

Tikrit University

The College of Petroleum Processes Engineering

Petroleum Systems Control Engineering

Department

Petroleum Refining Processes

Fourth Class

Lecture 16

By

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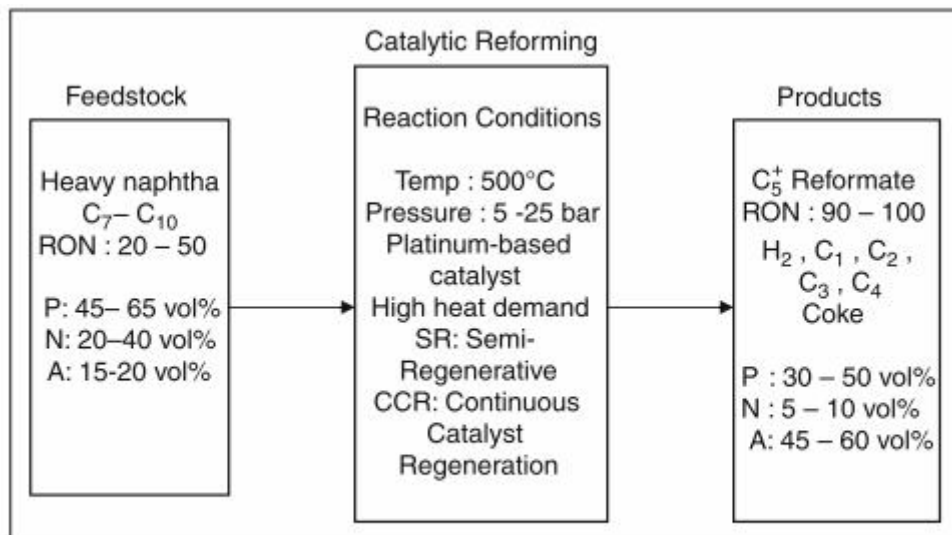
Catalytic Reforming

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. The process can be operated in two modes:

- ✚ A high severity mode to produce mainly aromatics (80–90 vol%).
- ✚ A middle severity mode to produce high octane gasoline (70% aromatics content).

The main feed comes from hydrotreated heavy naphtha C7-C10, and some feed comes from hydrotreated coker naphtha. It is important to remove C6 from the reformer feed because it will form benzene which is considered carcinogenic upon combustion

