Lecture 3

Recovery of Chemicals from FCC And Steam Cracker
LECTURE 3
RECOVERY OF CHEMICALS FROM FCC AND STEAM CRACKER

With the rising demand of ethylene and propylene, there has been a tremendous growth in the steam cracking of hydrocarbons during the last four decades. Similarly, FCC (Fluid Catalytic Cracking) has developed into a major upgrading process in the petroleum refinery industry for the conversion of heavy fuel oil into more valuable products ranging from light olefins to naphtha and middle distillate. Large amounts of C₄ and C₅ compounds are produced along with the production of ethylene in steam cracking and gasoline in FCC. C₄ & C₅ streams are an important source of feedstock for synthetic rubber and many chemicals.

With increasing demand of C₅ hydrocarbons and oxygenates, upgrading of C₄ and C₅ streams from steam crackers and catalytic cracker is important to the economic performance of the above processes. It also provides a rich resource of reactive molecules, which forms the backbone of the synthetic rubber industry. The quantity and composition of the C₄ and C₅ stream depends on the severity of the steam cracker operation and feedstock processed.

Product profile C4 and C5 hydrocarbons are given in Figure M-VII 3.1 and Table M-VII 3.1.
Figure M-VII 3.1: Product Profile of C4 and C5 Hydrocarbon

PRODUCT PROFILE OF C5 HYDROCARBON

C5 hydrocarbons – are an important source of synthetic rubber, solvents, chemical intermediate, MTBE, plasticisers, TAME, rubber chemicals, herbicides, lube oil additives, pharmaceuticals.

Table M-VII 3.1: Product Profile C5 Hydrocarbons

<table>
<thead>
<tr>
<th>C5 Hydrocarbon</th>
<th>Isoprene</th>
<th>Polyisoprene, as the cross linking agent in Butyl rubber As co-monomer in styrene-isoprene copolymers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Isopentane</td>
<td>Solvent, Chlorinated derivative, blowing agent for Polystyrene</td>
</tr>
<tr>
<td>1-Pentene</td>
<td>Organic Synthesis, blending agent for high octane fuel</td>
<td></td>
</tr>
<tr>
<td>2-Pentene</td>
<td>Polymerisation inhibitor, organic synthesis</td>
<td></td>
</tr>
<tr>
<td>CycloPentene</td>
<td>Organic synthesis, polyolefins, epoxies cross linking agent</td>
<td></td>
</tr>
<tr>
<td>2- Methyl-1-Butene</td>
<td>Synthetic mark, anyl benzene hydrogen synthetic mark, anyl benzene hydrogen peroxide catalyst, 2,4-diamyl phenol (photographs colour complex), pinacolone (Crop protection chemicals)</td>
<td></td>
</tr>
<tr>
<td>3- Methyl-1-Butene</td>
<td>Monomer for specialty homo-polymer</td>
<td></td>
</tr>
<tr>
<td>Cyclopentadiene</td>
<td>Chlorinated insecticides, Chemical intermediate, Antiviral agent</td>
<td></td>
</tr>
<tr>
<td>Piperylene</td>
<td>Polymers, maleic anhydride, chemical intermediate</td>
<td></td>
</tr>
</tbody>
</table>

FLUID CATALYTIC CRACKING

Fluid catalytic cracking (FCC) converts low value crude oil into a variety of higher value products which include gasoline, diesel, heating oil and valuable gases containing LPG, propylene and C4 and C5 gases. Various products from fluid catalytic cracking and their uses are given in Table M-VII 3.2. FCC units are versatile and can be operated in three main modes which are aimed at maximizing middle distillate, gasoline, or olefins respectively by means of the adequate combination of various parameters such as catalyst type, catalyst to oil ratio, rise of outlet temperature and recycle of fractionators bottom. FCC is the second largest source of propylene supplied for petrochemical application.

