

VISBREAKING

Definition Visbreaking is a **mild thermal cracking process to produce low viscosity and low pour point oils** which can be further processed in various units to get transportation fuels.

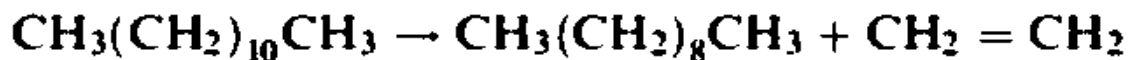
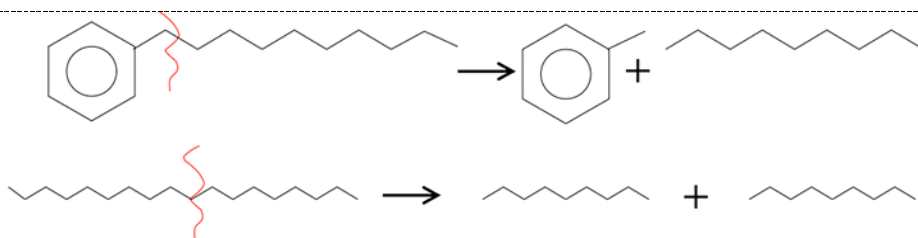
❖ Thermal cracking refers to cracking in presence of high temperatures.

Feedstocks **Vaccum fractionator residue** and sometimes Atmospheric residue (reduced crude oil) are visbreaker feed stock

Function

- ✓ Pour point reduction may be 15-35 °F
- ✓ Final viscosity may be reduced by 25-75% of the feed
- ✓ Degree of viscosity and pour point reduction = function(Composition of residual visbreaker feed)

Reactions



Products

1. Light ends (gas / Gasoline)
2. Light gasoils
3. Heavy gas oils
4. Vaccum cracked Residue

} Gasoils are with high aromatic- usually sent to hydrocracker

Note : Visbreaker products contain lot of olefins(alkenes/double bonded compounds)

Types of Processes 2 Types of Visbreaker Operations:

1. Coil – Cracking
2. Soaker Cracking

	Coil	Soaker
Furnace outlet temp	473-500 °C	427-443 °C
Reaction time	1-3 min	longer
Run times	3-6 months	6-18 months
Fuel consumption	100	85
Capital cost	100	90

Note : Runtimes mean the time after which unit will be shut down for maintenance purpose

Observations:

Coil visbreaker:

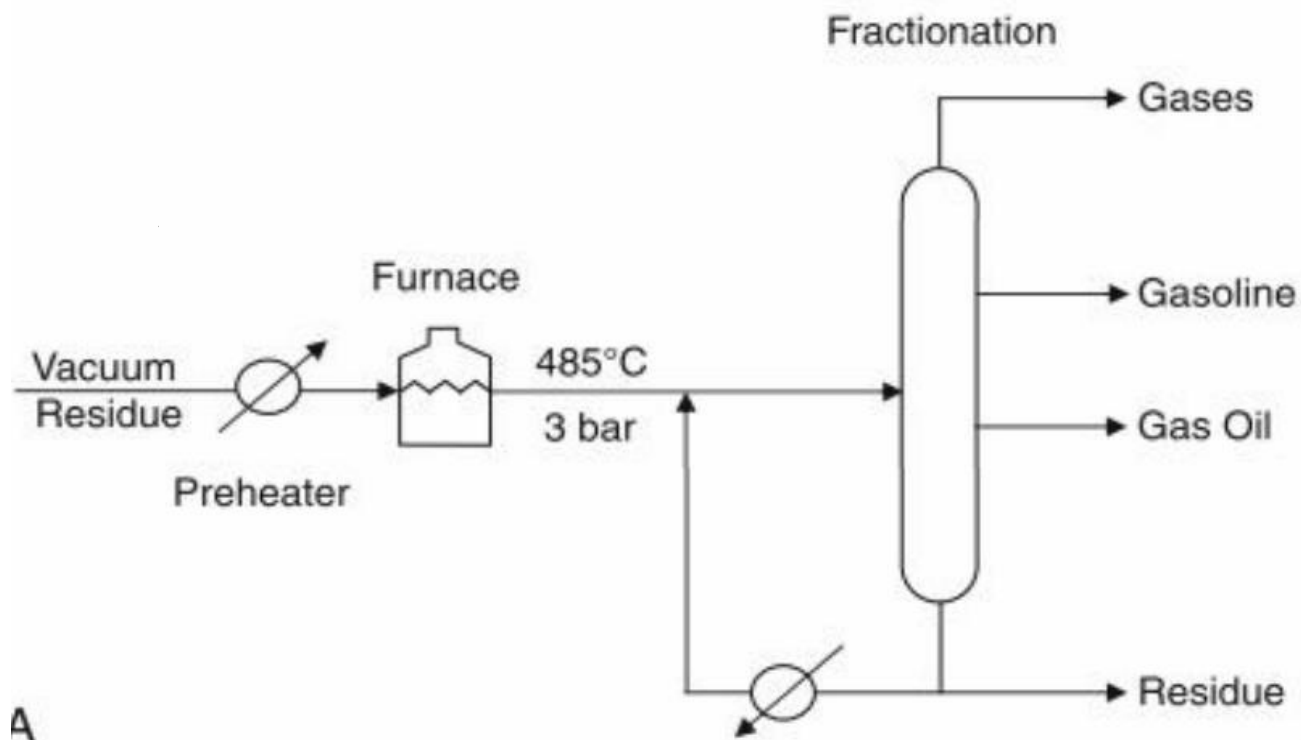
- High furnace temperature of **coil visbreaker leads to quicker reaction**
- But the runtime is less with **high capital and fuel consumption**

