# Hydrodesulphurization of diesel 22000 Bbl./day in conformance with Euro-VII specification



2k15-2k19

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# Approval Certificate



**Session 2015-2019**

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# ACKNOWLEDGEMENT

Any accomplishment requires the effort of many people and there are no exceptions. The design report **Hydrodesulphurization of diesel 22000 bbl/day in conformance with Euro-VII specification** being submitted today is a result of combined effort of group. Although the report has been prepared by group efforts with the purpose of fulfilling the requirements of the course there are in numerous helping hands behind it who have guided us on our way. First we thank our head of department **"Engr. Dr. Sadiq Hussain"** for creating such an opportunity for the students to broaden their frame of skills. We are gratified with their efforts. Our sincere gratitude & thanks goes to our Supervisor **"Engr. Hidayatullah Mahar"** who helped us to prepare this report.

# **Dedicated to**

Beloved Parents

Our Respectable Supervisor

Engr. Sir Hidayatullah Mahar

&

Respectable Teachers

# Summary

The importance of the diesel fuel for meeting the energy demands needs no explanation. Due to increase in the number of vehicles, the environmental problems have become of immense concern for the whole world. Ministry of Petroleum Pakistan imposed Euro-V specifications for diesel oil to meet the environment regulations. Developed countries had introduced Euro-III and Euro-Iv diesel. So, there is a great need to produce such fuels which cause less pollution and hence there is great need to produce Euro-VII Diesel Oil. In this report a plant having capacity 22000 bbl/day has been designed for the removal of sulfur from diesel oil by hydrodesulphurization (HDS) process. In the reactor, hydrodesulphurization reactions occurring and all are exothermic. The hydrogen sulfide produced in the reactor is separated in the separator from the oil and is absorbed in the di-ethanol amine while hydrogen recovered is recycled back. In the stripper, light gases are removed from the oil and are sending in the naphtha treating unit. Desulphurized is obtained from the bottom of the stripper. Amount of hydrogen required is 6000 kg/hr.At the end light gases are also obtained along with desulphurized fuel 32580 kg/hr. and our desired product is 1149120 kg/hr. Total energy required for this project is 156424256.7 kJ/kg. Total capital cost required for the project is US $11050252.05. Major equipments are shell and tube heat exchanger having tubes OD 38mm and ID 34mm. Trickle bed reactor diameter 3.3 m, Tray absorber 18m height, separator 37.33 sec hold up time and stripper having 21 theoretical trays and 47.15 m height. For the safety, maintenance and the product optimization, the necessary process control loops are introduces on the major equipments. One limitation of this process is catalyst exhaust after a certain period of time. Some techniques are being developed to replace the process of hydrodesulphurization with solvent extraction. We are hopeful that this project will prove useful to the readers.

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# Chapter No.1

# Introduction

## 1.1 Historical background

The removal of sulfur compounds from crude oil is very important to improve its quality. The sulfur compounds (such as thiophenes, benzothiophenes, dibenzothiophene and their derivatives) are naturally present in the crude. In recent years, deep desulfurization of diesel fuel has attracted much attention due to the gradual reduction of the statutory sulfur content in most western countries. In the near future the maximum sulfur content will be limited down to 10–50 ppm compared to today's value of 5100 ppm. These efforts aim to limit $SO_2$ emission from diesel engines which has bad impacts on the environment like air pollution and acidic rain and other effects and also to protect equipment from corrosion. In industry, desulfurization of diesel is actually carried out by hydro-treating. Generally, this allows the elimination of aliphatic and alicyclic sulfur compounds. However, if $H_2S$ dissolved in the oil in the presence of air elemental sulfur is formed, and the removal of it difficult using distillation because the elemental sulfur change it structure with the temperature. Many other methods reported for the desulfurization [1].

## 1.2 Need of Low Sulfur Diesel

In today's era, increasing environmental pollution is galvanizing the researcher to find efficient ways for producing fine quality fuels which must be environment friendly.

## 1.3 Health effects of sulfur

During combustion, the sulfur compound in the fuel burns to form acidic by-products (such as sulfur dioxide, sulfur tri-oxide), and also sulfates, in the exhaust. The exhaust emissions contain $SO_x$, $NO_x$, CO, $CO_2$, PM and unburned hydrocarbons (HC). Several studies have shown that the amount of $SO_x$ emissions is directly proportional to the amount of sulfur contained in the fuel-II. Sulfur dioxide affects human health when it is breathed in. It irritates the nose, throat and airways to cause coughing, wheezing, shortness of breath, or a tight feeling around the chest. The effects of sulfur dioxide are felt very quickly and most people would feel the worst symptoms in 10 or 15 minutes after breathing it in.

Petroleum fractions contain various amounts of naturally occurring contaminants including organic sulfur, nitrogen, and metal compounds. These contaminants may contribute to increased levels of air pollution, equipment corrosion, and cause difficulties in downstream processing of the material.

The best option for preventing exposure to diesel exhaust is to prevent it from being generated. This can be accomplished through several different means. First diesel engines can be replaced with engines that use alternative fuels such as liquid propane or compressed natural gas. Second, diesel fuels can be reformulated to reduce the amount of sulfur and other contaminant generating compounds that they contain. Third, diesel engines can be redesigned to reduce the amount of

pollutants that they generate. Finally, emissions control equipment can be added to existing diesel engines. These engines emit far fewer pollutants than diesel engines, particularly diesel exhaust. Diesel fuel reformulation can be a relatively simple and straightforward process. The reformulation most commonly used today and required by the EPA for On Road diesel engines in 2007 is to reduce the sulfur content of diesel fuel from as high as 3000 ppm to less than 15 ppm. Diesel fuel reformulation may allow better emissions control technology such as particulate traps and catalytic converters to be used. The particulate traps can remove up to 95% of the particulates that are present in diesel exhaust. Traps that have a catalytic action can remove up to 90% of carbon monoxide, 90% of hydrocarbons, and 10% of nitrogen oxides present in diesel exhaust. Oxidation catalysts can be used light in light trucks and cars in addition to heavy-duty vehicles. These catalysts are able to remove up to 90% of carbon monoxide, 90% of hydrocarbons, and 25-50% of particulate matter in diesel exhausts.

All living things need sulfur. It is especially important for humans because it is part of the amino acid methionine, which is an absolute dietary requirement for us. The amino acid cysteine also contains sulfur. The average person takes in around 900 mg of sulfur per day, mainly in the form of protein. Elemental sulfur is not toxic, but many simple sulfur derivates are, such as sulfur dioxide ($SO_2$) and hydrogen sulfide.

Sulfur can be found commonly in nature as sulphides. During several processes sulfur bonds are added to the environment that are damaging to animals, as well as humans. These damaging sulfur bonds are also shaped in nature during various reactions, mostly when substances that are not naturally present have already been added. They are unwanted because of their unpleasant smells and are often highly toxic.

Globally sulfuric substances can have the following effects on human health:
- Neurological effects and behavioral changes
- Disturbance of blood circulation
- Heart damage
- Effects on eyes and eyesight
- Reproductive failure
- Damage to immune systems
- Stomach and gastrointestinal disorder
- Damage to liver and kidney functions
- Hearing defects
- Disturbance of the hormonal metabolism
- Dermatological effects
- Suffocation and lung embolism [2].

## 1.4 Effect of Sulfur on Environment

Sulfur can be found in the air in many different forms. It can cause irritations of the eyes and the throat with animals, when the uptake takes place through inhalation of sulfur in the gaseous phase. Sulfur is applied in industries widely and emitted to air, due to the limited possibilities of destruction of the sulfur bonds that are applied. The damaging effects of sulfur with animals are

mostly brain damage, through malfunctioning of the hypothalamus, and damage to the nervous system.

Laboratory tests with test animals have indicated that sulfur can cause serious vascular damage in veins of the brains, the heart and the kidneys. These tests have also indicated that certain forms of sulfur can cause fetal damage and congenital effects. Mothers can even carry sulfur poisoning over to their children through mother milk. Finally, sulfur can damage the internal enzyme systems of animals [2].

## 1.5 Chemical and Physical Properties of Sulfur

Sulphur is a multivalent non-metal, abundant, tasteless and odorless. In its native form sulfur is a yellow crystalline solid. In nature it occurs as the pure element or as sulfide and sulfate minerals. Although sulfur is infamous for its smell, frequently compare to rotten eggs, that odor is actually characteristic of hydrogen sulfide ($H_2S$).

The crystallography of sulfur is complex. Depending on the specific conditions, sulfur allotropes form several distinct crystal structures [3].

**Table 1 Chemical and Physical Properties of sulfur**

| | |
|---|---|
| Atomic Number | 16 |
| Atomic mass | 32.06 g.mol$^{-1}$ |
| Electronegativity according to Pauling | 2.5 |
| Density | 2.7 gm.cm$^{-3}$ at 20 $^0$C |
| Melting Point | 113 $^0$C |
| Boiling Point | 445 $^0$C |
| Vander Waals Radius | 0.127 nm |
| Ionic radius | 0.184 (-2) nm; 0.029 (+6) |
| Isotopes | 5 |
| Electronic Shell | [Ne] $3s^2 3p^4$ |
| Energy of first ionization | 999.3 kJmol$^{-1}$ |
| Energy of second ionization | 2255 kJmol$^{-1}$ |
| Energy of third ionization | 3357 kJmol$^{-1}$ |
| Standard potential | -0.51V |
| Discovered by | The ancients |

### 1.5.1 Properties of Diesel Fuel

Fuels, as for any other type of substance, can be assigned some physical and chemical properties (e.g. density, thermal capacity, vapor pressure, chemical formula, etc. However, most of the times,

| | |
|---|---|
| Density | $830kg/m^3$ |
| Thermal expansion coefficient | $800\times10^{-6}\ K^{-1}$ |
| Boiling and freezing points | Not defined because they are mixtures |
| Viscosity (for diesel) | $3\times10^{-6}\ m^2/s$ ($2.0\times10^{-6}$ to $4.0\times10^{-6}\ m^2/s$ at 40 ℃) |
| Viscosity (for Biodiesel) | $4.0\times10^{-6}$ to $6.0\times10^{-6}\ m^2/s$ |
| Vapor pressure | 1 to 10 kPa at 38 ℃ |
| Cetane number | 45 (between 40-55) |
| Flash-point <br><br><br> Heating value. | 50 ℃ typical (40 ℃ minimum) <br> HHV=47 MJ/kg <br> LHV=43 MJ/kg |

combustion properties are also assigned to fuels, in spite of the fact that these properties depend on the oxidizer (e.g. air, pure oxygen) and the actual process (e.g. the explosion limits depend on the boundary conditions for a given fuel/oxidizer pair)

**Table 2 Properties of diesel fuel**

## 1.6 Sulphur in the Environment

Life on Earth may have been possible because of Sulphur. Conditions in the early seas were such that simple chemical reactions could have generate the range of amino acids that are the building blocks of life. Sulphur occurs naturally near volcanoes. Native Sulphur occurs naturally as massive deposits in Texas and Louisiana in the USA. Many sulphide minerals are known: pyrite and marcasite are iron sulphide, stibnite is antimony sulphide, galena is lead sulphide, cinnabar is mercury sulphide and sphalerite is zinc sulphide. Other, more important, sulphide ores are chalcopyrite, bornite, penlandite, millerite and molybdenite. The chief source of Sulphur for industry is the hydrogen sulphide of natural gas, Canada is the main producer [2].

## 1.7 Pakistan moving to EURO-II

Presently Pakistan is remaining around a mere value of 500ppm of sulfur contents. But now standards and research has changed the situation and the Pakistani government is also taking initial steps to take part in the race of cleaner fuels to produce a better environment. Government is inspiring and supporting the refiners to shift their facilities towards low sulfur contents diesel. By these steps Pakistan Refinery Limited (PRL), Pakistan's leading refinery decided in 2006 to invest US$182.5 million in the next three years "for the upgrading the facilities of the refinery to develop environment friendly and to meet the future diesel hydrotreating unit, visbreaking unit, hydrogen producing plant, deasphalting facility sulfur recovery plant, amino treatment facility and vacuum distillation unit. These facilities will add premium quality products for the local market as per the Euro-2 specification and will also produce exportable sulfur contents." Meanwhile, a report from Gulf News (UAE), "Pakistan's diesel demand is forecast to increase 70% in a decade to 15.07 million tones, as the overall fuel consumption almost doubles, forcing the country to boost imports" (National Refinery Manual 2012).

In Pakistan, NRL is presently producing HSD of around 1.0% sulfur content. In view of clean fuel quality requirements, NRL is planning up gradation of its facilities to enable production of HSD of 0.05 wt. % sulfur content. The ultimate aim is to reduce sulfur further to 50 parts per million. UOP-an international process designer & licensor-are carrying out the techno economic feasibility for conversion of redundant Kero Hydrobon unit to diesel service. After project completion, NRL will be the first refinery in Pakistan to produce diesel of low sulfur up to 500ppm and further to less than 50ppm-ULSD, i.e. Euro-IV specification (National Refinery Manual 2012)

## 1.8 Sulfur content of crude oils

### 1.8.1 Origin of sulfur

Sulfur in crude oil comes generally from the decomposition of organic matter, and with the passage of time and of gradual settling into strata, the sulfur segregates from crude oil in the form of hydrogen sulfide that appears in the associated gas, some portion of sulfur stays with the liquid. Another theory behind origin of sulfur compounds is the reduction of sulfates by hydrogen by bacterial action of the type desulforibrio desulfuricans:

$$4H_2 + SO_4 + (bacteria) \rightarrow H_2S + 2OH^{-1} + 2H_2O$$
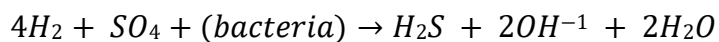
Hydrogen comes from the reservoir fluid and the sulfate ions are kept in the reservoir rock, as a result hydrogen sulfide is generated. The HS formed can react with the sulfates or rock to form sulfur that remains in composition of crude as in the case of oil from Goldsmith, Texas, USA. Moreover, under the conditions of pressure, temperature and period of formation of the reservoir $H_2S$ can react with the hydrocarbons to give sulfur compounds (Wauquier, 1995):

$$3H_2S + SO_4 \rightarrow 4S + 2OH^{-1} + 2H_2O$$

Sulfur compounds are among the most important non-hydrocarbon heteroatomic constituents of petroleum. There are significant amount of sulfur species found in crude oil and sulfur compounds of one type or another are present in all crude oils. Furthermore, only preferred type of sulfur exist in any particular crude oil, and this is dictated by the prevailing conditions during the formation, maturation, and even in situ alteration. In general, the higher the density of the crude oil, the lower

the API gravity of the crude and the higher the sulfur content. The total sulfur in crude oil can vary from 0.04% w/w for light crude oil to about 5% w/w for heavy crude oil and tar sand bitumen. Nevertheless, the sulfur content of crude oils which is produced from different locations varies with time, depending on the chemical composition of newly discovered fields, especially those in different geological environments (Speight, 2007).

**1.8.2 Nature of Sulfur compounds**

Sulfur compounds are substances of different chemical nature, from the elemental sulfur to hydrogen sulfide, sulfides, open-chain and cyclic disulfides, and heterocyclic derivatives of thiophene, thiophane and other more complex compounds. Free elemental sulfur is rarely found in crude oils. The emergence of free sulfur is associated with the decomposition of more complex sulfur compounds.

**1.8.3 The sulfur compounds determined in crude oil are classified into six chemical groups.**

## (i) Free elemental sulfur S:

Free elemental sulfur is rarely found in crude oil; however it can be present in a suspension or dissolved in the liquid. Sulfur, while crude oil is heated, partially reacts with hydrocarbons:
$$2RH + 2S \rightarrow R - S - R + H_2S$$
It is believed that determination of the presence of elemental sulfur in oil is a complex process and that any declaration of its presence has met with lack of confidence (Eccleston et al., 1992)

### (ii) Hydrogen Sulfide H$_2$S:

Hydrogen sulfide is a colorless, flammable, harmful gas that smells like rotten eggs (NPI, 2013). $H_2S$ is found in reservoir gas and dissolved in the reservoir liquid (<50 ppm by weight)

Often the appearance of $H_2S$ in petroleum fractions is a consequence of thermal decomposition of organosulfur compounds (Ryabov, 2009). It is itself and the sulfur dioxide ($SO_2$), the product of $H_2S$ combustion cause poisoning of humans, animals and plants. The presence of $H_2S$ in the reservoir crude determines the number of serious complications for production of oil, due to its high corrosiveness and toxicity. It causes corrosion of steel pipes and tanks, compressors, fittings and other surface equipment, particularly in the presence of carbon dioxide and water vapor in the feed, and under elevated temperatures.

**(iii) Thiols**

Thiols or mercaptans are organosulfur compounds that contain a sulfhydryl group (SH), also known as a thiol group, that is composed of a sulfur atom and a hydrogen atom attached to a carbon atom. This molecular structure is what distinguishes thiols from other organic chemical compounds with an oxygen-to-carbon bond configuration. It is also what gives many high velocity thiols a persistent and highly unpleasant odor that is reminiscent of rotten eggs (Mayer, 2013). The general formula of thiols is

$$R - S - H$$
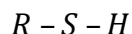
Where R stands for an aliphatic or cyclic radical. S–H group is responsible for their acidic behavior. The level of thiols in crude oil is very low, if not zero. However, they may appear from other organosulfur compounds during refining operations. It should be noted that the content of

mercaptans in crude varies from 0.1 to 15 % mass from total content of sulfur compounds (Ryabov, 2009).

**(iv) Sulfides**

The sulfides are organosulfur compounds which can have a linear or ring structure. They are chemically neutral. The boiling points of sulfides are higher than of mercaptans for molecules of equal carbon number. They create the bulk of sulfur containing hydrocarbons in the middle distillates (kerosene and gas oil), where their content is equal to 50-80% of total sulfur compounds (Ryabov, 2009).

**(v) Disulfides**

The disulfides (general formula: R–S–S–R') are found in small quantities in petroleum fractions with a boiling point up to 300˚C. They account for 7-15% of the total sulfur (Ryabov, 2009).

The disulfides are complex chemical compounds which are difficult to separate; as a result, few have been identified:

Dimethyl disulfide(2,3 dithiobutane)

$$CH_3-S-S-CH_3$$
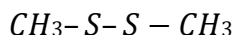
Diethyl disulfide(2,3 dithiohexane)

$$CH_3-CH_3-S-S-CH_2-CH_3$$
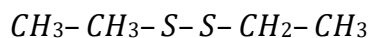
**(vi) Thiophene and derivatives**

Thiophene and its derivatives are neutral cyclic and temperature resistant compounds with five-membered ring. They do not dissolve in water, and their chemical properties are similar to aromatic hydrocarbons. The first determination of thiophene and its derivatives was in 1899, and it was believed that they came from the degradation of sulfides during refining operations. That was until 1953, the year when the methyl-thiophenes were identified in kerosene from Agha Jari crude oil, Iran. The existence of those sulfur compounds was no longer doubted after the identification of benzothiophenes and their derivatives [4].

## 1.9 Market Survey:

In Pakistan, high speed diesel (HSD) accounts for about 40 percent of total demand for petroleum products, Pakistan's annual diesel consumption is around 8 million metric tons. More than half (4.3 million metric tons) of the requirement is met through direct diesel import, chiefly by the PSO. The rest is produced by domestic refineries through import of crude. The government spends around $3-4 billion per annum on the import of diesel, out of total oil imports of over $11 billion. The country's total oil consumption during the current fiscal year is estimated to go up by about 26 per cent to 24 million tons from the last year's 19 million tons. More than 70 percent of the oil requirement is met through imports and the import bill for oil is estimated at about $11.6 billion this year against last year's 9.3 billion. Diesel is mainly used in the transport sector that accounts for about 90% and in other sectors that consist of the power, industry and other government. The market has grown by about 6.5% a year over the past 3 decades. However since fiscal year 1996 demand growth for petroleum products has slowed and declined in the past three years because of slowdown in economic growth to near 2%. HSP consumption increased by about of 1.6 % while

Fuel oil demand continued to grow at a relatively strong pace of 4% before declining in fiscal year 2007. As total domestic supply diesel was around 2.7 million tons per year as of 2008 compared to the domestic demand of around 7.0 million tons per annum. The ongoing heavy dependence on imports would continue.

**In Parco the production of diesel is 46000 bbl per day.**

**Table #3 Local Survey (FY 2016-2017)**

| Product | PSO | SHELL | PARCO | APL | ADMORE | HPL | ASKAR | ZOOM | BPPL |
|---------|-----|-------|-------|-----|--------|-----|-------|------|------|
| HSD (matric tons) | 3763.8 | 1020.3 | 63.4 | 834.6 | 88.9 | 898 | 24.5 | 8.4 | 291 |

**1.9.1 Market Share in Energy Products during FY 2016-17**

PSO with 55% market share, was the main supplier of POL products. It lost 1% of its market share during FY 2016-17 compared to 56% previous year.

Shell and BPPLs' market share was 9% and 3% respectively loosing 1% share each as compared to the previous year.

The main gainer was HPL whose market share has been increased by 2% to 8% during FY 2016-17.

APL and TPPL kept its market share at 8 and 4% respectively during current year.

Smaller OMCs jointly secured 8% of market share up from 7% in previous year.

GOPL has increased its share by around 1% during FY 2016-17 [5].

**1.9.2 World Wide Survey**

Total oil production averaged more than **97 million barrels per day (bbl/day)** in 2016-2017, the most recent year for which complete data are available, according to the Energy Information Administration (EIA).

The top five oil-producing countries were responsible for nearly half of the world's production.

Total oil production includes production of crude oil, lease condensate, unfinished oils, refined products obtained from the processing of crude oil, and natural gas plant liquids [6].

# CHAPTER NO 2

# PROCESS SELECTION

## 2.1 Desulfurization

Desulfurization is the removal of sulfur or sulfur compounds from hydrocarbons or hydrogen mixtures derived from petroleum or natural gas. Desulfurization process can also be used to treat hydrocarbons from other sources such as oil shale or coal

## 2.1.1 Purpose of Desulfurization

Crude oil consists of sulfur and various sulfur compounds. The presence of these sulfur compounds makes the oil sour. Removal of sulfur and its compounds from petroleum products is called sweetening.

The presence of sulfur compounds in petroleum is always objectionable due to their process and environmental problems. Sulphur occurs in many forms in petroleum like free sulfur, $H_2S$, marcaptans, sulfides, disulfide and thiophenes. These compounds are undesirable in the petroleum because of their potential corrosion problems in refining process.

Furthermore, these compounds are responsible for environmental problems, keeping in view the hazardous effects of the sulfur in petroleum, much attention is being paid to desulphurization in the recent years to protect the environment. Primitive techniques such as doctor sweetening was developed in 1860's, while the others developed later on were based on the oxidation of thioles to sulfides and disulfides. These processes were used to eliminate the corrosion and bad odor but not the sulfur compounds. Later on desulfurization in the presence of hydrogen was practiced. In conventional hydrodesulphurization (HDS), severe operating conditions of high temperature and pressure are unavoidable. Moreover, high consumptions of hydrogen and expensive cobalt molybdenum catalysts are other disadvantages of the method. Research is underway to improve the profitability of the process. Even with the conventional processes, it is difficult to reduce the sulfur content to less than 15 ppm. Therefore, new economical and more effective methods are sought throughout the world.

## 2.2 Methods of Desulfurization

1. Adsorption
2. Bio-desulfurization
3. Solvent extraction
4. Hydro-desulfurization

### 2.2.1 Adsorptive desulfurization from Diesel Oil

Although extensive efforts have been made to decrease the sulfur contents of diesel oil, the regulation on the fuel quality is going to be tightened faster than expected. Fruit kernel activated charcoal in batch process was used for desulfurization process. The results revealed the potential

for adsorbent as a low cost adsorbent and have a higher capacity for sulfur at gas oil concentrations than in kerosene. Naphtha desulfurization by adsorption was studied. They found that 13X zeolite have the highest capacity for sulfur a

t low concentration range and activated carbon at higher concentration range. The adsorptive desulphurization of gasoline over nickel based adsorbent, showed high capacity and selectivity for the adsorptive desulfurization of gasoline. The adsorption involves C-S bond cleavage as evidenced by the formation of ethyl benzene from benzothiophene in the absence of hydrogen gas. This work will focus on the adsorption desulfurization process of local diesel oil using activated carbon [7].

**Advantages**:

i. Not effective under high process conditions.

ii. More energy efficient because conducted at ambient temperature and atmospheric pressure.

iii. This process does not use hydrogen.

**Limitations**

i. Catalyst needs to be regenerated.

ii. Cannot achieve the ultra-low level sulfur content alone.

## 2.2.2 Bio-desulfurization

Microorganisms have evolved diverse biochemical strategies for dealing with sulfur, an essential element. The decreased availability of low sulfur crude oils has resulted in a need to refine heavier, higher sulfur crudes [8]. Which upon combination to produce sulfur oxides which cause air pollution.

One of the alternative options to remove sulfur from fossil fuel is by biological methods. Sulfur atom forms 0.5–1% of bacterial cell dry weight. Microorganisms require sulfur for their growth and biological activities. Sulfur generally occurs in the structure of some enzyme cofactors (such as Coenzyme A, thiamine and biotin), amino acids and proteins (cysteine, methionine, and disulfur bonds). Microorganisms consume sulfur from different sources depending upon their enzymes and metabolic pathways. Some microorganisms can consume the sulfur in thiophenic compounds such as DBT and reduce the sulfur content in fuel [9].

**Advantages**

i. Requires no hydrogen.

ii. BDS capital cost is about half of the HDS.

**Limitations**

i. Biocatalyst fermentor is required to regenerate the bacteria.

ii. Very much sensitive to the external conditions.

iii. Require a hydrotreater in order to have lower sulfur feed stock to the unit which make this process very costly.

iv. Rate of bio desulfurization are low.

v. Cannot achieve the ultra-low level sulfur content alone.

## 2.2.3 Extractive Desulfurization:

Extractive desulfurization (EDS) is probably the most studied technique, where a solvent is put contact with the fuel to remove the sulfur compounds by liquid-liquid extraction. Two classical

thermodynamic parameters for the evaluation of the performance of extracting solvents were calculated from the liquid–liquid equilibrium data: the solute distribution ratio, or simply solubility (related to the amount of solvent needed to carry out the extraction); and the selectivity (related to the separation power of the solvent to achieve the target separation). The desulfurization of simulated gasoline and diesel fuels was carried out in this work [10].

Extractive desulfurization is based on the polarity difference between the AAT (Alkylated Aryl Thiophenic) family of compounds and the hydrocarbons found in the diesel fraction. Because AATs comprise several dozen different compounds, they represent a range of solvent polarities, in some cases quite similar to the aromatic compounds found in diesel fuel. The critical "polarity difference" between individual hydrocarbon and thiophenic
 compounds is therefore variable, and in some cases may be insufficient to allow a functional separation by extraction. This polarity difference enables the extraction of these thiophenes from the diesel fuel. One such process of extraction is by using ionic liquids [11].

**Advantages**

i. Used in integration with the conventional HDS process to achieve lowest sulfur con tent.

ii. Economical when used as a standalone process for desulfurization [11].

**Limitations**

i. Depends on the boiling range of the feed stock.

ii. Depends on the density and composition of feed stock, i-e for the selection of solvent.

iii. Cannot achieve the ultra-low level sulfur content alone


## 2.2.4 Hydrodesulphurization

Hydrodesulphurization (HDS) is a catalytic chemical process widely used to remove sulfur (S) from natural gas and from refined petroleum products such as gasoline or petrol, jet fuel, kerosene, diesel fuel, and fuel oils. The purpose of removing the sulfur is to reduce the sulfur dioxide emissions that result from using those fuels in automotive vehicles, aircraft, railroad locomotives, ships, gas or oil burning power plants, residential and industrial furnaces, and other forms of fuel combustion. Another important reason for removing sulfur from the naphtha streams within a petroleum refinery is that sulfur, even in extremely low concentrations, poisons the noble metal catalysts (platinum and rhenium) in the catalytic reforming units that are subsequently used to upgrade the octane rating of the naphtha streams

**Reasons for Selecting HDS process**

We have selected HDS process because of following reasons

➢ ☐HDS process is most widely used in refineries.

➢ Extraction is not economically feasible for removing sulfur from heavier fractions of petroleum because of high yield losses

➢ ☐The very low sulfur levels required in feedstock for catalytic reforming and to meet environmental standards can only be achieved by HDS as it reduces the sulfur contents to PPM.

➢ Hydrogen is available in the refineries for hydro treating, therefore, the use of HDS process is economical.

## 2.3 The process chemistry

Hydrogenation is a class of chemical reactions in which the net result is the addition of hydrogen ($H_2$). Hydrogenolysis is a type of hydrogenation and results in the cleavage of the C-X chemical bond, where C is a carbon atom and X is a sulfur, nitrogen ($N_2$) or oxygen ($O_2$) atom. The net result of a hydrogenolysis reaction is the formation of C-H and H-X chemical bonds. Thus, hydrodesulfurization is a hydrogenolysis reaction. Using ethanethiol ($C_2H_5SH$), a sulfur compound present in some petroleum products, as an example, the hydrodesulfurization reaction can be simply expressed as

$$C_2H_5SH \ + \ H_2 \rightarrow \ C_2H_6 + H_2S$$
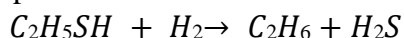
## 2.4 Catalysts and mechanisms

The main HDS catalysts are based on molybdenum disulfide ($MoS_2$) together with smaller amounts of other metals. At the edges of the $MoS_2$ crystallites, the molybdenum center can stabilize a coordinately unsaturated site (CUS), also known as an anion vacancy. Substrates, such as thiophene, bind to this site and undergo a series a reactions that result in both C-S scission and C=C hydrogenation. Thus, the hydrogen serves multiple roles - generation of anion vacancy by removal of sulfide, hydrogenation, and hydrogenolysis [12].

 Most metals catalyst HDS, but it is those at the middle of the transition metal series that are most active. Ruthenium disulfide appears to be the single most active catalyst, but binary combinations of Co-Mo are also highly active. Aside from the basic cobalt-modified $MoS_2$ catalyst, nickel and tungsten are also used, depending on the nature of the feed. For example, Ni-W catalysts are more effective for hydrodenitrification (HDN). Metal sulfides are "supported" on materials with high surface areas. A typical support for HDS catalyst is γ-alumina. The support allows the more expensive catalyst to be more widely distributed, giving rise to a larger fraction of the $MoS_2$ that is catalytically active. The interaction between the support and the catalyst is an area of intense interest, since the support is often not fully inert but participates in the catalysis.

**Table 4 Catalyst Characteristics**

|  | Co-Mo | Ni-Mo | Ni-Co-Mo | Ni-W |
|---|---|---|---|---|
| Cobalt (wt. %) | 2.5 | ----- | 1.5 | ---- |
| Nickle (wt. %) | ---- | 2.5 | 2.3 | 4 |
| Molybdenum (wt. %) | 10 | 10 | 11 | ---- |
| Tungsten (wt. %) | ---- | ---- | ---- | 16 |

## 2.5 Process Description
### 2.5.1 Process Description of Hydrodesulphurization Unit
All units comprise of a low pressure product fractionation section and high pressure reactor section. These two sections are described below in general terms

### 2.5.2 Process Flow diagram
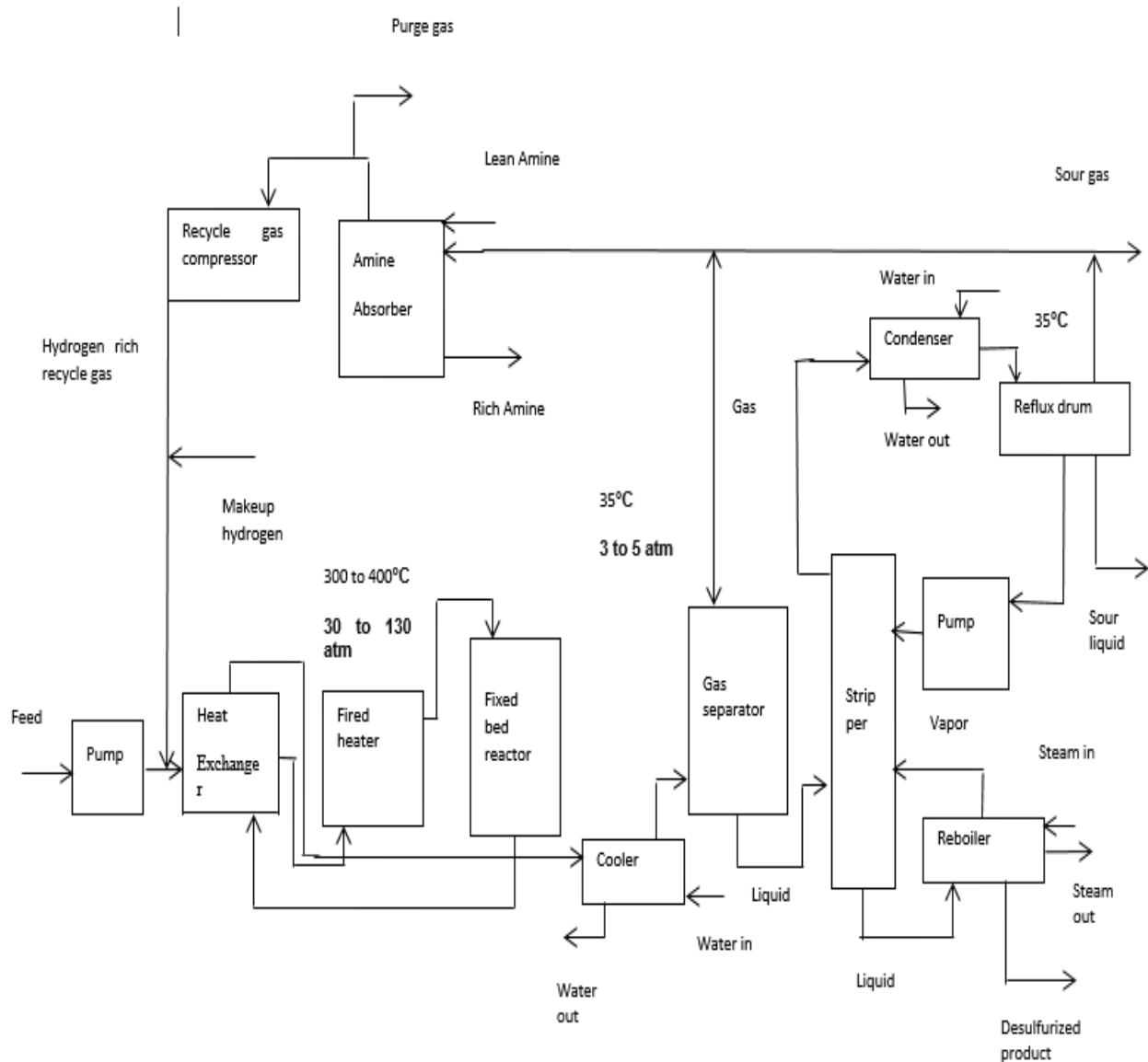
## 2.5.2 Piping and Instrumentation diagram
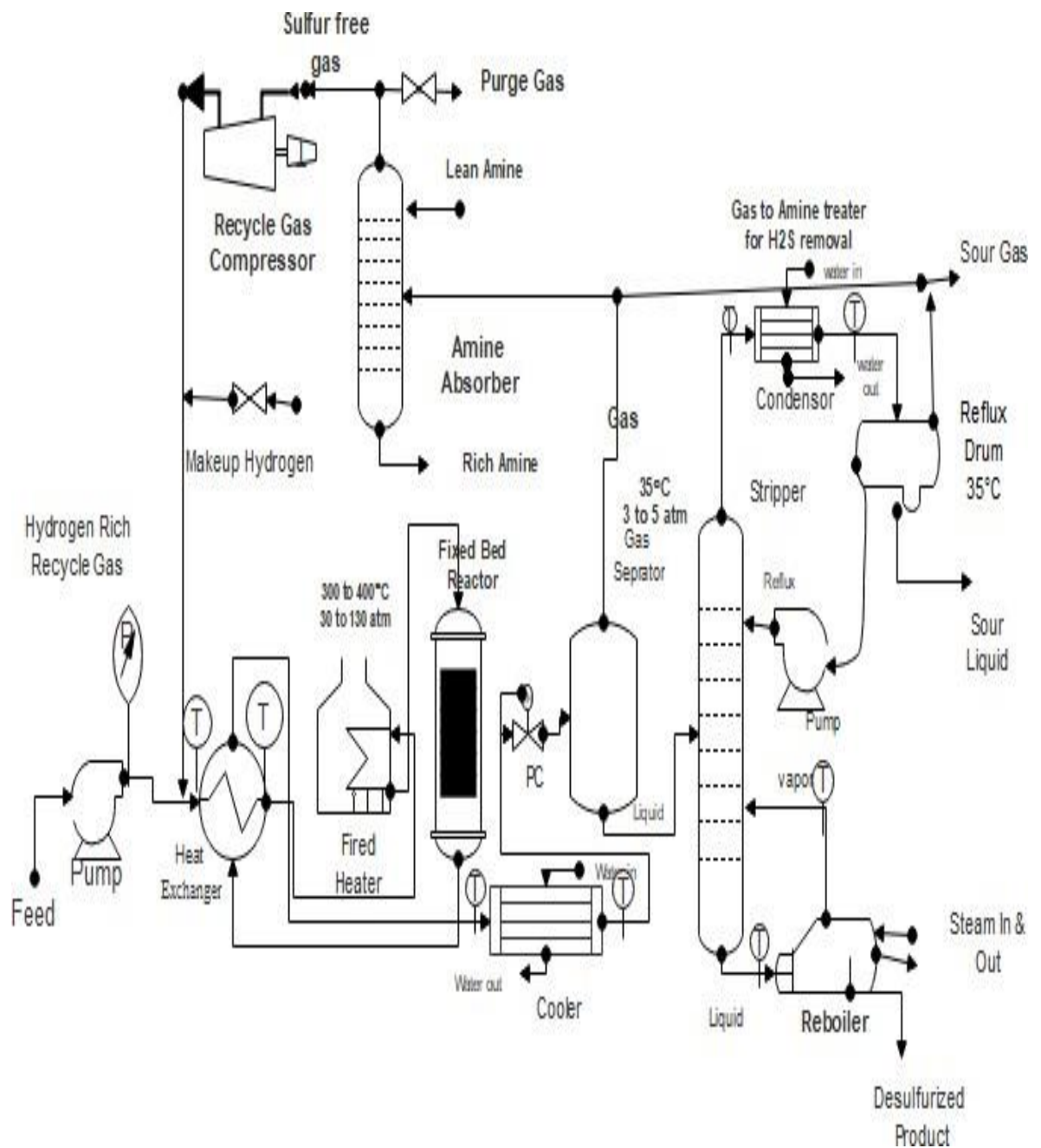
### 2.5.3 Reactor Section

Reactor is a heart of chemical process plant where reactants are converted into product

### 2.5.3.1 Fresh Feed System

The fresh feed comes from an upstream unit or storage unit. The fresh feed is then passed through filters to remove particulate and then is entered the gas into blanketed feed surge drum. If feed contains an appreciable quantity of solids material, twenty five micron of backwash filters may be specified as it is usually the case with coker gas oil. The feed from the surge drum is sucked by the reactor charge pumps and pumped to the combined feed heat exchanger. These charge pumps are high head machines and have the ability to pump large volumes of oil at pressures of over 70 kg/cm$^2$(1000 psig).

### 2.5.3.2 Feed Heat Exchanger

The charge of the reactor is reheated with the help of reactor effluent in a series of fee-effluent exchangers before entering the reactor charge heater. The combined feed stream typically enters a mixed inlet temperature. The better control of the charge heater outlet temperature is provided by the use of fresh feed bypass around one or more exchangers.

### 2.5.3.3 Make-up Hydrogen System

Make-up hydrogen is typically obtained from a naphtha reforming unit or a hydrogen manufacturing plant at a pressure of 14-28 kg/cm$^2$. As reactor [pressure may be greater than 70 kg/cm$^2$, the make-up gas is compressed before it can join the system. Reciprocating compressors are used to the pressure if the gas, with the number of compression stages varying in accordance the gas from the stage must be cooled to about 50°C before entering the second dotage.

### 2.5.3.4 Recycle Hydrogen System

After separation of the gas and liquid phases in the high pressure separator, the gas leaves from the top of the high pressure separator and flow suction of recycle gas compressor. In some cases the recycle gas will be sent to an amine scrubber to remove $H_2S$. After the recycle compressor discharge, some recycle gas will be slit off the main stream for use as quench gas between catalyst beds reactor to reduce temperature. The bulk of recycle gas is normally joined by the make-up gas. In cases, the make-up gas joins the recycle gas compressor if a make-up stage of compression can be saved

### 2.5.3.5 Recycle Gas Scrubbing.

The recycle gas stream contains $H_2S$ which reduces the partial pressure and suppresses the catalyst's activity. This effect is more pronounced with the high sulfur containing feed streams. For these cases, recycle gas amine scrubber may be specified. Recycle scrubbing is very unit specific, but would typically be specified when the recycle gas contains > 3 vol. % $H_2S$.

In the scrubbing unit, amine temperature is usually maintained 5°C above the gas temperature to minimize foaming. The amine and gas flowing up the tower come into contact over the trays where the intimate mixing between the two is achieved and $H_2S$ is absorbed by the amine. The rich amine falls to the bottom of the scrubber from where it is 18 sent to the amine regeneration unit. The $H_2S$ free gas goes into the top section of the scrubber for entrained amine removal through a demister pad. The amine free recycle gas then goes to recycle gas compressor section.

**2.5.3.6 Reactor**

Once the feed and recycle gas have been heated to desire temperature, the reactant enter the top of the reactor as a reactor floe downward through the catalyst bed, various exothermic reactions occur and the temperature increases. Multiple catalysts beds may be required depending upon the heat of the reaction and unit capacity (Rathi, 2007). In certain situation the heat if reaction will be large enough that the temperature increases across the reactor will be greater than the design. If this is allowed to happen, a reaction could become unstable and result in a temperature run away. Therefore, cold recycle gas at about 40 to 66°C is brought into the reactor at the interbred quench points in order to the reactants and thus control the reaction rates.

**2.5.3.7 Reactant Effluent Cooling**

Since all the hydro treating reactions are exothermic the temperature of the effluent stream is greater than the inlet stream. A no of heat exchangers are used to reduce the temperature of effluent stream by heating the feed.

**2.5.3.8 Reactor Effluent Water Wash**

Cooler is used to give final cooling touch to the reactor effluent. To avoid the deposition of salt wash water is introduced before entering to coolers. Sulfur and nitrogen compounds form ammonia and hydrogen sulfide that heat and produce ammonium salts which can solidify and precipitate when reactor effluent is cooled.

**2.5.3.9 Vapor/Liquid Separation**

A separator is utilized at specific flow pattern to disengage and remove steam, water and hydrocarbon liquid is collected in a shoe attached to a separator and is removed by level control and sent to treating unit. Gases are separated from the top and sent to absorber and diesel is sent to the stripper.

**2.5.3.10 Hydrogen Purification**

Since hydrogen gas coming from the absorber is contaminated so it should be purified because it will damage the catalyst. Additional measures are done to obtain hydrogen purity. These measures may include hydrogen enrichment and membrane separation.

**2.5.4 Fractionation Section**

In fractionation section feed which is coming from separator is fractionated into desulphurized products and light components. The feed is preheated by stripper bottom product and or effluent stream coming from the reactor. Steam is added at the bottom of the stripper that strips out the light components (Evans, 1980). The vapors of light components coming at the top of the stripper flow into the overhead receiver. The water is separated from the overhead receiver and sent to sour water stripping unit. Desulphurized diesel is obtained at the bottom of stripper. The diesel product obtained is dried with a salt prior to storage [13].

# Chapter No. 3
# Material and Energy Balance

## 3.1 Material Balance

Mass balance is simply an application of law of conservation of the mass which can be defined as "Mass neither be created nor destroyed, the total amount of the material remains" So we can write it in the equation form without chemical reaction

**Material in = Material out**

Some important definitions in this regard is

**System**:

Anything which is under observation is called system. There are three types of system

**Process:**

It consists of one or more series of actions which lead to the transformation of reactants into products. Process may be physical or chemical.

The more generalized material balance equation is

**Material in – Material out + Material generation – material Consumption = Accumulation**

For a steady state process the accumulation term is zero.

F12

F3    Reactor

F9

Mixer

Absorber F6

F8

F10

F2

Compressor

Furnace

F1

Heat Exchanger

Pump

F5

Stripper

F4

Mixer        Cooler        Separator F7

F11

Pump

| F1 | Feed (Diesel) |
|-----|---------------|
| F2 | Hydrogen gas |
| F3 | Effluent |
| F4 | Wash Water |
| F5 | Heavy Oil |
| F6 | Gases ($H_2$ + $H_2S$) |
| F7 | Sour Water |
| F8 | Rich Amine |
| F9 | Lean Amine |
| F10 | Light Gases |
| F11 | Desulphurized Oil |
| F12 | Recycle ($H_2$ Gas) |

| Designed by: M.Idrees, M.Adil |
|-------------------------------|
| Reviewed by:Sir Hidayatullah Mahar |
| Dated: 15 January, 2019 |

Figure 3-A: Block Diagram of Hydrodesulphurization Process

### 3.1.1 Material Balance around Reactor

Hydrogen reacts with sulfur compounds, nitrogen compounds and olefin in the diesel fuel to produce different products. The products formed are the corresponding contaminant of free hydrocarbon, along with $H_2S$ and $NH_3$. Along with hydrogen, it reacts with oxygen, metal and halide removal, and aromatic saturation. All the reactions are exothermic and heat is liberated.

**Basis 100kg/hr.**

$F_1$ (Feed) and $F_2$ ($H_2$ Gas) = 95+5 kg/hr.

Paraffin 58.15 %
Aromatics 25.7 %
Olefins 3.9 %
$N_2$ Compounds 2.4 %
Halides 3.9 %
$H_2$ 5 %
Sulfur compounds 0.95%
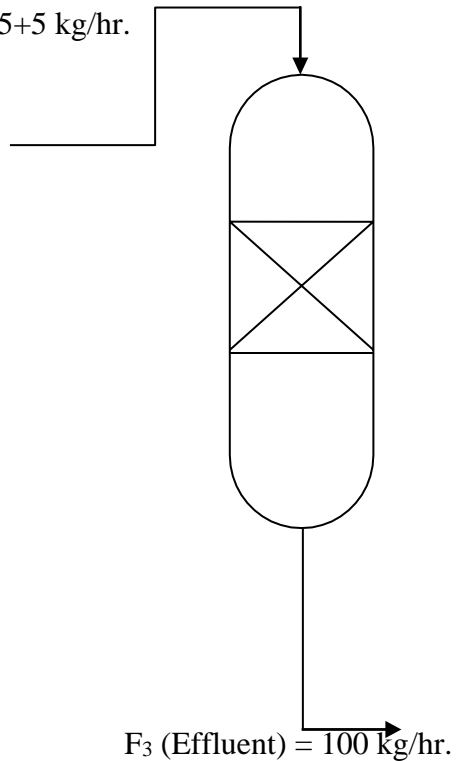
Ethane 0.22 %
Propane 1.99 %
Butane .95 %
Pentane 0.65 %
$H_2S$ 0.40 %
$NH_3$ 0.12 %
$H_2$ 2.46 %
$NH_4Cl$ 1.11 %
Oil 92.09 %

$F_3$ (Effluent) = 100 kg/hr.

Figure 3-B: Material Balance around Reactor

## Hydrogen Balance

Input=Output
At input $H_2$=5 kg/h
At output $H_2$ remain=2.46 kg/h
$H_2$ converted=2.14+0.4

**Input = Output**

5 kg/hr.=(2.46+2.14+0.4) kg/hr.
5 kg/hr.=5 kg/hr.

**Summary**

Table 3-A: Material Balance around Reactor

| Mass | Mass In (kg/hr.) | | Mass Out (kg/hr.) |
|---|---|---|---|
| Stream no | $F_2$ | $F_1$ | $F_3$ |
| Flow rate (kg/hr.) | 95 | 5 | 100 |

| Total (kg/hr.) | 100 | 100 |
|---|---|---|

## 3.1.2 Material Balance around Separator

$F_3$ (Effluent) and $F_4$ (Wash water) =105kg/hr.

$F_6$ (Gases $H_2$ + $H_2S$) = 2.715 kg/hr.

$F_7$ (Sour water) =6.32kg/hr.

$F_5$ (Heavy Oil) =95.76 kg/hr.
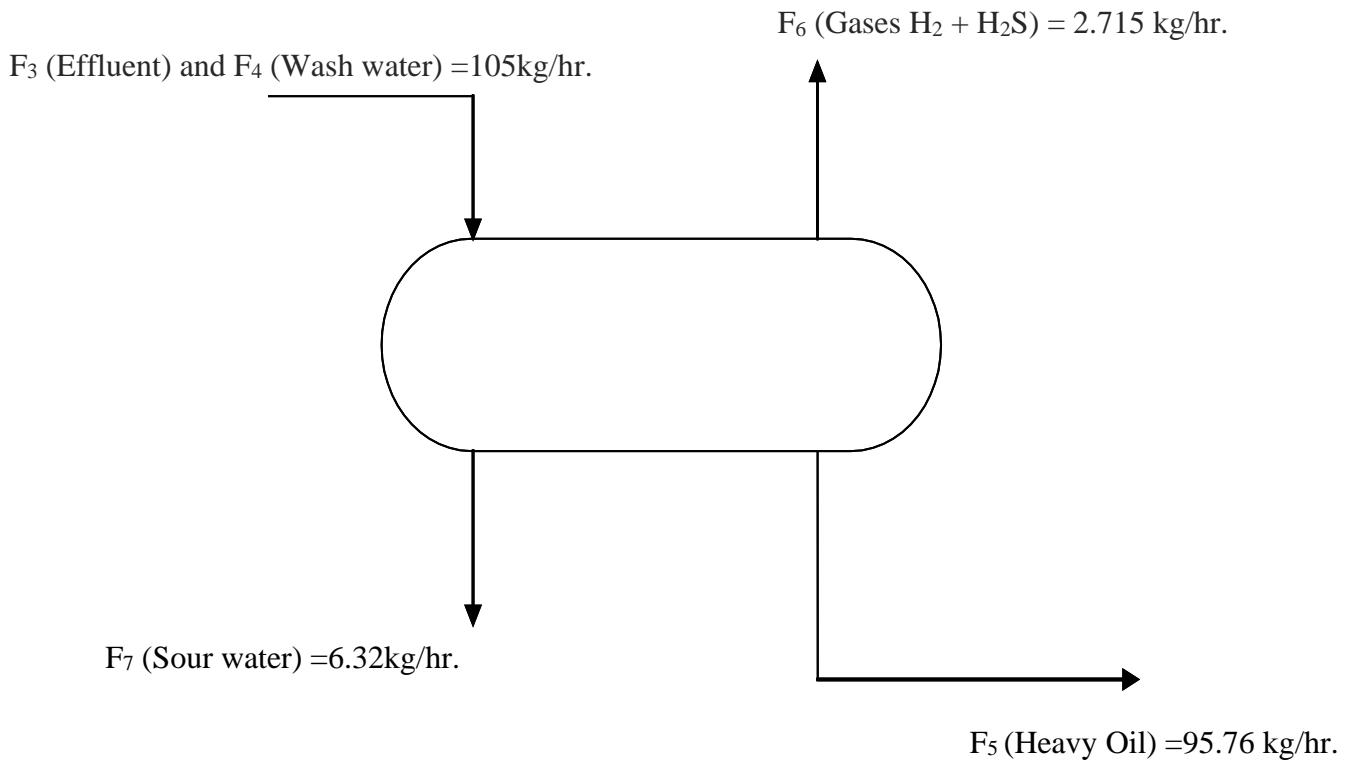
Figure 3-C: Material Balance around Separator

As we required at input

$F_3$=100kg/hr.

$F_4$=5kg/hr.

We obtain at output

$F_6$=2.715kg/hr.

$F_7$=6.63kg/hr.

$F_5$=95.76kg/hr.

Input=Output

105=95.76+2.715+6.63

105kg/hr.=105kg/hr.

**Summary:**

**Table 3-B: Material Balance around Separator**

| Mass | Mass In | | Mass Out | | |
|---|---|---|---|---|---|
| Stream no | $F_3$ | $F_4$ | $F_5$ | $F_6$ | $F_7$ |
| Flow rate (kg/hr.) | 100 | 5 | 95.76 | 2.715 | 6.63 |
| Total (kg/hr.) | 105 | | 105 | | |

### 3.1.3 Material Balance around   Absorber

$F_{12}$ (Recycle $H_2$)=2.624 kg/hr.                          $F_9$ (Lean Amine) =.104 kg/hr.

$F_6$ (Gases, $H_2$ + $H_2S$) =2.715 kg/hr.

$F_8$ (Rich Amine) =.194kg/hr.
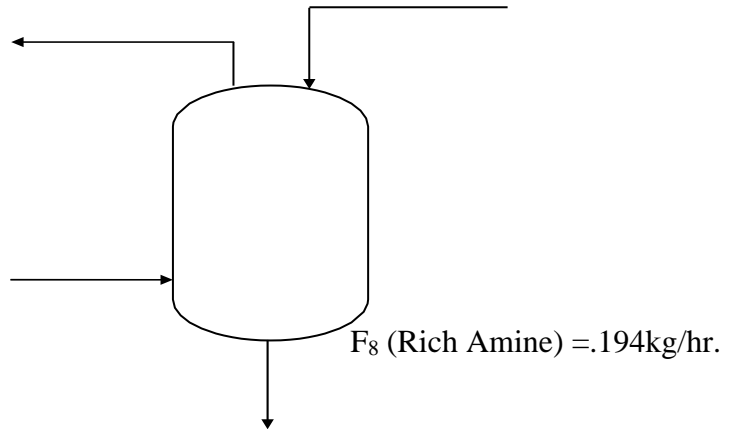
**Figure 3-D: Material Balance around Absorber**

3.86% Lean Amine is required for 2.715 ($H_2$+$H_2S$)
As we required at Input
$F_6$=2.715kg/h
$F_9$=.104kg/h
We obtain at output
$F_{12}$=2.624kg/h
$F_8$=.1944kg/h
Input=Output
2.7153+.104=2.624+.1944
2.814kg/hr.=2.814kg/hr.
**Summary**

### Table 3-C: Material Balance around Absorber

| Mass | Mass In | | Mass Out | |
|------|---------|---|----------|---|
| Stream no | $F_6$ | $F_9$ | $F_8$ | $F_{12}$ |
| Flow rate (kg/hr.) | 2.715 | .104 | .1944 | 2.624 |
| Total (kg/hr.) | 2.814 | | 2.814 | |

### 3.1.4 Material Balance around  Stripper

$F_{10}$ (Light Gases) = 3.962 kg/hr.

$F_5$ (Heavy Oil) = 95.76kg/hr.

$F_{11}$ (Desulphurized Oil) = 91.79 kg/hr
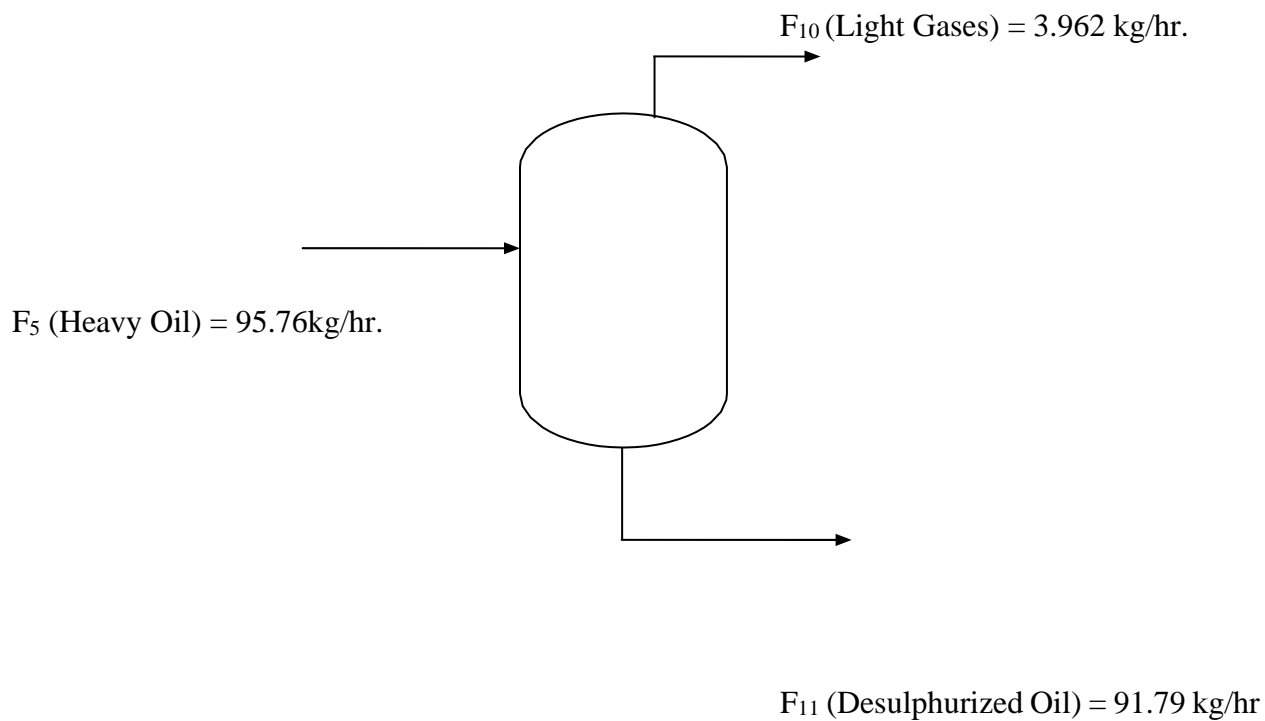
Figure 3-E: Material Balance around Stripper
As required at input
$F_5$=95.7kg/h
We obtain at output
$F_{10}$=3.962kg/h
$F_{11}$=91.79kg/h
Input=Output
95.76=3.962+91.79
95.75kg/hr. =95.7kg/hr.

## Summary

### Table 3-D: Material Balance around Stripper

| Mass | Mass In | Mass Out | |
|---|---|---|---|
| Stream no | $F_5$ | $F_{10}$ | $F_{11}$ |
| Flow rate (kg/hr.) | 95 | 3.964 | 91.79 |
| Total (kg/hr.) | 95.76 | 95.76 | |

### 3.1.5 Overall Material Balance

**Summary**

**Table 3-E: Overall Material Balance**

| Mass | Mass in | | Mass out | |
|---|---|---|---|---|
| | **Steams** | **Flow rate (kg/hr.)** | **Steams** | **Flow rate (kg/hr.)** |
| Reactor | $F_1$ <br> $F_2$ | 95 <br> 5 | $F_3$ | 100 |
| Separator | $F_3$ <br> $F_4$ | 100 <br> 5 | $F_6$ <br> $F_5$ <br> $F_7$ | 2.715 <br> 95.76 <br> 6.63 |
| Absorber | $F_6$ <br> $F_9$ | 2.715 <br> .104 | $F_8$ <br> $F_{12}$ | .1944 <br> 2.624 |
| Stripper | $F_5$ | 95.76 | $F_{10}$ <br> $F_{11}$ | 3.962 <br> 91.79 |
| | Total | 303.589 | Total | 303.4 |

**Input=Output**


303.589kg/hr.=303.589kg/hr.

As over capacity is 22000Bbl/day

22000Bbl/day = (22000Bbl/day)(42gal/Bbl)(ft³/7.48gal)(m³/3.28²ft³)(day/24hr.)(819.1kg/m³)

=1194500kg/h = 120000 kg/hr


    Total  capacity

  1200(303.587) = 364306.8kg/hr.

# 3.2 Energy Balance

Like Material balance, Energy balance can be defined as

"Energy can neither be created nor destroyed but it can be transformed from one form to another form and total amount of energy remains constant."

The generalized energy balance equation for open system can be written as

**Rate of Energy in – Rate of Energy out + Rate of Energy Generation – Rate of Energy Consumption = Accumulation**

Accumulation term is taken as zero for the steady state process.

Heat Energy can be calculated as:

$$\Delta H = mCp\Delta T$$

Where

$\Delta H$ = Enthalpy

M = Amount of Mass

Cp = Heat Capacity

$\Delta T$ = Operating Temp. – Ref. temp.

According to 1$^{st}$law of thermodynamics

$$Q = U + W$$

If W= 0

Then

Q= U

We know

$$H = U + PV$$

According to above equation

We write in the following form

mCpΔT= U + PV

As work is Zero

So

$$U = mCp\Delta T$$
$$Q = mCp\Delta T$$

## 3.2.1 Energy Balance around Reactor

**Reaction that takes place in Reactor**

Every reaction contains number of moles that are reacted, consumed, and produced during reactions:

| | Sulfur Removal | | | | | | |
|---|---|---|---|---|---|---|---|
| **RX 1** | $C_{18}H_{38}S$ 10.5572 | + | $H_2$ 10.5572 | = | $C_{18}H_{38}$ 10.5572 | + | $H_2S$ 10.5572 |
| **Rx 2** | $C_{14}H_{30}S$ 38.1229 | + | $2H_2$ 76.2457 | = | $2C_7H_{16}$ 76.2457 | + | $H_2S$ 38.1229 |
| **Rx 3** | $C_{10}H_{22}S_2$ 6.2212 | + | $3H_2$ 18.6637 | = | $2C_5H_{12}$ 12.4425 | + | $2H_2S$ 12.4425 |

$F_1$ (Diesel feed) and $F_2$ ($H_2$) = 120000 kg/hr.

$T_2$= 325°C

$F_3$ (Effluent stream) = 120000kg/h

$T_2$= 425°C

Final Pressure= 5 MPa
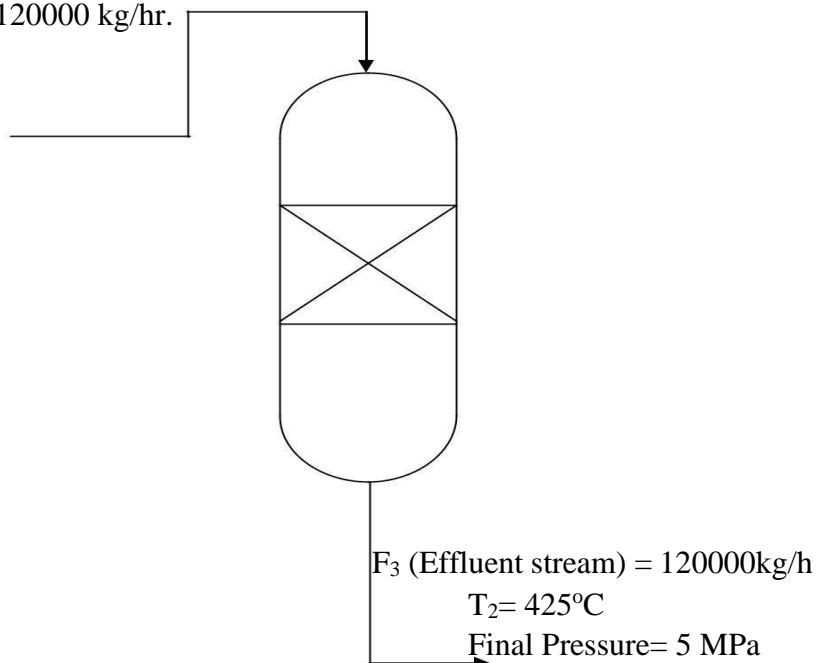
**Figure 4-B Energy Balance around Reactor**

**Heat in**

$$\Delta H = mCp\Delta T$$

=120000kg/hr. $\times$ 2.71kJ/kg°C $\times$ (325-25) °C

=97560000 kJ/hr.

**Heat Out**

$$Qout = mCp\Delta T$$

=120000kg/hr. $\times$ 2.78kJ/kg.C $\times$ (425-25)C

=130080000kJ/hr.

$$Q\ (Generated)\ =\ \Delta H \times X \times Feed\ mole$$

Mol.wt=211.5kg/kmol.

Feed mole=120000kg/hr. $\times$ (1/211.5kg/kmol)

=567.376kmol

X=0.96

**HEAT OF FORMATIONS DATA OF REACTANTS:**

| Components | $\Delta Hf$ At 25 °C ( KJ/mol ) |
|---|---|
| $C_{18}H_{38}S$ | -505.4 |
| $C_{14}H_{30}S$ | -403.3 |
| $C_{10}H_{22}S_2$ | -165.99 |
| $C_9H_7N$ | +141.22 |
| $C_{14}H_{22}$ | -95.76 |
| $C_{23}H_{46}$ | -400.83 |
| $C20H_{38}$ | -164.23 |
| $C_5H_{12}$ | -167.8 |
| $C_5H_{12}$ | -167.8 |
| $C_7H_{16}$ | -205.9 |
| $C_3H_8$ | -104.6 |
| $H_2$ | 0.0 |
| Total | -2240.42 |

**HEAT OF FORMATIONS DATA OF PRODUCTS :**

| Components | $\Delta Hf$ At 25 °C ( KJ/mol ) |
|---|---|
| $C_{18}H_{38}$ | -425.41 |
| $2C_7H_{16}$ | -205.9 * 2 = -411.8 |
| $2C_5H_{12}$ | -167.8*2 = -335.6 |
| $C_9H_{12}$ | -61.9 |
| $C_{14}H_{28}$ | -206.8 |
| $C_{23}H_{48}$ | -523.33 |
| $C_{20}H_{42}$ | -2230 |
| $4CH_4$ | -74.9*4 = -299.6 |
| $2C_3H_8$ | -104.6*2 = -209.2 |
| $C2H6$ | -83.7 |
| $N-C_4H_{10}$ | -125.5 |
| $I-C_4H_{10}$ | -134.3 |
| $4H_2S$ | -20.63 |
| $NH_3$ | -46.1 |
| Total | -5202.96 |

$Heat\ of\ Reaction\ at\ 25°C = \Sigma\ (Heat\ of\ formation\ of\ product \times Coefficient) – \Sigma\ (Heat\ of\ Formation\ of\ Reactant \times Coefficient)\ Heat\ of\ reaction\ at\ 25℃$

= -2962.54 kJ/mol.

Since Reactor is Adiabatic Reactor Q = 0

$$Input = Output + Generated + Accumulation – Quenched$$

Generated = $\Delta H \times X \times$ moles feed = -1962.54kJ/mol. $\times$ 0.96 $\times$ 576.376kmol= -1613622.69KJ

$$Quenched = mCp\Delta T$$

-30906377.93KJ/hr.

$$Input = Output + Generated + Accumulation – Quenched$$

97560000=130080000-1613622.04-30906377.93

97560000=97559999.38

## Summary

### Table 3.2-A: Energy Balance around Reactor

| Stream no | Description | ΔHin (kJ/kg) | ΔHout (kJ/kg) | Δ(ΔH) (kJ/kg) |
|---|---|---|---|---|
| F₁ and F₂ | Cold Feed | 97560000 | --- | |
| F3 | Hot Feed | ---- | 97559999.38 | 0 |

### 3.2.2 Energy Balance around Stripper

F̅₁₀= 4754.4 kg/hr  
T= 156ºC  
P= 0.1 MPa

Light Gases

F₅= 114912 kg/hr  
P= 0.5 M Pa

Heavy Oil Desulphrized diesel  
F₁₁= 110112 kg/hr.  
T= 245ºC T= 240.5⁰  
P= 0.1 MPa

**Figure 4-D: Energy Balance around Stripper**

**Heat In**

$$Feed = mCp\Delta T$$

=114912kg/hr. × 2.009kJ/kg°C × (245-25) °C  
=50788805.76kJ/hr.

$$Reflux = mCp\Delta T$$

=3492.825kg/hr. × 2.93KJ/kg. °C × (42-25) °C  
=173977.60kJ/hr.

$$Steam = m\ \lambda$$

$Heat\ of\ Reaction\ at\ 25°C = \Sigma\ (Heat\ of\ formation\ of\ product \times Coefficient) – \Sigma\ (Heat\ of\ Formation\ of\ Reactant \times Coefficient)\ Heat\ of\ reaction\ at\ 25℃$

= -2962.54 kJ/mol.

Since Reactor is Adiabatic Reactor Q = 0

$$Input = Output + Generated + Accumulation – Quenched$$

Generated = $\Delta H \times X \times$ moles feed = -1962.54kJ/mol. $\times$ 0.96 $\times$ 576.376kmol= -1613622.69KJ

$$Quenched = mCp\Delta T$$

-30906377.93KJ/hr.

$$Input = Output + Generated + Accumulation – Quenched$$

97560000=130080000-1613622.04-30906377.93

97560000=97559999.38

## Summary

### Table 3.2-A: Energy Balance around Reactor

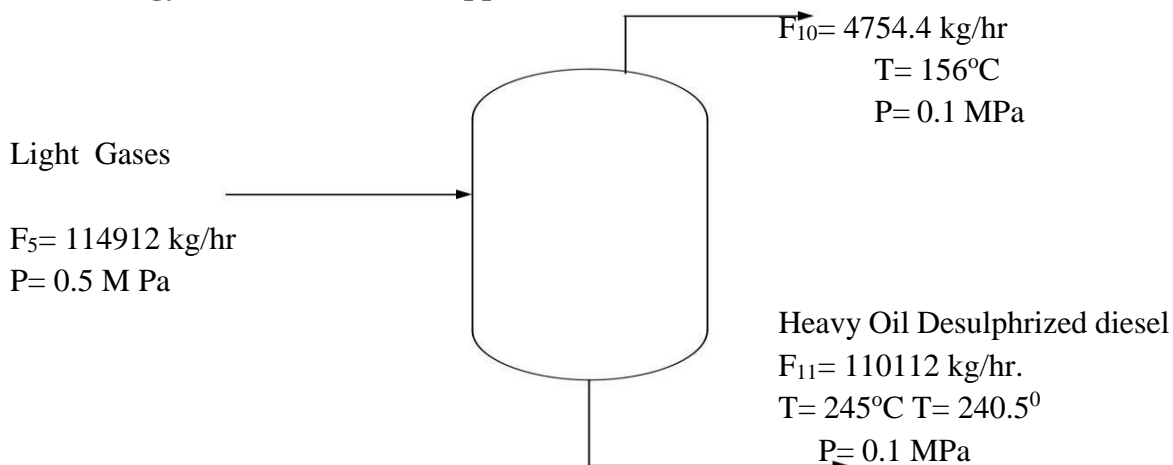| Stream no | Description | ΔHin (kJ/kg) | ΔHout (kJ/kg) | Δ(ΔH) (kJ/kg) |
|---|---|---|---|---|
| F₁ and F₂ | Cold Feed | 97560000 | --- | |
| F3 | Hot Feed | ---- | 97559999.38 | 0 |

### 3.2.2 Energy Balance around Stripper

F̅₁₀= 4754.4 kg/hr  
T= 156ºC  
P= 0.1 MPa

Light Gases

F₅= 114912 kg/hr  
P= 0.5 M Pa

Heavy Oil Desulphrized diesel  
F₁₁= 110112 kg/hr.  
T= 245ºC T= 240.5⁰  
P= 0.1 MPa

**Figure 4-D: Energy Balance around Stripper**

**Heat In**

$$Feed = mCp\Delta T$$

=114912kg/hr. × 2.009kJ/kg°C × (245-25) °C  
=50788805.76kJ/hr.

$$Reflux = mCp\Delta T$$

=3492.825kg/hr. × 2.93KJ/kg. °C × (42-25) °C  
=173977.60kJ/hr.

$$Steam = m\ \lambda$$

=1608768kg/hr. × 2013.35KJ/kg

=3239334.806kJ/hr.

**Heat Out**

$$Gases = mCp\Delta T$$

=4754.4kg/hr. × 1.758kJ/kg°C× (156-25) °C

=1094928.811kJ/hr.

$$Diesel = mCp\Delta T$$

=110112kg/hr. × 2.177kJ/kg. °C × (240.5-25) °C

=51658329.07kJ/hr.

**Summary**

**Table 3.2-B: Energy Balance around Stripper**

| Stream no | Description | ΔHin (kJ/kg) | ΔHout (kJ/kg) | Δ(ΔH) (kJ/kg) |
|---|---|---|---|---|
| Steam | Heat Source | --- | 53753257.88 | |
| F10 | Light Gases | 54202118.17 | --- | 0 |

### 3.2.3 Energy Balance around Absorber

Lean Amine + process gas = Rich Amine + process gas

**Heat input**

Lean amine heat = mCpΔT

=3258kg/hr. × 3.768KJ/kg. °C × (49-25) °C

=294627.456KJ/hr.

Process gas heat = mCpΔT

=124.8kg/hr. × 4.563KJ/kg°C× (43-25) °C

=10250.3232KJ/hr.°C

**Heat Output**

$$Rich\ amine\ heat = mCp\Delta T$$

=3148.8kg/hr.× 3.768KJ/kg. °C × (47-25) °C

=261022.92KJ/hr.

$$Process\ gas\ heat\ = mCp\Delta T$$

=233.28kg/hr. × 4.521KJ/kg°C× (50-25) °C

=26366.47kJ/hr

**Summary**

**Table 3.2-C: Energy Balance around Absorber**

| Stream no | Description | ΔHin (kJ/kg) | ΔHout (kJ/kg) |
|---|---|---|---|
| F6 | Lean amine | 294627.456 | |
| F9 | Process gas | 10250.3232 | |
| F8 | Rich amine | | 261022.92 |

| F12 | Process gas | | 26366.47 |
|---|---|---|---|
| **Total Heat** | | 304877.77 | 297389.392 |

## 3.2.4 Energy Balance around Separator
**Heat Input**

$$Feed\ heat = \ mCp\Delta T$$

=120000kg/hr. × 3.19kJ/kg°C × (60-25) °C

=13398000kJ/hr.

$$Water\ heat = mCp\Delta T$$

=6000kg/hr. × 4.33KJ/kg°C× (65-25) °C

=1039200KJ/hr.

**Heat Output**

$$Light\ gases = mCp\Delta T$$

=3258kg/hr. × 8035KJ/kg°C× (43-25) °C

=489677.4kJ/hr.

$$Heavy\ oil = mCp\Delta T$$

=114912kg/hr. × 2.9KJ/kg. °C × (60-25) °C

=11663568kJ/hr.

$$Sour\ water = \ mCp\Delta T$$

=7584kg/hr. × 4.35kJ/kg. °C × (60-25) °C

=1154664KJ/hr.

**Summary**

**Table 3.2-D: Energy Balance around Separator**

| Stream no | Description | ΔHin (kJ/kg) | ΔHout (kJ/kg) |
|---|---|---|---|
| F3 | Effluent | 13398000 | |
| F4 | Wash water | 1039200 | |
| F6 | Light gases | | 489677.4 |
| F5 | Heavy oil | | 11663568 |
| F7 | Sour water | | 1154664 |
| Total | | 14437200 | 14307909.4 |

## 3.3 Overall Energy Balance

**Table 3.2-E: Overall Material Balance**

| Equipment | ΔHin (kJ/kg) | ΔHout (kJ/kg) |
|---|---|---|
| Absorber | 304877.77 | 281022.92 |
| Reactor | 97560000 | 97559999.38 |

| | | |
|---|---|---|
| Separator | 14437200 | 13307909..4 |
| Stripper | 54202118.17 | 5275325.88 |
| Total | 166504195.9 | 156424256.7 |

# Chapter NO 4
# Equipment Design

## 4.1 Fixed Bed Reactor

The reactors in the DHDS contain desulphurization catalyst. They are constructed of Killed carbon steel. The process stream enters the reactor through an inlet distributor at the top of reactor and leaves from bottom. There is a vapor/liquid distributor tray installed above the catalyst bed to assure even distribution of the stream over the catalyst.

G+L feed

Reactor inlet

Catalytic zone

Interbed quenching /mixing zone

Catalytic zone
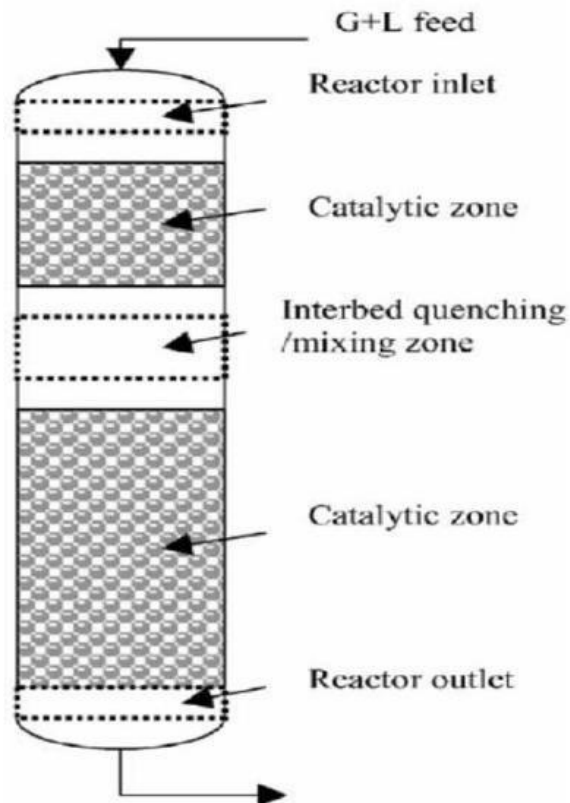
Reactor outlet

Inlet temperature = 325 °C
Outlet temperature = 425 °C
Volume of reactor
Mechanical design
I.D= 3.3m
L=13.3m

**Volume of Reactor**

$$Volume\ of\ reactor = cylindrical\ shell + 2(hemispherical)$$
$$(\pi/4\ LD2\ ) + 2(2/3\ \pi r3)$$

r=3.3/2
r=1.65m

$$V = \{\frac{3.14}{4} \times (13.3) \times (3.3)^2\} + 2\{\frac{2}{3}(3.14)(1.65)^3\}$$

V=133m³

**Thickness of head hemispherical**

$$t = pi\ di/2f - pi$$

f = maximum allowable working stress

f = 230 N/mm²

material of construction chromium and mollebednium

$p_i = 5.3 \times 10^6$ p

$p_i = 5.3$ N/mm²

$D_i = 3300$mm

t=5.3N/mm² ×3300mm×1/{2(230N/mm²)-(5.3N/mm²)}

t=38.4mm

**Thickness of hemisphere**

t=38.4/2

t=19.2mm

space time

$$T = volume\ of\ reactor/vol.flow\ rate$$

T = 133m³/hr ×1/146m³

T = 0.91 hr

**Space velocity**

$$S = 1/T$$

S = 1/0.91hr

S = 1.097/h

**Liquid hourly space velocity (LHSV)**

$$LHSV = Volume\ of\ feed\ change/volume\ of\ catalyst$$
$$Volume\ of\ catalyst = volume\ of\ reactor/\ (1 + \phi)$$

Opital Ratio $\phi = 0.3$

Volume of catalyst = 133/(1+0.3)

Volume of catalyst = 102.3m³

LHSV = 146m³/hr ×1/102.3m³

LHSV = 1.42/hr

LHSV = signifies the residence time of feed in react0r

L/D = 1.33/3.3

L/D = 4.03

## 4.2 Heat Exchanger Design

T1 = 425 °C

t1 = 30 °C
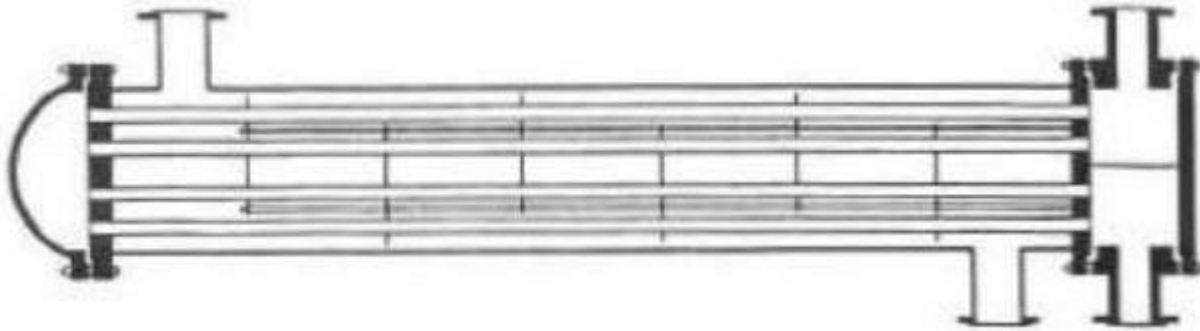


t2 = 120 °C

T2 = 373 °C

**Summary**

**Design Steps:**

1) Flow Rate & Physical Properties

2) Heat Load on Heat Exchanger

3) Log Mean Temperature Difference

4) Overall Heat Transfer Coefficient

5) Heat Transfer Area

6) Exchanger Type & Dimensions

7) Number of Tubes

8) Tube Side Velocity

9) Tube Side Heat Transfer Coefficient

10) Shell Bundle diameter

11) Shell Diameter

12) Shell side velocity

13) Equivalent diameter for square pitch arrangement

14) Shell Side Heat Transfer Coefficient

15) Overall Heat Transfer Coefficient

16) Tube Side Pressure Drop

17) Shell Side Pressure Drop

**1. Flow Rates & Physical Properties**

**Hot Stream**

Flow rate = 120000 kg/ hr

Inlet Temperature T1 = 425 °C

Outlet Temperature T2 = 373 °C

 **Cold Stream**

Flow rate = 114000 kg / hr

Inlet Temperature= t1 = 30 °C

Outlet Temperature= t2 = 120 °C

## 2. Heat Load on Heat Exchanger As,

From Cold Stream

$$Q = mCp\Delta T$$

Putting all value in formula,

Q = [114000×2.1×(120-30)]/3600

Q = 5985 kW

## 3. Log Mean Temperature Difference (LMTD)

As,

LMTD=$\frac{[(T1- t2) - (T2- t1)]}{ln\frac{(T1- t2)}{(T2- t1)}}$

Where,

T1=425°C

T2= 373°C

t1= 30 °C

t2= 120°C

Putting all the values in above formula,

$$LMTD = \frac{[(373- 30) - (425- 120)]}{ln\frac{(373 - 30)}{(425 - 120)}}$$

LMTD = 323.62 °C

Assume 1:2 shall and tube heat exchanger i.e. 1 shall pass and 2 tube pass

Since

$True\ temperature = Ft \times \Delta TLM$

Where Ft is the correction factor

For true temperature we must fine the values of R & S

$R = \frac{T1- T2}{t1 - t2}$

R= 425-373/120-30

R= 0.577

$S = \frac{t2- t1}{T1- t1}$

S= 120-30/425-30

S= 0.228

From graph (using the value of R & S)

Ft= 0.98

True temperature difference = ΔTm = 0.98 × 323.62 = 317.156 °C

## 4. Overall Heat Transfer Coefficient

Suppose,

Overall Heat Transfer Coefficient = 190 W/m2°C

## 5. Heat Transfer Area

As,

$$Q = U \times A \times \Delta TM$$
$$A = Q / (U \times \Delta TM)$$

Putting values,

A = 5985/ (190×317.156)

A = 99.32 m$^2$

## 6. Exchanger Type & Dimensions

Choosing "Shell & Tube Heat Exchanger",

Choosing standard dimensions of heat exchanger:

Inner diameter of tubes (i.d) =$d_i$= 34 mm

Outer diameter of tubes (o.d) =$d_o$= 38 mm

Length of tubes = L = 6.1 m

As,

$$Area\ of\ one\ Tube = Ao = pi \times do \times L$$

$A_o$= 3.14159×38x10$^{-3}$×4.8x(6.1)

$A_o$ = 0.728 m$^2$

## 7. Number of Tubes

Number of Tubes = $N_t$

$N_t$ = Heat Transfer Area/ Area Of One Tube

$$Nt = \frac{A}{Ao}$$

$N_t$ = 99.32/0.728

$N_t$ = 136

## 8. Tube Side Velocity

Tube Cross-sectional Area = $A_i$

$$Ai = \frac{pi \times di^2}{4}$$

$A_i$ = [3.14159×(34X10$^{-3}$)2]/4

$A_i$ = 9.08X10$^{-4}$m$^2$

Tubes per Pass = $T_{pp}$

$T_{pp}$ = $N_t$/2

$T_{pp}$=136/2

$T_{pp}$= 68

Total flow Area = A

$$At = Tpp \times Ai$$

At= 68×9.08X10$^{-4}$

$A_t$= 0.061744 m$^2$

Total tube area per pass = 0.061744 m$^2$

Volumetric Flow rate =Mass Flow Rate /density

= 120000/(50×3600)

= 0.667 m$^3$/sec

$$Tube\ side\ velocity\ Ut = \ Volumetric\ flow\ rate\ /\ Tube\ area\ per\ pass$$

= 0.667/0.061744

Tube Side velocity = $U_t$ = 10.79 m/sec

## 9. Tube Side heat transfer Coefficient

$$\frac{Hidi}{kf} = \ jh(Re)(Pr)^{0.33}(\frac{\mu}{\mu s})^{0.14}$$

$$Re = \frac{\rho u d i}{\mu}$$

Re= 50x10.79x38x10⁻³×1000/0.92x10⁻³

Re= 2.2 x10⁴

$$Pr = \frac{Cp\mu}{Kf}$$

Pr= 3.6X10⁻³x0.92x10⁻³/0.1562

Pr=21.2

As $\frac{L}{di} = \frac{6.1}{34x10^{-3}}$

=179.4

As, Jh= 3.8x10⁻³

$$Hi = (\frac{Kf}{di})\ jh(Re)(Pr)^{0.33}(\mu\frac{}{\mu s})^{0.14}$$

$H_i$ = 9410 W/m² K

## 10. Shell Bundle Diameter

Diameter of Bundle= $D_b$

$$Db = \ do \times [\frac{Nt}{K1}]^{\frac{1}{N1}}$$

Using square pitch & two tube passes

$K_1$= 0.156

$N_1$ = 2.291

So,

$D_b$= 38 × [136/0.156] ⁽¹/²·²⁹¹⁾

$D_b$= 729.87 mm =730 mm

## 11. Shell Diameter

Diameter of Shell =$D_s$

$D_s$ = $D_b$+ Clearance

Using split ring floating head type

For split ring floating head type:

Clearance = 65 mm

So,

$D_s$ = 730 + 65

$D_s$ = 795mm

## 12. Shell Side Velocity

Baffle Spacing = $L_b$

$L_b = D_s/5 = 795/5$

$L_b = 159$ mm

Tube Pitch = $P_t$

$P_t = 1.25 \times d_o$

pt = 1.25×38

pt = 47.5 mm

Cross-flow Area = $A_s$

$$As = (Pt - do) \times Ds \times \frac{Lb}{Pt}$$

$A_s = (47.5 - 38) \times (795\text{x}10\text{-}3) ( 159\text{x}10^{-3}) /47.5$

$A_s = 0.026$ m$^2$

## 13. Equivalent diameter for square pitch arrangement

Equivalent Diameter = $d_e$

$$de = (\frac{1.27}{do}) \times (Pt^2 - 0.785 \times do^2)$$

$d_e = (1.27/38) \times (47.5^2 - 0.785 \times 38^2)$

$d_e = 37.52$ mm

Volumetric Flow rate = Mass flow rate/density

$= 114000/(840 \times 3600)$

0.0377 m$^3$/sec

Shell Side velocity = volumetric flow rate/area

$= 0.0377/0.025281$

$= 1.49$ m/sec

## 14. Shell Side Coefficient

$$\frac{Hsde}{Kf} = jh\,(Re)(Pr)^{0.33} (\frac{\mu}{\mu w})^{0.14}$$

Reynolds Number = Re

$$Re = \frac{\rho v d}{\mu}$$

Re = (840×1.49×37.52x10$^{-3}$)/ 1.26x10$^{-3}$

Re = 37240

Prandtl Number = Pr

$$Pr = \frac{Cp \times \mu}{k}$$

$$Pr = \frac{2.1x10^{-3} \times 1.126x10^{-3}}{0.1298}$$

Pr = 20.4

For 25% baffle cut

$$\frac{Hsdo}{Kf} = jh\,(Re)(Pr)^{0.33} (\frac{\mu}{\mu w})^{0.14}$$

$H_s = 1005$ W/m$^2$ C

## 15. Overall Heat Transfer Coefficient

Overall heat transfer coefficient can be calculated as:

$$\frac{1}{Uo} = (\frac{1}{ho}) + (\frac{1}{hod}) + [\frac{\{do \times \ln(\frac{do}{di})\}}{2K}] + (\frac{do}{di}) \times (\frac{1}{hid}) + (\frac{do}{di}) \times (\frac{1}{hi})$$

Outside fouling factor = $h_{od}$ = 2000 W/m$^2$ $^{\circ C}$

Inside fouling factor = $h_{id}$ = 1000 W/m$^2$ $^{\circ C}$

Now, putting all value is the formula,

$$\frac{1}{Uo} = (\frac{1}{1005}) + (\frac{1}{1000}) + [\frac{\{38X10^{-3} \times \ln(\frac{38}{34})\}}{2} \times 16] + (\frac{38}{34}) \times (\frac{1}{1000}) + (\frac{38}{34}) \times (\frac{1}{9610})$$

$U_o$= 297.10 W/m$^2$. $^{\circ C}$

## 16. Tube-side Pressure Drop

$$\Delta Pt = Np[8jf(\frac{L}{di})((\mu/\mu w) + 2.5](Density \times \frac{ui^2}{2})$$

Np= No of tubes=2

Re=2.0086x10$^{-3}$

J$_i$=3.9x10$^{-3}$

$\Delta Pt$= 2 [8×3.9×10$^{-3}$(6.1/34×10$^{-3}$) + 2.5] (50×10.79$^2$/2)

$\Delta Pt$=47.606k Pa

## 17. Shell-side Pressure Drop

Re = 3.8X10$^4$

From graph

Jf= 4.1 ×10$^{-2}$

$\Delta P_s$ = 8jf ×(D$_s$/d$_e$)×(L/b)×(density×U$_s^2$ /2)

$\Delta P_s$ = 8×4.1×10$^{-2}$×(795/37.52)×(6.1/159)×(840×1.49$^2$/2)

$\Delta P_s$=248.6 kPa

# 4.3 Designing of Pump

Inlet Pressure (P1, N/m$^2$) = 350000

Outlet Pressure (P2, N/m$^2$) = 5300000

Volumetric flow rate (mv, m$^3$/hr) = 207

Density (Kg/m$^3$) = 779.88

Total dynamic head = H = (5300000-350000)/779.88 = 6347.13 N.m/Kg

Hence,

Shaft work of the Pump = Head ×Q

$$= \frac{6347.13Nm}{Kg} \times \frac{207m^3}{hr} \times 779.88\frac{Kg}{m^3} \times \frac{1hr}{3600sec} \times \frac{1watt}{Nm} \times sec \times \frac{1Kw}{1000}watt$$

=284.265 KW

Efficiency = 60 %

So,

the actual Power of the Pump = 284.265/0.6 = 475 KW

## 4.4 Stripper Design

Number of steps involved in the designing of stripper are as follows

### 1. Calculation of theoretical number of stages:

The main component which we want to be stripped from MDEA is $H_2S$. So, we take it as a reference.

Let us suppose that 100% of $H_2S$ is not stripped and very minute quantities remains in the lean MDEA coming back from Stripper.

Fraction of $H_2S$ stripped = Esi = 0.998

Minimum V/L for $H_2S$ $= (\frac{V}{Lo})\min = \frac{Esi}{Ki}$

Value of K depends on T & P.

So, average tower conditions for value of ki:

T = 230 °F

P = 26 psia.

Ki = 35

So, $(\frac{V}{Lo})\min \quad = \frac{Esi}{Ki}$

$= 0.998/35$

$= 0.0285$

Operating (V/Lo)= 1.25 (0.0285)

$\quad = 0.0356.$

Operating stripping factor

$Si = (\frac{V}{Lo}) \times Ki \ = \ 0.0356 \ x \ 35$

$\quad = 1.246.$

Theoretical stages at operating conditions.

$$ESi \ = \ \frac{Si^{N+1} - \ Si}{Si^{N+1} \ - \ 1}$$

$0.998 \ = \ \dfrac{[(1.246)^{N+1} - 1.246]}{[(1.246)^{N+1} - 1\ ]}$

(N+1) log 1.246 = log (1.246−0.998/1−0.998 )

(N+ 1)(0.0955) = 2.0969

N = 20.78

It means 21 theoretical trays are needed.

### 2. Calculation of Actual Number of Stages:

We take 70% efficiency.

So,

Actual number of stages = 30 stages.

### 3. Calculation of diameter of column:

Flooding velocity is given

$$UF = \frac{Ki\sqrt{Pt - Pv}}{\sqrt{Pv}}$$

Where,

Uf = Flooding vapor velocity in m/s, base on net column cross-sectional area.

K1 = Constant obtained from figure 11.27 vol.6 Coulson &Richardson.

$$F_{LV} = \frac{Lw}{Vw} \sqrt{(\frac{Pv}{PL})}$$

Where,

Lw =Liquid mass Flow rate, Kg/s

Vw = Vapor mass Flow rate, Kg/s

In this case,

Lw = 37.37 Kg/s

Vw = 0.3733 Kg/s

Pv= 1.9 Kg/m$^3$

PL = 914 Kg/m$^3$

$$F_{LV} = \frac{37.37}{0.3733}\sqrt{(\frac{1.96}{914})}$$

= 4.6

We use Plate Spacing 1500mm.

K1 = 0.03

Then,

$$UF = \frac{0.03\sqrt{914-1.96}}{\sqrt{1.96}}$$

= 0.65 m/s

We take actual velocity as 85% of flooding velocity

So, Uv = 0.85 x 0.65

= 0.55 m/s

Maximum volumetric vapor flow rate =0.37 1.96

=0.18 m$^3$ s

Net area required =A$_n$ = 0.18/0.55

= 0.33 m$^2$

We take down comer area as 12% of total area

Column cross sectional area = A$_c$ = 0.33/0.88

= 0.375 m$^2$

Down comer area = Ad = 2.67 – 2.35

= 0.045m$^2$

Active area, bubbling area = Aa= Ac – 2×Ad

= 0.285 m$^2$

Total hole area as 10% of active area, so

Hole area = A$_H$ = 0.10 x 0.285 = 0.0285 m$^2$

Column diameter = Dc = √Ac ×4 π

= √(0.375 ×4/3.14_

= 0.477 m.

**4. Calculation of Weeping Point:**

Maximum liquid flowrate = 37.37kg/s

Minimum liquid rate, at 70% turn down = 0.70 x 37.37

$$= 26.15\text{kg s}$$

$$(\frac{Ad}{Ac}) x100 \ = \frac{0.045}{0.375} x\ 100 = 12\%$$

$$\frac{Lw}{Dc} = 0.75$$

lw = 0.75 x 0.477 = 0.358m

We know

$$how = 750 \times [\frac{Lw}{pLLw}]^{2/3}$$

$L_w$ = weir length, m

$h_{ow}$= height over weir, mm liquid

$L_w$ = liquid flow rate

$$how = 750 \times [\frac{37.37}{914 \times 0.358}]^{2/3}$$

= 179mm.

We take, hw = 50mm

$h_w + h_{ow}$ = 179 + 50

$$= 229\text{mm.}$$

K2 = 31.2

$$U_{h(min)} = \frac{k2 - 0.9(25.4 - Dn)}{pv \times 1/2}$$

Uh = minimum vapor velocity through holes, m/s

Dh = hole diameter, mm

$$\text{Uh} = \frac{31.2 - 0.9(25.4 - 5)}{1.96 \times 1/2}$$

Uh = 9.17m/s

Actual minimum vapor velocity = Minimum vapour rate/ Ah

$$= (0.7 \times 0.67)/0.0285$$

$$= 16.52 \text{ m/s.}$$

So, minimum operating rate will be well above weeping point.

**5. Calculation of pressure drop:**

$\Delta Pt$= 9.81 x $10^{-3}$ht×$P_L$

$\Delta Pt$ = total pressure drop, Pa (N/m2)

ht = total pressure drop, mm liquid

Total pressure drop is given by

$$ht = hd + (hw + how) + hr$$

ht = total plate pressure drop

hd = dry plate pressure drop

hr = residual head

hw = height of weir

how = weir crest, mm liquid

$h_d = 51(\frac{Uh}{Co})^2(\frac{pv}{pL})$

Co = Orifice coefficient

Uh = Vapor velocity through holes, m/s

$Uh = \frac{0.18}{.0285}$

= 6.3m/s.

Ah/Ap≈Ah/Aa=0.0285/0.285

= 0.1

We take carbon steel plate, so

Plate thickness = 5mm

Hole diameter = 5mm

So, Plate thickness/hole diameter

= 1

Co = 0.84

$hd = 51(\frac{11.17}{0.84})^2(\frac{1.96}{914})$

= 19 mm

$$hr = \frac{12.5 \times 103}{\rho L}$$

= 13mm

ht = 229 + 13 + 19

= 261 mm liquid

ΔPt = 9.81 x 10$^{-3}$ x 261 x 914

= 2340.21 Pa

ΔPt = 78 Pa (per plate)

**6. Down comer Design:**

$hb = (hw + how) + ht + hdc$

Where,

$h_b$ = down comer backup, measured from plate surface, mm

$h_{dc}$= head loss in down comer, mm

$hdc = 166 \left[\frac{Lwd}{\rho L.Am}\right]^2$

Where,

$h_{dc}$ = head loss in down comer, mm

$L_{wd}$= liquid flow rate in down comer, kg/s

$A_m$ = either down comer area or clearance area under the down comer Aop which is smaller.

$A_{op}$= $h_{op}$ $L_w$

Where, $h_{op}$ = height of bottom edge of apron above plate

$L_w$ = length of weir

$h_{op} = h_w - 10$

$= 50 - 10 = 40mm$

So, $A_{op} = 0.040 \times 0.358m$

$= 0.0154m$

$H_{dc} = 166 [ 37.37/ 914 \times 0.0154 ]^2$

$= 306$ mm

So, backup in down comer = $h_b$ = 764 mm

Then, backup in downcomer < ½ (plate spacing + weir height)

$0.764 < ½(1.5 + 0.050)$

So, plate efficiency is acceptable.

## 7. Entrainment Calculation:

For checking entrainment, we calculate

$U_v = V_{max}/ A_n$

$U_v = 0.188/0.33$

$= 0.56$ m/s

% flooding $= \dfrac{\text{Actual velocity based on net surface area}}{Vf}$

$= 0.56 /0.65$

$= 86\%$

We already know FLV

$FLV = 4.6$

$\varphi = 0.08$

It is well below 0.1, so there is no chance of entrainment and process is satisfactory.

## 8. Calculation of Height of Column:

No. of plates = 30

Tray spacing = 1.5 m

Tray thickness = 0.005 m

Total thickness of trays = 0.15 m

Top clearance = 1m

Bottom clearance = 1 m

Total height = 47.15 m

# 4.5 Separator Design

Liquid Flowrate = 1200(105)=126000 kg/hr

Gas Flowrate = 1200(2.715)= 3258 kg/hr

Section of Lv/Dv

The most economical length to dia ratio depend upon operating pressure from 290 to 509.64 psi

Lv/Dv = 4

Hv=0.5Dv

$$liquid\ settling\ velocity = ut = 0.07 \times (\frac{\rho l - \rho v}{\rho v})^{\frac{1}{z}}$$

$$liquid\ settling\ velocity = ut = 0.07 \times (\frac{850 - 7}{7})^{\frac{1}{z}}$$

$$Ut = 0.754$$

Here Separator without demister is used which

$$Ua = 0.15\ x\ Ut$$

=0.15x 0.754=0.1131 m/s

Vapour Volumetric Flowrate

Vapour Flowrate = 3258 kg/hr

$$Qv = \frac{mass\ flowrate}{density}$$

Qv= 3258 kg/hr x 1 hr/3600s x m$^3$/7 kg

Qv= 0.129 m$^3$/sec

$$Cross\ Sectional\ area\ for\ vapor\ Flow\ =\ Av = \frac{\pi (Dv)^2}{4}(\frac{1}{2})$$

Av= 0.393 Dv$^2$

$$Vapor\ velocity =\ Uv\ = Qv/Av$$

$= 0.129$m$^3$/sec (1/0.393 Dv$^2$)

Uv= 0.3982 Dv$^{-2}$

Vapor resistance time required for liquid droplet to settle on liquid surface

$$Vapor\ resistance\ Time =\ vessel\ length\ /vapour\ Velocity\ =\ Lv\ /\ Uv$$

4Dv/0.3282Dv$^{-2}$

Vapor resistance time = 12.18 Dv$^3$

For satisfactory operation

Required resistance Time = Actual Resistance Time

4.33=12.18 Dv$^3$

Dv=0.59m ~ 1m

Lv = 4Dv = 4 (1) =4m

Liquid Hold up time

Liquid Volumetric Flowrate = Mass Flowrate/Density

$= 126000/820$x$3600 = 0.042$ m$^3$/sec

Al=Liquid Cross Sectional Area = ($\pi$Dv$^2$/4)0.5 = (3.142x1/4)0.5 = 0.392m$^2$

Hold Up Volume = length x Area

$= 4$x 0.393 = 1.568 m$^3$

Hold up time = Liquid Volume / Liquid Flowrate

$= 1.568$ /0.042 =37.33sec

## 4.6 Absorber Design

**1- Calculation of theoretical number of stages**

The main component is H₂S

H₂S:

In=.091×1200=109kg/hr

Out=2kg/hr

$$Efficiency = \frac{kg\ of\ H2S\ in - kg\ of\ H2S\ out}{kg\ of\ H2S\ in}$$

=(109-2)/109=.98=98%

Minimum L/V for H₂S

$$\left(\frac{Lo}{Vn+1}\right)min = KiEai$$

Lo=kg/hr lean liquid (amine) entering absorber

Vn+1=kg/hr rich gas entering absorber

Value of k depend upon T and P

So, average tower condition for Kij

T=110°F

P=432.5psia

So, Lo / Vn+1=1.6×0.98=1.568

$$Operating\ \left(\frac{Lo}{Vn+1}\right) = 1.25 \times 1.568 = 1.96$$

Operating absorbing factor

$$Aio = \left(\frac{Lo}{Vn+1}\right) \times \left(\frac{1}{Ki}\right) = \frac{1.96}{1.6} = 1.225$$

Theoretical stages at operating conditions

$$Eai = \frac{\{(Aio)^{N+1} - (Aio)\}}{\{(Aio)^{N+1} - (1)\}}$$

$$0.98 = \frac{(1.225)^{N+1} - 1.225}{1.225^{N+1} - 1}$$

(N+1)log1.225=log(1.225-.98/1-.98)

N=11

**2- Calculation of actual number of stages**

We take efficiency 70%

Actual number of stages=16

**3- Calculation of diameter of column**

Flooding velocity is given by

$$Uf = k1\sqrt{\frac{\rho l - \rho v}{\rho v}}$$

K1=constant obtain from fig 11.27 coulson &Richardson

$$Flv = \frac{Lw}{Vw}\sqrt{\frac{\rho v}{\rho l}}$$

Where Lw=liquid mass flow rate kg/hr.

Vw=vapor mass flow rate, kg/s

Vw=.905kg/s

Lw=0.104kg/hr×1200hr/3600s=.0346kg/s

Pv=2.4

Pl=1001.4kg/m$^3$

$$Flv = (\frac{.104}{.905}) \times (\frac{2.4}{1001.4})^{.5} = .00562$$

We used plate spacing 600mm

K1=.09

Then $Uf = .09 \times (1001.4 - \frac{2.4}{2.4})^{0.5} = 1.83$m/s

We take actual velocity 85% of flooding velocity

Uv=.85×1.836=1.55m/s

Maximum volumetric flow rate=.905/2.4=.377m$^3$/s

Net area required An=.377/1.55=.234m$^3$

Take down corner area 12% of total area

Column cross-sectional area =Ac=.243/.88=.276m$^3$

Down corner area =Ad=.276-.243=.033m$^2$

$$Active\ area = Aa = Ac - 2Ad$$

0.276-(2×.033)=.21Total whole area is 10% of active area

So Ah=.1*0.21=.021m$^2$

Column diameter=Dc= (4Ac/ π)$^{0.5}$=.59

**4- Calculations of weeping point**

Where  Lw=liquid mass flow rate kg/s=.0346kg/s

Minimum liquid rate,70% turn down=0.7×0.0346=.02422kg/s

$$Ad \times \frac{100}{Ac} = .033 \times \frac{100}{.276} = 11.95 = 12\%$$

$$\frac{Lw}{Dc} = .176$$

**5- Calculations of pressure drop**

ΔPt=9.85× (10$^{-3}$) ×Liquid density

ΔPt=total pressure drop, Pa

Ht=total pressure drop, mm liquid

Total pressure drop is given by

$$ht = hd + (hw = ho) = hr.$$

ht= total plate pressure drop

hd= dry pressure drop

hr= residual pressure drop

ho= weir crest ,mm liq

Co=orifice coefficient

Uh= vapor velocity through hole

Uh=maximum volumetric flow rate /hole area=.377/.021=17.95m/s

$$Ah/Ap = Ah/Aa$$

.021/.21=.1

We take carbon steel plate so,

Plate thickness=5mm

Hole diameter=5mm

So, plate thickness/diameter=5/5=1

Co=.84

Hd=51(Uh/Co)$^2$ × ρv/ρl=51[17.95/.84]$^2$× (1.4/1001.4)= 56

Hr=12.58×10$^3$/ ρl=12.58×10$^3$/1001.4=12.5

Ht=12.5+56+50+8=127

ΔPt= 9.81×10$^{-3}$ ×127.15×1001.4=1247pa

ΔPt= 1247/12=101pa per plate

**6- Down corner design**

$$hb = (hw + ho) + ht + hdc$$

where hb= down corner back up measured from plate surface, mm

hdc= head loss in down corner,mm

Lwd=liquid flow rate in down comer

Am=down comer area

Aap= hop×Lw

Lw= length of weir

hop= hw-10=50-10

Aap= .0135m

$$hdc = 166[Vw/1001.5 \times Aap]$$

=166[.905/1001.5×.0135]$^2$=.8mm

Backup in down corner<1/2(plate spacing+weir height)

.2006<1/2(1.2+.05)

0.2006<.626

So, plate efficiency is acceptable

**7- Calculations of height of column**

No plates=16

Trays spacing=1.2m

Trays thickness=.005m

Total thickness of trays =.1m

Top clearance =1m

Bottom clearance=1m

Total height=18m [14].

# Chapter No. 5
# Cost Estimation

## 5.1 Heat Exchange

Following equation is used to update the cost

Marshall and swift

Present cost/original cost =Index value at P.C/Index value at O.C

Cost of exchanger for 100 m$^2$ surface area in 2002 is = \$11500

Index value at original cost (2002) =1096.4

Current Index (2017) = 1593.7

Present cost = \$11500 × 1593.7/1096.4

Present cost = \$16716

## 5.2 Cost of pump

Centrifugal pump

Cost of pump (2012) = \$7000

Current cost (2017) = \$7000×1593.7/1096.4

Present cost = \$10175

## 5.3 Cost of Stripper

Column dia = 0.47m

Cost index (2002) = \$3000

Current cost (2017) = \$3000 ×1593.7/1096.4

Present cost = \$4360

## 5.4 Cost of Absorber

Dia = 0.59m

Cost index (2002) = \$3500

Present cost = \$3500 × 1593.7/1096.4

Present cost = \$5087.5

## 5.6 Cost of Separator

Hold up volume = 1.57 m$^3$

Cost index (2002) = \$11000

Present cost = \$11000× 1593.7/1096.4

Present cost = \$1598.93

## 5.7 Cost of Reactor

Cost of reactor in (1997) = \$12461841

Cost index (1997) = 1052.7

Cost index (2007) = 1593.7

Present cost = \$12461841 × 1593.7/1052.7

Present cost = \$18866.187

## 5.8 Cost of Furnace

Cost of furnace in (1990) = $100000

Present cost (2017) = $100000 × 1593.7/924

Present cost = $172478.35

## 5.9 Cost of Compressor

Cost index (1990) = $30000

Present cost (2017) = $30000 × 1593.7/924

Present cost =$51743.5

## 5.10 The Total Purchased Costs

**Table No 05 The Total Purchased Costs**

| EQUIPMENT | QUANTITY | PURCHASE COST ($) |
|---|---|---|
| Heat Exchanger | 4 | $66864 |
| Pump | 2 | $20350 |
| Compressor | 1 | $51743.5 |
| Furnace | 1 | $172478.35 |
| Stripper | 1 | $4360 |
| Absorber | 1 | $5087.5 |
| Separator | 1 | $1598.93 |
| Reactor | 1 | $18866.187 |
| Total | | $341348.447 |

## 5.11 Direct Cost

Total purchased equipment cost = $ 341348.447

Installation cost (40% of equipment cost) = $ 136539.38

Instrumentation and control cost (13% of equipment cost) = $ 44375.3

Piping cost (10% of equipment cost) = $ 34134.84

Electric Cost (10% of equipment cost) = $ 34134.84

Building Cost (29% of equipment cost) = $ 98991.05

Land Cost (6% of equipment cost) = $ 20480.91

Total Direct Cost = $ 710004.767

## 5.12 In-Direct Cost

Engineering and supervision Cost (32% of equipment cost) = $109231.5

Construction Expenses (30% of equipment cost) = $102404.53

Contractor fee (18% of equipment cost) = $61442.72

Contingency cost (30% of equipment cost) = $102404.53

**Total indirect cost =$375482.56**

## 5.13 Total Capital Investment

Fixed capital investment = Direct cost + Indirect cost

$$= \$710004.767 + \$375482.56$$
$$= \$10854873.327$$

Working capital (18% of fixed capital cost) = \$195387.72

Total capital investment = Working capital + Fixed capital cost

$$= \$195387.72 + \$10854873.327$$
$$= \$11050252.05$$

## 5.14 Plant Cost

Assume that the fixed capital investment depreciates by straight line method for 20 years. Assuming 5% salvage value at the end of plant life

Depreciation = $D = (V-V_s)/N$

V= Fixed capital investment

V= \$ 10854873.327

Vs= 0.05*Fixed capital cost

Vs= \$ 542743.666

N= no. of years = 10

D= (10854873.327 – 542743.666)/10

D= \$ 1031212.965

Total plant cost = Total capital investment + Depreciation

$$= \$ 10854873.327 + \$ 1031212.965$$
$$= \$ 11886086.29[15].$$

# Chapter No 6
# Instrumentation and Process Control

## 6.1 Instrumentation and Process Control

### 6.1.1 Introduction

Economics of the whole plant and processes depend on the instrumentation systems and control strategies. Therefore, specific needs of process control and measurement are developed for the petrochemical industries rapid expansion of chemical. Following are the points describing instrumentation,

1. Control the variables in industries automatically, normally or semi automatically.
2. Variables that require measurements.

A process is designed to get a require output. The desired efficiency is achieved sometimes by inference from the previous experience and sometimes by trial and error method. Instrumentation and the process control are responsible for the processes which are integrated and complex. In the manual control, the operation read the process variable input up or low to get a desired value of temperature. Manual control is used where the process is small and slow. The adjustments are made automatically on the continuous base processes for the automatic control system. There are different advantages to use automatic control.

1. Increase in the production rate.
2. By improvement of product quality.
3. Increase safety for equipment and personnel
4. Economical saving in energy, time and materials
5. Best efficiency of operation can't be possible by the manual control.

### 6.1.2 Objective of Process Control

Following are the objective of process control
1. To reduce the outside disturbance.
2. Operate the process in a stable manner
3. Optimize the process operation.

### 6.1.2 Components of Control System

#### 6.1.2.1 Process
Any operation or series of operations that produces a desired final result is a process.

#### 6.1.2.2 Measurement
Measurement is a functional requisite to process control whether that the control is affected automatically, semi automatically or manually. Therefore, all the parts of the control system, the ensuring element perhaps the most important. If measurement is not made properly, the remainder of the system cannot operate satisfactory.

**6.1.2.3 Process Variables**

The even operation of a process is dependent upon the control of the process variables. These are defined as conditions in the process materials or apparatuses, which are subjected to change. Temperature, pressure, flow and liquid level are the major variable, followed by perhaps a dozen less frequently encountered such as chemical composition, viscosity, density, humidity, moisture content and so forth. An automatic control is used to measure, correct and modify changes of the found principle types of process variables.

1. Temperature measurements.

2. Pressure measurements.

3. Flow rate measurements.

4. Level measurements.

Various type of measuring instruments for temperature, pressure, flow, and level are:

**1. Temperature Measurement**

Temperature is measured to control the temperature at the outlets and streams in equipment like heat exchanger, reactor etc. Thermocouple is mainly used in industry to measure the temperature. Different types of thermocouples are available for different purposes like equipment bimetallic or filled system thermocouple. Temperature sensors are used in order to measure the temperature of a system. There are the various types of the temperature sensors and which sensor is used is depends upon the criticality of the system. On industrial scale we generally use thermocouple, Resistance temperature detectors and for non-contacting purpose we always use pyrometer. All these sensors are used for the temperature measuring purpose but the working principle of all these sensors are different. It also depends on their accuracy, span, range, precision, reliability, life time and cost. The temperature measurement is used to control the temperature of outlet and streams in heat exchangers, reactors, etc. most temperature measurement in the industry are made by means of thermocouples to facilitate bringing the measurements to centralized location, for local measurements at the equipment bi-metallic or filled system thermocouple are used to a lesser extent usually, high temperature accuracy resistance thermometers are used. All these meters are installed with thermo-walls when used locally. This provides protection against atmosphere and other physical elements.

**2. Pressure Measurement Control**

Pressure sensors are used in order to measure the pressure of a system. Like temperature sensors, pressure sensors also have many types. Some famous types of the sensors are Differential pressure sensors, Bourdon gauges, C-gauges, Baro-meter, Manometer etc. which type of the sensor is used it depends upon the criticalities of the system. All these sensors are used for the pressure measuring purpose but the working principle of all these sensors are different. It also depends on their accuracy, span, range, precision, reliability, life time and cost.

**3. Level Measurement and Control**

Level sensors are used in order to measure the level of a system. There are various types of the level sensors but most famous are

1. Glass level Gauges

2. Displacer type

3. Ball type

4. Bubbler type

5. Dip stick

Which type of the sensor is used it depends upon the criticalities of the system. All these sensors are used for the level measuring purpose but the working principle of all these sensors are different. It also depends on their accuracy, span, range, precision, reliability, life time and cost

### 6.1.2.4 Controller

There are two types of control action;

### 1. Discontinuous Control

On/off or discrete controller The measured variable is compared to a set reference. When the variable is above the reference, the system is turned on, and when below the reference, the system is turned off, or vice versa, depending upon the system design. This could make for rapid changes in switching between states.

### 2. Continuous Control

- Proportional controllers.
- Integral controllers.
- Derivative controllers.

### Proportional Action

Continuous industrial process control action uses proportional control action. The Amplitude of the output variable from a process is measured and converted to an Electrical signal. This signal is compared to a set reference point, and any difference In amplitude between the two (error signal) is amplified and fed to a control valve (Actuator) as a correction signal. The control valve controls one of the inputs to the Process.

### Derivative Action

Proportional plus derivative (PD) action was developed in an attempt to reduce the correction time that would have occurred using proportional action alone. **Integral Action** Proportional plus integral (PI) action, also known as reset action, was developed to correct for long-term loads, and applies a correction that is proportional to the area under the change in the variable curve. **PID Action**

A combination of all three of the actions described above is more commonly referred to as PID action.

### 6.1.2.5 Transducers

Transducer is a device Used to convert either the electrical signal into pneumatic signals or pneumatic signals to electrical signals.

Examples are

1. Tungsten Filament in Electric Bulb

2. Electric Motor in Electrical Appliances

3. Microphones in telecommunication systems

4. Solar Cell

### 6.1.2.6 Transmitter

Transmitter is a device that receives the signals compare it with standard value amplified it transmit it.

### 6.1.2.7 Final Control Element

Final control elements are the devices which are used in order to control and achieve the set point value by altering the flow rate or by some other means. It may be valve, pump, compressor, turbine or motors.

## 6.2 Controllers

### 1. Control Loops (Feed Back):

In working with control, we should think of "control loops" When looking at a controller on a panel board we should think of the valve that the controller actuates, the part of the process that this Valve changes (pressure, flow etc.), the transmitter that sees this process change and back again to the controller on the panel board. Therefore, all of this is known as a "feedback control loop".

There are two important features of a control loop. First, all of the equipment is connected together in a loop form. Second, the operation of each piece of equipment takes place in succession after the one before it in the loop. As an example, when the process flow changes, the flow transmitter will measure it, the flow transmitter output signal to the flow controller will change, the flow controller output signal to the control valve will change and finally, the control valve position will change to correct the process flow. This completes the flow "control loop".

### 2. Manual Control:

It should be mentioned here that most controllers are designed to permit being put on manual control. Manual control is where the control valve is set by manually set air regulator. Panel mounted controllers have manual automatic air switches, knob or lever operated, through which the controller output or the output of the manually set regulator is selected to go to the control valve. Controllers mounted out in the field called local controllers, may have an air switch or may have a manual regulator in a pipe bypass manifold for manual control. Manual control may be wanted when starting up a control loop or when a controller needs to be worked on. It should be understood, however, that no one can manually control a process as good as a properly tuned controller in a well-designed control loop.

### 3. Flow Ratio Control:

This is a control system where two flow rates are involved. The first flow rate usually can be allowed to change and is called the primary flow. The second flow rate, called the secondary flow, is controlled at a certain ratio to (percentage of) the primary flow. This ratio is set by the operator.

