Lecture 6: Cracking

6.1 Introduction

A critical observation of the overall refinery process block diagram indicates that the straight run gasoline (this is the gasoline obtained from the CDU) does not have good octane number (40 – 60) and needs to be upgraded to obtain the desired octane number (85 – 95).

Typically, cracking, reforming and isomerisation are regarded as the three most important processes that contribute towards upgradation of the octane number.

In this lecture, we present an overview of the cracking operation in the refinery.

Typically cracking involves the thermal or catalytic decomposition of petroleum fractions having huge quantities of higher molecular weight compounds. Since heat is required, typically cracking reactions are carried out in furnaces that are supplied with either fuel oil or fuel gas or natural gas or electricity as heat source. Cracking facilitates initiation, propagation and termination reactions amongst the hydrocarbon themselves. However, when steam cracking is carried out, in addition to the energy supplied by the direct contact of steam with the hydrocarbons, steam also takes part in the reaction to produce wider choices of hydrocarbon distribution along with the generation of H_2 and CO.

6.2 What is cracking?

- Cracking involves the decomposition of heavier hydrocarbon feedstocks to lighter hydrocarbon feed stocks.
- Cracking can be carried out to any hydrocarbon feedstock but it is usually applied for vacuum gas oil (VGO)
- Cracking can be with or without a catalyst.
- When cracking is carried out without a catalyst higher operating temperatures and pressures are required. This is called as thermal cracking. This was the principle of the old generation refineries.
- Now a days, cracking is usually carried out using a catalyst. The catalyst enabled the reduction in operating pressure and temperature drastically.

6.3 Cracking chemistry

- Long chain paraffins converted to olefins and olefins
- Straight chain paraffins converted to branched paraffins
- Alkylated aromatics converted to aromatics and paraffins
- Ring compounds converted to alkylated aromatics

- Dehydrogenation of naphthenes to aromatics and hydrogen
- Undesired reaction: Coke formation due to excess cracking
- Cracking is an endothermic reaction

Therefore, in principle cracking generates lighter hydrocarbons constituting paraffins, olefins and aromatics. In other words, high boiling low octane number feed stocks are converted to low boiling high octane number products.

6.4 Operating conditions

- These very much depend upon the feed stock and type of cracking (thermal /catalytic) used.
- Cracking is a gas phase reaction. Therefore, entire feedstock needs to be vaporized.
- It was observed that short reaction times (to the order of 1 – 3 seconds only) provide good quality product and less coke formation.
- For vacuum gas oil, thermal cracking requires operationg at 600 ^{o}C and 20 atms gauge pressure.
- For vacuum gas oil, catalytic cracking is usually carried out at 480 ^{o}C and 0.7 – 1 atms gauge pressure.

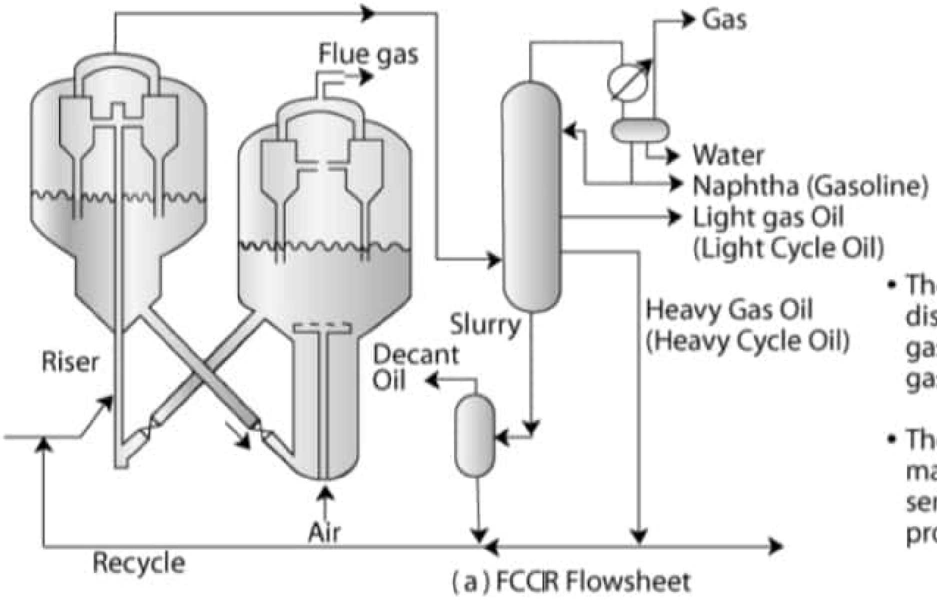
6.5 Catalyst

- Acid treated silica-alumina was used as catalyst.
- 20 – 80 mesh size catalysts used for FCCR and 3 – 4 mm pellets used for MBRs
- During operation, poisoning occurs with Fe, Ni, Vd and Cu

6.6 Process technology

The process technology consists of two flowsheets namely the cracking coupled with main distillation column and stabilization of naphtha.

Catalytic Cracking : Overview



(a) FCCR Flowsheet

- The products are distilled to give light gas, gasoline and light gas oil
- The heavier products may be recycled or sent for further processing elsewhere

Figure6.1 Flow sheet of Catalytic Cracking process

- Feed enters the cracking reactor.
- Old generation refineries used moving bed reactors
- Now a days, fluidized catalytic cracking (FCC) reactors are used.
- The cracked product from the reactor enters a main distillation column that produces unstabilized naphtha, light gas oil, heavy gas oil, slurry and gas.

