 2009; it is expected to average growth of 5.5 percent per year from 2009 to 2014, and 3.5 percent per year from 2014 to 2019 [Petrochemical overview, SRI consulting].

Global production and consumption of o-xylene in 2009 were approximately 3.7 million metric tons. Global capacity utilization was 66 percent in 2009. o-Xylene consumption is estimated to have increased slightly in 2009; it is forecast to average growth of 3.2 percent per year from 2009 to 2014, slowing to 2.4 percent per year from 2014 to 2019. Average global utilization rates are expected to remain in the 70s range throughout the forecast period [Petrochemical overview, SRI consulting].

ETHYLY BENZENE AND STYRENE
Ethyl benzene and styrene are two important aromatics. Ethyl benzene is mainly used for making styrene. Styrene which finds application in synthetic rubber and polymer industry for the manufacture of SBR and polystyrene, ABS plastic.

Major route for styrene manufacture is dehydrogenation of ethyl benzene which is manufactured by alkylation of benzene. Styrene plant consists of two major units. The process involves:

- Production of ethylene either from molasses route or by naphtha/natural gas cracking
- Production of ethyl benzene by alkylation of benzene
- Dehydrogenation of ethyl benzene to styrene

ETHYL BENZENE
Ethyl benzene is made by alkylation of benzene with ethylene. Ethylene can be produced from either from molasses route or naphtha/gas cracker. The convention alkylation catalysts are metal chlorides (BF3, AlCl3, etc) and mineral acids (HF, H2SO4). However, with development of zeolite, now the benzene alkylation I is done by using ZSM-5 catalysts using vapor-phase process [Mobil-badger Process] and liquid phase alkylation using MCM-22 zeolite proprietary catalyst based catalyst.
**Vapour Phase Alkylation of Benzene:** The process consists of vapor phase alkylation of benzene with ethylene using zeolite catalyst in a fixed bed catalytic distillation technology. Alkylation and distillation takes place in the alkylator. Unreacted ethylene, and benzene vapour are condensed and fed to the finishing reactor where the remaining alkylation is completed in the presence of a catalyst. The product stream goes to fractionating columns where ethyl benzene is separated from the higher ethylated benzene and heavy ends. Higher ethylated alkyl benzene is sent to the trans-alkylator where its trans-alkylated to produce additional ethyl benzene [Petrochemical Processes 2003” Hydrocarbon processing March1999, p.10]

**Liquid Phase Alkylation Of Benzene With Ethylene Using MCM-22 Catalyst:** In this process alkylation of ethylene takes place in a liquid filled alkylator reactor containing multiple fixed beds of MOBIL MCM-22 catalyst. During alkylation Ethyl benzene and small quantity of polyethylbenzene are formed which is converted to ethyl benzene using trans-alkylation catalyst. The product streams from alkylator and trans-alkylator are sent to various fractionating columns for separation of product ethyl benzene, polyethylbenzene, benzene, gases and heavy ends.

\[ C_6H_6 + C_2H_4 \rightarrow C_6H_5CH_2CH_3 \]

**STYRENE**

Styrene is one of the most important monomers for the production of polymers, resins and rubber. The biggest consumer of styrene monomer is polystyrene, other major derivatives are expanded polystyrene, Styrene butadiene(SB) latex, SB rubber, styrene block co-polymers (eg: ABS, MBS, SBS) [SNOW: an innovative technology for styrene synthesis, hydrocarbon asia,2007,p.42]

Styrene is made by catalytic dehydrogenation of ethyl benzene

\[ C_6H_5CH_2CH_3 \rightarrow C_6H_5CH=CH_2 + H_2 \]

