Unit 4. Fluidised Catalytic Cracking

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Introduction

Catalytic cracking is the process in which heavy low-value petroleum stream such as vacuum gas oil is upgraded into higher value products:

**FCC products:**
- gasoline
- olefins
- LPG

→ Alkylation unit → Ultra clean gasoline (C\textsubscript{7}–C\textsubscript{8} alkylates)

Catalytic cracking processes

- Fluidised catalytic cracking (FCC)
- Petro-FCC
- Residue FCC (RFCC)
- Deep catalytic cracking (DCC)
Role of FCC in the Refinery

Figure 1. Role of FCC in refining operation
**Feedstock**

The main feedstock is the gas oil boiling between 316 °C and 566 °C

Feed pre-treatment by hydrotreating is required in order to:

- protect the catalyst
- remove contaminants
- improve cracking characteristics and yields

Some possible feedstocks are:

- atmospheric distillates
- coking distillates
- visbreaking distillates
- vacuum gasoil
- atmospheric residue (desulphurised)
- vacuum residue (desulphurised, deasphalted)
# Products

<table>
<thead>
<tr>
<th>Products</th>
<th>Characteristics</th>
<th>Yield (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry gas + H$_2$S (C$_1$ + C$_2$ + C$_3$ + H$_2$) + H$_2$S</td>
<td>H$_2$S must be removed</td>
<td>3–5</td>
</tr>
<tr>
<td>LPG: C$_3$, C$_3^-$, C$_4$, C$_4^-$</td>
<td>Petrochemical feedstock</td>
<td>8–20</td>
</tr>
<tr>
<td>Gasoline</td>
<td>Main product, good octane number</td>
<td>35–60</td>
</tr>
<tr>
<td>Light cycle oil (LCO)</td>
<td>Rich in aromatics, high sulphur content, diluent for fuel</td>
<td>12–20</td>
</tr>
<tr>
<td>Heavy cycle oil (HCO) + slurry</td>
<td>Very rich in aromatics, slurry of solids, (mainly catalyst coke)</td>
<td>10–15</td>
</tr>
<tr>
<td>Coke</td>
<td>Consumed in regenerator</td>
<td>3–5</td>
</tr>
</tbody>
</table>
FCC Reactions

The main reaction in the FCC is the catalytic cracking of:

- paraffins
- olefins
- naphthenes
- side chains in aromatics

Figure 2. FCC reactions network
**Primary Reactions**

*Primary cracking occurs by the carbenium ion intermediates in the following steps:*

**(a)** Olefin is formed first by the mild thermal cracking of paraffin:

\[ nC_8H_{18} \rightarrow CH_4 + CH_3 - (CH_2)_4 - CH = CH_2 \]

**(b)** Proton shift:

\[ CH_3 - (CH_2)_4 - CH = CH_2 + H_2O + Al - O - Si \rightarrow \]

\[ CH_3 - (CH_2)_4 - CH^+ - CH_3 + [HO - Al - Si]^- \]

**Carbenium ion**

**(c)** Beta scission:

\[ CH_3 - (CH_2)_4 - CH^+ - CH_3 \rightarrow CH_3 - CH = CH_2 + CH_2^+ - CH_2 - CH_2 - CH_3 \]
Primary Reactions

*Beside paraffins, other hydrocarbons which are formed by primary cracking include the following:*

- **Olefins** – smaller olefins
  
  \[ \text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_3 \rightarrow \text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3 + \text{CH}_3 - \text{CH} = \text{CH}_2 \]

- **Alkylaromatics** – Dealkylation
  
  \[
  \begin{array}{c}
  \text{CH}_2\text{CH}_3 \\
  \text{Oll} \\
  \text{CH}_2\text{CH}_3
  \end{array}
  \rightarrow
  \begin{array}{c}
  \text{CH}_2\text{CH}_3 \\
  \text{Oll} \\
  \text{CH}_2\text{CH}_3
  \end{array}
  + \text{CH}_2 = \text{CH}_2
  
  
- **Alkylaromatics** – Side chain cracking
  
  \[
  \begin{array}{c}
  \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\
  \text{Oll} \\
  \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3
  \end{array}
  \rightarrow
  \begin{array}{c}
  \text{CH}_2\text{CH}_3 \\
  \text{Oll} \\
  \text{CH}_2\text{CH}_3
  \end{array}
  + \text{CH}_2 = \text{CH}_2
  
  
  

Primary Reactions

*Hydrogen transfer* plays a key role in the gas oil cracking process:

- it reduces the amount of olefins in the product
- contributes to coke formation
- influences the molecular weight distribution of the product

Through *intermolecular (bimolecular) hydrogen transfer*, highly reactive olefins are converted to more stable paraffins and aromatics as in the following reaction:

\[
3C_nH_{2n} + C_mH_{2m} \rightarrow 3C_nH_{2n+2} + C_mH_{2m-6}
\]

