POLITECNICO DI TORINO

Department of Environment, Land and Infrastructure Engineering

Master of Science in Petroleum Engineering

HEAT INTEGRATION OF HYDRODESULFURIZATION OF DIESEL FUEL

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Dedication

This thesis is dedicated to my Parents.

For their endless love,

Support and encouragement

Content

List of Figures

Abstract

Today in the industry, the trend has been developed to optimize the energy consumption by performing the heat integration through pinch analysis. The main objective to perform heat integration to reduce external utility and maximizing the heat recovery that directly leads to environmental and financial saving. Furthermore, the exact location of the heat exchanger and utilities can be known by designing the heat exchanger network (HEN) through pinch analysis.

Heat integration of hydrodesulfurization of diesel fuel is performed. In order to achieve this goal, pinch analysis was carried out using the ASPEN energy analyzer tool.

In this case, the comparison was made between the target set by the composite curve at a ΔTmin 10 °C and designed three heat exchanger networks (HENS). In terms of minimum hot duty (Qh), minimum cold duty (Qc), heat exchanger area and a number of heat exchangers. With respect to the target, the HEN-1, and HEN-3 has increased in a small percentage and are more close to our targets. Whereas, HEN-2 showed a significant amount of increase with respect to HEN-1, HEN-3.

Likewise, if look into these HENs from the perspective of an area, it is evident that HEN-1 and HEN-3 have the lower area requirements than that of target values, so these can be considered as potential candidates while suggesting for the optimum configuration. However, HEN-2 showed higher values than our desired target, therefore, we would be least interested in this network configuration.

In all three proposed configurations, we have seen the reduction in the heat-duty and cold-duty. In HEN-1 we could save 50.20% of heat duty and 40% cold-duty which is a major achievement if we compare it with the values of before heat integration.

The role of economic evaluation is of paramount importance and holds the key to the decision making factor of these networks. Out of these three designed networks, HEN-2 and HEN-3 have considerably higher values from the target annual cost. However, HEN-1 lies very close to our target value. Therefore, keeping in the account of all the parameters and cost analysis HEN-1 is the most feasible configuration and would provide the maximum throughput

1   Introduction:

Crude oil the primary energy source contributing over 80% of the world's total supply of energy. The depletion of conventional light crude oil reserves around the world increases the dependence on the heavy crude oil. Crude oil is a complex mixture containing a high amount of carbon-hydrogen, and some traces of heteroatom, i.e. Sulfur, nitrogen, and oxygen. Among all the heteroatom sulfur is the most detrimental compound. The sulfur compound must be removed. The presence of sulfur causes, corrosion in the refinery facilities, pipeline, and equipment, etc. Furthermore, sulfur dioxide (SO2) emission, during the combustion of the fuels in transportation causes air pollution. which are undesirable to the atmosphere.

Environment regulation has been introduced in many countries to reduce the sulfur-containing compounds from 10-15 ppm (gasoline & diesel). Petroleum companies in order to meet the stringent environmental regulation and safety requirements. There are different techniques to reduce the sulfur level from crude oil. The Commonly used conventional desulphurization method is hydrodesulfurization (HDS), it is expensive and does efficiently remove the sulfur compound in most cases. There are other efficient desulphurization methods, which remove sulfur compounds up to low-level i.e. biocatalytic desulphurization, oxidative desulphurization, etc. are being used in the refinery and commercial-scale projects.

The main objective of the to perform heat integration to reduce external utility and maximizing the heat recovery that directly leads to environmental and financial saving. Furthermore, the exact location of the heat exchanger and utilities can be known by designing the heat exchanger network (HEN) through pinch analysis

1.1   Quality of crude oil:

The quality of crude oil varies significantly with geographical location. The important properties which characterize the crude quality are API gravity and sulfur content. The Lower sulfur content of crude oil is highly preferred.

1.1.1 API gravity or density of crude oil:

Crude oil quality is determined in terms of density and divided into four different groups such as light crude, medium crude, heavy and extra-heavy crude, as shown in Figure-1. These are differentiated based on the API gravity. Density in-unit degree (API) is the dimension of oil density, is established by the American petroleum institute (API). It allows us to determine the relative density of oil with respect to the density of water at the equivalent temperature of 15 ⁰C. The API gravity of the crude oil is calculated with the following formula given below:

$$API = \frac{141.5}{SG} - 131.5$$

The SG is the specific gravity which is equal to the density of the substance divided by the density of water (1000kg/m3). The most value of the crude oil fall in between the API gravity of 10⁰ to 70⁰ (Duissenov 2013).
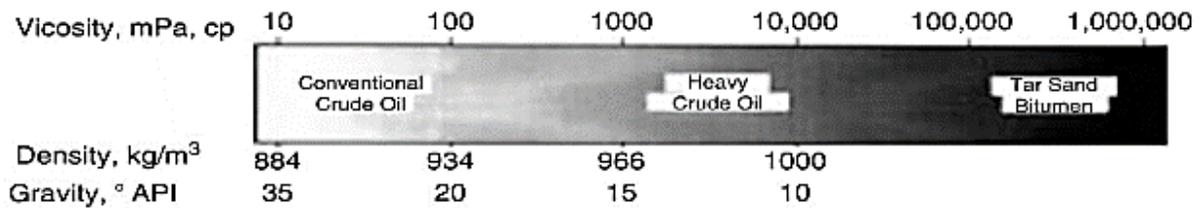
Figure 1: Classification of conventional crude, heavy crude oil, and bitumen by API gravity & viscosity (Schlumberge,2012)

Classification of API gravity of crude-oil as follows(Speight,2007):

- Light-crude API greater 31
- Medium-crude oil in between 22 API 31
- Heavy-crude oil less than 22.3
- Extra heavy crude with API less than 10.

1.1.2 Difference between Sweet and sour crude:

The amount of sulfur percentage present in the crude oil divides into the sour and sweet, show in Figure *2*. When the crude oil containing the total sulfur around 0.5 % it is known as sweet crude oil and if it is higher than that is known as sour crude, shown in Table-1. Sweet crude is more demanding in the refineries because it contains a higher number of distillates that are used for feedstock.

In the early times, the quality of the crude was tested by its odor. The crude oil with a pleasant smell would be determined as low sulfur crude. Sweet crudes are good to refineries because sulfur is easily extracted, transported and low maintenance than the sour crude.

The major location where the sweet crude is found includes North Africa, the North Sea of Europe, Appalachian Basin in Eastern-North America, Western Texas, the Bakken Formation of North Dakota and Saskatchewan, the North Sea of Europe, Australia, etc.Next, the major countries with a higher amount of sulfur content are the middle east (Kuwait, Saudi Arabia, Iran, Iraq, Egypt, and Syria), United States (part of the Gulf of Mexico), South America (Columbia and Venezuela).
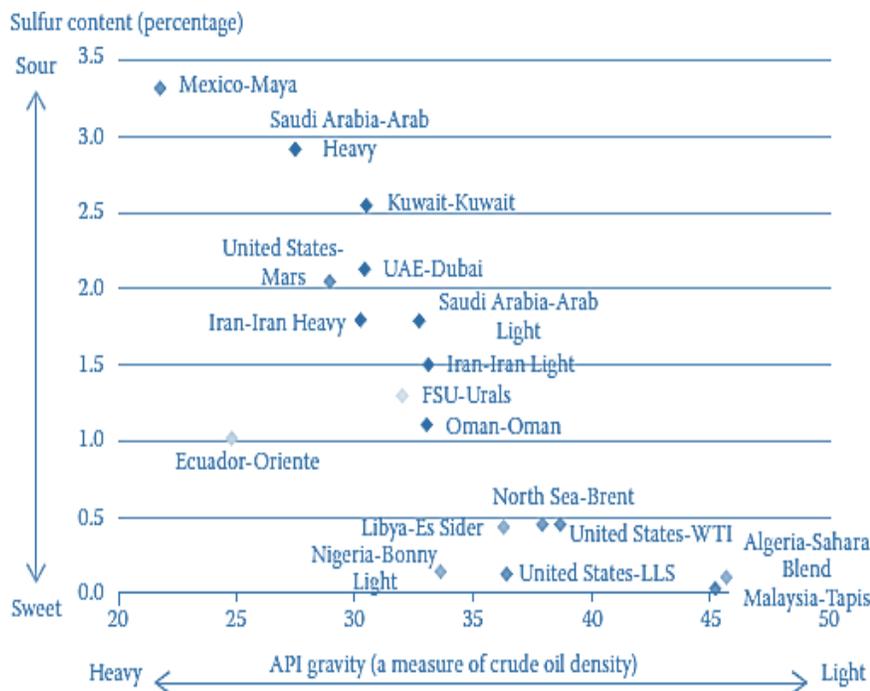
Figure 2: Quality levels - API gravity and sulfur content(EIA,2012.)

Table-1: (De Krom H,2002)

Organic Sulfur Content in Crude Oil from Various Countries

Source	Sulfur Content, % w/w
Argentina	0.06–0.42
Australia	0–0.1
Canada	0.12–4.29
Cuba	7.03
Denmark	0.2–0.25
Egypt	0.04–4.19
Indonesia	0.01–0.66
Iran	0.25–3.23
Iraq	2.26–3.3
Italy	1.98–6.36
Kuwait	0.01–3.48
Libya	0.01–1.79
Mexico	0.9–3.48
Nigeria	0.04–0.26
Norway	0.03–0.67
Russia	0.08–1.93
Saudi Arabia	0.04–2.92
United Kingdom	0.05–1.24
USA	0.05–5
Venezuela	0.44–4.99

1.2   Sulfur in crude oil:

In crude oil, sulfur present as a non-hydrocarbon constituent in different concentrations. The concentration of sulfur varies with the quality of crude oil. Generally, in the heavier crude oil, the sulfur percentage is higher than the lighter crude. Depending upon the source of crude oil or region the concentration ranges from tracer amount to approximately 8%.

According, to the nature of the sulfur in crude oil, it can be divided into two forms an organic and inorganic form shown in Figure-3. The elemental sulfur, H2S, and pyrites are called inorganic sulfur, found in dissolved or suspended form in the crude oil. The sulfur atom bonded to the hydrocarbon molecule as a heteroatom is classified as an organic sulfur compound that is in saturated or aromatic form e.g, thiols, sulfides R-S-R1, thiolanes, thiophene derivatives,

benzothiophene derivative, benzonaphthothiophene derivative, and alkylated derivatives.(Saleh 2016)

Next, based on reactivity, the sulfur present in the crude oil is divided into two classes, such as active, and inactive. The mercaptans and H2S are active sulfur compounds present in sour crude which causes corrosion when directly reacts with the metal. The advantage of these active sulfur compound can be easily removed from the crude oil. The aromatic sulfur (such as thiophene, benzothiophene, dibenzothiophenes, benzonapthothiophenes, and their alkyl-substituted derivatives, etc) comes under inactive sulfur compound which cannot react directly with the metals.

Figure 3: Types of sulfur compounds present in crude(Saleh 2016).
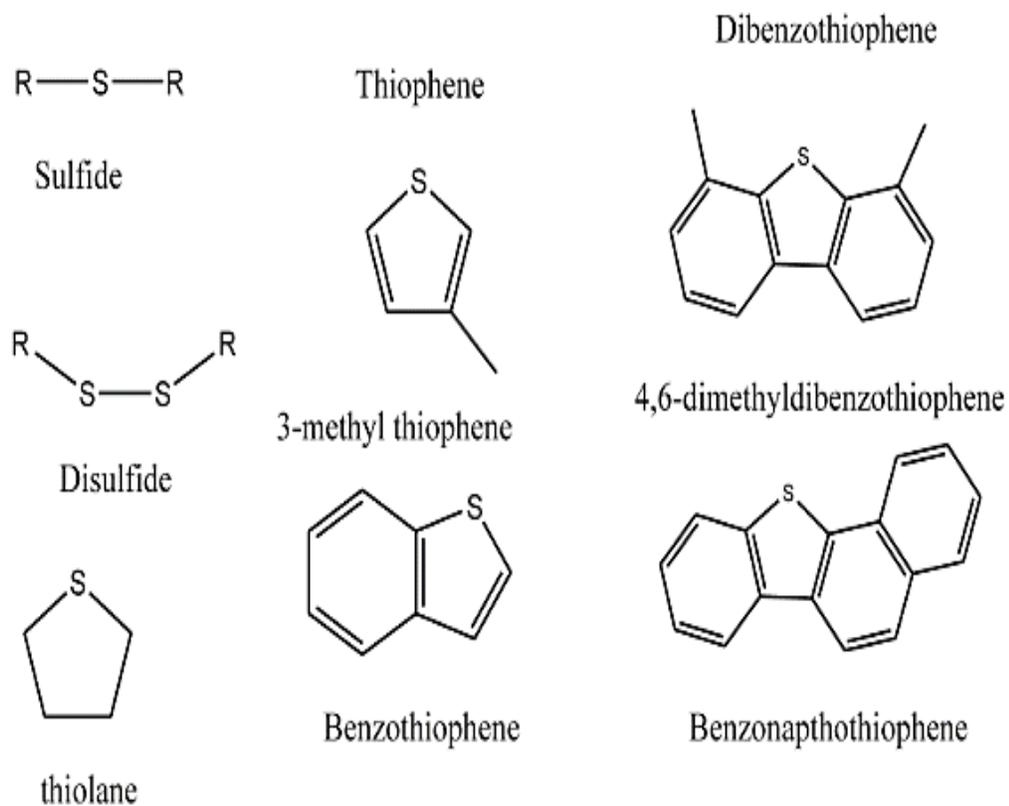
1.3 Effects of sulfur compound present in crude oil:

Sulfur causes a variety of problems present in the crude oil or petroleum distillates. Therefore, it must be removed. An overview of the major problems caused due to sulfur is discussed below.