- Conventional FCC 4-7% propylene and 1-2 % Ethylene
- High Severity FCC: 10% propylene
- Petro FCC™ (UOP): Ethylene 6%, Propylene 20-22%, Higher aromatics (18%) in Naphtha
- Higher C_{4,8} olefins yield which can be cracked to yield lower olefins by Total Petrochemicals ATOFINA/UOP Olefin cracking Process
- Although FCC is an important petroleum refining process, however, FCC gases have now become important petrochemical feedstock for production of LPG that can be converted to aromatics and C3, C4, & C5 hydrocarbons, i.e. propylene, butene, isobutene, pentene, etc.

Product distribution from FCC depends

- Reactor temp
- Feed preheat temperature
- Catalyst activity
- Catalyst circulation rate
- Catalyst activity
- Recycle rate

### Table M-VII 3.2: Various Petroleum Products from FCC and their uses

<table>
<thead>
<tr>
<th>Product</th>
<th>Composition and Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light gases</td>
<td>Primarily H_2, C_1 and C_2-s, ethylene can be recovered</td>
</tr>
<tr>
<td>LPG</td>
<td>C_{3-s} and C_{4-s} containing light olefins suitable for alkylations</td>
</tr>
<tr>
<td>Gasoline</td>
<td>C_{5+} high octane component for gasoline pool or light fuel</td>
</tr>
<tr>
<td>Light cycle oil (LCO)</td>
<td>Blend component for diesel or light fuel</td>
</tr>
<tr>
<td>Heavy cycle oil (HCO)</td>
<td>Fuel oil or cutter oil</td>
</tr>
<tr>
<td>Clarified oil</td>
<td>Carbon black feedstock</td>
</tr>
<tr>
<td>Coke</td>
<td>Used in regenerator to provide the reactor heat demand</td>
</tr>
</tbody>
</table>

**Propylene Recovery from FCC:** FCC gases has an important source of propylene from refinery and now FCC units are being operated both in gasoline mode and propylene mode. Details of propylene from FCC are given in Lecture 5 Module 6. Propylene from FCC may be as high as 25% with new FCC based propylene technologies.
olefins from FCC units have been achieved through changes in operations, base cracking catalyst and additive catalysts, and in hardware designs [Teng and Xie, 2006]

**UPGRADING OF C4 and C5 Streams**

C4 and C5 Streams from Steam Cracker and FCC contain C4 and C5 hydrocarbons recovery of which has become important steps for improving the overall economy of these processes. Some of the important C4 streams from Cracker and FCC butadiene (from cracker plant only), butene-1, 2- butane, isobutylene, mixed n-butene, isobutene. C4 stream of steam cracker contains appreciable amount of butadiene which is being recovered from naphtha cracker plants. Typical composition of C4 stream of naphtha cracker and FCC is given Table M-VII 3.3. The distribution product will depend on the feed stock, cracking severity and catalyst in case of FCC

**Table M-VII 3.3: Typical Compositions of C4 Fractions**

<table>
<thead>
<tr>
<th>Component</th>
<th>FCC</th>
<th>Steam Cracking</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutane</td>
<td>37.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Isobutene</td>
<td>24.0</td>
<td>26.0</td>
</tr>
<tr>
<td>1-Butene</td>
<td>15.0</td>
<td>13.6</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>0.2</td>
<td>36.0</td>
</tr>
<tr>
<td>2-Butenes (cis and trans)</td>
<td>11.0</td>
<td>12.0</td>
</tr>
<tr>
<td>n-Butane</td>
<td>12.0</td>
<td>9.8</td>
</tr>
<tr>
<td>others</td>
<td>balance</td>
<td>balance</td>
</tr>
</tbody>
</table>

