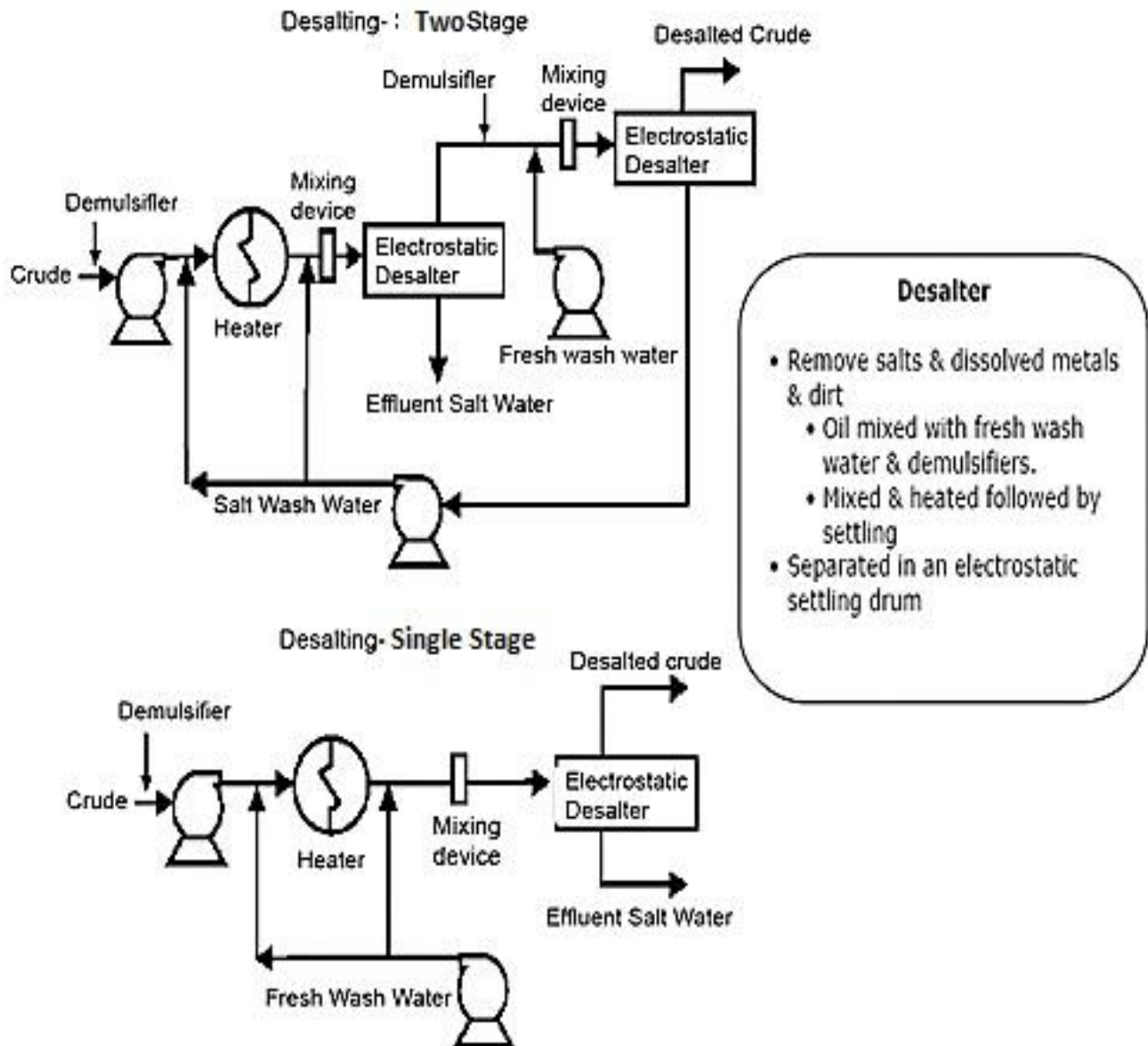


## CRUDE OIL PRETREATMENT (DESALTING)

### Purpose of Desalting

- ✓ Crude oil contains water, inorganic salts, suspended solids, and water-soluble trace metals.
- ✓ First step in the refining process is to remove salt and solids to reduce corrosion, plugging, and fouling of equipment and to prevent poisoning of the catalysts in processing units.
- ✓ Contaminants must be removed by desalting (dehydration).
- ✓ If the salt content of the crude is greater than 10 lb/1000 bbl (expressed as NaCl), the crude requires desalting to minimize fouling and corrosion caused by salt deposition on heat transfer surfaces and acids.



## **Methods of crude-oil desalting:**

**Chemical and Electrostatic separation:** Washing of the salt from crude oil with water. oil and water phases are separated in a settling tank by adding chemicals to assist in breaking up emulsion or by the application of electrostatic field to coalesce the droplets of saltwater more rapidly. Under charge condition polar molecules get oriented and get separated.

**Chemical desalting:** Water and chemical surfactant (demulsifiers) are added to the crude, heated so that salts and other impurities dissolve into the water or attach to the water, and then held in a tank where they settle out.

### **Electric Dehydration and desalting**

The feedstock crude oil along with water is heated to temperatures of 150 to 350°F to reduce viscosity and surface tension for easier mixing and separation of the water. Mixture is then sent to Settling vessel. The salts dissolved in the wash water and the oil and water phases separated in a settling vessel either by adding chemicals to assist in breaking the emulsion or by developing a high-potential electrical field across the settling vessel to coalesce the droplets of salty water more rapidly. The desalted crude is continuously drawn from the top of the settling tanks and sent to the crude distillation (fractionating) tower.

In Electrical desalting is the application of high-voltage AC or DC electric fields to concentrate suspended water globules at the bottom of the settling tank. Electric potentials from 12,000 to 35,000 volts are used to promote coalescence.

Surfactants are added if the crude has a large amount of suspended solids.

The dual field electrostatic process provides efficient water separation at temperatures lower than the other processes and as a result, higher energy efficiencies are obtained.

