HYDRODESULPHURIZATION OF NAPHTHA

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CERTIFICATE

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DEDICATION

To SCME, our beloved parents, our teachers and friends without their continual support it would not have been achieved.

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ABSTRACT

Naphtha is a brownish liquid which is a mixture of specific boiling range of hydrocarbons. It is highly flammable, has aromatic smell and is obtained from the fractionation of crude oil. Naphtha is major raw material for ethylene production around the world. It is used in the manufacture of many compounds like benzene, toluene and xylene as well as in hydrogen and ammonia production. It is also used not only as a fuel but also as a thinner to reduce the viscosity of crude oil for transportation purposes. SOx and NOx emission is destroying the environment. Hence the removal of the sulphur containing compounds from naphtha is major concern of the refineries all around the world. Sulphur present in naphtha also destroys the catalysts of cracking units and especially reforming units in industries. So its removal is essential to protect noble metal catalysts. Over the years, many processes have been developed for the removal of these compounds. The hydrodesulphurization process is chosen as suitable regarding the requirements by the industry and is studied in depth for this project. It is one of the oldest and most efficient process. Due to selectivity of catalyst towards sulphur removal, the final product has less than 1ppm sulphur. The hydrodesulphurization process is designed and optimized for this project. It is simulated using Aspen Hysys. Main focus is the design of reactor and distillation column. Research is being done on catalyst selection to ensure efficient removal of sulphur compounds. In the future, a reactive distillation scheme may be developed to integrate all plant units into one main vessel.

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CHAPTER 1

INTRODUCTION

The target of this project - Naphtha - is one of the main and most important feed stocks in the world and is the raw material for various products of petrochemical industry like ethylene and propylene, etc. About 10-25 % of aromatic compounds like benzene, xylenes, toluene and ethyl-benzene, etc. are produced from further purification of ethylene feed coming out of naphtha cracker.

Production of Naphtha plays a vital role in the petrochemical development of a country, all around the world. A number of different processes have been used over the past years for the removal of impurities like presence of sulfur and nitrogen in naphtha. Our main objective is to utilize the most suitable process according to Pakistan's requirements and situation.

1.1 Naphtha

It is a term used for the mixture of liquid-hydrocarbons of specific boiling point ranges and are highly flammable and volatile. It is usually derived from crude oil through fractional distillation process.

1.1.1 General Characteristics

- It is a reddish-brown liquid having aromatic smell.
- Boiling point ranges from 30-200 degree centigrade.
- It is highly carcinogenic.
- Carbon atom ranges from 5-12.
- Light Naphtha contains 5-6 carbon atoms or molecules having boiling point ranges from 30-90 degree centigrade.
- Heavy Naphtha contains 6-12 carbon atoms or molecules having boiling point ranges from 90-200 degree centigrade.
- Density of naphtha vary from 600-900 kg/m^3.

1.1.2 Uses of Naphtha

- Feedstock for high gasoline production.
- As an industrial solvent and cleaning fluid.
- An oil painting medium.
- As a fuel in gas turbine unit.
- An ingredient in some lighter fluids.
- As a feedstock for petrochemical products manufacturing.

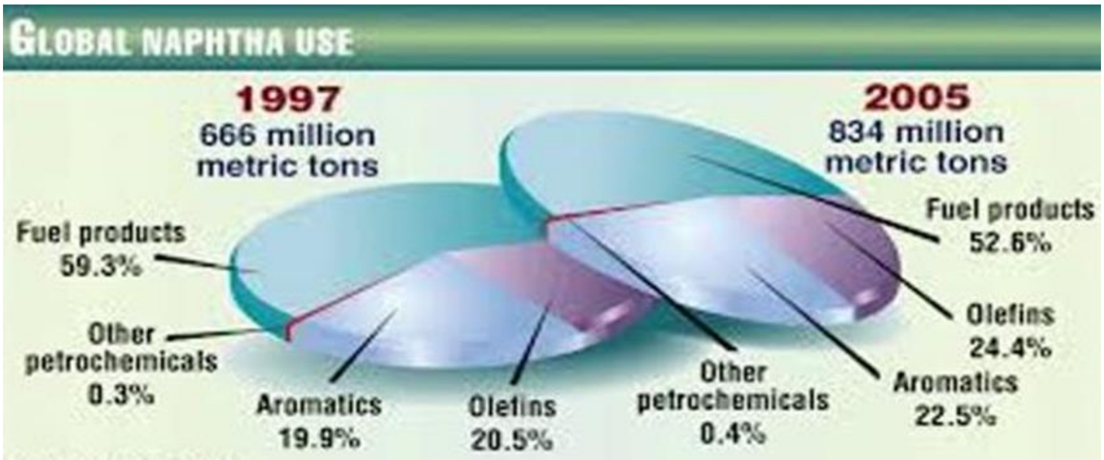


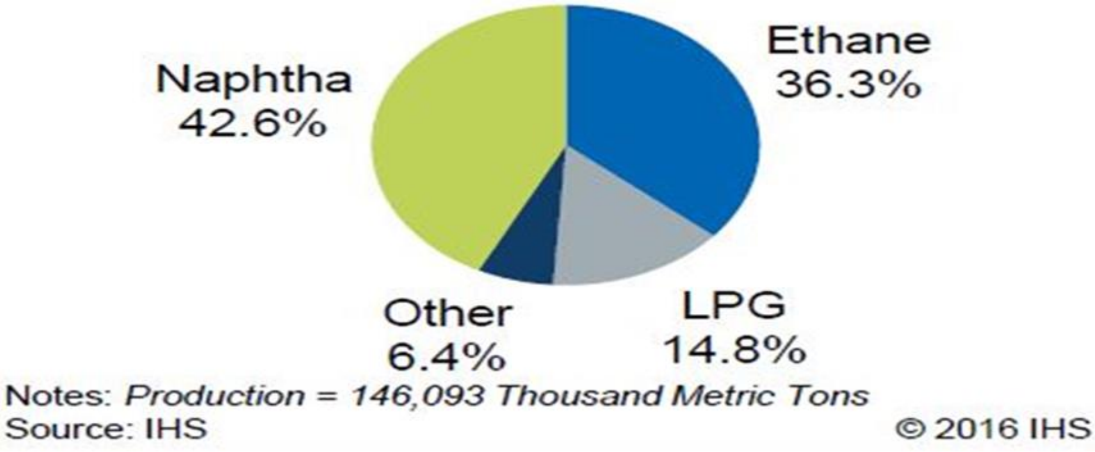
Figure 1. Uses of Naphtha (Oil and Gas Journel, n.d.)

1.2 Chemicals and Products being manufactured from Naphtha

In petroleum refineries, Naphtha can be used to produce hydrogen, ethylene and xylenes, etc. through catalytic reforming and cracking.

1.2.1 Ethylene Production

Production of Ethylene is seen as a direct measure of the petrochemical development of a country, all around the world. About 40 % of world's ethylene production is based on Naphtha.



Notes: *Production = 146,093 Thousand Metric Tons*
Source: IHS © 2016 IHS

Figure 2. Ethylene Production (IHS Market Inc., n.d.)

1.2.2 Benzene, Toluene and Xylene Production

These are aromatic hydrocarbons that are used as petrochemicals across the world. They are important forerunners for many chemicals and polymers such as nylon, trinitrotoluene, plastic and phenol. The given figure illustrate the importance of these chemicals in petrochemical industry.

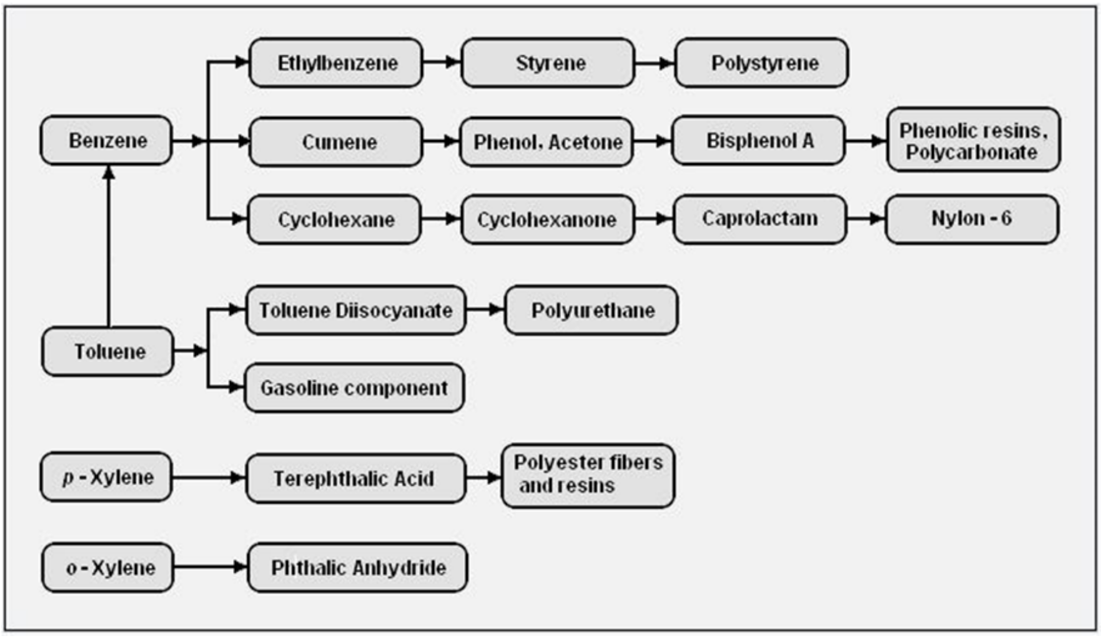


Figure 3. Uses of BTX (Wikipedia, n.d.)

Reformate obtained from catalytic reforming of straight run Naphtha is the major source of these aromatic compounds. The separation of aromatic compounds like benzene, toluene and xylene from reformate is done through the process of solvent extraction in a several steps. Different types of solvents can be used for this process like tetra-ethylene glycol and sulfolane, etc.

1.2.3 Hydrogen and Ammonia Production

Ammonia is one of the inorganic chemicals that is being manufactured world-wide in a very large quantity. In 2016, the production of it is about 175 million tonnes across the world. More than 80 percent of ammonia is used in fertilizer industries. The other usage of ammonia is in the manufacturing of chemicals like nitric acid, in production of explosives, plastics and fibers, etc.

The modern ammonia production plants have the steam reforming units for the production of hydrogen from Naphtha. In the end ammonia is produced as a result of reaction between hydrogen and nitrogen. (Haber's Process)

There are six major companies in Pakistan that are producing ammonia using natural gas or naphtha as a raw material.

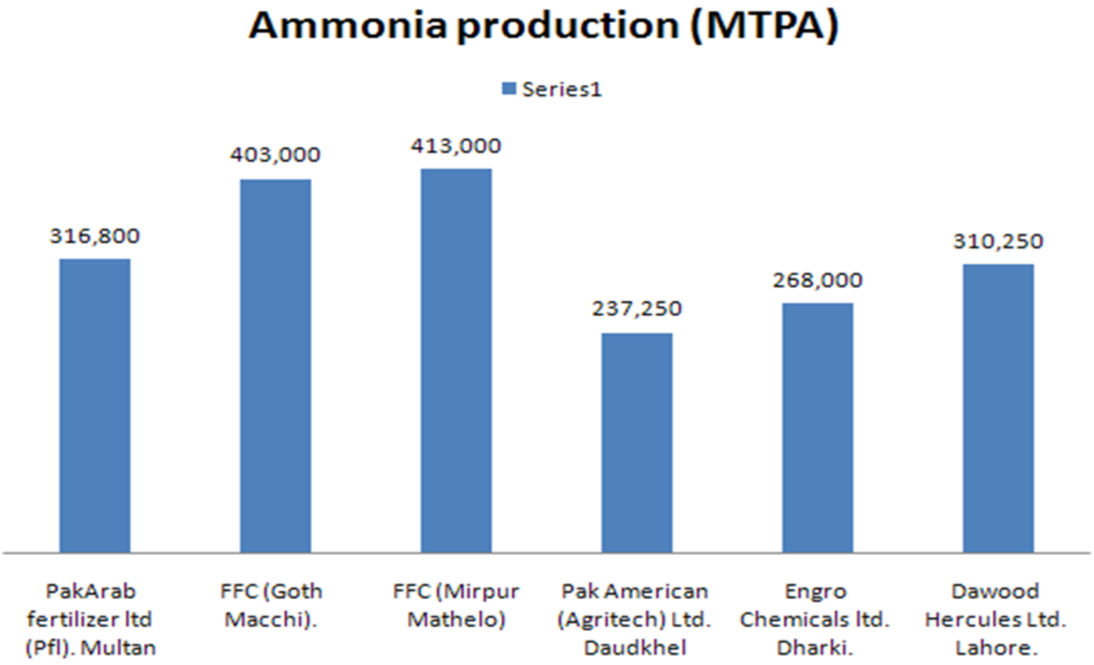


Figure 4. Ammonia Production in Pakistan (Academia, n.d.)

Pakistan also imports ammonia from other countries like China and Russia to meet its demands. Shortage of natural gas is one of the major problems in ammonia manufacturing, but it can be overcome to use naphtha as a feed which is also cleaner way of production when it is in desulfurized form.

1.3 Import Market of Naphtha and its Derivatives

To get an accurate idea of the impact created by Naphtha's trade market on Pakistan's economy, its derivatives must be incorporated in the overall estimation. The import market of Naphtha's derivatives and products formed from them are given below:

Table 1. Pakistan's imports in 2017 (UN data, n.d.).

Chemical Name	**Imports ($)**
Ammonia	453,313.00
Ethylene	86,834,361
Styrene	53,480,513
Ethyl benzene	76,565
Vinyl Chloride	8,394,108

About 4 billion US dollars are being spent by Pakistan on the import of chemicals. Most of the chemicals are being used as a feed-stock for other chemicals production. Many chemicals are being imported but six of them are imported in bulk quantity and their cost of import is around 2 billion US dollars. These chemicals include (Poly-Ethylene, Poly-Propylene, Para-Xylene, Ethylene Glycol) and a couple of more. These chemicals can be produced from cracking of naphtha.

1.4 Contribution of Naphtha in Export Market

Pakistan production of Naphtha is around one million tonnes most of which is being exported some of it is being converted into gasoline of high octane number.

Table 2. Pakistan's Naphtha Export (Academia, n.d.).

Refinery Export	**Tons/Annum**
NRL	300,000
PRL	178,460

Table 3. Pakistan's Naphtha Export (Academia, n.d.). (cont'd)

ARL	200,000
BOSICOR	37,000
DHODAK	83,000
TOTAL EXPORTS	798,460

Chemicals are being manufactured by companies in other countries from Naphtha that is exported by Pakistan to them and Pakistan import these chemicals on much higher rates. So we can say that such valuable feedstock is being wasted by Pakistan and billions of rupees are being spend on importing the same chemicals made from Naphtha.

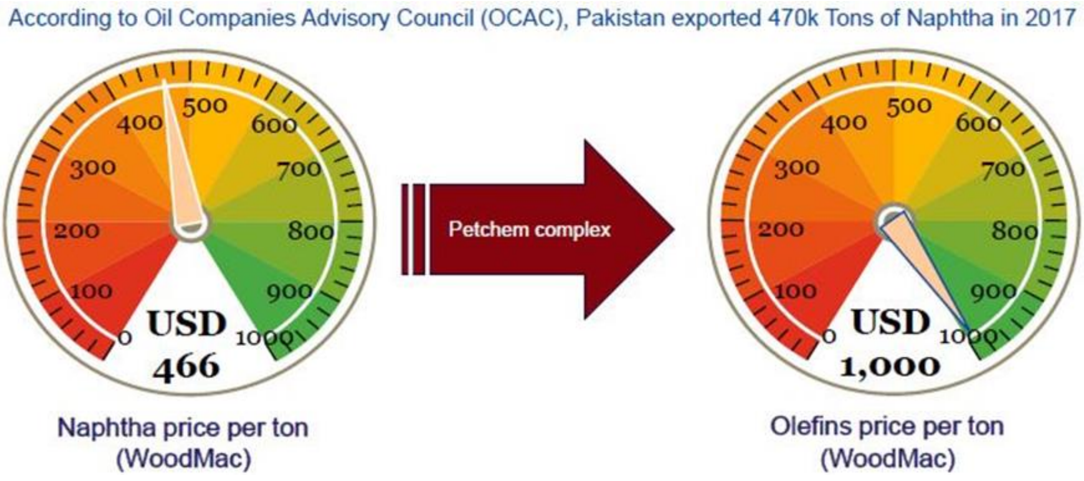


Figure 5. Comparison of Naphtha Market (Pakistan Economic Forum, n.d.)

As it can be seen clearly from above figure, there is huge price difference between Naphtha export and import of chemicals like olefins (ethylene, propylene, etc.). The major issue is the lack of Naphtha cracking complex unit. Pakistan can save up to 1.5 billion US dollars per year by building its own Naphtha Cracking Complex.

Pakistan's Naphtha exports decreases in a past few years but this may be the time that Pakistan can take advantage of that by effectively utilizing it as a clean feedstock for different industries and can also be used for power generation instead of using natural gas of which Pakistan is already facing shortage problems. The effective usage of Naphtha demands its purity. For this purpose different methods are available to remove impurities. The very aim of this project is to find suitable method for sulfur removal. The following chapter would now be explaining in detail the steps involved in process selection for removal of sulfur and other impurities from Naphtha.

CHAPTER 2

PROCESS SELECTION

Environment all around the world is suffering massive damage on daily basis due to the emission of greenhouse gases, NOx, SOx etc. Sulphur present in naphtha is a major source of acid deposition which is of prime concern here. It destroys crops, historical buildings and monuments, trees on high altitudes, contaminates fresh-water resources etc. So it has been a challenge for refineries to minimize sulphur content in petroleum products as much as possible. One way to do that is to use the crude oil containing very minor fractions of sulphur that makes the process easy to remove it and the end product is highly pure and according to government regulations. But in cases where that crude is not available the process has to be modified to achieve the desired purity of the product. This need of modification has encouraged engineers to develop new and efficient methods of sulphur removal. A brief explanation of all these processes is given below.

2.1 Extraction

Solvent Extraction method is extensively used in the industry for the separation of several mixtures or an undesired constituent from the mixture. Here in refineries a solvent whose tendency is to dissolve only sulphur containing compounds is used to separate sulphur compounds from the rest of the petroleum products. Solvent and sulphur compounds are then separated by distillation and solvent is recycled back to the naphtha feedstock. Process that is used for the efficient of removal of mercaptans, liquified gases and liquid fuel raw fractions is “UOP Merox extraction Process”. It has two steps:

I. Caustic soda is used as an extraction solvent to remove mercaptans
II. Mercaptans are oxidized with air to form disulphides in the presence of a catalyst.

$$2RSH \rightarrow RSSR$$

The product formed can then be hydrotreated or sold as a special product.

