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\textsubscript{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 H₂S, NH₃, H₂O 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 H₂S. Organic sulphur compounds such as mercaptans, sulphides, disulphides, thiophenes are converted to corresponding saturated hydrocarbons along with the generation of H₂S. Similarly, denitification reactions also take place during hydrotreating in which compounds such as pyrrole, pyridine and quinoline are converted 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, Molybdenum 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)

- 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 \( \text{H}_2\text{S} \) and \( \text{NH}_3 \) and will be sent out to a sour water processing unit to recover \( \text{H}_2\text{S} \) and \( \text{NH}_3 \). The sour water processing unit uses amine based absorption technology to recover \( \text{H}_2\text{S} \).
- 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 \( \text{H}_2 \), C1-C4, \( \text{H}_2\text{S} \) and \( \text{NH}_3 \).
- The gas stream emanating from the phase separator consists of 60 – 90 % \( \text{H}_2 \). 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 \( \text{H}_2\text{S} \) removal.
- When high sulphur feeds are used, \( \text{H}_2\text{S} \) removal is carried out by placing an additional absorber unit (with amine as an absorbent) to reduce higher concentrations of \( \text{H}_2\text{S} \) 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 unstabilized naphtha is produced as one of the products in the residue hydrotreating process.

### 8.4 Hydrocracking

#### 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)

- 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.
- 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$_2$S 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$_2$S, 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$_2$S rich) and the hydrotreated product (H$_2$S 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$_2$S 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 facilitated 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 hydrotreating feedstocks?

Ans: Depending upon the feedstocks, hydrotreating feedstocks would be fed with variant hydrogen requirements. For straight run naphtha, the \( \text{H}_2/\text{Naphtha} \) feed ratio is 1.4 – 5.7 \( \text{Nm}^3/\text{bbl} \) of feed. For Gas oil, it is 5.5 – 16 \( \text{Nm}^3/\text{bbl} \) feed. For kerosene, it is 2.7 – 11.2 \( \text{Nm}^3/\text{bbl} \) 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.

References:
