Term Project Report on

Crude Oil Refining

submitted on 15th November, 2021

as a part of the course

CHE313A: Mass Transfer and Its Applications

(2021-22-1)

at

Department of Chemical Engineering

Indian Institute of Technology Kanpur

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Abstract

The current scenario in the world shows that crude oil proves to be one of the most essential substances in the world. A fossil fuel, consisting mainly of hydrocarbons, varies in physical appearance such as color-from clear to tar-black and viscosity-from water to solid. Crude oil is mainly found in places which were once sea beds, and is a result of thousands of years of decomposition.

Crude oil consists of various components that differ in physical as well as chemical properties and each component consists of a specific range of hydrocarbon content by which they have a vast use throughout the world. For example, petroleum, a quite smooth and less dense liquid, is one of the major components and it has quite a number of uses, in automobile fuels, equipment, feedstock for chemicals, and a lot more. On the other hand, petroleum jelly, a relatively viscous and heavier component, is used for making moisturizers and other skin-care products. So, in order to improve the supply and quality of these components, crude oil needs to be refined well and purified to the farthest possible, with environmental hazards in mind.

These differences in physical properties of different components not only allows a variety of usage, but it also helps to adapt easier methods for refining, rather than separating each component through a series of chemical reactions. The most common method that is used in the industries nowadays is the **Fractional Distillation**. This method is based on the differences in the boiling point of different components in a given mixture which helps to separate them. This is a stepwise process, involving firstly the vaporization of crude oil to approximately 350^{o}C and is fed into the bottom of the column which consists of plates and trays at different sections. As the vapours rise, temperatures fall and the