<table>
<thead>
<tr>
<th>Olefin</th>
<th>Naphthene</th>
<th>Paraffin</th>
<th>Aromatic</th>
</tr>
</thead>
</table>

Further *loss of hydrogen* to olefins by aromatics or other hydrogen-deficient products results in more paraffins and coke:

- **Aromatics**: \(C_nH_{2n-6}\) or \(C_mH_{2m-2}\)
- **Cyclo-olefins**: Alkylation, condensation, Polymerization
- **Olefins**: \(C_nH_{2n}\) to \(C_nH_{2n+2}\)

**Paraffins**
Secondary Reactions

- **Isomerisation**

\[
R - CH_2 - CH_2 - CH^+ - CH_3 \rightleftharpoons R - CH_2 - C - CH_3 +
\]

Secondary Carbenium ion

Tertiary Carbenium ion

- **Cyclisation**

- **Coke formation**
FCC Reactions

The main reactions in the FCC reactor can be summarised as follows:

- **Paraffins**
  - Paraffin cracking → Paraffins + Olefins

- **Olefins**
  - Olefin cracking → LPG olefins
  - Olefin cyclisation → Naphthenes
  - Olefin isomerisation → Branched olefins + Branched paraffins
  - Olefin H-transfer → Paraffins
  - Olefin cyclisation → Coke

- **Naphthenes**
  - Naphthene cracking → Olefins
  - Naphthene dehydrogenation → Aromatics
  - Naphthene isomerisation → Restructured naphthenes

- **Aromatics**
  - Aromatics (side chain) → Aromatics + Olefins
  - Aromatic transalkylation → Alkylaromatics
  - Aromatic dehydrogenation → Polyaromatics → Coke
Thermodynamics of FCC Reactions

- **Cracking of relatively long-chain paraffins and olefins** can go up to 95% completion at cracking conditions.

- **Isomerisation, transalkylation, dealkylation and dehydrogenation** reactions are intermediate in attaining equilibrium.

- **Condensation reactions**, such as *olefin polymerization and paraffin alkylation*, are less favourable at higher temperatures.

- The occurrence of both *exothermic* and *endothermic* reactions contributes to the overall heat balance.

- The high volume of products caused by the cracking of larger molecules requires *low operating pressure* (1–5 bars).

- The high endothermic nature of cracking reactions requires that the reactor operates at *high temperatures 480–550 °C*. 
FCC Catalyst

The zeolite type catalyst

- In a powder form with an average particle size of 75 μm
- an average surface area of 800 m²/g
- it has a crystalline structure of aluminosilicates
- a matrix is added to the zeolite which acts as a binder and filler

FCC catalyst consists of

- zeolite
- matrix
FCC Catalyst. Zeolite

- The main active component in the catalyst is the Y-Zeolite.

**Y-Zeolite** is a crystalline structure of aluminosilicates which has the **Y-faujasite** structure.

- The highest pore size in the Y-faujasite structure is 8 Å, which is called the **super cage**.

- It can allow some C_{18}–C_{25} mono-, di- and tri-nuclear aromatics present in the vacuum gas oil to pass.

*Figure 3. Structure of Y-faujasite*
FCC Catalyst. Zeolite

In the cracking of *long chain paraffins*, a type of high silica zeolite ZSM-5 is added.

- is used to improve octane number
- it is composed of zig-zag channel systems

![Schematic representation of shape-selective cracking with ZSM-5 zeolite](image)

Figure 4. Schematic representation of shape-selective cracking with ZSM-5 zeolite

- the unreacted stream is enriched with *iso-paraffins* and *aromatics*, which contribute to an increase in the octane number

*Zeolite Socony Mobil-5* (Socony – Standard Oil Company of New York, the formula of the zeolite was patented by Mobil Oil Company)
FCC Catalyst. Matrix

The matrix is added to the zeolite to

- increase the body of the catalyst
- add some improved properties

Three types of substances constitute the matrix:

**Binder**
- is added as a glue
- provides cohesion for zeolite particles

**Filler**
- make up the body of the catalyst
- it is usually a clay (Kaoline)

**Additives**
- a small amount (ppm) of metal
- metallic oxides
- addition of 5% ZSM-5 zeolite

Function:
- provide physical integrity (density and attrition resistance)
- promotes the combustion of CO to CO\(_2\) in the regenerator
- fix SO\(_x\) on the catalyst
- leads to an increase of RON
FCC Configuration

The basic configuration of the FCC unit is a reactor (riser) and a regenerator.

