Lecture 3: Petroleum Refining Overview

In this lecture, we present a brief overview of the petroleum refining, a prominent process technology in process engineering.

3.1 Crude oil

Crude oil is a multicomponent mixture consisting of more than $10^8$ compounds. Petroleum refining refers to the separation as well as reactive processes to yield various valuable products. Therefore, a key issue in the petroleum refining is to deal with multicomponent feed streams and multicomponent product streams. Usually, in chemical plants, we encounter streams not possessing more than 10 components, which is not the case in petroleum refining. Therefore, characterization of both crude, intermediate product and final product streams is very important to understand the processing operations effectively.

3.2 Overview of Refinery processes

Primary crude oil cuts in a typical refinery include gases, light/heavy naphtha, kerosene, light gas oil, heavy gas oil and residue. From these intermediate refinery product streams several final product streams such as fuel gas, liquefied petroleum gas (LPG), gasoline, jet fuel, kerosene, auto diesel, lubricants, bunker oil, asphalt and coke are obtained. The entire refinery technology involves careful manipulation of various feed properties using both chemical and physical changes.

Conceptually, a process refinery can be viewed upon as a combination of both physical and chemical processes or unit operations and unit processes respectively. Typically, the dominant physical process in a refinery is the distillation process that enables the removal of lighter components from the heavier components. Other chemical processes such as alkylation and isomerisation are equally important in the refinery engineering as these processes enable the reactive transformation of various functional groups to desired functional groups in the product streams.

3.3 Feed and Product characterization

The characterization of petroleum process streams is approached from both chemistry and physical properties perspective. The chemistry perspective indicates to characterize the crude oil in terms of the functional groups such as olefins, paraffins, naphthenes, aromatics and resins. The dominance of one or more of the functional groups in various petroleum processing streams is indicative of the desired product quality and characterization. For instance, the lighter fractions of the refinery consist of only olefins and paraffins. On the other hand, products such as petrol should have high octane number which is a characteristic feature of olefinic and aromatic functional groups present in the product stream.
The physical characterization of the crude oil in terms of viscosity, density, boiling point curves is equally important. These properties are also indicative of the quality of the product as well as the feed. Therefore, in petroleum processing, obtaining any intermediate or a product stream with a defined characterization of several properties indicates whether it is diesel or petrol or any other product. This is the most important characteristic feature of petroleum processing sector in contrary to the chemical process sector.

The product characterization is illustrated now with an example. Aviation gasoline is characterized using ASTM distillation. The specified temperatures for vol% distilled at 1 atm. Are 158 °F maximum for 10 % volume, 221 °F maximum for 50 % volume and 275 °F maximum for 90% volume. This is indicative of the fact that any product obtained in the refinery process and meets these ASTM distillation characteristics is anticipated to represent Aviation gasoline product. However, other important properties such as viscosity, density, aniline product, sulphur density are as well measured to fit within a specified range and to conclude that the produced stream is indeed aviation gasoline.

3.4 Important characterization properties

Numerous important feed and product characterization properties in refinery engineering include

- API gravity
- Watson Characterization factor
- Viscosity
- Sulfur content
- True boiling point (TBP) curve
- Pour point
- Flash and fire point
- ASTM distillation curve
- Octane number

3.4.1 API gravity

API gravity of petroleum fractions is a measure of density of the stream. Usually measured at 60 °F, the API gravity is expressed as

\[ {^0}\text{API} = 141.5/\text{specific gravity} – 131.5 \]

where specific gravity is measured at 60 °F.

According to the above expression, 10 °API gravity indicates a specific gravity of 1 (equivalent to water specific gravity). In other words, higher values of API gravity indicate lower specific gravity and therefore lighter
crude oils or refinery products and vice-versa. As far as crude oil is concerned, lighter API gravity value is desired as more amount of gas fraction, naphtha and gas oils can be produced from the lighter crude oil than with the heavier crude oil. Therefore, crude oil with high values of API gravity are expensive to procure due to their quality.

3.4.2 Watson characterization factor

The Watson characterization factor is usually expressed as

\[ K = \frac{(T_B)^{1/3}}{\text{specific gravity}} \]

Where \( T_B \) is the average boiling point in degrees R taken from five temperatures corresponding to 10, 30, 50, 70 and 90 volume % vaporized.

Typically Watson characterization factor varies between 10.5 and 13 for various crude streams. A highly paraffinic crude typically possesses a K factor of 13. On the other hand, a highly naphthenic crude possesses a K factor of 10.5. Therefore, Watson characterization factor can be used to judge upon the quality of the crude oil in terms of the dominance of the paraffinic or naphthenic components.

3.4.3 Sulfur content

Since crude oil is obtained from petroleum reservoirs, sulphur is present in the crude oil. Usually, crude oil has both organic and inorganic sulphur in which the inorganic sulphur dominates the composition. Typically, crude oils with high sulphur content are termed as sour crude. On the other hand, crude oils with low sulphur content are termed as sweet crude. Typically, crude oil sulphur content consists of 0.5 – 5 wt % of sulphur. Crudes with sulphur content lower than 0.5 wt % are termed as sweet crudes. It is estimated that about 80 % of world crude oil reserves are sour.

The sulphur content in the crude oil is responsible for numerous hydrotreating operations in the refinery process. Strict and tighter legislations enforce the production of various consumer petroleum products with low quantities of sulphur (in the range of ppm). Presently, India is heading towards the generation of diesel with Euro III standards that indicates that the maximum sulphur content is about 500 ppm in the product. This indicates that large quantities of inorganic sulphur needs to be removed from the fuel. Typically, inorganic sulphur from various intermediate product streams is removed using hydrogen as hydrogen sulphide.

A typical refinery consists of good number of hydrotreaters to achieve the desired separation. The hydrotreaters in good number are required due to the fact that the processing conditions for various refinery intermediate process streams are significantly different and these streams cannot be blended together as well due to their diverse properties which were achieved
using the crude distillation unit. More details with respect to the hydrotreating units will be presented in the future lectures.

3.4.4 TBP/ASTM distillation curves

The most important characterization properties of the crude/intermediate/product streams are the TBP/ASTM distillation curves. Both these distillation curves are measured at 1 atm pressure. In both these cases, the boiling points of various volume fractions are being measured. However, the basic difference between TBP curve and ASTM distillation curve is that while TBP curve is measured using batch distillation apparatus consisting of no less than 100 trays and very high reflux ratio, the ASTM distillation is measured in a single stage apparatus without any reflux. Therefore, the ASTM does not indicate a good separation of various components and indicates the operation of the laboratory setup far away from the equilibrium.

3.4.5 Viscosity

Viscosity is a measure of the flow properties of the refinery stream. Typically in the refining industry, viscosity is measured in terms of centistokes (termed as cst) or saybolt seconds or redwood seconds. Usually, the viscosity measurements are carried out at 100 °F and 210 °F. Viscosity is a very important property for the heavy products obtained from the crude oil. The viscosity acts as an important characterization property in the blending units associated to heavy products such as bunker fuel. Typically, viscosity of these products is specified to be within a specified range and this is achieved by adjusting the viscosities of the streams entering the blending unit.

3.4.6 Flash and fire point

Flash and fire point are important properties that are relevant to the safety and transmission of refinery products. Flash point is the temperature above which the product flashes forming a mixture capable of inducing ignition with air. Fire point is the temperature well above the flash point where the product could catch fire. These two important properties are always taken care in the day to day operation of a refinery.

3.4.7 Pour point

When a petroleum product is cooled, first a cloudy appearance of the product occurs at a certain temperature. This temperature is termed as the cloud point. Upon further cooling, the product will ceases to flow at a temperature. This temperature is termed as the pour point. Both pour and cloud points are important properties of the product streams as far as heavier products are concerned. For heavier products, they are specified in a
desired range and this is achieved by blending appropriate amounts of lighter intermediate products.