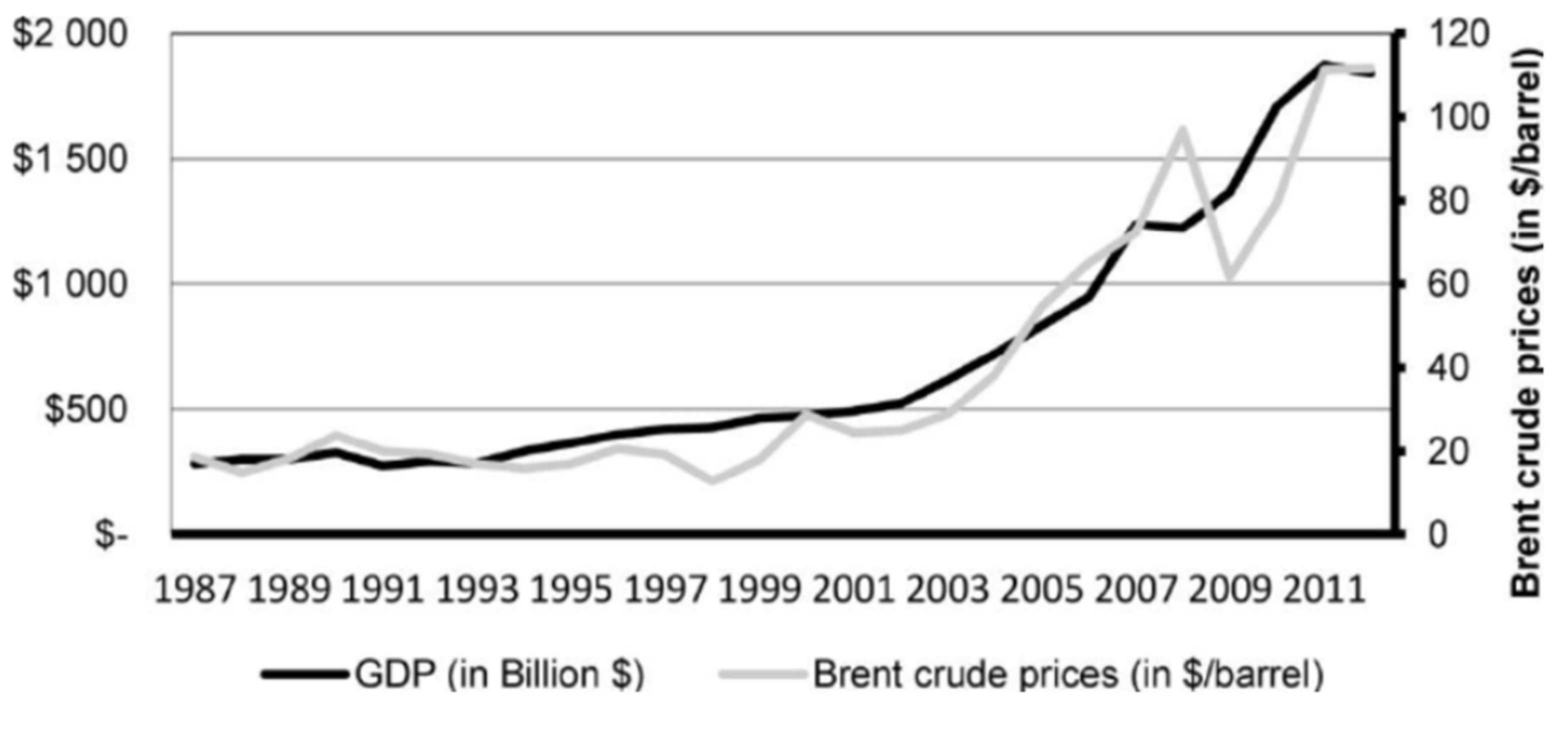
components begin to condense into liquids. The higher the boiling point, the faster and lower it condenses and thus the components are deposited at different sections in increasing order of boiling points-from top to bottom.
Even after this processing, the components separated are still not ready for the market as there is some mixing due to close boiling points and impurities, which needs to be resolved. For this, the different components are passed into various chemical processes as per need to remove impurities and increase purity. Major methods are **cracking** (breaking larger hydrocarbons into smaller ones) - consisting of thermal and catalytic cracking, **catalytic reforming** (hydrocarbons with low octane number into higher octane number hydrocarbons), **alkylation** (combining lighter hydrocarbons to give high octane number products) and **isomerization** (converting into a different isomer to increase octane number), **treating and blending** (to remove impurities, sulphur etc.). After these processes, the components are finally cooled and blended to make useful products.
This process is quite advantageous in itself as it reduces the labour of separating components by chemical reactions, avoiding the side-reaction and by-products. It is also economically good and increases the purity to a large extent. But it also has some drawbacks, such as if there are any sulphur-based hydrocarbons present in the feed, it leads to release of hazardous sulphur dioxide gas and contributes to environmental pollution. It also has some by-products such as nitrogen oxide, carbon dioxide, carbon monoxide, methane, dioxins, hydrogen fluoride, chlorine, benzene and others.
This report gives the details about crude oil and different methods to refine it, major components of crude oil, the most widely used method for refining and its working, different advantages-disadvantages of refining of crude oil along with some examples to support it.

Background

Economic Significance:

Crude oil is one of the most important fuel sources. If we consider its historical background, it has been contributing to around one-third of the world's energy consumption. It plays a significant importance to those industries and businesses that specifically rely on fuel, for e.g., airlines, plastic producers, etc. Since it is major contributor to the sources of energy, it has been a primary import and export for several countries. The importance of this commodity generates a large market financial trading market for oil and its derivatives.

Importance of crude oil to Indian economy can be clearly observed from the below figure:



Uses of various components of refined crude oil

- Sulphur: H_2S from the sour water stripper plant is converted into elemental sulphur in the Claus unit, it is used in making car batteries, fertilizers and mineral extraction and many other processes.

- Petroleum Gas: These are small alkanes with a number of carbon atom up to 4 and are used for heating, cooking etc. these are obtained from the sour water unit after removing sulphur from it.

