Lecture 7
Alkylation, Isomerisation And Polymerisation
ALKYLATION

Alkylation process commercialized in 1938, since then there has been tremendous growth in the process. In US and Europe about alkylate is about 11-12 percent and 6 percent in the gasoline pool respectively. Alkylate is a key component in reformulated gasoline. Alkylation processes are becoming important due to growing demand for high octane gasoline and requirement of low RVP, low sulphur, low toxics. Alkylate is an ideal blend stock to meet these requirement.

[D’Aquino & Mavridis, 2007]

The process of alkylation different iso-paraffins using olefins were developed during thirties using aluminium chloride catalyst, however, later catalyst was replaced by HF and sulfuric acid. Although butylenes alkylation is one of the most commonly used process, however, alkylation of amylene obtained from C5 fraction of FCC can be another route to increase the availability of alkylate. Alkylation of C5 cut from FCC can significantly reduce RVP of finished gasoline pool.

**C5 alkylate:** Amylene alkylation has two fold advantage: It increase the volume of alkylate available while decreasing Reid vapor pressure and olefinic content of gasoline blend stocks

The process of HF alkylation produces high octane blend stock for iso-paraffin (mainly iso butane) and olefin (propylene, butylene and amylene) in the process of HF catalyst to meet all the criteria of reformulated gasoline. Replacing high risk toxic liquid acids, such as hydrofluoric acid (HF) and sulphuric acid with solid acid catalysts is challenging goal iso-parraffin alkylation technology.

**Process**

The reaction involved in aliphatic alkylation consists of conversion of iso-butane and butylenes to iso-octanes using HF catalyst. Commonly alkylation process used are mention in Table M-VI 7.1.

\[ \text{i-C}_4\text{H}_4 + \text{i-C}_4\text{H}_8 \rightarrow \text{C}_8\text{H}_{18} \]

The side reaction results in increased iso-butane consumption increased acid consumption increased acid soluble formation, equipment handling and for the corrosion problem. Figure M-VI 7.1 gives the details of iso-parraffin alkylation mechanism [Mukherjee & Nehlsen, 2006]
Some of the other side reaction is the formation of paraffin, which boils above and below the desired product. Impurities in the feed acid and normal operating practices all can contribute to additional side reactions. Comparison of Alkyclean Technology with Modern Sulphuric Acid and Hydrofluoric Acid Technologies is shown in Table M-VI 7.2.

The key factors to be controlled in alkylation process are [Jezak, 1994]

- Maintaining proper composition of reaction mixture which include isobutene olefins and the HF acid
- Maintaining the proper reaction environment which includes adequate contacting, controlled temperature, and freedom from surges.
- Making a proper separation of the reactor effluent into its various components

### Table M-VI 7.1: Common Alkylation Processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONOCO Phillips process (ReVA Process)</td>
<td>Alkylation of propylene, butylenes, pentenes and isobutane to high quality motor fuel using HF catalyst</td>
</tr>
<tr>
<td>Stratco INC</td>
<td>Alkylation of propylene, butylenes and amylene with isobutane using strong sulfuric acid to produce high octane branched chain hydrocarbons using effluent refrigeration alkylation process</td>
</tr>
<tr>
<td>UOP HF Alkylation Process</td>
<td>Alkylation of isobutane with light olefins (propylene, butylenes and amylene to produce branched chain parafinic fuel) using hydrofluoric acid catalyst. More than 100 commercial process</td>
</tr>
<tr>
<td>UOP Alkylene™</td>
<td>UOP Alkylene process is based on solid catalyst(HAL-100) for alkylation of light olefins and isobutane to form a complex mixture of isoalkanes which are highly branched trimethylpentanes(TM)P) that have high octane blend values of approximately100</td>
</tr>
<tr>
<td>Exxon Alkylation</td>
<td>Alkylation of propylene, butylenes and penylene with isobutene in the presence of sulphuric acid catalyst using autorefrigeration. Products: a low sensitivity, highly iso, low RVP, high octane gasoline blend stock paraffinic</td>
</tr>
<tr>
<td>AlkylClean solid Acid alkylation technology (ABBLumus global)</td>
<td>The alkylation process uses a robust zeolite solid acid catalyst formulation coupled with a novel reactor processing scheme to yield a high quality alkylate product. The catalyst contains no halogen</td>
</tr>
</tbody>
</table>

Source: ABB Lumus Global www.abb.com/lumus
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Modern sulphuric acid technology</th>
<th>Modern hydrofluoric acid technology</th>
<th>Alkyclean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base condition</td>
<td>C4 feedstock</td>
<td>C4=feedstock</td>
<td>C4=feedstock</td>
</tr>
<tr>
<td>Product RON</td>
<td>95</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>Product MON</td>
<td>Base</td>
<td>Base or better</td>
<td>Base or better</td>
</tr>
<tr>
<td>Alkylate yield</td>
<td>Base</td>
<td>BASE</td>
<td>90% of base</td>
</tr>
<tr>
<td>Total installed cost</td>
<td>Base</td>
<td>85% OF BASE</td>
<td>50% of base</td>
</tr>
<tr>
<td>Total installed cost, including</td>
<td>Base</td>
<td>Less</td>
<td>None</td>
</tr>
<tr>
<td>OSBL (regeneration, facilities, and /or safety installations)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASO yield</td>
<td>Base</td>
<td>Less</td>
<td>None</td>
</tr>
<tr>
<td>Equipment maintenance</td>
<td>High</td>
<td>High</td>
<td>Much lower</td>
</tr>
<tr>
<td>Corrosion problems</td>
<td>Yes</td>
<td>Yes</td>
<td>Higher</td>
</tr>
<tr>
<td>reliability and on stream factor</td>
<td>Base</td>
<td>Base</td>
<td>Match fcc or better/shorter</td>
</tr>
<tr>
<td>Safety</td>
<td>Unit specific safety precautions as well as transport precautions unit specific precautions</td>
<td>C safety precautions required that extend throughout refinery very specific</td>
<td>No special precautions other than those for any refinery process unit</td>
</tr>
<tr>
<td>Catalyst</td>
<td>H₂SO₄</td>
<td>HF</td>
<td>Zeolite</td>
</tr>
<tr>
<td>Environmental</td>
<td>Significant waste streams generated</td>
<td>Significant waste streams generated</td>
<td>No emissions to air, water, or ground</td>
</tr>
</tbody>
</table>

ISOMERISATION

Petroleum fractions contain significant amounts of n-alkanes and the isomerisation of alkanes into corresponding branched isomers is one of the important process in refining [Mastuda, T., Sakagami, H. and Takahashi, N. Catalysis today 81, 2003 p.31]. The highly branched paraffins with 7-10 carbon atoms would be the best to fulfill the recent requirements of the reformulated gasoline [Rossini, S. Catalysis Today 2003, 77, 467]. The production of paraffin bases high – octane gasoline blend stock, such as isomers from isomerisation of light and mid cut naphtha might be a key technology for gasoline supply to cope with future gasoline regulation [Visanandham & Garg, 2010]

Light naphtha and paraffin isomerisation recognizes emerging technologies in order to boost octane in light gasoline fractions. Recent pricing trends show isomerisation could be a significant contributor to octane pool which will offset the loss from gasoline desulfurisation and aromatic reduction. Isomerate as % of gasoline used is USA 8percent, Western Europe 16percent.

Isomerisation involves

- Isomerisation of Light paraffins
- Isomerisation of C₅-C₆ paraffins
- Isomerisation of n-butane

Isomerisation of C₅-C₆ paraffins: Allow low octane number paraffins 5 and 6 carbon atoms into higher octane number paraffins

\[ n\text{-pentane} \rightarrow \text{isopentane} \]
n-hexane to 2-methyl pentane, 3 methyl pentane (low octane 75)
2,2 dimethyl butane, 2,3 dimethyl butane
Isomerisation of n-Butane; to produce isobutene feed for alkylation or as source of isobutene
dehydrogenation to manufacture MTBE

Isomerisation Catalyst
Two types of isomerization catalyst, zeolite and chlorinated alumina, has been used. Zeolite
catalyst requires higher temperatures and provide lower octane boost while chlorinated alumina’s
results in highest octane, however, it has higher sensitivity to feed stock impurities requiring
strict feed pretreatment to eliminate oxygen, water, sulphur and nitrogen is containing
compounds [Domergue & Matthews, 2001].
- Zeolite
- Chlorinated alumina
Zeolite catalyst requires higher temperatures and provide lower octane boost
Chlorinated alumina’s results highest octane, however, it has higher sensitivity to feed stock
impurities requiring strict feed pretreatment to eliminate oxygen, water, sulphur and nitrogen
containing compounds

