Lecture 11: Gas Processing and Polymerization

11.1 Introduction

- In this lecture, we present an overview of light end processing followed with gas processing and polymerization processes in the refinery
- Gas fraction is produced from various units. Some of them are
  - Crude distillation unit
  - Catalytic cracking unit
  - Catalytic reforming unit
  - Hydrocracking unit
  - Coking unit
- The light end streams are classified as
  - Streams rich in Butane: Sold as calor gas or LPG. Used internally for blending and alkylation units (isobutane only)
  - Streams rich in Propane
  - Light ends rich in olefins.
- We have already studied alkylation and isomerisation as important gas processing operations. Now we will study the additional units namely gas processing and polymerization units.

11.2 Gas processing technology (Figure 11.1)

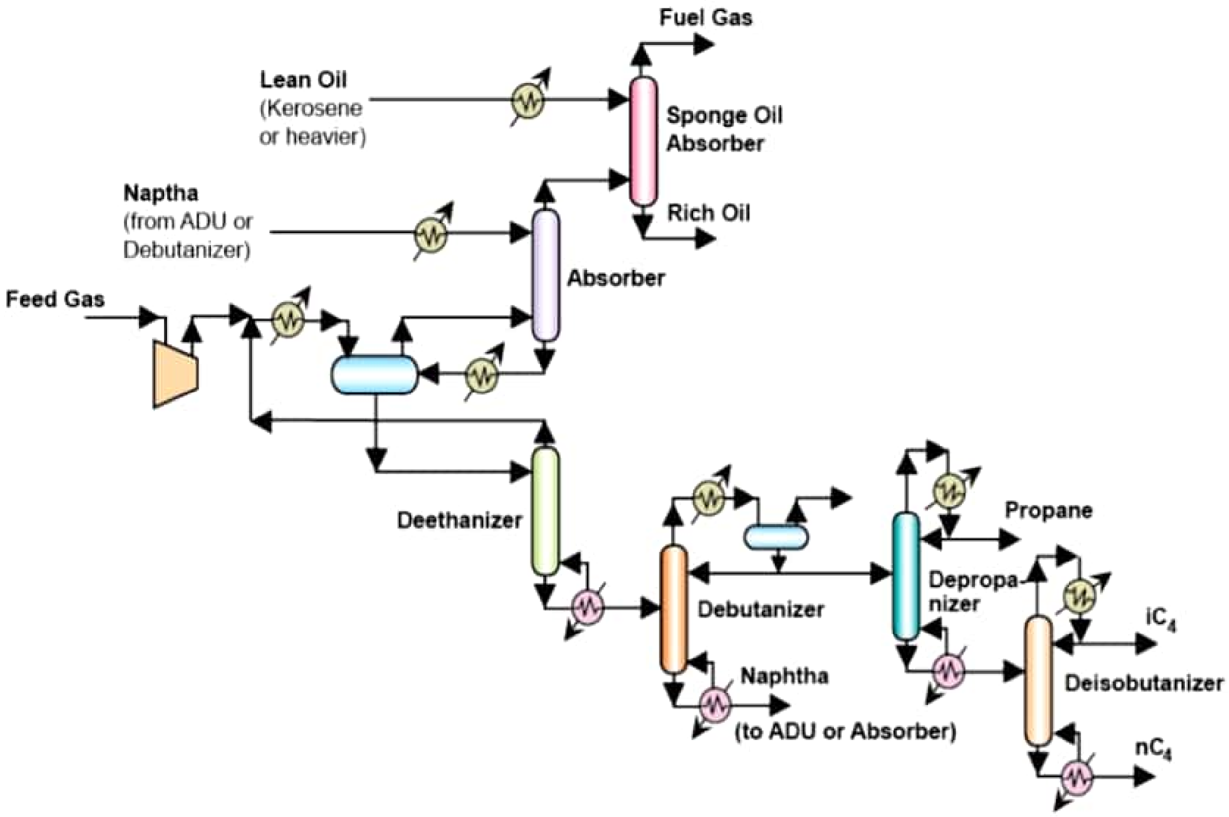

Figure 11.1 Gas Processing Technology

- The objective of gas processing is to produce ethane and methane.
- The produced ethane and methane is to serve later for fuel gas or hydrogen production
- The gas processing section consists mainly of two different sections
- Absorption using Naphtha and kerosene:
  - First, collected gases are compressed to be fed to an absorption.
  - The purpose of naphtha is to absorb heavier hydrocarbons in the gas fraction. These are C3s and C4s in the feed stream. To carry out absorption, first the gases are cooled and fed to a phase separator to facilitate early separation of lighter and heavier fractions.
  - From the phase separator two streams emanate namely a gas stream and a liquid stream.
  - The gas stream is fed to an absorber unit where naphtha is used as a solvent to absorb the left heavier hydrocarbons in the gas.
  - The naphtha rich with hydrocarbons is fed to the phase separator so as to stabilize the naphtha stream.
  - The gas from the absorber is fed to a second absorber where lean oil (such as kerosene) is used as a solvent to absorb any heavier hydrocarbons other than the methane and hydrogen. Eventually, fuel gas is produced as the gas product from this absorption. The other product from the absorber is the rich oil stream
- Naphtha rich stream processing:
  - The liquid product from the phase separator is fed to a deethanizer which generates ethane rich stream as the top product. This stream is recycled back to the gas processing unit i.e., mixing with the feed and subjected to cooling followed by phase separator.
  - The bottom product from deethanizer is naphtha rich stream with butanes and propanes.
  - This stream is subjected to fractionation using debutanizer, depropanizer and deisobutanizer to obtain propane, isobutane and naphtha. The stabilized naphtha can be used for absorption purposes.

11.3 Olefin Polymerization

- Olefin polymerization to yield polymer gasoline is primarily carried out to obtain polymers with good octane numbers.
- The octane number of the polymer gasoline product is not greater than the octane number of the products produced from reforming and alkylation. Instead, comparatively poor quality product is obtained. But for the sake of enhancing octane number polymerization is carried out.

- On the other hand, polymer gasoline has more vapour pressure than the corresponding alkylation products. Therefore, in both ways, polymer gasoline product quality is lower than that obtained from the alkylation unit.
- Typical feedstocks for polymerization process are C_3 and C_4 olefins that are obtained from catalytic cracking
- The end product from polymerization reactor is a dimer or a trimer of the olefins.

11.4 Reaction mechanism&Operating conditions

Reaction mechanism comprises of four basic steps

- Carbonium ion formation (Step 1): Here, olefin reacts with acid catalyst to yield carbonium ion.
- Additon reaction (Step 2): Carbonium ion reacts with olefin to generate intermediate carbonium ion
- Regeneration (Step 3): The intermediate carbonium ion converts to the dimer and generates back the proton on the catalyst surface
- Isomerization (Step 4): Straight chain proton substituted olefins convert to isomeric carbonium ions.
- Catalysts used: Acid catalysts (H_2SO_4) are used.
- Temperature: 150 – 220 ^{o}C are used. Too high temperatures give tar deposits.
- Pressure: 25 – 100 atms

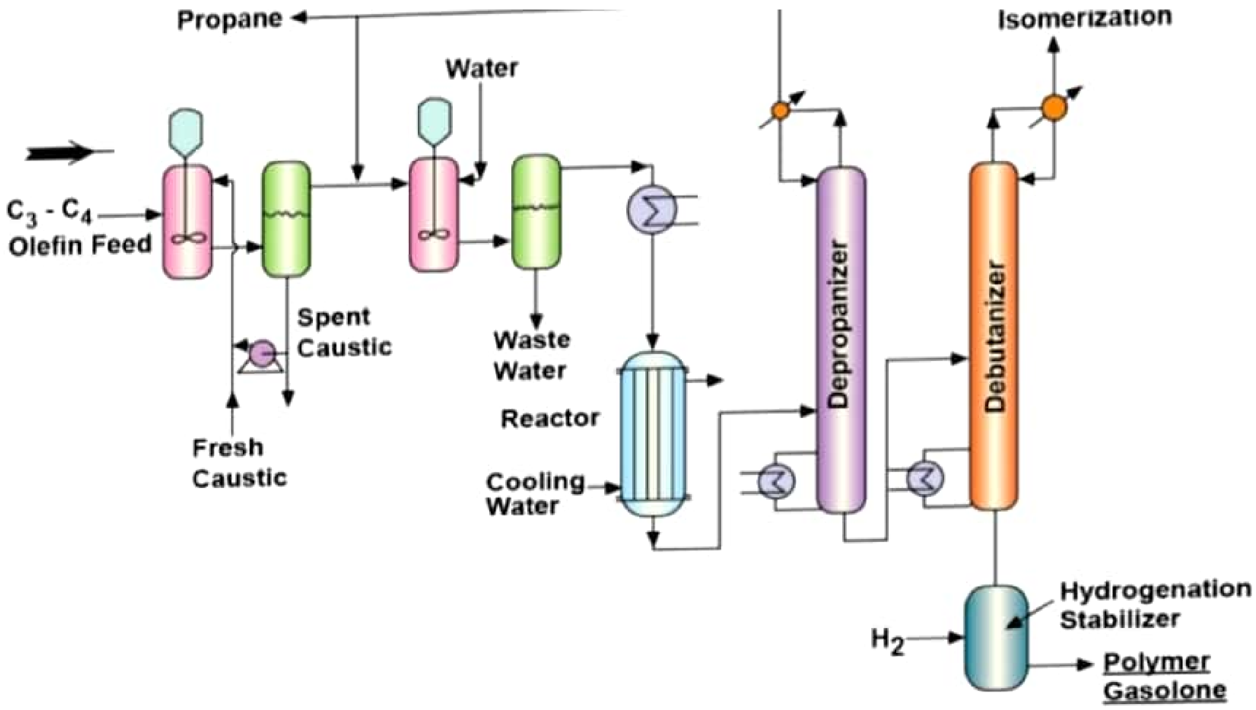

Figure 11.2 Flow sheet of Olefin Polymerization Technology

- Caustic wash: C3-C4 olefin feed subjected to caustic wash to remove H_2S and other sulphur compounds (such as mercaptans). These tend to poison the catalyst.
- **Water scrubbing:** Eventually water scrubbing is carried out to remove dissolved impurities and generate waste water.
- **Polymerization reactor:** The reaction mixture is heated, compressed and fed to a polymerization reactor. The reactor design is a shell and tube type design where catalyst is placed in the tube for the reaction to take place and cooling water is circulated in the shell side to control the temperature increase due to the exothermic reaction.
- **Fractionation:** Subsequently, the reactor product is fed to a depropanizer and debutanizer to produce propanes, butanes and polymer gasoline. The polymeric product is further stabilization using hydrogenation stabilizer which converts any freely available double bonds to single bonds. The end product is polymer gasoline
- The propane produced is partially recycled to the reactor and the other part taken out as a product.

11.6 Technical questions

1. **Why is the deethanizer top product recycled to the cooler followed with phase separator?**

Ans: The deethanizer top product consists of ethane rich stream but not a pure product. Therefore, instead of further distillation of the fraction, it is sent to the phase separator. This means that ethane is not produced as a product here. This is also practised in the refinery. Also, there are refineries that produce ethane as a product. It all depends on the subsequent operation that the refinery plans with the ethane generated.

2. **Why the sequence is followed to remove ethane, propane, butane and isobutene?**

Ans: This is an important question that one should understand. From a mixture of ethane, propane, butane and isobutane in naphtha, the easiest to separate is ethane followed with propane, butane and isobutane. Therefore, isobutane separation is the toughest.

3. **Why is naphtha rich with heavier hydrocarbons sent to the phase separator?**

Ans: The naphtha stream rich with heavier hydrocarbons is not a stream that consists of only heavier hydrocarbons. It also consists of lighter hydrocarbons. This is the problem we face always in chemical industry. Textbooks always enable a student to understand two component absorption, but in the real world we deal with multicomponent systems. The basic problem in multicomponent process is that we cannot dictate the absorption of a particular component only. For instance, when we absorb a mixture of NH_3 and CO_2, we see that both NH_3 and CO_2 get absorbed. We cannot dictate to the process to say that only NH_3 gets absorbed. Therefore, since it is possible that naphtha could absorb lighter hydrocarbons also due to the existing absorption factors for various components. Henceforth, it is important to note that naphtha rich with hydrocarbons needs to be stabilized. This stabilization requires either stripping or any other operation. By bringing in stripping, we are complicating of using another distillation unit and once again energy requirements for that column. Instead of that, simply the naphtha is fed to the phase separator to enable the stabilization of naphtha in the phase separator itself.

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Refinery Supporting Processes

12.1 Introduction

- In this lecture, we present a brief overview of the refinery supporting processes.
- If we analyze the petroleum refinery, other than hydrocarbon balances, two other components balances need to be considered.
- These are sulphur and hydrogen.
- It is a fact that the refinery has good number of hydrotreaters which needs to be fed with hydrogen to generate the H_2S. This hydrogen is primarily generated from the catalytic reforming unit.
- Now the question that are posed in the refinery are
  - How to handle H_2S for following environmental legislations
  - How to purify the reformer H_2 gas stream to meet the required inlet specifications in various hydrotreaters, hydrocracking and isomerisation units.
  - How to produce H_2 additionally, as the reformer off gas may not be able to meet the H_2 demands in various hydrotreaters.
- When the above question is answered, in due course, we get the two major supporting processes
  - Hydrogen production and purification process
  - Sulfur recovery process.
- We first discuss hydrogen production and purification process followed with the sulphur recovery process.