1.3.1 Malodorous from crude oil:

Crude oil containing malodorous or irritating pungent smell is termed as sour crude, due to the presence of the sulfur compound particularly hydrogen sulfide H2S, and mercaptans. These sulfur compounds not only malodorous but also toxic, and corrosive, during the processing and handling of crude oil they create health hazards and a nuisance to the workers. These malodorous can be removed from crude oil by the sweetening process.

1.3.2 Corrosion Problems:

The corrosive nature of sour crude and light distillate fractions is due to the presence of the sulfur compounds such as H2S, elemental sulfur, mercaptans, and aliphatic sulfides, which are highly reactive to the metals and thereby causes the problem of the corrosion in the distribution systems and equipment in the petroleum refineries. When these compounds are present abundantly in crude oil, they cause corrosion by reacting directly to the metals surfaces(Ahmad 2013). Corrosion damages pipes, storage tanks, and equipment, removal of sulfur reduce not only their durability but also there repair and maintenance costs. Such kind of corrosion in crude oil is assessed by employing the relative degree of corrosivity using the copper strip corrosion test (CSCT ASTM D 130). However, the direct corrosion, sulfur compounds also cause indirect corrosion by producing (Sox) which damages the boilers, internal linings of pipes, spare parts of the engine, and pipings.

1.3.3 Poisoning or deactivation of Catalyst:

The main disadvantage of sulfur compounds present in the crude oil or petroleum distillates is that they deactivate the catalyst used in the refineries for downstream processing and other catalytic operation of petroleum distillates. During the process, sulfur compound adsorbed on the surface

of the metal catalyst and reduces the activity or inactivation of the metal occurs. After the formation of metal sulfide, it leads to poisoning or deactivation of the catalyst. Generally, the poisoning of many catalysts(e.g Hg, Pb, As, etc) by the sulfur compound is an irreversible process. In some cases, this process is reversible for precious metals by the removal of sulfur compounds from the gas stream.

In other processes, such as hydrogenation, isomerization, reforming and alkylation, etc, sulfur compounds are adsorbed on the catalyst surface as organic sulfides, or H2S and blocks the adsorption of other material. Therefore, it leads to partial or complete loss in the activity of the catalyst. The deactivation of the catalyst depends on the extent of the surface coverage, which is categorized into geometric blocking or long-range electronic effects. In the case of a partially covered surface, deactivation results from the combined geometric blocking and long-range electronic effects. Next, under surface coverage, the loss inactivity is due to geometric blocking. Presulfidation of the catalyst can be used to reduce the deactivation of the catalytic problem up to some extent in certain processes.

1.3.4 Sulfur reduces octane number of gasoline:

Sulfur presence in the gasoline resists the susceptibility of octane boosters such as tetra- ethyl-lead (TEL), and tetra-methyl-lead (TML), are employed to increase the octane number. However, it leads to a decrease in the anti-knocking power. As we know that the higher the octane number of gasoline, the lower is the knocking of the engine.

1.3.5 Atmospheric pollution:

The sulfur dioxide (SO2) released during the combustion of petroleum distillate containing sulfur compounds is photo-catalytically oxidized to Sulfur trioxide(SO3) in the (H2SO4). The reaction is shown below:

$$2SO_2 + 2O_2 \rightarrow 2SO_3 \tag{1}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{2}$$

Acid rain mainly affects soil by leaching action. Acid rain dissolves and washes away the nutrients that are required for plant growth, thereby making the soil less fertile. However, acidic washing

also dissolves the harmful constituents present in some kind of soils i.e., Al, Pb, As, Hg etc., further polluting the vegetation, freshwater bodies, and finally reaching the human food chain. Consequently, microbial in soil that cannot survive under low pH conditions are also destroyed by acid rain(Ahmad 2013) .

2   Desulfurization techniques:

  The fossil fuels are a major cause to pollute the environment at a constant rate, as it contains the contaminated substance. Among all sulfur is a detrimental compound that causes corrosion in the refinery facilities, pipeline, and equipment, etc. Furthermore, sulfur dioxide (SO2) emission, during the combustion of the fuels in transportation causes air pollution. Thus, refineries are facing a huge problem to increase fuel quality and control all emissions and meet the given regulation and standards. In fact, all over the world environmental regulation is becoming more stringent to the removal of sulfur compounds. To meet, these regulations, good quality of crude with a low level of sulfur content is highly preferred. However, when it is not available, the alternative is to reduce the sulfur to a low level by using different desulfurization techniques, as shown in Figure-4 and in detail about each method will be discussed in this chapter.

        Desulfurization methods can be divided based on different aspects. Such as hydrogen, amount of sulfur to be reduced from the stream, and the type of processes (chemical or physical) and the operation cost. Also, the treating method of organic sulfur compound (separated without decomposition, decomposed, or both separated then decomposition). In general, hydrodesulfurization (HDS) is the most conventional method used in the refineries to remove the sulfur-containing compound from the stream and blending feedstocks. However, it has disadvantages, it is expensive to install, operate and requires high energy. The other alternative desulfurization techniques are extraction, adsorption, oxidative, and biological methods have also shown good substitution for HDS technology (El-Gendy and Speight 2015). Sulfur contains compounds can be removed by these methods from crude oil or before being refining of fuels. There is no universal approach to distinguish the desulfurization method. Therefore, it is based on the sulfur compound during desulfurization.
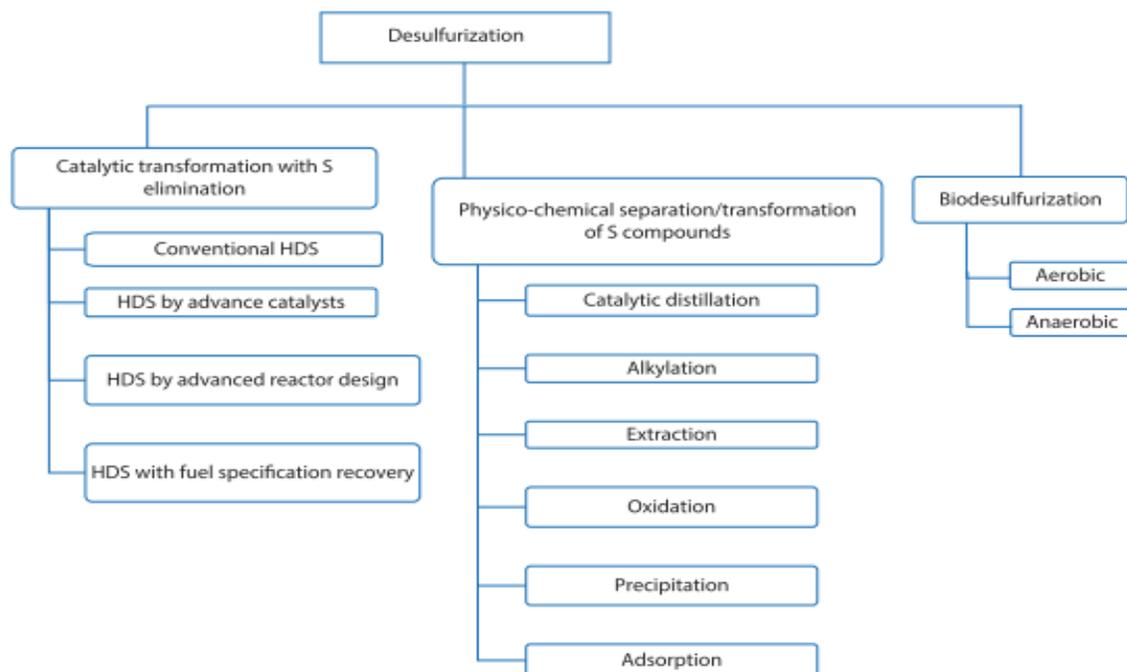
Figure-4: Different desulfurization techniques according to the nature of sulfur removal (El-Gendy and Speight 2015).

2.1   Hydrodesulfurization method:

The hydrodesulfurization (HDS) is a conventional catalytic method that is widely practiced in refineries to remove sulfur (such as, thiols, sulfides, and thiophenes derivatives) from crude oil and petroleum distillates (i.e. gasoline, kerosene, diesel, etc.).

2.1.1   Treatment Process:

Hydrodesulfurization (HDS) is a simple hydrotreating process as shown in figure-5, in this process the feedstock is first pressurized to pressure just above the reactor section. Next, the feedstock is completely mixed with the hot recycle gas and pre-heated to a temperature of reactor inlet. The combined hot feedstock is reacted with the catalyst (e.g. Ni-Mo, Co-Mo, impregnated on / Al2O3) in the reactor at an elevated temperature of (290–455°C) and pressure at an average of 150–3000 psi.

The reactor effluent is sent into the heat exchanger for cooling, next then desulfurized liquid components are separated at a pressure just below the reactor section. Hydrogen sulfide (H2S) and any light hydrocarbon gas are extracted from the recycle gas and the remaining gas is mixed with fresh hydrogen gas (H2), compressed, and mixed with the new feedstock(El-Gendy and Speight 2015).
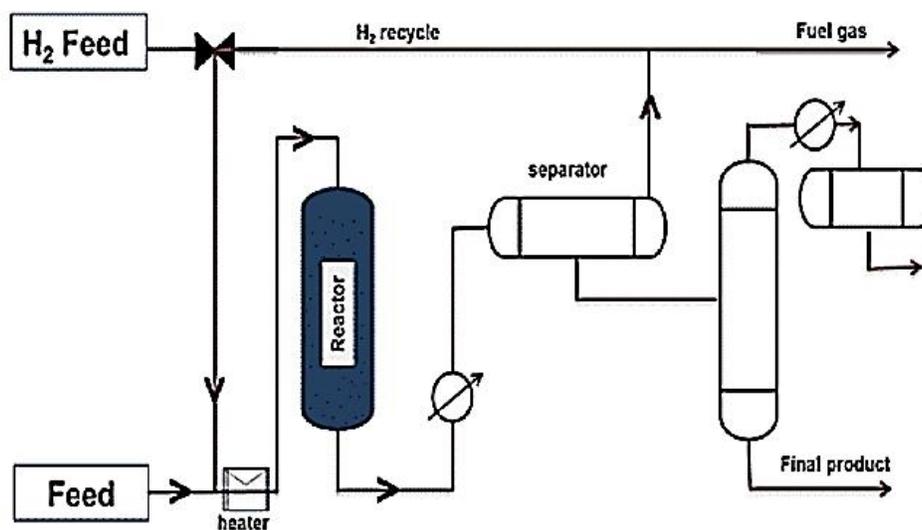
Figure-5: simple Hydrodesulfurization processing unit (Houda et al. 2018).

In the hydrodesulfurization process, the reaction mechanism as shown in Figure-6 of the organosulfur compound (such as thiols, sulfides,) where the sulfur atom is eliminated through the breaking of the C-S bond in the form of H2S gas. In the case, of thiophenic compound is complex and treated through two pathways: the hydrogenation and hydrogenolysis pathway. In the hydrogenolysis pathway, the sulfur element is removed through C-S bond breakage and formation of the S-H bond. In the hydrogenation pathway, the addition of hydrogen to the carbon element allows the removal of the sulfur atom from the ring. In the case of an aromatic sulfur compound, these two pathways can be put in parallel, depending on the reaction condition, nature of the sulfur compound and the catalyst used. The hydrogenolysis pathway favors the Ni-Mo catalyst, and the hydrogenation pathway favors the Co-Mo catalyst. Furthermore, the DBT sulfur compound is processed with the hydrogenolysis pathway and the other alkyl-DBT compound processed by both hydrogenation and hydrogenolysis pathways.

Figure-6: hydrotreating reaction mechanism of sulfur compound (Saleh 2016).

Hydrotreating pathways of organic sulfur compounds.