2.1.1 Advantages

- Since the treatment of aromatic sulphur compounds is very difficult via hydro desulphurization. So, these can easily be separated using a solvent and treated separately.
- The process avoids complications because organo-sulphur compounds have a high solubility in an appropriate solvent as compared to other hydrocarbons. So only a simple mixing process is required.
- The best aspect of using this technology is its applicability at low temperatures. And the chemical nature of components doesn't suffer any kind of change.

2.1.2 Disadvantages

- Large tanks (disperse phase contractors) can be used for desulphurization but it requires high solvent hold-up. Which requires large amount of extraction liquid.
- Formation of emulsions, unloading, flooding and foaming takes a lot of time.
- It is difficult to treat stable emulsions afterwards.

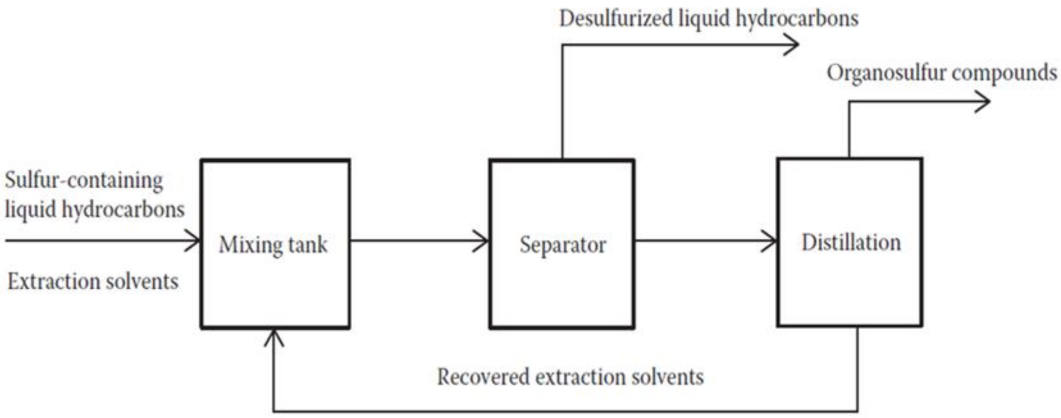


Figure 6. General Process Flow for Extractive Desulphurization

2.2 Desulphurization by Ionic Liquids

Most of the catalytic reactions take place in the presence of liquid solvents and mostly these solvents are present in liquid state at a lower temperature than 100°C. These solvents are able to extract sulphur containing compounds at low temperatures without the use of hydrogen at all. The ability of ionic liquids to remove compounds is strongly affected by the size and structure of its ions. Extensive research is being carried out on these liquids to get maximize benefit from their use.

2.2.1 Advantages

- This process will remove more quantity of thiophene type sulphur species as compared to a conventional desulphurization process.
- The ionic solvents have the flexibility in changing its structural nature according to the requirements.
- These solvents don't remain in their ionic phase after extraction that makes it easier to separate in distillation after desulphurization.
- The other characteristics of ionic liquids include high thermal stability and inflammable.

2.2.2 Disadvantages

- Major loss in octane number is suffered because of a large amount of olefins being saturated.

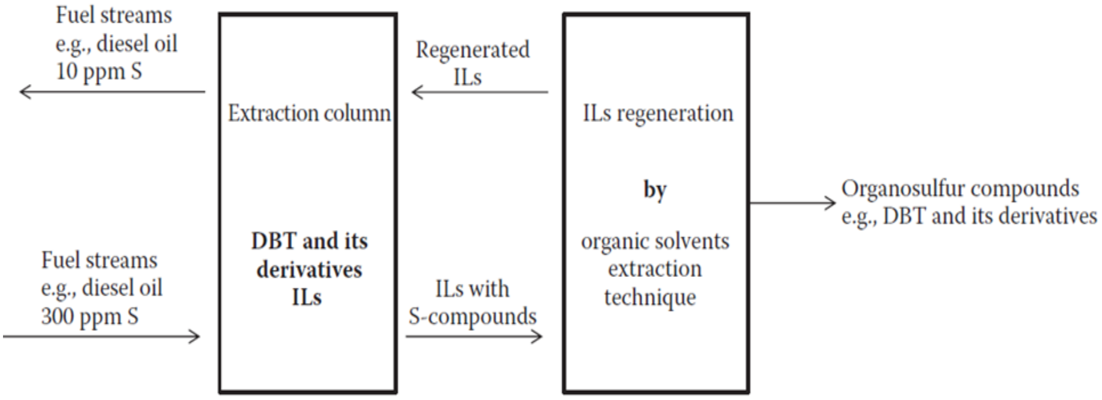


Figure 7. Desulphurization by Ionic Liquids

2.3 Alkylation

This technique utilizes the conversion of organo-sulphur compounds into very high boiling point compounds. So Alkylation is the separation of these compounds from light fractions of petroleum using distillation i.e to concentrate these compounds into the heavy fraction of distillate.

Thiophenic compounds react with olefins in the presence of catalyst to form high molecular compounds. The resulted alkylated thiophene derivatives have relatively high boiling points that upon separation by distillation are removed from main naphtha product. These derivatives can then be blended in diesel and hydrotreated because there won't be any problem regarding the octane number.

Assembly of OATS (Olefin Alkylation of Thiophene Sulphur) is shown below. It consists of following units:

- Pre-treatment unit
- Fixed bed reactor
- Product Separation Unit

The catalyst used to convert organo-sulphur compounds into thiophene derivatives are acidic in nature. Some examples are boron trifluoride (BF3), aluminium chloride (AlCl3), zinc chloride (ZnCl2), or antimony pentachloride (SbCl5) deposited on silica (SiO2), alumina (Al2O3), or silica–alumina (SiO2–Al2O3) supports.

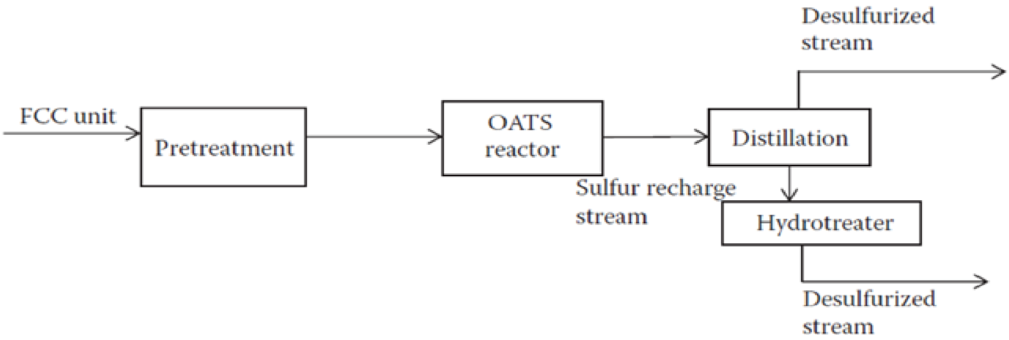


Figure 8. OATS Process

2.3.1 Advantages

- A relatively simple assembly where after alkylation the same conventional method is used to treat naphtha.
- Less amount of hydrogen is used in treating because minor amount of sulphur containing compounds.

2.3.2 Disadvantages

- Some other processes such as alkylation of aromatic hydrocarbons and polymerization of olefins also occur side by side with the desired reaction that could limit the efficiency of the process.

2.4 Desulphurization by Precipitation

This technique involves the formation of insoluble complex compounds that have the ability to transfer their charge and these compounds are subsequently removed from the product. For example, the reaction of methyl iodide with dibenzothiophene results in the formation of water soluble complex compound which can be removed easily and this reaction is carried out at room temperature in the presence of a catalyst.

2.4.1 Advantages

- Using high quantity of alkylating agent in the desulphurization reactor the amount of sulphur in the final product can be decreased approximately to 0.005% w/w.
- The removal of sulfur takes place in the form of alkyl sulfonium salts of thiols, disulphide derivatives, tetrahydrothiophene derivatives, thiophene derivatives, and benzothiophene derivatives.

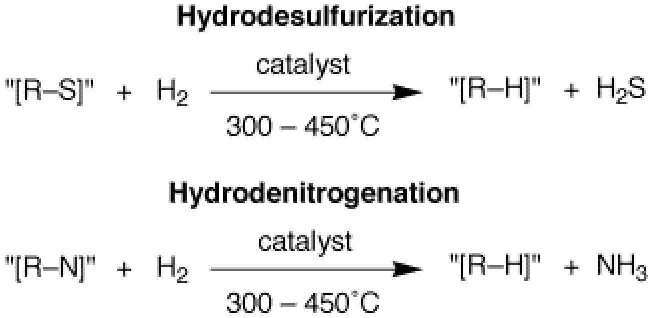
2.4.2 Disadvantages

- Octane number of naphtha remains the same as it was in the feedstock.

2.5 Hydrodesulphurization

The reactivity of organo sulphur compounds varies based upon their structure and environment. Low fractions of petroleum contain aliphatic organo-sulphur compounds, mercaptans, sulphides and disulphides. These compounds easily react which leads to almost complete removal of sulphur from the product. As we move towards higher fractions of petroleum, the form in which sulphur is present changes. In heavy straight run naphtha, straight run diesel and light FFC naphtha, sulphur is present in the form of thiophene rings and dibenzo thiophene derivatives. These are difficult to remove by simple hydrotreating as compared to mercaptans and sulphides.

One of the state-of-the-art technologies to reduce sulphur in middle distillate or diesel is known as hydro desulphurization. In this process, sulphur atoms present in organo-sulphur compounds in converted into hydrogen disulphide in the presence of catalyst and hydrogen gas. Catalysts used in this process is mostly of two types. One is $CoMo/Al_2O_3$ and the other is $NiMo/Al_2O_3$. The conditions of temperature and pressure may vary depending upon the type of hydrocarbons present and the limiting value of sulphur we want to achieve but normally it stays between 200°C and 450°C for temperature and 150 to 250psi for pressure. Generally more sulphur removal requires greater temperature and pressure values. When sulphur removal happens in the form of H_2S gas, the compounds which were attach to sulphur atom become hydrocarbons.



2.5.1 Advantages

- Ultra-low sulphur fuel can be obtained by this process.
- Process conditions are great not only for the removal of sulphur from organo-sulphur compounds but also
    i. for the removal of nitrogen and metallic substances from organic compounds,
    ii. to substances have unpleasant smell or colour,
    iii. Induce saturation of at least some carbon-carbon double bond.
- It also improves the cracking characteristic of the material.

2.5.2 Disadvantages

- In order to remove very small quantity of sulphur from diesel oil, a relatively large reaction vessel is required which of course will need longer residence time and more amount hydrogen gas and energy input.
- Higher values of temperatures and hydrogen pressures are required in case of refractory sulphur compounds which make the process costly.
- Under the extreme conditions of temperature and pressure, carbonaceous coke is formed that deposits on the catalyst thus rendering it inactive.
- Higher molecular weight hydrocarbons start cracking under severe conditions that is not desirable.

2.6 Selective Adsorption

It is basically a replacement of conventional hydrodesulphurization process. In this technique sulphur is removed by adsorption on some solid adsorbent and desulphurized naphtha is obtained. This process produces fuel cell grade gasoline and diesel. Several procedures are used for this process one of which is photodegradation adsorption. And a variety of adsorbents can be used according to the requirement. Generally activated alumina, silica gel, zeolites, bleaching clay, activated carbon are used in this application.

2.6.1 Advantages

- Relatively low temperature and pressure as compared to hydro desulphurization process.
- No use of hydrogen.
- It is a low cost and no pollution operation.

2.6.2 Disadvantages

- Regeneration of the adsorbent can be very difficult at times. If calcination is used to remove sulphur containing compounds, heating value of the fuel could be damaged.
- Aromatics can also get adsorbed on desulphurization adsorbent, so its selectivity has to be carefully designed.

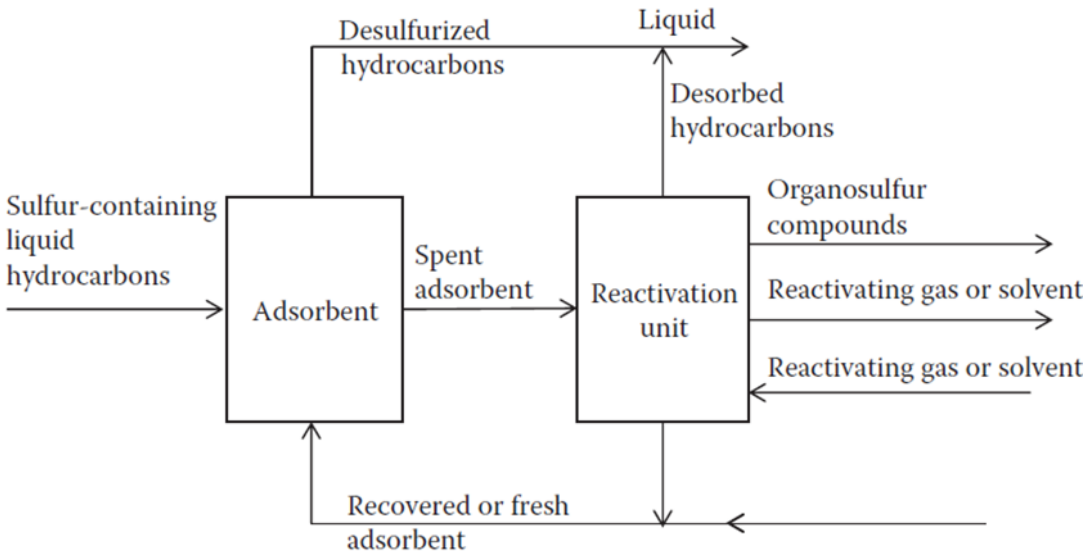


Figure 9. Desulphurization by Adsorption

2.7 Oxidative Desulphurization

Organo sulphur compounds in which sulphur is attached to benzene ring are particularly hard to deal with. Cleavage of carbon-sulphur bond is a tricky business that requires a lot of resources. Higher temperatures and pressures are required to achieve the desirable degree of sulphur removal. There are other problems like coking, cracking etc that come with severe conditions. Oxidative desulphurization process is an attempt to avoid these problems. In this process, organo-sulphur compounds react with oxidative reagents in the presence of a catalyst to form sulphones and sulfoxides. Catalyst can be homogeneous or heterogeneous. The economy of the process strictly depends on what type of oxidative reagent is being used for oxidation of aromatic type sulphur compounds and which process is being used for separation of product from sulphonic waste.

2.7.1 Advantages

- The end product formed in this process is polar due to which it easily separates from petroleum products.
- It also consumes less energy and produces ultra-low-sulphur product.
- There is no use of hydrogen which greatly reduce the cost of material and equipment.

- This process is safer as compared to conventional desulphurization process.
- High reactivity of aromatic sulphur compounds.

2.7.2 Disadvantages

- If extraction is used as separation process, a high product loss is encountered.
- Sulphonic compounds that are formed due to oxidation require special treatment.
- Sulphur compounds like disulphides are hard to remove because they oxidize very slowly. So unless it is being used as a second stage after hydrodesulphurization (for ultra-purification) it is not feasible.

2.8 Biocatalytic desulphurization

Biocatalytic desulphurization is another technique in the list of techniques that are considered as potential techniques to replace deep hydro desulphurization process. In this technique bacteria are used to remove sulphur compounds from petroleum feedstock. The moment from which oil reservoirs enter into the zone of formation and maturation, microbes come in contact with them. The highly specific activity of microorganisms enables them to efficiently transform and remove almost any compound that can be present in the crude oil. The microbes attack Sulphur in organo Sulphur compounds and form oxygenates. This process deals mostly with the removal of Sulphur from benzothiophene and dibenzothiophene in the petroleum refineries. The biocatalyst converts dibenzothiophene (DBT) into 2-hydroxybiphenyl (2-HBP) and sulfate in the presence of water and oxygen.

2.8.1 Advantages

- Efficient removal of sulphur without degrading carbon skeleton.
- Significant reduction in the formation of greenhouse gases.

2.8.2 Disadvantages

- The technology can't be used alone so it must be coupled with hydrodesulphurization unit.

- These micro-organisms also destroy significant amount of hydrocarbons if they are not sulphur selective

2.9 Membrane Separation

This technique is also used to remove sulphur compounds from petroleum fractions, but the difference is that feedstock for this process is refined before subjection. Feed can include naphtha, FCC naphtha, upstream distillation products etc. The reason being the sensitivity and fragility of membrane and easy vulnerability to damage. Polymeric membranes are used to selectively remove sulphur compounds from the feed. But they must be highly selective. Massive amount of energy is required to constantly push feed through membrane. Sulphur compounds pass through the membrane and are collected as permeate. Purified Product is collected as retentate. To increase diffusion of sulphur compounds through membrane a transport agent is sometimes added.

2.9.1 Advantages

- The technique is efficient in case of light naphtha.

2.9.2 Disadvantages

- Fouling occurs on the surface of membrane which greatly reduces mass transfer.

2.10 Why Hydrodesulphurization of Naphtha?

The main reason for choosing hydrodesulphurization process is the availability of hydrogen on plant site. The other reason is the proved efficiency of the process since it is the oldest technique and most widely used in industries to ensure ultra-low removal of sulphur compounds. Not only sulphur compounds, but nitrogen compounds and metallic impurities are also effectively removed. It also induces saturation of alkenes which in turn improves the cracking characteristics of naphtha as part of the naphtha is taken as product and other part is sent to cracking unit.

CHAPTER 3

PROCESS FLOW DIAGRAM

This chapter deals with the flow diagram that is used in this project.

3.1 Process Description

Hydrodesulfurization of naphtha is a catalytic process in which a hydrogen-rich gas stream is used to convert sulfur containing compounds into sulfur free compounds by the formation of hydrogen sulphide gas in the presence of a sulfur selective catalyst. This process also helps in removing other impurities like sulfur and oxygen containing compounds.

This process is basically used to prevent poisoning of Platforming unit catalysts by removing impurities from Naphtha stream that is usually used as a feedstock for Platforming unit. The catalysts usually used in hydrodesulfurization unit consist of an alumina base with Co-Mo or Ni-Mo, but the type of catalyst used along with process parameters are usually dependent on the type of feed.