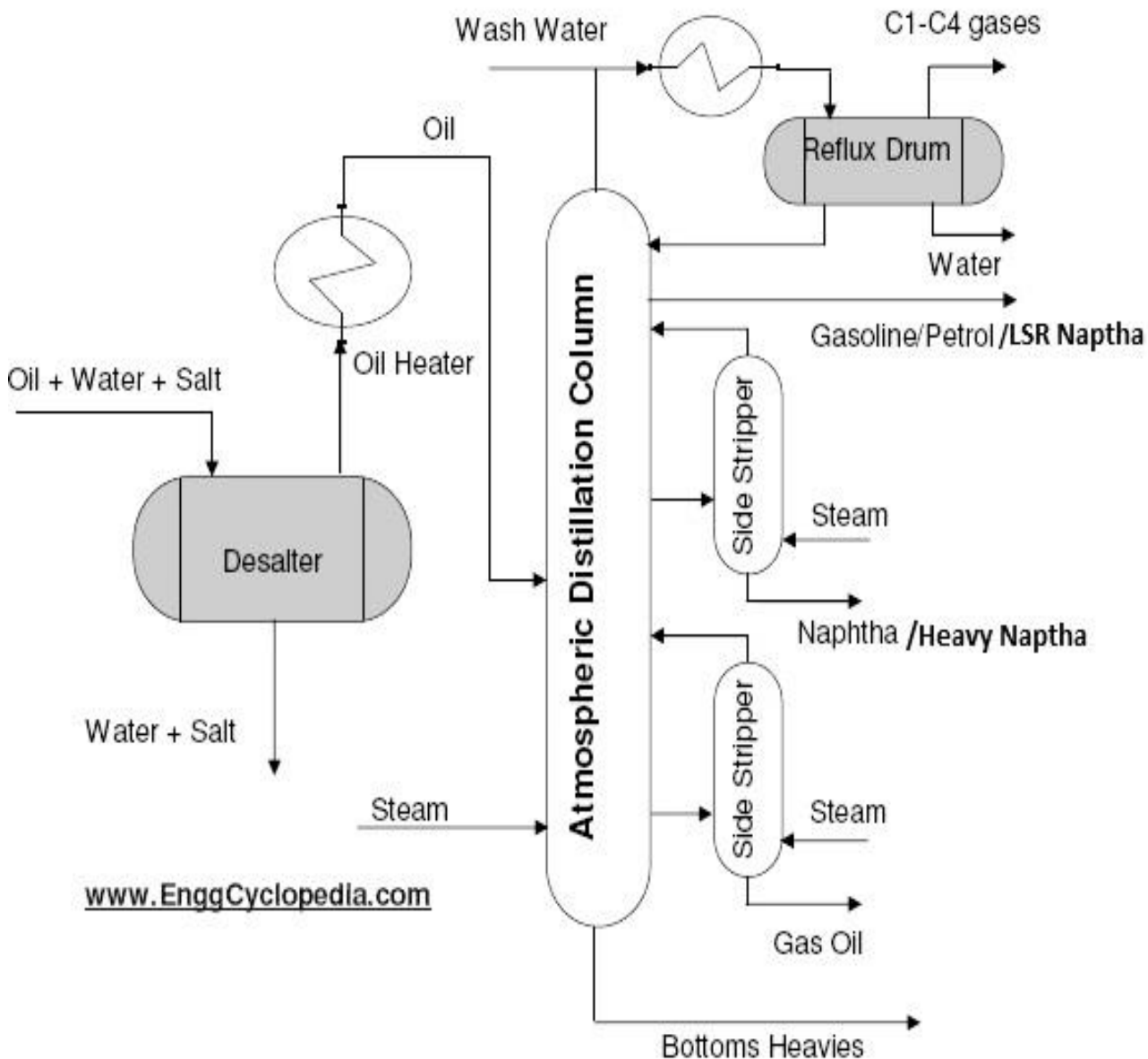
For single-stage desalting units 90 to 95% efficiencies are obtained and two-stage processes achieve 99% or better efficiency.

Heavy naphthenic crudes form more stable emulsions than other crudes. Higher temperature is required.

# Atmospheric Distillation/Atmospheric fractionation

<b>Definition</b>	Atmospheric distillation is the separation of various petroleum fractions from crude oil based on their boiling points (boiling ranges) at a pressure of 1 atmosphere/760mm of Hg.
<b>Feed contains</b>	<p>Feed is desalted crude oil. It contains paraffins, olefins, naphthenes and aromatics. These are chemical compounds each having different boiling points, volatility etc.</p> <p><b>Note:</b> <i>Lighter fractions – fractions having low carbon number, low molecular weight and low boiling point (can be a mixture of any of the lighter paraffins, olefins, naphthenes and aromatics). Opposite is true for heavier fractions</i></p>
<b>Reactions</b>	No reactions. <span style="float: right;">Separations of fractions only based on boiling points</span>
<b>Product contains</b>	<p>Products with increasing boiling point and molecular weight</p> <ol style="list-style-type: none"> <li>1. LPG</li> <li>2. Light straight run gasoline (LSR naphtha)/light naphtha</li> <li>3. Heavy naphtha</li> <li>4. Kerosene</li> <li>5. Light gas oil (LGO / Atmospheric LGO)</li> <li>6. Heavy gas oil (HGO / Atmospheric HGO)</li> <li>7. Reduced crude oil</li> </ol>
<b>Process</b>	<ol style="list-style-type: none"> <li>1. The crude oil is pumped through a series of heat exchangers and its temperature raised to about 550°F. It is further <b>heated</b> to about 750°F in a furnace.</li> <li>2. Heated feed (crude oil) is <b>charged to the flash zone of the atmospheric fractionator.</b></li> <li>3. Lighter fractions along with 20% heavy fractions vaporize in flash zone.</li> <li>4. <b>30 to 50 Trays</b> are present in tower which allow the contact of vapour and liquid.</li> <li>5. <b>Vapour-liquid equilibrium</b> is attained on trays (usually sieve tray/bubble caps tray etc.).</li> <li>6. Reflux is provided by condensing the tower overhead vapors to liquid at top of tower and pump around and pumpback will provide reflux for lower streams. Intermediate heat-removal streams are used to maintain temperature ranges on trays .</li> <li>7. Each product comes from set of tray which have certain boiling range.</li> <li>8. <b>Side stream products</b> removed from the tower. Overhead condenser on the atmospheric tower condenses the pentane and-heavier fraction of the vapors</li> <li>9. <b>Steam</b> is introduced below the bottom tray to <b>strip any remaining gas oil from the liquid.</b></li> <li>10. <b>Steam reduces the partial pressure</b> of the hydrocarbons and thus lowers the required vaporization temperature.</li> </ol>