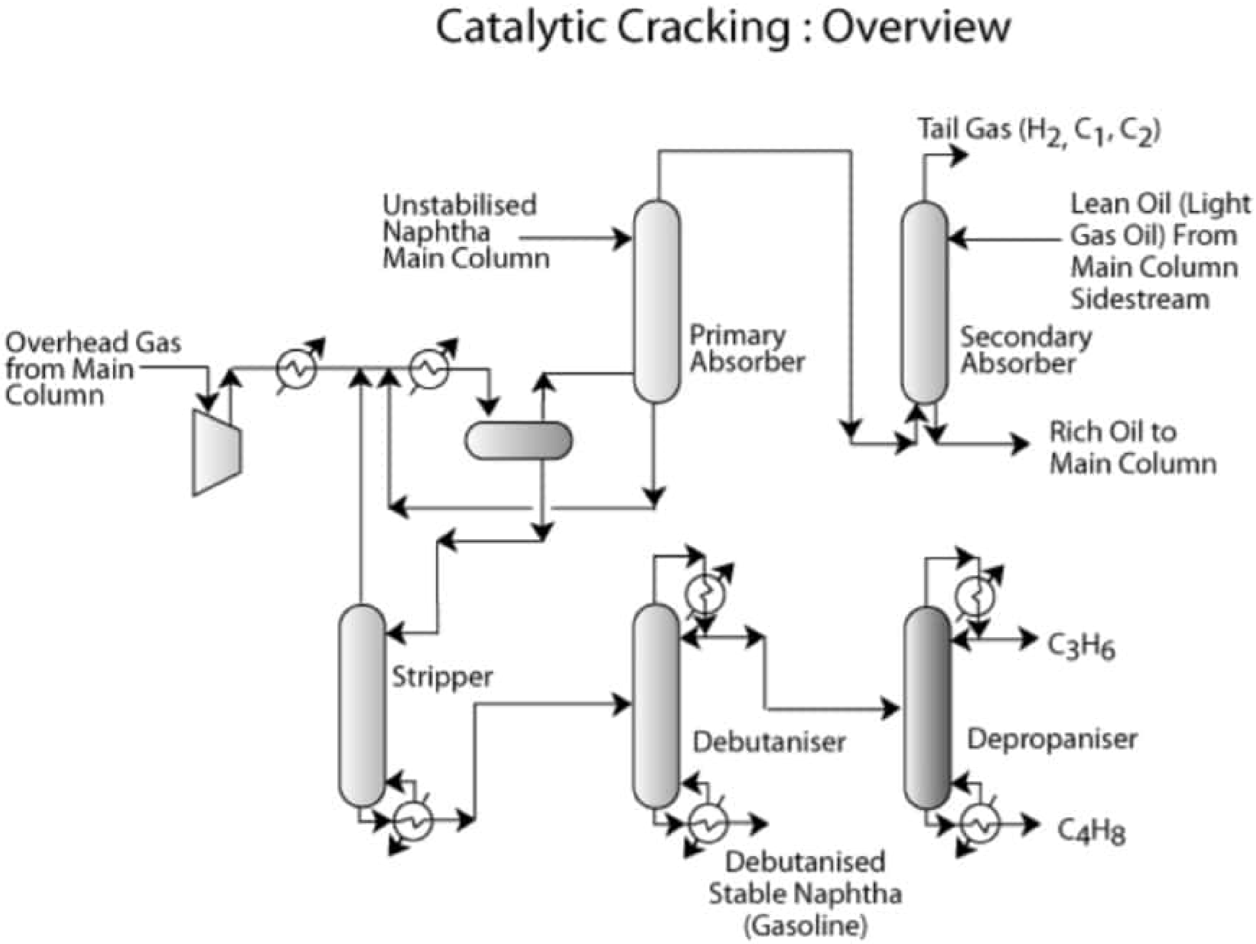
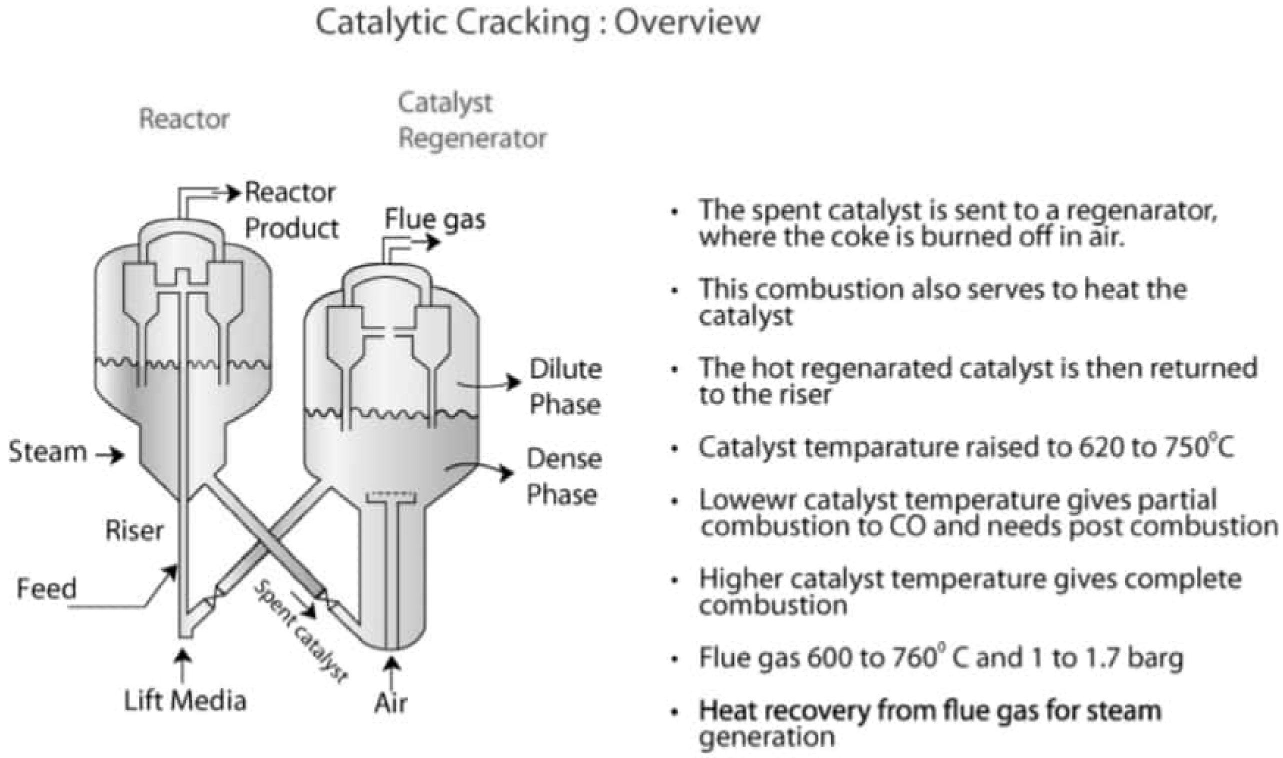