3.4.8 Octane number

Though irrelevant to the crude oil stream, the octane number is an important property for many intermediate streams that undergo blending later on to produce automotive gasoline, diesel etc. Typically gasoline tends to knock the engines. The knocking tendency of the gasoline is defined in terms of the maximum compression ratio of the engine at which the knock occurs. Therefore, high quality gasoline will tend to knock at higher compression ratios and vice versa. However, for comparative purpose, still one needs to have a pure component whose compression ratio is known for knocking. Iso-octane is eventually considered as the barometer for octane number comparison. While iso-octane was given an octane number of 100, n-heptane is given a scale of 0. Therefore, the octane number of a fuel is equivalent to a mixture of iso-octane and n-heptane that provides the same compression ratio in a fuel engine. Thus an octane number of 80 indicates that the fuel is equivalent to the performance characteristics in a fuel engine fed with 80 vol % of iso-octane and 20 % of n-heptane.

Octane numbers are very relevant in the reforming, isomerisation and alkylation processes of the refining industry. These processes enable the successful reactive transformations to yield long side chain paraffins and aromatics that possess higher octane numbers than the feed constituents which do not consist of higher quantities of constituents possessing straight chain paraffins and non-aromatics (naphthenes).

3.5 Crude chemistry

Fundamentally, crude oil consists of 84 – 87 wt % carbon, 11 – 14 % hydrogen, 0 – 3 wt % sulphur, 0 – 2 wt % oxygen, 0 – 0.6 wt % nitrogen and metals ranging from 0 – 100 ppm. Understanding thoroughly the fundamentals of crude chemistry is very important in various refining processes. The existence of compounds with various functional groups and their dominance or reduction in various refinery products is what is essentially targeted in various chemical and physical processes in the refinery.

Based on chemical analysis and existence of various functional groups, refinery crude can be broadly categorized into about 9 categories summarized as
3.5.1 **Paraffins:** Paraffins refer to alkanes such as methane, ethane, propane, n and iso butane, n and iso pentane. These compounds are primarily obtained as a gas fraction from the crude distillation unit.

3.5.2 **Olefins:** Alkenes such as ethylene, propylene and butylenes are highly chemically reactive. They are not found in mentionable quantities in crude oil but are encountered in some refinery processes such as alkylation.
3.5.3 Naphthenes: Naphthenes or cycloalkanes such as cyclopropane, methyl cyclohexane are also present in the crude oil. These compounds are not aromatic and hence do not contribute much to the octane number. Therefore, in the reforming reaction, these compounds are targeted to generate aromatics which have higher octane numbers than the naphthenes.
3.5.4 Aromatics: Aromatics such as benzene, toluene o/m/p-xylene are also available in the crude oil. These contribute towards higher octane number products and the target is to maximize their quantity in a refinery process.

![Benzene (C₆H₆)](image1)
![Toluene (C₇H₈)](image2)
![Para-Xylene (C₈H₁₀)](image3)

![Ortho-Xylene (C₈H₁₀)](image4)
![Meta-Xylene (C₈H₁₀)](image5)

3.5.5 Napthalenes: Polynuclear aromatics such as napthalenes consist of two or three or more aromatic rings. Their molecular weight is usually between 150 – 500.
Organic sulphur compounds: Not all compounds in the crude are hydrocarbons consisting of hydrogen and carbon only. Organic sulphur compounds such as thiophene, pyridine also exist in the crude oil. The basic difficulty of these organic sulphur compounds is the additional hydrogen requirements in the hydrotreaters to meet the euro III standards. Therefore, the operating conditions of the hydrotreaters is significantly intense when compared to those that do not target the reduction in the concentration of these organic sulphur compounds. Therefore, ever growing environmental legislations indicate technology and process development/improvement on the processing of organic sulphur compounds.

3.5.6 Oxygen containing compounds: These compounds do not exist 2 % by weight in the crude oil. Typical examples are acetic and benzoic acids. These compounds cause corrosion and therefore needs to be effectively handled.

3.5.7 Resins: Resins are polynuclear aromatic structures supported with side chains of paraffins and small ring aromatics. Their molecular weights vary between 500 – 1500. These compounds also contain sulphur, nitrogen, oxygen, vanadium and nickel.

3.5.8 Asphaltenes: Asphaltenes are polynuclear aromatic structures consisting of 20 or more aromatic rings along with paraffinic and naphthenic chains. A crude with high quantities of resins and asphaltenes (heavy crude) is usually targeted for coke production.

3.6 Technical Questions:

1. 3.6.1 Explain how crude quality affects the topology of refinery configuration?

A: This is a very important question. Usually, refinery crudes are characterized as light, moderate and heavy crudes. Light and moderate crudes are typically targeted for gas, naphtha, diesel, light and heavy gas oil fractions. Heavy crudes are targeted for coke and residue product streams. Therefore, the crude quality does affect the topology of the refinery configuration. According to the choice of the crude available, refineries are classified into four types namely

a) Those that target fuels. This is very prominent in a country like India
b) Those that target coke. This is very much targeted for refineries that supply coke as an important raw materials to other industries such as steel, catalysts etc.
c) Lubricants.
d) Petrochemicals.
According to the desired product palette, the refinery configuration and hence topology is affected with the crude quality.

2. **3.6.2 What is the basic difference between a chemical and a refinery process?**

A: A chemical process essentially involves streams whose composition is fairly known. As far as refinery processes are concerned, their chemical constituents are not exactly known but are estimated as functions of various measurable properties such as viscosity, cetane number, octane number, flash point, TBP/ASTM distillation etc.

Therefore, refinery process technology should accommodate the details pertaining to these issues in addition to the technology issues.

3. **3.6.3 Why are refinery process flow sheets very complex?**

A: Well, large refineries involve the production of about 30 to 40 refinery products with diverse specifications and needs of the consumers. And necessarily all these products are derived from the crude oil in a complex way. Due to complicated physical and chemical processes that are sequentially applied for various refinery process streams, refinery process flow sheets are very complex.

4. **3.6.4 How to analyze refinery process flow sheets in a simple way?**

Identify

a) Functional role of each process/operation
b) Plausible changes in property characteristics such as octane number or viscosity etc.

This way refinery technology will be easy to understand with maturity.

5. **3.6.5 Relate the important crude oil cuts and associated products**

a. Gases
   i. Fuel gas
   ii. LPG
b. Naphtha
   a. Gasoline
   b. Jet fuel
c. Kerosene
   a. Jet fuel
   b. Kerosene
d. Light gas oil
   a. Auto Diesel
   b. Tractor Diesel
   c. Home heating oil

e. Heavy gas oil
   a. Commercial heating oil
   b. Industrial heating oil
   c. Lubricants

f. Residues
   a. Bunker oil
   b. Asphalt
   c. Coke

References:


Lecture 4: Overview of Refinery Processes

4.1 Introduction

In this lecture, a brief overview of various refinery processes is presented along with a simple sketch of the process block diagram of a modern refinery. The sketch of the modern refinery indicates the underlying complexity and the sketch is required to have a good understanding of the primary processing operations in various sub-processes and units.

4.2 Refinery flow sheet

We now present a typical refinery flowsheet for the refining of middle eastern crude oil. There are about 22 units in the flowsheet which themselves are complex enough to be regarded as process flow sheets. Further, all streams are numbered to summarize their significance in various processing steps encountered in various units. However, for the convenience of our understanding, we present them as units or blocks which enable either distillation in sequence or reactive transformation followed by distillation sequences to achieve the desired products.

The 22 units presented in the refinery process diagram are categorized as

- Crude distillation unit (CDU)
- Vacuum distillation unit (VDU)
- Thermal cracker
- Hydrotreaters
- Fluidized catalytic cracker
- Separators
- Naphtha splitter
- Reformer
- Alkylation and isomerisation
- Gas treating
- Blending pools
- Stream splitters
A brief account of the above process units along with their functional role is presented next with simple conceptual block diagrams representing the flows in and out of each unit.