Soaker Visbreaker : (write the exact opposite to above sentences)

Process

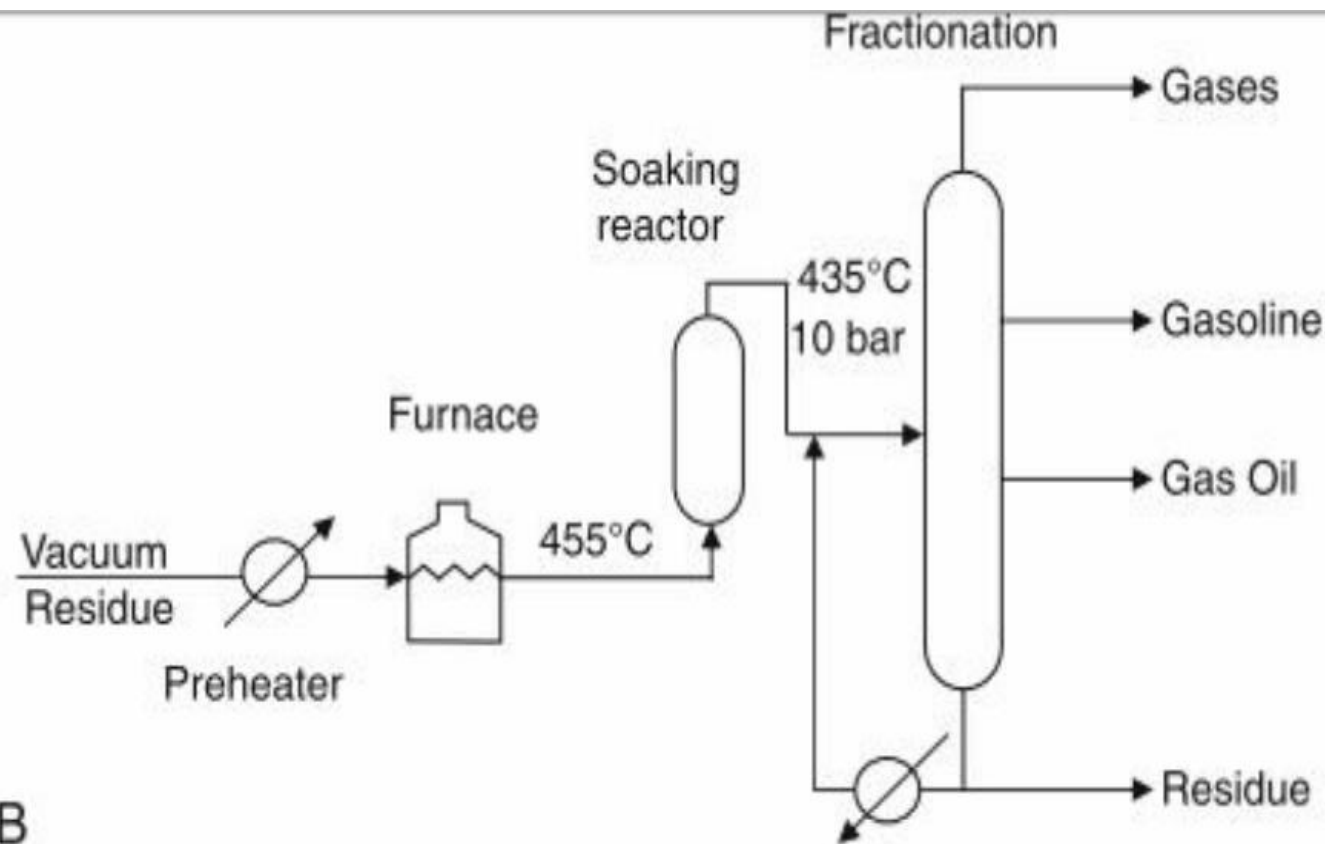
- Feed is heated in a preheater and fed to Furnace to heat it to required temperatures as given above table.
- Reaction will take place in furnace in coil visbreaker. In soaker visbreaker e ireactions will take place in Soaker
- The product produced is sent to fractionator to separate them in to various products based on boiling ranges.

Coil Cracker (Coil Visbreaker-A)



A

Soaker Cracker (Soaker Visbreaker)



B

FLUID CATALYTIC CRACKING

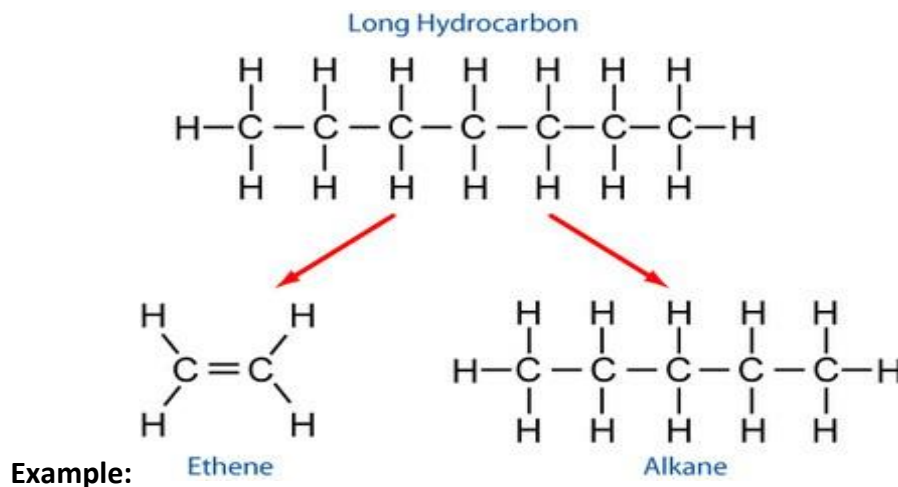
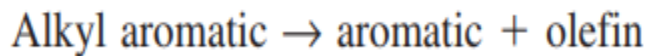
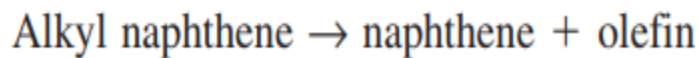
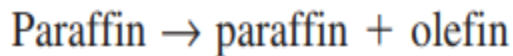
Catalytic cracking cracks low value **high molecular weight hydrocarbons** to low molecular weight products (more valuable products) like gasoline, LPG Diesel along with very important petrochemical feedstock like propylene, C4 gases.