Types of organic sulfur compounds and their chemical structure	Mechanism of hydrotreating reaction
R-SH Mercaptans	$R-S-H+H_2 \rightarrow R-H+H_2S$
R1-S-R2 Sulfides	$R^1-S-R^2+H_2 \rightarrow R^1-H^+R^2-H^+H_2S$
R^1-S-S-R^2	$R^1-S-R^2+H_2 \rightarrow R1-H^+R^2-H^+H_2S$
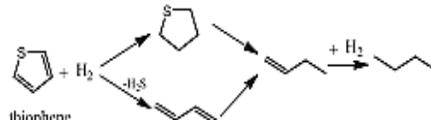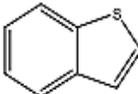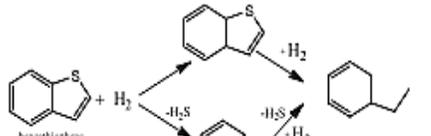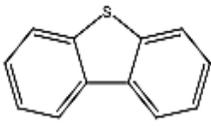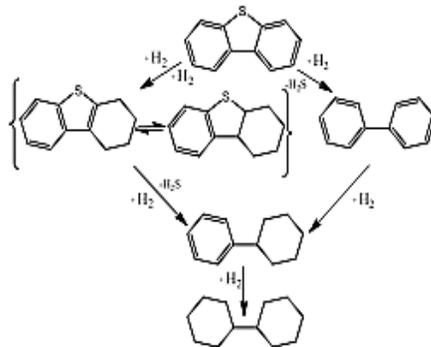
During the hydrodesulfurization HDS process, the order of reactivity of different organic sulfur compounds is in the following order

Th > R-Th > BT > R-BT > DBT > R-DBT > 4-R-DBT > 4, 6-R2-DBTWhere, Th = Thiophene, R = Alkyl group

2.1.2 Advantages of HDS method:

- Remove alphatic sulfur compound easily from the petroleum distillate .
- Remove nitrogen and metals from organic compounds
- Improve the cracking characteristics of the material.
- Remove substances having an unpleasant smell or color.
- Induce saturation of at least some carbon-carbon double bonds

2.1.3   Disadvantages if HDS method:

- The high cost of this process where it requires high pressure and temperature.
- The lack of selective catalysts that lead to more complex catalytic processes such as hydrogenation of aromatic compounds.
- Some of the gases resulting from cracking are harmful to the environment and cannot be reused, resulting in environmental problems.
- High capital costs to build a thick wall reactor to suit the high-pressure conditions.

2.2   Extraction desulfurization method:

The extractive desulfurization process involves the removal of the organosulfur compound from the hydrocarbons by the addition of solvent. As we know that the polar substance is soluble in the polar solvent and vice versa. Hence, extraction of the sulfur compounds from petroleum by addition proper solvent, because the organic sulfur compounds are more soluble in polar solvent then the hydrocarbon.

2.2.1   Treatment process:

In this process, as shown in the (figure -7 the feedstock with the solvent is mixed in the mixing tank. Next, the feedstock is separated from the solvent in the separator section. subsequently, the remaining solvent is recycled after the separation of the organic sulfur compound by distillation. The desulfurized feedstock can be used as the final product or can be blended to form other components.

The efficiency of extraction desulfurization is limited because it depends on the solubility of the organic sulfur compounds in the solvent. So, the proper solvent selection is important for efficient desulfurization. The commonly used solvents for extraction are, ethanol, acetone, and polyethylene glycols, etc. In addition, the combination of two or more solvent such as tetraethyleneglycol: methoxytriglycol, acetone: ethanol mixture, in order to improve the efficiency of extraction of the organic sulfur compound.
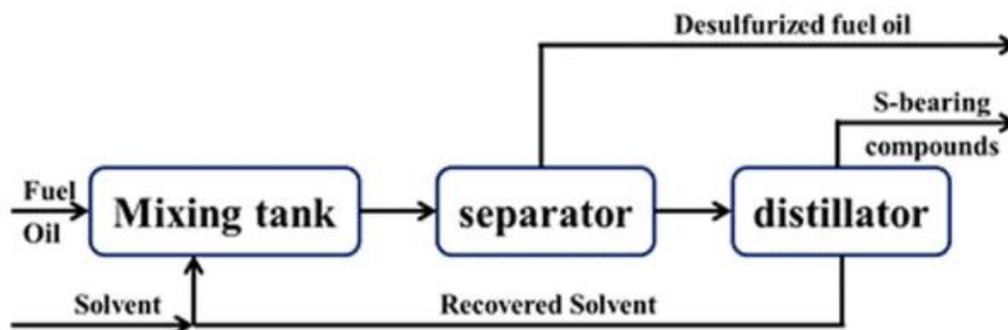
Figure-7: Treatment by extraction method (Houda et al. 2018).

2.2.2 Ionic Liquid extraction:

The ionic liquid extraction is an alternative method to the hydrodesulfurization as shown in Figure-8 Due, to its limitation towards the thiophenic sulfur compounds (e.g., benzothiophene, dibenzothiophene). Subsequently, the ionic liquid solvent can extract the aromatic sulfur compound from the fuels at ambient conditions and without hydrogen (H_2).

There are different types of ionic liquids has been introduced among these, imidazolium-based ionic liquids, such as [BMIM][PF6], [EMIM][BF4], [BMIM] [MeSO4], [BMIM][AlCl4], and [BMIM] [OcSO4], have demonstrated a high selective removal of heterocyclic sulfur compound such as dibenzothiophene, single β-, and di-β- methylated dibenzothiophene, etc. Selection of ions for ionic liquids used in organic sulfur removal from fuel oils is very important. Some of the chlorometallate ionic liquids—such as those with [BMIM] [AlCl4] structures—show good selectivity for sulfur removal; however, they are very sensitive to air and moisture and may cause alkene polymerization in fuels .The size of the anions in ionic liquids is also very important for the extraction of dibenzothiophene from an oil phase larger size anions tend to remove dibenzothiophene more effectively than smaller anions have reported that imidazolium ions with larger alkyl substitution groups are better solvents for dibenzothiophene removal. However, they found that alkyl groups beyond a certain size lowered the selectivity.Similarly, various pyridinium based ionic liquids containing tetrafluoroborate anion and various alkylpyridinum cations like N-hexylpyridinium, N-butylpyridinium, and N-octylpyridinium tetrafluo- roborate, have also been used for EDS of liquid fuels. Moreover, some of the I can be regenerated and reused. However,

theiroverall desulphurization efficiency is microorganisms, also resulting in the extraction of aromatic compounds.
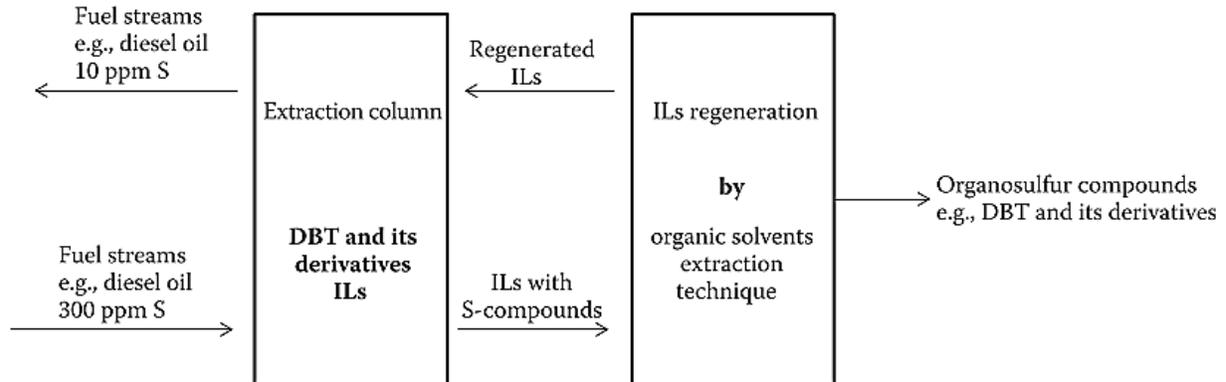
Figure-8: Ionic Liquid extraction (eh, 2016)

2.2.3 Advantages of extraction method:

- The biggest advantage of extractive desulfurization is the possibility of conducting it at relatively low temperatures and pressures, while the hydrocarbon compounds in the feed remain mainly intact.
- Ionic liquids can extract aromatic sulfur-containing compounds at ambient conditions without hydrogen consumption.
- ionic liquids are immiscible with fuel, and the used ionic liquids can be regenerated and recycled by solvent washing or distillation.
- The process equipment necessary for carrying out this process is conventional and can easily be integrated into refineries.

2.2.4 limitation of extraction method:

- In order for the process to be efficient, several conditions must be met: organic sulfur compounds must be fully soluble in the solvent, the solvent must have a different boiling point in relation to the removed organic sulfur compounds.
- The solvent must be nontoxic and relatively cheap so the process can be economically viable.
- The efficiency of extractive desulfurization is mainly restricted by the solubility of the organic sulfur compounds in the applied solvent.
- The choice of the solvent, which must take into account the nature of the organic sulfur compounds to be extracted.

2.3 Adsorptive desulfurization method:

Adsorptive desulfurization as shown in Figure-9 is an economically promising technique in comparison to the conventional hydrodesulfurization method. Due, to its simple operating conditions such as

(temperature, pressure) and high availability of adsorbent also high selectivity towards the sulfur compound. Furthermore, the selectivity of adsorbent also influences the efficiency of the adsorption process. Such as the capability of adsorption, regeneration, durability, etc.

The desulfurization process can be operated in batch or column mode where the feed gets intact with the adsorbent material, and the sulfur compound is adsorbed on the surface of the adsorbate. The interaction of the sulfur compound with adsorbent can be separated into two approaches physical adsorption and chemical or reactive adsorption.

2.3.1 Physical adsorption:

In physical adsorption, the Van-der Wall Forces are responsible for the binding of the sulfur compounds on the surface of the adsorbent. During, this interaction, there is no alteration of the

structure of the sulfur compound. The advantage of physical adsorption is, less energy is required to regenerate adsorbent.

2.3.2 Chemical adsorption:

In chemical adsorption, the sulfur compounds are attached to the adsorbent through chemical bonding and the structure of the sulfur compounds may be altered. The sulfur compounds that commonly interact with the adsorbent mostly as sulfides and can be extracted from the feedstock. Sometimes the chemosorbed sulfur compounds are further altered by treatments like hydrogenation etc. to set free the sulfur atom from the parental hydrocarbon molecule.

The regeneration of the adsorbent may be performed by strong heating in air or solvent washing, and the sulfur removal as hydrogen sulfide or sulfur oxides depends on the nature of the adsorbent and the sulfur compounds as well as on the and regeneration process employed. It has been found that the regeneration is easy, but selectivity is limited in case of physisorption based adsorptive desulphurization, whereas reactive adsorption is highly selective however regeneration is quite difficult and complex. In the literature, several different types of materials have been used as adsorbents for adsorptive desulfurization of various distillate fractions like model oil and gasoline, naphtha, diesel and jet fuel oil. The most common are activated carbon, zeolites 5A , Si2O3 & Al2 O3, MOF (metal organic framework) , modified composite oxides , SBA-15 (McKinley et al., 2003), ZSM-5, MCM-41,etc. Activated carbon is a very efficient adsorbent for high sulfur feed but generally attains low level of total desulfurization; in contrast, zeolite 13X is efficient in attaining deep desulphurization of low sulfur feeds. The application of these two adsorbents in a two-stage reactor constitutes an industrially viable process, where the first stage consists of a bed of activated carbon which merely lowers the sulfur contents of the feed and the second stage comprises of a bed of 13 X zeolite which further attains deep desulfurization. Activated carbon, silica and zeolites are very efficient in the removal of alkylated DBTs from the high sulfur feed.
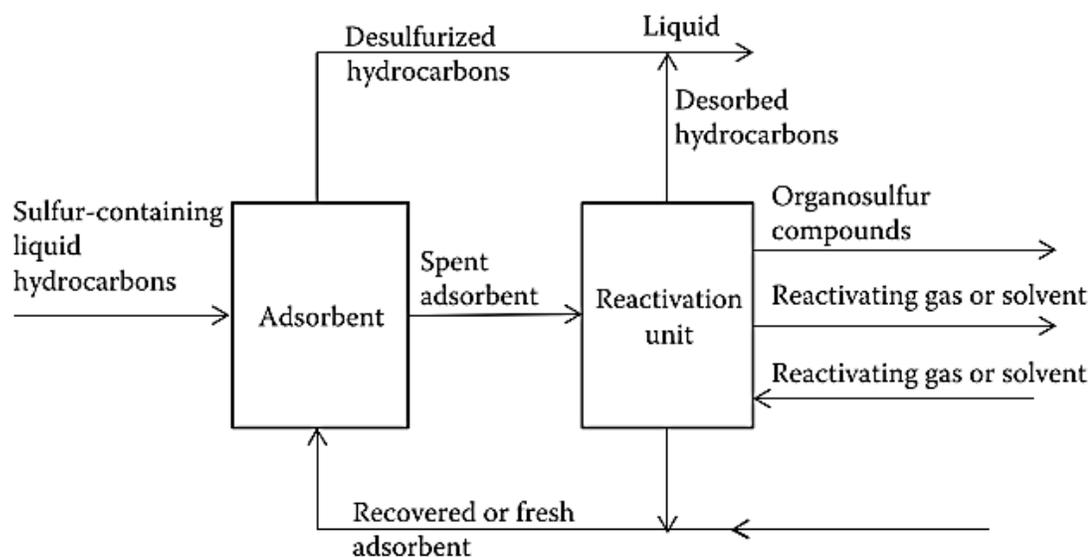
Figure-9: Adsorptive desulfurization method (eh, 2016)