Isomerisation of Light Naphtha
C₅/C₆ feed either from straight run crude distillation or from catalytic reforming. Table M-VI
7.3 gives details of isomerization of light paraffins catalyst.
Reformate: separated in lighter mostly benzene and heavier containing C7
Catalyst: Zeolite or Pt on Chlorinated alumina
Operating Condition:

<table>
<thead>
<tr>
<th></th>
<th>Pt on chlorinated alumina</th>
<th>Pt on zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature oC</td>
<td>120-180</td>
<td>250-270</td>
</tr>
<tr>
<td>Pressure</td>
<td>20-30</td>
<td>15-30</td>
</tr>
<tr>
<td>Space velocity h⁻¹</td>
<td>1-2</td>
<td>1-2</td>
</tr>
<tr>
<td>H₂ /HC ratio</td>
<td>0.1-2</td>
<td>2-4</td>
</tr>
<tr>
<td>Product RON</td>
<td>83-84</td>
<td>78-80</td>
</tr>
</tbody>
</table>
ONCE THROUGH PROCESS

Recycle Process: Unconverted n-paraffins and any single branched isomers from double branched isomers

Recycling with Distillation: Deisohexaniser

Recycling with Adsorption: Adsorption on Molecular sieve: n-paraffins are adsorbed and separated by desorption

Table M-VI 7.3: Isomerisation of Light Paraffins Catalyst

<table>
<thead>
<tr>
<th>Isomerisation Catalyst</th>
<th>1&lt;sup&gt;st&lt;/sup&gt; generation</th>
<th>Friedel and Crafts AlCl₃ catalysts, exhibit very high activity at low temp 980-1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt; generation</td>
<td>Metal/support bifunctional catalyst essentially Pt/alumina sensitivity to poisons are less acute, however, require higher temperature (350-550°C).</td>
<td></td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt; generation</td>
<td>Metal/support bifunctional catalysts with increased acidity by halogenation of the alumina support. Sensitive to poisons and need pretreatment, Corrosion problem. High activity at low temperature 91200°C to 160°C</td>
<td></td>
</tr>
<tr>
<td>4&lt;sup&gt;th&lt;/sup&gt; generation</td>
<td>Bifunctional zeolite catalysts, very resistant to catalyst poison and feed does not need pretreatment</td>
<td></td>
</tr>
</tbody>
</table>

Isomerisation of n-butane

To produce isobutene feed for alkylation or as source of isobutene dehydrogenation to manufacture MTBE

UOP Butamar Process:
Catalyst: Pt/chlorintated Al₂O₃
Operating Condition: Temperature: 180-220 °C,
Pressure: 15-20 bar
Spacevel: 2h⁻¹
H₂/HC: 0.5 to 2

UOP isomerisation Technologies:

Some of the UOP Light paraffin isomerisation technology are [Rajaram Panchapakesan, 2005]
**Penex™:** Higher octanes, higher product yields more than 120 licensed units

**Par-Isom™:** UOP introduced par-ISOM TM in 1996 using zeolite chloride sulfate of zirconium catalyst. It is characterized by lower equipment cost, multiple catalyst approach. Some advantage of Penex process Maximum octane bbls, high octane, best long-term profitability higher investment cost. It can handle undesired feedstocks including feed and process high benzene content feeds. It has wide range of operation. Penex once through Penex plus™ for extra high benzene levels DIH, DIP/DIH, MDEX TM

**Penex:** Para-ISOM process with PI-242 catalyst: Best LPG production, good octane, rapid payback, low investment cost

**POLYMERISATION**

Polymerization processes have received considerable interest in petroleum refining because of the higher requirement of reformulated gasoline and phasing of MTBE. The process may be attractive in two main areas [Leprince, 1998].

- Upgrading of C2 and C temperature: 150-200°C, Pressure: 30-50bar, space velocity 0.3-0.5 m³/h per m³ cuts from catalytic cracking for oligomerization ethylene & propylene to olefinic gasoline.
- Producing high quality middle quality

**REFERENCES**

1. D’Aquino & Mavridis, 2007
8. Mastuda, T., Sakagami, H., Takahashi, N., Catalysis Today, 81, 2003 p.31
11. “Refining processes”, Hydrocarbon processing November 1998, 53,
13. Rosini, S., Catalysis Today 2003,77, 467