Styrene can be also directly recover from raw pyrolysis gasoline derived from cracking of naphtha, gas oils Using GT styrene process
**Lumus/UOP EB One Process:** Styrene is made by catalytic dehydrogenation of ethylbenzene in the presence of steam. In Lumus/UOP EB one process involves first alkylating benzene with ethylene followed by dehydrogenating the EB to form styrene. The benzene and recycled benzene are preheated the liquid phase reactor containing zeolite catalyst. The polyethylbenzene formed during alkylkation is fed to another reactor for transalkylating with benzene. Transalkylation reaction is isothermal and reversible in distillation section. The reactor effluent from both reactions is sent to the distillation section for separating ethyl benzene from polyethylbenzene.

\[
\begin{align*}
\text{C}_6\text{H}_6 + \text{C}_2\text{H}_4 & \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 \\
\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 + \text{C}_6\text{H}_6 & \rightarrow 2\text{C}_6\text{H}_5\text{CH}_5 \text{CH}_3 \\
\text{C}_6\text{H}_5\text{CH}_5 \text{CH}_3 + \text{C}_6\text{H}_6 & \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3
\end{align*}
\]

Ethyl benzene and recycled ethyl benzene are then dehydrogenated to styrene in the presence of steam at high temperature (550-68\(^\circ\)C) under vacuum in a multistage reactor

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 & \rightarrow \text{C}_6\text{H}_5\text{CH} = \text{CH}_2 + \text{H}_2 \\
\text{H}_2 + \frac{1}{2}\text{O}_2 & \rightarrow \text{H}_2\text{O}
\end{align*}
\]

During dehydrogenation stages air or oxygen is introduced to partly oxidize the hydrogen to reheat the process gas and to remove the equilibrium constrain for dehydrogenation reaction. [HC,1999]. Reactor effluents are cooled to recover waste heat and condensed, uncondensed gases are used as fuel. The condensed product containing styrene is sent to distillation columns for separating styrene monomer, unconverted ethyl benzene is recycled.

Toluene is formed during the process which is recovered

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CHCH}_2 + \text{H}_2 & \rightarrow \text{C}_6\text{H}_5\text{CH}_3 \\
\text{C}_6\text{H}_5\text{CHCH}_2 & \rightarrow \text{C}_6\text{H}_5\text{CH}_3 + \text{C}
\end{align*}
\]
**GT Styrene Process:** Styrene can be also directly recovered from raw pyrolysis gasoline derived from cracking of naphtha, gas oils Using GT styrene process. Raw pyrolysis gasoline is fractionated into a heart cut C8 stream from which styrene is separated by extractive distillation.

**Innovative SNOW Technology:** The snow technology has been jointly developed by Snamprogetti and Dow represents a technological and economical breakthrough in styrene production and uses benzene and ethane as raw material which is dehydrogenated in the same reaction for EB dehydrogenation. SNOW reactor is rise type [SNOW: an innovative technology for styrene synthesis, hydrocarbon asia,2007, p.42].

**PHTHALIC ANHYDRIDE**

Phthalic anhydride first became commercially important during the nineteenth century as an intermediate for dyestuff industry. However, now phthalic anhydride is largely used for the manufacture of plasticizers, alkyd resins, and unsaturated polyester resins where about 95 percent of the phthalic anhydride production is consumed. With an aggregate installed capacity of 267,200-tpa across India, major PAN producers include IG Petrochemicals Ltd and Thirumalai chemicals Ltd. Consumption pattern of PAN is shown in Figure M-VII 8.2. List of the phthalic anhydride manufacturer in India is given in Table M-VII 8.2.

![Consumption pattern of PAN](image)

**Figure M-VII 8.2: Consumption pattern of PAN**

### Table M-VII 8.2: Phthalic Anhydride Manufacturer in India

<table>
<thead>
<tr>
<th>Company</th>
<th>Location</th>
<th>Installed Capacity (TPA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.G. Petrochemicals Ltd.</td>
<td>Taloja, Maharashtra</td>
<td>120,000</td>
</tr>
<tr>
<td>Thirumalai Chemicals Ltd.</td>
<td>Ranipet, Tamil Nadu</td>
<td>100,000</td>
</tr>
<tr>
<td>Asian Paints Ltd.</td>
<td>Ankleshwar, Gujarat</td>
<td>25,200</td>
</tr>
<tr>
<td>Mysore Petrochemicals Ltd.</td>
<td>Raichur, Karnataka</td>
<td>12,000</td>
</tr>
<tr>
<td>S.I. Group Ltd.</td>
<td>Thane, Maharashtra</td>
<td>10,000</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>267,200</strong></td>
</tr>
</tbody>
</table>


The basic raw material for the manufacture of phthalic anhydride is naphthalene and o-xylene. Phthalic anhydride was manufactured from naphthalene. With the availability of large amount of o-xylene as a byproduct during p-xylene production, now phthalic anhydride is made from o-xylene. Both vapor phase and liquid phase oxidation of o-xylene are available.

Phthalic anhydride is produced by oxidation of naphthalene in the gas phase using vanadium pentoxide catalyst supported on silica or silicon carbide promoted with various other metal oxides, e.g. titanium oxide (wire) in either a fixed bed multiple reactors or fluidized bed reactor.

\[
\text{C}_{10}
\text{H}_{8} + \frac{9}{2} \text{O}_2 \rightarrow \text{C}_{8}
\text{H}_{4} \text{O} + \text{CO}_2 + 2 \text{H}_2\text{O} \quad \Delta H^0_{298K} = -1790 \text{ KJ/mol}
\]

Production of phthalic anhydride from o-xylene is similar to naphthalene route. Catalytic oxidation of o-xylene is done either in fixed bed catalytic reactor having multi tube or fluidised bed reactor in the presence of vanadium pentoxide and titanium oxide catalyst.

\[
\text{C}_{6}
\text{H}_{5}
\text{CH}_3 + 3 \text{O}_2 \rightarrow \text{C}_8\text{H}_4\text{O} + 3 \text{H}_2\text{O} \quad \Delta H^0_{298K} = -1780 \text{ KJ/mol}
\]

**CUMENE**

Cumene is made by alkylating benzene with propylene using zeolite catalyst. Following three major processes are available
**Catalytic Distillation Technology:** The process uses a specially formulated zeolite alkylation catalyst in a proprietary catalytic distillation (CD) process and a trans-alkylator reactor using zeolite catalyst. In CD column combines both reaction and fractionation takes place.

**Liquid Phase Q-max Process:** In this process, cumene is produced by liquid phase alkylation of benzene with propylene in presence of azeolite catalyst.

**Cumene by Mobil Badger Process:** The process produces cumene from benzene and any grade of propylene using a new generation of zeolite catalysts from Exxon m Mobil. The process includes a fixed bed alkylation reactor and a fixed bed trans-alkylation reactor and distillation section.

**PHENOL**

According to SRI consulting report 2010 global production and consumption of phenol were both around 8.0 million tones with global capacity utilization of 77percent. Phenol consumption is expected to average growth of 5.1percent per year from 2009 to 2014 and around 2.5percent from 2014-19. Phenol is consumed mainly for production of bisphenol A and phenolic resins which accounted for 42percent and 28percent respectively of total phenol consumption in 2009.

Various routes for Phenol:
- Phenol from Cumene
- Phenol from Benzoic acid
- Phenol from chlorobenzene
- Benzene Sulphonation

With the availability of propylene now phenol is made by cumene route with added advantage of acetone as by product

**ANILINE**

The process of aniline manufacture involves two stages: Company which produce aniline is given in Table M-VII 8.3.
Table M-VII 8.3: Company-Wise Production of Aniline

<table>
<thead>
<tr>
<th>Company</th>
<th>Years</th>
<th>Production</th>
<th>Sales Quantity</th>
<th>Sales Value</th>
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<tr>
<td>Gujarat Narmada Valley Fertilizers Ltd.</td>
<td>2008-09</td>
<td>27077</td>
<td>27090</td>
<td>1865</td>
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<tr>
<td></td>
<td>2009-10</td>
<td>33848</td>
<td>33825</td>
<td>2167</td>
</tr>
<tr>
<td></td>
<td>2010-11</td>
<td>39896</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hindustan Organic Chemicals Ltd.</td>
<td>2009-10</td>
<td>5538</td>
<td>5231</td>
<td>309</td>
</tr>
<tr>
<td></td>
<td>2010-11</td>
<td>1833</td>
<td>1826</td>
<td>135</td>
</tr>
</tbody>
</table>