2.4   Oxidation method:
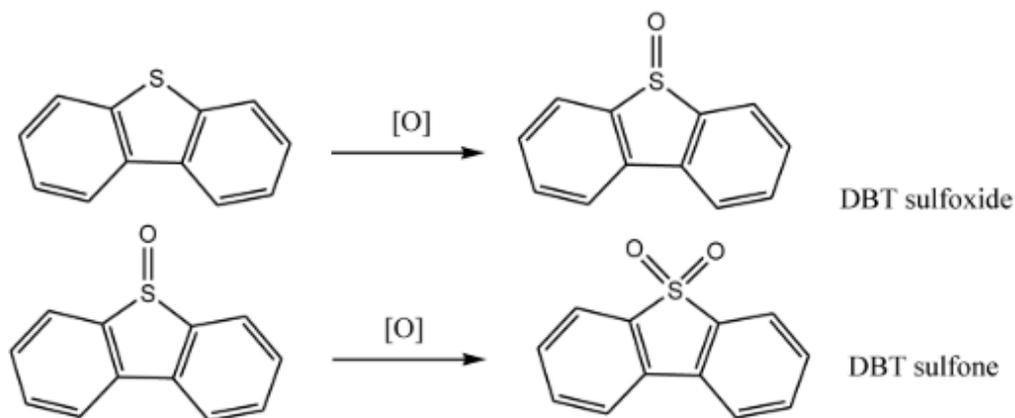
Figure-10: Oxidation mechanism (eh, 2016)

Maintaining selectivity and efficiency in the oxidation of sulfur compounds among the olefins, aromat-ics and cycloalkanes in non-polar medium and selection of the most appropriate oxidant is a challenging task in the ODS process. Extensive research in this field suggests the application of some novel oxidants, catalysts and use of different techniques in oxidation process. Many types of oxidation systems are utilized for efficient conversion of sulfur compounds. Somereported the use

of several of inorganic oxidants in the ODS process, which included nitric acid, nitric oxide KMnO4, sodium perchlorate) and ozone, etc.However, in most cases the inorganic oxidants requires a polar solvent or aqueous medium for enhanced efficiency, on the other limits the interaction of the oxidant and the sulphur compounds in the petroleum due to immiscibility. Many other oxidation systems used in the ODS process are mentioned below.

- ODS with Organic Peracids
- ODS with Air or Molecular Oxygen
- ODS with Organic Hydroperoxides

2.4.1   Advantages of ODS method:

- The ODS process do not require costly hydrogen and a specialized high temperature and high pres- sure reactor.
- The process operates under mild conditions of pressure and temperature, which makes it an eco- nomic process.
- The solvent and the extracted oxidized sulfur compounds can be recycled.
- The refractory sulfur compounds (alkyl-substituted dibenzothiophenes) can be efficiently removed by ODS, which are difficult to be treated by HDS under its normal operating conditions, hence the ODS can attain deep desulfurization.

2.5   Bio-desulfurization method:

The biodesulfurization method is a potential alternative to conventional hydrodesulfurization because in this process microorganisms, enzymes, etc. act as a microbial-catalyst to remove the organosulfur compounds (such as thiophene, benzothiophene, and dibenzothiophene, etc.) present in the crude oil or petroleum distillates without degrading the carbon skeleton of the sulfur-containing compound. The BDS method accounts for two different pathways aerobic and anaerobic.

2.5.1 Anaerobic (BDS) pathway:

In 1995 Kim et-al found the sulfur-reducing bacteria, known as Desulfovibrio desulfuricans M6, which anaerobically degraded the Dibenzothiophene to biphenyl and H2S as shown in the. Therefore, there are other microorganisms found such as (Desulfovibrio longreachii, and Desulfomicrobium escambium) have been reported that there was an absence of biphenyl after the desulfurization of DBT shown in figure-11.
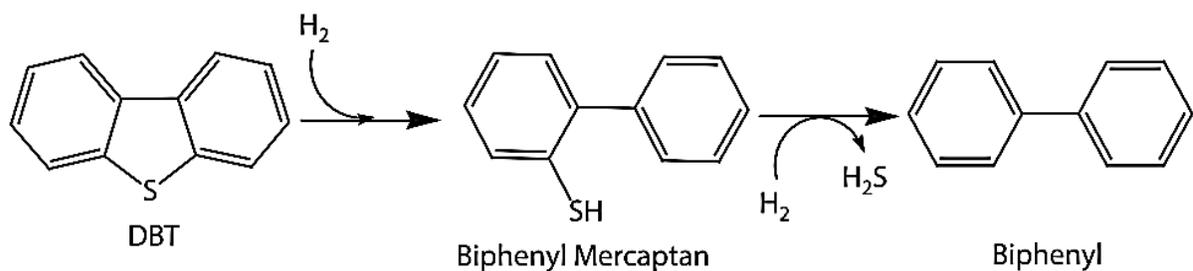
Figure-11: Anaerobic BDS of DBT by Desulfovibrio desulfuricans M6(eh, 2016)

In comparison, to Anaerobic BDS reactions proceed more slowly than aerobic reactions but forms the same products as the conventional hydrodesulfurization HDS method: hydrogen sulfide (H2S) and free sulfur oil. Although anaerobic BDS would be more attractive because it avoids costs of aeration, it has the advantage of liberating sulfur as gas and does not liberate sulfate as a by-product that must be disposed of by some appropriate treatment. However, it has low reaction rates, safety, cost concerns, and the lack of identification of specific microorganisms, genes that are responsible for anaerobic desulfurization, effective anaerobic microorganisms for practical petroleum desulfurization have not been found yet. Consequently, aerobic BDS has been the focus of most of the research in BDS.(Babich and Moulijn 2003)

2.5.2 Aerobic (BDS) pathway:

The aerobic BDS pathway has divided into two main pathways depending upon the utilization of the dibenzothiophene sulfur compound by the microorganism or bacteria. The two major aerobic pathways are sulfur specific oxidization pathway and ring destructive pathway.

2.5.2.1 Ring destructive or Kodama (BDS) pathway:

The ring destructive pathway is also termed as kodama pathway as shown in figure-12, where the breakage of thiophinic ring by oxidation of sulfur or carbon atoms in the ring. The oxidized substance is immiscible in the hydrocarbon phase because of the polar nature and can be removed by extraction with a polar solvent. The Pseudomonas stutzeri, and Rhodococcus erythropolis are more used microorganisms or bacteria strains for ring destructive BDS process. As shown in the figure-12 deoxygenation of the outlying aromatic ring of dibenzothiophene (DBT), following the breakage of the ring which finally leads to the formation of 3-hydroxybenzothiophene-2-carbaldehyde compounds that are miscible in the water with the low amount of carbon content than dibenzothiophene (DBT). In this pathway, no desulfurization occurs. But, the dibenzothiophene(DBT) is transformed into a more polar substance that can be removed by extraction with a polar solvent.
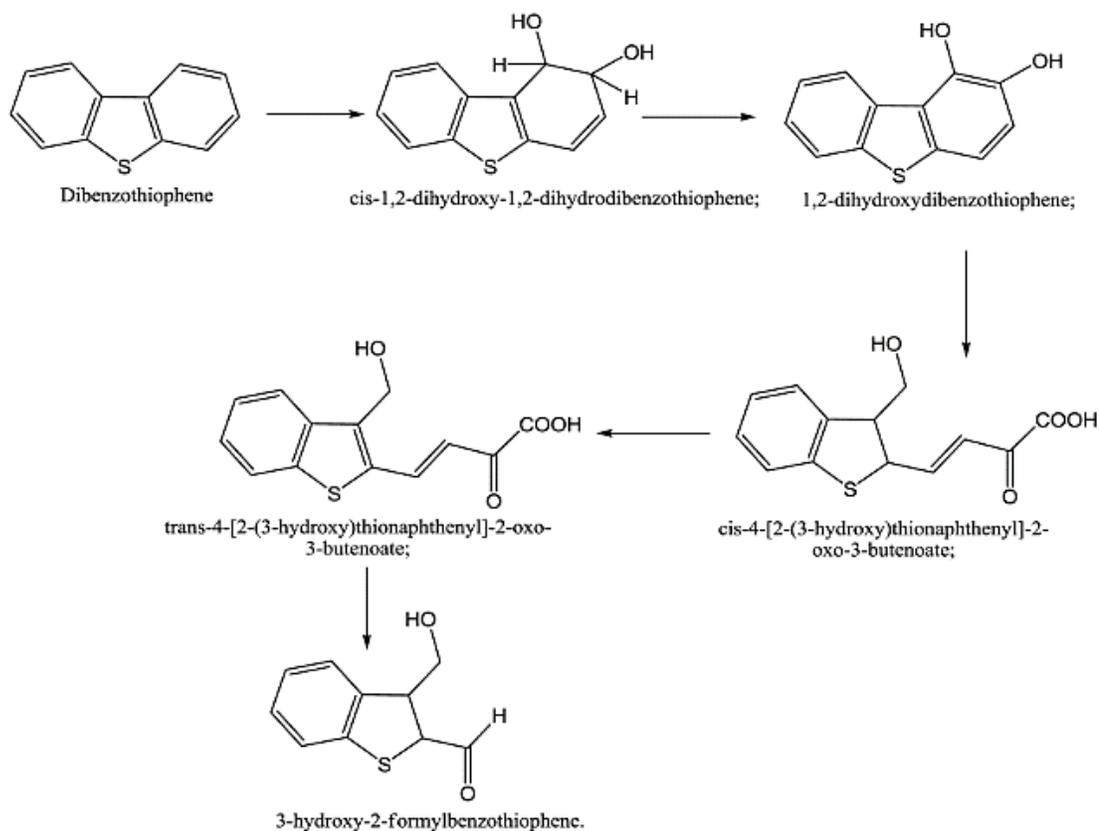
Figure-12: DBT metabolism via Kodama pathway (eh, 2016)