The operating cost and severity of operation in Platforming unit is greatly influenced by hydrodesulfurization unit. If the oxygen compounds are not completely removed then they may affect the performance of Platforming unit by increasing formation of water molecules. Similarly, if olefins are not treated then they may cause fouling by forming polymer chains. So, maintaining a good operation management is essential on hydrodesulfurization unit for maintaining catalyst life and product quality of Platforming unit.

Hydrodesulfurization unit also known as “Clean up” unit since it removes impurities and clean most of the refinery downstream feedstock. Naphtha produced from different units like FCC, visbreaking and delayed coking contains a lot of impurities like contaminants metals and also has a very high olefins content that needs to be removed by using this unit to produce valuable products.

3.2 Process Reactions

There are six types of reactions usually take place in this process. These include Sulfur removal, Nitrogen removal, Oxygen removal, Saturation of olefins, Metallic compounds removal and Hydrogen halides formation.

3.2.1 Sulfur Removal

Different types of sulfur removal reactions are shown below:

a. (Mercaptan)

$$\text{C-C-C-C-C-C-SH} + H_2 \longrightarrow \text{C-C-C-C-C-C} + H_2S$$

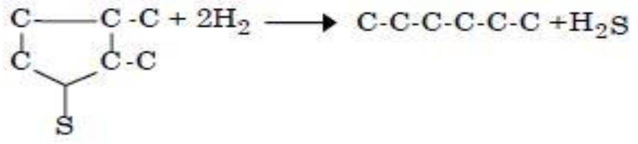
b. (Sulfide)

$$\text{C-C-C-S-C-C-C} + 2H_2 \longrightarrow 2\ \text{C-C-C} + H_2S$$

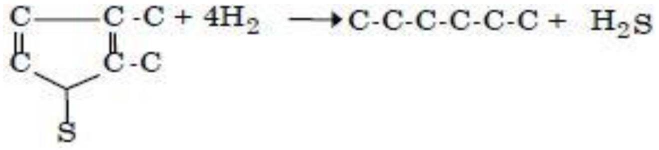
c. (Disulfide)

$$\text{C-C-C-S-S-C-C-C} + 3H_2 \longrightarrow 2\ \text{C-C-C} + 2\ H_2S$$

d. (Cyclic sulfide)



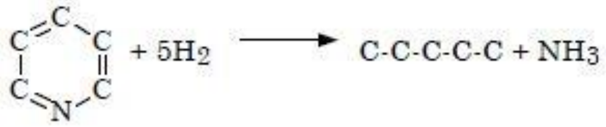
e. (Thiophenic)



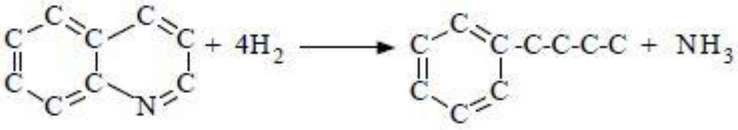
3.2.2 Nitrogen Removal

Nitrogen removal is very difficult in this process since rate of removal of nitrogen is very much lesser in hydrodesulfurization unit. Nitrogen removal results in the formation of ammonia which is usually removed by wash water from three phase separator. Most common nitrogen removal reactions are given below:

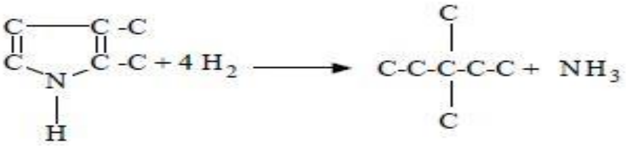
a. (Pyridine)



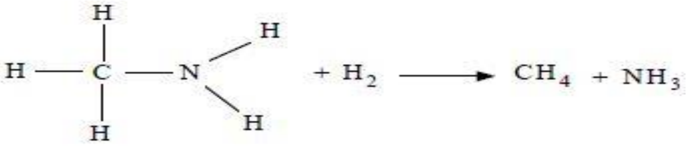
b. (Quinoline)



c. (Pyrrole)

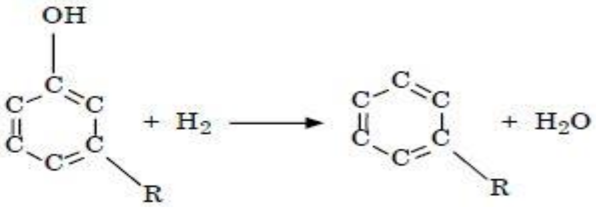


d. (Methylamine)



3.2.3 Oxygen Removal

Oxygen is usually present in the form of alcohol or phenol and its removal reaction is given as:



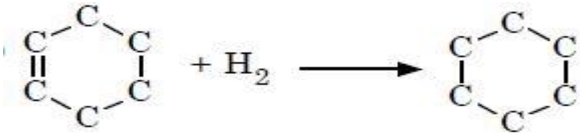
3.2.4 Olefins Saturation

In straight run naphtha, negligible amount of olefins are present in the form of either linear or cyclic olefins.

a. (Linear olefin)

$$C\text{-}C\text{-}C\text{-}C = C\text{-}C + H_2 \longrightarrow C\text{-}C\text{-}C\text{-}C\text{-}C\text{-}C$$

b. (Cyclic olefin)



3.2.5 Metallic compounds removal

Metallic compounds present in Naphtha stream needs to be removed to avoid catalyst poisoning but a higher temperatures of about 320°C or above are required. Using this process these metals can be removed up to 5 ppm by absorption on the catalyst and are separated during regeneration of catalyst.

3.2.6 Hydrogen halides formation:

Hydrocarbon halides presence in Naphtha feed stream can cause corrosion in the reactor outlet stream. In HDS unit these halides are converted into hydrogen halides. The halide decomposition reaction is given below:

$$\text{C-C-C-C-C-C-Cl} + H_2 \longrightarrow \text{HCl} + \text{C-C-C-C-C-C}$$

3.3 Process Variables

3.3.1 Reactor Pressure

Reaction rate and catalyst life is greatly influenced by the reactor pressure. Catalyst remains effective for a longer period of time at higher pressures and also reaction goes to near completion. Sulfur and nitrogen content present also determine the operating pressure. Higher sulfur content requires higher pressure and vice versa. Temperature ranges for different types of Naphtha are:

"Strait run: 300-500 psig" and "Cracked: up to 800 psig"

3.3.2 Reactor Temperature

Temperature effect is different for different kind of reactions but desulfurization is directly proportional to temperature. The reaction starts at 230°C and rate increases with increasing temperature. At higher temperature of about 320°C and above sulfur removal nearly goes to completion and also metal removal requires a minimum temperature of about 310°C. The maximum temperature range for both types of Naphtha is about 400°C.

3.3.3 Hydrogen to Feed Ratio

The minimum hydrogen to feed ratio required for straight run Naphtha is 40 nm^3/m^3 and its range is up to 75 nm^3/m^3. While this ratio is higher for cracked Naphtha because of higher sulfur contents and other impurities and its range is up to 500 nm^3/m^3. The minimum purity of hydrogen gas required is 70%.

3.4 Process Flow Diagram

First of all, Naphtha feed along with hydrogen gas is pumped through pump P-006 to the heat exchanger E-004 at desired pressure where it is preheated and is then sent to the fired heater or furnace FH-002 to heat it to the required reaction temperature. The vaporized feed is then entered into the fixed bed catalytic reactor in which hydrodesulfurization reactions take place and the catalyst is $CoMo/Al_2O_3$. The products formed are then cooled down first by exchanging heat with feed stream through exchanger E-004 and is then further cooled down by air cooler. This cooled stream is then sent to the three phase separator V-005 where most amount of hydrogen sulfide is absorbed into water and is separated from bottom while hydrogen gas stream containing some amount of unwanted gases like carbon dioxide is recycled back to the reactor while the other liquid products are sent to the stripper. (Note that the top stream of V-005 may also contain traces of H_2S so it must be removed by amine contractors so that recycle stream does not contains any H_2S).

The recycled hydrogen gas stream is passed through suction drum before it enter into compressor to remove any suspended particles that may damage the compressor. The stripper is basically a distillation column in which separation takes place on the base of volatility difference. The liquid stream from three phase separator V-005 is sent to stripper V-007 through pre-heating it by heat exchanger E-005.The unwanted gases are removed from the top while the desulfurized naphtha is removed from the bottom of the stripper and as it is at high temperature so it is used to preheat the stripper feed in heat exchanger E-005 before being sent to other units or storage.

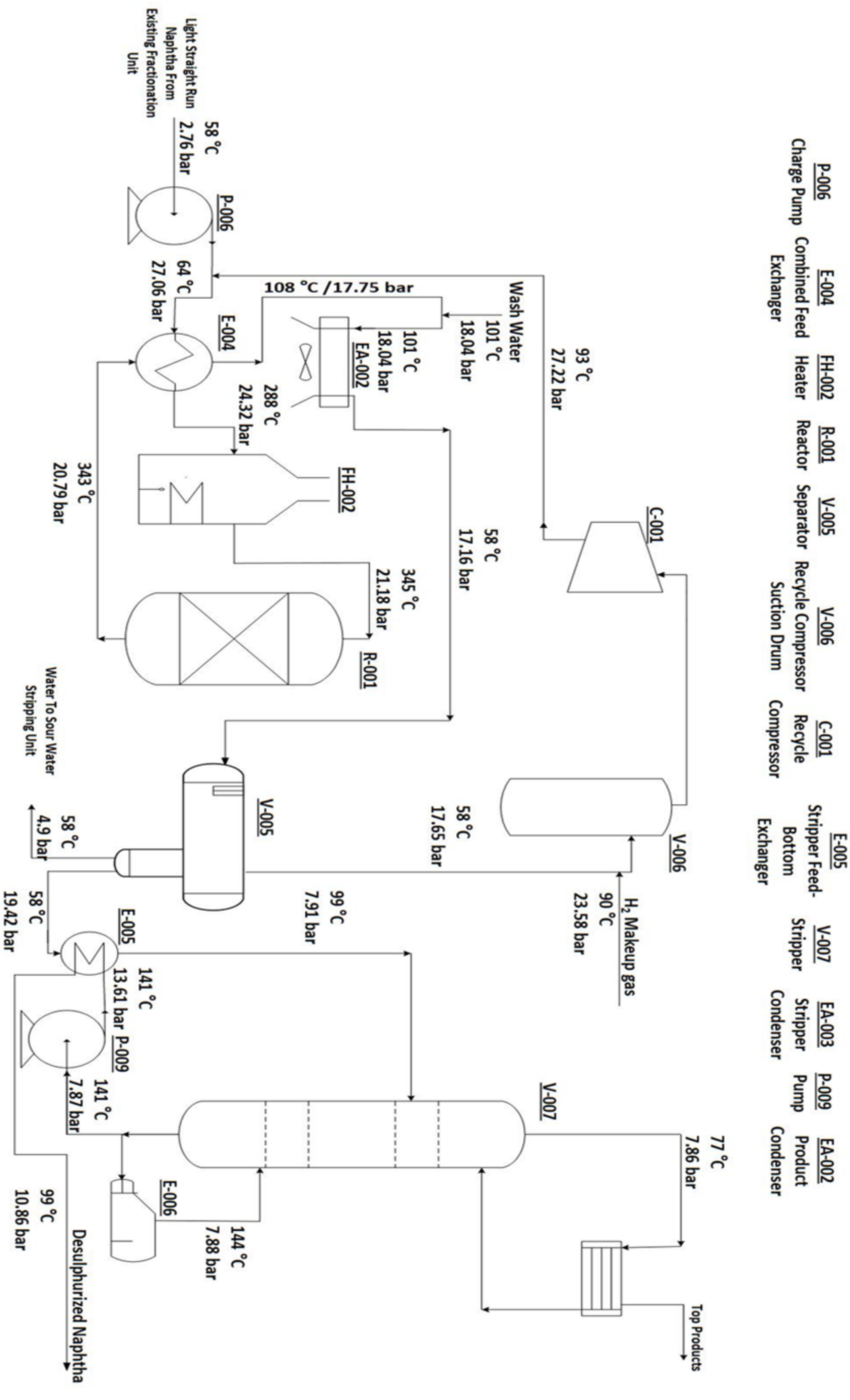


Figure 10. Process Flow Diagram

CHAPTER 4

MATERIAL BALANCE

The chapter discusses the masses moving in and out through various equipment. Mass balance calculations are employed to find the required masses in each stream. As there are many components in the feed so mainly the material balance is done through Aspen Hysys. All balances have been verified through Aspen Hysys simulation.

4.1 Feed Composition

According to given data from industry we have done material balance and energy balance. Naphtha feed ranges from C4-C11 hydrocarbons and is also separated into two ranges, one range being of light hydrocarbons from C4 to C7 and heavy ones from C7 to C11.In industry the feed composition varies depending on the reservoir from which the crude is extracted and so the composition of naphtha feed also varies. So on the basis of certain composition data provided by industry, we have assumed fixed composition of naphtha feed and have performed our calculations. Overall the calculations are based on 1 hour of feed. The hydrogen is provide in excess with 84 kg mole/hr. The feed composition is given below.

Table 4. Naphtha Feed Composition.

Naphtha Feed Composition	
Components	**Kg mole**
H2O	2
23-Mpentane	8.00E-02
33-Mpentane	0.13
24-Mpentane	3.67
22-Mpentane	2.18

Table 5. Naphtha Feed Composition. (cont'd)

23-Mbutane	4.98
22-Mbutane	2.57
H2S	0
Ammonia	0
Hydrogen	0
Methane	0
Ethane	0.8
Propane	6.95
i-Butane	0
n-Butane	22.83
i-Pentane	45.13
n-Pentane	57.03
1-Pentene	0
Cyclopentane	7.11
2-Mpentane	34.08
124-MBenzene	0
1M3-EBenzene	0
n-Nonane	0
p-Xylene	0
3-Mpentane	19.76
n-Hexane	46.51
1-Hexene	0
Mcyclopentan	27.67
Cyclohexane	32.36

Table 6. Naphtha Feed Composition. (cont'd)

Benzene	25.12
223-Mbutane	0.56
n-Heptane	0
3-Epentane	0
o-Xylene	0
m-Xylene	0
E-Benzene	0
n-Octane	0
Toluene	0
Ecyclopentane	0
Mcyclohexane	0
1-ci2-MCC5	0.65
1-Heptene	0
3-Mhexane	0.16
2-Mhexane	0.56
E-Mercaptan	0.1
diE-Sulphide	6.00E-02
Thiolane	3.00E-02
4-M-Pyridine	2.50E-03
Methylamine	5.00E-04
TOTAL (Kg mole)	343.08

4.2 Reactor

The feed undergoes a series of reactions in the fixed bed reactor where naphtha feed is hydrotreated. The inlet feed composition is given as follows along with the reaction set. The reaction set is as follows:

$$C_6H_6 + 3H_2 \rightarrow C_6H_{12}$$

$$C_2H_5SH + H_2 \rightarrow C_2H_6 + H_2S$$

$$C_2H_5SC_2H_5 + 2H_2 \rightarrow 2C_2H_6 + H_2S$$

$$C_4H_8S + 2H_2 \rightarrow C_4H_{10} + H_2S$$

$$C_6H_7N + H_2 \rightarrow C_6H_{14} + NH_3$$

$$CH_3NH_2 + H_2 \rightarrow CH_4 + NH_3$$

The material balance is done based on 97% conversion of sulphur compounds, 94% conversion of nitrogen compounds and 85% conversion of aromatics based on the CoMo/Al_2O_3 catalyst.

We have summarized the feed composition into paraffins, alkenes, aromatics, sulphur compounds, nitrogen compounds and hydrogen sulphide so that it will be easy for the reader to interpret.

Table 7. Reactor Material Balance.

Reactor Balance		
Composition	**Feed In (Kg Mole)**	**Feed Out (Kg Mole)**
Hydrogen Sulphide	0	0.1843
Ammonia	0	0.0027
Paraffins	315.77	337.401
Alkenes	0	0
Aromatics	25.12	3.768
Ethyl Mercaptan	0.1	0.003

Table 8. Reactor Material Balance. (cont'd)

Diethyl Sulphide	0.06	0.0018
Thiophene	0.03	0.0009
Pyridine	0.0015	0.0002
Methyl amine	0.0005	0.00005
Water	2	2
Hydrogen	84	19.66
Total (kg mole)	427.082	363.02195
Total (Kg)	26860	26860

4.3 Three Phase Separator

The material balance of three phase separator on Aspen Hysys is shown below.

Table 9. Three Phase Separator Balance.

Three Phase Separator				
Composition	**Feed In**	**Gas Phase**	**Liquid Phase**	**Aqueous Phase**
	kg mole	kg mole	kg mole	kg mole
Naphtha	341.153	5.08	336.073	0
Hydrogen	19.66	18.571	1.089	0
Water	2	0.4622	0.587	0.9508
Hydrogen Sulphide	0.1843	0.0442	0.1401	0
Ammonia	0.0027	0.0004	0.0023	0
TOTAL	363	24.1578	337.8914	0.9508

4.4 Distillation Column

The distillation column is essentially acting as stripper removing H_2S, NH_3 and light hydrocarbons till propane from top while the heavy hydrocarbons from butane to C7 which constitute the naphtha feed from bottom.

Table 10. Stripper/Distillation Column Material Balance.

Distillation Column			
Composition	**Feed In**	**Top**	**Bottom**
	kg mole	kg mole	kg mole
H2O	5.87E-01	1.28E-12	5.87E-01
23-Mpentane	7.98E-02	7.96E-02	1.41E-04
33-Mpentane	1.30E-01	1.29E-01	3.14E-04
24-Mpentane	3.66E+00	3.63E+00	2.06E-02
22-Mpentane	2.17E+00	2.16E+00	1.27E-02
23-Mbutane	4.94E+00	4.81E+00	1.29E-01
22-Mbutane	2.55E+00	2.46E+00	8.79E-02
H2S	1.40E-01	1.98E-07	1.40E-01
Ammonia	2.24E-03	6.39E-07	2.24E-03
Hydrogen	1.09E+00	3.13E-28	1.09E+00
Methane	1.62E-04	3.67E-21	1.62E-04
Ethane	7.34E-01	5.70E-08	7.34E-01
Propane	6.13E+00	5.72E-01	5.56E+00
n-Butane	2.19E+01	1.74E+01	4.54E+00
i-Pentane	4.43E+01	4.05E+01	3.77E+00
n-Pentane	5.61E+01	5.23E+01	3.87E+00

Table 11. Stripper/Distillation Column Material Balance. (cont'd)

Cyclopentane	7.03E+00	6.72E+00	3.12E-01
2-Mpentane	3.38E+01	3.30E+01	8.24E-01
3-Mpentane	1.96E+01	1.92E+01	3.96E-01
n-Hexane	4.62E+01	4.56E+01	6.86E-01
Mcyclopentan	2.75E+01	2.72E+01	3.15E-01
Cyclohexane	5.35E+01	5.31E+01	3.38E-01
Benzene	3.75E+00	3.70E+00	4.39E-02
223-Mbutane	5.58E-01	5.55E-01	2.56E-03
1-ci2-MCC5	6.49E-01	6.48E-01	3.86E-04
3-Mhexane	1.60E-01	1.59E-01	2.39E-04
2-Mhexane	5.58E-01	5.57E-01	1.03E-03
E-Mercaptan	2.91E-03	2.50E-03	4.12E-04
diE-Sulphide	1.79E-03	1.79E-03	4.02E-06
Thiolane	8.99E-04	8.99E-04	5.40E-08
4-M-Pyridine	2.50E-04	2.50E-04	7.62E-10
Methylamine	4.60E-05	1.88E-05	2.72E-05
TOTAL	337.88	314.42	23.45

4.5 Other Equipment

For the remaining equipment, like pumps, compressor, heat exchangers and air cooler, the mass going in is equal to the mass going out as there is no reaction so no generation and no accumulation is involved. Hence for pumps, compressor and heat exchangers' material balance is: In = Out

CHAPTER 5

ENERGY BALANCE

The chapter discusses the energy moving in and out through various equipment systems. Energy balance calculations are employed to find the required enthalpies in each stream. All balances have been verified through Aspen Hysys simulation.

5.1 Pumps

Formulae used: Isentropic Work: $W_s = \Delta H$

Actual Work: $W = W_s/\eta$

5.1.1 Pump P-006

Table 12. Pump P-006 Energy Balance.

Pump P-006		
Stream	**In**	**Out**
Temperature (°C)	58	59
Pressure (Bar)	4.58	27.11
Specific Enthalpy (KJ/Kg mole)	-154270.93	-153905.44
Isentropic Work (KJ/Kg mole)	365.49	
Isentropic Efficiency	75%	
Actual Work (KJ/Kg mole)	487.32	
Feed Flowrate (Kg mole/h)	343.1	
Power (KW)	46.44	

5.1.2 Pump P-009

Table 13. Pump P-006 Energy Balance

Pump P-006		
Stream	**In**	**Out**
Temperature (°C)	128.8	129.4
Pressure (Bar)	7.88	13.61
Specific Enthalpy (KJ/Kg mole)	-153552.06	-153442.52
Isentropic Work (KJ/Kg mole)	109.54	
Isentropic Efficiency	75%	
Actual Work (KJ/Kg mole)	146	
Feed Flowrate (Kg mole/h)	314.4	
Power (KW)	12.75	

5.2 Compressor

Formulae used: Isentropic Work : Ws =ΔH

Actual Work : W = Ws/η

Table 14. Compressor C-001 Energy Balance

Compressor C-001		
Stream	**In**	**Out**
Temperature (°C)	57.34	141.7
Pressure (Bar)	9.63	27.22
Specific Enthalpy (KJ/Kg mole)	-31270.53	-27104.53
Isentropic Work (KJ/Kg mole)	4166	

Table 15. Compressor C-001 Energy Balance (cont'd)

Isentropic Efficiency	75%
Actual Work (KJ/Kg mole)	5555
Feed Flowrate (Kg mole/h)	24.15
Power (KW)	37.26

5.3 Heat Exchangers

Formulae used:

$$H = mCp\Delta T$$

$$Q = \Delta H$$

$$\sum Qhot = \sum Qcold$$

5.3.1 Heat Exchanger E-004

Table 16. Heat Exchanger E-004 Energy Balance

Heat Exchanger E-004				
Stream	**Hot In**	**Hot Out**	**Cold In**	**Cold out**
Temperature (°C)	343	114.3	57.3	288
Pressure (Bar)	20.8	17.76	27.11	24.33
Cp (KJ/Kg. °C)	2.933	2.684	2.351	2.788
m (Kg)	2.69E+04	2.69E+04	2.69E+04	2.69E+04
H (KJ)	2.70E+07	8.24E+06	3.62E+06	2.16E+07
Q (KJ)	-1.88E+07		1.79E+07	
Error	0.044			

5.3.2 Heat Exchanger E-005

Table 17. Heat Exchanger E-005 Energy Balance

Heat Exchanger E-005				
Stream	**Hot In**	**Hot Out**	**Cold In**	**Cold out**
Temperature (°C)	129.4	88.6	57.34	99
Pressure (Bar)	13.61	10.86	9.63	7.91
Cp (KJ/Kg. °C)	2.793	2.487	2.307	2.585
m (Kg)	2.51E+04	2.51E+04	2.65E+04	2.65E+04
Latent Heat (KJ)	--		2.60E+05	
H(KJ)	9.07E+06	5.53E+06	3.50E+06	6.77E+06
Q (KJ)	-3.54E+06		3.53E+06	
Error	0.002			

5.4 Air Cooler

The formulae used are same as that for heat exchanger and the required energy removal is calculated.

$$H = mCp\Delta T$$

$$Q = \Delta H$$

Table 18. Air Cooler EA-002 Energy Balance

Cooler EA-002		
Stream	**Hot In**	**Hot Out**
Temperature (°C)	114.3	58
Pressure (Bar)	17.76	17.24
Cp (KJ/Kg. °C)	2.684	2.323
m (Kg)	2.69E+04	2.69E+04

Table 19. Air Cooler EA-002 Energy Balance (cont'd)

H (KJ)	8.24E+06	3.62E+06
Q (KJ)	-4.62E+06	

5.5 Fired Heater

The heat energy required to be given by the heater is calculated below.

Table 20. Fired Heater FH-002 Energy Balance

Heater FH-002		
Stream	**Hot In**	**Hot Out**
Temperature (°C)	288	345
Pressure (Bar)	24.33	21.24
Cp (KJ/Kg.°C)	2.788	2.935
m (Kg)	2.69E+04	2.69E+04
H(KJ)	2.16E+07	2.72E+07
Q (KJ)	5.63E+06	

5.6 Reactor

Formulae used:

$$Q = \Delta H$$

$$\Delta H^{O} = \Sigma\, n\Delta H_{\mathbf{f}}{}^{O}(\text{products}) - \Sigma\, n\Delta H_{\mathbf{f}}{}^{O}(\text{reactants})$$

Negative sign indicates that this much energy is released by reactor.

Table 21. Reactor R-001 Energy Balance

Reactor R-001		
Stream	**In**	**Out**
Temperature (°C)	345	343
Pressure (Bar)	21.24	20.8
Cp (KJ/Kg. °C)	2.935	2.933
Mass Flowrate(kg/h)	2.69E+04	2.69E+04
H(KJ)	2.72E+07	2.70E+07
Heat Of Reaction (KJ)	-4.50E+06	
Q(KJ)	-4.68E+06	

5.7 Distillation Column

The energy balance on streams of distillation column is as follows with condenser and reboiler duties. Where: Hf = Ht + Hb + Qr + Qc

Table 22. Distillation Column/Stripper V-007 Energy Balance

Distillation Column V-007			
Stream	**Feed**	**Top**	**Bottom**
Temperature (°C)	99	93	128.8
Pressure (Bar)	7.91	7.865	7.875
Cp (KJ/Kg. °C)	2.585	2.383	2.807
m (Kg)	2.65E+04	1.37E+03	2.51E+04
H(KJ)	-5.35E+07	-7.54E+06	-4.83E+07
Q Reboiler (KJ)	2.66E+06		
Q condenser (KJ)	-3.02E+05		

CHAPTER 6

EQUIPMENT DESIGN

Design calculations for the major equipment in the process flow diagram are described below.

6.1 Heat Exchanger

The following calculations are done to design the heat exchanger E-005 which is used to cool the bottom of distillation column by exchanging heat with the feed of column.

Mass flow of hot fluid = 25000 kg/h. Inlet and outlet temperatures of hot fluid are 130.8 °C and 89 °C respectively.

Mass flow of cold fluid = 26460 kg/h. Inlet and outlet temperatures of cold fluid are 57.34 °C and 90 °C respectively.

Tube outer diameter = ¾ in. Pitch = 1 in. square

Type of tubes = 13 BWG Length of a tube = 16 ft.

No. of tubes = 160 No. of passes = 2

Shell inner diameter = 17 ¼ in. Baffle spacing = 5 in.

1) Heat Balance:

$$Q = m\ Cp\ \Delta T = 25000 * 2.6455 * (130.8 - 89.71) = 2717590\ kJ/h$$
$$= 2575778\ Btu/h$$

2) Δt Calculation:

Table 16. Hot and Cold Fluid Temperatures and their Differences

Hot fluid		Cold fluid	Difference
130.8	Higher Temp	90	40.8
89.71	Lower Temp	57.34	32.37
41.09	Differences	32.66	8.43

$$LMTD = \frac{\Delta T1 - \Delta T2}{\ln\left(\frac{\Delta T1}{\Delta T2}\right)} \quad = \quad \frac{40.8 - 32.37}{\ln\left(\frac{40.8}{32.37}\right)} \quad = \quad 36.4℃ = \quad 97.52°\mathrm{F}$$

$$R = \frac{T1 - T2}{t2 - t1} \quad = \quad \frac{41.09}{32.66} \quad = \quad 1.26$$

$$S = \frac{t2 - t1}{T1 - t1} \quad = \quad \frac{32.66}{130.8 - 57.34} \quad = \quad 0.44$$

$F_T = 0.83$

$$\Delta t = F_T \times \mathrm{LMTD} \quad = \quad 0.83 \times 36.4 \quad = \quad 30.21℃ \quad = \quad 86.38°\mathrm{F}$$

3) Calorific temperatures:

$$\frac{\Delta tc}{\Delta th} = \quad \frac{32.37}{40.80} \quad = \quad 0.79$$

Kc = 1, Fc = 0.44

$$Tc = T2 + Fc \times (T2 - T1) = 89.71 + 0.44 \times 41.09 = 107.8℃ \quad = 226°\mathrm{F}$$

$$tc = t2 + Fc \times (t2 - t1) = 57.34 + 0.44 \times 32.66 = 71.7℃ = 161°\mathrm{F}$$

Shell side (hot fluid)

4) Flow area:

$a_s = I.D \times C'' \times {}^{B}/_{144P_T}$

$= 17.25 \times 0.25 \times {}^{5}/_{144 \times 1}$

$a_s = 0.1497\ ft^2$

5) Mass velocity:

$$G_s = \frac{W}{a_s}$$

$$= \frac{55000}{0.1497} = 367402\ {}^{lb}/_{hr.ft^2}$$

Tube side (cold fluid)

Flow area:

$a'_t = 0.247\ in^2$

$$a_t = \frac{N \times a'_t}{144 \times n} = \frac{160 \times 0.247}{144 \times 2}$$

$a_t = 0.137 ft^2$

Mass velocity:

$$G_s = \frac{W}{a_s}$$

$$= \frac{58212}{0.137} = 424286\ {}^{lb}/_{hr.ft^2}$$

6) Reynolds number:

At $T_c = 226°\text{F}$

$\mu = 0.3773\, {}^{lb}/_{ft.hr}$

$D_e = 0.079 ft$

$$Re_s = \frac{D_e G_s}{\mu}$$

$$= \frac{0.079 \times 367402}{0.3773}$$

$Re_s = 77122$

7) JH:

JH = 170

8) At $T_c = 226°\text{F}$

$c = 0.624\, {}^{Btu}/_{lb.°\text{F}}$

$k = 0.0502\, {}^{Btu}/_{hr.ft.°\text{F}}$

$$\left(\frac{c.\mu}{k}\right)^{1/3} = 1.654$$

9) Heat transfer coefficient:

$$\frac{h_0}{\emptyset_s} = \frac{J_H k}{D_e}\left(\frac{c.\mu}{k}\right)^{1/3}$$

$$\frac{h_0}{\emptyset_s} = 178.2$$

Reynolds number:

At $t_c = 161°\text{F}$

$\mu = 0.2042\, {}^{lb}/_{ft.hr}$

$D = 0.0467 ft$

$$Re_t = \frac{D G_t}{\mu}$$

$$= \frac{0.0467 \times 424286}{0.4942}$$

$Re_t = 40093$

JH:

${}^{L}/_{D} = 342.6$, JH = 120

At $t_c = 161°\text{F}$

$c = 0.573\, {}^{Btu}/_{lb.°\text{F}}$

$k = 0.056\, {}^{Btu}/_{hr.ft.°\text{F}}$

$$\left(\frac{c.\mu}{k}\right)^{1/3} = 1.716$$

Heat transfer coefficient:

$$\frac{h_i}{\emptyset_i} = \frac{J_H k}{D}\left(\frac{c.\mu}{k}\right)^{1/3}$$

$$\frac{h_i}{\emptyset_i} = 247$$

10) Tube-wall Temperature:

$$t_w = t_c + \frac{\frac{h_0}{\emptyset_s}}{\frac{h_0}{\emptyset_s} + \frac{h_i}{\emptyset_i}} \times (T_c - t_c)$$

$$= 161 + \frac{178.2}{178.2 + 247} \times (65)$$

$t_w = 188.25$°F

11) At $t_w = 188.25$°F

$\mu_w = 0.451 \, {}^{lb}/_{ft.hr}$

$$\emptyset_s = \left(\frac{\mu}{\mu_w}\right)^{0.14}$$

$$= \left(\frac{0.377}{0.451}\right)^{0.14}$$

$\emptyset_s = 0.975$

12) Corrected coefficient:

$$h_0 = \frac{h_0}{\emptyset_s} \times \emptyset_s = 178.2 \times 0.975$$

$h_0 = 173.75 \, {}^{Btu}/_{hr.ft^2.°F}$

$$\frac{h_{io}}{\emptyset_t} = \frac{h_i}{\emptyset_i} \times \frac{I.D}{O.D} = 247 \times \frac{0.560}{0.75}$$

$$= 247$$

At $t_w = 188.25$°F

$\mu_w = 0.432 \, {}^{lb}/_{ft.hr}$

$$\emptyset_t = \left(\frac{\mu}{\mu_w}\right)^{0.14}$$

$$= \left(\frac{0.494}{0.432}\right)^{0.14}$$

$\emptyset_t = 1.02$

Corrected coefficient:

$$h_{i0} = \frac{h_{i0}}{\emptyset_t} \times \emptyset_t = 184.4 \times 1.02$$

$h_{i0} = 188.1 \, {}^{Btu}/_{hr.ft^2.°F}$

13) Clean overall coefficient:

$$U_c = \frac{h_{i0} \times h_0}{h_{i0} + h_0}$$

$$= \frac{173.75 \times 188.1}{173.75 + 188.1}$$

$$U_c = 90.3 \, {}^{Btu}/_{hr.ft^2.°\text{F}}$$

14) Design overall coefficient:

$$a^{"} = 0.1963 \, {}^{ft^2}/_{lin.ft}$$

$$\text{Total surface, } A = N \times L \times a^{"} \quad = \quad 160 \times 16 \times 0.1963$$

$$A = 502.53 ft^2$$

$$U_D = \frac{Q}{A.\Delta T} = \frac{2575778}{502.5 \times 86.38}$$

$$U_D = 59.3 \, {}^{Btu}/_{hr.ft^2.°\text{F}}$$

15) Dirt factor Rd:

$$R_d = \frac{U_c - U_D}{U_c.U_D}$$

$$= \frac{90.3 - 59.3}{90.3 \times 59.3}$$

$$R_d = 0.0058 \, {}^{hr.ft^2.°\text{F}}/_{Btu}$$

After this pressure drop on both shell and tube side is found out to verify it the design is feasible and in the allowable pressure drop limitation of less than 10 psi.

Pressure Drop

Following calculations are carried to find out pressure drop across both sides of heat exchanger.

1) For $\boldsymbol{Re_s} = \mathbf{77122}$

$f = 0.00145$

$D_s = 1.4375ft$

$s = 0.5874$

2) No of crosses:

$N + 1 = 12 \times {}^{L}/_{B}$

$N + 1 = 12 \times {}^{16}/_{5}$

$N + 1 = 39$

3) $\boldsymbol{\Delta P_s}$

$$\Delta P_s = \frac{f.G_s^2.D_s.(N+1)}{5.22 \times 10^{10} \times D_e s \emptyset_s}$$

$\Delta P_s = 4.6Psi$

For $\boldsymbol{Re_t} = \mathbf{40093}$

$f = 0.0002$

$s = 0.6208$

$\boldsymbol{\Delta P_t}$:

$$\Delta P_t = \frac{f.G_t^2.L.n}{5.22 \times 10^{10} \times Ds\emptyset_t}$$

$\Delta P_t = 0.75Psi$

$\boldsymbol{\Delta P_T}$:

$G_t = 424286\ {}^{lb}/_{hr.ft^2}$

$$\frac{V^2}{2g'} = 0.024$$

$$\Delta Pr = \frac{4n}{s} \times \frac{V^2}{2g'}$$

$$= \frac{4 \times 2}{0.6208} \times 0.024$$

$\Delta Pr = 0.31Psi$

$\Delta P_T = \Delta Pr + \Delta P_t$

$\Delta P_T = 0.75 + 0.31$

$\Delta P_T = 1.1psi$

6.2 Three Phase Separator

The calculations shown below are for the design of three phase separator.

