Unit 1. Naphtha Catalytic Reforming

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Introduction

Catalytic reforming of heavy naphtha and isomerization of light naphtha constitute a very important source of products having high octane numbers which are key components in the production of gasoline.
Catalytic Reforming

- Catalytic reforming is the process of transforming C7–C10 hydrocarbons with low octane numbers to aromatics and iso-paraffins which have high octane numbers.
- It is a highly endothermic process requiring large amounts of energy.

**Feedstock**
- Heavy naphtha
  - C7-C10
  - RON: 20 – 50
- P: 45 – 65 vol %
- N: 20 – 40 vol %
- A: 15 – 20 vol %

**Catalytic Reforming**
- Reaction conditions
  - Temp: 500 °C
  - Pressure: 0.5-2.5 MPa
- Platinum-based catalyst
- High heat demand
- SR: Semi-Regenerative
- CCR: Continuous Catalyst Regeneration

**Products**
- C5+, Reformate
  - RON: 90 – 100
  - H2, C1, C2, C3, C4
  - Coke
- P: 30 – 50 vol %
- N: 5 – 10 vol %
- A: 45 – 60 vol %

*Figure 1. Catalytic reforming process*

- A high severity mode to produce mainly aromatics (80–90 vol%)
- A middle severity mode to produce high octane gasoline (70% aromatics content)
Role of Reformer in the Refinery

**Figure 2. Role of reformer in the refinery**

**CDU** – Crude distillation unit; **HT** – Hydrotreater; **D** – Distillation; **I** – Isomerization; **R** – Reformer; **F** – Flash **N** – Naphtha; **HTN** – Hydro Treated Naphtha; **LN** – Light Naphtha; **HN** – Heavy naphtha
Research Octane Number (RON)

- is the percentage by volume of iso-octane in a mixture of iso-octane and n-heptane that knocks with some intensity as the fuel is being tested.

Figure 3. Variations of research octane number (RON)

- n-heptane \( \text{RON} = 0 \)
- iso-octane \( \text{RON} = 100 \)
Reforming Reactions

- **Naphthene Dehydrogenation**
  
  \[
  \text{Methyl Cyclohexane} \rightleftharpoons \text{Toluene} + 3\text{H}_2
  \]

- **Paraffin Dehydrogenation**
  
  \[
  \text{n-C}_7\text{H}_{16} \rightleftharpoons \text{n-C}_7\text{H}_{14} + \text{H}_2
  \]

- **Dehydrocyclization**
  
  \[
  \text{n-C}_7\text{H}_{16} \rightleftharpoons \text{Toluene} + 4\text{H}_2
  \]

- **Isomerization**
  
  \[
  \text{n-C}_7\text{H}_{16} \rightleftharpoons \text{iC}_7\text{H}_{16}
  \]

**Endothermic Reactions:**
- Naphthene Dehydrogenation
- Paraffin Dehydrogenation
- Dehydrocyclization

**Exothermic Reaction:**
- Isomerization
Reforming Reactions

- Hydrocracking reactions *highly exothermic*

  **Paraffin hydrocracking:**
  \[ C_{10}H_{22} + H_2 \rightarrow C_2H_5 - CH - C_2H_5 + C_4H_{10} \]
  Decane \( \rightarrow \) Isohexane

  **Hydrocracking of aromatics:**
  \[ \text{Aromatics} + H_2 \rightarrow \text{CH}_4 \]

- Coke Deposition

  **Nemtsov’s reaction:**
  Olefin + Aromatics (500 °C) = Amorphous coke
  Olefin + Aromatics (900 °C) = Graphitize coke
Network of Reforming Reactions

M – Metal catalyst; A – Acid catalyst
I – Hydrocracking; II – Isomerization; III – Dehydro-cyclization
IV – Dehydrogenation

Figure 4. Network of Reforming Reactions
Thermodynamics of Reforming Reactions

- The dehydrogenation reactions are highly endothermic reactions and require a great amount of heat to keep the reaction going.
- For this reason three reactors are usually used in the reforming process with heating the product from each reactor before entering the other.