- Benefits : **High amount of High octane Gasoline** is produced

feed stock

Atmospheric gasoil, Vacuum gas oil (VGO), Hydro-treated VGO

Primary reactions



Catalyst: zeolite catalyst - lower residence time

Process

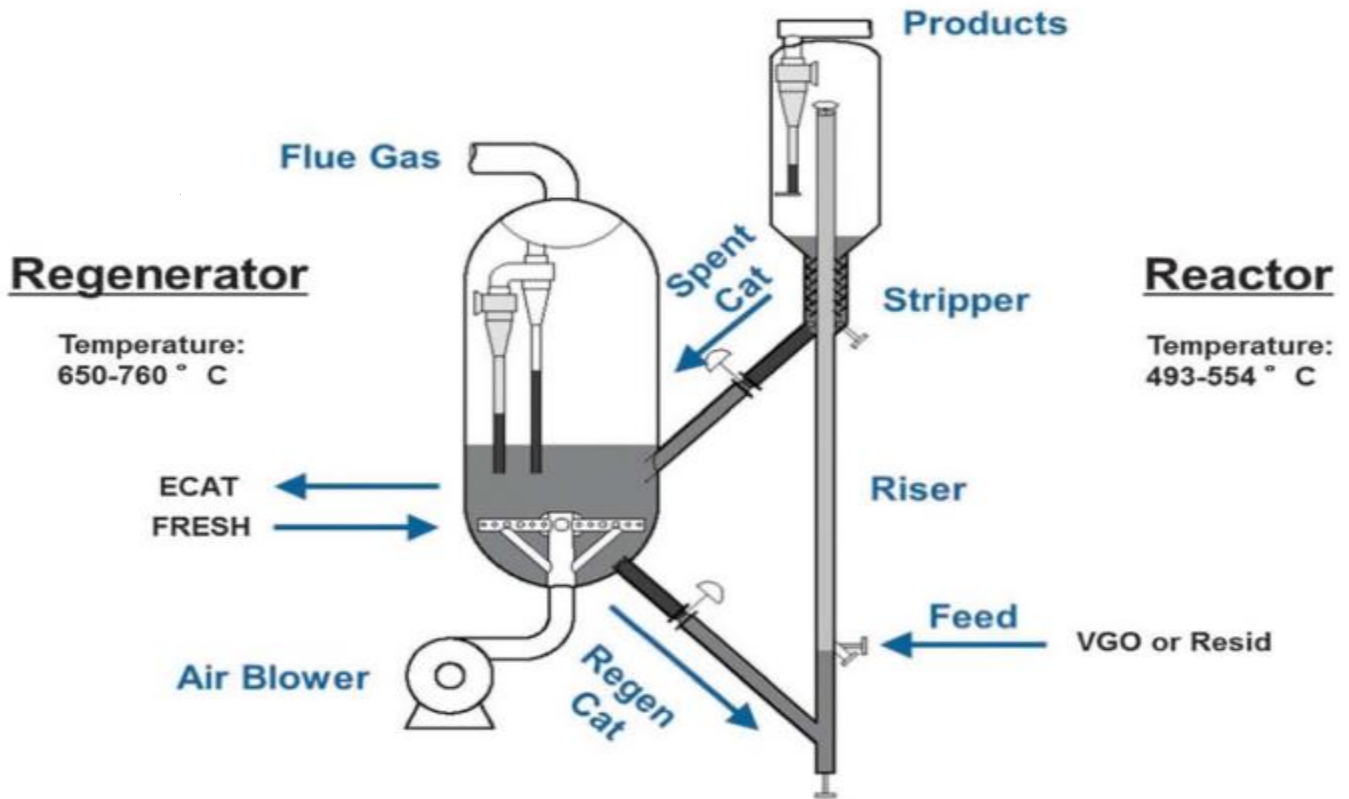
The feed along with recycle streams is preheated to temperature of 365°C-370°C . This mixture enters the riser where it comes in contact with hot regenerated catalyst (at a temperature of about 640-660° C). Finely divided catalyst is maintained in an aerated or fluidized state by the oil vapors. The reaction happens along the riser. Spent catalyst is sent to regenerator to get rid of coke that collects on the catalyst during the process. Spent catalyst flows to the regenerator, where most of the coke deposits burn off in presence of preheated air. Hot Regenerated catalyst is again sent to the riser. catalyst re-circulates between the reactor and regenerator. Cracked hydrocarbon stream from the reactor is sent to fractionator to separated Gasoline and by products like olefins, light cycle oil and heavy cycle oil etc.

