PROFESSIONAL COURSE IN ENGLISH
“FUNDAMENTALS OF PETROLEUM REFINING”

Unit 13. Alkylation

Assistant teacher
Belinskaya Nataliya Segeevna
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

Figure 1. Role of alkylation unit in the refinery

Table 1. Olefins and isobutane production from different units

<table>
<thead>
<tr>
<th>Unit</th>
<th>Isobutane</th>
<th>Olefins</th>
</tr>
</thead>
<tbody>
<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

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

Isobutylene Isobutane

\[
\text{CH}_2\text{=CH-CH}_2\text{-CH}_3 + \text{CH}_3\text{-CH-CH}_3 \rightarrow \text{CH}_3\text{-CH-CH-CH}_2\text{-CH}_2\text{-CH}_3
\]
(2,3-Dimethylnexane)

1-Butene Isobutane
ALKYLATION CHEMISTRY

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

2-Butene \hspace{1cm} \text{Isobutane} \hspace{1cm} 2,2,4-\text{Trimethylpentane}

or

\[ \text{CH}_3\text{CH}_3\text{CH}_3 \hspace{1cm} \text{CH}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_3 \hspace{1cm} 2,3,4-\text{Trimethylpentane} \]

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

\hspace{1cm} \text{Propylene} \hspace{1cm} \text{Isobutane} \hspace{1cm} 2,3-\text{Dimethylpentane} \]
ALKYLATION PROCESSES

❖ without a catalyst
  severe conditions: $T = 500 \degree C$ and $P = 20–40$ MPa

❖ a strong acid catalyst ($H_2SO_4$ or HF)
  $T < 50 \degree C$ and $P < 3$ 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
Figure 2: The reaction products are sent to an acid settler where the acid is recycled back to the reactor. Products are then separated into gaseous LPG propane and n-butane and the desired product of alkylate.
SULPHURIC ACID ALKYLATION PROCESS

- the auto-refrigeration process (Exxon)
  
  *the evaporation of iC$_4$ and C$_4$ induces cooling of the emulsion in the reactor*

- the effluent refrigeration process (Stratford)

  *a refrigeration unit provides cooling to the reactor*
The reactor operates at:

- a pressure of 0.69 bar (69 kPa)
- a temperature of 5 °C
- for up to 40 min
Figure 3: The olefin is fed to the first reactor in the cascades, together with the recycled acid and refrigerant. Recycled and make-up isobutanes are distributed to each reactor. Evaporated gases are compressed and fed back to the reactor along with the fresh olefin feed which is also cooled by this stream.
In this diagram the “effluent treating” section is used to remove free acid and alkyl sulphate to avoid corrosion and fouling.

The “blowdown” section is used to purge and neutralized spent acid.
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
HYDROFLUORIC ACID ALKYLATION

Two hydrofluoric acid (HF) alkylation processes are commonly available:
- Phillips process
- UOP process

- The hydrofluoric acid processes have no mechanical stirring as in the sulphuric acid processes.
- The low viscosity of HF and the high solubility of isobutane in the acid allow for a simpler design.
- The emulsion is obtained by injecting the hydrocarbon feed into the continuous HF phase through nozzles at the bottom of a tubular reactor.
- Reaction temperature is about 30 °C, allowing for the use of water as a coolant to the reactor.
- The two processes are quite similar. The flow diagram of the Phillips process is shown in Figure 6.
- The residence time in the reactor is 20–40 s.
- The hydrocarbon phase is sent to the main fractionation column to obtain stabilized alkylate.
ALKYLATION

- $\text{H}_2\text{SO}_4$ alkylation processes are favoured over the HF processes because of the recent concern about the mitigation of HF vapour.

- HF is a very hazardous material for humans because it can penetrate and damage tissue and bone.
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>
AlkyClean SOLID CATALYST TECHNOLOGY

Zeolite catalyst is used.

The reactor operates at

- a temperature of 50–90 °C
- liquid phase conditions
The process shown in **Figure 7** consists of four main sections:

- feedstock pretreatment
- reaction
- catalyst regeneration
- product distillation.

An olefin feed is preheated and fed with the isobutane recycle to the reactor. The reactor operates at 50–90 °C with liquid phase conditions. Multiple reactors are used to allow for the catalyst regeneration cycle. During regeneration, olefin addition is stopped and hydrogen is added to achieve a low reactor concentration of dissolved hydrogen while maintaining liquid phase alkylation reaction conditions. This minimizes energy consumption during the switching of the operation. The swing reactor coupled with long catalyst life allows the refiner to work without the need of taking the reactor off-line for moderate temperature regeneration that restores the catalyst activity completely.
EFFECT OF OPERATING 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 $C_3/iC_5$ feed mixture, the trend is interesting since sulphuric acid consumption decreases up to 82 vol% of the $C_3/iC_5$ mixture. However, the octane number also decreases.

- At lower acid consumption, it is better to separate the $C_3/iC_5$ mixture from $C_4$ and let it react with $iC_4$ in a separate reactor.
### EFFECT OF OPERATING CONDITIONS

#### Olefin Type

**Table 3. Effect of type of olefin on alkylate 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 $i\text{C}_4/\text{C}_4^-$ (isobutane to olefin) ratio has an important role regarding the quality of alkylate produced and the amount of sulphuric acid consumption.

- The $i\text{C}_4/\text{C}_4^-$ 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 ([iC\textsubscript{4}]) prevents olefin polymerization which results in low quality alkylate and high sulphuric acid consumption.

- Solubility of iC\textsubscript{4} \ll C\textsubscript{4}. Thus a high concentration of iC\textsubscript{4} is required in the mixed hydrocarbons to compensate for its low solubility.
Isobutane concentration

- The conversion to alkylate increases as $\delta (iC_4/C=4)$ 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
EFFECT OF OPERATING CONDITIONS

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 Alkylene™ 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

- A - CONTACTER REACTOR
- B - TUBE BUNDLE
- C - HYDRAULIC HEAD
- D - MOTOR
- E - IMPELLER
- F - CIRCULATION TUBE

EMULSION TO SETTLER

COOLANT OUT

COOLANT IN

ACID

HC

D
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