Basic types of FCC units:

- The ‘Side-by-Side’ type
  - the reactor and regenerator are separate vessels adjacent to each other

- The Staked (Orthoflow) type
  - reactor is mounted on the top of the regenerator

Figure 5. FCC type configuration
Fluidised Catalytic Cracking

Process Description

Figure 6. Main pieces of equipment for the fluid catalytic cracking
**Process Description**

![Fluid catalytic cracking process flowsheet](image)

**Figure 7. Fluid catalytic cracking process flowsheet**
### Process Operating Conditions

Table 2. Reactor and regenerator operating condition for max gasoline production

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor Feed Rate, MBPSD</td>
<td>40</td>
</tr>
<tr>
<td>Feed Temperature, °F</td>
<td>446</td>
</tr>
<tr>
<td>Catalyst/Oil Ratio</td>
<td>5.4</td>
</tr>
<tr>
<td>Catalyst Circulation Rate, tons/min</td>
<td>21.7</td>
</tr>
<tr>
<td>Catalyst Makeup Rate, tons/day</td>
<td>2.5</td>
</tr>
<tr>
<td>Riser Outlet Temperature, °F</td>
<td>991</td>
</tr>
<tr>
<td>Dispersion Steam, wt% feed</td>
<td>0.9</td>
</tr>
<tr>
<td>Stripping Steam, tons/ton catalyst</td>
<td>0.0213</td>
</tr>
<tr>
<td>Reactor Pressure, psig</td>
<td>30</td>
</tr>
<tr>
<td>Regenerator Pressure, psig</td>
<td>33</td>
</tr>
<tr>
<td>Regenerator Temperature, °F</td>
<td>1341</td>
</tr>
<tr>
<td>Flue Gas Temperature, °F</td>
<td>1355</td>
</tr>
</tbody>
</table>
## Modes of Fluidisation in FCC unit

**Table 3. Modes of fluidisation in FCC**

<table>
<thead>
<tr>
<th>Location in FCC</th>
<th>Mode of fluidisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regenerator</td>
<td>Turbulent fluidisation: to attain uniform burning temperature in bed.</td>
</tr>
<tr>
<td>Line for catalyst transport</td>
<td>Bubbling fluidisation</td>
</tr>
<tr>
<td>from regenerator to riser</td>
<td></td>
</tr>
<tr>
<td>Riser</td>
<td>Pneumatic transport: Catalyst and products are carried out from riser. Plug flow has a few seconds of residence time.</td>
</tr>
<tr>
<td>Stripper</td>
<td>Bubbling fluidisation: Steam is injected in the stripper to vaporise and recover heavy oil and reduce coke formation.</td>
</tr>
<tr>
<td>Lift line from regenerator to reactor</td>
<td>Pneumatic transport</td>
</tr>
</tbody>
</table>
New Technology

Deep Catalytic Cracking (DCC)

- DCC is a new FCC process using a new catalyst for heavy feed stocks to give light olefins.
- The yield of olefins depends greatly on the type of feedstock.
- Paraffinic feeds give the lightest propylene yield of 23 wt% and 6.9 wt% isobutylene.

Catalytic Pyrolysis Process (CPP)

- The CPP is an extension of DCC but with increased ethylene yield.
- C$_3$ can be produced up to around 20 wt% while C$_2$ can be adjusted between 10 and 20 wt%.
- It is suggested to optimise the use of crude oil as a petrochemical feedstock by using a combination of steam cracking (SC) and catalytic pyrolysis (CPP) (see Fig. 8).

Figure 8. Flowchart for crude to petrochemical
The process gives the highest yield of propylene, lighter olefins and aromatics for petrochemical operation from feedstocks which can include conventional FCC feeds and residual feeds.

Figure 9. UOP Petro-FCC complex
Comparison of FCC and Petro-FCC yields

Table 4. Yield patterns of conventional FCC and Petro-FCC units

<table>
<thead>
<tr>
<th>Component</th>
<th>Conventional FCC wt %</th>
<th>Petro-FCC wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S, H₂, C₁ &amp; C₂</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Ethylene</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>Propane</td>
<td>1.8</td>
<td>2</td>
</tr>
<tr>
<td>Propylene</td>
<td>4.7</td>
<td>22</td>
</tr>
<tr>
<td>Butane</td>
<td>4.5</td>
<td>5</td>
</tr>
<tr>
<td>Butene</td>
<td>6.5</td>
<td>14</td>
</tr>
<tr>
<td>Naphtha</td>
<td>53.5</td>
<td>28</td>
</tr>
<tr>
<td>Distillate</td>
<td>14</td>
<td>9.5</td>
</tr>
<tr>
<td>Fuel oil</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>Coke</td>
<td>5</td>
<td>5.5</td>
</tr>
</tbody>
</table>
References

  Fluidised Catalytic Cracking p.199-261

  KBR Fluid Catalytic Cracking Process p.146-176
  Deep Catalytic Cracking, The New Light Olefin Generator p. 178-188
  UOP Fluid Catalytic Cracking Process p. 189-211
  Stone & Webster-Institut Français Du Pètrole Fluid RFCC Process p. 212-235