12.2 Hydrogen production

- Hydrogen can be produced in many ways namely
  - Partial oxidation of heavy ends
  - Steam reforming of various product stocks
  - Methane steam reforming.
- Amongst these, methane steam reforming is more famous for hydrogen production
- Depending upon the process, the hydrogen production consists of four basic reactions
  - Reforming: Here, methane reacts with water molecules to form CO and H_2 at about 20 bar and 800 ^{o}C. The reacton is endothermic.
  - CO shift reaction: In this reaction, CO is converted to CO_2 and H_2 by reacting with water. The reaction is usually carried out on a catalyst. There are two types of shift reactions namely high temperature shift or low temperature shift. In the high temperature shift, the reaction is

carried out on iron oxide or chromia catalyst at about 350 – 550 °C. In the low temperature shift, the reaction is carried out at 200 – 250 °C using copper or zinc oxide on alumina.

  - Gas purification: The CO_2 is separated by passing the product gases through amine scrubber
  - Methanation: The remaining CO_2 and CO are converted back to methane using nickel-alumina catalyst in a reversible reaction scheme at 400 °C.

12.3 Hydrogen production technology (Figure 12.1)

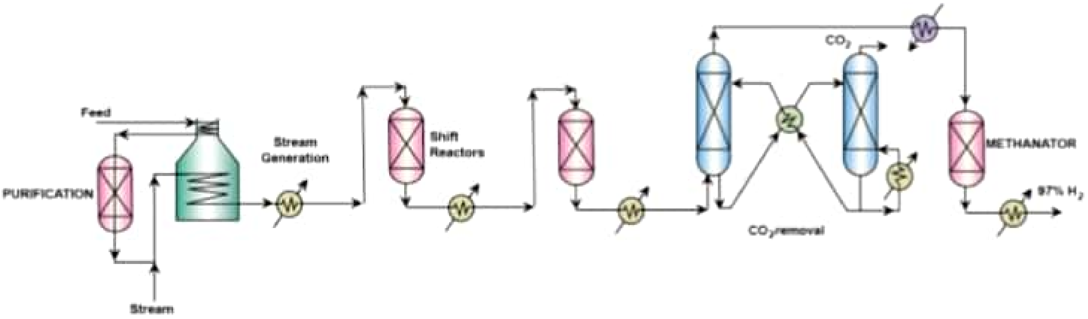

Figure 12.1 Flow sheet of Hydrogen Production Technology

- **Feed purification:** Feed pretreated to remove sulphur and halogens traces. H_2S is removed using zinc oxide catalysts. Organic sulphur removed by hydrotreating and H_2S removal from the feed. Halogens are removed using adsorption technique.
- **Furnace reactor:** The methane steam reforming reaction occurs in a furnace which is fed with the hydrocarbons mixed with steam. The steam to carbon ratio varies and is about 2.5 – 3.5. The furnace reactor consists of reactor tubes packed in the furnace chamber. The reactor tubes consist of the nickel oxide catalyst for carrying out the reaction.
- **Shift reactors:** The furnace reactor product is sent to both high temperature and low temperature shift reactors. It is interesting to note that these reactors operate at low temperatures. Therefore, cooling is carried out for the furnace reactor product and steam is generated. Similarly, steam is generated after the high temperature shift reactor also.
- **Absorber stripper:** The absorber stripper is used for CO_2 removal of the product emanating from the low temperature shift reactor.
- **Methanation reactor:** Here, traces of the CO_2 and CO are converted to CH_4 and H_2O using nickel catalyst and reversible reaction scheme. The product from methanation reaction consists of 97 % H_2.

- Alternatively, in some modern refineries, the low temperature shift reactor product is fed to a pressure swing adsorption (PSA) unit which produces 99.9 % hydrogen as a main product.
- The PSA also produces a tail gas which is used as a fuel in the furnace used in the reformer process.