- The dehydrogenation reactions are reversible and equilibrium is established based on temperature and pressure.

- In reforming, a high temperature around 500 °C and a low hydrogen pressure are required.

- The minimum partial pressure of hydrogen is determined by the amount of the desired aromatics conversion.
Catalytic Reforming of Naphtha

Reaction Kinetics and Catalysts

- **Iridium (Ir)** is added to boost activity
- **Rhenium (Re)** is added to operate at lower pressures
- **Tin (Sn)** is added to improve yield at low pressures
- **Pt/Re** is most common in semi-regenerative processes
- **Pt/Sn** is used in moving bed reactors
- **Impurities** include: coke, sulphur, nitrogen, metals and water

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**Bifunctional catalyst**

- Pt ≈ 0.1 to 0.6 % wt.
- Chlorinated alumina
- Platinum

Acidic site to promote structure changes, such as cyclization of paraffins and isomerization of naphthenes

≈ 1 % wt.
Catalytic Reforming Processes

Differences between commercial reforming processes

- catalyst regeneration procedure
- catalyst type
- conformation of the equipment

Process classification

Semiregenerative
- requires unit shutdown for catalyst regeneration

Cyclic (fully regenerative)
- utilizes a swing reactor for regeneration in addition to regular inprocess reactors

Continuous regenerative (moving bed)
- permits catalyst replacement during normal operation
### Catalytic Reforming Processes

#### Table 1. Summary of Naphtha Reforming Processes

<table>
<thead>
<tr>
<th>Process name</th>
<th>Licensor</th>
<th>Process type and key features</th>
<th>Installations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platforming</td>
<td>UOP</td>
<td>Semiregenerative and continuous reforming; CycleMax regenerator; product recovery system</td>
<td>Over 800 units with 8 million b/d</td>
</tr>
<tr>
<td>Octanizing; Aromizing</td>
<td>Axens</td>
<td>Semiregenerative and continuous reforming; dualforming for conventional process revamp</td>
<td>Over 100 licensed units</td>
</tr>
<tr>
<td>Houdriforming</td>
<td>Houdry Div. Air Products</td>
<td>Semiregenerative; high-octane gasoline and aromatics</td>
<td>0.3 million b/d</td>
</tr>
<tr>
<td>Magnaforming</td>
<td>Engelhard</td>
<td>Semiregenerative or semicyclic</td>
<td>1.8 million b/d</td>
</tr>
<tr>
<td>Powerforming</td>
<td>ExxonMobil</td>
<td>Semiregenerative or cyclic</td>
<td>1.4 million b/d</td>
</tr>
<tr>
<td>Rheniforming</td>
<td>Chevron</td>
<td>Semiregenerative; low-pressure operation</td>
<td>1 million b/d</td>
</tr>
<tr>
<td>Ultraforming</td>
<td>Amoco</td>
<td>Semiregenerative or cyclic</td>
<td>0.5 million b/d</td>
</tr>
<tr>
<td>Zeoforming</td>
<td>SEC Zeosit</td>
<td>Semiregenerative; zeolite-based catalyst</td>
<td>Few small units</td>
</tr>
</tbody>
</table>
Semiregenerative Process

- As the reactor temperatures reach end-of-cycle levels, the reformers are shut down to regenerate the catalyst in situ.

- Regeneration is carried out at low pressure (approximately 8 bar) with air as the source of oxygen.

- Semiregenerative reformers are generally built with three to four catalyst beds in series.

- Research octane number (RON) that can be achieved in this process is usually in the range of 85–100, depending on an optimization between feedstock quality, gasoline qualities, quantities required, the operating conditions required to achieve a certain planned cycle length (6 months to 1 year).
Cyclic (Full-regenerative) Process

- The cyclic process typically uses **three to six fixed catalyst reactor beds** with one additional swing reactor.

- The cyclic process may be operated at low pressures, may utilize a wide boiling range feed, and may operate with a low hydrogen-to-feed ratio.