	<p>11. <b>stabilization section:</b> butanes and propane are separated from the Light straight run gasoline (C<sub>5</sub>)</p>
<p><b>Process Variables</b></p>	<p><b>Feed (Preparation):</b> Before distillation Salt and suspended solids should be removed in feed (crude oil) by desalting process (in desalter). Removing salt prevents scaling and fouling of equipment.</p> <p><b>Temperature:</b> 550 – 750 °F should be maintained during heating in furnace according to feed composition. Higher temperatures above 750 °F may lead to thermal cracking and coke formation.</p> <p><b>Pressure:</b> Nearly 760 mm of Hg should be maintained in atmospheric distillation column/tower. Introduction of steam will reduce the partial pressure in the column, so fractionation takes place at low temperatures.</p>

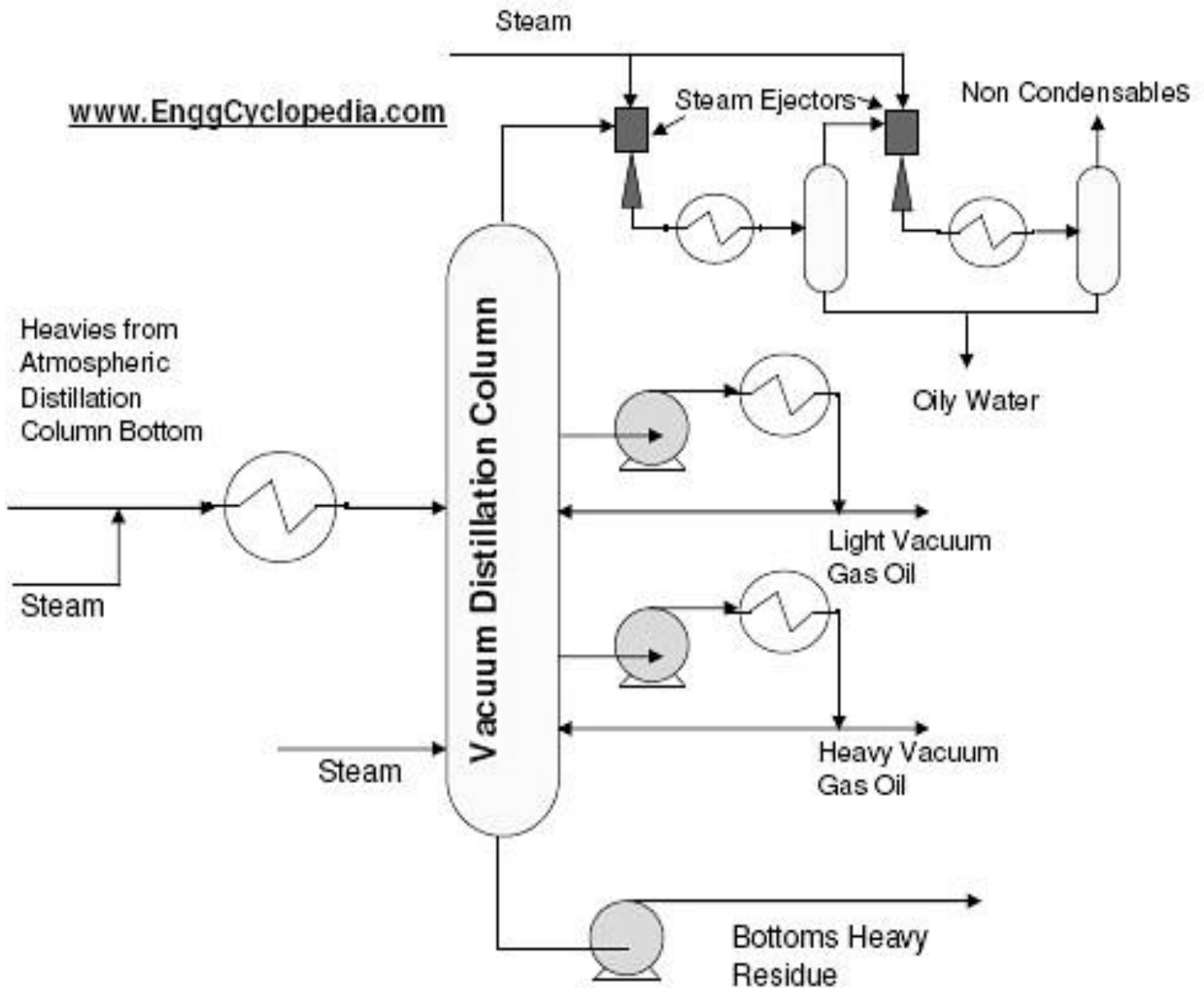


# Vaccum Distillation/Vaccum Fractionation

<b>Definition</b>	<p>Vaccum distillation is a method of separation of various high boiling petroleum fractions from reduced crude oil performed under reduced pressure.</p> <ul style="list-style-type: none"> <li>➤ Vaccum distillation is used when the boiling points of the compounds are too high.</li> <li>➤ It helps to separate the compounds without significant decomposition (without Thermal Cracking).</li> </ul>
<b>Feed contains</b>	<ul style="list-style-type: none"> <li>✓ Feed is reduced crude oil.</li> <li>✓ It is the bottom most and heaviest stream coming from Atmospheric fractionator.</li> <li>✓ It has high molecular weight compounds. Long Chain paraffins, Aromatics, Napthenes etc are present.</li> </ul>
<b>Reactions</b>	<p><b>No reactions.</b></p> <ul style="list-style-type: none"> <li>❖ Separations of fractions only based on boiling points under low pressure.</li> </ul>
<b>Product contains</b>	<p>Products with increasing boiling point and molecular weight are given below</p> <ol style="list-style-type: none"> <li>1. Non condensable gases</li> <li>2. Light vaccum gas oil (all gas oils are liquid products)</li> <li>3. Heavy vaccum gas oil</li> <li>4. Vaccum Residue/Asphalt</li> </ol>
<b>Process</b>	<ol style="list-style-type: none"> <li>1. Reduced crude oil from bottom of atmospheric tower is heated along with steam to temperatures of 730 to 850 °F in Heater (Furnace).</li> <li>2. Heated crude is introduced into flash zone of Vaccum tower (vaccum fractionator).</li> <li>3. Flash zone is maintained at a pressure of 25 mm of Hg by Steam ejectors and barometric condensers, vaccum pumps etc.</li> <li>4. Steam reduces the effective pressure of Vaccum tower which makes the heavier compounds boil at lower temperatures.</li> <li>5. Trays present in the tower are maintained at specific temperatures by pump around and pump back streams.</li> <li>6. Vapour liquid equilibrium (VLE) is attained on the top of the trays when liquid and gases contact each other.</li> <li>7. Each product is taken out from specific group of trays maintained at specific temperature ranges.</li> <li>8. Non condensable gases are produced at the top of the tower and oily water is condensed by condensing with cool water (cw).</li> </ol>