- Gasoline: It is the major product and is about 46% of the final products, gasoline consists mainly of alkanes and cycloalkanes (5-12 carbon atoms) it is majorly used as fuel in automobiles having spark ignition internal combustion engines.

- Kerosene: It is a mixture of aromatics and alkanes of about 10 to 18 carbon atoms and is mainly used in agricultural equipment, generators and also as starting material for some other products.

- Diesel: It is another important petroleum product used in engines and heating oil, it is the second highest fraction constituting 26% and it consists of alkane having 12 or more carbon atoms.

- Lubricating oil: these are long chain carbon molecules used as grease, motor oils and lubrication

- Fuel: these are carbon molecules with up to 70 carbon atoms used as industrial fuel and jet fuel

- Residue: these heavier fractions are used to make asphalt, tar, paraffin wax, etc. having multiple applications in road construction or waterproofing.

- Petroleum feedstocks like acrylic acid, ethylene, propylene is also produced which are used in polymer and plastic industry

Problems faced due to Crude oil refining process:

- **Air Pollution**: Oil refining causes smog which leads to air pollution. By-products of this process include hazardous elements such as lead and gases such as sulphur dioxide (SO2), nitrogen oxide, carbon dioxide, carbon monoxide, methane, dioxins, hydrogen fluoride, chlorine, benzene and others. They also include very small dust particles called PM10, that get deep into our lungs and harm our ability to breathe.
- **Health Effects**: Most of the gases emitted are harmful for humans and can cause permanent damage and even death in some cases. They can cause respiratory problems such as asthma, coughing, chest pain, choking, and bronchitis, skin irritations, nausea, eye problems, headaches, birth defects, leukaemia, and cancers.
- **Sulphur Dioxide (SO_2)**: When the sulphur containing crude oil or coal is heated at the refinery to produce fuel, the sulphur gets converted into SO_2 which can cause painful irritation of the eyes, nose, mouth and throat, difficulty in breathing, nausea, vomiting, headaches and even death.

Separation Process & Unit Operations:

Fractional Distillation:

The refining process starts with fractional distillation. The various components of crude oil have different boiling temperatures, weights and sizes. So, they can be easily separated by fractional distillation.

The fractional distillation of crude oil involves various steps:

- The crude oil containing various components, is first heated to high temperature of about 350°C so as to vaporize it. The vapor is then fed into the bottom of the fractional distillation column, that is filled with trays and plates.
- The vapor then starts rising through the distillation column. As the vapor travels up the column, the temperature decreases. When a component reaches a height where the temperature is equal to that component's boiling point, it will condense to form a liquid. As a result, the components with higher boiling point condense lower in the column while the components with lower melting points condense in the upper section of the column.
- The trays collect the liquid fractions, which may be further passed through condensers.

The components of crude oil having low boiling points, are obtained at higher levels of the column and are called light distillate. The boiling point of these components range from 70 °C to 200 °C. These include gasoline, naphtha (a chemical feedstock), kerosene, jet fuel, and paraffin.

The components having boiling point in the range 200-350 °C are collected somewhere in the middle of the column, and are called middle distillates. These include diesel oil and gas oil.

The components having boiling point above 350 °C are collected in the lowest part of the column, and are called heavy distillates. This includes fuel oil.

