Lecture 7

Aromatic Production
LECTURE 7
AROMATIC PRODUCTION

Aromatic hydrocarbons especially benzene, toluene, xylene, ethyl benzene are major feedstock for a 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.

Benzene also finds application in the manufacture of a large number of aromatic intermediates and pesticides. As per CMAI, demand for benzene is forecast to grow at an average annual rate of 2.8% per year through 2020 resulting in nearly 57 million tonnes of demand by 2020. Originally, the aromatics were produced from coal tar distillation, which is the by-product of destructive distillation (carbonisation).

Major application of toluene is as solvent. Other uses are in the manufacture of benzoic acid, chloro derivatives, nitro toluenes, toluene sulphonic acid, toluene sulphonamide, benzaldehyde, etc Xylenes are another important aromatics. Various sources of aromatics is mention in Table M-VII 7.1.

Amongst the xylenes, about 80% of the production is of p-xylene. Finds application in the manufacture of terephthalic acid/DMT. o-Xylene used in the manufacture of phthalic anhydride and m-xyleneisohthalic acid. Typical yield of benzene, toluene, xylene in kg per tonne of coal carbonised is about 2.8, 0.5-2, and 0.1-0.5 kg [Wiseman, 1986]

Table M-VII 7.1: Various Sources of Aromatics

<table>
<thead>
<tr>
<th>Processes</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal Carbonisation (Coke oven plant)</td>
<td>From coke oven plant during carbonisation, light oil is obtained as by product which contains about 2-8 kg, 0.5-2 kg, 0.1-0.5 kg of benzene, toluene and xylene respectively per tonne of coal.</td>
</tr>
<tr>
<td>Steam cracking of hydrocarbons</td>
<td>Steam cracking of naphtha and light hydrocarbon like ethane and propane produce liquid product (pyrolysis gasoline) rich in aromatics containing about 65% aromatics about 50% of which is benzene. About 30-35% of benzene produced worldwide is from pyrolysis gasoline.</td>
</tr>
<tr>
<td><strong>Catalytic Reforming</strong></td>
<td>Catalytic reforming is a major conversion process, which converts low octane naphtha to high-octane gasoline and produce aromatics rich in BTX. Major reactions involved are dehydrogenation of naphthalenes to aromatics, isomerisation of paraffins and naphthenes, dehydrocyclisation of paraffins to aromatics, and hydrocracking of paraffins.</td>
</tr>
<tr>
<td><strong>BP-UOP Cyclar Process</strong></td>
<td>In this process, BTX is produced by dearomatisation of propane and butane. The process consists of reaction system, continuous regeneration of catalyst, and product recovery. Catalyst is a proprietary zeolite incorporated with a non noble metal promoter.</td>
</tr>
<tr>
<td><strong>Dearomatisation of naphtha</strong></td>
<td>Process consists of extraction of aromatics from high aromatic naphtha feed without prior reforming. The process is useful for naphtha having high aromatics.</td>
</tr>
<tr>
<td><strong>Hydro dealkylation and disproportionation</strong></td>
<td>Hydrodealkylation: It involves production of benzene by dealkylation of toluene either by catalytic or thermal process. Catalytic process: Hydeal, Deltol Thermal process: HAD (ARCO), THDC Gulf Oil Disproportionation: It involves conversion of toluene into benzene and xylenes.</td>
</tr>
<tr>
<td><strong>Mitsubishi's Zforming Process</strong></td>
<td>This process consists of conversion of C₈ stream into valuable o- and p-xylene having isomerisation and isomer separation stage.</td>
</tr>
<tr>
<td><strong>KTI Pyroforming</strong></td>
<td>This process uses a shape selective catalyst to convert C₂ and C₃ paraffins to aromatics.</td>
</tr>
<tr>
<td><strong>Chevron's Aromax process</strong></td>
<td>It is similar to conventional catalytic reforming processes and L-type zeolite catalyst.</td>
</tr>
<tr>
<td><strong>Isomerisation and Isomer process</strong></td>
<td>This process consists of conversion of C8 stream into valuable o- and p-xylene having isomerisation and isomer separation stage.</td>
</tr>
</tbody>
</table>
CATALYTIC REFORMING

Catalytic reforming is a key conversion process in a petroleum and petrochemical industry. The catalytic reforming gives flexibility to meet gasoline octave number requirement. It can also make aromatics of high market value. Catalytic reforming is a refining process that uses selected operating conditions and selected catalysts to convert. Basic objective of catalytic reforming is

- To produce high octave blending stock for motor fuel
- To produce high value aromatic hydrocarbon such as BTX

**Process Description**

A typical catalytic reforming process includes following three sections:

- Naphtha Hydrotreating
- Catalytic Reforming
- Catalyst Circulation and Regeneration

Basic steps in catalytic reforming involve feed preparation, temperature control, reaction in reformer and product recovery, various types of catalytic reformer are – semi regeneration, non-regeneration cyclic moving bed two types of reformer reactors are in use radial flow and axial flow. Details of this has been covered in Module VI Lecture 6.

**Reactions in Catalytic Reforming Process**

Number of reactions takes place in catalytic reforming. Dehydrogenation is one of the major reactions. These reactions are discussed in detail in module VI lecture 6. Some of the major reactions are

**Dehydrogenation**

\[
\text{Methyl Cyclohexane} \rightarrow \text{Toluene} + \text{H}_2
\]
MCP $\rightarrow$ Benzene $+$ H$_2$

Isomerisation

$n$-Hexane $\rightarrow$ Neohexane

Dehydrocyclisation of paraffins, $i$-paraffins to aromatics

$n$-heptance $\rightarrow$ Toluene $+$ H$_2$

Hydrocracking

**BTX FROM PETROLEUM**

**Major Units of Aromatic Complex**

- Heavy Naphtha Pretreatment Unit
- Catalytic reforming (Platformer Unit, CCR Unit Continuous Catalyst Regenerator)
- Recovery Plus
- PSA (Pressure Swing Adsorption)
- BTX separation
- Xylene Fractionation Unit for separation of o-xylene from m- and p- xylene
- p-xylene and m-xylene separation by crystalisation, adsorption

**Process steps in aromatic production:** Figure M-VII 7.1 gives the details description of aromatics complex. The various steps involved in aromatic production are given below:

- First step in making BTX is to distill off a suitable fraction rich in naphthenes which serves as precursors for aromatics
- Catalytic reforming or a team cracking to produce an aromatic gasoline. Detail of the catalytic reforming is given in Lecture 6, Module VI Lecture 6,
- Preliminary treatment of this cut: fractionation and/or selective hydrogenations essentially pyrolysis gasoline
- Solvent extraction to eliminate non-aromatic from aromatics
- Distillation to produce pure benzene and toluene and in cased reformates used alone or blended art a pyrolysis gasoline, the following additional treatment
- Distillation aromatic C$_8$ to yield by super fractionation ethyl benzene and O-xylene, after passage through a separation column in a light cut and a heavy cut (splitter)
• Production of p-xylene at low temperature with a mother liquor by product rich in m-xylene
• Isomerisation / delakylation /disporportionation of m-xylene to p-xylene

Separation of Aromatics: As non aromatics and some of the aromatics have close boiling points, various methods used for their separation are
• Liquid – Liquid Extraction (DEG, TEG, Tetra methylene Sath NMP-EG, Monoethyle methyl forma midamorphine, DMF)
• Distillation,Extractive or Azeotropic distillation.
• Adsorption
• Crystallisation

Process Variables:
Various process variables in the catalytic reforming for the production of aromatics are
• Feed quality and N+2A
• Temperatures:
• Space velocity
• Hydrocarbon hydrogen ration
• presence of impurities

Details of these parameters are discussed in Module VI Lecture 6

EFFECT OF FEED QUALITY ON AROMATIC YIELD
• Naphthenes dehydrogenate very fast and give rise to aromatics. Therefore, N + 2A is taken as index of reforming. Higher the N + 2A, better is quality to produce high aromatics.
  \[ N = \text{Naphthenes } \% \quad \text{A} = \text{Aromatics } \% \]
• Lighter fraction have a poor naphthene and aromatic content are, therefore, poor feed for reforming. Low IBP feed results in lower aromatics and H₂ yield
• Heavy fractions have high naphthene and aromatic hydrocarbon content. Therefore, good reforming feed but tendency of coke formation is high