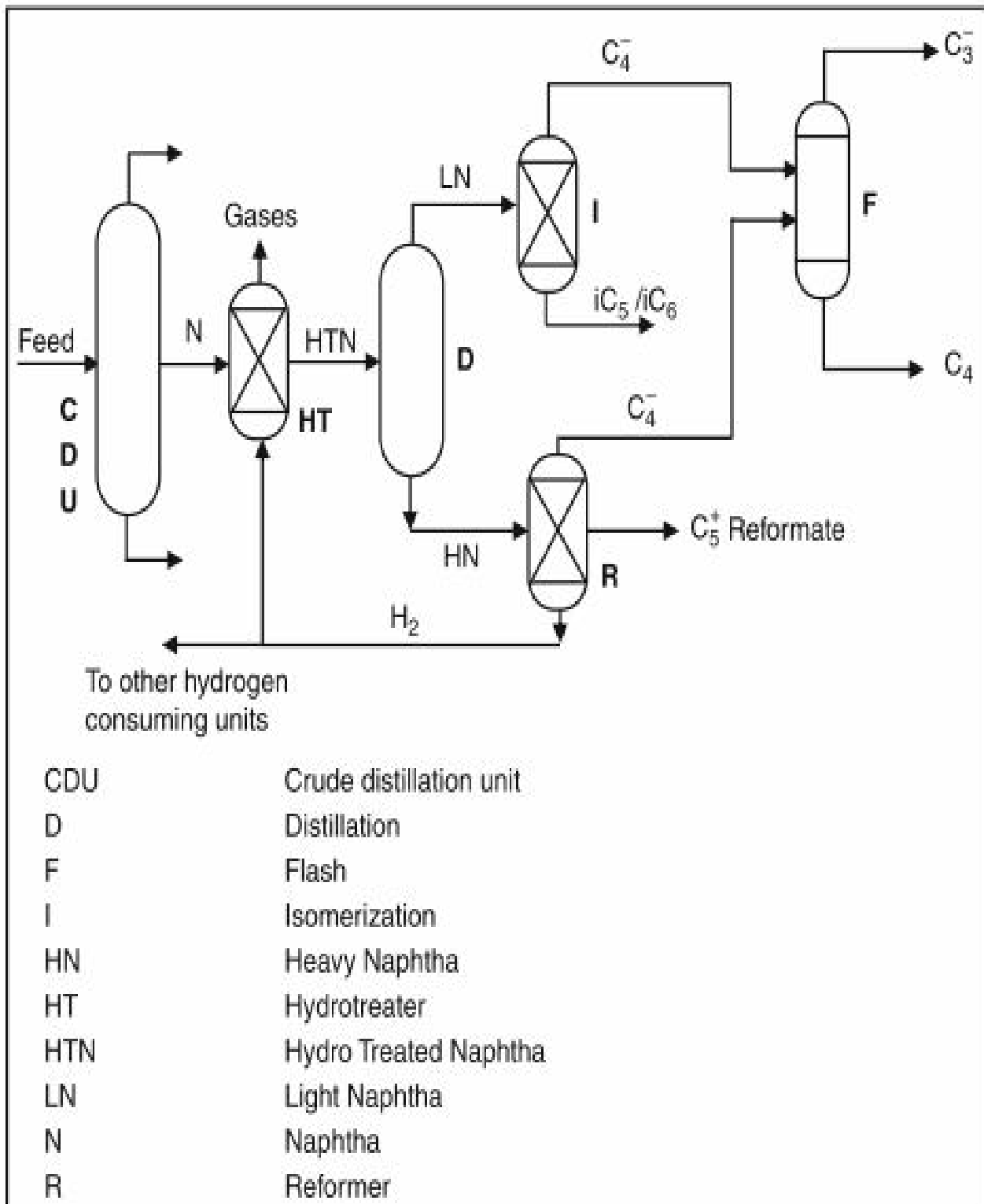
Feedstock and products properties



Catalytic reforming process

Role of Reformer in the Refinery and Feed Preparation

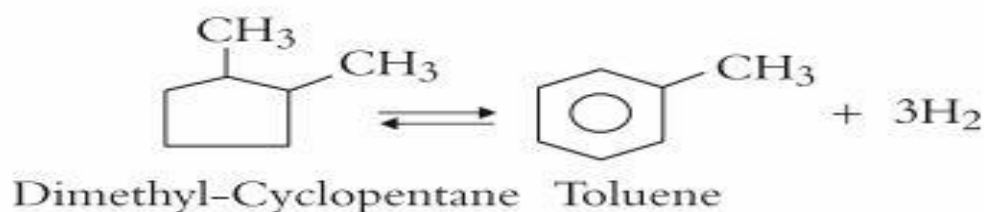
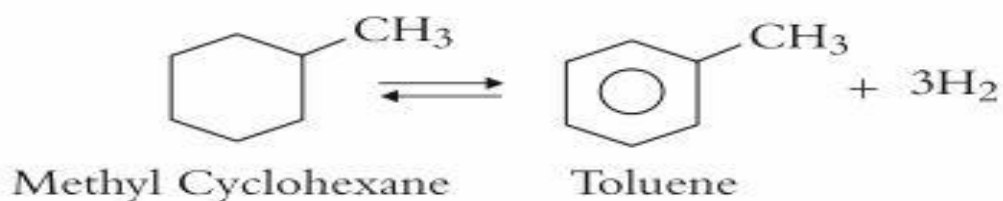
The catalytic reformer is one of the major units for gasoline production in refineries. It can produce 37 wt% of the total gasoline pool. Other units such as the fluid catalytic cracker (FCC), the methyl ter-butyl ether (MTBE) production unit, alkylation unit and isomerization unit, also contribute to 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 sulfur, nitrogen and oxygen which can all deactivate the reforming catalyst. The hydrotreated naphtha (HTN) is fractionated into light naphtha (LN), which is mainly C5 –C6, and heavy naphtha (HN) which is mainly C7 –C10 hydrocarbons. It is important to remove C6 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.



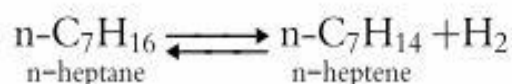
Role of reformer in the refinery

Reforming Reactions

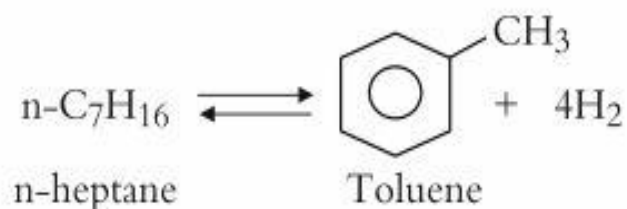
Naphthene Dehydrogenation of Cyclohexanes



Paraffin Dehydrogenation

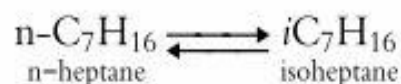


Dehydrocyclization



All the above reactions are highly endothermic.

Isomerization



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

- ✚ Impurities that might cause deactivation or poisoning of the catalyst include: coke, sulfur, nitrogen, metals and water. Therefore, reformer feed has to be severely hydrotreated to remove most of these impurities, and should be operated at high temperature and low pressure to minimize coke deposition.