Product Obtained

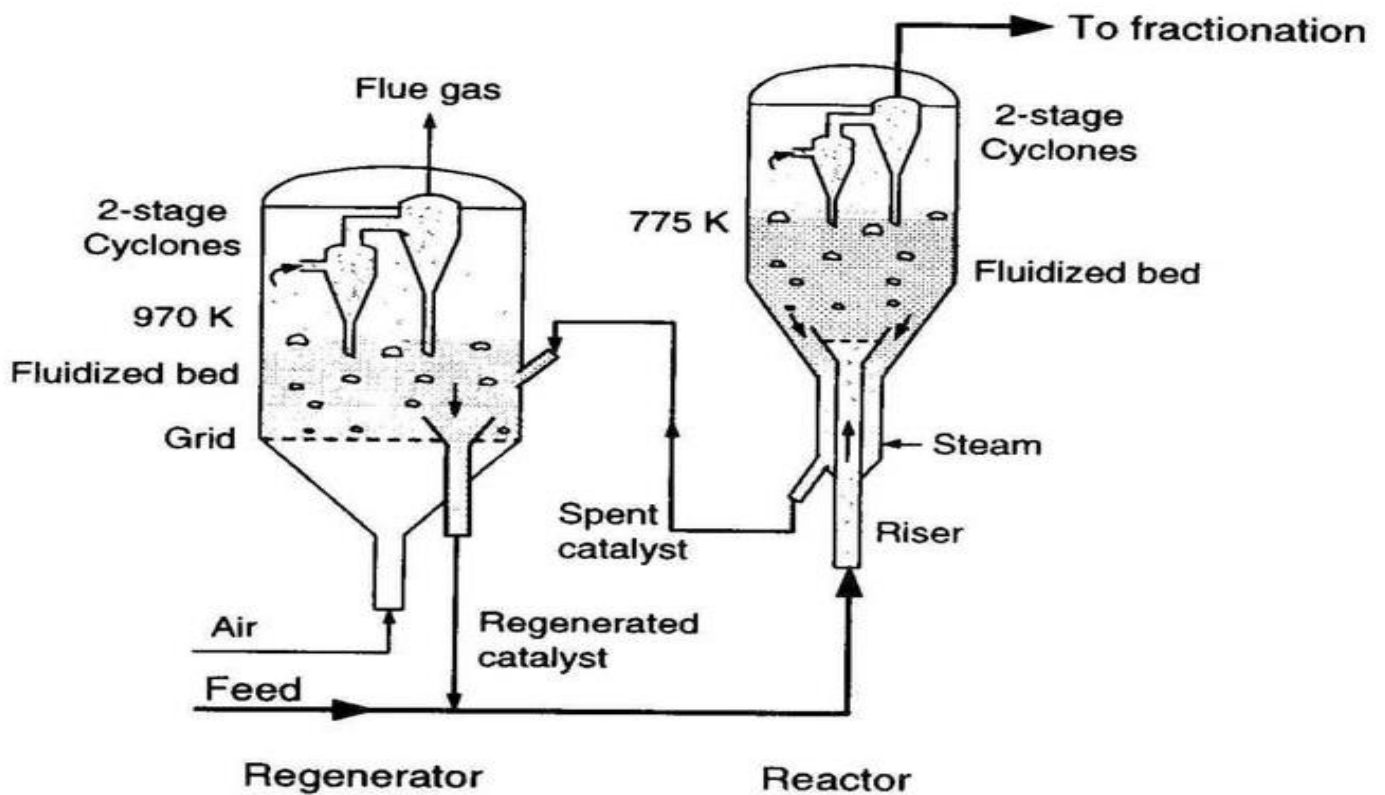
1. Light gas -H₂, C₁, and C₂
2. LPG C₃S and C₄S – includes light olefins
3. Gasoline C₅+ high octane component for gasoline pool or light fuel
4. Light cycle oil (LCO) blend component for diesel pool or light fuel
5. Heavy cycle oil (HCO) Optional heavy cycle oil product for fuel oil or cutter stock
6. Clarified oil (CLO) or decant oil: slurry for fuel oil

Coke by-product consumed in the regenerator to provide the reactor heat demand

Fluid Catalytic Crackers



Or



DELAYED COKING

Coking refers to extreme thermal cracking process.

- ✓ Feed is heated to 480 – 510°C and left for some time so that coke and lighter products form.
- ✓ Since coking is a batch reaction, there can be different ways to carry out coking.
- ✓ There are two types of refinery coking processes namely delayed coking and fluid coking.

Delayed coking:

The feed is heated along with steam in furnace. The heated feed is fed to a coke drum and coke forms in the drum. The lighter products are withdrawn from the top section of the delayed coker. After coking, the coke drum is full of coke and it is then removed using water jets. The process is called delayed coking because in this process the feed is heated using a much more complex system, and it consists of multiple furnaces or coke drums. Usually the coal is heated at a lower temperature for shorter periods of time, which removes water and other by – products more slowly than the conventional process, thereby increasing the overall time span.

