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Comparative Study on Technologies for Crude Oil Desulphurization in Modular Refineries

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Abstract:- This study compares the performance and economic viability of two different sulphur removal methods from crude oil, namely, hydrodesulphurization (HDS) and oxidative desulphurization (ODS) processes. The results indicate that HDS is more effective in removing dibenzothiophene, achieving an absorption rate of 90%, while ODS achieved an absorption rate of 80%. However, both methods were equally effective in removing other sulphur compounds such as B and P-Disulphide, and Thiophene. Economic comparison suggests that ODS is a more cost-effective process compared to HDS. The study highlights the importance of considering various factors, including crude oil composition, required degree of desulphurization, and environmental regulations, in choosing the appropriate sulphur removal method. Overall, the study concludes that both HDS and ODS are effective methods for removing sulphur-containing compounds from crude oil, and the choice of method depends on specific application requirements and environmental considerations.

***Keywords*:-** *Hydrodesulphurization, Oxidative-Desulphurization, Crude Oil, Sulphur, Aspen Hysys and Modular Refinery.*

I. INTRODUCTION

Sulphur compounds and dispersed particles constitutes less than 0.1% to around 5% of composition of crude oil samples depending on the specific composition of the oil and its source. Different geological conditions yield different types of crude oil, and even repeated extractions from the same well yield different types of crude oil due to the passage of time. Despite this, all crude share the same underlying physical properties [1]. After carbon and hydrogen, sulphur is the most common non-hydrogen ingredient in fossil fuels [2]. Thiophene, thiols, and sulphides predominate among the organic sulphur molecules found in crude oil. Both organic and inorganic sulphide substances can be found in crude oil. Crude oil may contain a mixture of pyrite and hydrogen sulphide. This is due to the presence of organic sulphur molecules in the oil [3]. There is a direct correlation between the API (American Petroleum Institute) gravity of petroleum oil (a measure of its specific gravity) and the sulphur content of that oil, which in turn directly affects its market value [4]. One of the four main groups of sulphur compounds, thiophenes, comes in several different types. The remaining sulphur molecules can be broken down into methacrylic acid, sulphides, and disulphides. The existence of sulphur compounds in gaseous fuels has a negative effect on cars not only because of their harmful influence but also because of their toxicity.

According to the International Energy Agency (IEA) in 2020, fossil fuels accounted for approximately 80% of global primary energy consumption. Most hydrocarbon oil is used to produce transportation fuels like gasoline, diesel, and aeroplane fuel. Sulphur-containing gasoline significantly affects how well catalytic converters in cars work [5]. Because of their tendency to inactivate crude oil processing and cause rust in pipes, pumping equipment, and refinery equipment, sulphur compounds are not accepted in the refining process. Sulphur oxide emissions result from unburned sulphur compounds in gasoline and diesel fuel [6]. When these gases combine with atmospheric water, they produce sulphates and acid rain, which in turn harm buildings, eat away at car paint, make dirt acidic, and lead to the death of trees and other habitats [7].

To comply with environmental requirements, reduced sulphur concentrations in transportation fuels must be achieved, and this requirement serves as the primary impetus for the efforts that are being made to achieve this goal today. To ensure access to affordable clean energy, innovative techniques for removing sulphur from materials of poorer quality are required. The pollution that is produced by automobiles has a significant impact on the quality of the air that is available to us to consume in our urban areas [4]. Combustion turns sulphur compounds into sulphur oxides, which in turn contribute to acid rain and other environmental problems. Sulphur compounds also contribute to the formation of sulphuric acid [8].

When sulphur compound fuels are consumed, sulphur dioxide and other pollutants related to combustion are generated. Sulphur dioxide and other combustion-related pollutants contribute to haze, as well as global warming and environmental contamination [3]. Exhaust gas from diesel engines contains a significant amount of particulate matter (PM), which has been linked to an increased risk of lung cancer in people who operate diesel vehicles [4]. As a result,

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the desulphurization of products derived from hydrocarbons is an absolute requirement.

Sulphur affects these pollution control systems because it firmly adsorbs to the valuable metal catalysts, stopping the uptake and reaction of various pollutants like hydrocarbons, nitrogen oxides, and carbon monoxide. In addition to this, sulphur compounds found in petroleum can be corrosive to the components of internal combustion engines and refineries. This is because sulphur oxyacids are formed when the products of combustion react with sulphur compounds [9].