First we have to select the Retention time of both fluids:

Retention time of oil = (tr)o = 0.16 min (10 sec)

Retention time of water = (tr)w = 0.16 min (10 sec)

Calculate (ho)max:

$$(ho)\ \max = \frac{320 * (tr)o * (\Delta \mathrm{S.G})}{\mu \mathrm{o}}$$

$$\mathrm{(tr)o} = 0.16\ \mathrm{min}$$

$$\Delta\ \mathrm{S.G} = (\mathrm{S.G})\mathrm{w} - (\mathrm{S.G})\mathrm{o} = 1 - 0.647 = 0.353$$

$$\text{Viscosity of oil} = 0.2331\ \mathrm{cp}$$

$$(ho)\ \max = \frac{320 * 0.16 * 0.353}{0.2331} = 77.5\ inch$$

Calculate Aw/A (fraction of vessel cross-section occupied by the water phase).

$$\frac{Aw}{A} = \frac{0.5 * Qw * (tr)w}{(tr)o * Qo + (tr)w * Qw}$$

$$\mathrm{Qw} = 17.13\ \mathrm{kg/hr} = 0.000168\ \mathrm{ft3/s}$$

$$\mathrm{Qo} = 26460\ \mathrm{kg/hr} = 0.71\ \mathrm{ft3/s}$$

$$\frac{Aw}{A} = \frac{0.5 * 0.000168 * 0.16}{0.16 * 0.71 + 0.16 * 0.000168} = 1.2 * 10 - 6$$

Calculating dmax

$$dmax = \frac{(ho)max}{\frac{ho}{d}}$$

ho/d is taken from the following graph

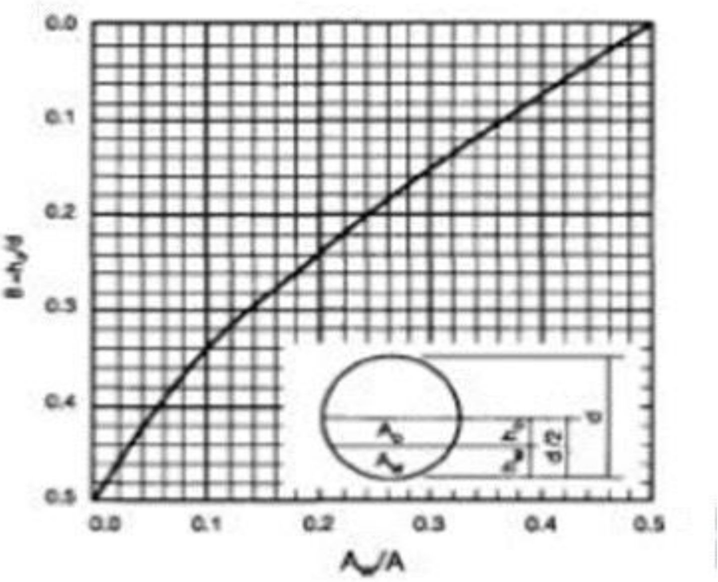


Figure 11. Graph of Aw/A

Which turns out to be 0.499 against the value of Aw/A = 1.2* 10^{-6}

$$dmax = \frac{77.5}{0.499}$$

$$= 158\ inch$$

For gas capacity

$$d * l_{eff} = 420 * \left(\frac{T * Z * Q_g}{P}\right)[\left(\frac{\rho_g}{\rho_l - \rho_g}\right) * \frac{C_D}{d_m}]^{\frac{1}{2}}$$

Calculating l_{eff} for $d<d_{max}$

T = 57.34oC = 594 oR

P = 9.82 kg/cm2 = 139.7psia

Density of gas = 5.535 kg/m3 = 0.3455 lb/ft3

Density of liquid = 650 kg/m3 = 41.2 lb/ft3

dm = 100 micron

Qg = 380 kg/hr = 0.01 MMScf

$$Z = 0.997$$

$$C_D = 1.5$$

$$d * l_{eff} = 420 * \left(\frac{594 * 0.997 * 0.01}{139.7}\right)[\left(\frac{0.3455}{41.2 - 0.3455}\right) * \frac{1.5}{100}]^{\frac{1}{2}}$$

$$d * leff = 201.2$$

For Liquid Capacity

$$d^2 * l_{eff} = 1.42 * [(t_r)_o * Q_o + (t_r)_w * Q_w$$

$$Q_o = 6279 \text{ B/D}$$

$$Q_W = 2.631 \text{ B/D}$$

$$d^2 * l_{eff} = 1.42 * [0.16 * 6279 + 0.16 * 2.631 = 1427$$

Calculating Lss

Lss = Leff + d/12 for gas capacity

Lss = 4/3*Leff for liquid capacity

Calculating slenderness ratio (12Lss//d) which should be between 3 and 5 for both gas and liquid capacities.

Table 17. Vessel Length based on Liquid Capacity

D (inch)	**L_{eff} (ft)**	**L_{ss} (ft)**	**$12L_{ss}/d$**
24	8.38	10.38	5.19
20	10.06	11.72	7.032
16	12.57	13.9	10.42
30	6.7	9.2	3.68

Table 18. Vessel Length based on Gas Capacity

D (inch)	L_{eff} (ft)	L_{ss} (ft)	$12L_{ss}/d$
24	2.47	3.2	1.6
30	1.58	2.06	0.82
20	3.56	4.63	2.78
16	5.57	7.2	5.4
18	4.4	5.7	3.8

Comparison of tables shows that liquid capacity is dominant parameter, so

18in * 5.7ft vessel is sufficient

18in * 6ft (rounded figure)

Weir's Height:

$$\Delta h = h_o\, [1 - \rho_o/\rho_w]$$

We know that

$$ho/d = 0.499$$

$$ho = 0.499 * d$$

$$d = 18$$

$$\text{ho} = 0.499 * 18 = 9 \text{ inch}$$

$$\Delta h = 9 * 0.535 = 3 \text{ inch}$$

So oil weir should be placed at 9 inches while water weir should be placed at 6 inches radial distances.

Demister Sizing:

$$V_m = K_d \sqrt{\frac{\rho_l - \rho_g}{\rho_g}}$$

K_d = demister capacity factor, ft/s

Vm = maximum velocity, ft/s

k_d = 0.1m/s = 0.35 ft/s

$$V_m = 0.35\sqrt{\frac{41.2 - 0.3455}{0.3455}} = 3.8\text{ft/s}$$

Now calculating area of demister

$$A_d = \frac{0.327 * \frac{T * Z * Q_g}{P}}{V_m} = 3.65 \text{ ft2}$$

A demister having this much area is required for our job.

Nozzle Sizing:

Nozzles are generally sized depending on the momentum of the incoming feed. It normally lies in the range of 600-700 lb/ft.s^2

Momentum = $\rho_m * {V_m}^2$

= 42 * 3.8^2

= 606 lb/ft.s^2

6.3 Fixed Bed Reactor

The reactor we have chosen is isothermal fixed bed reactor.

The catalyst is CoMo with alumina base with name tag S-12 and the shape is extrudate form with size of 1/16 in.

The average bulk density of catalyst is 45 lb/ft3.

We know that LHSV (liquid hourly space velocity) is given by

$$LHSV = \frac{Volume\ of\ (liquid)\ Feed\ flowing\ per\ hour}{Volume\ of\ Catalyst}$$

For straight run naphtha, LHSV is between 4-12 hr^{-1} .Taking value of 8 hr^{-1}, and volume of feed flowing at STD is 43.91 m^3/h.

Hence Volume of catalyst is

$$Volume\ of\ Catalyst = \frac{43.91\ m^3/hr}{4\ /hr} = 10.98\ m^3$$

Weight of catalyst is given by

$$Weight\ of\ Catalyst = Density \times Volume$$

$$Weight\ of\ Catalyst = 45\ \frac{lb}{ft^3} \times 10.98\ m^3$$

Using conversion factors:

$$1\ lb = 0.453\ kg$$

$$1\ \mathrm{m}^3 = 35.31\ \ ft^3$$

So we get $Weight\ of\ Catalyst = 7903\ kg$

In industrial scale plant a guard bed is usually required to remove impurities

Vguard bed = 0.2Vcatalyst

$$Vguard\ bed\ =\ 0.2(10.98\ m^3) =\ 2.2\ m^3$$

$$V\ bed = Vcatalyst\ +\ Vguardbed$$

$$V\ bed = 10.98\ m^3 + 2.2\ m^3 = 13.18\ m^3$$

Allowing for top and bottom clearance, considering 10% space on entrance and 10% space on exit of reactor, we get volume of reactor as

$$Vreactor = 20\%\ more\ of\ Vbed = 13.18\ m^3 + (0.2 *\ 13.18\ m^3) = 15.8\ m^3$$

Dimensions of Reactor:

$$V = \left(\frac{\pi * \mathrm{d}^2}{4}\right) * h$$

Where:

d= diameter of the reactor and h= height of the reactor

According to the literature, the height is double of the diameter:

So,

$$V = \left(\frac{\pi * \mathrm{d}^2}{4}\right) * h$$

$$V = \left(\frac{\pi * d^2}{4}\right) * 4d$$

$$15.8\ m^3 = \left(\frac{\pi * d^2}{4}\right) * 4d$$

$$d = 1.71\ m$$

$$h = 6.84\ m$$

6.4 Distillation Column

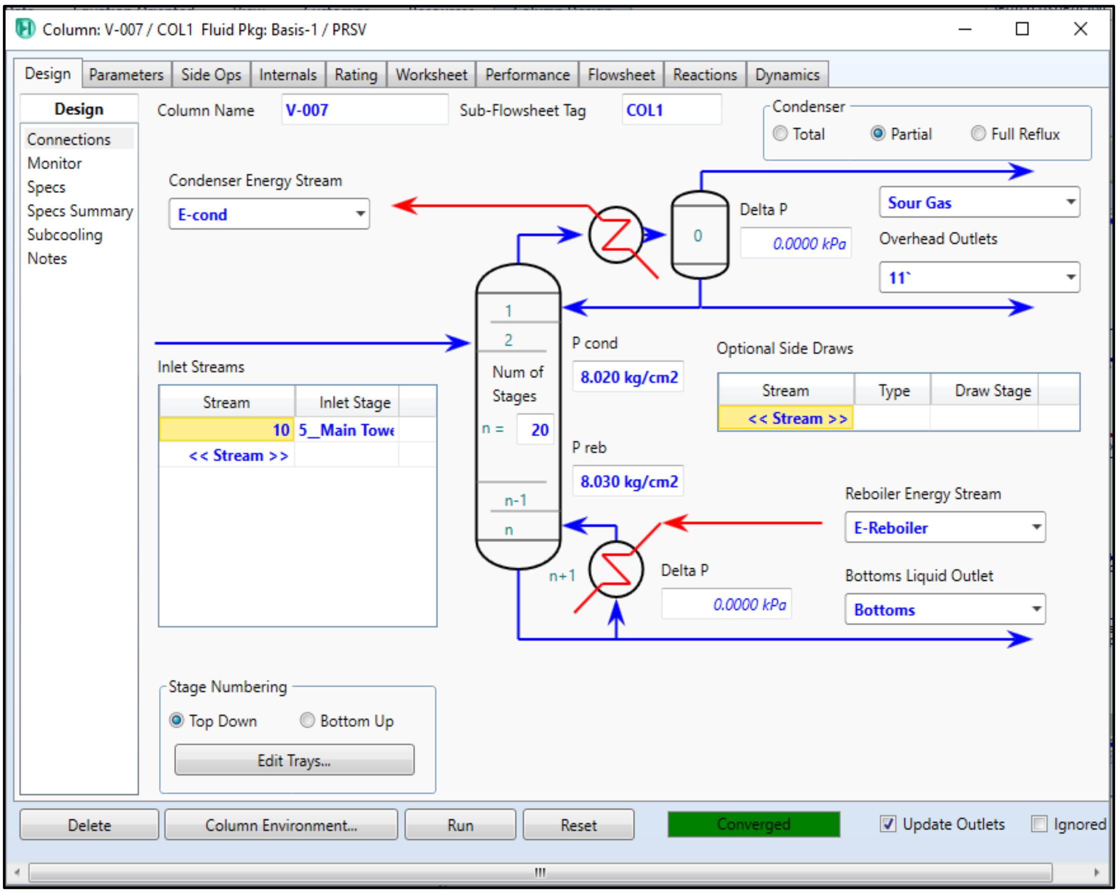
It was not possible to design the column manually using design equations to find number of trays and other required parameters as the feed is complex. Hence the design of column is done through Aspen Hysys by doing several simulations and then optimizing the design to obtain best results.

Other than temperature, pressure and flow rates, following parameters were fixed after doing hit and trial to obtain desired bottom product. Initially reflux ratio was set to 0.49 which was then changed to 1 after optimizing the column.

Reflux Ratio = 1

Distillate rate = 4 kg mole /h

Bottom Product Rate= $2.5*10^4$ kg/h



Column Name: V-007

Sub-Flowsheet Tag: COL1

Condenser: ○ Total ● Partial ○ Full Reflux

Condenser Energy Stream: E-cond

Delta P (condenser): 0 — 0.0000 kPa

Overhead Outlets: Sour Gas, 11`

Inlet Streams

Stream	Inlet Stage
10	5__Main Towe
<< Stream >>	

Num of Stages: n = 20

P cond: 8.020 kg/cm2

P reb: 8.030 kg/cm2

Optional Side Draws

Stream	Type	Draw Stage
<< Stream >>		

Reboiler Energy Stream: E-Reboiler

Delta P (reboiler): 0.0000 kPa

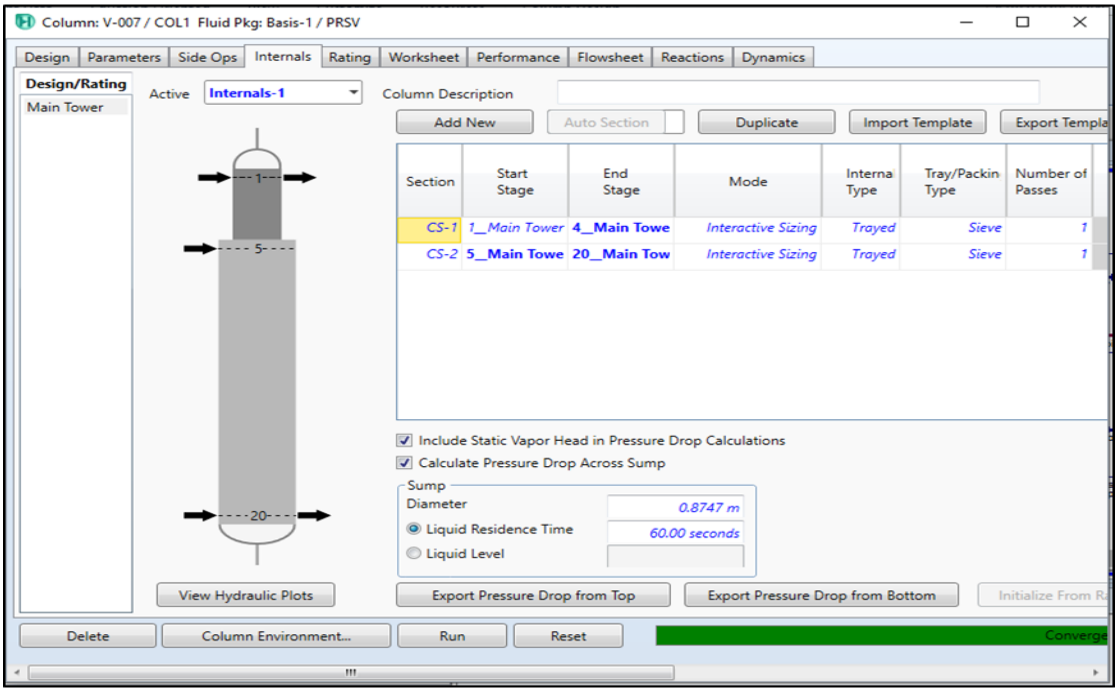
Bottoms Liquid Outlet: Bottoms

Stage Numbering: ● Top Down ○ Bottom Up

Edit Trays...

☑ Update Outlets ☐ Ignored

Figure 12. Distillation Column connections on Aspen Hysys.



Active: Internals-1

Column Description:

Section	Start Stage	End Stage	Mode	Interna Type	Tray/Packin Type	Number of Passes
CS-1	1__Main Tower	4__Main Towe	Interactive Sizing	Trayed	Sieve	1
CS-2	5__Main Towe	20__Main Tow	Interactive Sizing	Trayed	Sieve	1

☑ Include Static Vapor Head in Pressure Drop Calculations

☑ Calculate Pressure Drop Across Sump

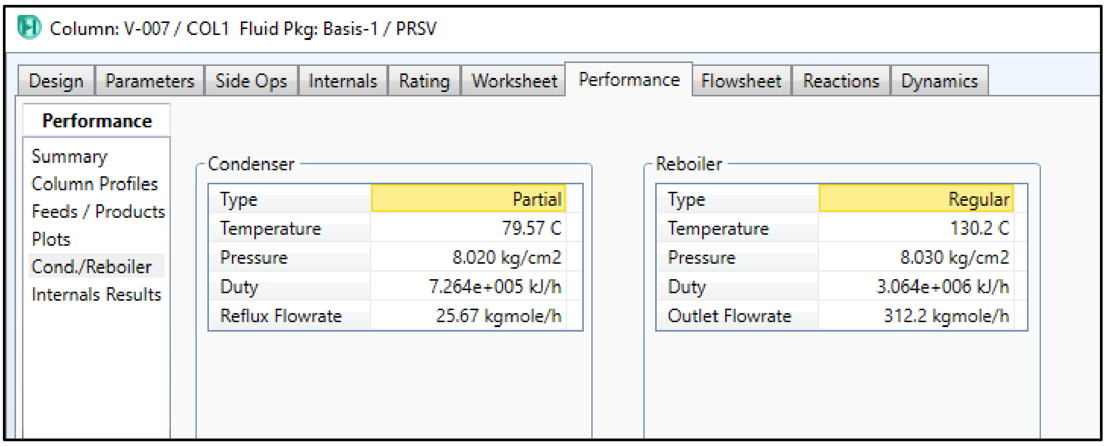
Sump

Diameter: 0.8747 m

● Liquid Residence Time: 60.00 seconds

○ Liquid Level:

Figure 13. Distillation Column Internals on Aspen Hysys..