Typical C5 cuts from steam cracking contain C4 (1%), n-pentene (26%), isopentane (24%), n-pentenes (4.5%), methyl butenes (12%), cyclopentenes (1.5%), isoprene (13.5%), pentadiene (piperylene) (9.0%), cyclopentadiene (7.5%), C6+ (1%) [Chauvel & Lefebvre, 1989]. Cyclopentadiene is easily dimerised to higher boiling dicyclopentadiene and separated from C5 stream by simple distillation. Typical composition of C5 cuts from catalytic cracking may be C4 (2%), n-pentane (5.5%), isopentane (31.5%), n-pentenes (22.5%), methyl butenes (37.5%), C6+ (1%) [Chauvel & Lefebvre, 1989]. Naphtha feed gives higher yield of C4 (8-10%) than ethane feed (2-3%)

- Upgrading of C4 Olefins:
• The production of chemical intermediates
• Butene-1, isobutylene, mixed n-butene
• Production of motor fuel component (alkylate, dimate, MTBE)

**Processing of C₄ cut from Steam Cracker and FCC**

There is not much difference in the processing of C₄ streams after the recovery of butadiene from the steam cracker and C₄ streams from the FCC. C₄ stream Butadiene from C₄ stream of naphtha cracker/ gas cracker is first recovered, followed by separation Isobutylene, isobutanee, butane, butane-1 and butene-2 from C₄ stream/ FCC and cracker using various process like etherification, hydrolusis, cracking, adsorption distillation etc. plant by various C₄ cut from steam cracker and FCC is shown in Figure M-VII 3.2 [Briggs et al., 1987; Convers, 1987; Vermilion and Niclaes, 1977; Chauvel& Lefebvre, 1989]. Isobutene recovery includes either hydration of the C₄ stream and subsequent decomposition or etherification with methanol to yield MTBE, which is cracked to give isobutene. Separation of 1-butene is done by selective hydrogenation followed by adsorption for separation of 1-butene and further processing for separation of isobutene and 2-butene by distillation. Separation of 2-butene involves hydro-isomerisation and subsequent distillation for separation of isobutene and 2-butene.
Figure M-VII 3.2: Separation of C4 hydrocarbons from FCC and Steam Cracker plants

After separation of butadiene, the C₄ streams from cracking and FCC is processed for production of n-butene, 1-butene, 2-butene, and isobutene. Process flow diagram for treatment of...
BUTADIENE

Butadiene is important raw material for production of a larger number of synthetic rubber and polymers such as styrene butadiene rubber (SBR), poly butadiene, chloroprene rubber, nitrile rubber, acrylonitrile butadiene styrene plastic. Other fastest growing use is in the manufacture of adiponitrile used in the manufacture of Nylon 66, Steam cracker and catalytic dehydrogenation of butenees are the two major sources of butadiene. Butenes can be recovered from C4 stream or produced by dehydrogenation of butanes.

According to SRI consulting global production and consumption of butadiene in 2009 was approximately 9.2 million tones and 9.3 million tones respectively. Butadiene is expected to average growth of 4.9 per year from 2009-2014. Styrene –butadiene rubber accounted for more than 33% of global butadiene consumption in 2009 and butadiene rubber for about 25%.

**Polymerisation Grade Butadiene**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3 Butadiene % min</td>
<td>99.6%</td>
</tr>
<tr>
<td>Butenes ppm max</td>
<td>4000</td>
</tr>
<tr>
<td>Methyacetylenes ppm.max.</td>
<td>25</td>
</tr>
<tr>
<td>Vinyl acetate ppm max</td>
<td>200</td>
</tr>
<tr>
<td>C5 dimers ppm max</td>
<td>2000</td>
</tr>
<tr>
<td>Carbonyl compounds (as aldehyde) max.</td>
<td>50</td>
</tr>
<tr>
<td>Inhibitor (p-tertiobutyl catechol)</td>
<td>100-200</td>
</tr>
<tr>
<td>Non-volatile residue ppm</td>
<td>2000</td>
</tr>
</tbody>
</table>

There are four major routes for production of butadiene:

- Steam cracking of naphtha
- Catalytic dehydrogenation of butenes
- Catalytic dehydrogenation of butanes
- Dehydrogenation-dehydration of ethanol (molasses route)
Butadiene from C₄ stream of Cracker Plant

C₄ cut from the steam cracker is first sent for butadiene recovery, which includes selective hydrogenation of acetylenics in the presence of palladium catalyst, then separation of butadiene extractive distillation process steps involved are [Chavel & Lefebvre, 1989]

- Extractive distillation in which acetylnic compound and butadiene are extracted in one or two stages
- Recovery of solvent
- Super fraction of butadiene stream for removal of acetylnic impurities
- Water scrubbing butadiene depleted cut to recover the solvent.

Various solvents used for separation of butadiene are furfural, dimethyl formamide (DMF), n-methyl pyrrolidone (NMP), and dimethyl acetamide. Selective hydrogenation results in overall improvement in the economy with higher butadiene yield.

Catalytic dehydrogenation of Butenes

Reaction:

\[
\begin{align*}
\text{H}_2\text{C} &= \text{C} - \text{C} - \text{CH}_3 \\
\text{H}_3\text{C} &= \text{C} - \text{C} - \text{CH}_3
\end{align*}
\]

\[\xrightarrow{\text{H}_2} \quad \text{H}_2\text{C} &= \text{C} - \text{C} - \text{CH}_2 + \text{H}_2 \quad \text{H}^0_{298} = 124 \text{ kJ/mol}
\]

Yield = 75-85%

Catalytic dehydrogenation of butanes two stages process:

1. Catalytic dehydrogenation of butanes to butenes

\[
\begin{align*}
\text{H}_2\text{C} &= \text{C} - \text{C} - \text{CH}_3 \\
\text{H}_3\text{C} &= \text{C} - \text{C} - \text{CH}_3
\end{align*}
\]

\[\xrightarrow{\text{H}_2} \quad \text{H}_2\text{C} &= \text{C} - \text{C} - \text{CH}_3 + \text{H}_2
\]

2. Catalytic dehydrogenation of butenes to butadiene

\[
\begin{align*}
\text{H}_2\text{C} &= \text{C} - \text{C} - \text{CH}_3 \\
\text{H}_3\text{C} &= \text{C} - \text{C} - \text{CH}_3
\end{align*}
\]

\[\xrightarrow{\text{H}_2} \quad \text{H}_2\text{C} &= \text{C} - \text{C} - \text{CH}_2 + \text{H}_2 \quad \text{H}^0_{298} = 124 \text{ kJ/mol}
\]

Yield = 75-85%
ISOBUTYLENE

Isobutylene is present in the C4 stream naphtha cracker and FCC. Major application of isobutene is in the manufacture of gasoline blending component such as MTBE, ETBE, alkylation, polymer gasoline. Polymer grade isobutylene can be made by cracking MTBE or for manufacture of polyisobutylene. Isobutylene is used in manufacture butyl rubber which is made by copolymerization of isobutylene with small amount of isoprene.

Various Routes for Isobutylene

**Extraction of C4 cuts from steam cracking / FCC:** Isobutylene is separated from C4 cuts from naphtha cracker after extraction of butadiene and from FCC gases after propylene recovery. First isobutenes is converted to MTBE by etherification and the recovered by cracking of MTBE to get polymer grade isobutylene it is also obtained by hydration of isobutylene containing stream and then cracking.

**Isomerisation of Butene:** isobutylene can be also produced from butane by isomerisation using zeolite ferrierite (zeolite of medium pore size) [Maulijanet al.2001]

**Dehydrogenation of Isobutene:**

**BUTENE -1**

Butene-1 is co-monomer in the production of low density polyethylene and high density polyethylene. Butene-1 can be separated from C4 stream of cracker after extraction of butadiene

**SHB-CB process:** This process selectively hydrogenate the butadiene in the C4 cut by converting it to butane-1 and butane-2. Acetylenes and dienes are likewise hydrogenated. If the process is optimized to produce butane-1, about 60% of butadiene is converted to butane-1. The process is operated in the liquid phase mild temperatures and moderate pressures.