Diesel fuel and gasoline in the United States have to have at least a 25% reduction in sulphur content because of rules from the United States Environmental Protection Agency (USEPA). In 2006, the Environmental Protection Agency (EPA) set a limit on the amount of sulphur that could contain no more than 15 parts per million (ppm). By the year 2020, the sulphur concentration of petrol was expected to decreased to less than 10 parts per million (ppm), as stipulated by new laws passed by the European Union (EU). Additional sulphur regulations for on-road diesel fuel and gasoline entered into force on June 1, 2006, in Canada and the United States, respectively. Gasoline and diesel fuel for on-road cars were included in the scope of these rules. The restrictions resulted in a decrease in sulphur concentration of 500 mg kg-1 to 15 mg kg-1 and, correspondingly, 350 mg kg-1 to 30 mg kg-1. Both in the United States and in Europe, the maximum amount of sulphur that can be present in diesel gasoline is now capped at 10 milligrams kg-1. The most recent legislation to be implemented in India was in 2010, and it resulted in a reduction in the amount of sulphur found in petrol and diesel in India's most populous regions from 150 to 50 parts per million (ppm) and 350 to 50 parts per million, respectively (ppm) [10]. In Nigeria, the Department of Petroleum Resources (DPR) is the regulatory body responsible for setting and enforcing the limits on sulphur content in petroleum products. Gasoline (Petrol) is set at a maximum of 150 parts per million (ppm) or 0.015% sulphur content, the sulphur limit for diesel fuel used for on-road vehicles in Nigeria is set at a maximum of 50 ppm or 0.005% sulphur content. The sulphur limit for kerosene used as a household fuel in Nigeria is set at a maximum of 2000 ppm or 0.2% sulphur content.

There are four different methods of desulphurization: hydro, extractive, oxidative, and biological [11]. Elemental sulphur can be recovered from a variety of materials, including molten metals, hydrocarbon oil, and exhaust fumes. A variety of desulphurization methods available to eliminate sulphur from crude oil is necessary because the presence of sulphur in crude oil increases the heating range and is harmful to the ecosystem [12]. The desulphurization of aromatic sulphur compounds is much more challenging than that of aliphatic sulphur compounds due to the presence of high viscosities and API gravities [13]. Sulphur, in the form of acyclic aliphatic sulphides like thioethers and cyclic thiolate, is abundant in crude oil.

The process of hydrodesulphurization (HDS) is currently used in industry to purge fuels of sulphur. HDS is a chemical process that operates at high temperatures and pressures to remove sulphur from fuels. This means that HDS (desulphurization at high temperatures) is a capital-intensive process. The toxic substance 4,6-dimethyldibenzothiophene (DMDBT) and its parent component dibenzothiophene (DBT) are not being adequately cleared from the environment. (4,6-DMDBT). Desulphurization methods such as oxidative (ODS), oxidation-extraction (OEDS), adsorptive (ADS), and bio-desulphurization (BDS) can be used to create ultra-clean fuels. Sulphur-containing substances in ODS can be oxidised with the help of oxidants like hydrogen peroxide (H_2O_2), sulphuric acid (H_2SO_4), and other sulphur-containing molecules. For ADS, adsorbents utilised in this procedure are created with sulphur extraction in mind. Adsorption capacity can be increased by stacking active adsorbents on top of a permeable, non-reactive base. The molecules of sulphur adhere to the adsorbent on the substrate through a process called adsorption, and they stay there for the length of the reaction, whether a fuel is present. BDS has been in the news a lot lately for its innovative and environmentally favourable methods of handling natural fuels. However, a major drawback of the BDS method is the elimination procedure itself [5].