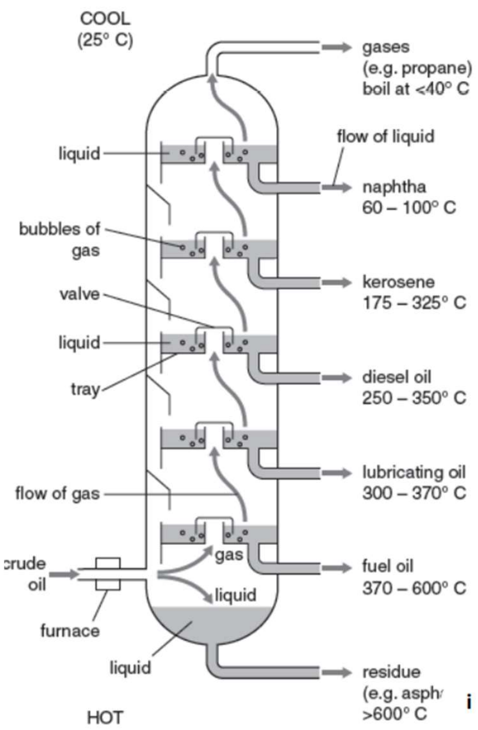


Figure 1: Fractional distillation of Crude Oil

Most of the components that come out of the fractional distillation column are not ready for market. For example, gasoline is one of the important products for oil companies so other fractions of the distillation column are chemically processed to convert them to gasoline and also to remove impurities.

Chemical processing involves the following steps:

- **Cracking**: It involves breaking of large hydrocarbons into smaller ones. Two types of cracking can be done:
  - **Thermal cracking**:
    Thermal cracker is used to carry out this process. In this, large hydrocarbons are heated to high temperatures (also high pressure if needed) until they break apart.
    (a) High temperature steam at around 816 °C is used to break naphtha, ethane and butane into ethylene and benzene. These are further used for manufacturing chemicals.
    (b) Vis breaking: This process aims to reduce the viscosity of vacuum residues and heavy weight oils. It involves heating the residue from distillation tower to around 482 °C, then cooling with gas oil and lastly, rapidly burning (or flashing) in distillation tower.
    (c) Coking: This leads to upgrade of materials from vacuum distillation column to higher value products. In this, residues are first heated to around 480 °C , until they crack into heavy oil, gasoline and naphtha. After the completion of this process, coke (heavy and pure carbon residue) is formed.

    <u>Operating conditions</u>: Temperature of around 450 °C to 500 °C and pressure of 2-3 bar should be maintained for the large hydrocarbons to break spontaneously.

  - **Catalytic cracking**:
    Fluidized catalytic cracker is used for this process. This process involves making use of catalysts like zeolite, aluminium hydro silicate, bauxite and silica-alumina to speed up the cracking reaction.
    (a) Fluid catalytic cracking: A hot, fluid catalyst heated to about 538 °C is used to crack heavy gas oil into diesel oils and gasoline.
    (b) Hydrocracking: It involves breaking of hydrocarbon molecules into simpler molecules by the addition of hydrogen gas under low temperatures and high pressures. It is similar to fluidized catalytic cracking, just that it uses different catalyst. It cracks heavy oil resulting in kerosene (jet fuel) and gasoline.
    <u>Operating conditions</u>: Temperature of around 34 °C with pressure ranging from 75kPa to 180kPa should be maintained. Also, this process should be carried out in relatively wet environment.

- **Catalytic Reforming**:
  This process is used to convert naphtha (having low octane number) into high octane liquid products (called reformates) which are premium grade gasoline. It also converts paraffins with low octane number into branched

alkanes and naphthenes, which can result into high octane aromatic on subjecting to dehydrogenation. A significant amount of hydrogen gas is also released as by product which can be used for hydrocracking.
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 ^{o}C-520^{o}C.

- **Alkylation and Isomerization**:
  Alkylation process stabilizes the unsaturated hydrocarbons produced during fluidized catalytic cracking. Isobutane is used to convert unsaturated low molecular weight compounds, like propylene and butylene to high octane alkylates, which are used in gasoline to reduce knocking. Isomerization reaction is also carried out to generate isobutane, which has been utilized during alkylation. The process is carried out in presence of catalyst such as hydrofluoric acid or sulfuric acid.