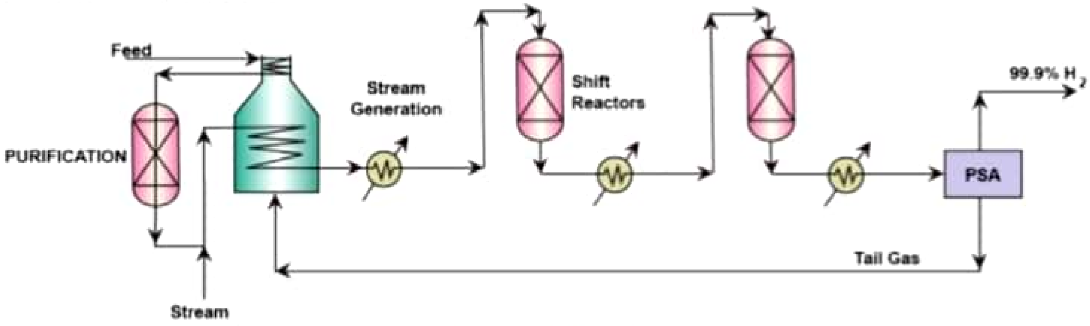

Figure 12.2 Methanation Reactor

- PSA technology also is incapable for CO and CO_2 removal as the adsorbents are not competent enough to separate these components to a large extent. But they can effectively do separation when hydrocarbons are present but not oxides in the hydrogen rich stream. Therefore, from PSA perspective as well it is important to remove CO_2 bulk with amine scrubbing followed with methanation reaction for both CO and CO_2 conversion.

12.4 Claus sulphur recovery process technology (Figure 12.3)

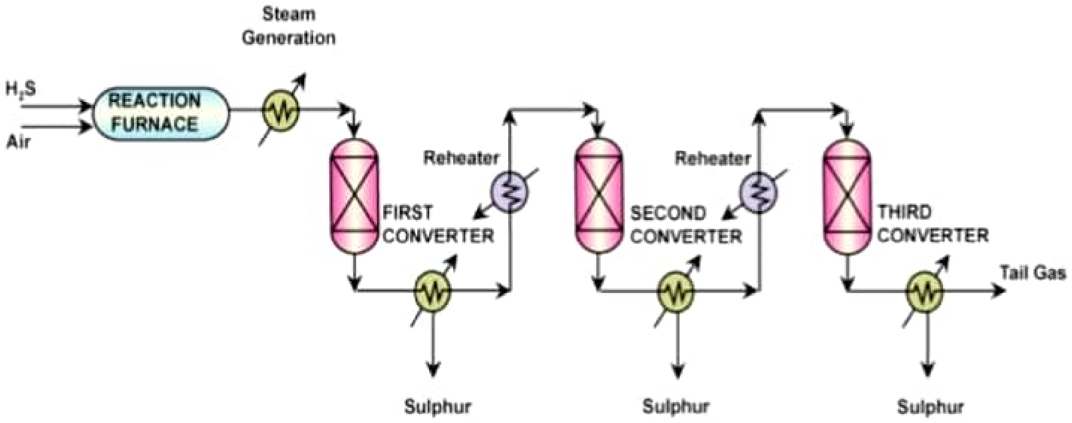

Figure 12.3 Flow sheet of Claus Sulphur Recovery Process Technology

- In a furnace reactor, H_2S is partially oxided with air to produce water and SO_2. The reaction is highly exothermic. Therefore, steam is generated using the products from the furnace reactor.
- The remaining H_2S is then sent to a converter at about 250 °C to allow the reaction between H_2S and SO_2 and produce Sulfur and water. The emanating product is at 290 °C
- The second reactor (H_2S to SO_2) is having severe equilibrium limitations. Therefore, it is sent to two to three reactors for maximizing conversion.
- After each converter, the product stream is cooled and sent to another reactor. Subsequently, Sulphur is removed as a product from the coolers.
- Finally tail gas is obtained from the last converter which consists of unreacted H_2S, N_2 and O_2.
- The tail gas requires treatment as well. This is because the gas consists of components such as H_2S, CS_2 etc. The tail gas is fed with air to another burner and converter that converts sulphur compounds to H_2S.The H_2S thus generated is separated using amine scrubbers. The H_2S thus recovered is sent as a recycle stream to the partial oxidation reactor.

12.5 Technical questions

1. **How good is conversion in the steam methane reforming reaction?**

Ans: By maintaining good process conditions, the conversion of the methane steam reforming reaction can be achieved to about 60 – 80 % in a single furnace reactor. Therefore, a single furnace reactor is sufficient to achieve the desired conversion.

2. **Why methanation cannot be avoided in the hydrogen production process?**

Ans: The trace gases CO and CO_2 are reactive towards the catalysts due to the presence of oxygen molecule. Therefore, H_2 sent to various other units should be bereft of the CO and CO_2 which can poison the catalyst due to the reactive oxygen molecule.

3. **Why CO_2 bulk removal is targeted in the hydrogen production process?**

Ans: CO_2 bulk production if avoided will affect the product quality. The methanation catalyst is not competent to fully convert CO_2 back to methane due to the reversibility of the reaction. Therefore, CO_2 removal is required.

4. **What oppurtunites exist for heat integration in the hydrogen production process?**

Ans: The feed to the process needs pre-heating therefore, is a cold steam. Now this stream can be integrated with the furnace itself where the combustion gases can be used to pre-heat the stream. Other than this the