Figure6.2 Naphtha stabilization flow sheet

- The naphtha obtained is unstabilized, as it consists of various hydrocarbons. It is therefore subjected to stabilized by continued processing.
- The slurry enters a phase separation unit which separates decant oil and a heavier product. The heavier product is recycled back to the cracking reactor.
- The unstabilized naphtha subsequently enters a unsaturates gas plant
- In the unsaturates gas plant, the gas obtained from the main distillation column is sent to a phase separator. The phase separator separates lighter hydrocarbons from heavier hydrocarbons.
- The phase separator is also fed with the unstabilized naphtha. The unstabilized naphtha from the main column is first fed to a primary absorber to absorb heavier hydrocarbons in the gas stream emanating from the phase separator.
- The gas leaving the primary absorber is sent to a secondary absorber where light gas oil from main distillation column is used as a absorbent to further extract any absorbable hydrocarbons into the light gas oil. Eventually, the rich light gas oil enters the main distillation column (not shown in the figure a).
- The naphtha generated from the phase separator is sent to stripping to further consolidate and stabilize naphtha
- The stabilized naphtha is further subjected to distillation in debutanizer and depropanizer units

- The debutanizer unit removes butanes and lower hydrocarbons from the naphtha. The naphtha obtained as bottom product in the debutanizer is termed as debutanized stable naphtha or gasoline.
- The butanes and other hydrocarbons are sent to a depropanizer unit where butanes are separated from propanes and other lighter hydrocarbons. Thus, butanes are obtained as lower product and propanes along with other lighter hydrocarbons are obtained as the top product in the depropanizer unit.

6.7 Fluidized catalytic cracking reactor (FCCR) (Figure 6.3)


Catalytic Cracking : Overview

- The spent catalyst is sent to a regenarator, where the coke is burned off in air.
- This combustion also serves to heat the catalyst
- The hot regenarated catalyst is then returned to the riser
- Catalyst temparature raised to 620 to 750°C
- Lowewr catalyst temperature gives partial combustion to CO and needs post combustion
- Higher catalyst temperature gives complete combustion
- Flue gas 600 to 760° C and 1 to 1.7 barg
- Heat recovery from flue gas for steam generation

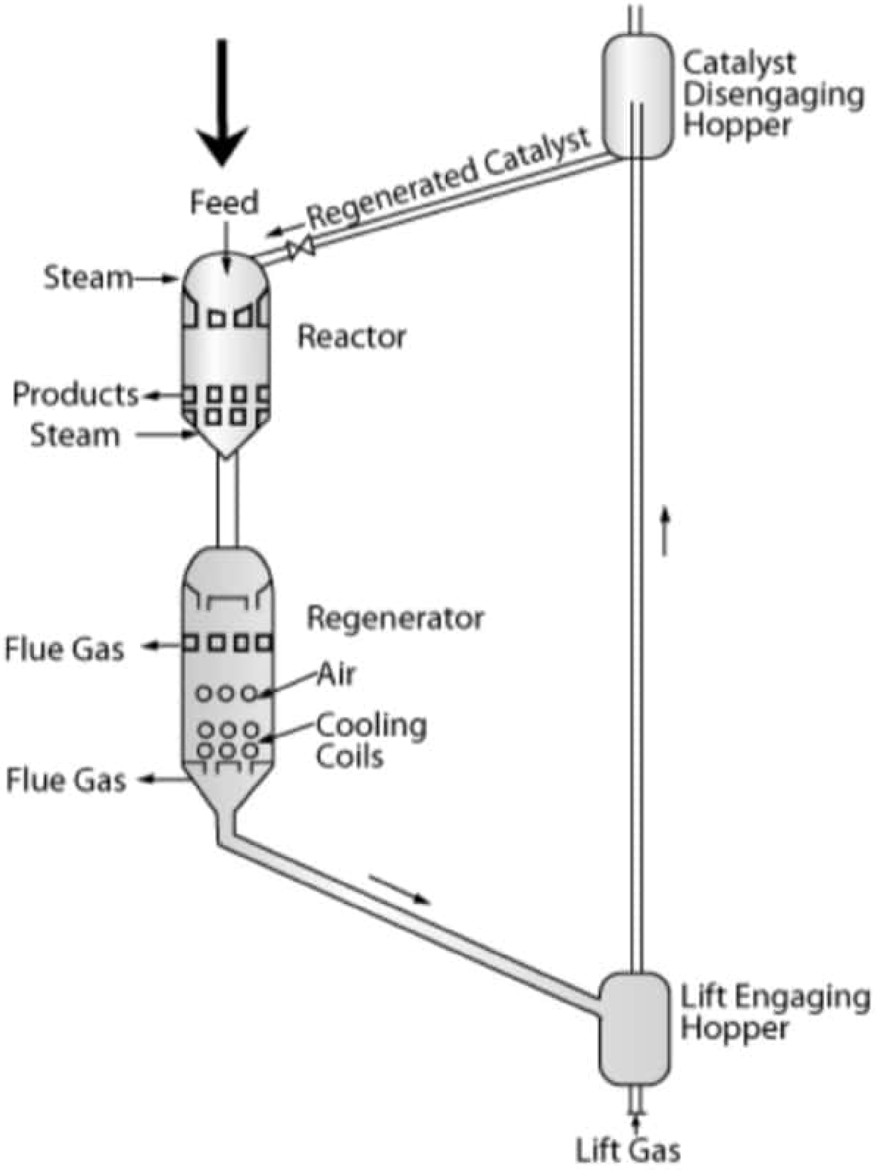
Figure6.3 Fluidized Catalytic Cracking Reactor

- The basic principle of the FCCR is to enable the fluidization of catalyst particles in the feed stream at desired pressure and temperature.
- Another issue for the FCCR is also to regenerate the catalyst by burning off the coke in air.
- Therefore, the reactor unit should have basically two units namely a reactor (FCCR) and a catalyst regenerator (CR).
- The FCCR consists essentially of two important components in a sophisticated arrangement. These are the riser and the cyclone unit assembled in a reactor vessel.
- Riser: In the riser (a long tube), the feed is allowed to get in contact with the hot catalyst. The hot catalyst is enabled to rise through lift media in the riser. The lift media is usually steam or light hydrocarbon gas.
- The riser contact time is about 250 milliseconds.
- The riser is eventually connected to cyclone units.