2.5.2.2 Sulfur specific oxidization pathway:

Sulfur specific oxidization pathway is also termed as the 4-S pathway. The process involves the selective oxidization of thiophinic ring. In the case of dibenzothiophene as shown in figure-13 is converted into sulfoxide-DBTO, sulfone-DBTO2, sulfinate-HPBSi, and/or sulfonate-HPBSo, and then finally forming into the oil-soluble product 2-HBP 2,2′dihydroxybiphenyl, is possible. Furthermore, the bacteria termed as (Brevibacterium Sp) for oxidizing DBT to DBTO and next to $DBTO_2$, releasing free sulfur as $SO3^{-2}$ or $SO4^{-2}$ from $DBTO_2$. Various aerobic microorganisms and removal of sulfur percentage are shown in figure-13.Rhodococcus erythropolis can remove the sulfur atom from the thiophinic ring without losing any carbon atom. Rhodococcus species encode a set of genes, named as Dsz. These genes produce four types of enzymes, DszA, DszB DszC and dszD. These enzymes consecutively oxidize DBT to DBTO, DBTO2, 2-(2-

hydroxybiphenyl)-benzenesulfinate (HPBS),and 2-hydroxybiphenyl, respectively and finally, inorganic sulfur is released. The DszC and DszA are monooxygenase enzymes.
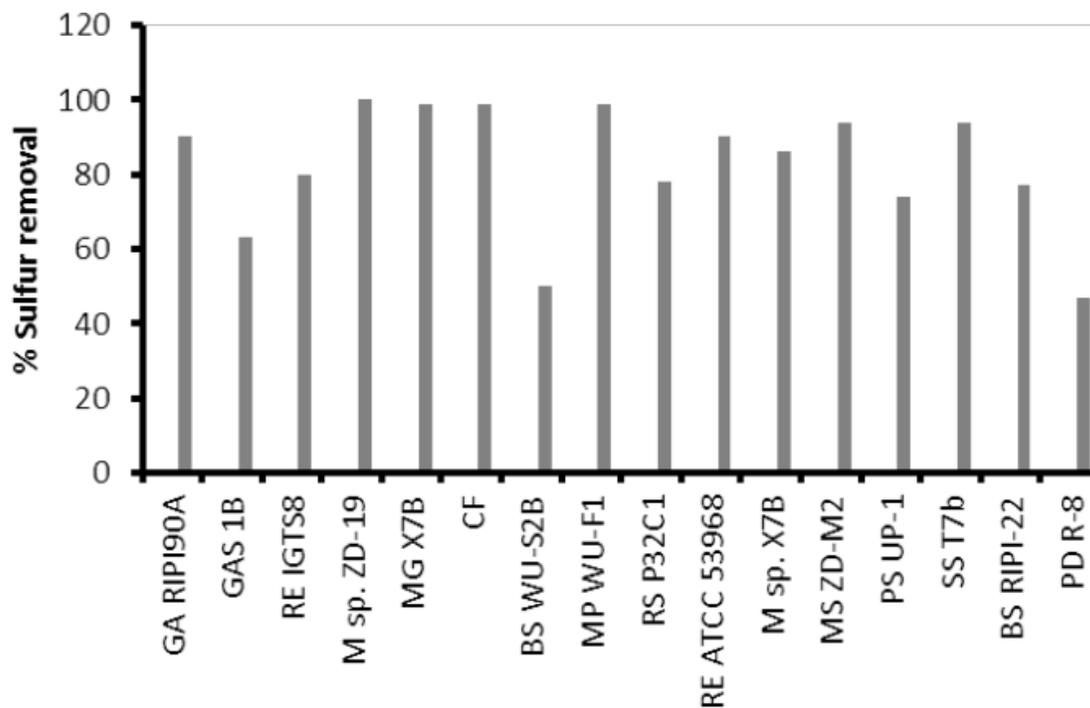
Figure 13: Percentage of sulfur removal with different micro-organism(eh, 2016)

The DszC enzymes oxidizes DBT to DBTO and DBTO2, and it requires oxygen and FMNH2. The DszA also requires oxygen and NADH, and it converts sulfones into sulfinate i.e. HBPS. The DszB is a sulfinse enzyme, which catalyzes the conversion of HBPS to HBP. Similarly, the DszD is an oxidoreductase enzyme that oxidizes NADH and reduces FMNH2. The oxidation pathway involves these enzymes to remove the sulfur compounds as shown in figure-14.
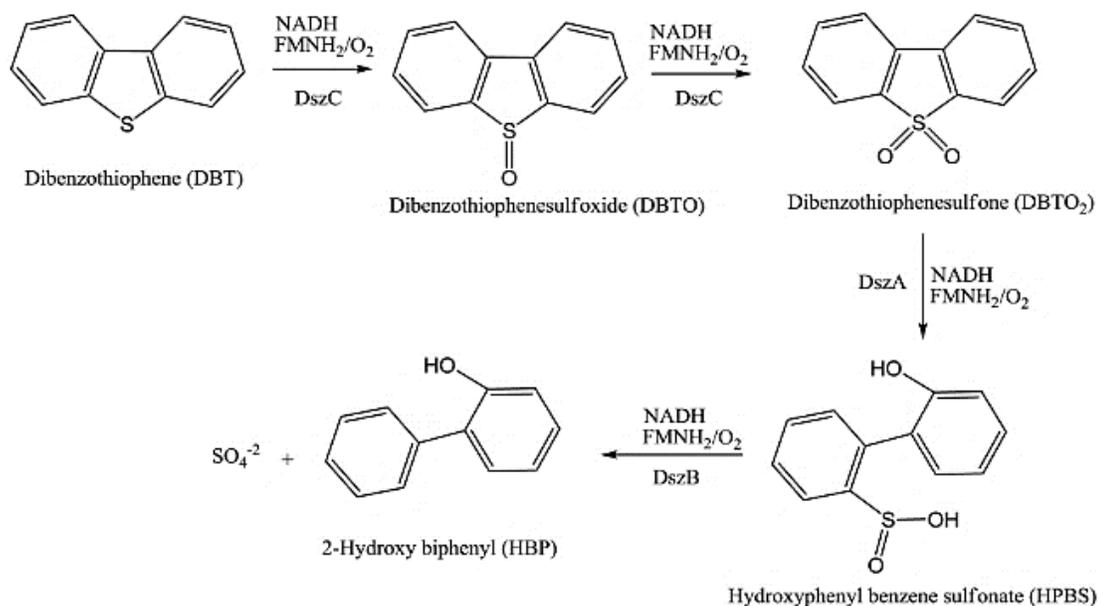
Figure-14: Sulfur specific oxidization pathway (eh, 2016)

The other following microorganisms are ; Rhodococcus erythropolis IGTS8 (RE IGTS8),Pseudomonas delafieldii R-8 (PD R-8),Gordonia alkanivorans RIPI90A (GAR 190A), Bacillus subtilis WU-S2B (BS WU-F1),Gordonia alkanivorans strain 1B (GAS 1B), Pseudomonas stutzeri UP-1 (PS UP-1) Mycobacterium sp. X7B (M sp. X7B),Mycobacterium sp. ZD-19 (M sp ZD-19), Mycobacterium goodii X7B (MG X7B), Caldariomyces fumago (CF), , Mycobacterium phlei WU-F1 (MP WU-F1), Rhodococcus sp. strain P32C1 (RS P32C1), Rhodococcus erythropolis ATCC 53968 (RE ATCC 53968), , Microbacterium strain ZD-M2 (MS ZD-M2), , Sphingomonas subarctica T7b (SS T7b), Bacterium, strain RIPI-22 (SS RIPI-22).(Hossain, Park, and Choi 2019)

2.5.3 Biocatalytic treatment process:

The biocatalytic treatment process, starting first with the charging of oil, a small amount of water, air, and biocatalyst in the batch reactor as shown in Figure-15.Next in the reactor aromatic sulfur compounds are oxidized to form water-soluble products, and the sulfur is dissolved in the aqueous phase. The mixture of oil, a small amount of water, air, and biocatalyst from the reactor is separated into two streams. The oil is further filtered and brought to the refinery and the other is water, biocatalyst and sulfur by-product stream. A second separation process is required to recycle the

water and biocatalyst into the reactor for reuse. Furthermore, the Air-lift bioreactors with other microorganisms and different operating conditions(temperature and pressure) have also been used and achieved 50–100% w/w sulfur removal.
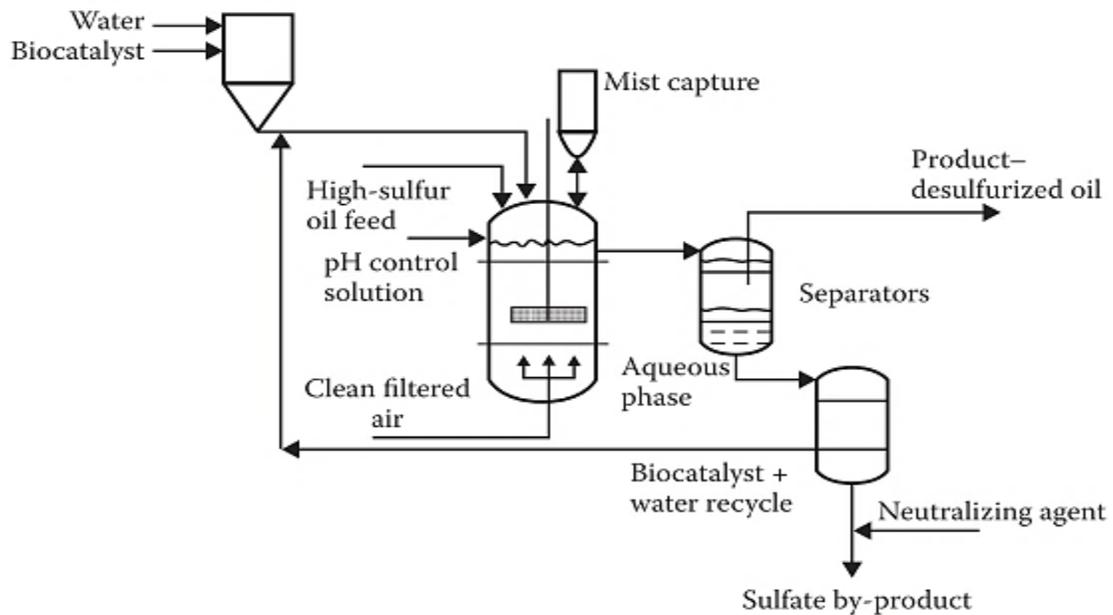
Figure -15: Biocatalytic treatment process(saleh, 2016)

2.5.4   Advantages of Bio-desulfurization:

- Bio-desulfurization offers the specificity of enzymes or microorganisms.
- Relative lower capital and operating costs.
- Mild operating conditions, as well as reduce the requirement of hydrogen. Both these features would lead to high energy savings in the refinery.
- significant reductions in greenhouse gas.

2.5.5 Limitation of biodesulfurization:

- Production of active resting cells (biocatalysts) with high specific activity;
- Preparation of a biphasic system containing oil fraction, aqueous phase and biocatalyst;
- Bio-desulfurization of a wide range of organosulfur compounds at a suitable rate.
- Separation of desulfurized oil fraction, and recovery of the biocatalyst and its return to the bioreactor.
- Efficient wastewater treatment.

3   Literature Review:

Elin and Simon performed heat integration to optimize the energy of the partly crafted pulp and paper mill. The main objective of this review was to optimize energy efficiency and reduce the requirement of the steam. Another objective was to find out the retrofit model for the heat exchanger network and calculate the capital investment for the optimized retrofit solution. To perform a heat integration reMIND simulation tool was used. The reMIND simulation tool contains mixed-integer linear programming that allows minimizing the cost of the system. The overall energy saving by heat integration was up to 18.5 MW. Demanding 12% of steam. Therefore, two alternative retrofit options were provided. The first retrofit model is easy to install and gives a benefit of 5.8 MW of steam and 0.13€ million per MW of steam is saved. The second retrofit model could give the benefit of 11MW of steam saving 0.14€ million per MW of steam is saved. Finally, the heat integration reduced the fuel and power boiler and the payback period for both retrofit model was assessed to be less than 16 months. (Svensson and Harvey 2011)

Sajjad Keshavarzian et al. analyses the effectiveness of the pinch analysis on a small petrochemical Para-xylene separation unit in terms of energy efficiency and the economic aspect of change or modification of the unit. The evaluation is done by seeing the composite curve that reducing the Δt min difference 30 °C and 16.5 °C respectively, the amount of energy recovery increases and external utility decreases. The main idea was to recover heat from the system by adding an extra stream. The stream of cooling water at 48 °C is selected and the mass flow rate of the selected stream is increased to make the heating load to zero. The new mass flowrate with additional stream case. heat exchanger network was designed and heat transfer are was calculated Finally, the capital cost and payback period has computed, which was almost 17 months in the optimized case.(Keshavarzian et al. 2015)

Hyun-Wook Ryu et al. performed hydrodesulfurization through heat exchanger network synthesis for ultra-low sulfur of diesel. First, the exergy analysis was conducted to know about energy-saving from the conventional hydrodesulfurization of the diesel process. Since the exergy analysis gave a possible indication of energy saving from conventional HDSD. Therefore, heat exchanger network synthesis HEN was applied. Two heat exchanger was added to the process, by replacing

with heater and cooler. The capital cost was increased by \$782,186 and \$791,244 for each heat exchanger. The payback period was 1-year and 1.2-year capital cost savings were \$746,996 yr−1 and \$585,263 yr−1 from each heat exchanger. Finally, there was 5% of energy-saving from the conventional process through Heat exchanger network synthesis. However, there was not much saving, but simple modification enhances energy efficiency.(Ryu et al. 2019)

Vishal.G et al. processed heat integration of the vinyl chloride monomer (VCM) unit. In this case, Aspen energy analyzer V8.0 software was used to design the Heat exchanger network HEN through pinch technology. Several HEN was designed with different minimum temperature difference and the total annual cost was compared to obtain an optimum design. The heat exchange network with a minimum temperature difference of 9 °C with the most optimum utility saving
 Of 15% for hot utilities and 47% for cold utilities compared with the conventional plant design). The total Percentage reduction in operating cost is 18%. From calculation Payback Period for the new design is 3.1 years. This saving can be obtained through a plant revamp, by the addition of two heat exchangers. This improvement is not done in the process by using only advance unit operation, but to perform a heat integration scheme. The Pinch method can be used to give designs in a quick time and with the minimum data.(Bokan and Pople 2015)

 K. Nagamalleswara Rao et al. proposed the work on cumene production and the objective was to perform heat integration network HEN through pinch analysis using ASPEN energy analyzer. The retrofit model was designed in comparison to the base case to save energy and minimize the operating cost. In the retrofit model, seven new heat exchanger was added that reduced the operating cost. The total capital cost for the improved HEN was 2.664×10^5 with a payback period of 0.1797 years.(Rao et al. 2015)

Akpa Jackson G et al. performed the heat integration on the Butene-1 unit through pinch analysis using HINT software. The research shows, that in the existing HEN there are three across pinch violations.The removal of the pinch violation in the new design for maximum energy recovery by matching of streams that are feasible. Improving the heat exchanger network HEN by identifying the loops and paths and breaking the feasible loop match to reduce the number of the heat exchanger. (Journal and Vol 2014)

4 Case study:

4.1 Introduction to pinch analysis:

Today in the industry, the trend has been developed to optimize the energy consumption by performing the heat integration through pinch analysis. The main objective to perform heat integration to reduce external utility and maximizing the heat recovery that directly leads to environmental and financial saving. Furthermore, the exact location of the heat exchanger and utilities can be known by designing the heat exchanger network (HEN) through pinch analysis.