**a) Crude distillation unit**
The unit comprising of an atmospheric distillation column, side strippers, heat exchanger network, feed de-salter and furnace as main process technologies enables the separation of the crude into its various products. Usually, five products are generated from the CDU namely gas + naphtha, kerosene, light gas oil, heavy gas oil and atmospheric residue (**Figure 4.1a**). In some refinery configurations, terminologies such as gasoline, jet fuel and diesel are used to represent the CDU products which are usually fractions emanating as portions of naphtha, kerosene and gas oil. Amongst the crude distillation products, naphtha, kerosene have higher product values than gas oil and residue. On the other hand, modern refineries tend to produce lighter components from the heavy products. **Therefore, reactive transformations (chemical processes) are inevitable to convert the heavy intermediate refinery streams into lighter streams.**

**Operating Conditions :** The temperature at the entrance of the furnace where the crude enters is 200 – 280°C. It is then further heated to about 330 – 370°C inside the furnace. The pressure maintained is about 1 barg.

**b) Vacuum distillation unit (VDU)**
The atmospheric residue when processed at lower pressures does not allow decomposition of the atmospheric residue and therefore yields LVGO, HVGO and vacuum residue (**Figure 4.1b**). The LVGO and HVGO are eventually subjected to cracking to yield even lighter products. The VDU consists of a main vacuum distillation column supported with side strippers to produce the desired products. **Therefore, VDU is also a physical process to obtain the desired products.**

**Operating Conditions :** The pressure maintained is about 25 – 40 mm Hg. The temperature is kept at around 380 – 420°C.
c) **Thermal cracker**

Thermal cracker involves a chemical cracking process followed by the separation using physical principles (boiling point differences) to yield the desired products. Thermal cracking yields naphtha + gas, gasoil and thermal cracked residue (**Figure 4.1c**). In some petroleum refinery configurations, thermal cracking process is replaced with delayed coking process to yield coke as one of the petroleum refinery products.

**Operating Conditions**: The temperature should be kept at around 450 – 500°C for the larger hydrocarbons to become unstable and break spontaneously. A 2-3 bar pressure must be maintained.

d) **Hydrotreaters**

For many refinery crudes such as Arabic and Kuwait crudes, sulfur content in the crude is significantly high. Therefore, the products produced from CDU and VDU consist of significant amount of sulfur. Henceforth, for different products generated from CDU and VDU, sulfur removal is accomplished to remove sulfur as H2S using Hydrogen. The H2 required for the hydrotreaters is obtained from the reformer unit where heavy naphtha is subjected to reforming to yield high octane number reforme product and reformer H2 gas. In due course of process, H2S is produced. Therefore, in industry, to accomplish sulfur removal from various CDU and VDU products, various hydrotreaters are used. In due course of hydrotreating in some hydrotreaters products lighter than the feed are produced. For instance, in the LVGO/HVGO hydrotreater, desulfurization of LVGO & HVGO (diesel) occurs in two blocked operations and desulfurized naphtha fraction is produced along with the desulfurized gas oil main product (**Figure 4.1 f**). Similarly, for LGO hydrotreating case, along with diesel main product, naphtha and gas to C5 fraction are obtained as other products (**Figure 4.1e**). Only for kerosene hydrotreater, no lighter product is produced in the hydrotreating operation. It is further interesting to note that naphtha hydrotreater is fed with both light and heavy naphtha as feed which is desulfurized with the reformer off gas. In this process, light ends from
the reformer gas are stripped to enhance the purity of hydrogen to about 92% (Figure 4.1d). Conceptually, hydrotreating is regarded as a combination of chemical and physical processes.

**Operating Conditions:** The operating conditions of a hydrotreater varies with the type of feed.

For Naphtha feed, the temperature may be kept at around 280-425°C and the pressure be maintained at 200 – 800 psig.

e) **Fluidized catalytic cracker**

The unit is one of the most important units of the modern refinery. The unit enables the successful transformation of desulfurized HVGO to lighter products such as unsaturated light ends, light cracked naphtha, heavy cracked naphtha, cycle oil and slurry (Figure 4.1i). Thereby, the unit is useful to generate more lighter products from a heavier lower value intermediate product stream. Conceptually, the unit can be regarded as a combination of chemical and physical processes.

**Operating Conditions:** The temperature should be maintained at 34°C with pressure ranging from 75 kPa to 180 kPa. Moreover, the process is to be carried out in a relatively wet environment.

f) **Separators**

The gas fractions from various units need consolidated separation and require stage wise separation of the gas fraction. For instance, C4 separator separates the desulfurized naphtha from all saturated light ends greater than or equal to C4s in composition (Figure 4.1g). On the other hand, C3 separator separates butanes (both iso and nbutanes) from the gas fraction (Figure 4.1j). The butanes thus produced are of necessity in isomerization reactions, LPG and gasoline product generation. Similarly, the C2 separator separates the saturated C3 fraction that is required for LPG product generation (Figure 4.1k) and generates the fuel gas + H₂S product as well. All these units are conceptually regarded as physical processes.

**Operating Conditions:** Most oil and gas separators operate in the pressure range of 20 – 1500 psi.
g) Naphtha splitter
The naphtha splitter unit consisting of a series of distillation columns enables the successful separation of light naphtha and heavy naphtha from the consolidated naphtha stream obtained from several sub-units of the refinery complex (Figure 4.1n). The naphtha splitter is regarded as a physical process for modeling purposes.

Operating Conditions: The pressure is to be maintained between 1 kg/cm² to 4.5 kg/cm². The operating temperature range should be 167 – 250°C.

h) Reformer
As shown in Figure 4.1o, Heavy naphtha which does not have high octane number is subjected to reforming in the reformer unit to obtain reformate product (with high octane number), light ends and reformer gas (hydrogen). Thereby, the unit produces high octane number product that is essential to produce premium grade gasoline as one of the major refinery products. A reformer is regarded as a combination of chemical and physical processes.

Operating Conditions: The initial liquid feed should be pumped at a reaction pressure of 5 – 45 atm, and the preheated feed mixture should be heated to a reaction temperature of 495 – 520°C.

i) Alkylation & Isomerization
The unsaturated light ends generated from the FCC process are stabilized by alkylation process using iC₄ generated from the C4 separator. The process yields alkylate product which has higher octane number than the feed streams (Figure 4.1r). As isobutane generated from the separator is enough to meet the demand in the alkylation unit, isomerization reaction is carried out in the isomerization unit (Figure 4.1q) to yield the desired make up iC₄.

j) Gas treating
The otherwise not useful fuel gas and H₂S stream generated from the C2 separator has significant amount of sulfur. In the gas treating process, H₂S is successfully transformed into sulfur along with the generation of fuel gas (Figure 4.1m). Eventually, in many refineries, some fuel gas is used for
furnace applications within the refinery along with fuel oil (another refinery product generated from the fuel oil pool) in the furnace associated to the CDU.

**Operating Conditions: Gas treaters may operate at temperatures ranging from 150 psig (low pressure units) to 3000 psig (high pressure units).**

**k) Blending pools**
All refineries need to meet tight product specifications in the form of ASTM temperatures, viscosities, octane numbers, flash point and pour point. To achieve desired products with minimum specifications of these important parameters, blending is carried out. There are four blending pools in a typical refinery. While the LPG pool allows blending of saturated C3s and C4s to generate C3 LPG and C4 LPG, which do not allow much blending of the feed streams with one another (Figure 4.1t). The most important blending pool in the refinery complex is the gasoline pool where in both premium and regular gasoline products are prepared by blending appropriate amounts of n-butane, reformate, light naphtha, alkylate and light cracked naphtha (Figure 4.1u). These two products are by far the most profit making products of the modern refinery and henceforth emphasis is there to maximize their total products while meeting the product specifications. The gasoil pool (Figure 4.1v) produces automotive diesel and heating oil from kerosene (from CDU), LGO, LVGO and slurry. In the fuel oil pool (Figure 4.1w), haring diesel, heavy fuel oil and bunker oil are produced from LVGO, slurry and cracked residue.

**l) Stream splitters**
To facilitate stream splitting, various stream splitters are used in the refinery configuration. A kerosene splitter is used to split kerosene between the kerosene product and the stream that is sent to the gas oil pool (Figure 4.1h). Similarly, butane splitter splits the n-butane stream into butanes entering LPG pool, gasoline pool and isomerization unit (Figure 4.1p).
Unlike naphtha splitter, these two splitters facilitate stream distribution and do not have any separation processes built within them.