➢ *Some Essential Necessities for a Modular Refinery to Operate Profitably and Sustainably are:*

- *Types of available crude Oil. Crude oils are classified according to their API, which is based on their viscosity; the greater the API number, the lighter the petroleum is [13]. The production of more outputs from heavy crude oil results in a product of lesser value, which requires additional distillation and incurs additional costs. On the other hand, the production of high-value products from light crude oil does not require any additional distillation [9].*
- *The complexity of a modular refinery can be inferred from its structure.*
- *Classification of finished goods.*
- *Finished goods quality.*

Refineries, from a purely economic standpoint, need to strike a balance between the production cost and the market worth of refined goods to maximise their refining profits [6]. A refinery's only recourse, given that the price of petroleum is set by uncontrollable factors like supply and demand on global markets or the spot price system, is to keep running costs as low as possible. This means that a refiner should always aim to maximize efficiency. The administration of the supply chain is an essential component of the company that needs to be optimized and systematically managed to maintain profitable operations over time. Although they are standard across the board, it goes without saying that each refinery is highly specialized and one of a kind in every aspect.

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The economic viability of a proposed production method, product, or service is evaluated through a techno-economic analysis, (Abbreviated TEA). Software modelling, which is affected by both technical and financial input variables, is commonly used to make estimates of income, routine expenses, and capital costs. Many software packages exist to facilitate TEA, including but not limited to Aspen HYSYS, Aspen Plus, Prosimplus, and Umberto. In addition, the introduction of Industrial Revolution 4.0 is transforming conventional manufacturing into what is known as "smart manufacturing".

The purpose of this research is to investigate the various strategies for recovering sulphur, including how they function, how effective they are, how much energy they require, the components that they make use of, how much it will cost to implement them based on previous studies, and both their positive and negative aspects in general.

II. METHODOLOGY

Aspen Hysys version 11 was used in this work to simulate the design of two desulphurization units namely HDS and ODS. HDS is used in refineries to reduce sulphur in fuels. It involves treating sulphur compounds with hydrogen under high temperature and pressure, converting them to H_2S. A modified Claus process is used to handle the resulting H_2S and convert elemental sulphur. ODS refers to Oxidative Desulphurization, which is another process used in refineries to remove sulphur from fuels. In ODS, sulphur compounds are oxidized using an oxidizing agent, such as hydrogen peroxide or air, to convert them into water-soluble compounds that can be easily separated from the fuel. This method offers an alternative approach to reducing sulphur content in fuels.

The energy analysis for the processes were performed using the aspen energy analyzer which is a sub software installed along with aspen hysys. It is used in energy management for optimizing energy consumption based on a user's input. Pinch technology helps accomplish this goal by providing insights and energy saving recommendations that lead to increased efficiency and decreased pollution.

Tables 1 - 3 show the input data used for the work. The crude oil used in the process has an API gravity of 37.27 (which signifies SG of 0.838 and it is a light crude). The temperature of the feed stream is 38 degrees Celsius, and the pressure is 8.172 atmospheres per square centimetre. The feed streams' flow rate is 39486.387 bbl/d which is within the normal flow rate range for modular refineries. To provide a fair comparison of the desulphurization processes, the input flow rate was kept constant for both processes

Table 1 Inlet Feed Condition and Flow Rates of Crude Oil

Phase Fraction	**0**
Feed Temperature (°C)	80
Feed Pressure (kPa)	828
Feed flow rate	39486.387bbl/d, (261.6m3/hr)

(Source: Hernandez, C. P. 2020)

Table 2 Major Feed Composition for HDS and ODS Process

Components	Flow Rate (Kg/Hr)
n-Eicosane	56508.002
n-Triacontane	9301.578
1-Eicosene	83314.147
t-Decalin	17834.250
c-Decalin	17834.250
n-Pcychexane	0.000
n-Bcychexane	0.000
n-BBenzene	4026.660
n-PBenzene	3605.820
1-Tetradecen	0.000
Anthracene	16219.203
B-diSulphide	3567.000
DiBZThiphene	552.783
Quinoline	2583.200
Pyrrole	134.182
Thiophene	420.680
P-diSulphide	3006.000
Phenol	188.226

(Source: Aspen Hysys Assay Databank, Version 11)

➢ *Step by Step Procedure Used for HDS Simulation*

- *Step 1:*
  Open Aspen hysys software environment (interactive section) for component selection for the process.

- *Step 2:*
  The component list was clicked to gain access to the required components used in the desulphurization process from the library.

- *Step 3:*
  Begin the desulphurization procedure by initiating the necessary processes. All reactions were conversion reactions and were also balanced (to gain balance error of zero).

