

T.R
VAN YUZUNCU YIL UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES
CHEMICAL ENGINEERING DEPARTMENT

**IMPLEMENTING OF DECREASING SULPHUR FROM HEAVY FUEL OIL
OF ZAKHO BY OXIDATION DESULPHURIATION (ODS) METHOD**



M.Sc. THESIS

PREPARED BY: Rebeen Ramzi ALI
SUPERVISOR: Prof. Dr. Nahit AKTAŞ
SECOND SUPERVISOR: Prof. Dr. Lokman A. ABDULKAREEM

VAN-2018

T.R
VAN YUZUNCU YIL UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES
CHEMICAL ENGINEERING DEPARTMENT

**IMPLEMENTING OF DECREASING SULPHUR FROM HEAVY FUEL OIL
OF ZAKHO BY OXIDATION DESULPHURIATION (ODS) METHOD**



M.Sc. THESIS

PREPARED BY: Rebeen Ramzi ALI

VAN-2018

ACCEPTANCE and APPROVAL PAGE

This thesis entitled "IMPLEMENTING OF DECREASING SULPHUR FROM HEAVY FUEL OIL OF ZAKHO BY OXIDATION DESULPHURIATION (ODS) METHOD" presented by Rebeen Ramzi ALI under supervision of Prof. Dr. Nahit AKTAŞ in the department of Chemical Engineering has been accepted as a M. Sc. thesis according to Legislations of Graduate Higher Education on 03/04/2018 with unanimity of the members of jury.

Chair: Prof. Dr. Abdulkerim KARABAKAN

Signature:

Member: Prof. Dr. Nahit AKTAŞ

Signature:

Member: Assoc. Prof. Dr. Suha Orçun MERT

Signature:

This thesis has been approved by the committee of The Institute of Natural and Applied Science on 21.04.2018 with decision number 2018/29-I

Signature:
Director of Institute

THESIS STATEMENT

All information presented in the thesis obtained in the frame of ethical behavior and academic rules. In addition all kinds of information that does not belong to me have been cited appropriately in the thesis prepared by the thesis writing rules.

Signature

Rebeen Ramzi ALI



ABSTRACT

IMPLEMENTING OF DECREASING SULPHUR FROM HEAVY FUEL OIL OF ZAKHO BY OXIDATION DESULPHURIATION (ODS) METHOD

ALI, Rebeen Ramzi

M. Sc. Thesis, Chemical Engineering Department

Supervisor: Prof. Dr. Nahit AKTAŞ

Second supervisor: Prof. Dr. Lokman A. ABDULKAREEM

April 2018, 47 pages

In fact, all fuel oil contains a significant amount of sulfur. Because of the requirement for low sulfur content of fuel oil, it is necessary to develop alternative method for desulfurization of heavy fuel oil. Due to the disadvantage of ODS technologies such as safety, cost and easy process and green environment. new method have been developed. Elimination of sulfur compounds in this process to reach about 96%. Oxidative desulfurization method process have two-step: the number one step is reaction step where the fuel, chemicals (acidic acid and proxide and formic acid) agents and the catalyst mixing and react with each other to form sulfones, the number two step is the extraction of these sulfone combination using a solvent agent. These reactions are rather slow in nature, In this study, the mixtures were stirred with one thousand fifty RPM the speed of reaction will be increase. Finally, while the examination of several elements and parameters of the interaction where sulfur was totally removed from heavy fuel dully via Oxidative desulfurization method, after that outwardly: the natural sulfur content of 4.7% (w) was reduced to 2.54% (w), and for this project using H_2O_2 with CH_3COOH yielded much better results than H_2O_2 with $HCOOH$. Another effect is quantity of oxidant amount, catalyst, and the temperature was also evaluated in terms of their effects on the performance. One interesting finding out of these inquiries was the fact that increasing the reaction temperature yielded better results up to 65 C° , where the highest efficiency in elimination of sulfur through Oxidative desulfurization method for the Zakho refiner fuel oil was achieved.

Keywords: Acidic acid, Catalyst, Fuel Oil, Hydrogen Desulfurization, Oxidative Desulfurization, Peroxide, Sulfur.

ÖZET

OKSİDATİF KÜKÜRTSÜZLEŞTİRME TEKNİĞİNİ (ODS) KULLANARAK ZAKHO PETROL RAFİNERİSİNDE AKARYAKITTAN KÜKÜRTÜN ARINDIRILMASI

ALI, Rebeen Ramzi
Yüksek Lisans Tezi, Kimya Mühendisliği Bölümü
Tez Danışmanı : Prof. Dr. Nahit AKTAŞ
İkinci Danışman: Prof. Dr. Lokman A. ABDULKAREEM
Nisan 2018, 47 sayfa

Normal şartlarda ağır yakıtlar önemli miktarda Kükürt içermektedir. Yakıt, eliminasyon sürecinde problemlere sebep olan ağır karbon katmanlarından oluştuğu için bu kükürtün tasfiye edilmesi oldukça zordur. Bu çalışmada akaryakıtlardan kükürt oranının azaltılmasında sıklıkla kullanılan Oksidatif Kükürt Giderme tekniği (ODS) incelenecektir. ODS İki adımlı bir tekniktir: birinci adım sülfonları oluşturmak için yakıtın, kimyasal maddelerin ve katalizatörün birbiriyle etkileşime geçtiği adımdır. İkinci adım ise çözücü bir madde kullanarak bu sülfon kombinasyonunun ortadan kaldırıldığı adımdır. Bu reaksiyonlar doğal olarak çok yavaştır ancak bu reaksiyonların hızını arttırmak için süreçte bazı ek önlemler bulunmaktadır. Bu çalışmada, reaksiyonu hızlandırmak amacıyla karışımlar 1500 RPM ile karıştırılmıştır. ODS yoluyla ağır yakıttan kükürtün neredeyse tamamen ayrıştırıldığı reaksiyonun çeşitli faktörleri ve parametreleri incelendikten sonra sonuç belirgin olmuştur: %4.7 oranındaki kükürt içeriği %2.54'e indirilmiştir. Ayrıca asetik asitli H₂O₂ formik asitli H₂O₂'den daha iyi sonuçlar kazandırmıştır. Performans üzerindeki etkileri bağlamında katalizator miktarı, oksidan miktarı ve sıcaklık gibi diğer faktörler de değerlendirilmiştir. Bu incelemelerden ortaya çıkan ilginç biri bulgu şudur ki reaksiyonu sıcaklığını 65 C°'ye kadar arttırmak daha iyi sonuçlar doğurmaktadır ki bu Duhok rafinerisinde ODS tekniğiyle kükürtün ayrıştırılması işleminde görülmüştür.

Anahtar kelimeler: Akaryakıt, Asetik Asit, Formik Asit, Hidrojen Kükürtsüzleştirme, Katalizator, Kükürt, Oksidatif Kükürtsüzleştirme, Peroksit.



ACKNOWLEDGEMENT

First of all, I thank my God, Allah, for support and help that motivated me and gave me strength all the time to complete this work successfully. I would like to express my sincere gratitude to my supervisor Prof. Dr. Nahit AKTAŞ for his continuous academic and moral support. This thesis work is a tribute to his exceptional guidance and mentorship; in addition, I owe gratitude, respect, and thanks to my second supervisor Prof. Dr. Lokman A. Abdulkareem, for his continuous support, and valuable efforts being done to finish this work.

I also extend my heartfelt thanks to my family and well-wishers.

2018

Rebeen Ramzi ALI



CONTENTS

	Pages
ABSTRACT	i
ÖZET	iii
ACKNOWLEDGEMENT	v
CONTENTS	vii
LIST OF TABLES	ix
LIST OF FIGURES	xi
SYMBOLS AND ABBREVIATIONS	xiii
1. INTRODUCTION	1
1.1. Aim and Objective	2
2. LITERATURE REVIEW	3
2.1. Sulfur Categories in Oil.....	3
2.2. Influences of Sulfur	4
2.2.1. Health	4
2.2.2. Enviroment and climate.....	5
2.2.3. Effects of sulphur - containing fuels on economy	6
2.3. Desulfurization of Crude Oils	6
2.4. Oxidative – Desulfurization (ODS) Process.	7
2.5. General Description of The ODS Process.....	7
2.6. Formic Acid/ H ₂ O ₂ Oxidation System:.....	9
2.7. H ₂ O ₂ / Organic Acid system	10
2.8. Comparative Studies on Reduction of Sulphur Content	22
2.9. Benefits of ODS Compared to Other Methods	22
2.10. Disadvantages of The ODS Process	22
3. MATERIALS AND METHODS	23
3.1. Introduction	22
3.2. Material	23
3.2.1. Chemical compounds	23
3.2.2. Instruments used in this experiment	23

	Pages
3.3. Method	24
4. RESULTS AND DISCUSSION	27
4.1. Introduction	26
4.2. Effectiveness of Formic Acid - Hydrogen Peroxide Combination	27
4.3. Effectiveness of Acetic Acid - Hydrogen Peroxide Combination	29
4.4. Effect of Temperature on ODS Process	30
4.5. Effect of String	32
5. CONCLUSION	35
REFERENCES	37
EXTENDED TURKISH SUMMARY(GENİŞLETİLMİŞ TÜRKÇE ÖZET).....	41
CURRICULUM VITAE	47

LIST OF TABLES

Tables	Pages
Table 4.1. Sulfur removal performance of formic acid when used in conjunction with hydrogen peroxide.....	28
Table 4.2. Sulfur removal performance of acetic acid when used in conjunction with hydrogen peroxide.....	30
Table 4.3. The effects of temperature level on the sulfur removal performance of hydrogen peroxide in conjunction with formic acid.....	31
Table 4.4. The stirrer size ODS performance in conjunction of formic acid and hydrogen peroxide.....	33

LIST OF FIGURES

Figures	Pages
Figure 2.1. The ideal reaction in ODS process for dibenzothiophenes and methyl substituted derivatives.	8
Figure 2.2. Simplified diagram of the CED technology	11
Figure 2.3. Hetero-atom compounds found in crude oil	17
Figure 2.4. Organometallic compounds found in crude oil [Robinson PR.(2013)]	18
Figure 2.5. Structure of 4, 6-DMDBT [Sami M.2000].....	20
Figure 3.1. position of field petroleum	24
Figure 3.2. Laboratory collocate	24
Figure 3.3. Schematics of oxidative-desulfurization ODS process.	26
Figure 4.1. Sulfur measurement device	27
Figure 4.2. The amount of formic acid used plotted against sulfur removal performance	29
Figure 4.3. Sticky substance forming on the fuel sample after sulfur removal with formic acid..	29
Figure 4.4. The amount of formic acid used plotted against sulfur removal performance	30
Figure 4.5. Sample of fuel oil after sulfur reduction with acetic acid	31
Figure 4.6. ODS process test temperature plotted against remaining sulfur content within the sample	32
Figure 4.7. Measurement of sulfur in the fuel sample via sulfur measurement device	33
Figure 4.8. Sample under stirring effect.....	33
Figure 4.9. Stirrer size No 6.....	34



SYMBOLS AND ABBREVIATIONS

Some symbols and abbreviations used in this study are presented below, along with descriptions.

Symbols	Description
SO₂	Sulphur dioxide
HDS	Hydrodesulphurization
BTs	Benzothiophenes
DBTs	Dibenzothiophenes
ODS	Oxidative desulfurization
H₂S	Hydrogen sulphide
CS₂	Carbon disulphide
C₄H₄S	Thiophene
H₂O₂	Hydrogen peroxide
SH	Sulfhydryl
SO_x	Sulphur oxide
NO_x	Nitrogen oxide
CO	Carbon monoxide
VOC_s	Volatile organic compounds
SO₄	Sulphate
PM	Particulate meter
LGO	Light gas oil
CLO	Commercial light oil
LCO	Light cycle oil

Symbols	Description
DMSO	Dimethylsulfoxide
DMF	Dimethylformamide
Ti-HMS	Hexagonal mesoporous
Ti-WMS	Wormhole mesoporous silica
TS-1	Titanium silica -1
DMDBT	Dimethyl-dibenzothiophene



1. INTRODUCTION

Presence of sulfur in heavy fuel oils leads to emission of SO_x which endangers public health. In order to control air pollution because of heavy fuel oils combustion, most of the countries released a new regulation requiring the use of low sulfur fuel oils. Desulfurization of crude oil is one of the important processes in the refining of crude oil to final product. In recent times, the required specifications for transportation fuels have become increasingly stringent with respect to sulfur content. Efforts are being made to produce petrochemical products and transportation fuels to be almost sulfur free. Consequently, the removal of sulfur from the crude oil has become one of the prime processes and consequently, the price of a crude oil is influenced by its sulfur content (Javadli et al., 2012). The stringent environmental regulation has limited the level of sulfur content in many countries. The limit has been less than 15 µg/g since 2006 in US, less than 10 µg/g in Europe since 2005, and less than 50 µg/g in Beijing and Shanghai in China since 2008 (Jiang et al., 2011).

The new regulation in India since April 1, 2010 has prescribed the sulfur content limit for gasoline and diesel to be 50 µg/g with the limit reducing to as low as 10 µg/g in near future (Kumaret et al., 2012). The sulfur content can poison the noble metal catalyst used in the reforming and transforming process of fuel and the electrode catalysts used in fuel cell stacks (Jiang et al., 2011). Due to this stringent condition, the refineries are facing the major problem in treating the sulfur content crude oil and the need for ultra-deep desulfurization of liquid hydrocarbon fuels has become an increasingly important subject worldwide. The main traditional and widely used method available is hydrodesulfurization which employs the use of hydrogen at an elevated pressure (20-100 atm of H₂) and high operating temperature of 300-400 °C. The method is highly effective for aliphatic and acyclic S-compound but less effective for the treatment of aromatic sulfur compound. However, the existing hydrodesulfurization technique requires much harsher operating conditions to remove the last 100 ppm of sulfur due to the presence of refractory sulfur compounds such as benzothiophenes (BT) and dibenzothiophene (DBT), which demand higher hydrogen pressure, temperature and/or contact time to achieve a fuel with sulfur concentration of less than 10 ppm.

(Aysar et al., 2011; Chica et al., 2006), ultimately increasing the initial and operating investment cost. Therefore there is a need to develop alternative cost efficient method which operates at normal range temperature and pressure for ultra-deep desulfurization process. Many efforts have been made in these direction and new methods such as reactive adsorption or adsorptive desulfurization (Gao et al., 2013; Naviri, et al., 2015), extractive distillation (Shen et al., 2013), oxidative desulfurization (Filippis et al., 2003) biodesulfurization (Bordoloi et al., 2014) has gained much recognition in recent times. Oxidative desulfurization (ODS) is the most interesting desulfurization technique among the researcher. Many researches are being carried on this subject. ODS process primary include two stages: (i) Oxidation of sulfur compound and (ii) Liquid extraction. The process makes use of oxidant to oxidize the organic sulfur present in fuel oil and is subsequently removed by adsorption or extraction. The primary focus of this review is to summarize the various oxidative system used in ODS. The sulfur compound like benzothiophene, dibenzothiophene, 4, 6- Dimethyldibenzothiophene (4, 6-DMDBT) are oxidized using selective oxidant to a compound that can be preferentially extracted using suitable solvent. The various oxidative systems such as Formic acid/ H_2O_2 , Ionic liquid/ H_2O_2 , Heteropolyacid (HPA)/ H_2O_2 , Molecular sieve/ H_2O_2 , Poloxometalates/ H_2O_2 , TS-1/ H_2O_2 , Ultrasound/ H_2O_2 is deeply analyzed based upon the literature survey in the present review work.

This study will therefore focus on the Oxidative Desulphurization method for the desulphurization of local fuel oil of Northern Iraq.

1.1. Aim and Objective

The aim and objective of the present work is to decrease sulphur from the Zakho heavy fuel oil of Northern Iraq by Oxidation Desulphurization (ODS) method. Two steps are involved in utilizing ODS method, these steps are oxidation and extraction. The Oxidation, which is the first step, employs hydrogen peroxide as an oxidant (H_2O_2) in the existence of either acetic acid or formic acid as a catalyst. The second step will involve a liquid-liquid extraction which will be conducted by applying acetonitrile solvent.

2. LITERATURE REVIEW

2.1. Sulfur Categories in Oil

Presence of sulfur in heavy fuel oils leads to emission of SO_x which endangers public health. In order to control air pollution because of heavy fuel oils combustion, most of the countries released a new regulation requiring the use of low sulfur fuel oils. It is well known that sulfur in fuel oil is created through the breakdown of organic matter, as time strata initiates to form in time, and the sulfur separates from the fuel oil in the form of Hydrogen Sulphide. It seems not all of the sulfur is separated from the fuel in this way, though, as some sulfur remains with the fluid phase left behind. One more idea is that the sulphate ions that are in the tank rock are reduced by hydrogen, which comes from the tank fluid through bacterial action of *Desulfotribrio desulphuricans*.

Hydrogen gas + sulphate ions = (bacteria) → Hydrogen Sulphide + Hydroxide ion + Water

As a consequence of this reaction, Hydrogen Sulphide (H₂S) is produced. The H₂S thusly formed can correspondingly react with the sulphates in the bedrock to form Sulfur that stays in liquid configuration of fuel oil. Furthermore, under certain circumstances like pressure, temperature and a long period of time, these can occur naturally within the bedrock as well. H₂S can also react with the hydrocarbons to discharge Sulfur mixtures (Wauquier, 1995).

Hydrogen Sulphide + sulphate ions → Sulfur + Hydroxide ion + Water

Sulfur mixtures are one of the most significant non-hydrocarbon heteroatom constituents of fuel oil. There are many types and formations of sulfur compounds in the many layers of petroleum. Furthermore, it seems like the type and amount of sulfur compounds that exist in any given fuel oil is based on certain circumstances like period of creation, period of maturing, and even in situ alterations.

Usually, fuel oil with higher density has less API importance and higher sulfur content. The amount of sulfur in fuel oil can fluctuate from 0.04% w/w for light fuel oil to about 5% w/w for heavy fuel oil. Sulfur within fuel oil also varies contingent on the

chemical arrangement of recently uncovered fields, especially between those in different geological places (Speight, 2007).

2.2. Influences of Sulfur

Sulfur is dangers to humans, ecologically disastrous, and corrodes infrastructure. The existence of high sulfur-containing compounds in the process streams could have a lot of damaging effects, which is dangerous to health. This section presents and discusses the effects of sulfur with respect to mankind and its environment.

2.2.1. Health

Petroleum-based fuels, such as diesel and gasoline are used by internal combustion engines to power most automobiles. The emission of particulate matter (PM), nitrogen oxides (NO_x), and carbon monoxide (CO), non-methane hydrocarbons, airborne toxins, and sulfur oxides (SO_x) are usually caused by high temperature in cylinder of incomplete combustion of fuel. Some health issues and chronic diseases that are associated with exposure to these pollutants can eventually lead to early death (Sharaf, 2013) Particulate matter (PM) is the most dangerous among the vehicle emissions. These categories of solid and liquid particles, lesser than 2.5 microns in aerodynamic diameter, (PM_{2.5}) can easily infiltrate into the lungs, stirring up inflammation and oxidative stress. In addition, the continuing exposure to PM 2.5 causes a series of chronic illnesses in adults. These include respiratory infections, aggravation of existing asthma, lung cancer, ischemic heart disease, chronic bronchitis, as well as cerebrovascular disease Chambliss, (Sharaf, 2013). The reduction of sulfur-containing compounds from transportation fuel is essential in the petroleum industry. International Agency for Research on Cancer has confirmed that PM_{2.5} is a recognized carcinogen, which is mainly caused by diesel exhaust in transportation fuel (McClellan et al., 2012). Exposure to high concentrations of PM_{2.5} has been discovered to be connected to increase in hospital admissions that are related to infections of the respiratory organs (Chien et al., 2016) stroke, nonfatal heart attacks, and other acute outcomes (Lisabeth et al., 2008) Undesirable effects on reproduction, including reduced

birth weight and increased death of children are also as a result of the emission of PM_{2.5} (Geer et al., 2012). New investigation into the impacts of black carbon on climate gives stronger proof that, if diesel particulate emissions can be controlled, it will reduce global warming. Over the years, diesel black carbon has been extensively reduced in carbon dioxide equivalent emission by diesel engine polices in the state of California. Therefore, the implementation of vehicle emission standards equivalent to Euro 6/VI for the international fleet would reduce the rate of premature mortality to between 120,000 and 280,000 in 2030 (McClellan et al., 2013) at a worldwide standard.

2.2.2. Environment and climate

The quality of the air is seriously affected by the pollution emitted by vehicle engines. There is a release of the sulfur oxides (SO_x) and NO_x into the atmosphere during the combustion of fuel. This could form sulfuric acid and nitric acid in the atmosphere when combined with water that lead to acid rain (Koch et al., 1996). In addition, the release of sulfur-containing compounds in fuels into the environment leads to environmental concerns, such as water pollution (due to oil spillage) and global warming (Shiraishi et al., 1998). The vehicle manufacturers request for the removal of sulfur-containing compounds from petroleum, so as to reduce the global emissions of these compounds from vehicles (Parkinson et al., 2000). These emission control devices are affected since sulfur is intensely adsorbed onto the metal catalysts, which inhibit the reaction and the adsorption of carbon monoxide, Nitrogen oxide (NO_x), and hydrocarbons. Furthermore, production of the oxy-acids of sulfur from combustion products causes the internal combustion engines parts to corrode (Collins et al., 1997). Likewise, compounds of sulfur deactivate the catalysts that are used in hydrocarbon upgrading. In addition, they add to the formation of sticky deposits in petroleum products (Tam et al., 1990). Therefore, sulfur compounds are unwanted in refining processes and their removal from petroleum distillates is important to the refineries and for human welfare.

2.2.3. Effects of sulphur-containing fuels on economy

Some of the economic impacts of SO_x that are emitted due to the incomplete combustion of high-sulfur fuels have negative impacts on the economy of the nation. The acid rain as a result of this emission dissolves the calcium carbonate in monuments and buildings that are made with limestone and marble (Bravo et al., 2006). Sulfuric acid can cause huge economic losses owing to the occurrence of metal corrosion in machineries and vehicles in oil plants. Crude oils are refined and extracted by oil companies at varying levels. However, it is cheaper to refine crude that has lower sulfur content first, before refining crude with higher concentrations of sulfur. Since this is done the other way round, the oil reserves with lower sulfur contents would have been used up, leaving only high-sulfur concentrated crude oil to be used (Jones et al., 2010). From estimation, the use of low sulfur fuels would be economically useful since it will prevent hospital emergencies and thousands of hospital admissions, lost working days, reduction of agricultural crop, and damage to commercial forest.

2.3. Desulfurization of Crude Oils

Desulfurization of crude oils (fuels) is a process employed for the elimination of sulfur and/or sulfur-containing compounds in crude oils during the petroleum refining process. Crude oils contain a large variety of sulfur-containing compounds (thiols, thioethers, disulfides and thiophenes), which generate a serious environmental concern because of the emission of sulfur oxides (SO_x) and airborne particulate during combustion to the atmosphere. The reduction of these gases in the atmosphere is currently being addressed through the elimination of source compounds (sulfur-containing compounds) present in fuels. The desulfurization process is extremely important in the petroleum-refining industry for the production of cleaner fuels. The three methods of desulfurization are described below (Booth et al., 2001).

2.4. Oxidative-desulfurization (ODS) Process

Oxidative-desulfurization (ODS) has been considered as a new technology for desulfurization of fuel oils. The ODS process includes two stages: (i), oxidation of the sulfur atoms in the first step; and (ii), liquid extraction of the polar products at the final step. The utmost advantages of the ODS process is that the refractory sulfur-containing compounds can be oxidized and it operates at a low reaction temperature, and pressure, and in the absence of hydrogen which is expensive. With HDS being able to desulfurize thiophene and acidic sulfur compounds at relatively moderate conditions and the ODS process being capable of desulfurizing refractory sulfur compounds, then the ODS process has great potential to be a complementary process to HDS for producing deeply desulfurized crude oil.

2.5. General Description of The ODS Process

In the ODS process, sulfur-containing compounds in crude oils are oxidized using selective oxidants such as nitric acid, (Tam et al., 1990; Baxendale et al., 1946) nitrogen oxides, organic hydroperoxides, peroxyacids, hydrogen peroxide, and/or ozone in the presence of a catalyst to produce sulfone compounds that can be preferentially extracted due to their increased relative polarity.

For oxidation to take place, the oxidant needs to be in contact with fuel oils under optimum conditions, and the oxidant donates oxygen atoms to the sulfur in benzothiophenes, dibenzothiophenes and its derivatives to form sulfoxides and/or sulfones (figure 2.1). Some of the by-products generated by oxidant influence the quality of the fuels; for example *tert*-butyl alcohol which is a potential octane booster for fuels is generated as by-product of *tert*-butylhydroperoxide (Aida et al., 1994).

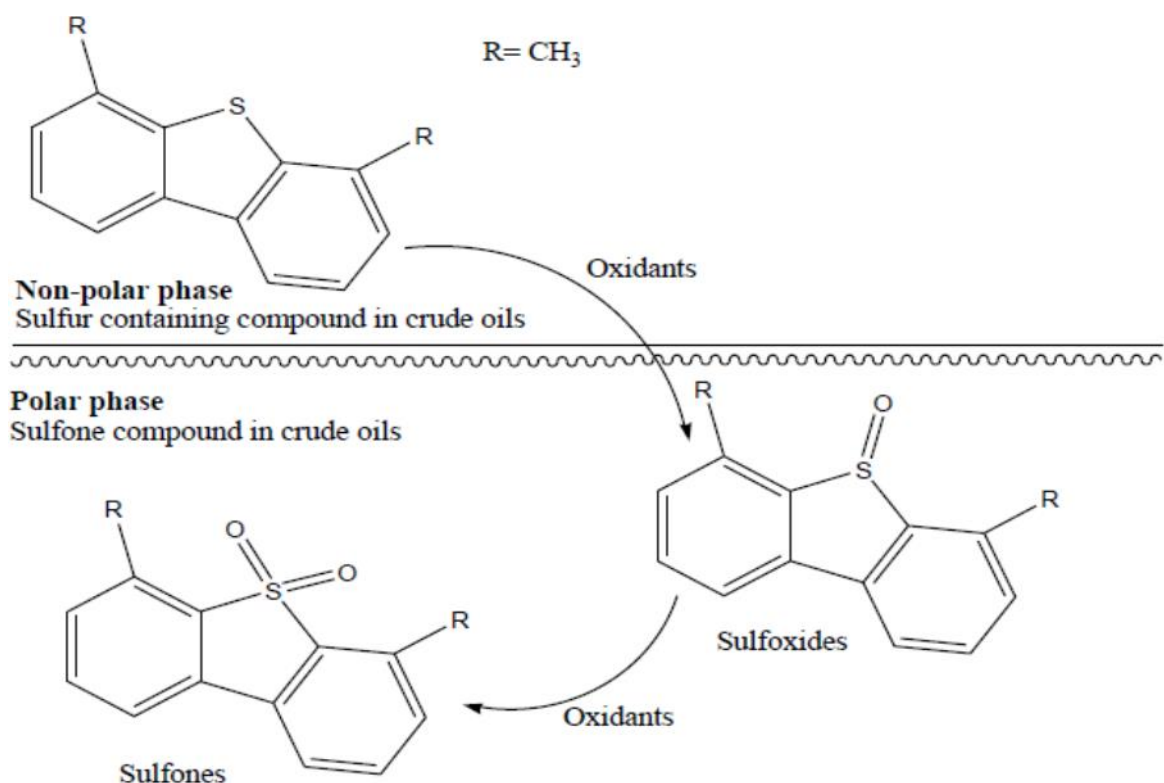


Figure 2.1. The ideal reaction in ODS process for dibenzothiophenes and methyl substituted derivatives.

A practical industrial flow system for oxidative desulfurization of hydro-treated crude oil (Figure 2.2), where catalyst in the crude oils are extracted and washed, unused oxidant are also separated in the separator section before further oil processing can take place.

Liquid-liquid extraction of the oxidized compounds (sulfones and sulfoxides) was carried out by contacting oxidized crude oil with a non-miscible solvent which is selective for the polar oxidized sulfur compounds. The desulfurized crude oil is water washed to recover any traces of dissolved extraction solvent and then polished either by absorption using silica gel and alumina to produce high quality clean sulfur free oil.

The choice of solvent for the extraction of sulfone in crude oils is critical. A solvent must be thermodynamically compatible with the compound to be extracted. Water-soluble polar solvents such as *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), and acetonitrile are usually employed for the desulfurization of crude oils. The former two solvents have a high extractability for sulfones but have a high boiling point (above 200°C), which is close to the boiling point

of the sulfones, and thus may not be re-used for further extraction based on the solvent recovery by distillation. Acetonitrile was, however, a preferred solvent for the extraction of sulfones despite its high cost because of its relatively low boiling point (82°C) making solvent recovery by distillation possible. However, it extracts a large quantity of aromatics along with sulfones, thereby giving rise to a low quality fuel. Several solid adsorbent materials have also been developed for the adsorption of sulfone compounds in order as to eliminate the limitations posed by the liquid extractants. The adsorbents for organosulfur compounds are discussed in details. Oxidative-desulfurization demonstrates that it is possible to remove sulfur compounds from fuels to meet strict regulation limits, though a high oxidant-to-sulfur (O/S) ratio is required to oxidize sulfur compounds to their corresponding sulfoxides and sulfones. However, this drawback (i.e. high oxidant constraint) can be avoided by use of suitable catalysts (Campos-Martin et al., 2010).