### 4. Cascade Control:

Cascade control is the name used when the output of one controller is connected to adjust the set point of a second controller. The first controller is called the primary controller, (the master) and the controller whose output actuates a control valve is called the secondary controller (the slave). Take the example of a tower bottoms cascade control system where the primary controller (tower level) output sets the set point of the secondary controller (bottoms flow). It can be seen that the tower level controller could actuate the bottoms draw-off control valve directly without using a flow controller. However, cascade control minimizes process disturbances.

## 5. Split Range Control:

At times it is desired to have one controller actuate two control valves and not at the same time.
Control valves generally are operated full open to close directly by the 3 –15 psig output of the controllers. However, two valves with petitioners can be operated so that the positioned of one can be calibrated so that its output is from 3 –15 psig while sensing from 3 –9 psig from the controller. Then when the controller output goes above 9 psig, the positioner on the second valve is calibrated to put out 3 –5 psig while sensing 9 –15 psig from the controller. Therefore, one valve goes through its full stroke before the other one starts. Actually these spans can be altered a little so that there is some overlap or there can be a dead band, say, between 8½ psig and 9½ psig where one valve has completed its stroke and the other does not begin until the controller output has changed another pound.

## 6. Computerized Control Systems:

In the previous chapters discussion on process controllers was based on pneumatic and electronic panel mounted instruments. In modern industries, however, computers are used to control process and equipment. Instead of large control panels spread over a large area of space in a control room, operators now control their plants from a workstation consisting of a set of TV screens. Process variables, measurements are transmitted in to the control room and displayed in the screens and they are controlled from these work stations.

## 7. Distributed Control Systems (DCS):

Process variables are measured and controlled in digital units. This has brought in greater precision in measurement and control. Reading through linear and square root changes has become totally unnecessary as they are always displayed in digits to the accuracy of decimals. DCS has the capability of internal calculations thus can give information in a wider range and can control process variables in very complex loops.

## 8. Advanced Control Strategies (ACS):

Using DCS, control strategies can be designed for further advanced type of controls in order to achieve greater profits for the organization and greater safety in operation. An introduction to
ACS is given below.

## Basic Regulatory Controls:

All the process plants are normally controlled using parameters such as pressure, temperature, flows and levels. These are called the basic regulatory controls. Operator usually adjusts these basic controllers like the column top temperature, product flow rates, vessels pressure and levels to control the product quality and maintain the unit throughput.

## Advanced Control Strategies:

ACS aims to achieve the following objectives automatically by adjusting the basic regulatory controls.

- Effective tangible reduction in operation cost, by lower utility consumption, higher catalyst
- Life and higher unit operating factor.
- Observe and follow critical plant constraints.
- Maximize the unit capacity.
- Calculate the important product qualities and control them at their target.
- Ensure the safety of operation.

- Integrates the process operation.
- Generate lots of meaningful information related to the plant performance.

## 6.3 Control Valves

### 6.3.1 General:

The control valve is the final control element in a control loop. It is the device used to regulate the flow in a line. The same control valve could be used in temperature, level flow or pressure control.

In a sense, process control is a form of flow control. The controller determines what position opening the control valve should have to maintain the process at the set point. The output from a pneumatic controller is an air pressure that varies between 3 and 15 psig. Control valves are designed to range from fully open to fully close when an air pressure of 3 to 15 psig is applied to their diaphragm motor. Control valves are known as single seated, double seated, three-way throttle plug type, linear plug type etc. on the basis of the difference in their construction.

### 6.3.2 Air-Fail-Safe Action:

The choice of the air action of a control valve depends on whether the valve should open or close in the event of an instrument air failure. This air-fail-safe action needs not necessarily be the right action for process operations but it will be the better of the two. The general logic applied in process units are, to close the heating mediums (temperature control valves), to open reflux and to open or close pressure control valves and the feed control valves, if the air to the diaphragm fails.

## 6.4 Alarms & Shutdown Devices

### 6.4.1 Purpose and Function of Alarm:

Alarms are provided in control panels of modern process plants, to alert the operator of an abnormal situation. He then can initiate remedial actions to return the operations to normalcy.

Process variables – flow, pressure, level, temperature, quality analysis etc, which are critical, can be arranged for an alarm to be given by sounding a hooter and flashing a light.

### 6.4.2 ESD and Selective Alarms:

In some cases, a severe condition can develop which necessitates the shutdown of equipment or a system or even a whole plant. This can be arranged to take place automatically by emergency shutdown (ESD) systems.

There can be several variables connected to an ESD circuit. For example a compressor may be shut down for any one of the following reasons.

- Low lube oil pressure.
- High lube oil temperature.
- High suction drums level.
- High discharge temperature / pressure.
- High bearing temperature / axial displacement.
- In case like this, the operator might have trouble in determining the cause of shutdown, unless it was obvious.

For example a high level in the suction drum might stop a compressor in which case the lube oil pressure also might drop (where the lube pump is driven by the main shaft) and the alarm be given for this too. To avoid this, it is possible to arrange such alarm groups so that the first alarm only flashes. The others light

but do not flash. It is very important that the operator does not push the "ACKNOWLEDGE bottom until he has noted which alarm has caused the shutdown. (I modern computerized control system, a "sequence of events" print out provides the information regarding the cause of a shutdown[16].

# Chapter No. 7
# Safety & Environmental Consideration

## 7.1 Environmental & Safety Considerations:

Chemical industry in addition to being a capital investment related with risks, special measures should be adopted to ensure safe operation in the chemical and process industries. Following are the factors which contribute to overall plant safety.

- Design
- Construction
- Plant Maintenance
- House Keeping
- Training
- Safety Devices

### 7.1.1 Design:

The planning and design is vital, here is the first opportunity to rule out accidents. Selection of Material of construction can be added by several publishing guidelines. These guidelines are codes for different equipment which are essential for proper design. One factor usually overlooked is the necessary actions of men using the equipment. If frequent access to an elevated place is necessary, perhaps a stairway should be considered rather than a ladder.

### 7.1.2 Construction:

The next opportunity to build safety to the plant is during construction. At this time errors in design can be corrected. Several questions should be asked during the construction process to make sure all areas have been covered. Is there provision to install blank flanges to isolate the equipment? Are sample points as accessible as they appeared in the design? If for example these points are missed in the design phase they can be corrected during construction.

### 7.1.3 Plant Maintenance:

Plant maintenance is also another critical phase in plant safety. It is vital that the plant maintenance and repairs be conducted in a manner to preserve the integrity of the equipment and plant.

Maintenance practices in themselves offer many opportunities to improve safety performance.

Emphasis should be on using correct tools and equipment should be in good condition. Shields should be in place and goggles worn. When using a ladder with an elevation more than 6 feet handrails should be provided.

### 7.1.4 House Keeping:

Housekeeping is an area related to safety which must be kept in mind by maintenance and operations alike. Cluttered walkways, oil spills and just plain dirt do nothing to improve the safety attitudes of people. Housekeeping can generate into a safety problem if ignored. One thing dirt and clutter will not go away by itself. In fact it will attract more dust every day. Each man should have his own areas of responsibility for a clean and ordinary workplace.

### 7.1.5 Training:

Training is very important. Well trained men are more confident and competent in all phases of jobs. Hence a well-trained person has a lesser probability of being involved in an accident.

Be sure to provide the necessary equipment and tools for each job, otherwise you cannot expect the job to be done right or with safety.

### 7.1.6 Safety Devices:

Special clothing and equipment should be used where necessary and available. This again is a part of training. Devices which should be used include goggles, hard hat, proper shoes, gloves, safety belts or harness.

### 7.1.7 Unsafe Acts:-

- Running in the plant.
- Horseplay in the plant.
- Smoking in unauthorized area.
- Using defective tools.
- Injury not reported.
- Unprotected equipment
- Working at unsafe position or unstable position.
- Using unauthorized exit.
- Standard procedures not followed.

### 7.1.8 Unsafe Conditions:-

- Spills (water, oil etc.)
- Machine guards altered or removed.
- Door exits blocked.
- Safety equipment removed.
- Defective equipment.
- Fire hazards.
- Flammable liquids not in safe cans.
- Chemicals not labeled.
- Poor Housekeeping.
- Improper use of danger tags.
- Improper light.
- Inadequate ventilation

### 7.1.9 Fire description:

Fire or burning is a form of rapid oxidation of a substance that produces much heat and light energy. The release of heat energy in a fire may be so rapid as to cause an explosion (a violent expansion of the gases produced). Oxidation is the chemical reaction combining oxygen with another element or compound. This reaction is almost invariable accompanied by a release of heat energy (exothermic reaction). The amount of heat energy released depends on the oxidizing (burning) compounds. Among the hottest heat energy

releases are those occurring when oxygen combines with carbon,hydrogen, or a compound of both elements.

If the chemical combination of carbon and oxygen is complete, carbon dioxide, a colorless gas, is produced. If hydrogen and oxygen combine, water vapor or steam is produced. If the chemical combination includes both carbon and hydrogen and the reaction is complete, then carbon dioxide and water vapor are produced and the resulting smoke is white. If the combustion is incomplete, the products of combustion are carbon monoxide, carbon dioxide, water vapor, and particles of free carbon, and then the resulting smoke is grey or black.

In firefighting, fires are organized into several fire classes that describe what kind of fuel or heat source it has, and by extension what methods will be necessary to contain it or put it out.

# HAZOP Study

## 7.2 What is HAZOP?

A Hazard and Operability (HAZOP) study is a structured and systematic examination of a planned or existing process or operation in order to identify and evaluate problems that may represent risks to personnel or equipment, or prevent inefficient operation. The HAZOP technique was initially developed to analyze chemical process systems, but has later been extended to other types of systems and also to complex operations and to software systems.

A HAZOP is a qualitative technique based on guide-words and is carried out by a multi-disciplinary team (HAZOP team) during a set of meetings.

### 7.2.1 When to perform a HAZOP?

> ➤ The HAZOP study should preferably be carried out as early in the design phase as possible to have influence on the design. On the other hand; to carry out a HAZOP we need a rather complete design. As a compromise, the HAZOP is usually carried out as a final check when the detailed design has been completed.

> ➤ A HAZOP study may also be conducted on an existing facility to identify modifications that should be implemented to reduce risk and operability problems.

### 7.2.2 HAZOP studies may also be used more extensively, including:

1. At the initial concept stage when design drawings are available.
2. When the final piping and instrumentation diagrams (P&ID) are available.
3. During construction and installation to ensure that recommendations are implemented.
4. During commissioning.
5. During operation to ensure that plant emergency and operating procedures are regularly reviewed and updated as required.

### 7.2.4 HAZOP Team members and responsibilities:

HAZOP team leader Responsibilities:

- Define the scope for the analysis
- Select HAZOP team members
- Plan and prepare the study
- Chair the HAZOP meetings

Trigger the discussion using guide-words and parameters

Follow up progress according to schedule/agenda

Ensure completeness of the analysis

- The team leader should be independent (i.e., no responsibility for the process and/or the performance of operations)
- Depending on the actual process the team may be enhanced by:

Operating team leader

Maintenance engineer

### 7.2.5 How to be a good HAZOP participant

Be active! Everybody's contribution is important

Be to the point. Avoid endless discussion of details

Be critical in a positive way - not negative, but constructive

Be responsible. He who knows should let the others know

**7.2.6 Process HAZOP**

Prerequisites

As a basis for the HAZOP study the following information should be available:

- Process flow diagrams
- Piping and instrumentation diagrams (P&IDs)
- Layout diagrams
- Material safety data sheets
- Provisional operating instructions
- Heat and material balances
- Equipment data sheets Start-up and emergency shut-down Procedures

**7.2.7 HAZOP procedure**



HAZOP report
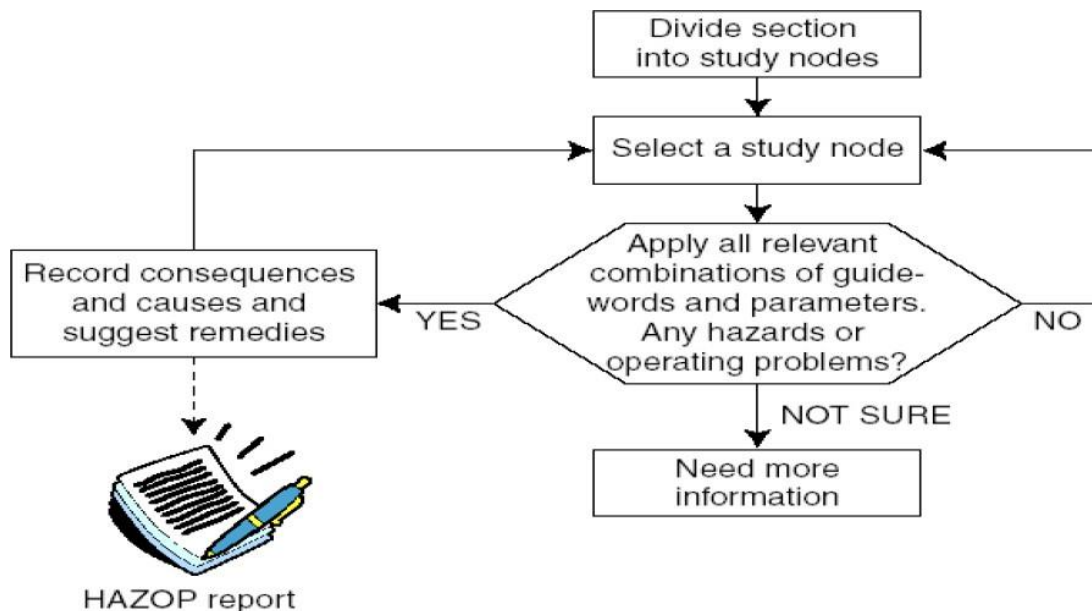
**7.2.8 Modes of operation:**

The following modes of plant operation should be considered for each node:

- Normal operation
- Reduced throughput operation
- Routine start-up
- Routine shutdown
- Emergency shutdown
- Commissioning

- Special operating modes

## 7.2.9 Process HAZOP worksheet:

| Study title: | | | | | | | | | Page: of | |
|---|---|---|---|---|---|---|---|---|---|---|
| Drawing no.: | | | Rev no.: | | | | | Date: | | |
| HAZOP team: | | | | | | | | Meeting date: | | |
| Part considered: | | | | | | | | | | |
| Design intent: | | | Material: Source: | | Activity: Destination: | | | | | |
| No. | Guide-word | Element | Deviation | Possible causes | Conse-quences | Safeguards | Comments | Actions required | Action allocated to |
| | | | | | | | | | | |

— Source: IEC 61882

## 7.2.10 Process parameters:

Process parameters may generally be classified into the following groups:

- Physical parameters related to input medium properties
- Physical parameters related to input medium conditions
- Physical parameters related to system dynamics
- Non-physical tangible parameters related to batch type processes
- Parameters related to system operations
- These parameters are not necessarily used in conjunction with guide-words:

Instrumentation
Relief
Start-up / shutdown
Maintenance
Safety / contingency
Sampling

**Example of process**

- Parameter
- Flow
- Pressure
- Mixing

- Stirring
- Transfer
- Level
- Viscosity
- Reaction
- Composition
- Addition
- Separation
- Time
- Phase
- Speed
- Particle size
- Measure
- Control
- PH
- Sequence
- Signal
- Start/stop
- Operate
- Maintain
- Services
- Communication

## 7.3 The basic HAZOP guide-words are:

**Table No 06 The basic HAZOP guide-words**

| Guide-word | meaning | Example |
|---|---|---|
| No (not, none) | None of the design intent is achieved | No flow when production is expected |
| More (more of ,higher) | Quantitative increase in a parameter | Higher temperature than designed |
| Less (less of ,lower) | Quantitative decrease inn a parameter | Lower pressure than normal |
| As well as (more than ) | An additional activity occurs | Other value closed at the same time (logic fault or human error) |
| Part of | Only some of the design intention is achieved | Only part of the system is shut down |
| Reverse | Logical opposite of the design intention occurs | Back-flow when the system shut down |

| Other than (other) | Complete substitution another activity take place | Liquid in the gas piping |
| --- | --- | --- |

**Table No 07 Guide word meanings**

| Guide-word | Meaning |
| --- | --- |
| Early/late | The timing is different from the intention |
| Before/after | The step (or part of it) is effected out of sequence |
| Faster/slower | The step is done /not done with the right timing |
| Where else | Applicable for the flows, transfer, source and destinations |

## 7.4 HAZOP Results

. Improvement of the system or operations

- Reduced risk and better contingency
- More efficient operations
- Improvement of procedures
- Logical order
- Completeness
- General awareness among involved parties
- Team building

## 7.5 Advantages

- Systematic examination
- Multidisciplinary study
- Utilizes operational experience
- Covers safety as well as operational aspects
- Solution to the problem identified may be indicated
- Consider operational procedures
- Covers human error
- Study led by independent person
- Results are recorded

## 7.6 Pitfalls and objections

- Time consuming
- Focusing too much on solutions
- Team member allowed to divert into endless discussion of details

- A few of the team members dominate the discussion
- This is my design/procedure
- Defending a design/procedure HAZOP is not an audit
- No problem
- Wasted time[14].

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