With these conceptual diagrams to represent the refinery, the refinery block diagram with the complicated interaction of streams is presented in Figure 4.2. A concise summary of stream description is presented in Table 4.1.

### 4.2 Technical questions:

1) How to remember the refinery process flow sheet in a simple way?

Ans: Well, visualize the refinery into four blocks namely the separation block, the treating block, the reactive transformation block and the rest.

The separation block consists of CDU, VDU, naphtha splitters, C4, C3 and other separators.

The treating block consists of all hydrotreaters and gas treating unit.

The reactive transformation block consists of thermal cracker (termed as cracking), alkylator, isomerizer and reformer.

The last block consists of other units such as blending units, kerosene splitter, n-butane splitter.

This way the refinery can be easily remembered after thoroughly understanding the functional role of each process.
(c) Thermal Cracker

(d) Naphtha HDS

(e) LGO Hydrotreater

(f) HGO Hydrotreater

(g) C4 Separator

(h) Kerosene Splitter

(i) FCC Unit

(j) C3 Separator
<table>
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<tr>
<th>(k) C2 Separator Unit</th>
<th>(m) Gas treating Unit</th>
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<tr>
<td><strong>SEP-C2</strong></td>
<td><strong>GT</strong></td>
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<tr>
<td>[Image 101x680 to 237x717]</td>
<td>[Image 90x411 to 226x472]</td>
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<thead>
<tr>
<th>(n) Naphtha Splitter</th>
<th>(o) Catalytic Reformer</th>
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<tr>
<td><strong>NS</strong></td>
<td><strong>CR</strong></td>
</tr>
<tr>
<td>[Image 323x528 to 459x599]</td>
<td>[Image 90x526 to 226x586]</td>
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<th>(p) n-Butane Splitter</th>
<th>(q) Isomerization Unit</th>
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<td><strong>B-SP</strong></td>
<td><strong>ISO</strong></td>
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<tr>
<td>[Image 323x667 to 459x730]</td>
<td>[Image 90x411 to 226x472]</td>
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<th>(r) Alkylation Unit</th>
<th>(s) LVGO Splitter</th>
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<td><strong>LVGO-SP</strong></td>
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<td>[Image 90x526 to 226x586]</td>
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<th>(u) Gasoline Pool</th>
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<td><strong>LPGP</strong></td>
<td><strong>GP</strong></td>
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<td>[Image 90x411 to 226x472]</td>
<td>[Image 323x528 to 459x599]</td>
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Figure 4.1: Summary of prominent sub-process units in a typical petroleum refinery complex.

(v) Gasoil Pool

(w) Fuel Oil Pool
<table>
<thead>
<tr>
<th>Stream Make</th>
<th>Source</th>
<th>Destination</th>
<th>Functional Role</th>
</tr>
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<tbody>
<tr>
<td>Crude oil</td>
<td>Market</td>
<td>CDU</td>
<td>Separation</td>
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<td>Gas + Naphtha</td>
<td>CDU</td>
<td>N-HDS</td>
<td>Sulfur removal</td>
</tr>
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<td>Kerosene</td>
<td>CDU</td>
<td>L-HDS</td>
<td>Sulfur removal</td>
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<td>Light Gas oil</td>
<td>CDU</td>
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<td>CDU</td>
<td>VDU</td>
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<td>Light Vacuum Gas oil (LVGO)</td>
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<td>H-HDS</td>
<td>Sulfur removal</td>
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<td>N-HDS</td>
<td>Sulfur removal</td>
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<td>Treatment</td>
<td>Product</td>
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<td>L-H DS</td>
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<td>Cracked residue</td>
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<td>Hydrogen</td>
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<td>H-H DS</td>
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<td>K-SP</td>
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<td>L-H DS</td>
<td>G OP</td>
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<td>Desulfurized Gas + Naphtha</td>
<td>H-H DS</td>
<td>N-H DS</td>
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<td>LV - SP</td>
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<td>H- FC</td>
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<td>Process</td>
<td>Symbol</td>
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<td>Reactant 2</td>
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<td>d HVGO</td>
<td></td>
<td>HD S</td>
<td>C</td>
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<tr>
<td>Saturated light ends</td>
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<td>SE P-C3</td>
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<tr>
<td>Heavy cracked naphtha</td>
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<td>FC C</td>
<td>GP</td>
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<tr>
<td>Cycle oil</td>
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<td>FC C</td>
<td>G-OP</td>
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<tr>
<td>Process</td>
<td>Slurry</td>
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<td>Saturated light ends (≤ C3s)</td>
<td>SE P- C3</td>
<td>SE P- C2</td>
<td>To separate C3s from the stream</td>
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<td>SE P- C3</td>
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<td>To by-pass the stream</td>
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<td>Fuel gas + H₂S</td>
<td>SE P- C2</td>
<td>GT</td>
<td>To recover sulfur and produce Fuel gas</td>
</tr>
<tr>
<td>C3s</td>
<td>SE P- C2</td>
<td>LP GP</td>
<td>To recover sulfur and produce Fuel gas</td>
</tr>
<tr>
<td>Fuel gas</td>
<td>GT</td>
<td>Fuel gas storage tank</td>
<td>Storage</td>
</tr>
<tr>
<td>Sulfur</td>
<td>GT</td>
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<td>Storage</td>
</tr>
<tr>
<td>Desulfurized LN</td>
<td>NS</td>
<td>GP</td>
<td>To prepare Premium and Regular gasoline products</td>
</tr>
<tr>
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<td>Process Description</td>
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<td>Description</td>
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<td>Refiner off-gas</td>
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<td>Cracked Light ends</td>
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<td>Reformate</td>
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<tr>
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<td>Desulfurized LVGO</td>
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<td>C3 LPG product</td>
<td>LP GP</td>
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<td>C4 LPG product</td>
<td>LP GP</td>
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<td>Premium gasoline</td>
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<td>Auto diesel</td>
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<tr>
<td></td>
<td>Heating oil</td>
<td>GO P</td>
<td>Storage</td>
</tr>
</tbody>
</table>

K products generate premium and regular gasoline products. LVGO products generate Auto diesel and heating oil products. FO products generate haring diesel, heavy fuel oil and bunker oil.
Table 4.1: Summary of streams and their functional role as presented in Figures 4.1 and 4.2.

<table>
<thead>
<tr>
<th>Stream Type</th>
<th>Process</th>
<th>Storage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haring diesel</td>
<td>FO P</td>
<td>Storage tank</td>
</tr>
<tr>
<td>Heavy fuel oil</td>
<td>FO P</td>
<td>Storage tank</td>
</tr>
<tr>
<td>Bunker oil</td>
<td>FO P</td>
<td>Storage tank</td>
</tr>
</tbody>
</table>

Figure 4.2: Overall refinery process block diagram (Dotted lines are for H₂ stream).

References:


Lecture 5: Crude distillation

5.1 Introduction

In this section, we present a brief overview of the crude distillation process.

The first essential task for the crude oil consisting of more than $10^8$ compounds is to separate its major components based on boiling point differences. This principle is exploited in the crude distillation unit which involves energy intensive operation. Since crude distillation involves the processing of the entire feed, it remains as the most significant operation in a refinery.

Process flowsheet

The conceptual process flowsheet for the petroleum refinery is shown in the Figure 5.1. It consists of the following important sub-processes:

- Crude desalter
- Furnace
- Pre-flash column
- Crude distillation column supplemented with side columns. These columns produce the desired products
- Pump around heat exchanger units
- Heat exchanger network that facilitates energy recovery from hot product and reflux streams to heat the crude oil.
We next present the functional role of various sub-processes in the crude distillation unit.