2.6. Formic Acid/ H₂O₂ Oxidation System

The reactivity of sulfur compounds for oxidation increases with increase of electron density on sulfur atom. The reactivity of refractory sulfur compounds decreases in order of 4,6-DMDBT > 4-MDBT > DBT. The order of reactivity in HDS of sulfur compounds is reverse of the above pattern. (Yao Xiuqing et al. 2003] studied the desulfurization process for DBT and its derivatives such as MDBT, 4,6-DMDBT by using formic acid as catalyst and H₂O₂ as an oxidant. Model sulfur compounds of BT, DBT and 4,6-DMDBT is dissolved in nheptane to prepare the model oil. The results shows that under the condition of the reaction temperature of 600C, the molar ratio of hydrogen peroxide to sulfur of 7:1, and volume ratio of hydrogen peroxide to formic acid of 1:1, and the reaction time 40min. The conversion achieved for 4,6- DMDBT, DBT and BT were 100%, 96% and 58% respectively. (Alireza et al., 2013) studied the oxidative desulfurization of model fuel by using of formic acid as a catalyst and H₂O₂ as an oxidant. For deep desulfurization of sulfur containing compounds (BT, DBT,4,6-DMDBT) sulfuric acid was used to increase the acidity of model sulfur compounds and catalytic activity with formic acid. The sulfur containing compounds is oxidized to sulfones followed by liquid-liquid extraction using acetonitrile to remove sulfones from

model oil. The result shows that under operating condition, reaction temperature of 650C, molar ratio of H₂O₂ to sulfur of 2:1, ratio of formic acid to sulfur of 22:1 and reaction time of 56min, 100% conversion is achieved. H₂O₂-organic acid oxidative system has relatively mild reaction conditions and strong oxidizing ability, to achieve high desulfurization rate, but the organic acids in the oilsoluble part impact the fuel quality. And the liquid organic acids have several disadvantages such as unrenewable and a high reclaiming cost, so catalyst which can be recovery is one indispensable choice (Zhang et al., 2009).

2.7. H₂O₂/Organic Acid System

The major organic acids used in ODS are acetic acid and formic acid. For example, conversion/extraction desulfurization (CED) technology began in 1996 when Petro Star Inc. combined conversion and extraction to remove sulfur from diesel fuel (Bonde et al., 2002). First, the fuel is mixed with H₂O₂/acetic acid (peroxyacetic acid) and the oxidative reaction takes place below 100 °C under atmospheric pressure. This is followed by a liquid/liquid extraction to obtain a fuel with low sulfur and an extract with high sulfur. Finally, the low sulfur fuel may require additional treatment. The extraction solvent is then removed from the extract for re-use and the concentrated extract is made available for further processing to remove sulfur and to produce hydrocarbon (Fig. 2.3). In a laboratory-scale experiment the fuel did not change significantly and it remained within the quality guidelines. The sulfur levels were markedly reduced from 4720 $\mu\text{g/g}$ to 70 $\mu\text{g/g}$ after processing and the American Petroleum Institute (API) gravity as well as the cetane number improved. The extraction solvent is also important for the success of this process. In the CED process the production of cost effective solvent cocktails is most important. High desulfurization

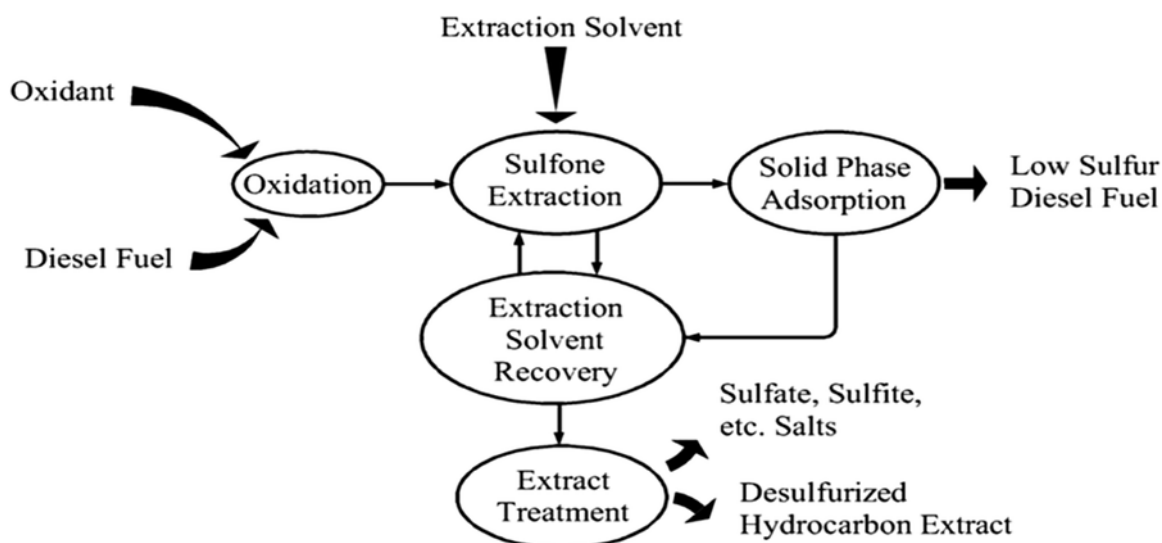


Figure 2.2. Simplified diagram of the CED technology.

Efficiencies are required and only a slight influence on the non-polar fuel constituents is allowed. The reactivity of the different sulfur-containing compounds including methyl phenyl sulfide, thiophenol, diphenyl sulfide, 4-methyldibenzothiophene (4-MDBT), DBT, benzothiophene (BT), 2-methylthiophene (2-MT), 2,5-dimethylthiophene (2,5-DMT), and thiophene was investigated for selective oxidation using hydrogen-peroxide and formic acid by Otsuki and colleagues (Otsuki et al., 2000). The relationship between the electron densities of the sulfur atoms, which was estimated by molecular orbital (MO) calculations, and the oxidative reactivities of the sulfur-containing compounds was also investigated. The electron densities on the sulfur atom of the sulfur compounds are shown in Table 1. The electron densities of the thiophene derivatives varied between 5.696 (thiophene) and 5.760 (4,6-DMDBT). 2,5-DMT, 2-MT, and thiophene usually oxidize with difficulty because of their lower electron densities. BT (electron density 5.739) and other model compounds with higher electron densities were oxidized to form their corresponding sulfones. These apparent rate constants (k) decrease as follows: 4,6-DMDBT > 4-MDBT > DBT > BT. This result indicates that the rate constant increases with an increase in electron density. A hydrogen peroxide and formic acid oxidizing system was also used to study the influence of the solvent on the oxidation rate of the sulfur-containing compounds in the organic phase (Filippis et al., 2003). The results indicate that heterocyclic sulfur-containing compounds such as benzo- and dibenzothiophene have different kinetic

processes compared with thiols and sulfides. The aromaticity of organic solvents has a considerable influence on oxidation rates.