- *Step 4:*
  Select a suitable fluid package (i.e the thermodynamic relation that will help to carry out background calculations where necessary) was selected and it was believed that the process would remain in a constant condition throughout.

- *Step 5:*
  The simulation environment was entered to create the process flowsheet.

- *Step 6:*
  The crude oil feed is pumped into a mixer where it is mixed with, heated, and sent to the reactor for reaction to occur. Here, sulphur compounds were converted to H_2S.

- *Step 7:*
  The product from the reactor was used to carry out a preheating process on the feed stream and further cooled before sending it to the knockout (KO) drum.

- *Step 8:*

The Product from the reactor was then sent to a knockout (KO) drum to flash out light ends of the stream and the vapour from the KO was sent to an absorber to carry out amine treatment process using the DEAmine. The light ends which consist of majorly hydrogen is recycled to the hydrogen line.

- *Step 9:*

The liquid product from the KO was sent to a 25-stage distillation column unit to remove any trace of H_2S and other light components from the oil stream. Steam (3% of the quantity of the feed to the column) was added to the distillation column to add the required amount of heat needed to cause the separation. The desulphurized oil was collected at the base of the column. When these steps are followed, and there is convergence, the process flow will be as shown in Figure 1.

Table 3 Extra Feed Inlets for ODS

Stream	Flow rate (kg/hr)
H_2O_2	10664.5
H_2O	53.198
$ZnCl_2$	21791.21
1-n-Butyl-3-Methylimidazolium Chloride	21596.26

(Source: Gao et al., 2019)

➢ *Step by Step Procedure Used for ODS Simulation*

- Step 1 to Step 5 in HDS process was repeated in the ODS setup before entering the simulation environment. Step 6. After the above reaction sets were carried out in the properties section of the process, the components were also selected before entering the simulation environment.
- Step 7. Three material streams (oil feed, H_2O_2 and ionic Liquid (IL)) were created and sent into the reactor, wherein the reactions were performed under the various circumstances shown in Table 3.
- Step 8: The reactor products were collected and sent to a decanter where the de-sulphurised oil was separated from the sulfone, sulfolane and IL.
- Step 9: The stream from the decanter containing sulfone, sulfolane and IL is mixed with water and sent to a filtration unit where the sulfone was filtered out.
- Step 10: The IL (which absorbed the sulfone and sulfolane compounds) stream and water was sent to a heater where it was heated up to the required regenerated temperature, thereafter it was sent to a regenerator to separate the remaining water, sulfone and sulfolane compounds from IL compounds.
- Step 11: To keep the procedure going, the IL is returned to the IL input source.
- Step 12: To aid in the sorting process, water was introduced as an entrainer. The IL with water mixture was heated to raise the temperature and pressure and sent into a flash drum to knock off water vapor from the IL stream.

When these steps are followed, and there is convergence, the process flow will be as shown in Figure 2.

➢ *Basis for Comparing Both Processes*

The basis for comparison is the energy saving potential, the capital and utilities cost, and the estimation of equipment cost. The processes are compared based on the capacity to capture the sulphur compound present in the crude oil stream and the total cost which covers the equipment cost, operating cost, installation cost, utility cost and the CO_2 emission from the process.

The cost estimation calculation was done using the Aspen Hysys software and it was based on the equipment index as indicated in the software. The costing was based on major equipment such as compressors, reactors, columns, and pumps.

The cost of equipment has increased over the years because of inflation. The method usually used to update historical cost data makes use of published costs, which relates present costs to past costs:

$$\textbf{Cost in Year} = \frac{\textbf{Cost in Year } \boldsymbol{X} \times (\textbf{Index year } \boldsymbol{Y})}{(\textbf{index year } \boldsymbol{X})}$$

To account for developments in technology, building methods, labour efficiency, and the index's own formulation, experts advise only utilizing the index for the previous five years, see Figure 3 (Chemical Engineering Plant Cost Index).

III. RESULTS & DISCUSSIONS

The HDS and ODS results for energy analysis, economic analysis for utilities, equipment costing, and sulphur content analysis for ODS can be found in the full work [14].

Figure 4 shows the cost comparison between HDS and ODS processes. The costs include those associated with operation, utilities, equipment, and installation. This indicates that, compared to hydrodesulphurization, oxidative desulphurization may be the more cost-effective option. It is worth noting, however, that other variables, such as the application at hand, environmental considerations, and the degree of sulphur elimination sought, may influence the final decision.