- The cyclone units receive the catalyst and finished product. The catalyst that enters the cyclone unit is fully coked and needs to be sent to a regenerator to regain its lost activity.
- After cyclone operation (which separates the hydrocarbon vapors and catalyst as a solid fluid operation), the catalyst falls down to the vessel that houses the riser and cyclone units.
- The catalyst in the vessel is subjected to stream stripping in which direct contact with steam is allowed to remove hydrocarbons from the catalyst surface.

6.8 Catalyst regenerator (CR)

- The spent catalyst which is relatively cold enters the regenerator unit.
- Here air enters the vessel through a sparger set up.
- The catalyst is subsequently burnt in the air. This enables both heating the catalyst (which is required to carry out the endothermic reaction) and removing the coke so as to regain the activity of the coke.
- The catalyst + air after this operation will enter the cyclone separator unit. Unlike the FCCR, the CR does not have a riser. Therefore, air enters a dense phase of catalyst and also enables the movement of the catalyst to a dilute phase of catalyst + air
- The cyclone separators separate the flue gas and catalyst as a solid fluid operation.
- The activity regained catalyst is sent to the riser through a pipe.
- During this entire operation, the catalyst temperature is increased to 620 – 750 ^{o}C
- The flue gas is obtained at 600 -760 ^{o}C and is sent for heat recovery unit to generate steam.



(d) Moving Bed Reactor

Figure 6.4 Moving bed reactors (MBR)

- These are old generation catalytic cracking reactors
- There are basically four sections namely reactor, generator, catalyst engaging hopper and catalyst disengaging hopper.
- The catalyst disengaging hopper feeds the regenerated catalyst to the reactor.
- After reaction, the products are recovered from the unit.
- The bed moves to the regenerator unit where air is used to regenerate the catalyst
- The regenerated catalyst enters the engaging hopper unit from where using lift media the catalyst is moved to the disengaging hopper unit.

6.9 Technical questions

1. **Why the naphtha stream after absorption and phase separation enters a stripping unit?**

Ans: The stabilization process involves enabling naphtha to possess only those components that do not flash off in due course of storage. Therefore, naphtha possessing any lighter hydrocarbons other than those desired should be totally eliminated. The unstabilized naphtha obtained from the main distillation column is not given enough time to equilibriate towards stabilization cause. Even after the phase separator and absorber units, the stabilization needs one more unit for processing and hence a stripper unit is used to remove any lighter gases that exist after phase separation.

It is further interesting to note that phase separators do not always meet the product requirements. The phase separators only enable the separation of gas and liquid streams based on their operating temperature and pressure which may not correspond to the exact conditions required to equilibrate. Therefore, additional processing is mandatory.

2. **Why steam stripping is carried out in the FCCR?**

Ans: The purpose of stream stripping is to facilitate the removal of hydrocarbons adsorbed on the catalyst surface. If this is not done, they will be burnt in the CR unit and this will be loss of product value. In petroleum processing, always we don't wish to loose any valuable money in the processing. That's also the reason why the flue gas from CR is sent to the flue gas heat recovery unit for steam generation.

3. **Comment on process intensification in the FCCR?**

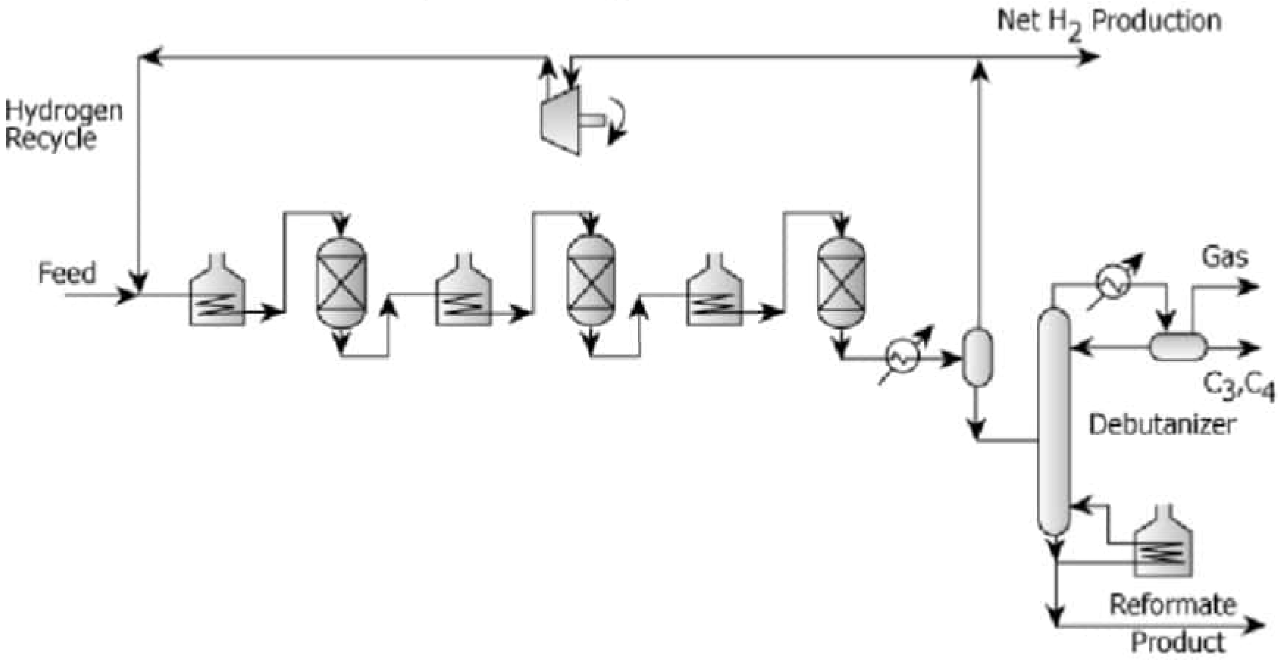
Ans: The FCCR is a complicated arrangement of the riser (where the reaction takes place), the cyclone separator (where solid fluid separation takesplace) and the stripper (where again stripping the catalyst takes place a physical process). Therefore, we can see that the reactor and separator are packed into a single vessel applying the finer principles of process intensification.

4. **What are the main advantages of catalytic cracking over thermal cracking?**

- Good product quality
- Less coke formation
- Temperature and pressure uniformity in operation

Lecture 7: Reforming and Isomerization

Catalytic Reforming : Flowsheet



- Products from reactor cooled (often by heat exchange with feed), partially condensed to separate hydrogen-rich gas from the liquid products.
- Reformate separated from C_4^- by distillation.