Catalytic Reforming Catalysts

- ✚ Bi-functional catalyst composed of platinum metal on chlorinated alumina.
- ✚ Platinum acts as the center for the dehydrogenation reaction, and chlorinated alumina acts as an acidic site to promote structure changes, such as cyclization of paraffins and isomerization of the naphthenes.
- ✚ Hydrocracking catalysts have a cracking function and a hydrogenation-dehydrogenation function. The cracking function is provided by an acidic support, whereas the hydrogenation–dehydrogenation function is provided by active metals.
- ✚ 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 wppm. In addition to Pt, modern multi-metallic catalysts contain highly dispersed rhenium (Re) and in some cases tin (Sn) can be used.

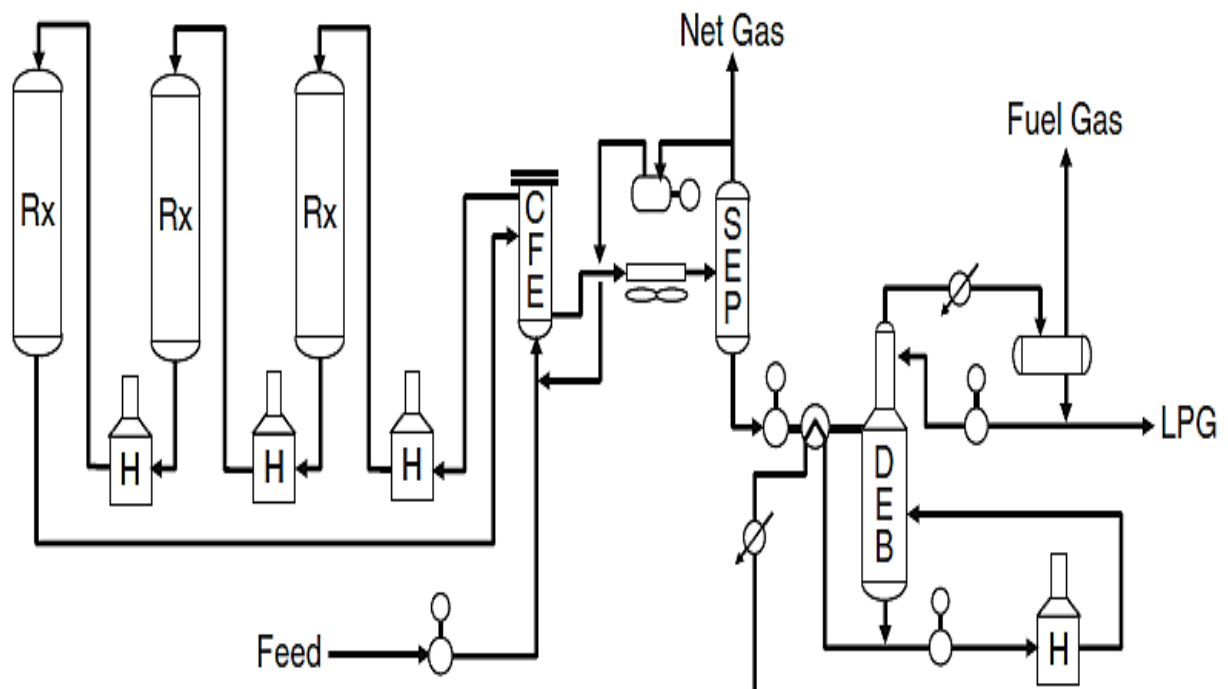
Process Technology

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.

Process Configuration

1. Semi-regenerative Fixed Bed Process

- ✚ 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.
- ✚ The feed is mixed with recycled hydrogen and heated before sending to reactor.
- ✚ Since the reactions are highly endothermic, several combinations of reactor + heaters are used.
- ✚ 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.
- ✚ The liquid stream from the phase separator is sent to a debutanizer distillation column that separates butanes and lower alkanes from the reformat product.
- ✚ The hydrogen produced in the phase separator is compressed and sent back to the first reactor.



