Unit 2. Light Naphtha Isomerization

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Isomerization of Light Naphtha

Isomerization is the process in which light straight chain paraffins of low RON (C$_6$, C$_5$ and C$_4$) are transformed with proper catalyst into branched chains with the same carbon number and high octane numbers.

Light naphtha C$_5$ – 80 °C is used as a feed to the isomerization unit.

There are two reasons for this fractionation:

- light hydrocarbons tend to hydrocrack in the reformer;
- C$_6$ hydrocarbons tend to form benzene in the reformer.

Gasoline specifications require a very low value of benzene due to its carcinogenic effect.
Thermodynamic of Isomerization

- The isomerization reactions are **slightly exothermic** and the reactor works in the **equilibrium** mode.

- There is no change in the number of moles and thus the **reaction is not affected by pressure change**.

- Better conversions are achieved at **lower temperature**.

- **Paraffin recycle** substantially increases the conversion.

Figure 1. Thermodynamic equilibrium with and without recycling normal paraffin.
Isomerization Reactions

- Isomerization is a reversible and slightly exothermic reaction

\[ \text{n-paraffin} \rightleftharpoons \text{i-paraffin} \]

- The conversion to iso-paraffin is not complete since the reaction is equilibrium conversion limited.

- It does not depend on pressure, but it can be increased by lowering the temperature.

- However operating at low temperatures will decrease the reaction rate.

- For this reason a very active catalyst must be used.
Isomerization of Light Naphtha

Isomerization Catalysts

Standard catalyst
- Platinum
- Chlorinated alumina

Zeolite catalyst
- Platinum
- Zeolite

Operating conditions
- Temperature, °C
  - 120-180
- Pressure (bar)
  - 20-30
- Space velocity (h^{-1})
  - 1-2
- H₂/HC (mol/mol)
  - 0.1-2
- Product RON
  - 83-84

- Sensitivity to impurities (water, sulphur)
- Feed must be treated
- Carbon tetrachloride must be injected in the reactor

- Low activity

Hydrogen transfer centres
Acidic centres

+ Resists impurities
- Does not require feed pretreatment
Isomerization activity of SI-2 catalyst is much higher than that of zeolite catalysts and is as good as that of chlorinated ones.

SI-2 catalyst is tolerant to catalytic poisons, the catalyst restores its activity even after short-time water skip-ups up to 100 ppm and sulfur skip-ups up to 5 ppm.

Supply of acid reactants is not required and thus there is no off gas alkalization block.

High yield of commercial isomerate – 97-99%.

SI-2 catalyst service life is 10-12 years.
### Table 4. Comparative table for process flow diagram

<table>
<thead>
<tr>
<th>PROCESS DIAGRAM</th>
<th>Once-through</th>
<th>DIP+DP</th>
<th>DIH</th>
<th>DIP+DIH</th>
<th>DIP+DP+DIH</th>
<th>DIP+SuperDIH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isomerate RON</td>
<td>81-85</td>
<td>86-88</td>
<td>87-88</td>
<td>89-90</td>
<td>91-92</td>
<td>90.5-91.5</td>
</tr>
<tr>
<td>Space velocity, hour⁻¹</td>
<td>2.0-3.0</td>
<td>2.0-3.0</td>
<td>2.0-3.0</td>
<td>2.0-3.0</td>
<td>2.0-3.0</td>
<td>2.0-3.0</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>120 - 180</td>
<td>120 - 180</td>
<td>120 - 180</td>
<td>120 - 180</td>
<td>120 - 180</td>
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<tr>
<td>Pressure, MPa</td>
<td>3.0 - 3.5</td>
<td>3.0 - 3.5</td>
<td>3.0 - 3.5</td>
<td>3.0 - 3.5</td>
<td>3.0 - 3.5</td>
<td>3.0 - 3.5</td>
</tr>
<tr>
<td>Circulation ratio H₂ gas/HC, nm³/m³</td>
<td>450-500</td>
<td>450-500</td>
<td>450-500</td>
<td>450-500</td>
<td>450-500</td>
<td>450-500</td>
</tr>
<tr>
<td>Isomerate yield, wt. %</td>
<td>98-99</td>
<td>98-99</td>
<td>97-98</td>
<td>97-98</td>
<td>97-98</td>
<td>97-98</td>
</tr>
<tr>
<td>H₂ consumption, wt. %</td>
<td>0.15-0.25</td>
<td>0.20-0.25</td>
<td>0.20-0.25</td>
<td>0.15-0.25</td>
<td>0.20-0.35</td>
<td>0.20-0.35</td>
</tr>
<tr>
<td>Catalyst service cycle, years</td>
<td>5-6</td>
<td>5-6</td>
<td>5-6</td>
<td>5-6</td>
<td>5-6</td>
<td>5-6</td>
</tr>
<tr>
<td>Catalyst service life, years</td>
<td>10-12</td>
<td>10-12</td>
<td>10-12</td>
<td>10-12</td>
<td>10-12</td>
<td>10-12</td>
</tr>
</tbody>
</table>

**DIP** – Deisopentanization  
**DP** – Depentanization  
**DIH** – Deisoheexanization
Isomalk-2 ONCE-THROUGH

- Least capital and operating costs
- Production of isocomponent with RON 81 – 85
- Yield is at least 98 wt. %

Figure 2. Isomalk-2 ONCE-THROUGH
Isomalk-2 N-PENTANE RECYCLE (DIP+DP)

- Production of isocomponent with RON 86 – 88
- Yield is not less than 98 wt. %

Figure 3. Isomalk-2 N-PENTANE RECYCLE (DIP+DP)
Isomalk-2 RECYCLE OF LOW-BRANCHED HEXANES (DIH)

- RON of isocomponent 87 – 88

- Installation of Deisohexanizer is optimum technical solution for processing of feed, containing 50-70% of hexanes and with high content C7+ hydrocarbons and benzene
Isomalk-2 N-PENTANE AND LOW-BRANCHED HEXANES RECYCLE (DIP+DP+DIH)

Figure 5. Isomalk-2 N-PENTANE AND LOW-BRANCHED HEXANES RECYCLE (DIP+DP+DIH)

- RON of isocomponent 91 – 92
Figure 6. Isomalk-2 PFD - N-PENTANE AND LOW-BRANCHED HEXANES RECYCLE (DIP+SuperDIH)

- RON of isocomponent 90.5 – 91.5
Issues for Self Study and Revision

  - UOP Butamer™ process p. 432-438
  - UOP Penex™ process p. 439-451

- ISOMALK-2 Pentane-Hexane Fractions Isomerization Technology
  http://nefthim.com/developments/slot1-0

- UOP Isomerization Technology and Catalysts
  http://www.uop.com/products/catalysts/isomerization/