	<p>9. Light vacuum gas oil and heavy vacuum gas oil comes from middle portion of the tower.</p> <p>10. Vacuum residue/Asphalt comes from the bottom of the tower.</p>
<p><b>Process</b></p> <p><b>Variables</b></p>	<p><b>Feed (Preparation)</b></p> <p><b>Dry operation:</b> high furnace outlet temperatures with no steam addition.</p> <p><b>Wet operation:</b> lowest furnace temperatures with steam addition.</p> <p><b>Damp operation:</b> Intermediate furnace temperatures with no steam addition at furnace inlet only.</p> <p><b>Pressure:</b> Reduction in pressure in V.Tower reduces the boiling point of fractions and increases the efficiency of tower.</p> <p>Pressure range - 25 to 40 mm of Hg</p> <p>Addition of steam lowers the effective pressure to below 10 mm of Hg.</p>

**Note:** Draw any one of the two flow sheets. But names of the feed and products should not change.

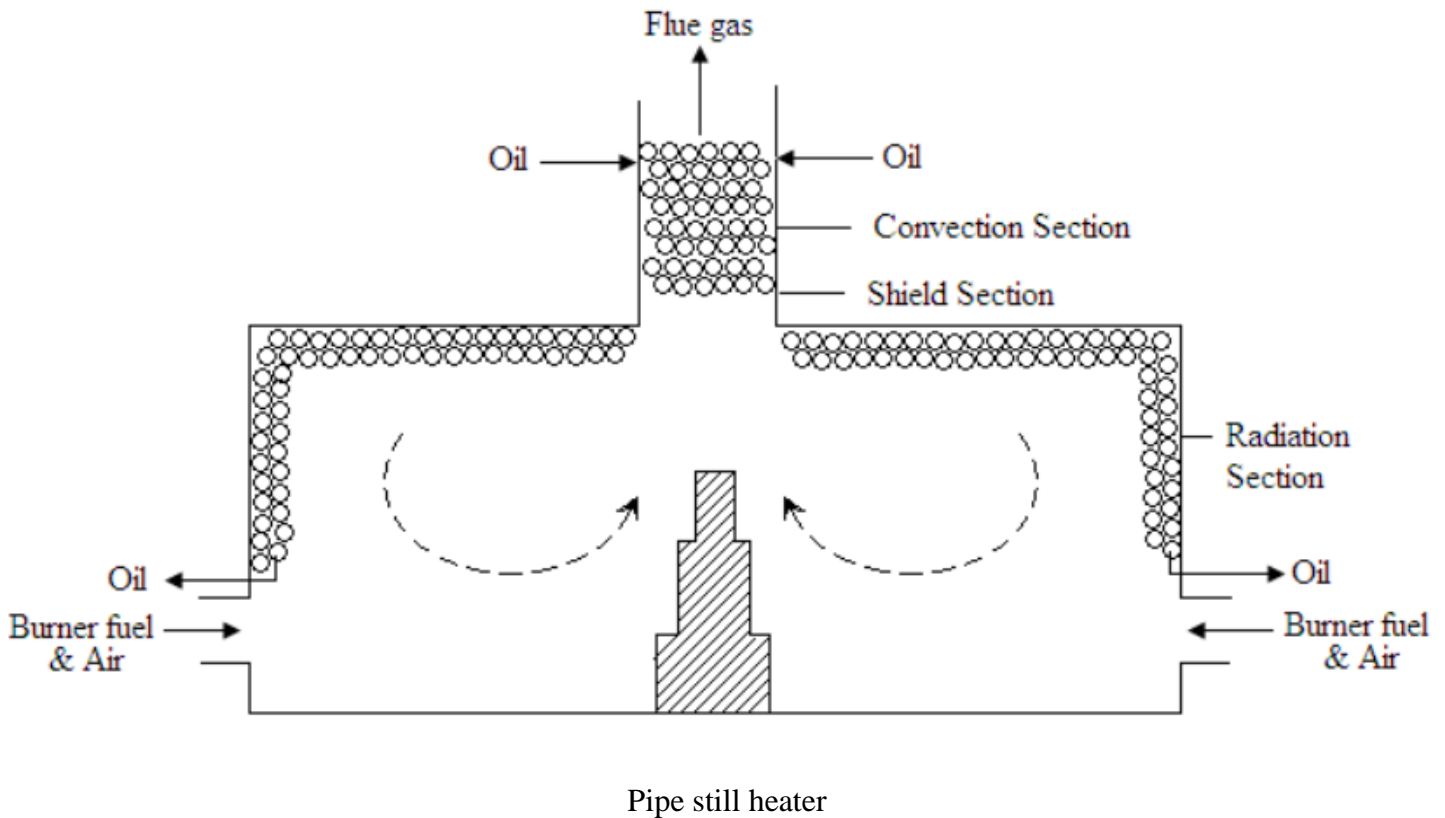




# Pipe still heaters

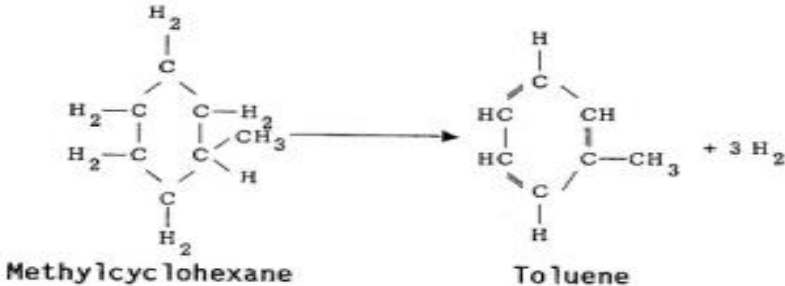
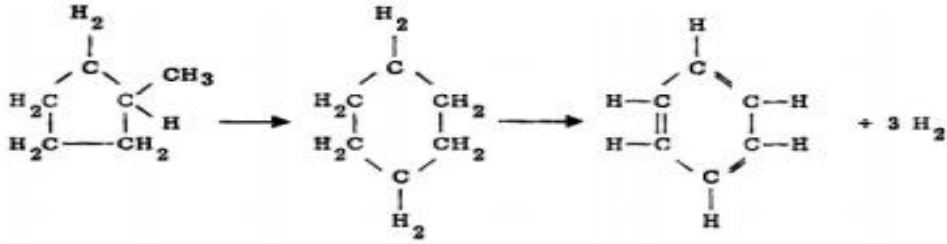
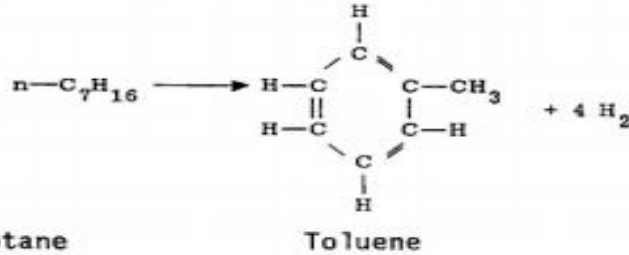
<b>Purpose</b>	<p>This heater is a <b>special type of furnace</b> which <b>heats crude oil upto about 350°C</b> depending on the type of feed.</p> <ul style="list-style-type: none"> <li>❖ Crude oils are heated in pipe still heater before entering into the atmospheric distillation column.</li> </ul>
<b>Process</b>	<ol style="list-style-type: none"> <li>1. Crude oil is pumped into the furnace through the tubes at the convection section.</li> <li>2. At this section the crude is preheated and then goes to the radiation section to be heated upto 350°C..</li> <li>3. The Atmospheric Heater receives crude at about 260°C and sends it to the atmospheric column at about 350°C.</li> </ol>
<b>Description</b>	<p>A <b>large number of tubes connected through bends</b> are housed within the furnace in multiple rows.</p> <p>Two distinct heating sections are present in Heater</p> <ol style="list-style-type: none"> <li>1. <b>Convection section :</b> <ul style="list-style-type: none"> <li>➤ Takes heat from the hot gases travelling to the stack</li> <li>➤ Gases circulate at high speed through a tube bundle before leaving the furnace through the stack</li> </ul> </li> <li>2. <b>Radiant section:</b> <ul style="list-style-type: none"> <li>➤ Receive heat directly from the flame</li> </ul> </li> </ol> <p><b>Note :</b> Shield or shock section separates the two major heating sections. It contains two to three rows of bare tubes that are directly exposed to the hot gases</p>
<b>Heater types</b>	<p>Types of heaters <b>based on geometrical configuration</b></p> <ol style="list-style-type: none"> <li>1. <b>Vertical cylindrical or box-type heaters</b> <ul style="list-style-type: none"> <li>✓ Square or a rectangular cross section</li> <li>✓ Burners are located on the floor</li> <li>✓ Tubes in the radiation section may be arranged horizontally or vertically along the heater walls</li> </ul> </li> <li>2. <b>Cylindrical-type furnace</b> <ul style="list-style-type: none"> <li>✓ Radiation section is of the shape of a cylinder</li> <li>✓ Burners are situated on the floor at the base of the cylinder</li> </ul> </li> </ol>
<b>Problems</b>	<p>The fired heaters have corrosion and material problems due to the high temperatures.</p>





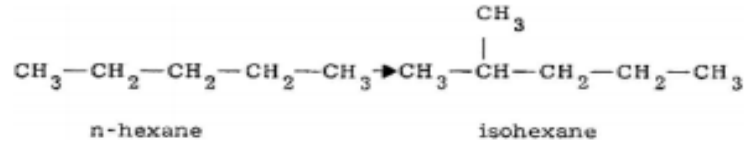
## Catalytic Reforming processes

<b>Purpose</b>	Hydrocarbon molecular structures are rearranged to form <b>higher-octane Aromatics</b>
<b>Feedstocks</b>	<p><b>Feed:</b></p> <ol style="list-style-type: none"> <li>1. heavy straight-run (HSR) Gasolines and Naphthas (comes below Light Naptha/LSR Naptha)</li> <li>2. heavy hydrocracker naphthas</li> </ol> <p><b>Note:</b> Usually heavy naphthas from any refinery unit can be feed depending on feed properties</p> <hr/> <p>Feed contains four major hydrocarbon groups: (PONA)</p> <ol style="list-style-type: none"> <li>1. Paraffins</li> <li>2. Olefins</li> <li>3. Naphthenes,</li> <li>4. Aromatics</li> </ol> <p><b>Feed Pretreatment: (Write incase feed pretreatment is asked)</b></p> <ul style="list-style-type: none"> <li>✓ Hydrotreating, of feed is usually performed before feed enters reforming unit.</li> <li>✓ This hydrotreating process removes metals, hydrogen sulfide, ammonia, and organic nitrogen and sulfur compounds.</li> <li>✓ These substances if present in feed will deactivate the reforming catalyst.</li> </ul>