**UPGRADING OF C₅ CUTS**

The steam cracker C5 stream is a rich resource of olefins and diolefins which can be upgraded to produce elastomers, resins and fine chemical intermediates. In steam crackers during cracking process along with ethylene, propylene, C4 stream, aromatics and pyrolysis gasoline bare also formed. Apart from aromatics, Pyrolysis gasoline stream also contains C5 stream [Morgan,
1996]. The quantity and composition of the stream depend on the nature of the cracked product and severity of cracker operation C₅ stream.

**Various Steps in the recovery of C₅ chemicals are [Chauvel & Lefebvre, 1985]**

- Separation of C₅ stream from pyrolysis gasoline by distillation
- Separation of cyclopentadiene: In first stage cyclopentadiene is dimerised to dicyclopentadiene followed by cracking of dicyclopentadiene to cyclopentadiene.
- Extractive distillation of cyclopentadiene free C₅ stream produce isoprene-piperylene stream. Distillation removes the light acetylenes
- Separation of isoprene and piperylene extract by distillation
- Absorption at atmospheric pressure in the presence of NMP
- Purification of Isoprene rich paraffin
- Periodic regeneration of solvent

Solvents used in extraction of isoprene are Acetonitrile, N-methylpyrroldone, Dimethylformalnide.

**OXYGENATES FROM REFINERY C₄ AND C₅ STREAM**

Several oxygenated fuel components have figured prominently in refinery reformulated gasoline planning. Methyl tertiary butyl ether (MTBE), tertiary amyl methyl ether (TAME) and ethyl tertiary butyl ether (ETBE). All oxygenated fuels reduce hydrocarbons in the automobile exhaust. MTBE was considered one of the most important oxygenates used in the production of lead free gasoline and was used produced on a large scale throughout the world. There has been because of environmental problem. The oxygenated MTBE and ETBE are produced by the reaction of methanol/ethanol and isobutylene.

**METHYL TERTIARY BUTYL ETHER (MTBE)**

MTBE is one of the important oxygenates and originally its use started as a substitute of tetraethyl lead. MTBE increases the oxygen content of gasoline results in the reduction of harmful emissions. MTBE which is made by etherification of C₄ gases from cracker and FCC is also used for production of polymer grade isobutylene for synthetic rubber.
MTBE is produced by the reaction of methanol with isobutylene contained in C_4 streams from thermal crackers in the presence of ion exchange resin at 40-90°C and a pressure of 5 to 10 kg/cm². Catalytic cracking butylenes and field butanes are additional possible source of isobutylene. Convention process and catalytic distillation are the two commercial processes available. **Figure M-VII 3.3** shows the process flow diagram for MTBE conventional methods.

![Chemical Structures]

**Figure M-VII 3.3: MTBE Conventional Methods**

**ETHYL TERTIARY BUTYL ETHER (ETBE)**

ETBE is made by etherification of isobutylene with ethanol similar to MTBE.

Isobutylene + Ethanol → ETBE
TERIARY AMYL METHYL ETHER (TAME)

TAME is produced by etherification of isoamylene recovered from C₅ stream of FCC and steam crackers. Two reactive components of isoamylenes are 2-Methyl butene-1 and 2-Methyl butene-2. Catalytic distillation process is used for the manufacture of TAME.

Reaction Involve:

TERIARY AMYL METHYL ETHER (TAME)

TAME is produced by etherification of isoamylenes recovered from C₅ stream of FCC and steam crackers. Two reactive components of isoamylenes are 2-Methyl butene-1 and 2-Methyl butene-2. Catalytic distillation process is used for the manufacture of TAME.

Reaction Involve:
REFERENCES
4. Convers, A., “Make chemicals from C4olefinic fractions”, Chemical Age of India,