- **Treating and blending**:
  Now, these distilled and chemically processed products can be further treated to remove impurities and other organic compounds, such as sulphur, nitrogen, inorganic salts or other dissolved metals. Firstly, the products are passed through a column filled with sulphuric acid to remove unsaturated compounds, nitrogen and oxygen compounds and residues. Then, the products are further passed into an absorption column filled with drying agents so as to remove water. Lastly, these products are subjected to sulfur treatment to remove sulfur and its compounds.

After going through all these processes, the final product are cooled and blended together to yield various useful products: gasoline, lubricating oils, diesel fuel, jet fuel, kerosene, heating oil and chemical of various grades.

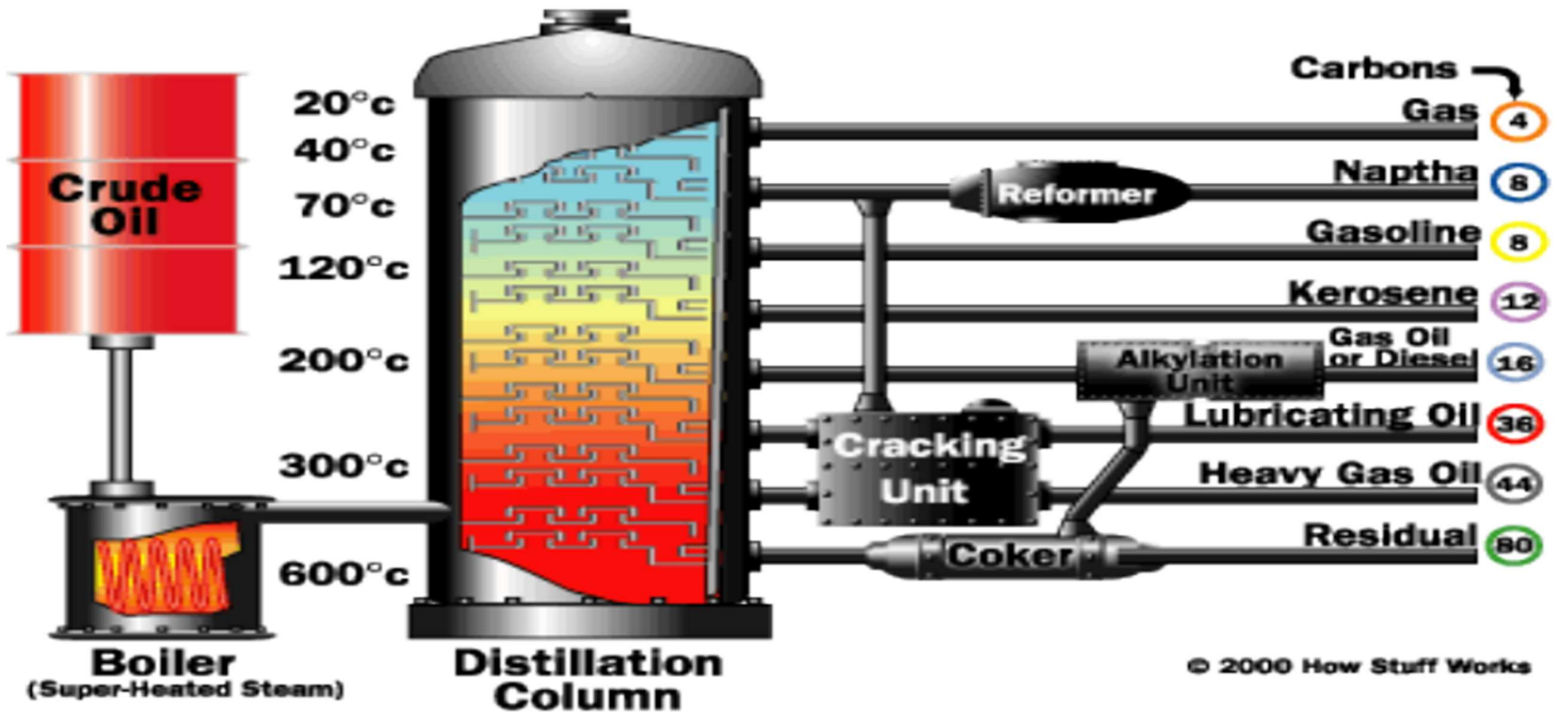


Figure 2: Complete refining process of Crude oil

Analysis and Calculations:

The design of fractionation columns is usually decided by using following two steps

a. Process design – This is done to find out number of required theoretical stages to carry out required distillation. Other quantities like reflux ratio, heat reflux can also be calculated using this.
b. Mechanical design- This is used to choose the tower internals and also calculate column height and diameter.

PROCESS DESIGN ANALYSIS:

Analysis (or assumptions)

Let us consider a fractional distillation setup filled with tray columns. We will carry out the analysis on a two-component fractional distillation column because the correct design of multi-component column involves multiple feeds and side streams. The design is also quite complex. Moreover, there are a large number of different compounds involved which are really difficult to take care of.

We can later generalise this two-component design for LDUs.

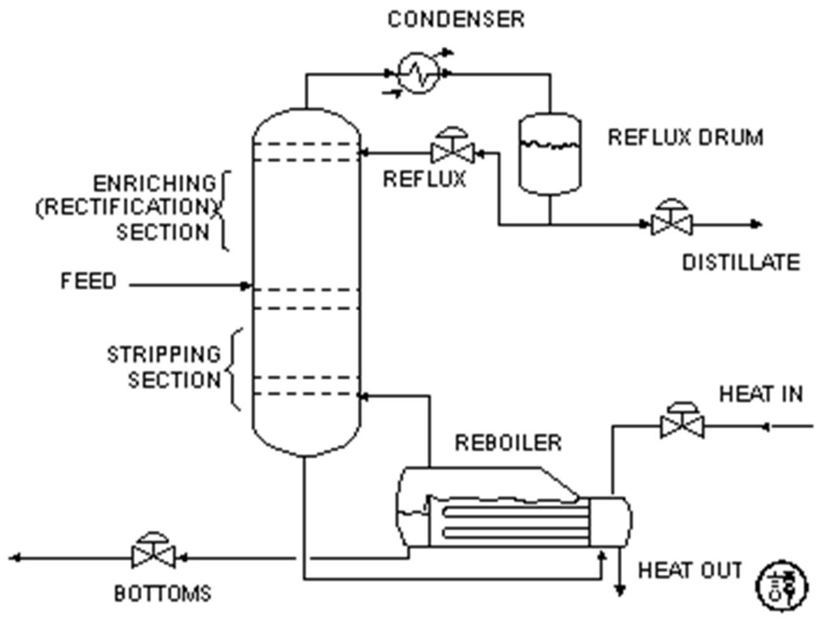


Figure 3: Design of distillation tower

For the enriching section, assuming G1, G2…Gm gas flow rates and L1, L2...Lm liquid flow rates,

For the stripping section assuming Gm, G(m+1)..Gmp gas flow rates Lm, L(m+1)..Lmp liquid flow rates.

Performing mass balances for various sections-

Enriching section:

Mass balance: $G_{n+1}y_{n+1} = Dz_D + L_n x_n$

Enthalpy balance: $G_{n+1}H_{Gn+1} = L_n H_{Ln} + DH_D + Q_c$

Stripping section:

Mass balance: $\overline{L_m}x_m = \overline{G_{m+1}}y_{m+1} + \mathrm{W}x_w$

Enthalpy balance: $\overline{L_m}x_m + Q_b = wH_w + \overline{G_{m+1}}H_{Gm+1}$

Simplifying the equations using **Mc-Cabe Thiele** approximations, i.e., assuming the molar flow rates in the enriching and the stripping sections to remain the same, we get the equations of operating lines as follows-

Enriching section:

$$y_{n+1} = \frac{R}{R+1}x_n + \frac{x_D}{R+1}$$

Stripping section-

$$y_{m+1} = \frac{\bar{L}}{\bar{L}-w} - \frac{w}{\bar{L}-w}x_w$$

The feed line equation from the overall mass balance can thus be written as-

$$y = \frac{q}{q-1}x - \frac{x_f}{q-1}$$

Where q is the amount of liquid present in feed, given by

$$q = \frac{H_G - H_F}{H_G - H_L}$$

The number of ideal trays thus required for the given conditions is obtained by plotting the operating lines and obtaining the number of optimal stairs on the curve.