Figure 7.1 Reforming

7.1 Introduction

- The catalytic cracking involves enhancing the octane number of the product
- Heavy naphthas are used are typical feed stocks
- The reaction is carried out on a catalyst
- Reforming reaction produces hydrogen as a by product which is used elsewhere in the refinery
- Usually Platinum supported on porous alumina is used as a catalyst
- Catalyst activity enhanced using chloride

7.2 Cracking Chemistry

- Paraffin isomerisation takes place
- Naphthene isomerisation also takes place to produce cycloalkanes
- Cyclo alkanes undergo dehydrogenation to generate aromatics
- Dehydrocyclization takes places to convert side chained alkanes to cyclo alkanes and hydrogen
- In summary lower octane number feeds are converted to high octane products
- The reformate thus produced has high octane and aromatics (benzene, toluene and xylene) content.

- The reactions are endothermic. Therefore, heat needs to be supplied

7.3 Process technology (Figure 7.1)

- The feed is mixed with recycled hydrogen
- Subsequently, it is heated before sending to reactor
- Since the reactions are highly endothermic, several combinations of reactor + heaters are used.
- The products from the final reactor are cooled. Often this is carried out with heat recovery principle in which heat is recovered using the fresh feed to the first reactor.
- After this, the product mixture enters a phase separator which separates the hydrogen gas stream from the liquid stream.
- The liquid stream from the phase separator is sent to a debutanizer distillation column that separates butanes and lower alkanes from the reformate product.
- The hydrogen produced in the phase separator is compressed and sent back to the first reactor.
- Excess hydrogen generated in the reactions is taken out as a bleed stream
- Catalyst regeneration (not shown in the flow sheet) needs to be carried out to regain catalyst activity. This can be in different modes of operation namely cyclic, semi-regenerative or continuous. When continuous mode of catalyst regeneration is carried out (as in UOP continuous catalytic reforming process), the moving bed designs are used for the reforming reactor. Additional complexity in the moving bed reactors is to enable process intensification to club the sequence of three reactors + heaters into one single unit.

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7.4 Process parameters

- Reactor pressure: 4 – 24 barg
- Reactor temperature: 500 – 525 °C
- H_2/Hydrocarbon molar ratio: 2 – 3

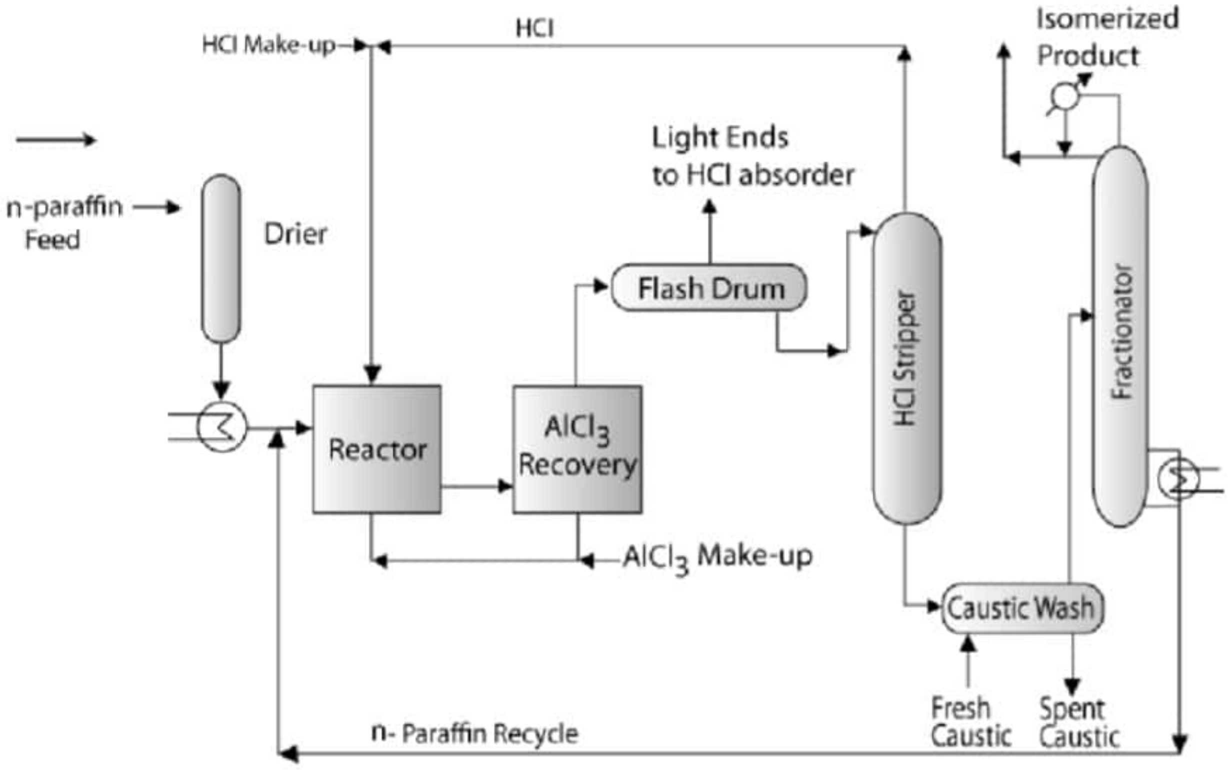

Figure 7.2 Flow sheet of Isomerization of n-paraffin

7.5 Introduction

- The basic principle of Isomerization is to straight chain alkanes to side chain paraffins. This enhances the octane number substantially
- For instance, n-pentane has an octane number of 61.7 where asiso-pentane has an octane number of 92.3
- Usually light naphtha is used as a feed stock

7.6 Catalyst

- Platinum base catalysts are used
- $AlCl_3$ is used as a promoter for the catalyst
- During reaction, part of the $AlCl_3$ gets converted to HCl
- Therefore, completely dry conditions shall be maintained to avoid catalyst deactivation and corrosion.
- Catalytic reaction takes place in the presence of hydrogen to suppress coke formation