5.1.1 Crude desalter

- Crude oil consists of dissolved salts and they tend to cause fouling and corrosion in various process equipments. Therefore, dissolved salts need to be removed using a separation process.
- The crude desalting unit is a separation process. Here, water along with other trace chemicals such as caustic and acid are allowed to enter a mixing unit along with the crude oil.
- The mixture of crude oil and water is subsequently passed through an electrostatic precipitator cum gravity settler. The electrostatic field enables the agglomeration of water droplets and aids faster gravity settling.
- An essential issue for the good performance of crude desalter is the temperature of the operation. Usually, high efficiency of salt removal is possible between 100 – 300 °F.
- Therefore, the crude oil is heated to about 250 °F before it enters the desalter unit.
- The clean desalted crude oil flows from the top of the gravity settler and the water along with other dissolved impurities is removed as a bottom product from the gravity settler unit.
- A high degree of salt removal is desired (95 – 99% removal of the dissolved salt in the crude oil). Usually, a two stage desalting process is deployed. When higher salt removal efficiencies are desired, three stage units are deployed.

5.1.2 Furnace

- The furnace is an important constituent in the crude distillation unit.
- Here, fuel oil and fuel gas (heavier products) obtained from the refining process itself are burnt to increase the crude oil temperature.
- Typically in refineries, the crude oil is heated to a temperature that enables overflash conditions in the main crude distillation column.
- The concept of overflash is that the crude is heated to such a temperature that enables an additional 5 % vaporization with respect to the residue product. In other words, the residue fraction vapoors amounting to 5 % of the total volume of the crude oil are desired.
- Depending upon the quality of the crude, the desired temperature for the crude oil is about 600 – 700 °F.
5.1.3 Pre-flash column

- The crude oil enters the pre-flash column after leaving the furnace.
- The pre-flash tower separates the lighter fractions of the already heated crude oil.
- The heavier fractions of the crude oil leave from the bottom section of the pre-flash tower.
- Both lighter and heavier streams emanating from the pre-flash tower are fed to the main crude distillation column at various sections.
- Pre-flash column enables better refluxes in the main column by distributing the streams effectively between various processing zones of the crude oil.
- Pre-flash column may or may not be included i.e., it is optional. In other words, the pre-flash column can be avoided and the heated crude oil from the furnace can be fed to the main column directly.

5.1.4 Main and Secondary distillation columns

- The distillation columns consisting of both main and secondary crude distillation columns are one of the most complex circuitries in distillation.
- The complex arrangement of distillation columns is based on research carried out with pilot plants and simulation software.
- The crude distillation columns (both main and primary) are regarded to an indirect sequence of thermally coupled distillation sequences to obtain the desired products.
- Effective distribution of vapor and reflux in the main column is a serious issue.
- The effective distribution of vapor and reflux is aided through pump around heat exchanger units.
- Live steam is also used in the recent designs. The live steam is usually at about 50 psig.
- The basic principle of using live steam stems out from several facts. Firstly, upon condensation, oil and water are very easy to separate. Secondly, steam can take significant amount of heat in terms of enthalpy. Thirdly, steam enables enhancement in relative volatility, a principle that is used in steam distillation laboratory experimental set ups. These principles together are anticipated to provide good dividends technically.
- Live steam cannot be just fed at one section of the CDU. It needs to be fed at various sections to ensure both good heat distribution and reduce relative volatilities of the hydrocarbons at various sections of the main and secondary towers.
- Therefore, live steam will enable good product quality as lighter hydrocarbons with higher relative volatilities in the bottom heavy product liquid streams will be easily stripped and carried along with the vapor.
- The only condenser in the main column is a partial condenser to facilitate the production of both gas and naptha+water stream.
- The circuitry totally avoided the existence of reboilers by introducing live steam. Therefore, much fixed costs of the column have been reduced. However, higher operating costs due to higher steam utilization rates are evident.

5.1.5 Pump-around units

- Pump around units are most essential units in the crude distillation column.
- They are used to maintain good reflux conditions in the main column and therefore the desired product quality.
- They also provide a good heat source as the liquid streams are at higher temperatures. Therefore, they are also important units in the heat exchanger network.
- The cooled liquid is sent back to a section above.
- Usually two pump arounds are used in conventional designs. However, there are crude distillation units with even three pump around units.

The circuitry connections between primary and secondary towers along with relevant pump around units are presented in Figure 5.2. It can be seen that very complex interactions exist between the main and secondary columns.
Figure 5.2: Design architecture of main and secondary columns of the CDU.

a) The main column consists of 45 trays and the secondary columns (side strippers) consist of 4 trays each. Three side strippers are used to strip the light ends from kerosene, LGO and HGO products.

b) The main column has two sections that are distinguished with respect to a flash zone. The flash zone is where the crude oil partially vaporized is fed to the main column. There are about 4 trays below the flash zone and 41 trays above the flash zone of the main column. The bottom most tray (residue
stripping tray) is numbered as 1 and the top tower tray is numbered as 45. Trays 1 to 4 process the atmospheric residue portion of the crude in the section below the flash zone.

c) Trays 5 to 10 (6 trays above the flash zone) process the HGO product portion of the crude. From tray 10, HGO draw off product is taken out (as liquid) and enters the HGO side stripper unit. From tray 10 as well, the liquid stream is drawn and sent to tray 12 via a bottom pump around unit that enables cooling of the liquid stream. The steam + light ends from the HGO side stripper enter tray 11 of the main column.

d) Trays 13 to 22 (10 trays above the HGO processing zone) process the LGO product portion of the crude. From tray 22, LGO draw off product is taken (as liquid) and sent to the LGO side stripper unit. Also, from tray 22, another liquid stream is taken out and sent to tray 24 via a top pump around unit (TPA) that enables cooling of the liquid stream. The steam + light ends from the LGO side stripper enter tray 23 of the main column.

e) Trays 24 to 34 (10 trays above the LGO processing zone) process the kerosene product portion of the crude. From tray 34, the kero draw off stream is taken and sent to the kerosene side stripper unit. The steam + light ends of the kerosene side stripper enter tray 35.

f) Trays 34 to 45 (12 trays above the Kerosene processing zone) process the naphtha product portion of the crude. **It is interesting to note that tray 34 is regarded as a tray processing both LGO as well as naphtha processing zone. This is because there is no pump around associated to the tray 34. Where pump around is associated, that tray is often ignored in counting, as it affects to a large extent the tray hydraulics and contributes less towards the separation of the components.**

g) It is interesting to note that steam enters main column at trays 1, 11, 23, 35 and therefore is present along with the vapor stream along with the hydrocarbons. Therefore, **steam balances throughout the column are very important.**

h) The cold naphtha stream obtained from the phase separator is sent back to the main column as reflux stream.
5.1.6 Heat exchanger networks

- Two heat exchanger networks exist in the crude distillation unit, one before the crude desalter and one after the crude desalter.

- The heat exchanger networks facilitate energy recovery from hot product, naphtha+steam vapor and reflux streams to heat the crude oil in an indirect heat transfer mode i.e, using heat exchangers.

- Therefore, the design and operation of a heat exchanger network is very important in the crude distillation unit.

- Further, it needs to be understood that the naphtha heat integrated condenser is a partial condenser where as all others are heat exchangers without any phase change streams.

- The heat exchanger networks enable to increase the crude oil stream temperature to about 200 – 230 °C which is significantly higher than the crude oil source temperature (about 20 – 30 °C).

- Crude distillation units without heat exchanger networks have higher furnace load targets. They also cause more pollution due to burning more fuel oil and fuel gas streams.

5.2 Technical questions

1. What is the most important aspect of main column in the CDU?

Ans: The column hydraulics with a good distribution of liquid and vapor in the CDU is the most important aspect. The entire concept of live steam at various sections, top and bottom pump arounds, over-flash is centered around this designed basic feature.

2. What similarities are there for the CDU with vacuum distillation unit?

Ans:: Both crude and vacuum distillation units have similar architecture of the main and secondary columns i.e., both have complex stream circuitries with pump arounds, heat exchanger networks and utilization of steam. Only basic difference is that while we operate the VDU at lower pressure (30 – 40 mm Hg), the operating temperatures will be lower than those in the CDU. Otherwise, the basic principles remain the same.