2.8. Comparative Studies on Reduction of Sulphur Content

In recent time clean fuels research such as desulfurization, oxidative desulphurization and dearomatization has become one of the essential focus of environmental catalysis studies globally (Chunshan, 2002). The level of sulphur content is one of the major essential factors of crude oils marketing price. Nowadays there are different kinds of sulphur compounds in crude oil that can be further divided into four categories for examples: disulfides, mercaptanes, sulfides, and thiophenes, moreover, Sulphur compounds in the refining process are unwanted due to their capability of leading to deactivation of the catalyst and also causes environmental pollution (Hosseini et al., 2014). Heavy crude oil exploitation is a remarkable topic dealing with the scarcity of energy in the globe. Heavy crude oil reservoirs are abundant in the world, they account for 70% of the total quantity of petroleum. Heavy crude oil contain mainly hydrocarbon with little amount of heteroatoms such as sulphur (S), oxygen (O) and nitrogen (N) compounds, present of sulphur compound in the heavy oil molecules has become the challenges of many refinery and petroleum industry during the exploitation as well as during refine processing. Hence, several techniques such as thermal recovery, chemical recovery, microbial recovery, Toe to Heel Air Injection (THAI), Steam Assisted Gravity Drainage (SAGD), in-situ combustion and cyclic steam stimulation (CSS) etc., have been developed and adopted for heavy crude oil derailing (Desouky et al., 2013). Sulphur content is among the major important characteristics of the crude oil and natural gas due to their high effect to environment as well as affecting human health, and it also devalue quality of the crude oil fraction when found in excess. Nowadays, there is a negative trend of increase of sulphur content in hydrocarbons worldwide, many nations of the world are moving towards environmentally friendly alternative transportation fuels. New transportation fuel policies are being put into consideration worldwide. As a result of those contra guiding factors, such as hydrocarbon quality and reducing the maximum allowable level of sulphur occurrence making the condition bad (Darkhan, 2013). Sulphur has been known to be among the

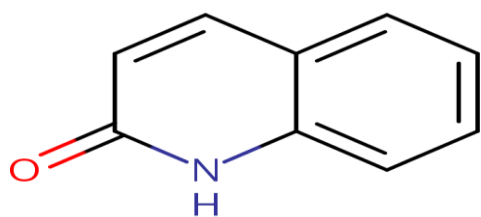
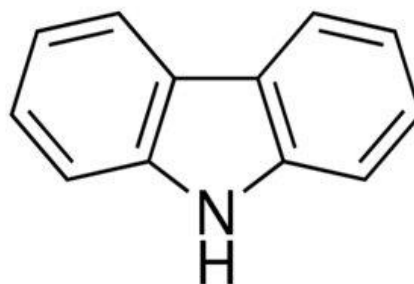
major impurity affecting the quality of the final refined product and as well, contributes to high cost dispensation, additionally sulphur compounds in the crude oil generates many operational problems, as well lead to environment pollution when refined product are used by internal combustion engine, the smoke were released to air which lead to air pollution. Sulphur content in petroleum destroys the catalyst by affecting catalyst to be came inactivation (Abdullahi et al., 2012). Higher sulphur content in petroleum products contributes to large emissions of sulphur dioxides (SO₂) and as a result produce acid rain to the environment, as well as providing poor performance of vehicle emissions control systems. Refining instruments across corrosion problems when handling heavy crude oil with huge amount of high sulphur compounds, besides, sulphur compounds are extremely unwanted in commercial products due to their nasty smell or ruthless odour (Hanni et al., 2004). The occurrence of sulphur has an implication effect on the price of the crude oils, due to its adverse environmental consequence as well as the outcome of end refined products, thus led to severe environmental protocols passing large regulations on refinery operatives globally to decrease sulphur contents of crude oil products (Huang et al., 2006). In the previous era, many strict laws on the standard and benchmark of sulphur level in fusel fuels have been introduced in many countries, nowadays the production of ultra-low sulphur fuel has become an essential mission of refines industries (Germain et al., 2013). Generally crude oils has unrelated quantities and forms of sulphur compounds, however as a guideline the quantity, stability, and complexity of the compounds are much higher in heavy crude oil fractions (Abdullahi et al., 2012). When petroleum products comprise up sulphur compounds undergo combustion, may produces undesirables compound like sulphuric acid (H₂SO₄) and sulphur dioxide (SO₂), many refineries implemented hydro-treating processes or hydrodesulphurization (HDS) reaction which includes catalytic alteration of many sulphur compounds to nonsulphur no-inclusive materials at the occurrence of hydrogen, however some amount of sulphur remain in the products, thus another methods with simple operating conditions is also needed as well as the practice of dynamic catalyst and imaginable advanced technologies were also required (Nicholas et al., 2008). In current time, many research has try to discover advance and cheapest process that could replace hydro-treating in other to reduce the cost of production, as well to reduce the level of sulphur. One of the alternative that have the golds of meeting

the demand was oxidative desulphurization by using organic or inorganic peroxide as oxidants in the present of ideal catalyst (Hanni et al., 2004). It is recognised that reacting a petroleum fuels with an oxidant alters the organo-sulphur and nitrogen compounds present in fuels to sulphones compound (or sulphoxides compound) as well as organic nitric oxides. These polar organic oxides can be separated from the fuels by solvent extraction and/or by adsorption. Moreover, oxidative desulphurization can simply oxidize and remove thiophenic sulphur compounds, which cannot be remove by HDS due to the stereo hindrance (interference) effect within the sulphur atom in the molecule (Abdullahi et al., 2013). For instance, it has been testified that the action of thiophenic compounds in reacting to HDS treatment occur in this order: DBT (dibenzothiophene) > 4-MDBT (4-methyl dibenzothiophene) > 4, 6 DMDBT (4, 6-dimethyl dibenzothiophene). Additionally, it has been testified that the activity of thiophenic compounds in responding to oxidative treatment is just the reverse, for example: 4, 6-DMDBT > 4- MDBT > DBT. These interpretations advise that oxidative desulphurization can be active in eliminating the most challenging residual sulphur compounds from hydrotreated oils to produce ultra-low sulphur products (Germain et al., 2003). Although, the oxidants used in the oxidative desulphurization process can be active in aqueous intermediate or in non-aqueous intermediate. It has been recognised that via aqueous oxidant involves a phase transfer agent (catalyst) to carry out the oxidant from the aqueous phase to the oil phase where it reacts the organosulphur compounds, beside one of the problem related with the use of aqueous oxidants is the precipitation of important portion of the sulphones from the liquid phases which disturb the process (Gore et al., 2003). Crude oil is a complex mixture comprised of thousands number of hydrocarbons compound (C-C bond), nonhydrocarbon compounds (S, N, O, etc.) as well as heavy metals (Pb, Cu, Ca, etc.). Or crude oils are flammable liquid recognised to contain mainly hydrocarbons mixed with little amount of sulphur-, nitrogen-, and oxygenated compounds (Haruna et al., 2017). Heavy metals are in the forms of inorganic salts or organometallic compounds like porphyrinate complexes were present in the complex mixture of crude oil in small quantities, it is forecast that crude oil will be existing as a source of energy for many decades to subsequent era, on the other hand, there has been additional needs for crude oil quality disintegration as the left behind contents of the recognised reservoirs tend to be of substantial and sourer

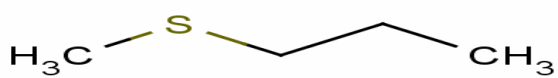
composition and new wells are rarely to be across (Barbara et al., 2011). By the increase awareness that oil is a limited resource, it is well essential to try to use it as efficiently as potential by controlling its environmental impact by processing productivity, by reducing sulphur content in different fuels.