7.7 Process technology (Figure 7.2)

- Light naphtha and hydrogen (make up) are totally dried and sent to an isomerisation reactor after pre-heating the feed mixture in a heat exchanger
- Reaction operating conditions: 150 – 200 °C and 17 – 28 barg
- Typical conversions: 75 – 80 % for pentanes.
- After reaction, $AlCl_3$ is recovered from the product using condensation or distillation
- The basic principle for $AlCl_3$ recovery is that at the reactor operating conditions, the $AlCl_3$ is in volatile conditions and is soluble in hydrocarbons
- After $AlCl_3$ is recovered from the product, it is sent back to the reactor along with the make- up $AlCl_3$
- Eventually, the product enters a flash drum where bulkly light ends along with little quantities of HCl are separated from the liquid product.
- The light ends recovered from the flash drum are sent to aHCl absorber where HCl is absorbed into caustic solution to generate the light end gases. The light end gases can be further used for other processes in the refinery.
- The bottom product then enters aHCl stripper where most of the HCl is stripped from the isomerisation product rich stream. The HCl is recycled back to the reactor to ensure good catalyst activity. Make-up HCl is added to account for losses
- Subsequently, caustic wash is carried out to remove any trace quantities of HCl
- The isoermized product rich stream is then sent to a fractionators that separates the isomerized product from the unreacted feed.
- The unreacted feed from the fractionators is sent back to the reactor.

Lecture 8: Hydroprocessing

8.1 Introduction

- In this lecture, we present a brief overview of the hydroprocessing operations in the petroleum refinery. The hydroprocessing operations mainly involve hydrotreating and hydrocracking units.

- From reforming and cracking reactions, the gasoline yields have been predominantly increased. However, their quality has not been addressed.

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

- The undesired materials mainly include (a) organic sulphur containing compounds (b) organic nitrogen containing compounds and (c) metals.

- Other undesired materials include olefins (double bond compounds) and metals.

- The sulphur removal from various refinery intermediate process streams is desired for several reasons. Firstly, the fuel specifications with lower sulphur content should be met. Secondly, the shelf life of sulphur sensitive platinum catalysts need to be increased.

- Similarly, nitrogen removal from various process streams is desired to improve yields, reduce catalyst poisoning, reduce NO_x formation in combustion etc.

- The metals such as Vanadium and Nickel need to be removed as they tend to poison the catalyst and can cause environmental problems after combustion.

- The olefin removal is primarily desired to obtain clean products after combustion. Other than this, the formation of polymeric (gum type) compounds in fuel combustion be avoided.

- Aromatics removal is desired primarily to meet the desired specifications.

8.2 Definitions of hydroprocessing, hydrotreating and hydrocracking

- 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.

- During hydrotreating, sulphur and nitrogen concentration in the final products is reduced along with the saturation of olefins and aromatics. However, boiling range of the final products will be similar to that of the feed stock.

- During hydrocracking, heavier molecules react with hydrogen to generate lighter hydrocarbons.

8.3 Hydrotreating

8.3.1 Introduction

- In hydrotreating, sulphur, nitrogen and metals removal is targeted along with the saturation of olefins and aromatics. Thus the operating conditions of the hydrotreater unit will be the same for the simultaneous removal of S, N & O as H_2S, NH_3, H_2O respectively. These products will be separated in the off gas and the off gas will be further subjected to gas treating.
- The boiling point range of the products is not significantly different from that of the feedstocks.
- From chemistry perspective, inorganic sulphur is converted to H_2S. Organic sulphur compounds such as mercaptans, sulphides, disulphides, thiophenes are converted to corresponding saturated hydrocarbons along with the generation of H_2S. Similarly, denitification reactions also take place during hydrotreating in which compounds such as pyrrole, pyridine and quinoline are convered to saturated hydrocarbons. Ammonia is generated as a byproduct in the denitrification reactions.
- The olefins are converted to both cyclic and non-cyclic saturated hydrocarbons. Similarly, aromatic hydrocarbons such as toluene, naphthalene and tetrahydronaphthalene are converted to corresponding cyclic hydrocarbon compounds
- The removal of vanadium and nickel is usually difficult. This is due to the reason that they are held within asphaltene molecules and intense operating conditions (higher T, P and molar ratio of hydrogen to hydrocarbon feed) are required.

8.3.2 Process Conditions

- 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: Cobalt, Molbdenum catalysts are used when effective sulphur removal is targeted. Nickel, molybdenum catalysts are used when effective nitrogen removal is targeted
- The hydrotreating reactions are exothermic and therefore, the reactor product needs to be cooled.