- Coke lay-down rates at these low pressures and high octane severity are so high that the catalyst in individual reactors becomes exhausted in time intervals of from less than a week to a month.
Cyclic (Full-regenerative) Process

**Advantages**

- Low unit pressures to gain a higher $C_{5+}$ reformate yield and hydrogen production
- The overall catalyst activity, conversion, and hydrogen purity vary much less with time than in the semiregenerative process

**Drawbacks**

- All reactors alternate frequently between a reducing atmosphere during normal operation and an oxidizing atmosphere during regeneration. This switching policy needs a complex process layout with high safety precautions and requires that all the reactors be of the same maximal size to make switches between them possible.
Continuous Catalyst Regeneration Process

The continuous reforming process is characterized by:

- high catalyst activity
- reduced catalyst requirements
- more uniform reformate of higher aromatic content,
- high hydrogen purity

- In this process, small quantities of catalyst are continuously withdrawn from an operating reactor, transported to a regeneration unit, regenerated, and returned to the reactor system.

- In the most common moving-bed design, all the reactors are stacked on top of one other.

- The reactor system has a common catalyst bed that moves as a column of particles from top to bottom of the reactor section.
Continuous Catalyst Regeneration Process

- Coked catalyst is withdrawn from the last reactor and sent to the regeneration reactor, where the catalyst is regenerated on a continuous basis.

- Fresh or regenerated catalyst is added to the top of the first reactor to maintain a constant quantity of catalyst in the reactor train.

- Catalyst transport through the reactors and the regenerator is by gravity flow, whereas the transport of catalyst from the last reactor to the top of the regenerator and back to the first reactor is by the gas lift method.

- Catalyst circulation rate is controlled to prevent any decline in reformate yield or hydrogen production over time onstream.
Continuous Catalyst Regeneration Process

- In another design, the individual reactors are placed separately with modifications for moving the catalyst from the bottom of one reactor to the top of the next reactor in line.

- The continuous reforming process is capable of operation at low pressures and high severity by managing the rapid coke deposition on the catalyst at an acceptable level.

- Operating pressures are in the 3.5- to 17-bar range and design reformate octane number is in the 95–108 range.
Typical operating conditions of the UOP CCR process are:

- Reactor pressure 6.8 bar
- LHSV 1.6 h⁻¹
- H₂/H₃ molar ratio 2–3
- RON 100–107
Axens Reforming Technology – Octanizing and Aromizing Processes

The Axens catalytic reforming technology is used for the upgrade of various types of naphtha to produce:
- high octane reformate
- BTX (benzene, toluene, xylene)
- liquefied petroleum gas (LPG)

<table>
<thead>
<tr>
<th>Semiregenerative</th>
<th>Continuous</th>
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</thead>
<tbody>
<tr>
<td>+ Catalyst is regenerated in situ at the end of each cycle</td>
<td>+ continuous regeneration of the catalyst</td>
</tr>
<tr>
<td>+ The product RON is 90–100</td>
<td>+ high aromatics yields</td>
</tr>
<tr>
<td>+ Multimetallic catalyst formulations for semiregenerative applications offer higher selectivity and stability</td>
<td>+ low investment and operating costs</td>
</tr>
<tr>
<td>- decrease in the reformate yield during the run cycle</td>
<td>- and high onstream factor</td>
</tr>
</tbody>
</table>
Axens Reforming Technology – Octanizing and Aromizing Processes

The overall process comprises the following:

- A conventional reaction system consisting of a series of four radial flow reactors that use a stable and selective catalyst suitable for continuous regeneration.
- A catalyst transfer system using gas lift to carry the catalyst from one reactor to the next and finally to the regenerator.
- A catalyst regeneration section, which includes a purge to remove combustible gases, followed by catalyst regeneration.
Issues for Self Study and Revision

  [Licensed Reforming Processes p. 477-494]

  [UOP Platforming Process p. 237-265]

- [UOP Reforming](http://www.uop.com/products/catalysts/reforming/)