Moreover many strict laws to reduce levels of sulphur content in fuels have been offered by environmental regulating agencies in many countries of the world, all pointing toward limiting levels of sulphur content in crude fractions to was ultra-low level between 10-15ppm by 2015 (Barbara et al., 2011). Many criteria have been used to categorise crude oils; which are differences in form and viscosity of oils from one oil reservoir to another as well as chemical composition present, these differences in form are range in aroma and colour, but the viscosity and gravity of the crude can be classified based on American Petroleum Institute (API) gravity and viscosity. For instance, if the API gravity of the crude oil is between 0-20 degrees are placed as heavy crude oil, while those above API gravity ≥ 40.1 degrees are placed as light crude oil and if the oil fall between 20 and 40.1 degrees was categorised as medium crude oil (intermediate crude) (Dysard et al., 2009). Classifications may be based on chemical properties present in the crude, for instance, vanadium-to-nickel ratio (V: Ni), nitrogen and sulphur content (N, S). It is identified that crude oil with low content of sulphur is call sweet, but crude with high presence sulphur content is call (sour), respectively every crude oil poses different compound, composition or properties that is not correspond with other sample of crude, moreover chemical and physical composition of crude oil vary not only with the site and In the substantial fractions such as resins and asphaltenes organometallic compounds like nickel (Ni) and vanadium (V) are originate and their concentrations have to be condensed by altering the oil to transportation fuel form. The oldness of the oil field, but also varies with the depth of the different well, besides, two neighbouring oil reservoirs may produce hydrocarbons with different properties (Hosseini et al., 2014). In order to know the behaviour of sulphur compounds present in crude oil the basic knowledge of all crude oil composition were required. The major compounds found in crude oils are hydrocarbons mostly (C1 to C6). The hydrocarbon content may be much as 97% by weight in light paraffinic oils or lower as 50% by weight in heavy crude oil and bitumen, other non-hydrocarbon compound include small amount of organic compounds such as sulphur (S), oxygen (O), and

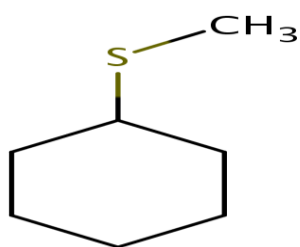
nitrogen (N), as well as compounds with metallic elements like vanadium (V), nickel (Ni), iron (Fe), and copper (Cu) (Speight, 2007). Crude oils contain some extents of organic non-hydrocarbon elements, those elements exist in organic compounds, such as hetero-atoms (carbon and hydrogen atoms) with either sulphur, nitrogen, and oxygen compounds present in the ring, with high boiling point, but tend to distillate mostly in the heavier fractions (Speight, 2011). Even though they are little constituents of crude oil, their increased processing or operation costs, most of the sulphur and nitrogen compounds increasing high operational cost to crude oil refiners and petrochemical industries. Fuels with higher sulphur, if burned by combustion engine in vehicles or power plants, also pollute the environment, beside lead to acid rain. For several refining processes, sulphur is a promoter poison likewise nitrogen is also promoter of poison, thus, refiners offer a large quantity of time and money to eliminate heteroatoms from intermediate streams and finished concentration of metal compounds ranges between little ppm to 200 ppm for nickel (Ni) and up to 1200 ppm for vanadium (V) (Robinson, 2013).

2(1*H*) Quinolin-one

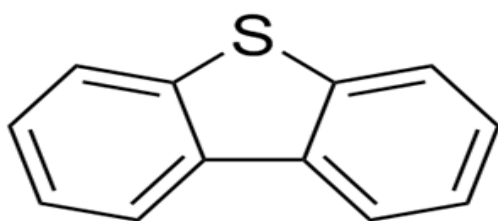
Carbazole



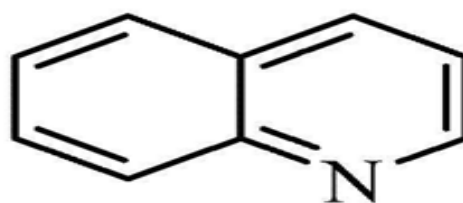
Methyl propyl sulfide



3-methylthiacyclohexane



Dibenzothiophene



Quinoline

Figure 2.3. Hetero-atom compounds found in crude oil.

Concentration of metal compounds ranges between little ppm to 200 ppm for nickel (Ni) and up to 1200 ppm for vanadium (V) (Robinson, 2013).

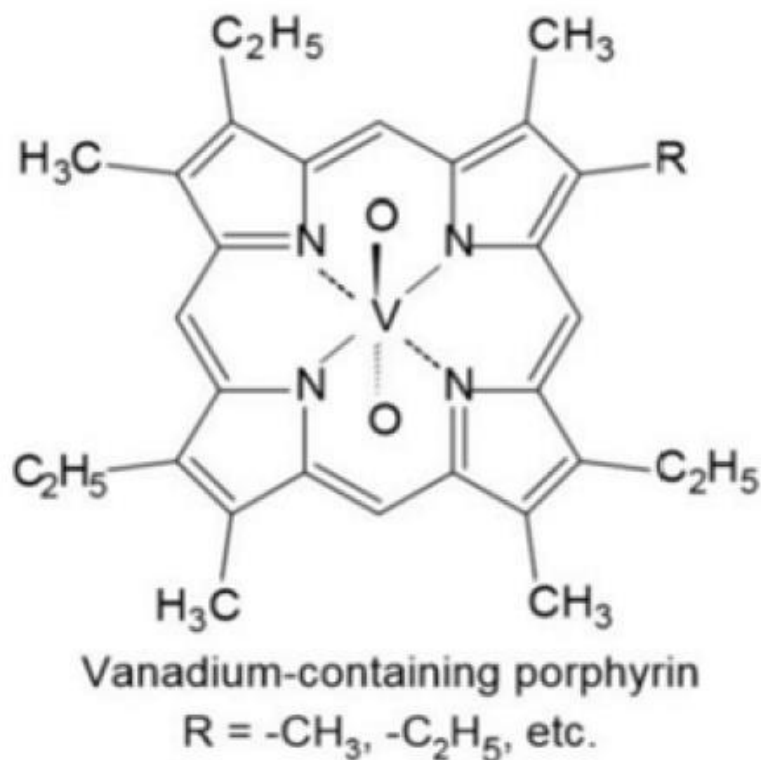


Figure 2.4. Organometallic compounds found in crude oil [Robinson PR. (2013).].