8.3.3 Process Technology for Naphtha & Gas oil hydrotreating (Figure 8.1)

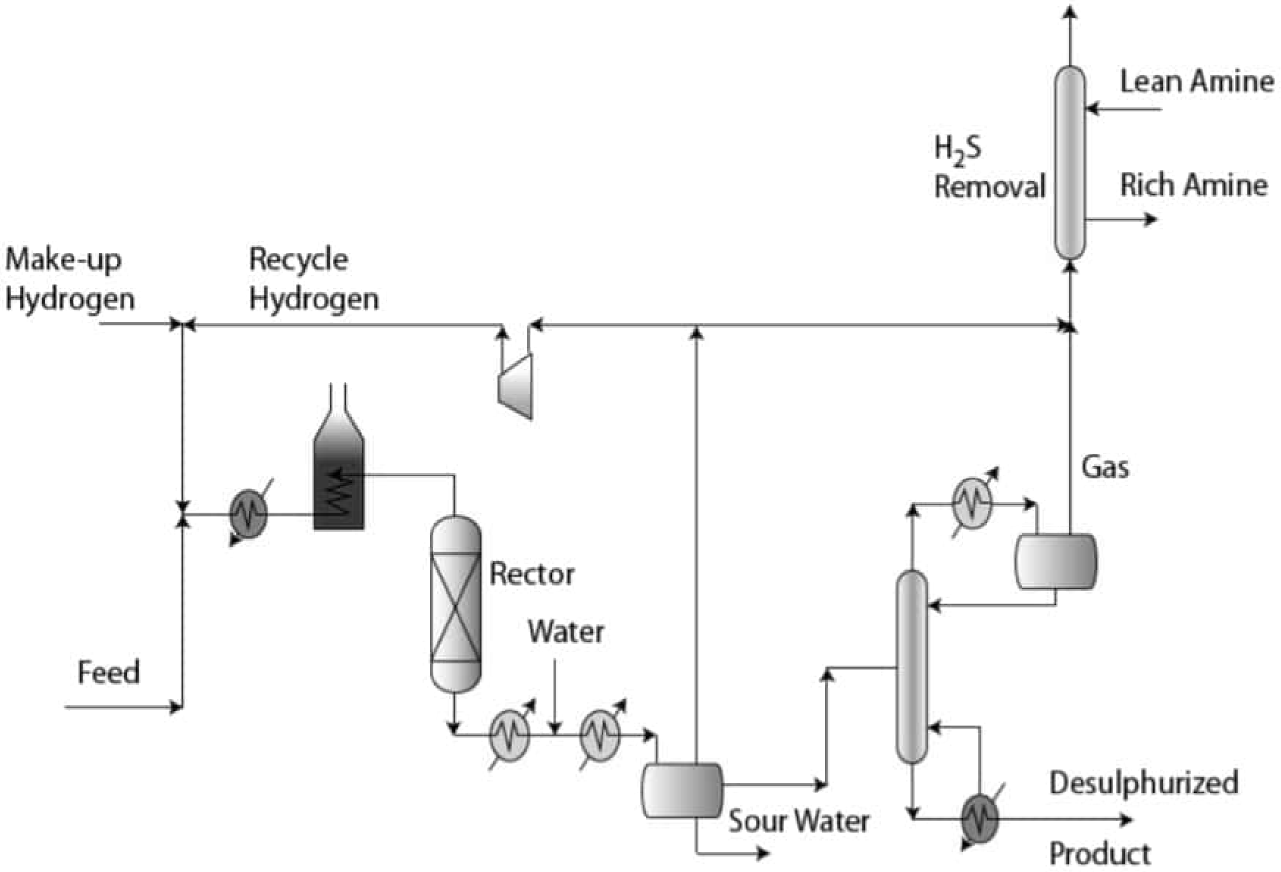

Figure 8.1 Flow sheet of Naptha and Gas Oil hydrotreating

- Feed is mixed with recycle hydrogen stream
- Sent to heat exchange in a furnace for heating the same
- Eventually the heated feed mixture is sent to the hydrotreating packed bed reactor
- The reactor outlet is cooled and mixed with water.
- Eventually the water mixed reactor stream is further cooled and 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 and will be sent out to a sour water processing unit to recover H_2S and NH_3. The sour water processing unit uses amine based absorption technology to recover H_2S.
- The hydrotreated product is the organic stream enters a fractionator to stabilize the hydrotreated product. Eventually the stabilizing fractionator produces a gas stream from the partial condenser 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. Majority of this stream is recycled using a compressor to mix with the make-up hydrogen and enter the heat exchanger and furnaces. 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.
- 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. In this case, a purge stream is allowed to balance off the additional gas available as another by product from the process.

8.3.4 Process technology for Residue hydrotreating

- Heavier hydrocarbon hydrotreating is carried out using guard reactors
- Guard reactors have catalysts with larger pore size first and then have decreasing pore size along the reactor length.
- The guard reactors are followed with conventional packed bed reactors.
- 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
- Except the guard reactors, the remaining flow sheet for residue hydrotreating remains the same. Live steam is used in the fractionator and unstablized naphtha is produced as one of the products in the residue hydrotreating process.

8.4Hydrocracking

8.4.1 Process summary

- Cycle oils and coker distillates are the typical feedstocks
- High quality jet fuel and diesel production is targeted
- Overall reaction is exothermic

- Cracking is promoted on silica-alumina sites of the catalyst. Hydrogenation promoted by palladium, molybdenum sulphide or tungsten sulphide compounds
- Since catalyst gets poisoned with organic nitrogen compounds, hydrotreater catalytic reactors are used before hydrocracking reactors to safeguard the hydrocracking catalysts
- Excess hydrogen also aids in preventing catalyst coking.
- Operating conditions of the hydrocracking reactor: 340 – 425 °C and 70 – 200 bar