**Nitrobenzene Route:**

- Nitration of benzene with nitric acid
- Hydrogenation of nitrobenzene to aniline

\[
\text{C}_6\text{H}_5 + \text{HNO}_3 \xrightarrow{180 \degree \text{C}} \text{C}_6\text{H}_4\text{NO}_2 + \text{H}_2\text{O} \\
\text{C}_6\text{H}_4\text{NO}_2 + 3\text{H}_2 \xrightarrow{250 \degree \text{C}} \text{C}_6\text{H}_4\text{NH}_2 + \text{H}_2\text{O}
\]

**Ammonylation of Chlorobenzene**

\[
\text{C}_6\text{H}_5\text{Cl} + 2\text{NH}_3 \xrightarrow{200 \degree \text{C}} \text{C}_6\text{H}_4\text{NH}_2 + \text{NH}_4\text{Cl}
\]
**Ammonolysis of Phenol**

![Chemical reaction](image)

**BENZOIC ACID (C₆H₅COOH)**
Benzoic acid is the simplest member of the aromatic carboxylic acid. Benzoic acid, which is used in the manufacture of caprolactam, phenol, terephthalic acid and used as mordant, is manufactured by liquid phase catalytic oxidation of toluene in presence of cobalt acetate at 165 °C and 11.2 atm pressure. Major processing steps in the manufacture of benzoic acid consist of:

- Catalytic liquid phase air oxidation of toluene
- Stripping of unreacted toluene and light end precursors from the benzoic acid for recycle
- Distillation to recover benzoic acid as a pure overhead product

![Chemical reaction](image)

**BISPHENOL**

Bisphenol is an important building block and its measure use is in the manufacture of polycarbonate plastic and epoxy resins. Other uses include in flame retardants, unsaturated polyester resin and polyacrylate, polyetherimide and polysulphone resin [Chemical weekly, 2008].

**India and Global demand of Bisphenol** [Chemical business, 2012]
Demand of bisphenol in India during 2010-11 was 30,000 tonnes per annum
Global installed capacity: around 5.2 million tones
Global demand around 4.2 million tones
Global growth rate in demand 5 to 6 percent

Polycarbonate resin are the largest and fast growing BPA market, consuming 60 percent of the global production.

**Process Technology**

Various process technologies available for manufacture of bisphenol are:

- Condensation of phenol with acetone
- Condensation of phenol with alkenyl phenol
- Condensation of phenol with ethylene and acetylenes
- Condensation of phenol with alkyl benzene

**Bisphenol From Phenol And Acetone:** Bisphenol is synthesized by a condensation reaction between phenol and acetone using proprietary cation exchange resin-base catalyst (4PET) in a packed bed reactor. The catalyst has higher acetone conversion, higher BPA selectivity and longer life. Reactor effluents are process in series of distillation column for separation of product bisphenol, unreacted acetone, water, phenol. Phenol and acetone are recycled. Bisphenol is purified by crystallization where bisphenol crystals are separated from the impurities. Although the impurities are removed with mother liquor, however two stage crystallisation can lower the impurities captured in the crystal. Bisphenol is sent to prilling tower to get final bisphenol in the form of spherical prill.

**REFERENCE**

1. “Petrochemical Processes 2003” hydrocarbon Processing
2. Chemical Business, January 2012, p.12
9. SNOW: An innovative technology for styrene synthesis, hydrocarbon Asia, 2007, p.42
10. Styrene market & Asian demand to drive global benzene markets, Chemical weekly
   November 22, 2011, p. 205