Fundamentals of Petroleum Refining
Unit 5. Alkylation

Assistant lecturers
Belinskaya Nataliya Sergeevna
Kirgina Maria Vladimirovna

2015
INTRODUCTION

Alkylation is the process of producing gasoline range material (alkylates) from olefins such as

- propylene ($C_3$)
- butylenes ($C_4$)
- amylene ($C_5$)

and isobutane.
ROLE OF ALKYLATION UNIT IN THE REFINERY

![Diagram showing the role of alkylation unit in the refinery](image)

Figure 1. Role of alkylation unit in the refinery

Table 1. Olefins and isobutane production from different units

<table>
<thead>
<tr>
<th></th>
<th>IV %</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Isobutane</td>
<td>Olefins</td>
</tr>
<tr>
<td>Hydrocracker</td>
<td>3</td>
<td>–</td>
</tr>
<tr>
<td>FCC</td>
<td>6</td>
<td>15</td>
</tr>
<tr>
<td>Coker</td>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>Hydrotreater</td>
<td>1</td>
<td>–</td>
</tr>
<tr>
<td>Reformer</td>
<td>2</td>
<td>–</td>
</tr>
<tr>
<td>Isomerization</td>
<td>1</td>
<td>–</td>
</tr>
<tr>
<td>Crude unit</td>
<td>0.5</td>
<td>–</td>
</tr>
</tbody>
</table>
ALKYLATION CHEMISTRY

\[
\begin{align*}
\text{CH}_3\text{C}=\text{CH}_3 & + \text{CH}_2\text{-CH-CH}_3 \rightarrow \text{CH}_3\text{-C-CH}_2\text{-CH-CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{(Isooctane)} \\
\text{Isobutylene} & \quad \text{Isobutane} & \quad 2,2,4\text{-Trimethylpentane}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2=\text{CH-CH}_2\text{-CH}_3 & + \text{CH}_3\text{-CH-CH}_3 \rightarrow \text{CH}_3\text{-CH-CH-CH}_2\text{-CH}_2\text{-CH}_3 \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{1-Butene} & \quad \text{Isobutane} & \quad 2,3\text{-Dimethylhexane}
\end{align*}
\]
ALKYLATION CHEMISTRY

\[
\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3 + \text{CH}_3-\text{CH}-\text{CH}_3 \rightarrow \text{CH}_3-\text{C}-\text{CH}_2-\text{CH}-\text{CH}_3
\]

2-Butene  Isobutane  2,2,4-Trimethylpentane

or

\[
\text{CH}_3\text{CH}_3\text{CH}_3
\]

\[
\text{CH}_3-\text{CH}-\text{CH}-\text{CH}-\text{CH}_3
\]

2,3,4-Trimethylpentane

\[
\text{CH}_3-\text{CH}=\text{CH}_2 + \text{CH}_3-\text{CH}-\text{CH}_3 \rightarrow \text{CH}_3-\text{CH}-\text{CH}-\text{CH}_2-\text{CH}_3
\]

Propylene  Isobutane  2,3-Dimethylpentane
ALKYLATION PROCESSES

- **without a catalyst**
  
  _severe conditions:_ $T = 500 \, ^\circ\text{C}$ and $P = 20–40 \, \text{MPa}$

- **a strong acid catalyst** ($\text{H}_2\text{SO}_4$ or HF)
  
  $T < 50 \, ^\circ\text{C}$ and $P < 3 \, \text{MPa}$

- **a solid catalyst**
  
  _zeolite type catalyst is used_
ALKYLATION PROCESSES

The alkylation process

- consists of running the hydrocarbons in **liquid form**
- at **low temperature**
- with a high **isobutane to olefin ratio**

Figure 2. Block diagram of alkylation process
SULPHURIC ACID ALKYLATION PROCESS

- the auto-refrigeration process (Exxon)
  
  *the evaporation of *i*C*₄ and *C*₄* induces cooling of the emulsion in the reactor*

- the effluent refrigeration process (Stratford)
  
  *a refrigeration unit provides cooling to the reactor*
Figure 3. Auto-refrigerated sulphuric acid alkylation process

The reactor operates at
- a pressure of 0.69 bar (69 kPa)
- a temperature of 5 °C
- for up to 40 min
Figure 4. Block diagram for Stratco effluent refrigerated sulphuric acid alkylation unit
The reactor operates at
- a pressure of 4.13 bar (0.41 MPa)
- a temperature of 10 °C
- for 20–35 min
SULPHURIC ACID ALKYLATION PROCESS

STRATCO contactor reactor for sulfuric acid alkylation
Figure 6. Simplified diagram of the Phillip’s HF alkylation process
The overall process scheme is similar to the liquid acid base process scheme, except for the regeneration section, which is necessary for solid acid catalysts because of rapid deactivation.

Table 2. Solid acid alkylation processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction temperature (°C)</th>
<th>iC₄/olefin</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>UOP alkylene</td>
<td>10–40</td>
<td>6–15</td>
<td>HAL-100</td>
</tr>
<tr>
<td>Lurgi Eurofuel</td>
<td>50–100</td>
<td>6–12</td>
<td>Faujasite-derived</td>
</tr>
<tr>
<td>Haldor Topsoes FBA</td>
<td>0–20</td>
<td></td>
<td>CF₃SO₃H/SiO₂</td>
</tr>
<tr>
<td>ABB Lummus</td>
<td>50–90</td>
<td>8–15</td>
<td>Zeolite-derived (SAC)</td>
</tr>
<tr>
<td>AlkyClean</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Zeolite catalyst is used.