8.4.2 Process Technology (Figure 8.3)

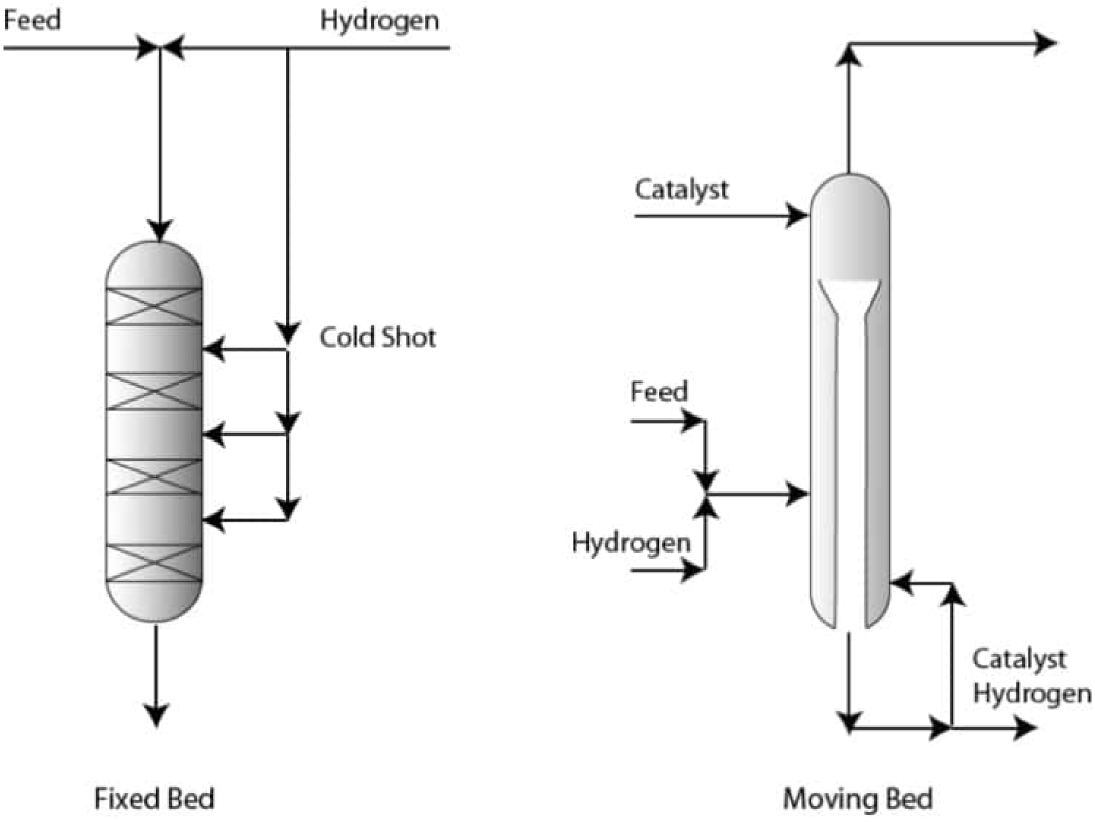

Figure 8.2 Fixed Bed and Moving Bed

- Reactors use fixed or moving bed reactors in which fixed beds are more common.
- Packed beds: Cold shot reactors are used in which cold H_2 is used to cool the hot streams. Guard reactors are used before hydrocracking catalyst within the reactor column itself
- Moving beds: Feed allows movement of the catalyst for good mixing.
- After reaction, the product gets mixed with water and enters a three phase separator.

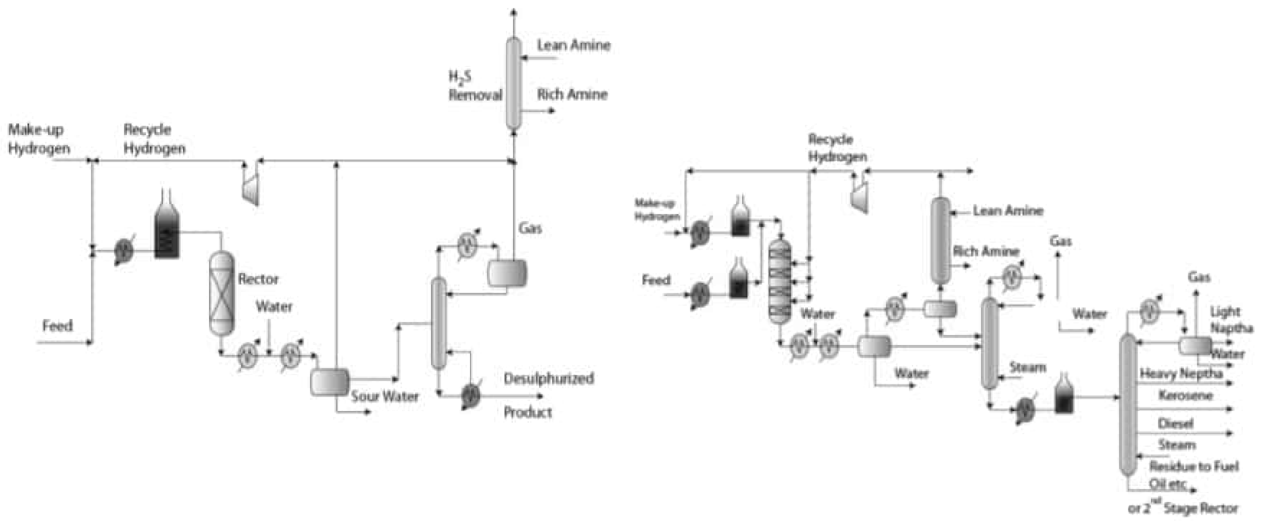

Figure 8.3 Flow sheet of hydrocracking

- The three phase separator generates three streams namely sour water stream, organic stream and a gas stream.
- The gas stream again enters a phase separator to remove entrained organic stream after cooling.
- The gas stream is subjected to H_2S removal using amine scrubber. The organic stream eventually enters a steam stripper further stabilize the organic stream. In this fractionator, a gas stream and a sour water stream are generated.
- Eventually, the stabilized organic stream is sent to a multi-product fractionators to generate light naphtha, heavy naphtha, kerosene, diesel and residue. Steam is used to enhance the product quality.

8.4.3 Technical questions

1. Why the phase separator emanates two streams?

Ans: Here, the principle of maximizing H_2S, NH_3 removal by absorption into water is facilitated. All other hydrocarbons and hydrogen do not have much solubilities in water when compared to these two gases. Usually, a phase separator is assumed to produce two phases namely gas or liquid or two separate liquids based on densities. But here, due to injection of water and cooling, three phases are existent. These are gas (hydrogen rich), water (NH_3 and H_2S rich) and the hydrotreated product (H_2S and H_2 lean).

2. Explain why one heat exchanger is used before mixing water and one is used after mixing?

Ans: This is a very intelligent question. After years of research and process simulation studies, such optimal conditions of mixing and cooling have been obtained. Cooling the reactor product first is targeted for mixing and cooling after mixing is targeted to maximize solubilities of NH_3 and H_2S in the water stream.

3. Can we use steam instead of reboiler in the fractionator?

Ans: This is also an important question. Steam utilization instead of reboilers is usually carried out for heavier hydrocarbons but not for the light hydrocarbons such as naphtha and gas oil. This is to ensure that lighter hydrocarbons are easily stripped from the heavier desulphurized product and good product quality is obtained in the top and bottom products of the fractionators.

4. Do we produce only gas when steam stripping facilitiated in the fractionators?

Ans: No, we produce three products from the partial condenser of the fractionator. These are (a) sour water (steam condenses to form water), unstabilized naphtha (this will again enter a stabilization unit) and a gas stream.

5. Comment upon hydrogen requirements for various hydrotreatingfeedstocks?

Ans: Depending upon the feedstocks, hydrotreatingfeedstocks would be fed with variant hydrogen requirements. For straight run naphtha, the H_2/Naphtha feed ratio is 1.4 – 5.7 Nm^3/bbl of feed. For Gas oil, it is 5.5 – 16 Nm^3/bbl feed. For kerosene, it is 2.7 – 11.2 Nm^3/bbl feed.

6. Why two phase separators are used for the reactor product in hydrocracking flowsheet?

Ans: The first phase separator provides three streams based on its temperature and pressure. However, when the temperature of the gas stream is again reduced, again two phase streams would emanate. This is due to the heat removal and due to this reason, adiabatic flash conditions would exist and two streams would be generated. The second phase separator could be optional as well, but it will affect the catalyst performance. Long term performance studies along with process simulation studies provide such minor changes in the process flow sheet which are important to eventually phase out long term profitability of the hydrocracking flow sheet.

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