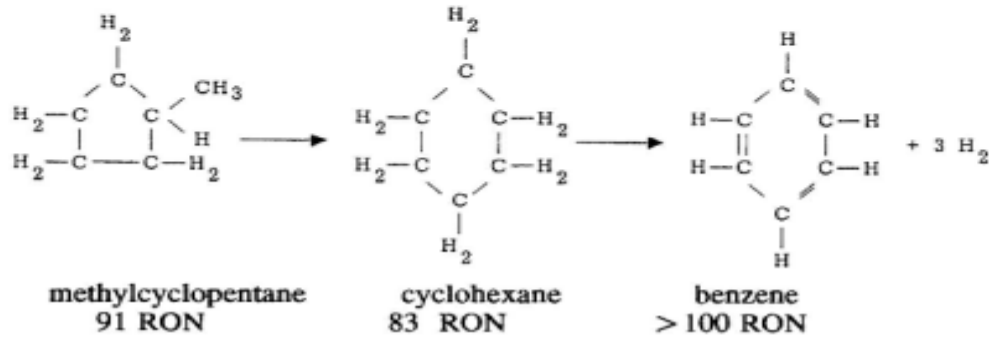
	<ul style="list-style-type: none"> <li>✓ Hydrotreating catalyst: cobalt–molybdenum (Co -Mo)</li> <li>✓ Reactions : Organic Sulphur → hydrogen sulphide ( S → H<sub>2</sub>S)</li> <li style="padding-left: 40px;">Organic Nitrogen → ammonia (N→ NH<sub>3</sub>)</li> </ul>
<b>Product</b>	<p><b>Reformate</b> which is rich in Aromatics and high in octane rating</p> <ul style="list-style-type: none"> <li>✓ Usually blended (mixed) with gasoline to improve engine performace</li> </ul>
<b>Reactions</b>	<p>There are four major reactions that take place during reforming.</p> <p>They are:</p> <ol style="list-style-type: none"> <li>(1) dehydrogenation of naphthenes to aromatics</li> <li>(2) dehydrocyclization of paraffins to aromatics</li> <li>(3) isomerization</li> <li>(4) hydrocracking</li> </ol> <p>Note: dehydrogenation reactions are highly endothermic (reaction consumes heat) and cause a decrease in temperature as the reaction progresses. This the reason for presence of heaters in between the fixed bed reactors.</p> <p><b>The major dehydrogenation reactions are:</b></p> <ol style="list-style-type: none"> <li>1. <b>Dehydrogenation of alkylcyclohexanes to aromatics:</b> <div style="text-align: center; margin: 10px 0;">  <p style="display: flex; justify-content: space-around; width: 100%;"> <span>Methylcyclohexane</span> <span>Toluene</span> </p> </div> </li> <li>2. <b>Dehydroisomerization of alkylcyclopentanes to aromatics:</b> <div style="text-align: center; margin: 10px 0;">  <p style="display: flex; justify-content: space-around; width: 100%;"> <span>Methylcyclopentane</span> <span>Cyclohexane</span> <span>Benzene</span> </p> </div> </li> <li>3. <b>Dehydrocyclization of paraffins to aromatics:</b> <div style="text-align: center; margin: 10px 0;">  <p style="display: flex; justify-content: space-around; width: 100%;"> <span>n-heptane</span> <span>Toluene</span> </p> </div> </li> </ol>

Major Isomerization reactions are

1. **Isomerization of normal paraffins to isoparaffins:**



2. **Isomerization of alkylcyclopentanes to cyclohexanes, plus subsequent conversion to benzene:**



**Types of Processes**

Reforming processes are classified in to 3 types based upon the frequency of catalyst regeneration

1. **Continuous** - Removal and replacement of catalyst during normal operation.
2. **Cyclic** - Swing reactor is used in addition to those on-stream reactor to regenerate the catalyst without shutting down the unit.
3. **Semiregenerative** - Unit to be taken off-stream (shutdown) and catalyst is regenerated.

**Process**

Catalytic reforming unit consists of a feed system, several heaters, reactors in series, separator and a fractionator.

Part of the flashed hydrogen is recycled to the feed before it enters the first heater. As the feed flows through the catalytic bed in the reactor, the major reaction, dehydrogenation of naphthenes to aromatics occurs. Reforming reactions are fast and highly endothermic, so temperature decreases within the reactor. Several heaters are used to maintain the reactor temperature at the desired levels (400 to 500°C). The product from the first reactor is reheated and fed to the following reactor. As the feed passes through the reactors in series, the reaction rates decrease. The liquid product is sent to the fractionation section (stabilizer). The reformate is obtained as a bottoms product from the stabilizer. Off-gas and liquefied petroleum gas (lpg) are recovered from the top of the stabilizer.

nd the reactors become larger, the reaction becomes less endothermic, and the temperature differential across them decreases, while the amount of heat required between the reactors also decreases.