4.2 Concept of pinch analysis:

Heat integration is also termed as process integration or pinch technology. Therefore, this technique is used to save the energy cost of the chemical process plants by reusing the energy from the process to process stream and reducing the external utilities. In addition, to perform heat integration, the initial required data for each stream is, supply temperature ⁰C, target temperature ⁰C, Heat duty or enthalpy Btu or KW of the existing plant.

## 4.3 Process flow of hydrodesulfurization unit of diesel:

Hydrodesulfurization (HDS) is a hydrotreating process as shown in figure-15. In this process the untreated diesel feedstock is first pressurized to pressure just above the reactor section. Next, the feedstock is completely mixed with the hydrogen gas and pre-heated to a temperature of reactor inlet. The combined hot feedstock is reacted with the catalyst (e.g. Ni-Mo, Co-Mo, impregnated on / Al2O3) in the reactor at an elevated temperature of (290–455°C) and pressure at an average of 150–3000 psi.

The reactor effluent containing unreacted feedstock along with hydrogen is cooled before sending it into the separation system. The separation system contains high hot pressure separator (HHPS), cold high-pressure separator (CHPS), low-pressure separation unit and a distillation column. First, the high-pressure separator splits the stream into light and heavy products. This reactant product is sent from high-pressure separator to low-pressure separator and then to the

distillation column. The final treated diesel product is removed from the bottom of the column. The vapor from the high-pressure flash separator is first cooled and sent into the cold high-pressure separator. Hydrogen sulfide (H2S) and any light hydrocarbon gas are extracted from the recycle gas and the remaining gas is mixed with fresh hydrogen gas (H2), compressed, and mixed with the new feedstock(El-Gendy and Speight 2015).

Figure-16 Process flow of hydrodesulfurization unit of diesel
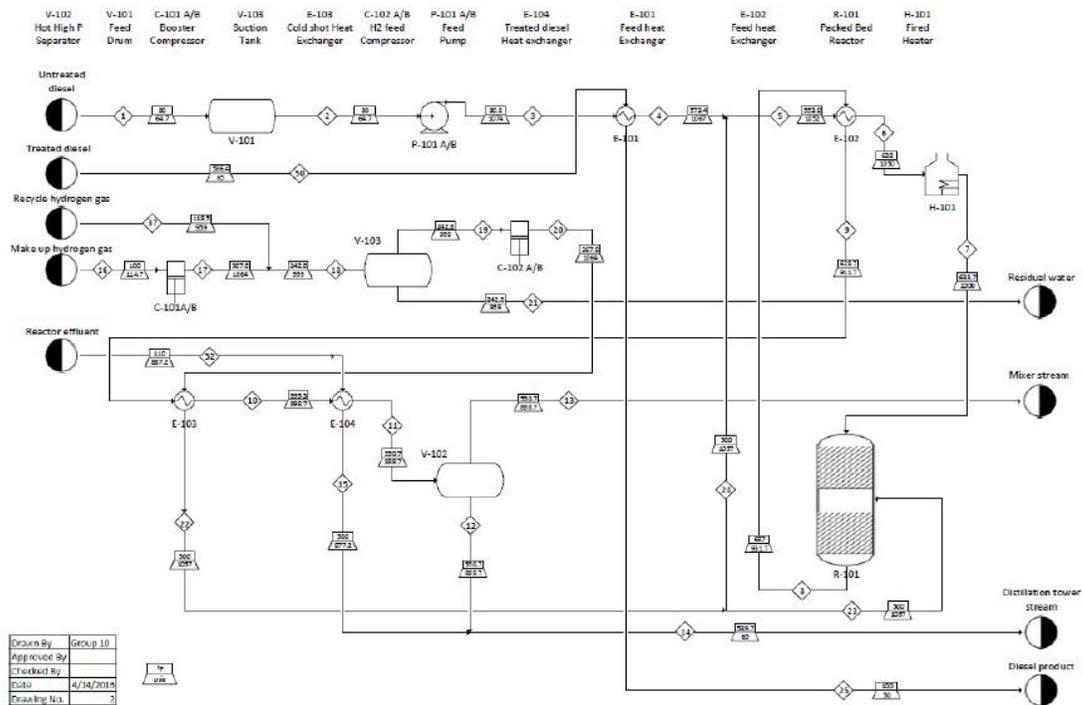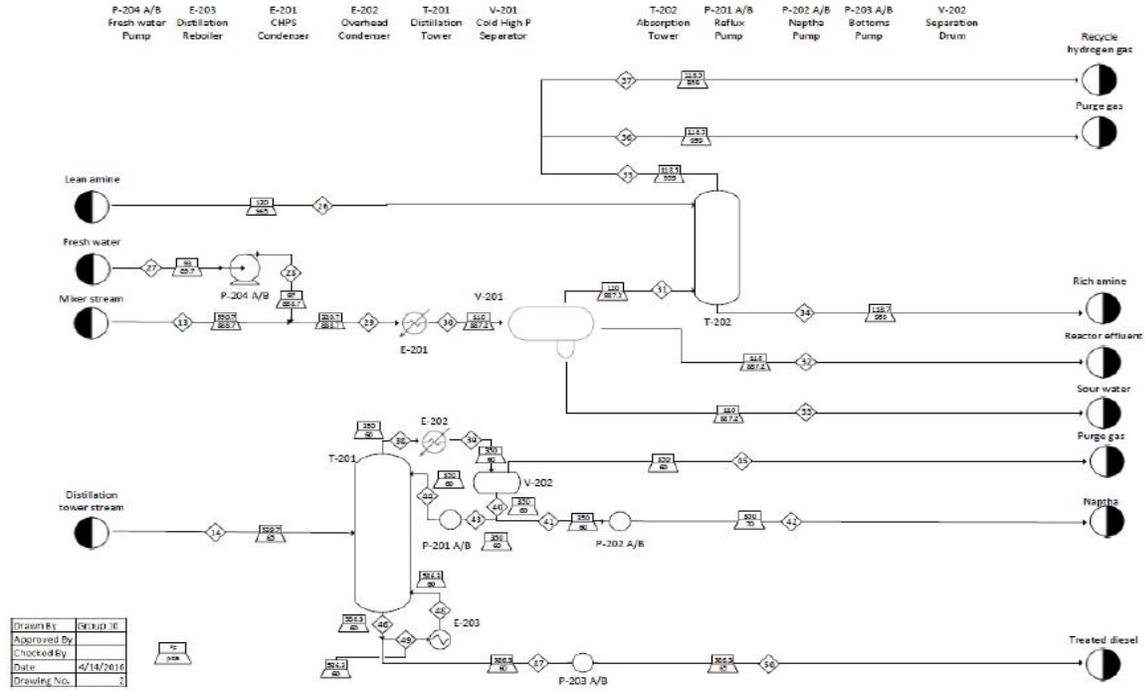
4.4 Data extraction for pinch analysis

To perform heat integration the hot and cold stream data need to be extracted from the existing flow diagram. Therefore, considering the stream that needs to heat or cold. In my thesis, working on the hydrodesulfurization of the diesel unit. The extracted cold and hot streams are listed in the table below (Table 2). There are four hot streams that need to be cooled down and three cold streams that need to be heated. In addition, the hot duty and heat capacity flow rate is also listed in the table. There many tools to perform heat integration, in my case using ASPEN energy analyzer. Furthermore, to reduce the total hot utility and cold utility demand the targeted procedure needs to be applied. There is two procedure to know the target minimum utility demand-based composite curve and the grand composite curve.

Table-2: process stream data of hydrodesulfurization of diesel fuel

Streams	Supply temperature (ºC)	Target Temperature (ºC)	Heat duty (KW)	Mcp (KW/ºC)
Cold streams:				
Diesel Feed	27.1	300.7	3627.76	13.26
Diesel & H2 mixture	289.8	331.11	8239.43	199.8
H2 & Make up H2	131.1	260	4693.7	36.5
Hot streams:				
Reactor effluent	363.8	331.5	815.8	25.18
Diesel & H2s	288.16	43.33	14235.9	58.5
H2s	331.5	312	379.18	20.4
Treated diesel	308	37	5065	18.7

Table-3: Utility stream data of hydrodesulfurization of diesel fuel

streams	Supply temperature (ºC)	Target temperature (ºC)	Heat duty (KW)	Flow rate (Kg/hr)
Cooling Water	20	40	11171	472099.4
HP Steam	371	348.8	7036	669.34

4.5   Composite curve and Grand composite curve(GCC):

Composite curves are plotted with respect to temperature ºC against the enthalpy or heat duty KW. There are two composite curves hot and cold, which are the sum of the individual streams integrated based on the temperature interval. Therefore, the hot composite curve is always above the cold composite curve following the thermodynamic laws. The hot composite curve that sets to remove the heat and need to be cool down.Similarly, to the cold composite curve that needs to be heated by the hot stream. In the composite curve where the minimum temperature difference between hot and cold composite curves is termed as a pinch point.

The grand composite curve is plotted with respect temperature ºC vs enthalpy or heat duty KW. It is like the composite curve that shows the minimum requirement of hot and cold utility to be supplied. The top shows in the curve are the net heat flow and the bottom shows that

the heat needs to be supplied. It also gives an idea about the selection cooling and heating utility stream at a temperature.

Figure-17: composite curve (CC)
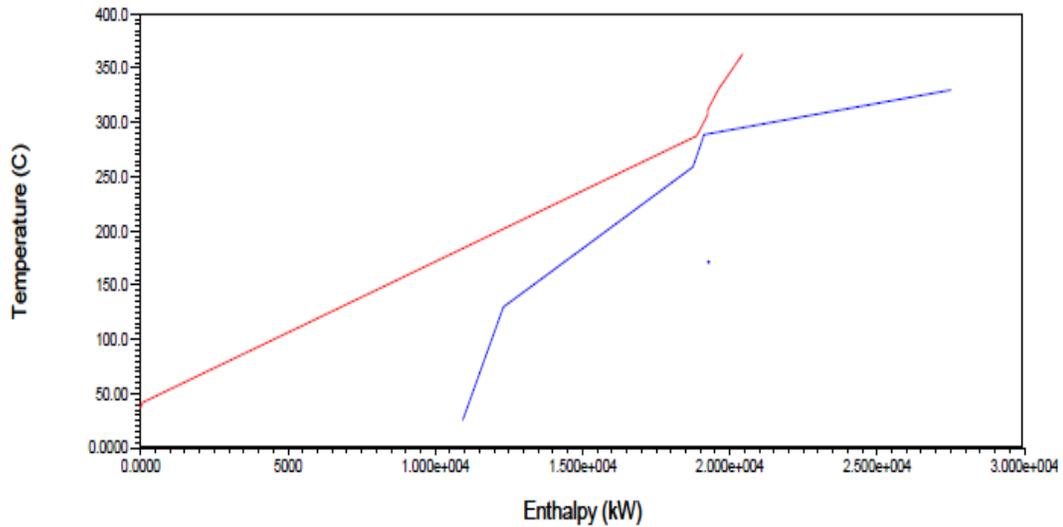
Figure-18: Grand composite curve(GCC)
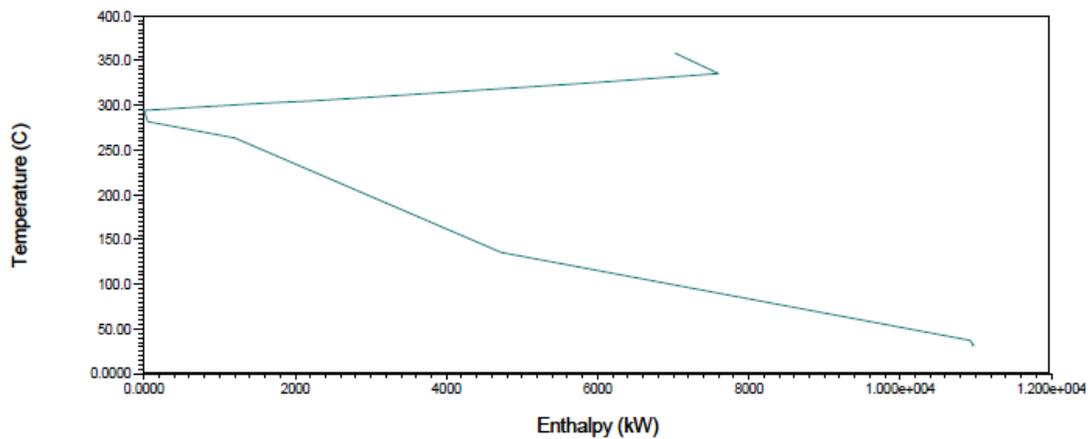
The targeted parameters obtained from the composite curve and the grand composite curve to design the heat exchanger network (HEN)

- Minimum heating load Q_H= 7037KW
- Minimum cooling load Q_C= 11171 KW

- Pinch temperature =299.9-289.8 ºC
- Total minimum number of units = 9

4.6 Heat exchanger network (HEN) design :

To perform heat integration through pinch analysis, the ASPEN energy analyzer software was used to design the heat exchanger network (HEN). According to the target set by the composite curve with the ΔTmin of 10 ºC based on that the minimum heating load Q_H of 7037KW and Q_C of 11171 KW needs to be supplied from the external source.