The results for removing sulphur-containing molecules from crude oil are shown in Figure 5. The results indicate that the HDS process was more effective in removing dibenzothiophene, with an absorption rate of 90%, compared to ODS, which achieved an absorption rate of 80%.

Furthermore, both methods showed complete removal of B and P-Disulphide compounds from the crude oil, indicating that both HDS and ODS are effective in removing these types of sulphur compounds. Another sulphur-

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containing substance that was eliminated during both procedures was thiophene.

The mechanism of sulphur removal in the HDS process involves the conversion of sulphur-containing compounds to hydrogen sulphide (H_2S), which can be easily separated from the crude oil (Figure 1). On the other hand, the ODS process converts sulphur-containing compounds to sulfone, which is then absorbed by the ionic compound used in the process (Figure 2).

Overall, the results suggest that both HDS and ODS are effective methods for removing sulphur-containing compounds from crude oil, although HDS appears to be more effective in removing dibenzothiophene. The choice of method may depend on various factors, including the composition of the crude oil, the required degree of desulphurization, and the environmental regulations in place.

IV. CONCLUSION

In this study, we use a computer programme (Aspen Hysys) to model and compare the techno-economic benefits of two desulphurization processes—hydrodesulphurization (HDS) and oxidative desulphurization (ODS). Both processes remove sulphur and its derivatives from crude oil as much as possible.

The results obtained from Aspen Hysys (version 11) and the database from Aspen Plus simulates how a modular refinery can most effectively remove huge amounts of sulphur from its feed – crude oil. The conclusions drawn from this study are:

- The associated costs of operating a modular refinery that removes sulphur from crude oil using the process of hydrodesulphurization is higher compared to the associated costs when using oxidative desulphurization. So, ODS is more cost effective since it involves milder reaction conditions.
- The modelling findings (Figure 5) show that HDS is superior in its ability to remove the cancer compounds dibenzothiophene (DBT) and 4,6-dimethyl dibenzothiophene (DMBT). ODS have an absorption rate of 80% while HDS have an absorption rate of 90% making HDS a more effective process.

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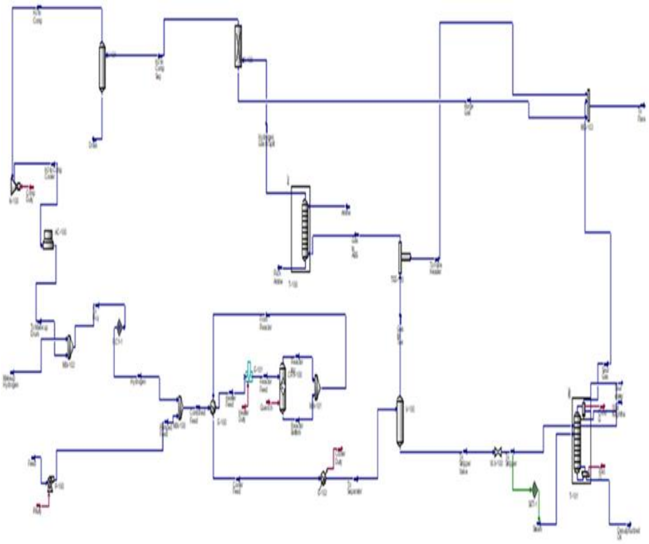