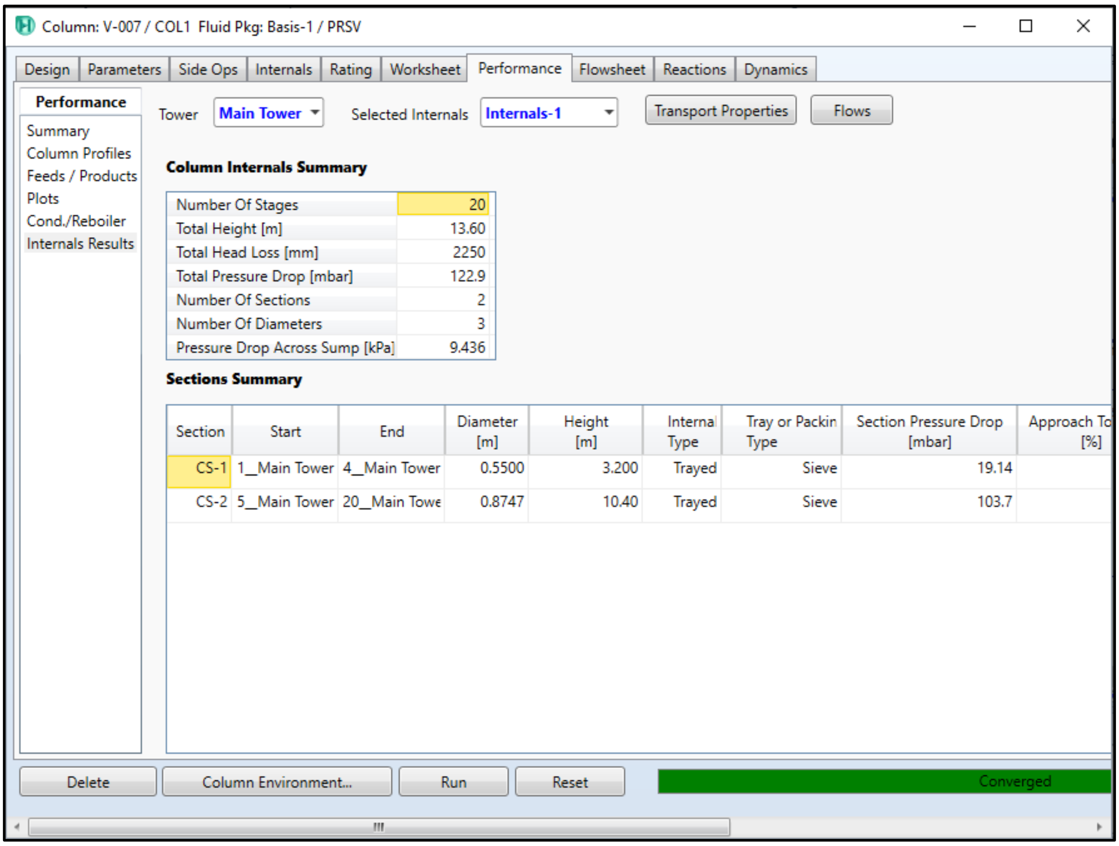
Condenser

Type	Partial
Temperature	79.57 C
Pressure	8.020 kg/cm2
Duty	7.264e+005 kJ/h
Reflux Flowrate	25.67 kgmole/h

Reboiler

Type	Regular
Temperature	130.2 C
Pressure	8.030 kg/cm2
Duty	3.064e+006 kJ/h
Outlet Flowrate	312.2 kgmole/h

Figure 14. Condenser and Reboiler specifications on Aspen Hysys.



Tower Main Tower

Selected Internals Internals-1

Column Internals Summary

Number Of Stages	20
Total Height [m]	13.60
Total Head Loss [mm]	2250
Total Pressure Drop [mbar]	122.9
Number Of Sections	2
Number Of Diameters	3
Pressure Drop Across Sump [kPa]	9.436

Sections Summary

Section	Start	End	Diameter [m]	Height [m]	Internal Type	Tray or Packin Type	Section Pressure Drop [mbar]	Approach To [%]
CS-1	1__Main Tower	4__Main Tower	0.5500	3.200	Trayed	Sieve	19.14	
CS-2	5__Main Tower	20__Main Towe	0.8747	10.40	Trayed	Sieve	103.7	

Converged

Figure 15. Distillation Column with Internals Specifications on Aspen Hysys

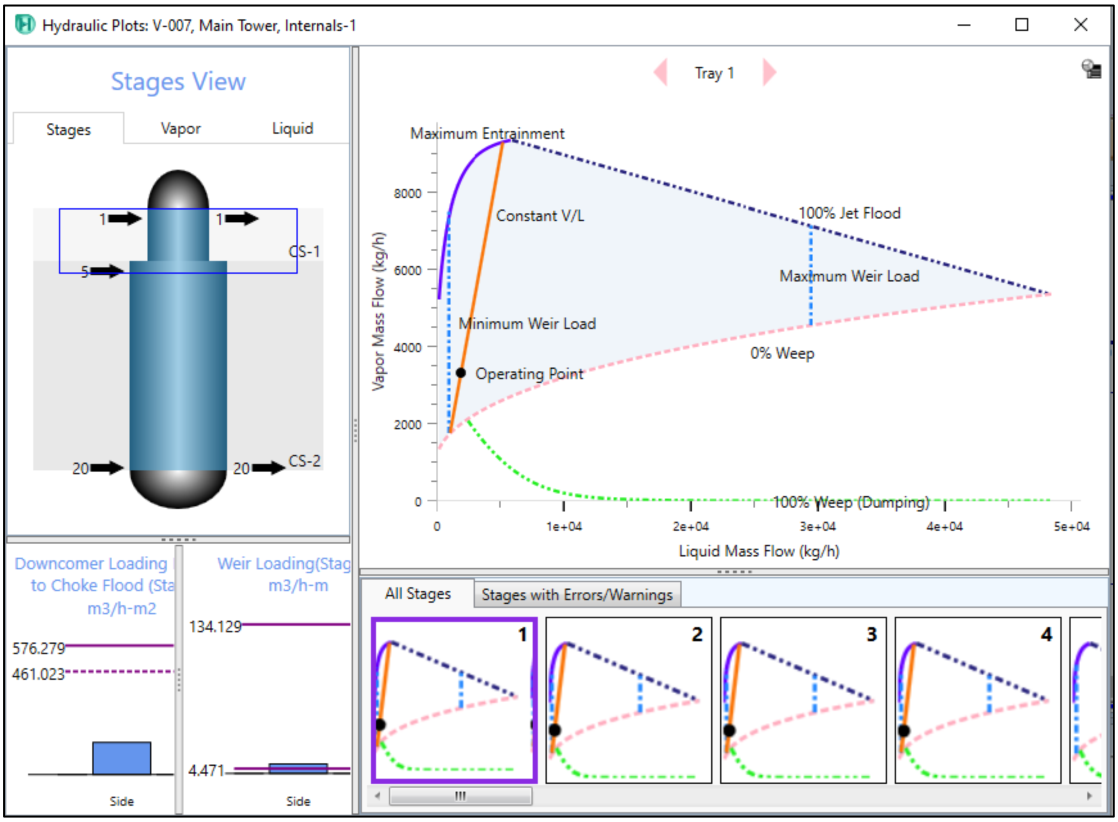


Figure 16. Hydraulic Plots of Distillation Column on Aspen Hysys.

As you can see from the above hydraulic plots, all the trays are working efficiently without any problem such as weeping or flooding. Hence the design that we have specified after hit and trial is quite effective one. The table below shows the overall parameters of the distillation column.

Table 19. Overall Distillation Column Specification Summary

Parameters	**Specifications**
No. of Ideal stages with reboiler	20
Actual No. of stages	24 (assuming 85 % efficiency)
Minimum Reflux ratio	0.49
Actual Reflux Ratio	1
Feed Point Location	5
Height of Column	13.6 m

Table 19. Overall Distillation Column Specification Summary (cont'd)

Number of Diameters	2
Diameter of upper section (D1)	0.55 m
Diameter of lower section (D2)	0.87 m
Type of trays	Sieve
Weir height for D1	66 mm
Weir length for D1	0.39 m
Weir height for D2	54 mm
Weir length for D2	0.79 m
Total Pressure Drop	122.9 mbar

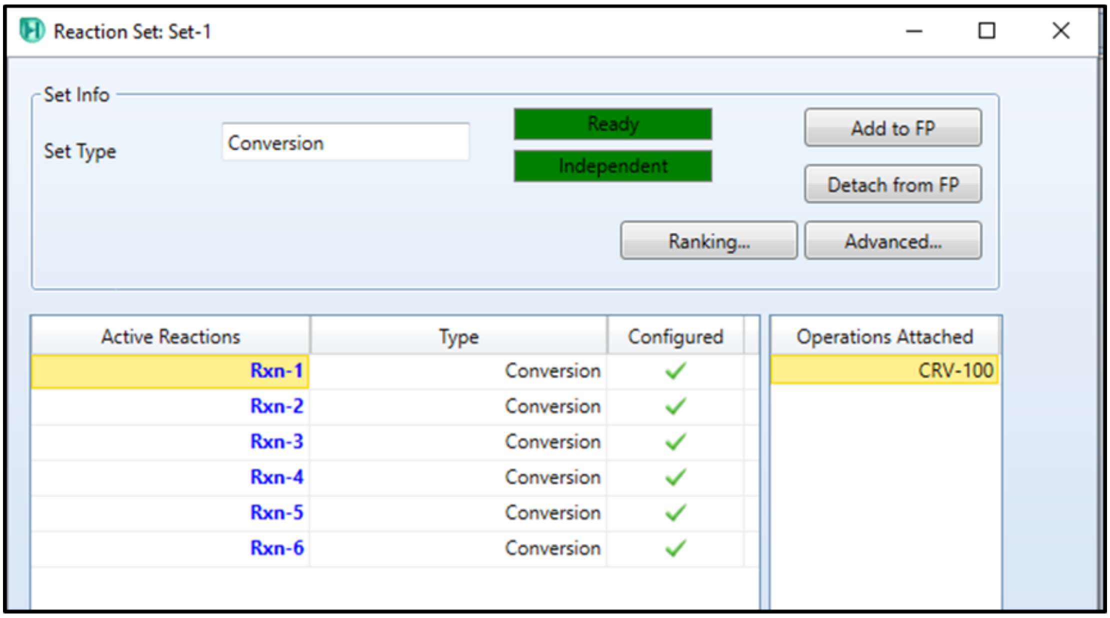
CHAPTER 7

SIMULATION

The simulation was done on Aspen Hysys. The results obtained were pretty close with the values which were calculated through material and energy balance and equipment design.

The fluid package used in this simulation was the PRSV property package employing the Peng-Robinson equation model as referred from the literature, and the other main reason was the presence of sulphur compounds, employing other suitable fluid package resulted in loss of properties of compounds like thiolane etc. Conversion reactor was used and conversions were employed to reactions which were previously determined by the CoMo/Al_2O_3 catalyst.

The following shows the reactions set and property package selected.

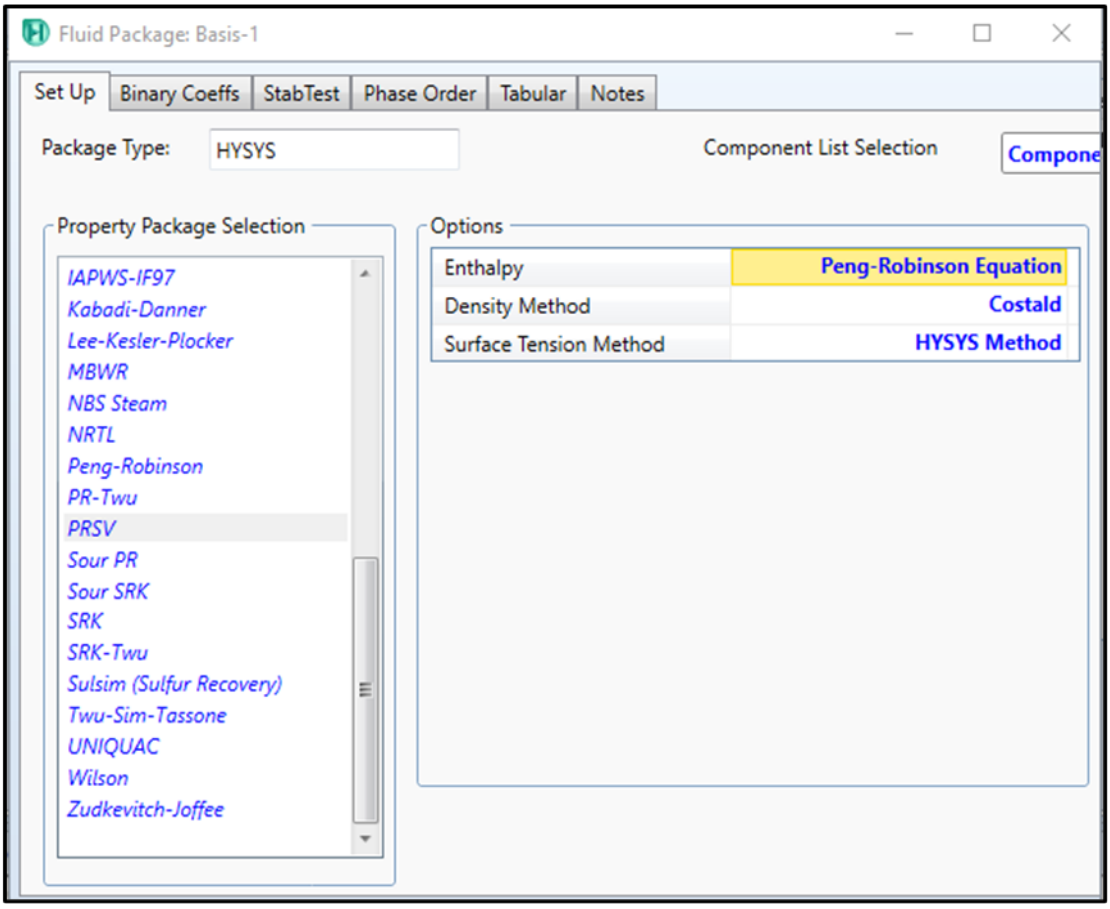


Set Type: Conversion

Active Reactions	Type	Configured
Rxn-1	Conversion	✓
Rxn-2	Conversion	✓
Rxn-3	Conversion	✓
Rxn-4	Conversion	✓
Rxn-5	Conversion	✓
Rxn-6	Conversion	✓

Operations Attached
CRV-100

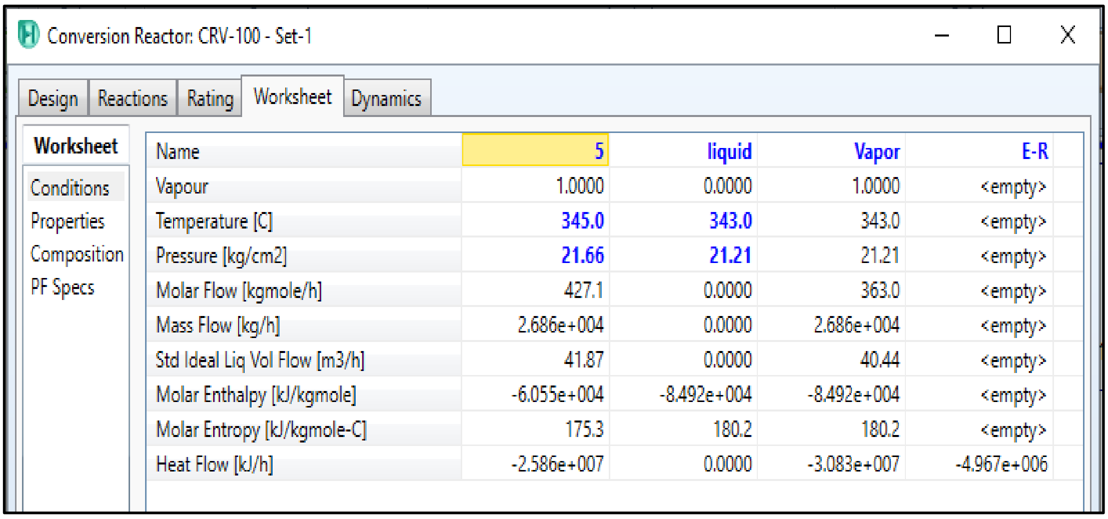
Figure 17. Reaction set on Aspen Hysys



Package Type: HYSYS

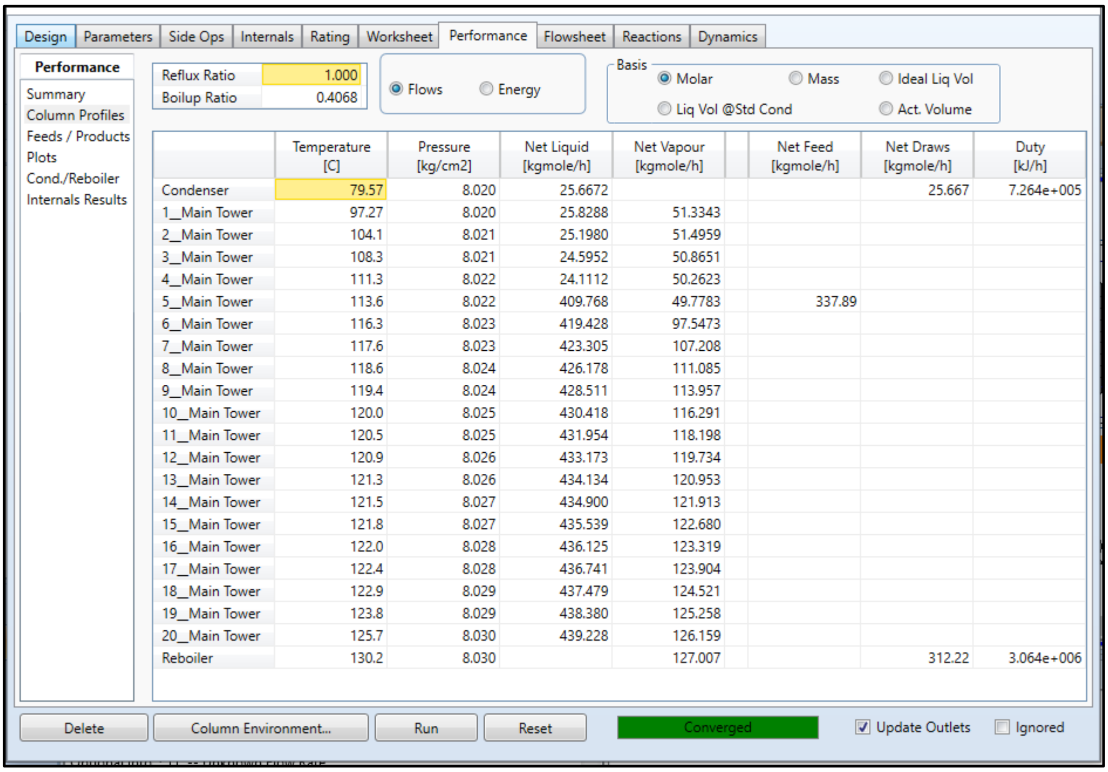
Enthalpy	Peng-Robinson Equation
Density Method	Costald
Surface Tension Method	HYSYS Method

Figure 18. Property package on Aspen Hysys



Name	5	liquid	Vapor	E-R
Vapour	1.0000	0.0000	1.0000	<empty>
Temperature [C]	345.0	343.0	343.0	<empty>
Pressure [kg/cm2]	21.66	21.21	21.21	<empty>
Molar Flow [kgmole/h]	427.1	0.0000	363.0	<empty>
Mass Flow [kg/h]	2.686e+004	0.0000	2.686e+004	<empty>
Std Ideal Liq Vol Flow [m3/h]	41.87	0.0000	40.44	<empty>
Molar Enthalpy [kJ/kgmole]	-6.055e+004	-8.492e+004	-8.492e+004	<empty>
Molar Entropy [kJ/kgmole-C]	175.3	180.2	180.2	<empty>
Heat Flow [kJ/h]	-2.586e+007	0.0000	-3.083e+007	-4.967e+006

Figure 19. Reactor Worksheet on Aspen Hysys



Reflux Ratio 1.000
Boilup Ratio 0.4068

● Flows ○ Energy

Basis: ● Molar ○ Mass ○ Ideal Liq Vol ○ Liq Vol @Std Cond ○ Act. Volume

	Temperature [C]	Pressure [kg/cm2]	Net Liquid [kgmole/h]	Net Vapour [kgmole/h]		Net Feed [kgmole/h]	Net Draws [kgmole/h]	Duty [kJ/h]
Condenser	79.57	8.020	25.6672				25.667	7.264e+005
1__Main Tower	97.27	8.020	25.8288	51.3343				
2__Main Tower	104.1	8.021	25.1980	51.4959				
3__Main Tower	108.3	8.021	24.5952	50.8651				
4__Main Tower	111.3	8.022	24.1112	50.2623				
5__Main Tower	113.6	8.022	409.768	49.7783		337.89		
6__Main Tower	116.3	8.023	419.428	97.5473				
7__Main Tower	117.6	8.023	423.305	107.208				
8__Main Tower	118.6	8.024	426.178	111.085				
9__Main Tower	119.4	8.024	428.511	113.957				
10__Main Tower	120.0	8.025	430.418	116.291				
11__Main Tower	120.5	8.025	431.954	118.198				
12__Main Tower	120.9	8.026	433.173	119.734				
13__Main Tower	121.3	8.026	434.134	120.953				
14__Main Tower	121.5	8.027	434.900	121.913				
15__Main Tower	121.8	8.027	435.539	122.680				
16__Main Tower	122.0	8.028	436.125	123.319				
17__Main Tower	122.4	8.028	436.741	123.904				
18__Main Tower	122.9	8.029	437.479	124.521				
19__Main Tower	123.8	8.029	438.380	125.258				
20__Main Tower	125.7	8.030	439.228	126.159				
Reboiler	130.2	8.030		127.007			312.22	3.064e+006

☑ Update Outlets ☐ Ignored

Figure 20. Distillation Column on Aspen Hysys

In the simulation fired heater is not used rather a heater with Fired Heat (1000) as utility type is used because the fuel composition which is used in industry is not given so it was not possible to determine the composition of fuel which is used in case of fired heater.