3. What primary disadvantage exists by using live steam in the CDU columns?

- Live steam once it enters the column does not condense anywhere, as we don’t want any condensation to happen.

- When live steam is used, vapor load increases significantly in the column
- This increases the diameter of the column at various sections. There will be of course a section that has maximum vapor load and this section will have the maximum diameter.

References:


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 H₂ 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 operation at 600 °C and 20 atms gauge pressure.
- For vacuum gas oil, catalytic cracking is usually carried out at 480 °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

- 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.
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 an 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 deutanized 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 regenerator, where the coke is burned off in air.
- This combustion also serves to heat the catalyst.
- The hot regenerated catalyst is then returned to the riser.
- Catalyst temperature raised to 620 to 750°C.
- Lower 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.

- 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 °C.
- The flue gas is obtained at 600 -760 °C and is sent for heat recovery unit to generate steam.
Figure 6.4 Moving bed reactors (MBR)

(d) Moving Bed Reactor

- 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 equilibrate 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 lose 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 takes place) 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
5. **What are the advantages of FCCRs with respect to MBRs?**
- Uniformity in heat and mass transfer (fluidization)
- Compact design
- Lower erosion
- Lower steam requirements
- Higher steam efficiency

**References:**


Lecture 7: Reforming and Isomerization

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.
### 7.4 Process parameters

- Reactor pressure: 4 – 24 barg
- Reactor temperature: 500 – 525 °C
- \( \text{H}_2 / \text{Hydrocarbon molar ratio: } 2 – 3 \)

![Flow sheet of Isomerization of n-paraffin](image)

**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 \( \text{asiso} \)-pentane has an octane number of 92.3
- Usually light napththa is used as a feed stock
7.6 Catalyst

- Platinum base catalysts are used
- AlCl₃ is used as a promoter for the catalyst
- During reaction, part of the AlCl₃ 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, AlCl₃ is recovered from the product using condensation or distillation
- The basic principle for AlCl₃ recovery is that at the reactor operating conditions, the AlCl₃ is in volatile conditions and is soluble in hydrocarbons
- After AlCl₃ is recovered from the product, it is sent back to the reactor along with the make- up AlCl₃
- 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.
7.8 Technical questions

1. Why is hydrogen used in the reforming reaction?

Ans: Hydrogen reduces the coke formation on the catalyst and therefore increases the shell life of the highly expensive platinum catalyst.

2. Why is reforming a very important process in the refinery?

Ans: The reforming is one of the most important operation in the refinery to enhance product quality. Further, the total hydrogen requirement in the refinery for various hydrotreaters is produced in the reforming process. Therefore, the reformer contributes to both most important requirements of the refinery.

3. Looking at the process flow-sheet of the reforming and isomerisation process, what insights you gain towards the flowsheet evolution?

Ans: Both reforming and isomerisation flow sheets are typical examples of reactor-separator-recycle systems that are extensively studied in process synthesis and evaluation studies. These flow sheets are candidate examples to illustrate the process development required for other non-conventional and novel technologies such as bio-fuel processing etc.

4. What research contributions can be provided by chemical engineers to both reforming and isomerisation reactions?

Ans: Both reforming and isomerisation reactions are centrally built upon the catalyst. Therefore, catalyst engineering is the most important area where research contribution by chemical engineers will be of paramount significance. In fact, process modifications of the entire petroleum refinery are dictated by catalyst engineering and energy integration research.

5. Why is make up AlCl₃ required in the isomerisation process?

Ans: A part of the AlCl₃ gets converted to the HCl and therefore gets lost. The make up AlCl₃ therefore replaces the lost HCl in the process.

6. Comment upon the HCl distribution between light ends and bottom liquid product in the flash drum?

Ans: Most of the HCl distributes towards the liquid phase only. Little quantities of HCl enter the light end stream (gas phase). The distribution of HCl is dictated by the operating conditions of the flash drum.
References:


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 tetrahydrofuran 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 H\textsubscript{2}S and NH\textsubscript{3} and will be sent out to a sour water processing unit to recover H\textsubscript{2}S and NH\textsubscript{3}. The sour water processing unit uses amine based absorption technology to recover H\textsubscript{2}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 H\textsubscript{2}, C1-C4, H\textsubscript{2}S and NH\textsubscript{3}.
- The gas stream emanating from the phase separator consists of 60 – 90 % H\textsubscript{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\textsubscript{2}S removal.
- When high sulphur feeds are used, H\textsubscript{2}S removal is carried out by placing an additional absorber unit (with amine as an absorbent) to reduce higher concentrations of H\textsubscript{2}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 H₂ 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 \( \frac{H_2}{Naphtha} \) 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:


Lecture 9: Alkylation

9.1 Introduction

- In this lecture we present a brief overview of the alkylation process.
- In an alkylation process, olefins are reacted with isoparaffins to yield alkylate product.
- The basic purpose of alkylation is to enhance the octane number of the feed stock.
- For instance, octane number of butane alkylate is about 92 – 97. This is due to the formation of a hydrocarbon with side chain arrangement of carbon and hydrogen atoms.

9.2 Reaction Mechanism

- There are three basic reaction steps to achieve alkylation
- Step 1 involving Carbonium ion formation: In this reaction, alkene reacts with a proton (acid catalyst) to produce a proton substituted olefin. The proton substituted olefin reacts with isoparaffin to generate a reactive carbonium ion and alkane.

\[
\begin{align*}
  &\text{C} = \text{C} - \text{C} + \text{H}^+ \quad \xrightarrow{\text{acid catalyst}} \quad \text{C} - \text{C}^+ - \text{C} \\
  \begin{array}{c}
    \text{C} \\
    \text{C} - \text{C} + \text{C} - \text{C}^+ - \text{C} \\
    \text{C}
  \end{array} & \Rightarrow & \begin{array}{c}
    \text{C} \\
    \text{C} - \text{C}^+ + \text{C} - \text{C} - \text{C}
  \end{array}
\end{align*}
\]

- Step 2 involving carbonium ion intermediate formation: In this reaction, the carbonium ion formed in step 1 reacts with the olefin to produce an intermediate carbonium ion.
Step 3 involving regeneration of carbonium ion: In this reaction, the intermediate carbonium ion reacts with the isoparaffin to produce alkylate product and carbonium ion. Thus carbonium ion is again regenerated to take part in step 2 reactions along with other additional unreacted olefin molecules.

9.3 Reaction conditions

- To avoid olefin polymerization, high isobutane to olefin ratios are used.
- Typical isobutene to olefin ratios are 5:1 to 15:1.
- Acid catalysts are used. Primarily sulphuric acid \( \text{H}_2\text{SO}_4 \) or HF are used.
- Depending on the acid catalysts chosen, the process complexity varies. We present both process technologies to indicate the pertinent process complexity.
- Reaction operating temperature: 10 - 20 °C using \( \text{H}_2\text{SO}_4 \) and 25 – 40 °C using HF
- Reaction temperature: 4.4 bar for \( \text{H}_2\text{SO}_4 \) and 7.8 bar for HF
- When \( \text{H}_2\text{SO}_4 \) is used, refrigeration is used.
- When HF is used, refrigeration is not used.
9.4 Sulfuric acid based alkylation process technology (Figure 9.1)

- **Caustic wash**: The feed mixture (olefin + C4 compounds) are first subjected to caustic wash. During caustic wash, sulphur compounds are removed and spent caustic is recycled back to the caustic wash. Fresh caustic solution is added to take care of the loss.

- **Refrigeration**: The olefin feed enters a refrigeration unit to reduce the feedstock temperature.

- **Alkylation reactor**: The reactor is arranged as a series of CSTRs with acid fed in the first CSTR and feed supplied to different CSTRs. This arrangement is for maximizing the conversion.

- In the alkylation reactor it is important to note that the olefin is the limiting reactant and isoparaffin is the excess reactant.

- The alkylator unit therefore will have two phases in due course of reaction namely the olefin + isoparaffin mixture which will be lighter and the alkylate stream which will be heavier and will be appearing as a bottom fraction if allowed to settle.