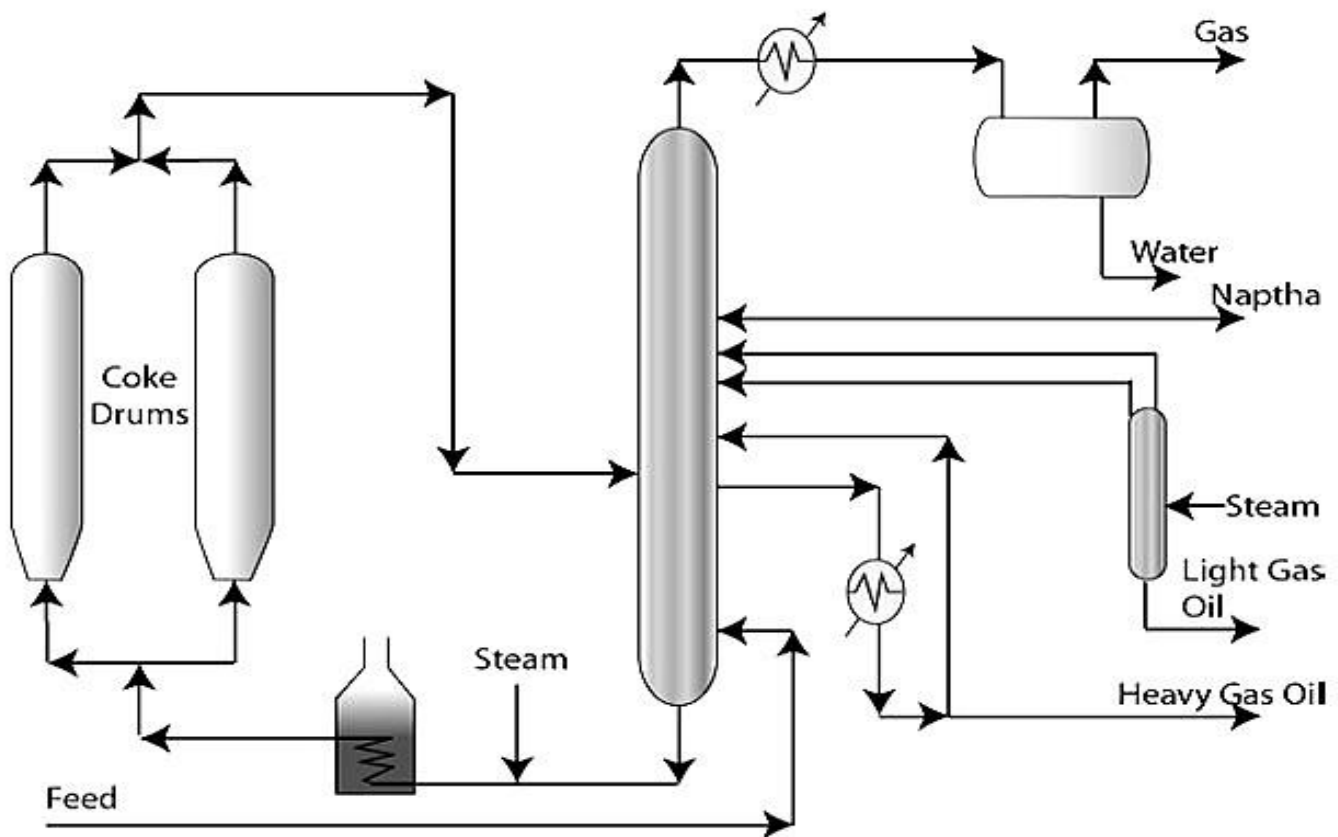


Figure 10.2 Delayed Coker

or

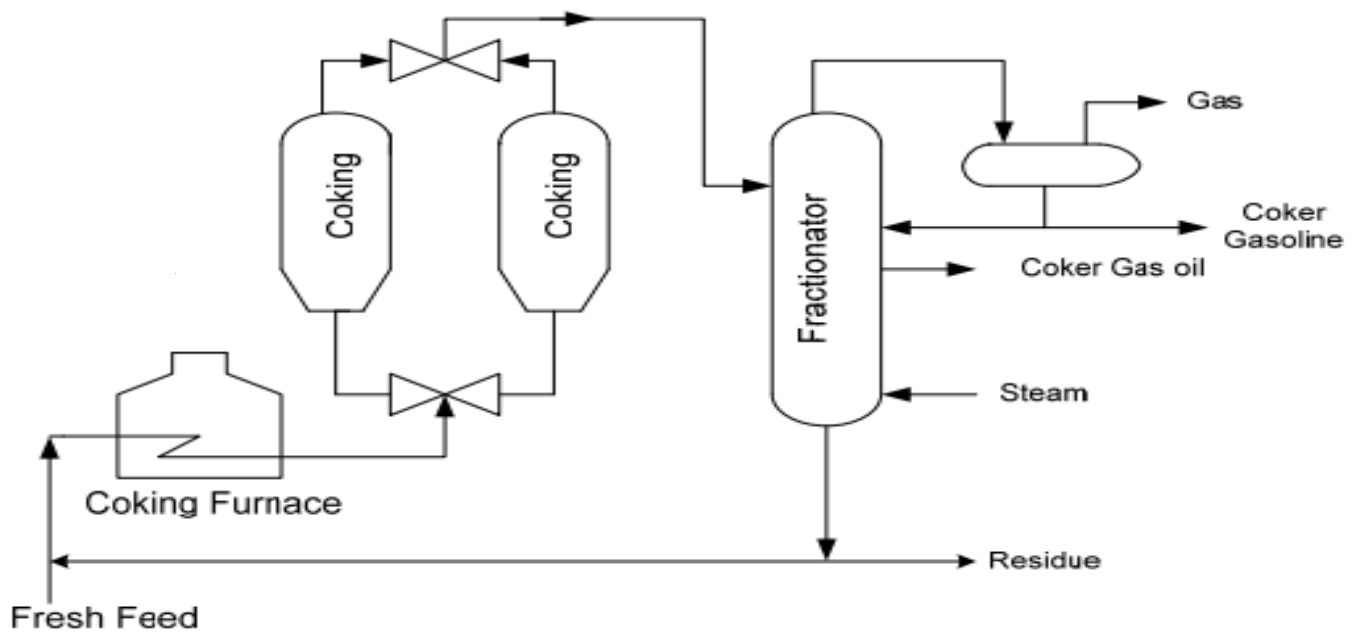


Figure M-IV 4.2: Process Flow Chart of Delayed Coking

Fluid coking: The heated feed is fed to a fluidized bed where coke particles with finer particle sizes would aid fluidization. After coking, lighter products are withdrawn as overhead vapour and coke thus formed is removed continuously. The fluid coker also has an additional scrubber which will remove heavier compounds from the vapour (if any) and send them back with the feed stream. Here, the feed stream absorbs heavier hydrocarbons from the vapour generated. The coke after coking reaction is cold coke. Therefore, to generate hot coke, a burner unit is used to heat the coke using exothermic CO₂ reaction. The offgases from the burner are sent to cyclones, scrubbing and then to the vent. The hot coke thus obtained is recycled back to the fluidized bed or taken out as a net coke product.