MECHANICAL DESIGN ANALYSIS-

The design and operation of fractionation towers is accomplished on an empirical basis.

Column Diameter-

The proper sizing of the column diameter is essential because it ensures efficient performance and operation of fractionation columns. Column diameter also influences costs of fractionation equipment. Moreover, desired separation will not be achieved if the column diameter is not sized properly.

Souders and Brown equation is used usually for the calculating column diameter and it is given by:

$$U_V = \frac{K}{3600}\left(\frac{\rho_L - \rho_V}{\rho_V}\right)^{0.5}$$

Where:

ρ_V = Vapour density (kg/m3 or lb/ft3)

ρ_L = Liquid density (kg/m3 or lb/ft3)

K = entrainment-related factor

U_v = Maximum allowable superficial vapour velocity (ft/sec or m/sec)

K factor can be defined in terms of plate spacing and is given by following equation:

$$K = 3600(-0.171T^2 + 0.27T - 0.047)$$

where: T = plate spacing (m).

After calculating U_V, the column diameter can then be calculated using the following equation:

$$D = \left(\frac{4V}{3600\pi\rho_V U_V}\right)^{0.5}$$

Where: V = Maximum allowable vapour flow rate (kg/h or lb/h)

D = Column diameter (m or ft)

The diameter obtained in the following problem is the minimum acceptable diameter for operation.

Analysis/Assumptions:

- Fractionating column operating at 141°C.
- Plate spacing comes out to be 22 inch(using process design)
- Liquid flow rate: 65.3kg/h, Vapor flow rate:29m^3/hr.
- Let us assume that maximum allowable vapour flow rate is 83.3 kg/h.
- Average molecular weight of the crude oil = 110 gm
- Assuming liquid density to be approximately 684 kg/m^3 and vapor density to be 2.9kg/m^3.

Calculations:

Let T be plate spacing = 22 in. = 56 cm

Vapour volume flow rate = QV = 29 × 102 m3/h = 10 × 104 ft3/h

L =65.3 × 102 kg/h = 14.4 × 103 lb/h

V = 83.3 × 102 kg/h = 18.3 × 103 lb/h

ρL =42.7 lb/ft3

ρV =2.9 kg/m3 = 0.18 lb/ft3

t = 141°C (t is temperature)

M = Averages molecular weight = 110

Using the above approximate formulas, the column diameter is determined to be as follows-

$$K = 3600(-0.171T^2 + 0.27T - 0.047)$$

$$K = 3600 \times (-0.171 * 56 * 56 + 0.27 * 56 - 0.047)$$

$$K = 182.068$$

$$U_V = \frac{K}{3600}\left(\frac{\rho_L - \rho_V}{\rho_V}\right)^{0.5} = \frac{182.068}{3600}\left(\frac{42.7 - 0.18}{0.18}\right)^{0.5}$$

$$U_V = 0.7773$$

$$D = \left(\frac{4V}{3600\pi\rho_V U_V}\right)^{0.5} = \left(\frac{4 * 83.3 * 102}{3600 * 3.14 * 2.9 * 0.7773}\right)^{0.5}$$

$$D = 1.155m$$

Result:

The column diameter for the above values of the variables were also calculated using more accurate charts, MATLAB and various calculation methods given in literature. Therefore, the real value obtained was 1.2 m.