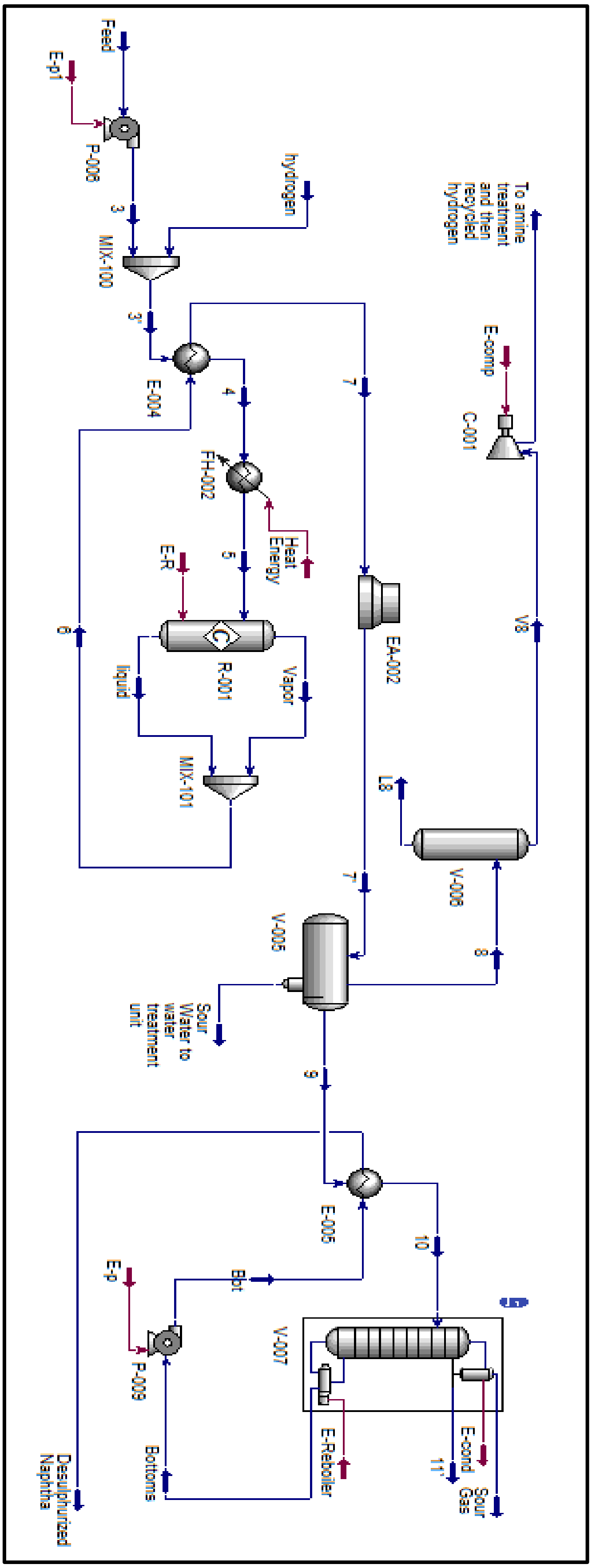


Figure 21. Simulation flow sheet from Aspen Hysys

CHAPTER 8

PROCESS CONTROL & INSTRUMENTATION

The importance of process control and instrumentation and how this is employed process employed in the hydrodesulphurization process is described in this chapter. The instrumentation ensures that the process remains safe.

8.1 Objectives of Process Control.

One of the main objective to apply controls and instrumentation process is to ensure the desired quality product and the improving the lifetime of the unit by neutralizing threats or minimizing the chances of equipment failure by providing safety measures through it. Following measures can be taken to do so:

1. A set point is to be specified and process variable is to be controlled to maintain it in limits.
2. A quick solution should be provided in the form of a control system or shutdown of a process in case of a large deviations from the set point.
3. The control system is put in place to avoid any human errors from the operators that may result the process to go outside of the safe operating conditions.

The major controlling parameters that have been manipulated in our project are:

1. Flow rate
2. Temperature
3. Level
4. Pressure

The above parameters can be controlled through different mechanisms or equipment like using controlling valves, different kind of alarms or indicators can be used to detect any deviations and hence the necessary measures can be done to maintain the set point within specified limit through control systems and instrumentation process.

8.2 Implementation of Control Systems in Design

In our process design, the control systems implemented are cascade, feed-forward and feedback. In cascade control system, the output of one process variable is controlled by altering the other variable. In other words, two different variables are interlinked with each other. In forward control system, only one of the variable is being manipulated whereas in feedback control system, the upstream variable is being manipulated according to the information provided by the downstream variable.

The best example of feedback control is the parallel pump system. The parallel pumps have been installed to run the process smoothly in case of a pump failure. The feed-backward control valves have implemented on the both pump lines with flow indicators to open and close valves according to the requirements in case of one pump failure or during maintenance. Our main feed pump initially was P-006A only but we have implemented another pump P-006B by keeping failure factor in our mind and similarly four valves have been installed to control the flow rate. Two valves: V-001 and V-002 for controlling flow of pump P-006A and the other two valves: V-003 and V-004 for controlling flow through pump P-006B and in this way by switching flow path we can ensure smooth and continuous flow across the whole desulfurization unit. This system is applied across all the pumps installed in our process design.

Following are the list of different types of controllers installed in our plant design.

Table 20. Controllers installed in the plant on different equipment

Equipment	**Name of Controller**	**Type of Controller**	**Manipulated Variable**	**Controlled Variable**
Fired Heater	TC	PI	Fuel Gas Flow rate	Temperature
	FC	PI	Valve opening	Fuel Gas Flow rate
Heat Exchangers	TC	PI	Streams Flow rate	Temperature
	FC	PI	Valve opening	Streams Flow rate
Reactor	PC	PI	Feed Flow rate	Reactor Pressure
	FC	PI	Valve opening	Feed Flow rate
Three Phase Separator	LC	PI	Flow rate	Liquid Level
	PC	PI	Valve opening	Pressure
Surge Drum	PC	PI	Valve opening	Pressure
Distillation Column	TC	PI	Flow rate of air	Temperature of inlet
	PC	PI	Flow rate of vapor stream	Pressure
	LC	PI	Flow rate of Inlet	Level
	FC	PI	Valve opening	Inlet Flow rate
	FC	PI	Valve opening	Reflux Flow rate
	TC	PI	Air Flow rate	Reflux Temperature
	FC	PI	Valve opening	Reboiler Outlet Flow rate
	TC	PI	Steam Flow rate	Reboiler Outlet Temperature

8.3 Distillation Column Control

In the distillation column design, the role of cascade control system is really important since many process variables are interlinked with each other especially around condenser and re-boiler. The temperature of the different streams like re-boiler and reflux streams have major impact on the performance of the distillation column and therefore it is need to be controlled very carefully and the cascade of control is the best choice to control the temperature of the recycle streams. It helps in controlling temperature by manipulating the flow rate of cooling and heating media which in our case is air and steam respectively. The controlling of flow rate is much easier by implementation of cascade control which can be done by simply opening and closing of valves otherwise it will be much difficult to control temperature directly.

The controlling pressure of the column is also an important task which is made easier through cascade control system which helps in controlling of pressure by manipulating the flow rate of the vapour stream leaving from top of the distillation column. Since the vapour build-up inside the column may result in higher pressure and these vapours need to be removed effectively within time at a proper flow rate to maintain constant pressure.

8.4 Reactor, Heater & Pre-heater Control

Flow control valve along with flow indicator is installed on the reactor feed stream to maintain constant flow of feed at constant pressure. HIC control system is also installed here to control the valve manually. This valve also helps in maintaining constant heat exchange from preheater and that’s why temperature indicator is also installed here. At fired heater flow control system is installed to controlled fuel flow rate which helps in maintain constant rise of temperature to preheated feed stream. Here pressure control system can also be used but it has more risks involved as compared to flow control system. The reactor control parameters are directly manipulated by these two control systems.

The simplified control system diagram of this whole loop is shown below:

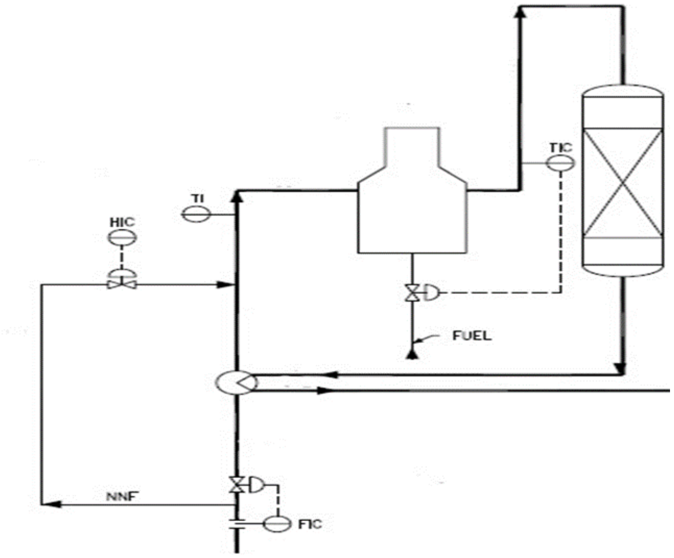


Figure 22. Control loop comprising of Reactor, Heater and Pre-heater

8.5 Three Phase Separator Control

Normally two phase separators have only two types of controllers and both of them are level controllers but three types of controllers are involved in three phase separators because of gas separation that happens on the base of pressure. One level controller is for water and other is for oil since both have density difference. Since the gases have higher pressure contained in vessel and they try to escape from top, that's why pressure control systems are there. The pressure relief valve is installed to the top of separator which allows them to escape from top and these gases are then recycled.

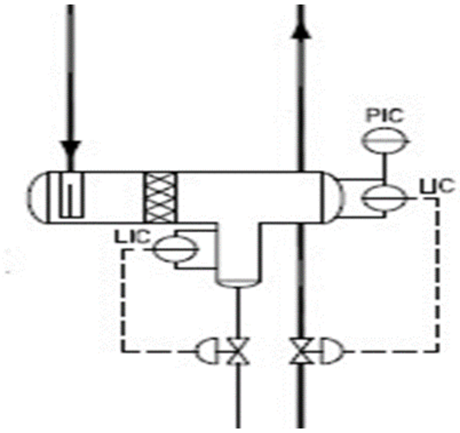


Figure 23. Controllers on Three phase separator

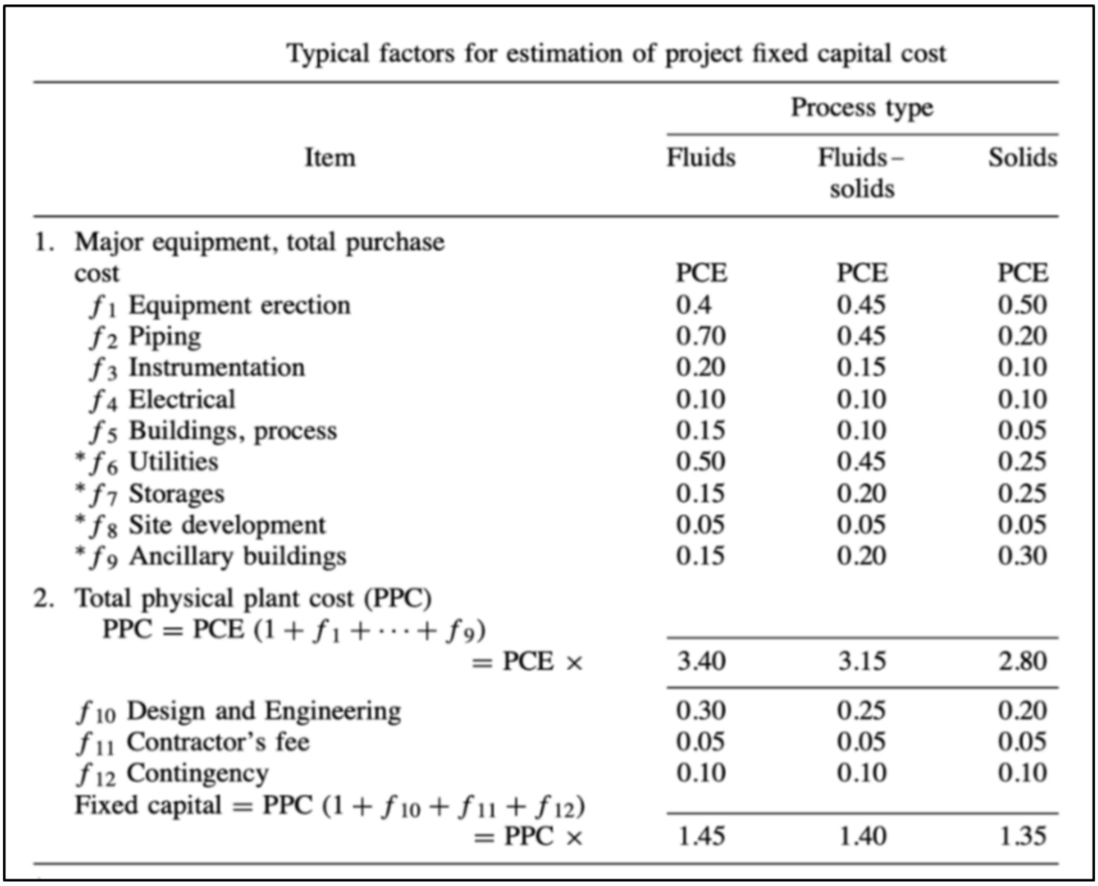
CHAPTER 9

COSTING & ECONOMIC ANALYSIS

This chapter deals with the cost and economic analysis of our plant, in order to determine whether it is feasible or not. All types of costs are included to calculate overall cost of process design. These different costs include variable costs, capital costs, working capital and engineering costs etc. Further, rate of investment and payback periods are calculated as well in order to show the profitability of the proposed process.

9.1 Costing

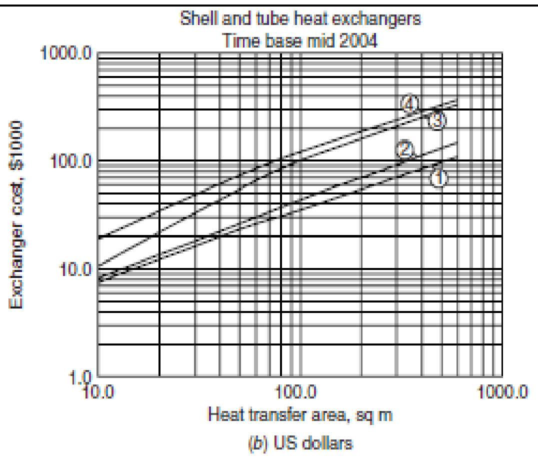
The costing was done both manual and through Aspen Hysys. The following data was used.



