**Catalytic Reforming**

Catalytic reforming is the process of transforming C\textsubscript{7} – C\textsubscript{10} 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. A schematic presentation of the feedstock, products and process condition is shown in Figure below. The process can be operated in two modes: a high severity mode to produce mainly aromatics (80–90 vol\%) and a middle severity mode to produce high octane gasoline (70% aromatics content).

![Catalytic Reforming Schematic](image)

**Role of Reformer in the Refinery and Feed Preparation**

The catalytic reformer is one of the major units for gasoline production in refineries. It can produce 37 wt\% of the total gasoline pool. Other units such as the fluid catalytic cracker (FCC), the methyl ter-butyl ether (MTBE) production unit, alkylation unit and isomerization unit, also contribute to this pool. These units will be covered in other chapters of the book.

The straight run naphtha from the crude distillation unit is hydrotreated to remove sulphur, nitrogen and oxygen which can all deactivate the reforming catalyst. The hydrotreated naphtha (HTN) is fractionated into light naphtha (LN), which is mainly C\textsubscript{5} – C\textsubscript{6}, and heavy naphtha (HN) which is mainly C\textsubscript{7} – C\textsubscript{10} hydrocarbons. It is important to remove C\textsubscript{6} from the reformer feed because it will form benzene which is considered carcinogenic upon combustion. Light naphtha (LN) is isomerized in the isomerization unit (I). Light naphtha can be cracked if introduced to the reformer. The role of the heavy naphtha (HN) reformer in the refinery is shown in Figure below. Hydrogen, produced in the reformer can be recycled to the naphtha hydrotreater, and the rest is sent to other units demanding hydrogen.

**Research Octane Number**

The research octane number (RON) is defined as 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. A list of the RON of pure hydrocarbon is given in Appendix D. It is seen from this appendix that the RON of paraffins, iso-paraffins and naphthenes decrease as the carbon number of the molecule increases. Aromatics have the opposite trend.
Role of reformer in the refinery

Reforming Reactions

Naphthene Dehydrogenation of Cyclohexanes

\[
\begin{align*}
\text{Methyl Cyclohexane} & \rightleftharpoons \text{Toluene} + 3\text{H}_2 \\
\text{Dimethyl-Cyclopentane} & \rightleftharpoons \text{Toluene} + 3\text{H}_2
\end{align*}
\]
Paraffin Dehydrogenation

\[ n-C_7H_{16} \rightleftharpoons n-C_7H_{14} + H_2 \]

Dehydrocyclization

\[ n-C_7H_{16} \rightleftharpoons \begin{array}{c} \text{CH}_3 \\ \text{Toluene} \end{array} + 4H_2 \]

All the above reactions are highly endothermic.

Isomerization

\[ n-C_7H_{16} \rightleftharpoons \text{iso-C}_7H_{16} \]

Isomerization is a mildly exothermic reaction and leads to the increase of an octane number.

Hydrocracking Reactions

Hydrocracking reactions are the main sources of $C_4^-$ hydrocarbons ($C_1$, $C_2$, $C_3$ and $C_4$). The reactions are highly exothermic and consume high amounts of hydrogen. Cracking results in the loss of the reformate yield.

Paraffin hydrocracking:

\[ C_{10}H_{22} + H_2 \rightarrow C_2H_5 \cdot \text{CH} - C_2H_5 + C_4H_{10} \]

\[ \begin{array}{c} \text{Decane} \\ \text{Isohexane} \end{array} \]

Hydrocracking of aromatics

Other paraffins can crack to give $C_1$–$C_4$ products.
**Coke Deposition**
Coke can also deposit during hydrocracking resulting in the deactivation of the catalyst. The catalyst in this case has to be re-activated by burning off the deposited coke. The catalyst is selected to produce a slow hydrocracking reaction. Coke formation is favoured at low partial pressures of hydrogen. Hydrocracking is controlled by operating the reaction at low pressure between 5–25 atm (74–368 psia), not too low for coke deposition and not too high in order to avoid cracking and loss of reformate yield.

**Catalytic Reforming Catalysts**
Catalytic reforming catalysts contain highly dispersed platinum (Pt), the activity of which is inhibited by sulfur. Therefore, an upstream hydrotreater lowers the sulfur content of reformer feeds to <1 ppm. In addition to Pt, modern multi-metallic catalysts contain highly dispersed rhenium (Re) and in some cases tin (Sn).

**Process Technology**
There are several commercial processes available for reforming. These include Platforming (UOP), Powerforming (Exxon), Magna forming (Engelhard), Catalytic reforming (IFP), Rheniforming (Chevron) and Ultra forming (Amoco). The old technologies are fixed bed configuration. Moving bed technology has also recently been introduced.

**Semi-regenerative Fixed Bed Process**
The schematic flow diagram of this process is shown in Figure below. The name semi-regenerative comes from regeneration of the catalyst in the fixed bed reactors after shut down by burning off the carbon formed on the catalyst surface. Reactions such as dehydrogenation of paraffins and naphthenes which are very rapid and highly endothermic occur in the first reactor, with high temperature drop. Reactions that are considered rapid, such as paraffin isomerization and naphthens dehydroisomerization, give moderate temperature decline in the second reactor. Furthermore, slow reactions such as dehydrocyclization and hydrocracking give low temperature decline in the third reactor.
To prevent catalyst coking, the hydrogen partial pressure is maintained at a level such that the \( \frac{H_2}{HC} \) is greater than 25 for monometallic catalyst. This is done by recycling some of the hydrogen produced. Some light hydrocarbons \((C_1 - C_4)\) are separated from the reformate in the stabilizer. At the top of the stabilizer residual hydrogen and \(C_1\) to \(C_4\) are withdrawn as condenser products, which are then sent to gas processing, and part of the liquid product \((C_3\) and \(C_4)\) is returned from the reflux drum back to the stabilizer. The main product of the column is stabilized reformate, which is sent to the gasoline blending plant. A slight modification to the semi-regenerative process is to add an extrareactor to avoid shutting down the whole unit during regeneration. Three reactors can be running while the forth is being regenerated. This modified process is called the “cyclic fixed bed” process.