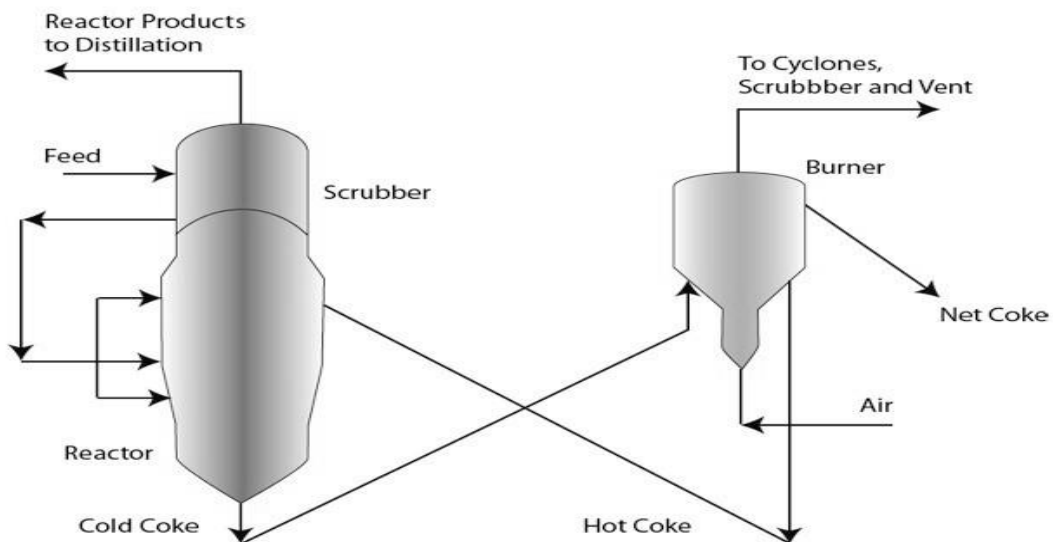


Figure 10.3 Fluid Coking

HYDROPROCESSING

HYDROPROCESSING operations mainly involve **HYDROTREATING** and **HYDROCRACKING UNITS**.

Gasoline and other products from intermediate operations have good number of undesired materials.

The undesired materials mainly include

1. Organic sulphur containing compounds
 2. Organic nitrogen containing compounds and
 3. Metals.
 4. Other undesired materials include olefins (double bond compounds) and metals.
- ❖ The sulphur removal from various refinery intermediate process streams is desired.
 - ❖ Fuel specifications with lower sulphur content should be met.
 - ❖ Nitrogen removal from various process streams is desired to improve yields, reduce catalyst poisoning, reduce NO_x formation in combustion
 - ❖ Metals such as Vanadium and Nickel need to be removed as they tend to poison the catalyst and can cause environmental problems
 - ❖ The olefin removal is primarily desired as they form polymeric (gum type) compounds

Hydroprocessing Process Sequence

- ✓ In hydroprocessing, feedstocks are sent to a catalytic reactor in the presence of hydrogen.
- ✓ Depending upon the intensity of the hydroprocessing operation, the hydroprocessing is termed as hydrotreating or hydrocracking.

Hydrocracking: Heavier molecules react with hydrogen to generate lighter hydrocarbons.

Hydrotreating

In Hydrotreating, the hydrogen on reacting with feed reduces the sulphur and nitrogen concentration in the final products. Hydrogen saturates the olefins and aromatics. However, boiling range of the final products will be similar to that of the feed stock.

- ✓ The operating conditions of the hydrotreater unit will be the same for the simultaneous removal of S, N & O as H₂S, NH₃, H₂O respectively.

Reactions:

1. Inorganic and organic **sulphur** is converted to **H₂S**.

2. **Ammonia** (NH_3) is formed by reactions of **nitrogen** compounds with hydrogen
3. The olefins are converted to both cyclic and non-cyclic saturated hydrocarbons.

Depending upon the feed conditions, the operating conditions are

- Temperature: 290 – 430°C
- Pressure: 7 – 180 bar

Higher pressure and temperature are used when heavier feed stocks are used.

Catalysts:

1. Cobalt, Molybdenum (Co-Mo) catalysts -effective sulphur removal is targeted.
 2. Nickel, molybdenum catalysts (Ni-Mo) -when effective nitrogen removal is targeted.
- The hydrotreating reactions are **exothermic** and therefore, **the reactor product needs to be cooled**.