Typical factors for estimation of project fixed capital cost

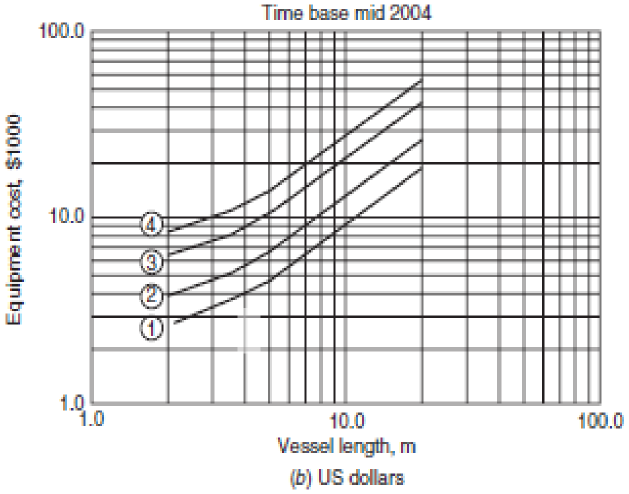
Item	Process type		
	Fluids	Fluids–solids	Solids
1. Major equipment, total purchase cost	PCE	PCE	PCE
f_1 Equipment erection	0.4	0.45	0.50
f_2 Piping	0.70	0.45	0.20
f_3 Instrumentation	0.20	0.15	0.10
f_4 Electrical	0.10	0.10	0.10
f_5 Buildings, process	0.15	0.10	0.05
*f_6 Utilities	0.50	0.45	0.25
*f_7 Storages	0.15	0.20	0.25
*f_8 Site development	0.05	0.05	0.05
*f_9 Ancillary buildings	0.15	0.20	0.30
2. Total physical plant cost (PPC)			
PPC = PCE $(1 + f_1 + \cdots + f_9)$			
= PCE ×	3.40	3.15	2.80
f_{10} Design and Engineering	0.30	0.25	0.20
f_{11} Contractor's fee	0.05	0.05	0.05
f_{12} Contingency	0.10	0.10	0.10
Fixed capital = PPC $(1 + f_{10} + f_{11} + f_{12})$			
= PPC ×	1.45	1.40	1.35

Figure 24. Factors for estimation of fixed capital cost



Materials		Pressure factors		Type factors	
Shell	Tubes				
① Carbon steel	Carbon steel	1–10 bar	× 1.0	Floating head	× 1.0
② C.S.	Brass	10–20	× 1.1	Fixed tube sheet	× 0.8
③ C.S.	Stainless steel	20–30	× 1.25	U tube	× 0.85
④ S.S.	S.S.	30–50	× 1.3	Kettle	× 1.3
		50–70	× 1.5		

Figure 25.PCE for Shell and Tube HE



Diameter, m

①—0.5 ③—2.0
②—1.0 ④—3.0

Material factors	
C.S.	× 1.0
S.S.	× 2.0
Monel	× 3.4
S.S. clad	× 1.5
Monel clad	× 2.1

Pressure factors	
1–5 bar	× 1.0
5–10	× 1.1
10–20	× 1.2
20–30	× 1.4
30–40	× 1.6
40–50	× 1.8
50–60	× 2.2

Temperature up to 300°C

Figure 6.6*a*, *b*. Horizontal pressure vessels. Time base mid-2004. Purchase cost = (bare cost from figure) × Material factor × Pressure factor

Figure 26. PCE for Horizontal Vessels

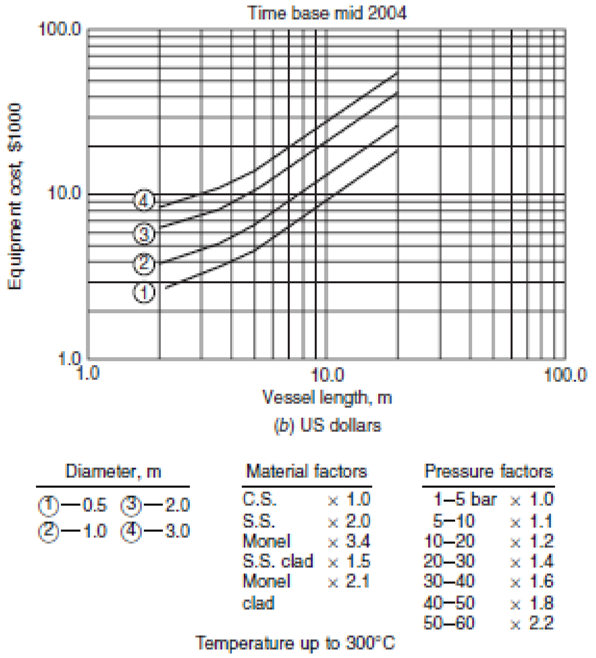


Figure 6.6*a*, *b*. Horizontal pressure vessels. Time base mid-2004.
Purchase cost = (bare cost from figure) × Material factor × Pressure factor

Figure 27. PCE for Horizontal Vessels

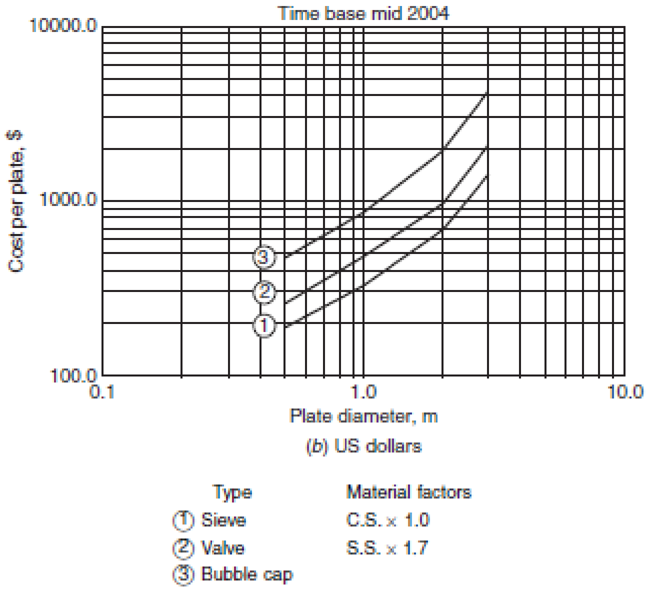
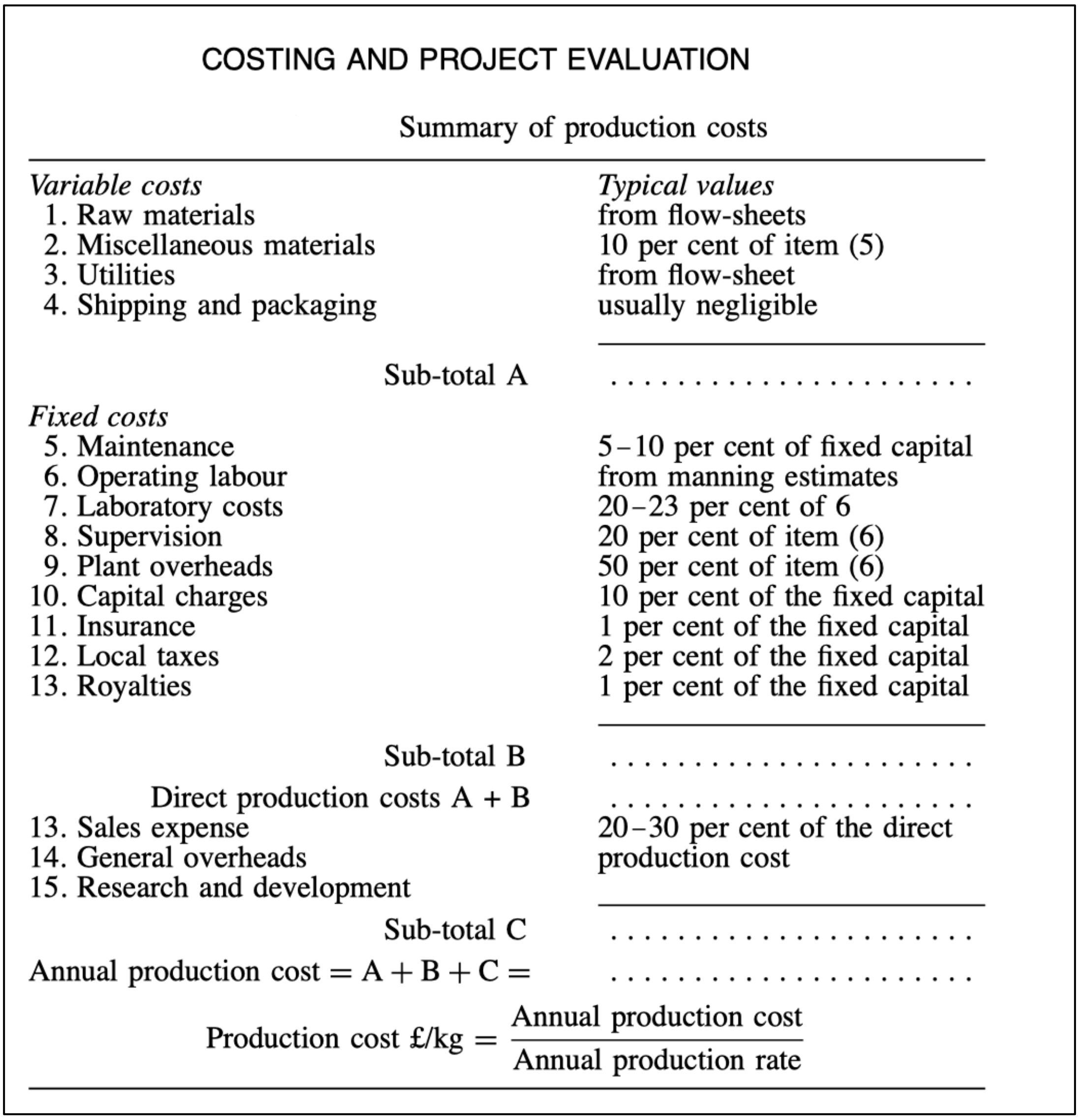


Figure 6.7*a*, *b*. Column plates. Time base mid-2004 (for column costs see Figure 6.4)
Installed cost = (cost from figure) × Material factor

Figure 28. PCE for Column Plates



COSTING AND PROJECT EVALUATION

Summary of production costs

Variable costs	*Typical values*
1. Raw materials	from flow-sheets
2. Miscellaneous materials	10 per cent of item (5)
3. Utilities	from flow-sheet
4. Shipping and packaging	usually negligible
Sub-total A	. . . .
Fixed costs	
5. Maintenance	5–10 per cent of fixed capital
6. Operating labour	from manning estimates
7. Laboratory costs	20–23 per cent of 6
8. Supervision	20 per cent of item (6)
9. Plant overheads	50 per cent of item (6)
10. Capital charges	10 per cent of the fixed capital
11. Insurance	1 per cent of the fixed capital
12. Local taxes	2 per cent of the fixed capital
13. Royalties	1 per cent of the fixed capital
Sub-total B	. . . .
Direct production costs A + B	. . . .
13. Sales expense	20–30 per cent of the direct production cost
14. General overheads	
15. Research and development	
Sub-total C	. . . .
Annual production cost = A + B + C =	. . . .

$$\text{Production cost £/kg} = \frac{\text{Annual production cost}}{\text{Annual production rate}}$$

Figure 29. Summary of Production Costs

Table 21. Annual Costs of Feed and Product

Material with mass flow	Annual costs= USD /year
Naphtha product =25000kg/hr	117165000
Naphtha feed=26689kg/hr	77155452
Hydrogen=169kg/hr	18839413.68

The following table shows all the individual and then total purchased cost of our plant equipment.

Table 22. Equipment Costs of Project

Equipment Costs of Project		
Name	**Equipment Cost (2004) [USD]**	**Equipment Cost (2020) [USD]**
Charge Pump P-006	41353.00	66029.26
Heat Exchanger E-004	65000.00	103786.95
Cooler EA-002	18788.49	30000.00
Heater FH-002	68554.00	109461.71
Reactor R-001	45243.00	72240.51
Three phase Separator V-005	3240.00	5173.38
Suction Drum V-006	3638.00	5808.88
Compressor C-001	34697.00	55401.48
Heat Exchanger E-005	50000.00	79836.12
Reboiler E-006	42712.00	68199.21
Condenser EA-002	18788.49	30000.00
Distillation column V-007	37000.00	59078.73
Bottoms Pump P-009	14713.00	23492.58
TOTAL (PCE)	**443726.98**	**708508.79**

Table 23. Production Costs of Project

COSTING AND PROJECT EVALUATION			
Summary of production costs			
	Variable costs	**Typical values**	**Costs ($)**

1	Raw materials.	from flow-sheets	95994865
2	Miscellaneous operating materials.	10 % of item (5)	15126
3	Utilities (Services).	from flow-sheet	65982
4	Shipping and packaging.	usually negligible	0
	Sub-total A		**96075974**
	Fixed costs		
5	Maintenance (labour and materials).	5 -10 % of fixed capital	151266
6	Operating labour.	from manning estimates	200000
7	Laboratory costs.	20 23 % of (6)	40000
8	Supervision	20 % of item (6)	40000
9	Plant overheads	50 % of item (6)	100000
10	Capital charges.	10 % of the fixed capital	302533
11	Rates (and any other local taxes).	1% of the fixed capital	30253
12	Insurance.	2 % of the fixed capital	60506
13	License fees and royalty payments.	1 % of the fixed capital	30253
	Sub-total B		**954813**
	Direct production costs A + B		**97030787**
14	Sales expense	20 -30% of the direct production cost	19406157
15	General overheads		0
16	Research and development		0

Table 23. Production Costs of Project (cont'd)

	Sub-total C		**19406157**
	Annual production cost A + B + C		**116436945**
	Production Cost (USD/kg)		**0.99**

9.2 Cost Evaluation

The following equations were used to find out the production cost and the payout period of our plant.

$$Cost\ in\ year\ 2019\ =\ Cost\ in\ year\ 2004\ \times \frac{CPE\ Index\ 2020}{CPE\ Index\ 2004}$$

$$\frac{CPE\ Index\ 2020}{CPE\ Index\ 2004} = 1.59$$

$$Production\ Cost\ (\frac{USD}{kg}) = \frac{Annual\ Production\ Cost}{Annual\ Production\ Rate}$$

$$Payout\ Period = \frac{Total\ Investment}{Average\ Cash\ Flow}$$

$$Purchase\ Cost\ of\ equipment\ =\ PCE =\ 708509\ USD$$

$$Total\ Physical\ Plant\ Cost\ = PPC =\ 2160951\ USD$$

$$Fixed\ Capital = 3025333\ USD$$

$$Working\ Capital = 151267\ USD$$

$$\begin{aligned} Total\ investment\ required &=\ Fixed\ capital\ + Working\ capital \\ &= 3176599\ USD \end{aligned}$$

$$Total\ Income\ =\ 117165000\ USD$$

$$Annual\ Profit =\ 728055\ USD$$

$$Payback\ Period = 4.3\ years$$

A pay out period of 4.3 years shows that the designed plant is highly feasible in both economic and efficiency terms.

CHAPTER 10

HAZOP STUDY

This chapter will describe the possible hazards that can take place when the process is functional on a plant. The Hazop study carries out a detail risk assessment of what hazards might occur when a process is fully functional.

Hazard and operability study analysis (HAZOP) is a qualitative technique, done to determine the potential hazard of equipment. HAZOP is done on both on and off-site equipment. The main aim of the HAZOP is to identify the hazardous situations and to determine the efficient working of the safeguards to prevent unwanted scenarios or to control those scenarios.

HAZOP is important to operate the plant within safe limits. We have developed the HAZOP for different nodes which would explain the methodology. HAZOP is necessary before building a chemical plant. In other words, it's a legal requirement to quantify all the hazards and risk present on the plant.

10.1 Course of action

In the HAZOP analysis, the most important parameter is to select the critical nodes. We have selected the inlet of reactor as our first node since it's the most critical one due to high pressure and temperature variables and the second node selected is the inlet of the distillation column.

The parameters included in the study are:

- Flow
- Temperature
- Pressure

And the "Guide Words" selected are:

- None
- More
- Less

These guide words were applied and then the deviations, possible causes and consequences were studied and then recommendation plan was devised.

Table 24. Hazop Study at Reactor Inlet

Guide Word	**Parameter**	**Deviation**	**Possible Causes**	**Consequences**	**Action Required**
No	Flow	No flow to Reactor	Pump failure, Line Failure	Loss of feed to reactor, No product formation	Installation of standby pump and shift load on it, Maintenance of plant piping
More		Excess flow to reactor	Control faults	Damage to valves , Low conversion in reactor	Inspection of valves, Installation of flow control between reactor & heater
Less		Less flow to reactor	Leakage, Line damage	Production Loss	Regular patrolling and inspection of transfer line
More	Pressure	High pressure of inlet stream	Malfunctioning of valve	Explosion of reactor	Installation of pressure relief valve, Installation of rupture disc on reactor

Table 24. HAZOP Study at Reactor Inlet (cont'd)

Less	Pressure	Low pressure of inlet stream	Control faults	Low conversion, Decrease in catalytic activity	Pressure relief valve installation using differential pressure control to ensure safe limit
More	Temperature	High temperature of inlet stream	Failure of pressure reduction valve	Increased temperature in reactor leading to excess heat	Ensure temperature warning and Installation of Pressure relieve valves
Less		Low temperature of inlet stream	Control failure of heater temperature	Decrease in conversion	Installation of temperature controls

Table 25. Hazop study at Distillation Column Inlet

Guide Word	**Parameter**	**Deviation**	**Possible causes**	**Consequences**	**Action Required**
No	Flow	No flow to the column	Pipe failure	Distillation would not occur	Maintenance of plant piping

Table 25. HAZOP study at Distillation Column Inlet (cont'd)

More	Flow	Excess flow to the column	Control faults	Low efficiency for separation, Flooding	Inspection of valves, Installation of flow controller which regulates valve opening
Less		Less flow to column	Leakage in pipe, Valve partially open	Production Loss	Regular inspection of line
More	Pressure	High pressure of inlet stream	Malfunctioning of valve, Control faults	Explosion of column	Installation of pressure relief valve
Less		Low pressure of inlet stream	Control faults	Poor Separation	Using differential pressure control to ensure safe limit
More	Temperature	High temperature of inlet stream	Fire situation, Valve failure	It will lead to separation of both the top and bottom as vapours, Damage to equipment, Explosion	Ensure there is adequate warning of high temperature, Pressure relief valves
Less		Low temperature of inlet stream	Control faults of cooler	Poor Separation	Installation of temperature controls

CONCLUSION

The proposed process has been efficiently designed to meet the requirements i.e. the final product which is desulphurized naphtha contains less than 1 ppm sulphur. The process has also been optimized with main focus on reactor and distillation column. Process optimization is also done in terms of production, cost and energy efficiency while taking into consideration the environmental hazards at the same time.

- The use of $CoMo/Al_2O_3$ catalyst ensures the conversion of sulphur compounds up to 97% while being cost effective as well.
- The process is made energy efficient by use of heat exchangers for preheating reactor inlet and for preheating distillation column inlet with column bottom product thereby reducing energy requirements.
- The process is environment friendly since the hydrogen sulphide which is highly toxic gas is sent to sour gas treatment section where it is treated to form H_2S water. Hence in this way it is made sure that it does not directly release into environment.
- The results of the process simulation validated the calculations and design of the process and verified the operability of the process.
- The process is evaluated for a pay-out period of 4.3 years which indicate that the process is not only feasible but economically profitable as well.
- Different controllers are used throughout the process in order to make sure that the designed process works within safety regulations so that there is not unnecessary downtime or equipment failure.
- Hazop analysis of the process was also done in order to make sure that the possible hazards can be dealt efficiently while maintaining safe environment for the hydrodesulphurization of naphtha.

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