- Since excess isoparaffin is used, the isoparaffin can be easily allowed as a bypass stream.
Eventually, the alkylate product from the last reactor will be taken out as a heavy stream.

Thus, the alkylation reactor produces two streams. These are (a) isoparaffin rich organic phase and (b) alkylate rich phase along with acid and isobutane phases.

These streams should be subjected to further purification.

**Phase separator:** It so happens that the acid enters the organic rich stream and will be subjected to phase separation by settling. Similarly, the olefin/isoparaffin mixture will be also separated by gravity settling. Thus the phase separator produces three streams namely (a) olefin + isoparaffin rich phase (b) acid rich stream (c) alkylate rich stream.

**Olefin + Paraffin processing:** The olefin + paraffin stream is first subjected to compression followed by cooling. When this stream is subjected to throttling and phase separation, then the olefin + paraffin rich stream will be generated. The propane rich stream from this stream is generated as another stream in the phase separator.

**Propane defractionator:** The propane rich stream after cooling is fed to a fractionator where propane is separated from the olefin+isoparaffin mixture. The olefin+isoparaffin mixture is sent back to mix with the olefin feed.

**Caustic wash for alkylate rich stream:** The caustic wash operation ensures to completely eliminate acid concentration from the alkylate.

**Alkylate fractionation:** The alkylate is fed to a distillation column that is supplied with isobutane feed and alkylate feeds to produce isobutane as a top product and alkylate + butane mixture as a bottom product.

**Debutanizer:** The debutanizer separates butane and alkylate using the concept of distillation.
9.5 HF process technology (Figure 9.2)

- The process is similar to the sulphuric acid plant. However, additional safety issues make the process complex.
- The feed is first subjected to drying followed by pre-cooling.
- After pre-cooling the reaction mixture, the reaction mixture is fed to a reactor.
- Unlike CSTRs in series here impeller reactors are used. The reactor consists of cooling tubes to absorb the heat generated.
- The reaction products enters a settler where oil and the HF are separated.
- Since there can be traces of HF in the oil rich phase and vice-versa additional processing is followed.
- The HF rerun column removes traces of oils from the bulk of the HF. Thus HF purified will be recycled back to the reactor. The bottom product thus generated in this unit is acid oils.
- A HF stripper is used to remove the HF in lower quantities from the alkylate product. Eventually, the HF stripper produces HF that is sent back to the reactor and the alkylate product.
- The alkylate product is sent to a deisobutanizer and depropanizer units. The final alkylate product is produced by using a deflourinator which is basically a caustic wash or adsorption unit. Finally n-butane + alkylate is produced as the bottom product.
9.6 Technical questions

1. **Why isobutane is fed to the deisobutanizer unit in the sulphuric acid flow sheet?**

   Ans: The isobutane feed consists of n-butane and it should be separated so that the alkylation reactor is fed with only isobutane. Now, the issue is to use a separate distillation column for separating isobutane feed into isobutane and butane. This will incur additional costs. Therefore, instead of two separate columns, both separations are carried out in the same distillation column. Of course, costs will be saved by this concept in processing.

2. **Explain how compression and cooling will enable the separation of propane and olefin+isoparaffins mixture?**

   Ans: The separation of propane from isoparaffins and olefins is very difficult due to close boiling points of these streams. Now, compression is also required so as to avoid refrigeration system in the condenser of propane. This is also due to the fact that higher pressures increasing boiling point of the propane and enable the usage of cooling water in the condenser. On the other hand, removing heat from the system will enable adiabatic flash conditions which can be exploited to separate the propane and olefin+isoparaffin mixture. This entire operation has significant research in the field of thermodynamics and mass transfer subjects. Probably, good number of simulation studies have finally yielded the flowsheet to obtain such configurations.

3. **What are the advantages of H$_2$SO$_4$ process when compared to the HF process?**

   - Additional equipment is not need in this process. This is not the case in HF process where HF recovery or neutralization requires additional processes.
   - HF can form a toxic vapour cloud therefore, safety parameters need to be more effectively considered.
   - Higher capital costs in HF process
   - Good quality product is produced in sulphuric acid process but not the HF process.

4. **Why is deisobutanizer placed before the depropanizer?**

   Ans: Isobutane is used in excess. If propane is removed first then both the columns have high flow rates. Since column costs are proportional to the flow rates, deisobutanizer is placed before depropanizer so that the depropanizer can process less feed and hence have lower diameters and cost.
5. What additional units are there in the HF process flow sheet when compared to the sulphuric acid flow sheet?
   a. Drier
   b. Deflourinator
   c. Safety instrumentation and accessories

References:


Lecture 10: Visbreaking and Coking

10.1 Introduction

- In this lecture, we present two important processes that are used to upgrade the residue product obtained from the vacuum distillation unit.
- Significant amounts of vacuum residue is obtained from various crude oils. For instance Arabian heavy oil produces 23.2 vol% vacuum residue product.
- The residue consists of heavier hydrocarbons with molecular weights ranging from 5000 – 10000.
- Thermal cracking is most preferable for the vacuum residue.
- The vacuum residue also consists of other metals such as vanadium and nickel.
- Typically, vacuum residue is subjected to six different operations namely
  - Vacuum residue desulphurization (VRDS)
  - Residue fluid catalytic cracking (RFCC)
  - Visbreaking
  - Coking
  - Deasphalting
  - Gasification
- Amongst these, Visbreaking and coking are prominent operations that exist in many refineries and we restrict our discussion to these processes only.

10.2 Visbreaking

- In Visbreaking operation, a mild thermal cracking is carried out.
- Visbreaking produces Naphtha, Gasoil and a residue. The residue has lower viscosity and pour point and hence can easily meet the requirements of the fuel oil specifications in the fuel oil blending pool.
- Visbreaking basically breaks the long paraffinic side chains attached to aromatic structures. Due to this the residue pour point and viscosities are considerably reduced.
- Two classes of reactions occur during visbreaking
  - Cracking of side chained aromatic compounds to produce short chained aromatics and paraffins
  - Cracking of large molecules to form light hydrocarbons
10.3 Process technology (Figure 10.1)

- Visbreaking is carried out either in a coil or in a soaker.
- When coil technology is used, the mild thermal cracking is carried out in the furnace coils.
- When soaker technology is adopted, the cracking is carried out in a soaker unit that is kept immediately after the furnace.
- After cracking, the products are at high temperatures (480 °C for coiled furnace case or 430 °C for the soaker).
- After cracking, the products are cooled using quenching operation.
- Quenching is a direct heat transfer mechanism in which a hot stream is cooled with a hydrocarbon or water to reduce the temperature of the system drastically.
- After quenching, the mixture is fed to a distillation column supplemented with a side column and a partial condenser.
- From partial condenser, water, naphtha and gas are produced. Naphtha liquid stream is sent as a reflux for the column.
The side column is fed with steam and produces gas oil. Steam enhances hydrocarbon volatility as explained before in the lecture devoted towards crude distillation process.

### 10.4 Coking (Figure 10.2, 10.3)

- Coking refers to extreme thermal cracking process
- Coking is a batch reaction. 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 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 coal 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.
- 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 vapors (if any) and send them back with the feed stream. Here, the feed stream absorbs heavier hydrocarbons from the vapors generated. This is required as it is difficult to keep heavier hydrocarbons in the feed phase only due to pertinent high temperatures. 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.
- The coker products are fed to a complex distillation column i.e., main column supplemented with side columns. From the complex distillation column, naphtha, water, light gas oil and heavy gas oil are obtained.

- Additional complexities in the distillation unit are
  - Feed entering the distillation column but not the coker unit: This is to facilitate the removal of light ends from the feed (if any) and don’t subject them to cracking. This is also due to the reason that light ends are valuable commodities and we don’t want to loose them to produce cheap coke product. In this case, the bottom product from the distillation column is fed to the furnace for pre-heating and subsequent coking operation.
  - Live steam in distillation: This is to facilitate easy removal of lighter hydrocarbons in various sections.
  - Circulatory reflux (Pump around units): This is to facilitate good amount of liquid reflux in various sections of the main column. For further details, of the above two issues, please refer to the crude distillation lecture notes.
10.5 Technical questions

1. Why thermal cracking is most preferable for vacuum residue than catalytic cracking?

Ans: Since heavier compounds are present in the vacuum residue, they can totally poison the catalyst with coke deposition. Therefore, thermal but not catalytic cracking is preferred.