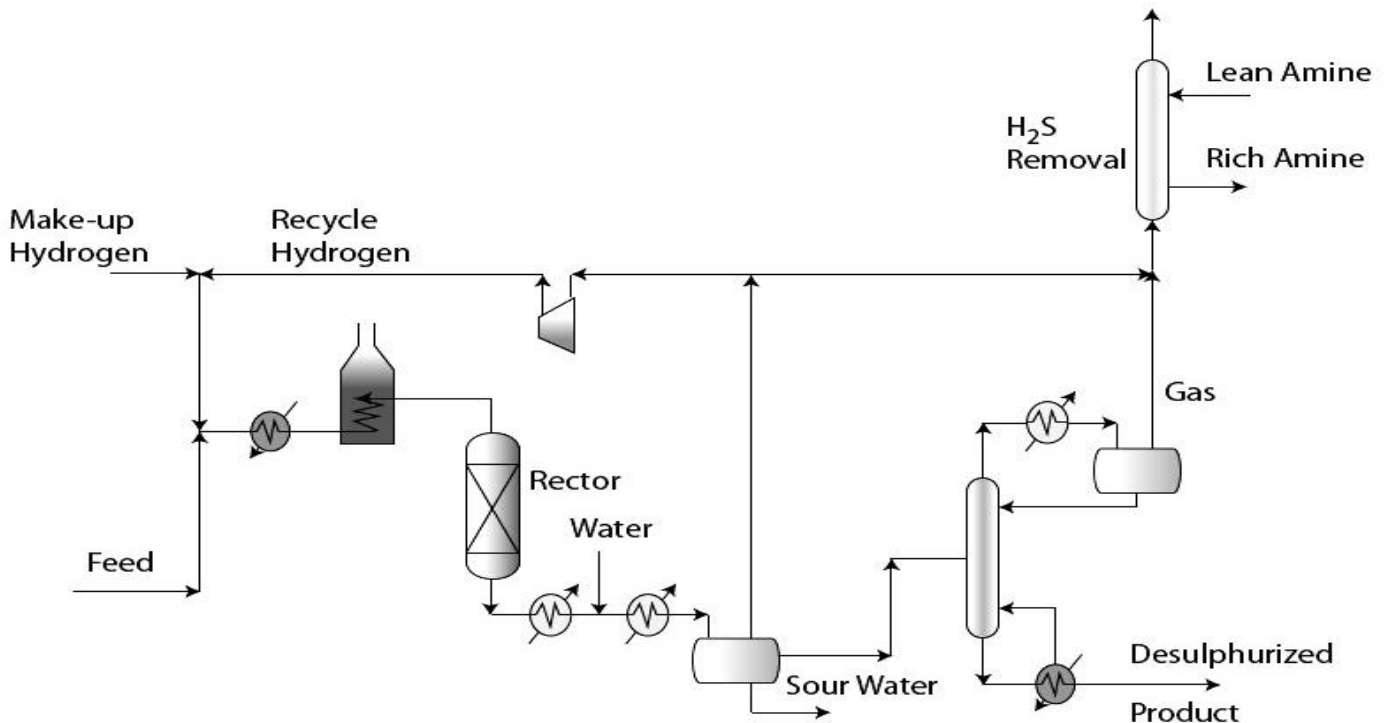


Figure 8.1 Flow sheet of Naptha and Gas Oil hydrotreating

Feed is mixed with recycle hydrogen stream and sent to **heat exchanger and furnace**. Heated mixture is sent to the hydrotreating **packed bed reactor**. The reactor outlet is cooled and **mixed with water**. Mixture is sent to a **phase separator**. The phase separator splits the feed stream to three separate streams namely a gas phase

stream, an organic stream and an aqueous stream. The aqueous stream is rich of H_2S and NH_3 will be sent out to a **sour water** processing unit. The **hydrotreated product enters a fractionator**. Eventually the stabilizing fractionator produces a gas stream consisting of H_2 , C1-C4, H_2S and NH_3 .

- The gas stream emanating from the phase separator **consists of 60 – 90% H_2** . This stream is recycled using a compressor to mix with the make-up hydrogen. The other part of the gas stream from the phase separator is purged to mix with the gas generated from the fractionators and enter the absorption unit for H_2S removal.

Note: When high sulphur feeds are used, H_2S removal is carried out by placing an additional absorber unit (with amine as an absorbent) to reduce higher concentrations of H_2S in the gas stream.

Process Technology for RESIDUE HYDROTREATING

- ✓ Heavier hydrocarbon hydrotreating is carried out using guard reactors followed with conventional packed bed reactors.
- ✓ Guard reactors have catalysts with larger pore size first and then have decreasing pore size along the reactor length.
- ✓ This is due to the reason that heavier fractions could form coke and damage the catalyst totally.
- ✓ Here, Nickel and Vanadium would stay back on the surface of the catalyst.

Note: Except the guard reactors, the remaining **flow sheet for residue hydrotreating remains the same**.

HYDRO CRACKING

Heavier molecules react with hydrogen to generate lighter hydrocarbons.

1. **Cycle oils and coker distillates** are the Hydrocracker **feedstocks**.
2. **High quality jet fuel and diesel production** is targeted.
3. Overall reaction is **exothermic**. (almost in all cases where hydrogen reacts reactions are exothermic-heat releases)
4. **silica-alumina** catalyst. Hydrogenation promoted by **palladium, molybdenum sulphide or tungsten sulphide compounds**.
 - Excess hydrogen also aids in preventing catalyst coking.
 - Operating conditions of the hydrocracking reactor:

5. Temp : **340 – 425°C** and Pressure: **70 – 200 bar**.

6. Guard reactors are used

Reactors

1. fixed bed reactors (more common)
2. moving bed reactors

Fixed bed Hydrocracker

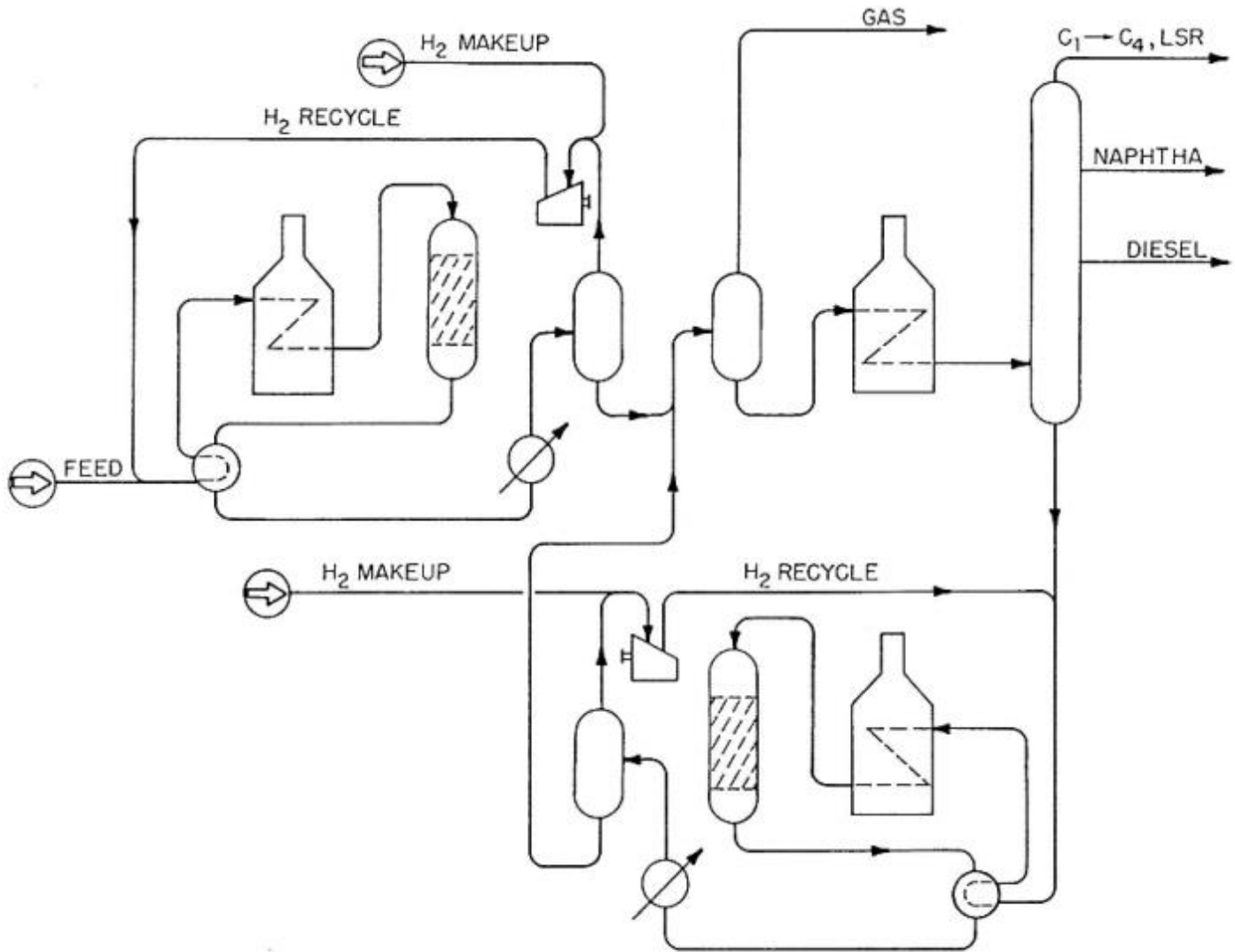
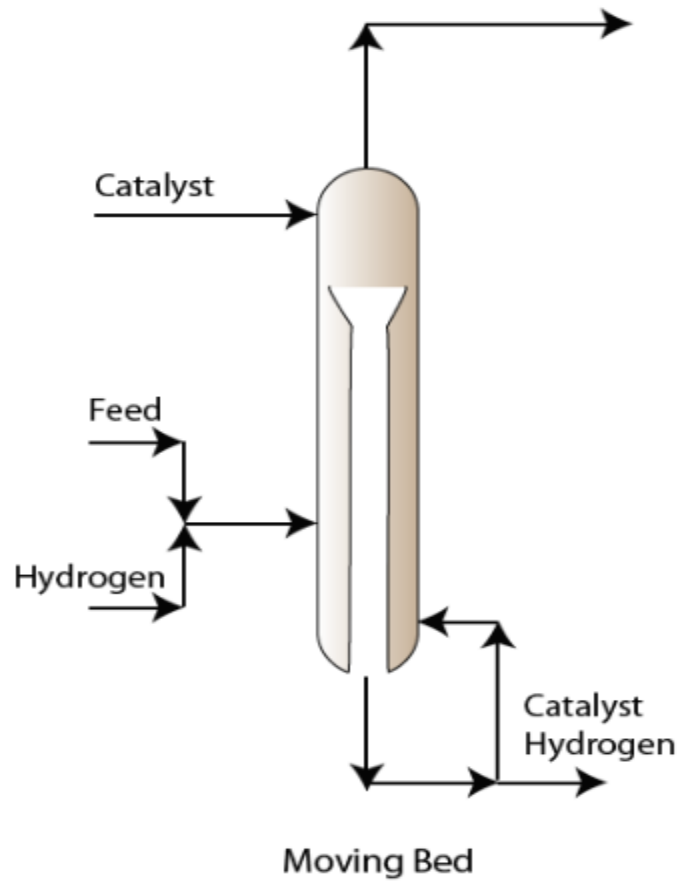


Figure 7.2 Two-stage hydrocracker.

Note:

- In the above figure the top portion is repeated in bottom portion with fractionator bottom as feed.
- Hydrotreating and hydrocracking process are same the only difference is stages
- For moving bed Hydrocracking draw Hydrotreating. Replace reactor with Reactor shown below.



This reactor is also known as ebullated bed reactor