The heat exchanger network is a set of hot and cold process streams and utility streams. The HEN is separated by a pinch point temperature 299.9-289.8 ºC into the above pinch is also termed as the hot side and below pinch as a cold side.

In order to perform heat integration, there are certain constraints that need to be followed, such as tick off rule, maximum heat duty to be supplied from the hot stream in order to satisfy the target temperature and to minimize the heat exchangers units. Next, the number stream above the pinch should be greater than the cold stream, and below the pinch, the cold streams need to be greater than the hot stream. Conversely, no hot utility stream should be used below the pinch point and no cold utility should be used above pinch point.

The HEN design show in figure-19, starting the stream match above the pinch point. First, the hot stream (reactor effluent) has 815.5KW of heat duty to reach the target temperature 331.5ºC is matched with the cold stream(H2 & makeup H2) cross to the pinch and it has reached the temperature of 153.5 ºC.Second hot stream(Fresh H2) with a heat duty 379.2KW to reach the target temperature of 312.9 ºC is exchanged the heat with cold stream(diesel feed) to reach the temperature of 260 ºC cross to the pinch.The third hot stream(trated diesel) with hot duty of 3248.6 KW and the target temperature of 299.9 ºC with the cold stream(diesel feed).Finally, the cold stream(diesel and H2 mixture) is heated by hot utility with a heat duty of 8239.4KW to reach target temperature of 331.1ºC.

Below the pinch point,the hot stream (treated diesel) is cooled by cooling water to reach the target temperature of 37.8 ⁰C with a cooling duty 1816 KW.Second hot stream (diesel and H2s) is cooled by the cooling water with a cooling duty of 10357.3KW to rech the target temperature of 43.3 ⁰C.

Figure-19: Heat exchanger network (HEN)
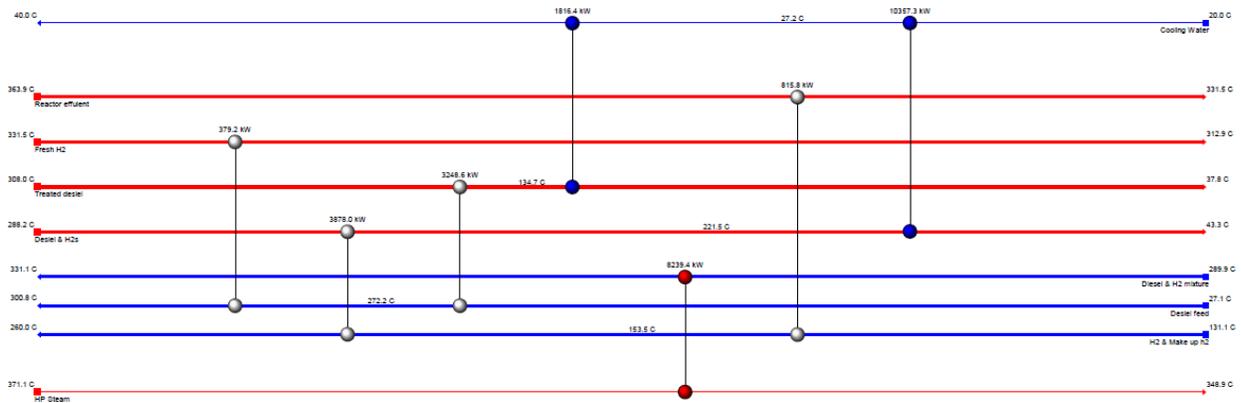
4.7 Comparison of the targeted parameter to the achieved parameters:

The comparison of three achieved heat integration networks (HEN-1, HEN-2 & HEN-3) design parameters, such as cold duty (KW), hot duty (KW) and total heat exchanger area (m2) with the target parameters. Starting with the target hot duty is 7037 KW in comparison to the HEN-1 and HEN-3 has achieved with the same hot duty with 8239 KW is increased by 14.5%. On the other hand, HEN-2 hot duty obtained is 8779.9 KW increased by 19.85 %.

Secondly, the target cold duty is 11171.52 KW comparing with the HEN-1 and HEN-3 has the same cold duty obtained is 12173.7 KW. Therefore, it is increased by 8.2 %. Furthermore, the cold duty of HEN-2 is 12714.3KW is increased a little bit in comparison to HEN.1 and HEN-3 with the target increased by 12.13%.

Finally, the total target heat exchanger area (m2) is 7247.37 and the total minimum number of heat exchangers is 9. In comparison, the HEN-1 area achieved is 6182.7 and the number of units is 7. The total decrease in the area of HEN-1 is around 14.6%. On the other hand, the total

area of HEN-2 obtained is 8015(m2) and the number of units is 10. The total increase, in the area

Type	Heat duty (KW)	Cold duty (KW)	Area (m2)	Heat exchangers
Target	7037	11171.5	7247.37	9
HEN-1	8239	12173.7	6182.7	7
HEN-2	8779.9	12714.3	8015	10
HEN-3	8239	12173.7	6000.8	8

of HEN-2, is increased by 10.59 %. Likewise, the total area of HEN-3 is 6001(m2) and decrease by 17.197 % with total heat exchangers 8.

Table-4: Comparison of the targeted parameter to the achieved parameters
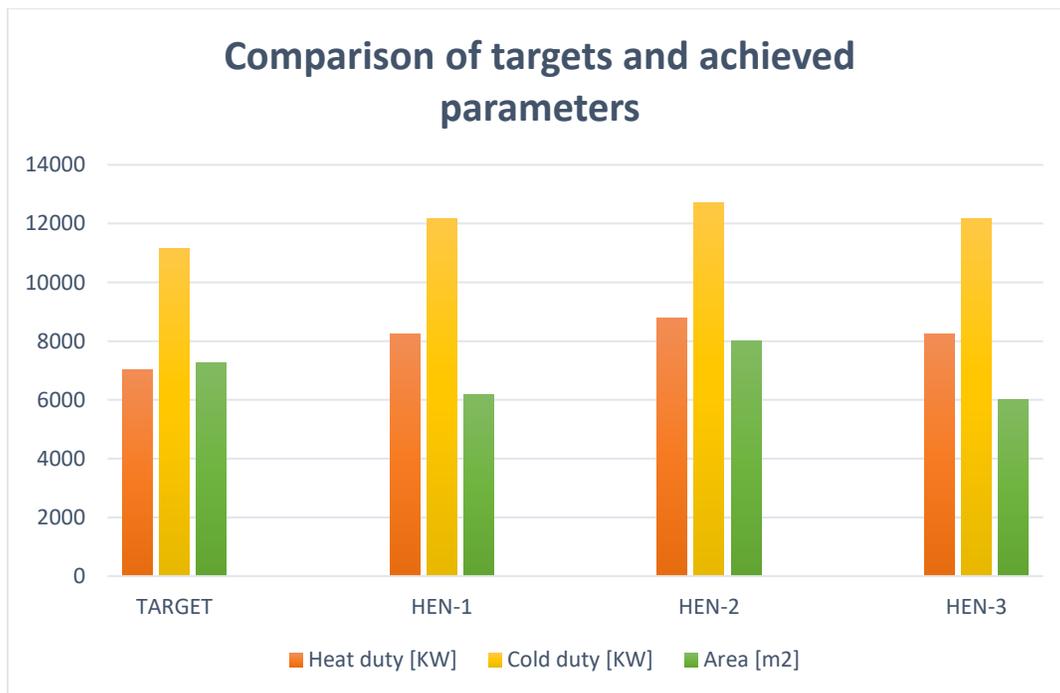

*Figure-20: Comparison of the targeted parameter to the achieved parameters*
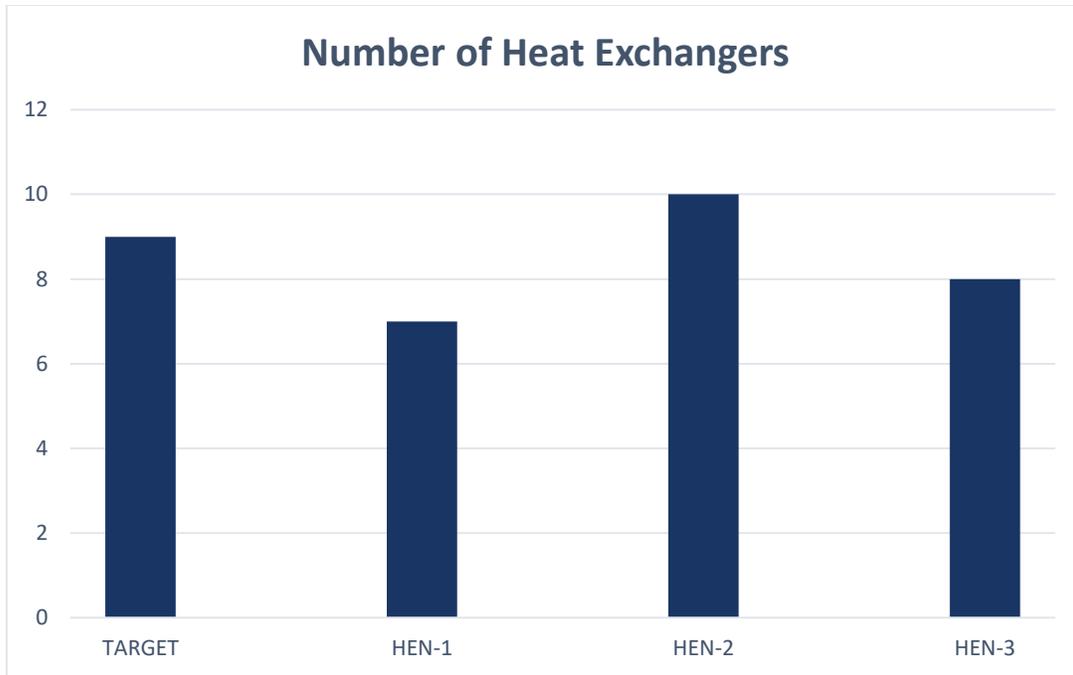
Figure- 21: Number of Heat Exchangers