2. Provide technical insight for quenching?

Ans: Quenching is one of the oldest technique to control temperatures of a stream without involving indirect heat transfer. The basic advantage of the quenching is that if a cold fluid with similar chemical constitution is mixed, then it reduces the temperature of the cold fluid and increases the temperature of the quenching fluid. Quenching is also an instantaneous operation which is not the case of indirect heat transfer. Also, in indirect heat transfer, losses could be significant due to additional process resistance for heat transfer. This is not the case in quenching where the hot fluid directly comes in contact with the cold fluid. The basic disadvantage in quenching is that if a cold fluid of different chemical constitution is used then additional separation (downstream) is required. If that can be avoided, quenching is an excellent operation.

3. Are there any heat integration opportunities existent for the visbreaking operation?

Ans: No, the reason is that the vapour from the fractionators is a hot stream and the quenching stream is also a hot stream. We need atleast one cold stream and hot stream to enable heat integration.

4. Explain the reason behind recycling of intermediate process streams in fluid coker?

Ans: An essential issue in fluidization is to maintain a uniform temperature throughout the fluidized bed. To do so, partial recycle of intermediate vapour streams is carried out so that uniform temperatures are maintained.

5. Do opportunities exist in coking operation for heat integration?

Ans: Yes, they exist very much. The hot products from the complex distillation unit as well as the vapors generated from the coke drums are the hot streams. The cold stream is the feed which is subjected to pre-heated. Since we have a cold stream and good number of hot streams, we can have a good heat integration opportunity in the coking operation.
6. What is flexicoking?

Ans: In flexi coking, coke is fed to a gasifier to react with air and steam. Eventually, the coke produces hydrogen, CO, CO$_2$, N$_2$, H$_2$O and H$_2$S. The gas thus obtained is used as a fuel gas in the refinery itself for various furnace operations. Therefore, flexicoking refers to flexibly alter the coking process to produce additionally gas using an extra gasification unit.

Flow sheets to Dekaji

1. Coil visbreaker
2. Fluid coking process

Delayed coker

References:


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](image)

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\textsubscript{3} and C\textsubscript{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.
- Addition 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\textsubscript{2}SO\textsubscript{4}) are used.
- Temperature: 150 – 220 °C are used. Too high temperatures give tar deposits.
- Pressure: 25 – 100 atms.
11.5 Olefin polymerization process technology (Figure 11.2)

Figure 11.2 Flow sheet of Olefin Polymerization Technology

- **Caustic wash**: C3-C4 olefin feed subjected to caustic wash to remove H2S 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.
4. **What modification you can think in the polymerization reactor process instead of using a shell and tube design?**

Ans: Well, this is an important question. If we analyze the shell and tube design, we want to achieve simultaneous cooling of the olefin stream in the tube. Instead of cooling, we can also try cold shot technique or diluent in the stream. When diluents is used, then the diluents or inert carrier needs to be separated and its an additional task in the process. Therefore, the best possibility is to target either a cold shot feed or a cold shot product with recycle. Since conversions are low, doing cold shot with feed is not beneficial. Therefore, cold shot product will be the optimal arrangement to replace the shell and tube design. In that case, the product should be cooled and send back to the reactor.

5. **Can optionally propane be fed to the polymerization reactor?**

Ans: Few process flowsheets involve propane as well fed to the polymerization reactor, but conversions are expected to significantly low for propane. Therefore, as such much gain will not be there by feeding propane to the polymerization reactor.

**References :**


Jones D.S.J., Elements of Petroleum Processing, John Wiley & Sons, 1995


Lecture 12: 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 °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 CO₂ is separated by passing the product gases through amine scrubber
- Methanation: The remaining CO₂ 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](image)

- **Feed purification:** Feed pretreated to remove sulphur and halogens traces. H₂S is removed using zinc oxide catalysts. Organic sulphur removed by hydrotreating and H₂S 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 CO₂ removal of the product emanating from the low temperature shift reactor.

- **Methanation reactor:** Here, traces of the CO₂ and CO are converted to CH₄ and H₂O using nickel catalyst and reversible reaction scheme. The product from methanation reaction consists of 97 % H₂.
- 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.

- PSA technology also is incapable for CO and CO\textsubscript{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\textsubscript{2} bulk with amine scrubbing followed with methanation reaction for both CO and CO\textsubscript{2} conversion.

### 12.4 Claus sulphur recovery process technology (Figure 12.3)

![Figure 12.3 Flow sheet of Claus Sulphur Recovery Process Technology](image)
- In a furnace reactor, $\text{H}_2\text{S}$ is partially oxidized with air to produce water and $\text{SO}_2$. The reaction is highly exothermic. Therefore, steam is generated using the products from the furnace reactor.
- The remaining $\text{H}_2\text{S}$ is then sent to a converter at about 250 °C to allow the reaction between $\text{H}_2\text{S}$ and $\text{SO}_2$ and produce Sulfur and water. The emanating product is at 290 °C.
- The second reactor ($\text{H}_2\text{S}$ to $\text{SO}_2$) 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 $\text{H}_2\text{S}$, $\text{N}_2$ and $\text{O}_2$.
- The tail gas requires treatment as well. This is because the gas consists of components such as $\text{H}_2\text{S}$, $\text{CS}_2$ etc. The tail gas is fed with air to another burner and converter that converts sulphur compounds to $\text{H}_2\text{S}$. The $\text{H}_2\text{S}$ thus generated is separated using amine scrubbers. The $\text{H}_2\text{S}$ 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 $\text{CO}_2$ are reactive towards the catalysts due to the presence of oxygen molecule. Therefore, $\text{H}_2$ sent to various other units should be bereft of the CO and $\text{CO}_2$ which can poison the catalyst due to the reactive oxygen molecule.

3. **Why $\text{CO}_2$ bulk removal is targeted in the hydrogen production process?**

Ans: $\text{CO}_2$ bulk production if avoided will affect the product quality. The methanation catalyst is not competent to fully convert $\text{CO}_2$ back to methane due to the reversibility of the reaction. Therefore, $\text{CO}_2$ removal is required.

4. **What opportunities 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
furnace product, high and low temperature shift reactor products are also available. The choice of heat integration and steam generation at various sites in the process is a complex optimization problem and has to be addressed by solving separate problems to finally arrive at the one optimal solution. Mostly, the furnace combustion gases will be integrated for energy recovery with the feed stream and steam generation is effected from the high and low temperature shift reactors.

5. Explain how using three reactors in series will enhance equilibrium conversion of the second conversion reaction i.e, \( \text{H}_2\text{S} \) to \( \text{S} \) in Claus process?

Ans: Equilibrium conversion is a function of temperature and pressure. There are two types of equilibrium reactions namely exothermic and endothermic reactions. For exothermic reactions, the conversion increases with decreasing temperature. Therefore, after first converter, the product is cooled and sulphur is also removed. The reduction in temperature and elimination of sulphur moves the process conditions to a shift equilibrium to the right hand side. Therefore, series of chemical reactors followed with product cooling will enhance equilibrium conversion. By the by, the same concept is also used in hot and cold shot reactors. The only difference between this arrangement and the shot reactor arrangement is that there direct heat transfer by quenching or heating is allowed where as in the shown flow sheet, indirect heat transfer is facilitated only.

6. Why burner and converter are required in the tail gas processing unit?

Ans: The burner enhances the temperature of the stream and produce \( \text{H}_2 \). The produced \( \text{H}_2 \) reacts with sulphur compounds to thereby produce \( \text{H}_2\text{S} \).

References:


Jones D.S.J., Elements of Petroleum Processing, John Wiley & Sons, 1995