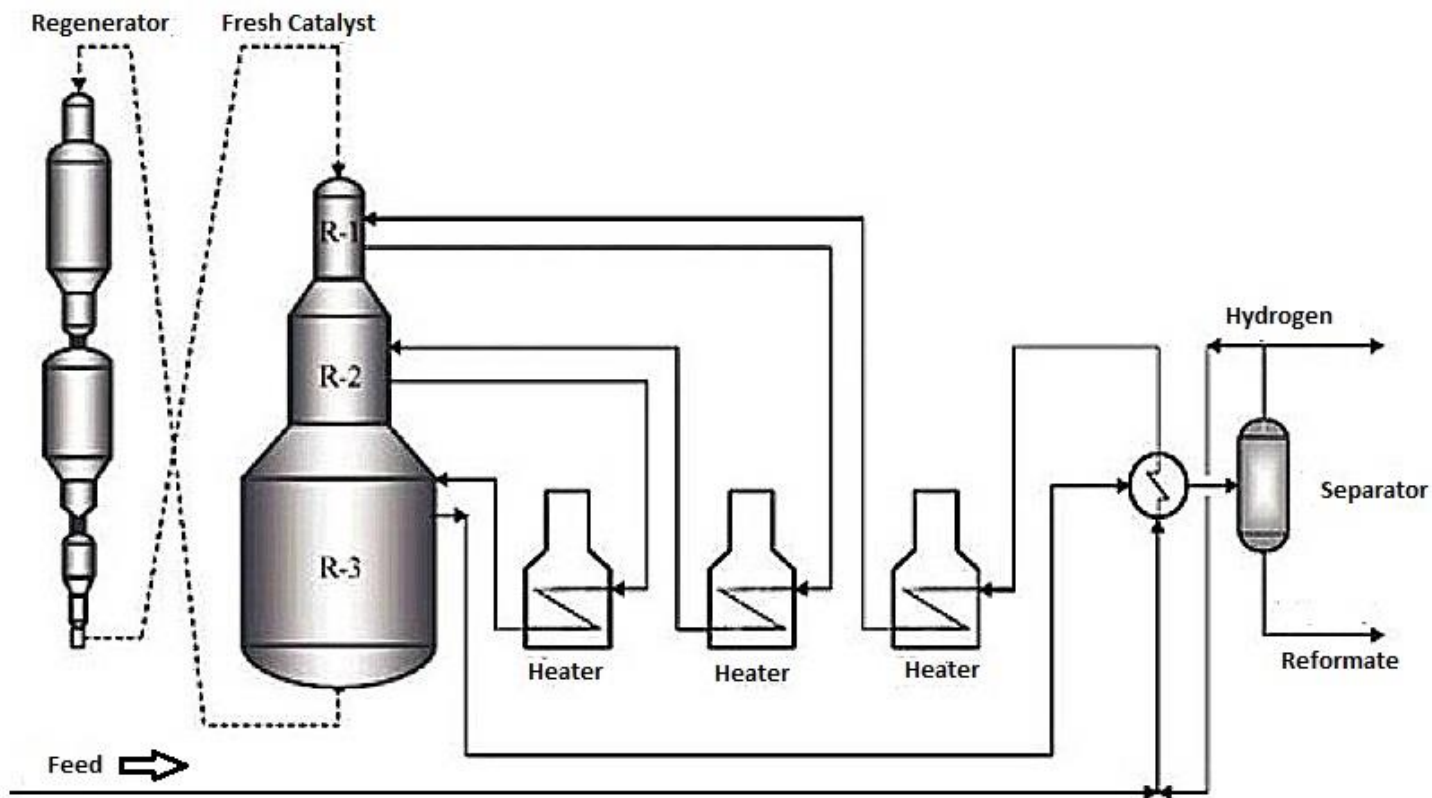
### **Continuous Catalytic Reforming**

- This type of process uses **moving-bed reactor design**, in which the reactors are stacked.
- **Catalyst bed moves by gravity flow** from top to bottom of the stacked reactors
- The **spent catalyst** (deactivated catalyst) is withdrawn from the last reactor and sent to the top of the regenerator to burn off the coke.
- Transport of catalyst between reactors and regenerator is done by the **gas lift method**.
- During normal operation, small quantities of catalyst are withdrawn continuously. Fresh or regenerated catalysts are added to the top of the first reactor.

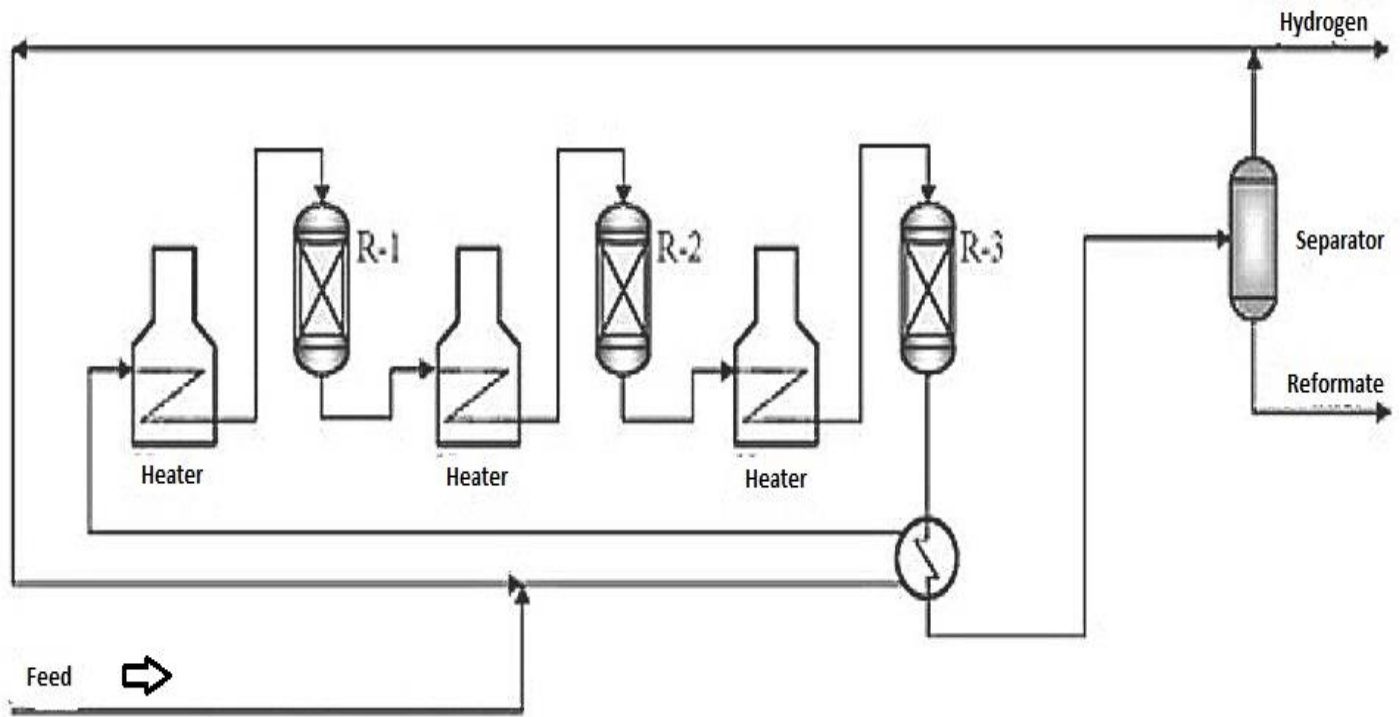
### **Semi-Regenerative Catalytic Reforming Process**

A semi regenerative catalytic reforming process usually has three or four reactors in series with a fixed-bed catalyst system and operates continuously (cycle length) from six months to one year.