The reactor operates at:
- a temperature of 50–90 °C
- liquid phase conditions
The *process conditions* that influence the quality of alkylate product and acid consumption rate are

- olefin type
- dilution ratio $\delta (iC_4/iC^=4)$
- mixing temperature
- impeller speed
- space velocity (or residence time)
- acid strength
EFFECT OF OPERATING CONDITIONS

Olefin Type

- The presence of propylene or pentene with butane will lower the octane number and increase the acid consumption.

- Butene in sulphuric acid as a catalyst gives the best octane numbers.

- The presence of propylene with butene increases acid consumption and lowers the alkylate octane number.
EFFECT OF OPERATING CONDITIONS

Olefin Type

- In the case of a $\text{C}_3/i\text{C}_5$ feed mixture, the trend is interesting since sulphuric acid consumption decreases up to 82 vol% of the $\text{C}_3/i\text{C}_5$ mixture. However, the octane number also decreases.

- At lower acid consumption, it is better to separate the $\text{C}_3/i\text{C}_5$ mixture from $\text{C}_4$ and let it react with $i\text{C}_4$ in a separate reactor.
## Table 3. Effect of type of olefin on alkylation octane number

<table>
<thead>
<tr>
<th>Types of Olefin</th>
<th>RON</th>
<th>MON</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HF</td>
<td>H$_2$SO$_4$</td>
</tr>
<tr>
<td>Propylene</td>
<td>91–93</td>
<td>91–92</td>
</tr>
<tr>
<td>Butene–1</td>
<td>90–91</td>
<td>97–98</td>
</tr>
<tr>
<td>Isobutene</td>
<td>94–95</td>
<td>90–91</td>
</tr>
<tr>
<td>Amylene</td>
<td>90–92</td>
<td>91–92</td>
</tr>
</tbody>
</table>
EFFECT OF OPERATING CONDITIONS

Isobutane concentration

The $i\text{C}_4/C_4^=$ (isobutane to olefin) ratio has an important role regarding the quality of alkylate produced and the amount of sulphuric acid consumption.

- The $i\text{C}_4/C_4^=$ ratio is kept in industrial operation between 5:1 and 15:1 as the external isobutane to olefin (I/O) ratio.
- Inside a reactor with high circulation, this ratio becomes 100–1000:1.
EFFECT OF OPERATING CONDITIONS

Isobutane concentration

- High isobutane concentration ([iC₄]) prevents olefin polymerization which results in low quality alkylate and high sulphuric acid consumption.

- Solubility of iC₄ << C₄. Thus a high concentration of iC₄ is required in the mixed hydrocarbons to compensate for its low solubility.
EFFECT OF OPERATING CONDITIONS

Isobutane concentration

- The conversion to alkylate increases as $\delta \left( \frac{iC_4}{C_4} \right)$ is increased.

- The rate of alkylate formation increases while the rate of formation of undesirable heavy alkylates decreases as $iC_4$ increases.

- As isobutane increases, alkylate MON increases and sulphuric acid consumption decreases.
EFFECT OF OPERATING CONDITIONS

Acid strength

An *optimum value of acid strength* of 90 wt% $\text{H}_2\text{SO}_4$ is maintained by adding fresh concentrated acid (98–99 wt%).

- As the strength of the acid decreases, the acid consumption increases with the octane number decreases.

- Although water lowers the acid activity, 1–2 wt% *water is added to ionize the acid*.

- The acid strength decreases because of the formation of gums and other products resulting from the reaction with other impurities.
EFFECT OF OPERATING CONDITIONS

Degree of agitation

- When the hydrocarbons \((iC_4\) and \(C_4=\)) are dispersed in sulphuric acid, the speed of the impeller determines the dispersed phase size (droplet diameter) and hence, the interfacial contact area.

- The reaction rate of \(iC_4\) and \(C_4=\) is quite fast, and the reaction is controlled by mass transfer.

Figure 8. Emulsion of hydrocarbon in sulphuric acid
Space velocity

- Since the alkylation reaction is very fast, the *residence time* is not a limiting parameter.

- However, as the *space velocity increases*, the *octane number tends to decrease* while *acid consumption tends to increase*.

- Residence time for sulphuric acid is usually from *5 to 40 min*, and for hydrofluoric acid, it is *5–25 min*. 
EFFECT OF OPERATING CONDITIONS

Reaction temperature

The reaction thermodynamics and kinetics are favoured at low temperatures.

- **Sulphuric acid alkylation** units are operated at 5–10 ºC.

- Above 10 ºC, oxidation and side reactions are promoted, and the deteriorate-alkylate yield and quality while acid consumption increases.

- Above 21 ºC, the polymerization of olefin will occur, and the octane number of alkylate decrease.

- For **HF alkylation**, the reaction temperature is less significant and is between 21 and 38 ºC.
REFERENCES

  Alkylation p. 263-283

  NexOctane™ Technology for Isooctane Production p. 3-9 
  Stratco Effluent Refrigerated H₂SO₄ Alkylation Process p. 10-23 
  UOP Alkyiene™ Process for Motor Fuel Alkylation p. 24-30 
  UOP Alkylation Technology p. 31-53
Figure 1. NExOCTANE process
Figure 2. Block flow diagram of STRATCO Inc. effluent refrigerated alkylation process
Figure 3. STRATCO Contactor reactor
Figure 4. Alkylene process flow scheme
Figure 5. Alkylene process flow diagram
Figure 6. UOP C₄ HF Alkylation process
Figure 7. UOP C3-C4 HF Alkylation process
Figure 8. Sulfuric acid alkylation process using a conventional reactor
Figure 9. Sulfuric acid alkylation process using a cascade reactor
Figure 10. The effluent refrigeration alkylation process
Figure 11. Hydrogen fluoride alkylation process