General recommended feed ranges for production
<table>
<thead>
<tr>
<th></th>
<th>Compound</th>
<th>Temperature Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzene</td>
<td>60-90°C Fraction</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>90-110°C Fraction</td>
</tr>
<tr>
<td>3</td>
<td>Xylenes</td>
<td>110-140°C Fraction</td>
</tr>
<tr>
<td>4</td>
<td>Octane blending stock</td>
<td>90-140°C Fraction</td>
</tr>
</tbody>
</table>
Figure M-VII 7.1: Aromatics Complex
Source: Mall, 2007 courtesy Macmillan India
P-XYLENE

The p-xylene plant consists of five units are:

**Pretreatment Unit:** This unit is used for reducing sulphur content to 5 ppm (max.) by dehydro - desulphurisation which takes place at 330–370 °C and 24 kg/cm² pressure in presence of cobalt molybdenum catalyst.

**Reformer Unit:** To get maximum amount of C₈ aromatics by reforming process (Process similar to described earlier).

**Fractionation Unit:** For separation of o-, m-, and p-xylanes from combined C₈ reformate and isomerisate from isomerisation unit (after clay treatment).

**Parex Unit:** This unit is for the separation of p-xylene by selective adsorption using molecular sieve followed by desorption. Other method for separation of p-xylene is by crystallisation process.

**Isomerisation:** Isomerisation of C₈ stream from Parex unit rich in m- and o-xylene and ethyl benzene to p-xylene, which is sent to fractionation unit for separation of high component. The bottom of the column is recycled for further recovery of xylanes.

AROMATIC CONVERSION PROCESSES

Because of higher demand of benzene and p-xylene in comparison to toluene and m-xylene various processes are commercially available for conversion of toluene and m-xylene to more value added products like benzene and p-xylene. processes are also available for conversion of paraffins into aromatics. Some of the major processes are:

<table>
<thead>
<tr>
<th>Aromatic conversion Process</th>
<th>Process details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isomeration</td>
<td>Isomerization of meta xylanes to para and ortho xylanes</td>
</tr>
<tr>
<td>Transalkylation and Disproportion</td>
<td>Transalkylation and Disproportionation of C₇ and C₉</td>
</tr>
<tr>
<td>Toluene Disproportionation</td>
<td>Toluene disproportion to xylanes and benzene</td>
</tr>
</tbody>
</table>
Selective Toluene Disproportionation
Selective conversion of toluene to para xylene by disproportionation

Xylene Isomerizations
Maximization of p-xylene, ethyl benzene (EB) conversion and EB dealkylation process

Aromatization
Conversion of light hydrocarbons to benzene, tolenes and xylenes

Paraffin Aromatization processes:

<table>
<thead>
<tr>
<th>Process</th>
<th>Licensor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycler</td>
<td>UOP-BP</td>
</tr>
<tr>
<td>Aroforming</td>
<td>IFP-Sheddon Technology Management</td>
</tr>
<tr>
<td>M-2 Forming</td>
<td>Mobil</td>
</tr>
<tr>
<td>Z-Forming</td>
<td>Research Association of</td>
</tr>
</tbody>
</table>

CYCLAR PROCESS

Cyclar process inexpensive and plentiful LPG requires minimal feed pretreatment and product purification requirements and simplicity in operation. Reaction involved in the cycler process is shown in Figure M-VII 7.2. Process flow diagram of UOP-BP cycler process for LPG aromatisation is shown is Figure M-VII 7.3.

Feed: Propane, Butane, Pentanes or mixture

Liquid Product: Largely BTX essentially free from C₆-C₉ paraffinic & naphthalenes

Preparation of Benzene Toluene and xylene charges very little with the composition of feed.

Aromatic yield:

- 63.6% of Feed for Propane
- 67.5% of Feed for Butane

→ Very high H₂ yield of 5.5 – 6% for feed
→ H₂ purity of about 95%.
Feed
Propane
Butanes

Pentanes

Intermediate
Unsaturated Oligomers

Highly reactive oligofinsoligmerised

C – C – C

C – C – C – C = C

+ 2H₂

C – C – C

Products
Cyclics

Hydrogen

+ Aromatics

By products
Methane

Ethane

Figure M-VII 7.2: Reactions involved in Cyclar Process

Courtesy: Hydro carbon processing [Gosling et al., 1991]
Figure M-VII 7.3: UOP-BP Cyclar Process for LPG Aromatisation

Courtesy: Hydrocarbon processing [Gosling et al., 1991]

REFERENCE