During this period, the activity of the catalyst diminishes due to coke deposition, provoking a decrease in aromatics yield and in hydrogen gas purity. To minimize the catalyst deactivation rate, the semiregenerative units operate at high pressure (200 to 300 psig). To compensate for catalyst activity decline and to keep conversion more or less constant, the reactor temperatures are increased continuously. When the end- of-cycle reactor temperatures are reached, the unit is shutdown and the catalyst is in situ regenerated. A catalyst cycle ends when the reforming unit is unable to meet its process objectives: octane and yield reformat. Catalyst regeneration is carried out with air as the source of oxygen. A catalyst can be regenerated five to ten times before it is removed and replaced.



Continuous Reforming process



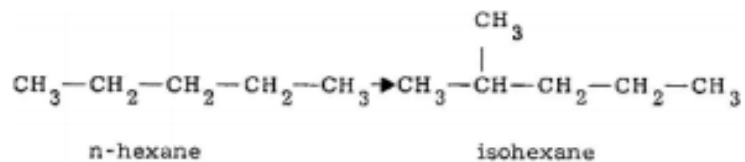
Semi regenerative Reformer

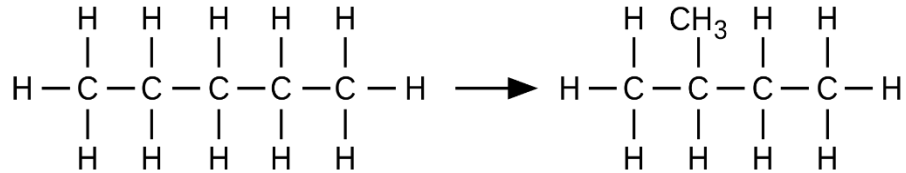
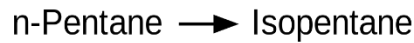
## Isomerization

**I**somerization is the process of conversion of normal paraffins to isomers.

The Octane number of Light Straight Run Naptha (C<sub>5</sub>-180 °F) (also called LSR Naptha) can be improved by isomerization process. Octane number of LSR Naptha increases from 70 to about 82-84.

**Isomerization of normal paraffins to isoparaffins:**





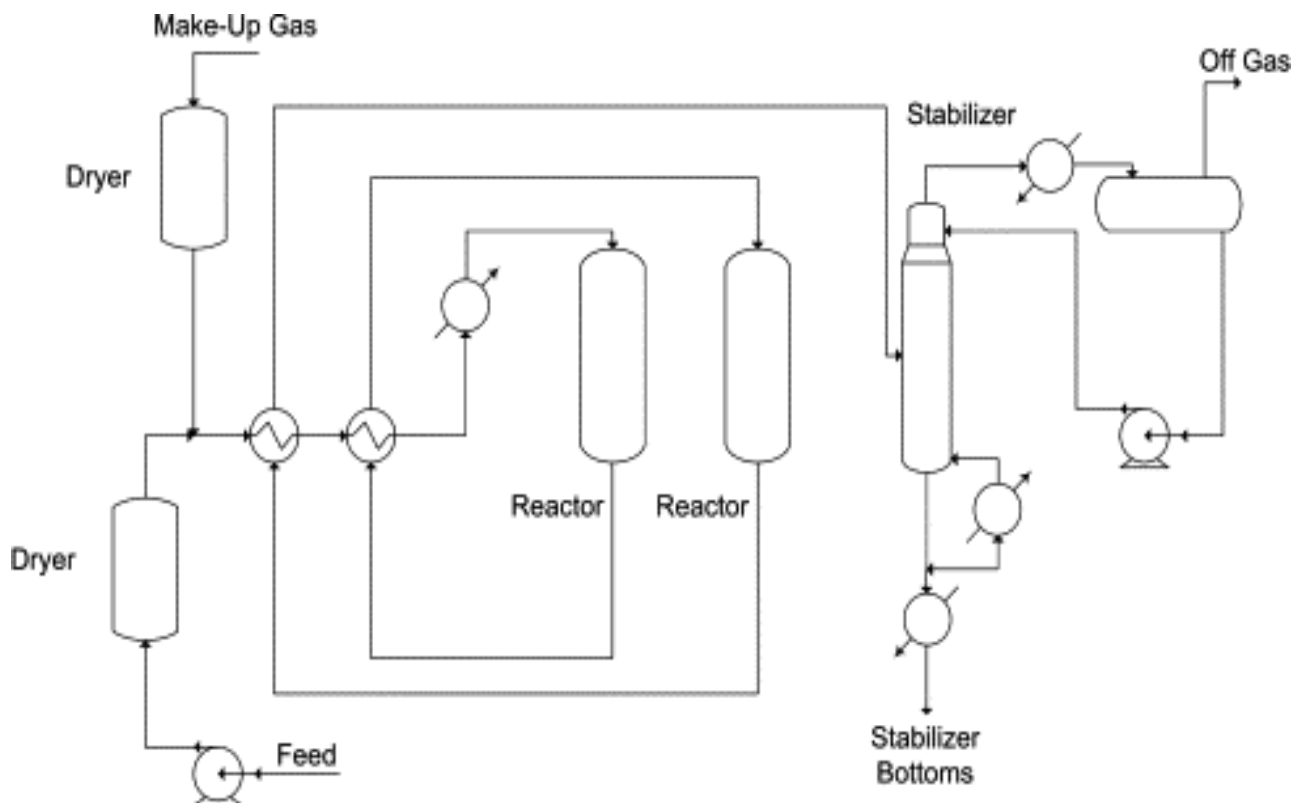
Process:

LSR naphtha and hydrogen are first sent to dryers to remove moisture.

This feed mixture is heated in a series of heat exchangers and fed into reactors which are maintained at a temperature of 200-400 °F. These low temperatures are maintained as the isomerization reactions are enhanced at lower temperatures. Platinum on various bases is used as isomerization catalyst to increase reaction rates. Two reactors in series are used to increase the conversion of reactants to products. The product stream from second reactor is sent to stabilizer to separate lighter and heavier components of the product. Heavier isomerate comes from bottom and lighter off gases comes from the top of the stabilization column.

Note:

An atmosphere of hydrogen is maintained in reactor to minimize carbon deposits on the Catalyst. But hydrogen consumption is negligible.



Penex isomerization process