4.8 Targeting of minimum temperature difference ΔTmin:

The minimum temperature difference is an important parameter to fix the energy targets and heat recovery targets for the heat exchanger network. As shown in the figure-22&23. The increase in the ΔTmin, Hot (Qh) and cooled (Qc) utility target increase. On the other hand, there is a decrease in the heat exchanger network area. In this case, the value of ΔTmin is taken as 10 ⁰C that gives the minimum hot utility target Qh of 7037 KW and cold utility target Qc of 11171 KW. That needs to be supplied from the external source.
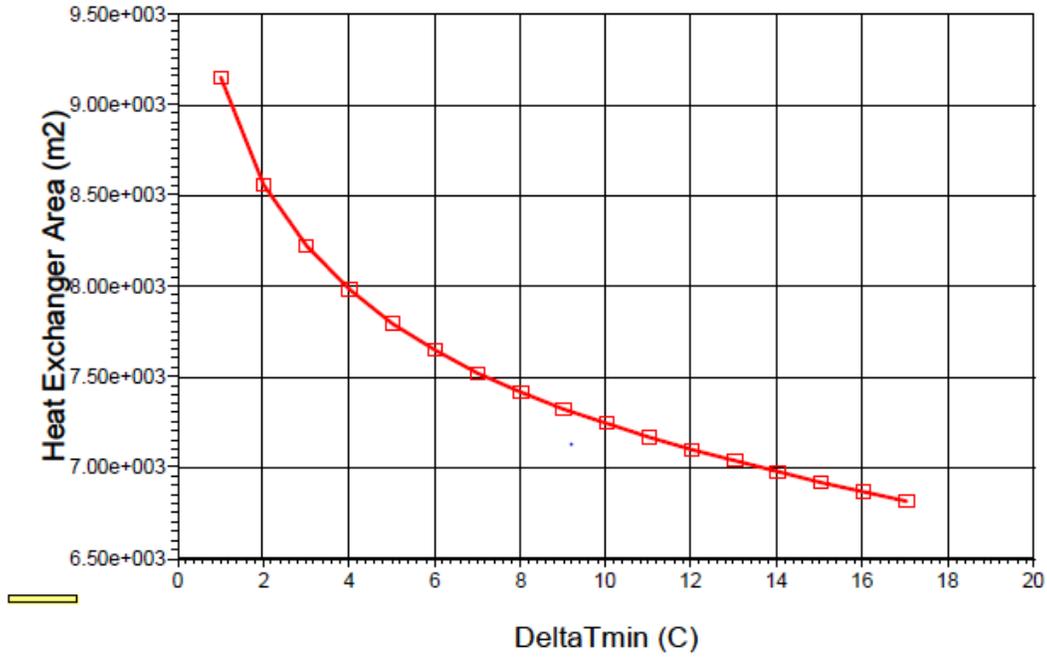
Figure-22: Heat integration VS Delta Tmin (C)

Figure-23: Utility target VS Delta Tmin (c)

4.9 The Economic evaluation of heat exchanger network (HEN):

The operating cost accounts for the minimum hot and cold utility employed during the heat exchanger network at a ΔTmin of 10 °C. In this case, the cooling water used at a temperature inlet 20 °C and the outlet temperature 40 °C. The cost index of cooling water is 6.7 $/ kW Y^{-1}. The minimum cold duty required is Qc = 11127 kW. The annual cost of cold duty is calculated by multiplying the cost index with the minimum cold duty Qc and the obtained value is 7.4× $10^4$$/ year.

In the same way, hot steam has used for hot utility at an inlet temperature of 371.1C and the outlet temperature 348.9 °C. The cost index of hot steam is 78.84 $/kW Y^{-1}. The minimum hot duty required is Qh 7037 KW. The annual cost calculated for hot steam in a similar manner and the total hot utility annual cost obtained is 5.5× 10^5 $/ year. Finally, the total annual operating cost is the sum of hot and cold duty cost that is equal to 5.73398.2 × 10^5 $/ year.
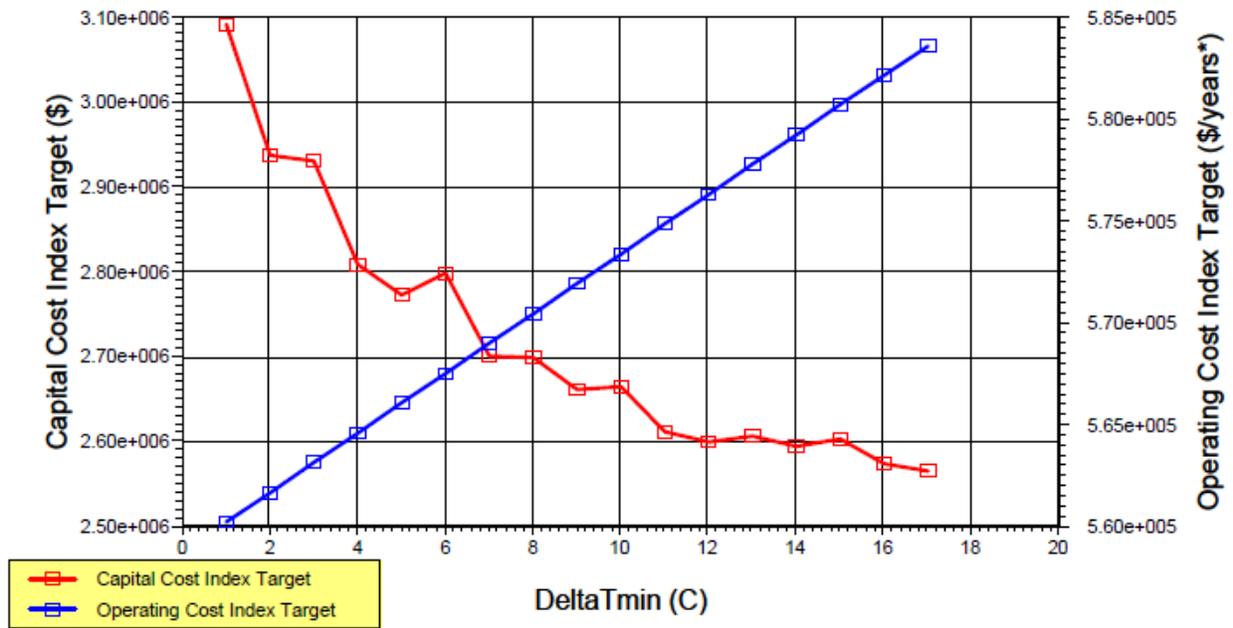
*Figure-24: capital cost vs operating cost with respect delta Tmin*

The operating costs listed in the table below for all the heat exchanger network HENS. As shown in Figure -24 there is a trade-off between operating cost and capital cost with a change in ΔTmin. In addition, ΔT min increase there is an increase in operating cost and a decrease in capital costs.

To calculate the total annual cost which is capital cost plus the operating cost for the heat exchanger network.

Table-5 The Economic evaluation of heat exchanger network (HEN

| Type	TARGET	HEN-1	HEN-2	HEN-3
Operating cost ($/year)	573398.2	667288.2	709488	667288.2
Total annual cost ($/Year)	923904.5	963795.7	1116925	970952.9
capital cost ($)	2665979	2255259	3099002	2309698
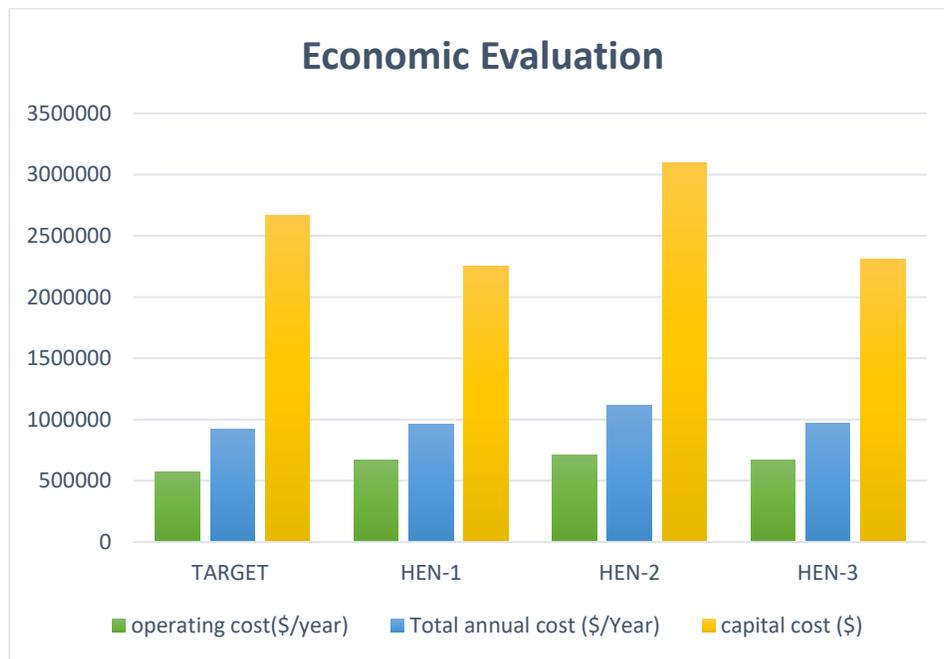
Figure-25: The Economic evaluation of heat exchanger network (HEN

The above bar chart shows the comparison of the operating cost, capital cost, and total annual cost in between the target and the achieved HENS. Starting with the comparison of target operating-cost with respect to the HEN-1 and HEN-3 has increased by 14%. On the other hand, the HEN-2 operating cost has increased more, about 19.18% of the remaining two HENS.

Next, correlating the target capital cost with the achieved HENS. Likewise, HEN-1 capital cost has decreased by 18.2%. conversely, HEN-2 capital has increased to 13.9 %. On the other hand, HEN-3 capital cost has decreased to 13.3 %.   After the comparison of operating-cost and capital-cost, the total annual cost needs to be compared because selecting the HEN based on the minimum total annual cost in comparison to the target.

Finally, the comparison of the target total-annual cost (TAC) with the HENS. Where the total annual cost of HEN-1 has increased slightly above the target of 3.56%. On the other hand, HEN-3 has not much difference to the HEN-1 is increased by 4.8%. Conversely, the HEN-2 has increased more than HEN-1 and HEN-2 comparing to the target of about 17.2%.

4.10 Comparison of utility required before and after heat integration:

The main objective of the thesis was to reduce the cold and hot utility by the heat integration process. The total hot and cold utility was required for heating and cooling the stream before integration was 16561KW of hot utility and 20500 kW of cold utility. After performing heat integration through pinch analysis the minimum utility target requirement in the hot case reduced to 7037KW and cold utility is 11173.7KW. Therefore, the comparison of three HENS in terms of total saving of hot and cold utility is shown in the below graph. The maximum hot utility saving was 50.2% and cold utility of 40%.
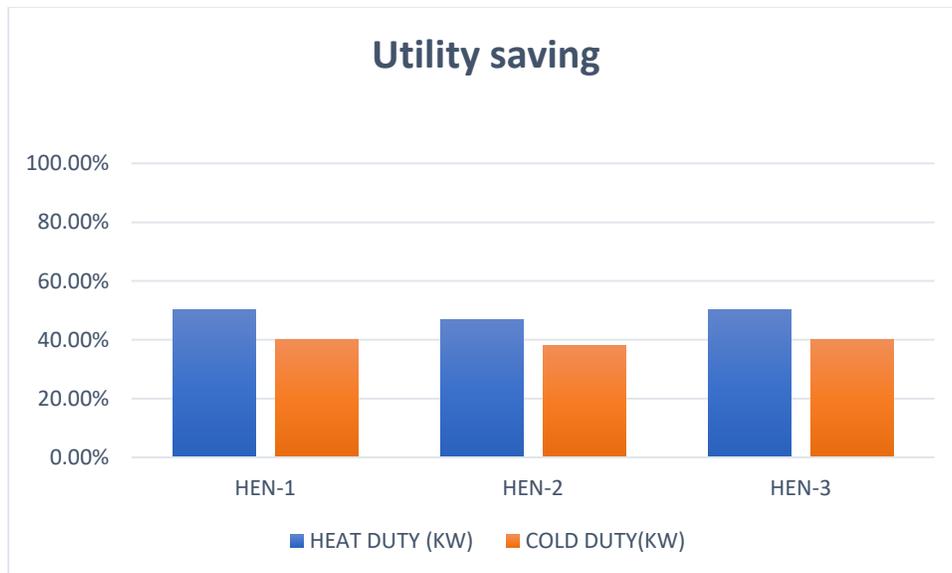

Figure-26: Utility saving

5   Conclusion:

Heat integration of hydrodesulfurization of diesel fuel is performed. In order to achieve this goal, pinch analysis was carried out using the ASPEN energy analyzer tool.

In this case, the comparison was made between the target set by the composite curve at a ΔTmin 10 ⁰C and designed three heat exchanger networks (HENS). In terms of minimum hot duty (Qh), minimum cold duty (Qc), heat exchanger area and a number of heat exchangers. With respect to the target, the HEN-1, and HEN-3 has increased in a small percentage and are more close to our targets. Whereas, HEN-2 showed a significant amount of increase with respect to HEN-1, HEN-3.

Likewise, if look into these HENs from the perspective of an area, it is evident that HEN-1 and HEN-3 have the lower area requirements than that of target values, so these can be considered as potential candidates while suggesting for the optimum configuration. However, HEN-2 showed higher values than our desired target, therefore, we would be least interested in this network configuration.

In all three proposed configurations, we have seen the reduction in the heat-duty and cold-duty. In HEN-1 we could save 50.20% of heat duty and 40% cold-duty which is a major achievement if we compare it with the values of before heat integration.

The role of economic evaluation is of paramount importance and holds the key to the decision making factor of these networks. Out of these three designed networks, HEN-2 and HEN-3 have considerably higher values from the target annual cost. However, HEN-1 lies very close to our target value. Therefore, keeping in the account of all the parameters and cost analysis HEN-1 is the most feasible configuration and would provide the maximum throughput.

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