Legend

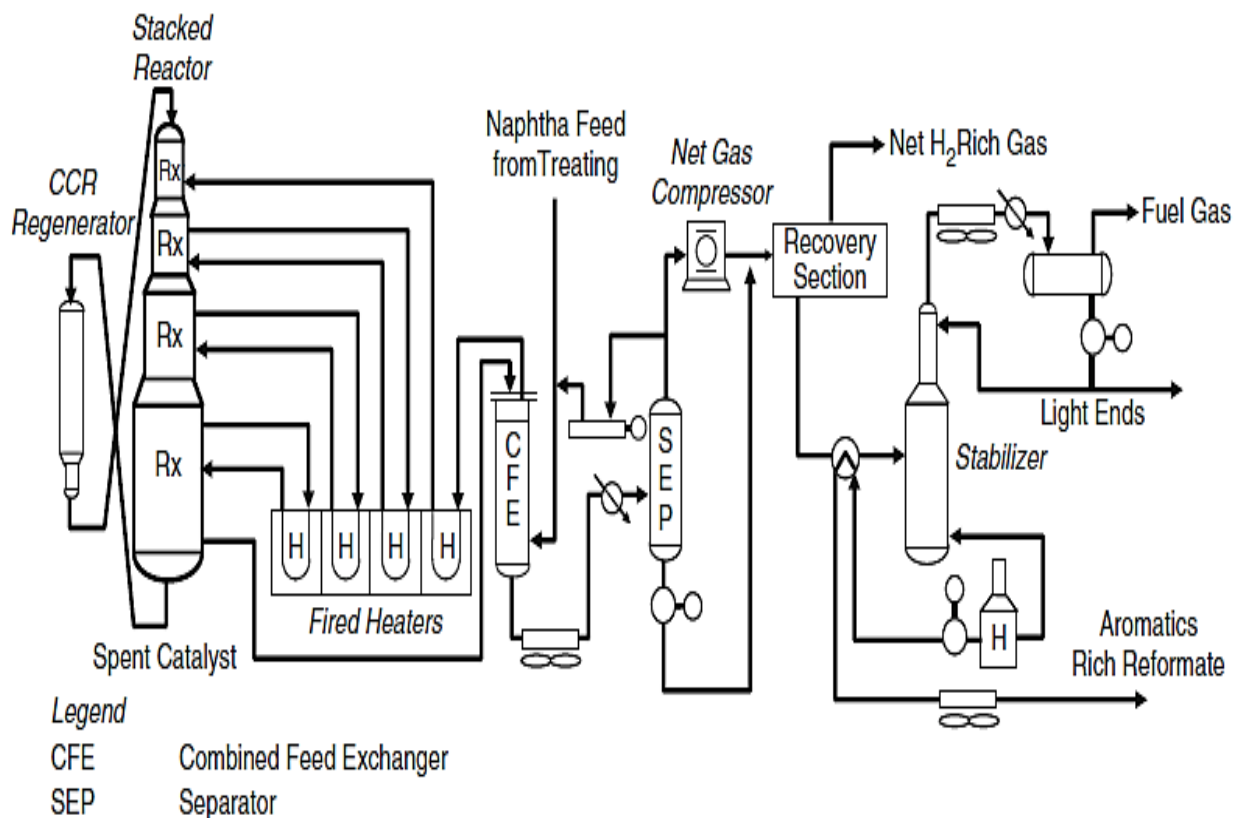
- Rx Reactor
- H Heater
- CFE Combined Feed Exchanger
- SEP Separator
- DEB Debutanizer

Semi-regenerative (SR) fixed bed reforming unit

2. Continuous catalyst Regenerative (moving bed) CCR

Reforming UOP Process

- ✚ In this process, three or four reactors are installed one on the top of the other.
- ✚ The effluent from each reactor is sent to a common furnace for heating.
- ✚ The catalyst moves downwards by gravity from the first reactor (R1) to the fourth reactor (R4).
- ✚ The catalyst is sent to the regenerator to burn off the coke and then sent back to the first reactor R1.
- ✚ The final product from R4 is sent to the stabilizer and gas recovery section.



CCR reforming unit

Process variables

Pressure

- The lower the pressure the higher the reformat yield.
- Low pressure increases hydrogen producing reactions such as dehydrogenation, dehydrocyclization, and coking. While it reduce cracking reactions.

Temperature

The primary control for product quality in catalytic reforming is the temperature of the catalyst beds. The reactor temperature is usually expressed as the weighted average inlet temperature WAIT.

Space velocity

The combination of space velocity and reactor temperature is used to adjust the conversion of the naphtha feed in order to achieve the target product octane number.

H₂/HC ratio

- (H₂/HC) mole ratio is the ratio of moles of hydrogen in the recycle gas to moles of naphtha charged to the unit.
- The recycle hydrogen is necessary to maintain catalyst life stability by removing coke precursors from the catalyst.
- Lower H₂/HC ratios can provide higher C₅+ and hydrogen yields.
- CCR units can operate under more severe conditions including lower H₂/HC ratio because catalyst is being continuously removed from the last reactor and sent to the regenerator while fresh catalyst is continuously being fed back to the first reactor.

	Feed Composition			Reaction Conditions			
	Paraffins (wt. %)	Naphthene s (wt. %)	Aromatics (wt. %)	WAIT (°F)	Pressure (psig)	H ₂ :HC (molar ratio)	LHSV (h ⁻¹)
Range	27-60	23-38	17-35	925- 975	420-460	3-5	1.4-20
Average	50.0	30.0	20.0	950	440	4.1	1.8