It can thus be seen that the above empirical equations give an approximate determination of the column diameter required. For satisfactory operation in the industrial conditions, the maximum flow rate may be multiplied by 1.05 to 1.15 which tolerates the loss in fractional efficiency due to entrainment.

Conclusion

In this report, we have tried to outline the importance of crude oil, uses of its various components and also the importance of its refining processes. Crude oil refining forms an important part of the industry as the petroleum products formed from it play an important role in transportation, heating and generating electricity. Despite being an energy intensive process, it is not possible to replace fractional distillation method in petrochemical industries. We have also done some analysis and calculations to calculate some of the distillation column design parameters like number of trays, trays spacing and column diameter.

Further, we will try to elaborate future prospects and challenges faced in process of crude oil refining.

Future prospects:

A constant demand of high-octane number products from the gasoline pool has driven a lot of research in the area of petroleum refining. The light fraction obtained from distillation consists of hexanes and pentanes which have a low octane number; hence they are converted into iso forms to increase the octane number but equilibrium considerations limit the conversion to 60-65 percent in one pass. So, three novel processes are being studied to overcome such problems.

- **Pennex Hydroisomerisation Process:** High activity catalyst especially Type-3 platinum containing catalyst is used in place of conventional catalysts. The equilibrium is reached at several hundred degrees lower than in catalytic reforming and a very high yield of around 90-95 percent is obtained. The entire process is eco-friendly with low investments involved.
- **Pentafining Process:** A highly selective catalyst comprising of alumina, silica and platinum is used to minimize the yield losses involved in conversion of pentane and hexane to their isomers. After reaching a certain octane number, further increase in pool-octane can be obtained economically through paraffin isomerisation. Thus, this process can be used to obtain fuels with high anti-knock properties for super –premium fuels.
- **Iso-kel Process:** In this process, for minimizing the cracking side reactions and enhance the life of conventional catalyst, copper and platinum are added in appropriate proportions. The process is carried out at the same pressure range as that of conventional catalytic reforming but at lower temperature range with increased space velocities.

Challenges:

The energy market in today's scenario is highly competitive and volatile so the oil refining industry is under constant demand to increase the efficiencies of different operations, produce better products at an economical cost along with maximizing space velocities and productivity.

- With the advent of unconventional methods of crude oil extraction, the variability in feedstock is rising rapidly. The refiners have to work with great quantities of raw material with no fixed quality parameters, thereby increasing the cost burden of refineries involved in research and development. The variability adversely affects the product quality, unit reliability and greatly hinders the process optimization efforts of refineries. The refining process has to undergo significant change in order to meet the new composition of crude oil but due to the unavailability of sufficient time for developing the new techniques has led to unexpected shutdowns, product loss and shorter running time.
- Oil refining process is energy intensive so it naturally has a lot of impact on environment. In order to, protect the earth's environment strict regulations on air and water contamination such as minimizing sulphur concentration in fuels, detoxifying the effluents before releasing into the environment and eradicating the usage of lead-based catalysts are being enforced. As a result of which, operational reconfigurations are required in many refineries which involve a lot of capital investment. As further global fuel standards are being implemented it has become very difficult to produce quality fuels at an economical rate.

Learnings:

- The products obtained from the column are further processed via cracking, reforming, alkylation, isomerization and many others to obtain variety of products such as natural gas, kerosene, diesel, residue etc. which have significant use in various industries.
- The design and the temperature and pressures the fractionating column need to be operated at needs to be carefully accessed based on different inlet/outlet compositions, flow rates, reflux ratio and many other properties. Thus, the mechanical as well as the physical design of the system can be analysed using empirical corelations available in the literature.
- The column diameter as well as other parameters for the mechanical design can be analysed, approximating the process as a two-component system and calculating variables such as the number of trays required, the height of the tower and the tray spacing. These corelations provide a good approximation to the real values and thus are widely used.

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