Fig 1 Complete Flowsheet of Hydrodesulphurization Process Using Aspen Hysys

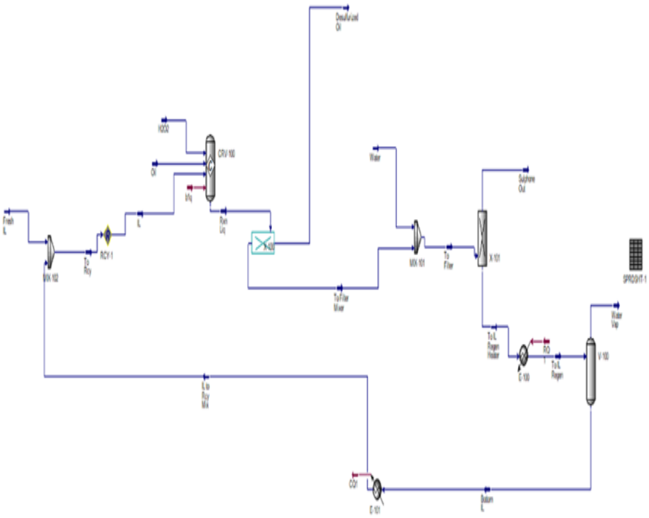

Fig 2 Complete Flowsheet of Oxidation Desulphurization Process Using Aspen Hysys

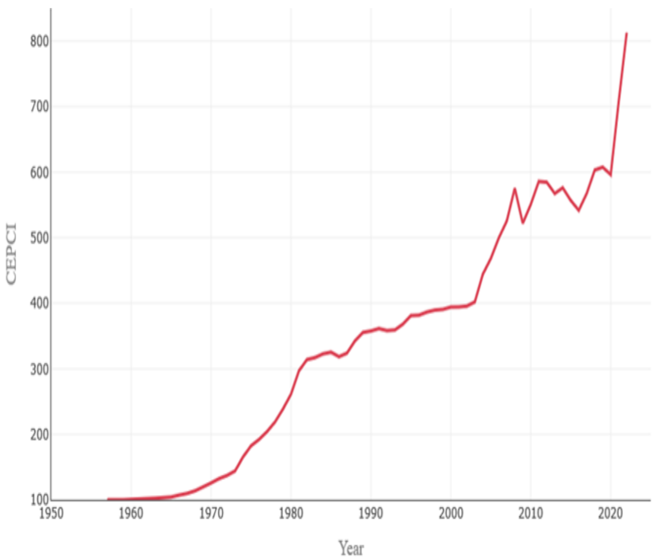

Fig 3 Chemical Engineering Plant Cost Index

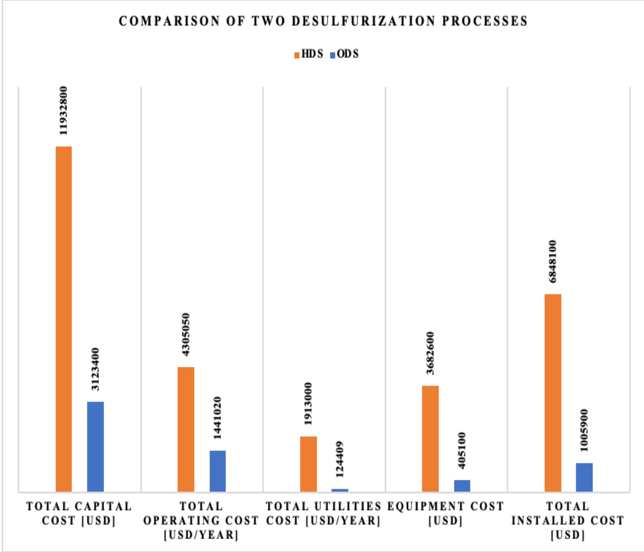

Fig 4 Cost Comparison between Both Processes

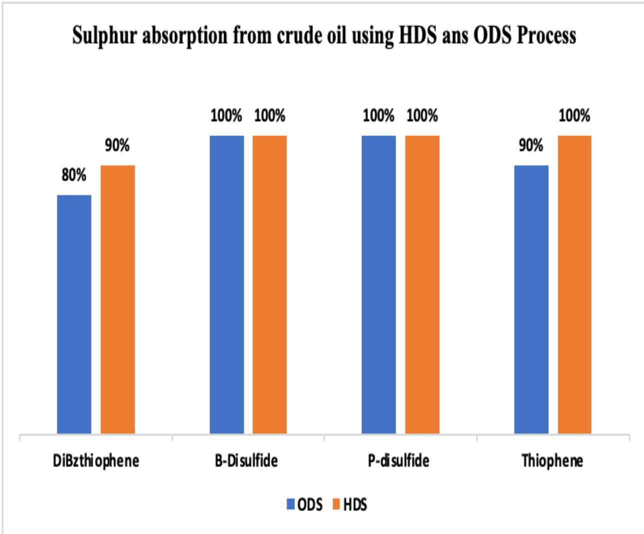

Fig 5 Comparison of the Sulphur Absorption from the Crude Oil Using HDS and ODS