Hydrodesulphurization (HDS) also refers as hydro-treating process, is one of the well-known desulfurization methods that have been run by refinery processes since the 1950s, hydrodesulphurization (HDS) can be achieved by using fixed bed reactor (Zhu et al., 2014). The sulphur bearing hydrocarbon feed (heavy crude oil) and hydrogen gas are past to the reactor, the sulphur bearing hydrocarbon feed are pump and high pressurised between the range 13 to 130 atmospheres. The high pressurised feed are link with hydrogen gas and then pass over heat exchanger to heat up the liquid-gas mixture at temperatures ranging between 300 to 400°C, in the reactor, catalyst cobalt and molybdenum over alumina (CoMO/Al₂O₃) base are used to enhance (speed) the reaction which convert organic sulphur compounds (OSCs) to hydrogen sulphide (Chen

et al., 2008). Besides mixture of hydrocarbons, hydrogen gas and hydrogen sulphide in the reactor were further pass through gas separator in order to separate the fuel from hydrogen gas and hydrogen sulphide, the separated phases of hydrogen and hydrogen sulphide are treated with amine gas in order to purify hydrogen gas for recycling in the reactor and hydrogen sulphide are oxidized to sulphur dioxide (SO₂) by air, and sulphur is formed, the process is known as Claus process, the overall reaction is show below (Raja et al., 2015). $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} (\text{s}) + 2\text{H}_2\text{O}$ Fuel produced from the gas separator are further treated in stripper distillation unit with reflux in an attempt to remove gases such as hydrogen (H), hydrogen sulphide (HS), methane (CH₄), ethane (CH₃CH₃), propane (CH₃CH₂CH₃) and other volatile organic compounds, In the same way, the gas mixture are treated with amine gas to recover hydrogen sulphide, the residual fraction may be utilised for other purposes like refinery fuel gas. Even though hydrodesulphurization (HDS) has been utilised to synthesed low sulphur fuel for years, the approaching tautened regulations will be the big challenge on this process, even do hydrodesulphurization (HDS) was recognised to desulfurize mercaptans, sulphides and thiophene, Still, the more condensed by-products are benzothiophenes (BTs) and dibenzothiophenes (DBTs) are major challenging compound to eradicate by hydrodesulphurization (HDS), it is well-known that reactivity of the one- to three-ring organic sulphur compounds (OSCs) reduce by Thiophenes > Benzothiophenes > Dibenzothiophenes (Girgis et al., 1991). It is reported that low sulphur diesel fuel produced by hydrodesulphurization (HDS) contains approximately 500ppmw of sulphur, mostly alkyl derivatives of DBTs which are considered as refractory compounds and cannot be easily desulfurized through hydrodesulphurization (HDS) (Ma et al., 2001). Moreover 4-alkyl DBTs, 6-alkyl DBTs and 4, 6-alkyl DBTs have very low reactivity which can be illuminated by mixtures of electronic density, bond order, and spatial, geometric and steric interference around the sulphur atom (Schulz et al., 2009). 4, 6-dimethyl-dibenzothiophenes are familiar for its high stability against hydrodesulphurization (HDS). Therefore, traditional hydrodesulphurization (HDS) is not applicable to produce ULSD needed by new sulphur regulations (Sami, 2000). The structure of 4, 6-DMDBT is shows in figure 2.5.

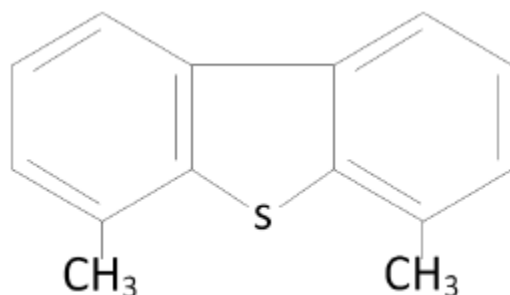


Figure 2.5. Structure of 4, 6-DMDBT [Sami M.2000].

Adjustments on hydrodesulphurization (HDS), including increase of hydrogen, catalyst quantity, and as well as operating pressure, have been studied, overall, hydrogen usage is the main operational cost of hydrodesulphurization (HDS), as to reduce the sulphur content from 500ppmw to 15ppmw, an increase of 25% to 45% of hydrogen gas is needed (Muhammad, 2015). This indicates that the operational cost will be doubled up, then again, doubling catalyst quantity can only lower the sulphur content by 100ppmw, and hence, an affected increase in catalyst dosage is also necessary to produce ULSD (Whitehurst et al., 1998). As proposed by the National Petroleum Council, operating pressure has to be improved from 1100psi to 1200psi so as to produce diesel with low than 30ppmw sulphur, thus this needs a specific thick-walled reactor to withstand with high pressure, and as a result increasing the investment and operational costs, also the massive increase in cost, safety issue is also a big problems for hydrodesulphurization (HDS) which involves high operating temperature and pressure with the use of hydrogen gas, moreover reactor failure as well as explosion can be occurred if uncontrollable (hot-spots) phenomenon, or any other operation errors will happen (Ojinnaka et al., 2012). Nowadays petroleum industry begin to give new attention to the advance of cost operational alternatives as a replacement of depended totally traditional hydro-treating operation, oxidative desulfurization is among the best substitute methods proposed, although research on developing industrial futures golds of this method was initiated in the 1990s (Lin et al., 2007). Oxidative desulfurization (ODS) is deliberated as the upto-date alternative desulfurization process which consist of chemical oxidation of divalent organic sulphur compounds to the equivalent hexavalent sulphur, also well-known as sulphone, those physical and chemical properties of sulphones, are boiling points, polarity and solubility in different solvents,

and are entirely diverse from the original sulphur compounds, generally, sulphones poses higher boiling points and improved polarity which leads to higher solubility (Zapata et al., 2005). Ideally, oxidation desulphurization (ODS) can be accomplished by many type of oxidants such as nitric acid catalyst and nitrogen oxides were among the common oxidants used to remove both organic sulphur compounds and organic nitrogen compounds in nineteen century, because of the poor selectivity, low yield and loss in heating value for the treated heavy crude oil, these oxidants have not been usually used today (Tam et al., 1990). Even though oxidative desulfurization can be achieved by noncatalytic oxidation or catalytic oxidation of OSCs, noncatalytic oxidative desulfurization processes involves high temperature of about 200°C and high pressure (Paniv et al., 2006). When compare, catalytic oxidative desulfurization needs moderately slight environments at temperature between 25°C to less than 100°C under ambient pressure. Different types of ODS catalysis such as aldehydes (Murata et al., 2004), transition metal salts (Chen et al., 2007), polyoxometalate acids (Rosa et al., 2206) and carboxylic acids, but organic acids -and polyoxometalate acids are the major ones generally used. This research work was aimed at reducing the sulphur content of heavy crude oil prior to processing using combination of two alternative oxidants for the oxidative desulphurization process potassium permanganate and hydrogen peroxide ($\text{KMnO}_4/\text{H}_2\text{O}_2$) as oxidants over formic acid and acetic acid as a catalyst for oxidative desulphurization (ODS) of heavy crude oil, and then solvent extraction with DMSO. The objectives of the research are summarised below: i. To compare the effect of mix oxidants; potassium permanganate and hydrogen peroxide ($\text{KMnO}_4/\text{H}_2\text{O}_2$) on oxidative desulphurization. ii. To examine the effect of two acid catalysts; acetic acid and formic acid, on oxidative desulphurization as well as to compare their efficiency in reducing the sulphur content present in heavy crude oil. iii. To study the effects of reactions temperature at 60°C on the efficiency of desulphurization of the heavy oil. iv.

To measure the amount of sulphur content of the untreated and desulphurized crude sample. v. To investigate the effect of the oxidation-extraction system on the oil quality and distribution of the sulphur compounds

2.9. Benefits of ODS Compared to Other Methods

Easy removal of sulfur compounds which are resistant against HDS method

- Refineries contain more than enough air.
- Very strong sulfur elimination, resulting in significantly lower sulfur content.
- Applicable even for small and medium size refineries.
- May become the best desulfurization process with advancements in the sector (Rang et al., 2006).

2.10. Disadvantages of The ODS Process

- Since ODS was not widely utilized until recently, most other ancillary technologies are built around HDS.
- A significant amount of chemicals are used in ODS processes, and feasible methods of elimination of the effects of these chemicals were not available until recently.

3. MATERIALS AND METHODS

3.1. Introduction

This study was conducted to investigate and removal of sulphur from fuel oil. This chapter consists the experimental work and data collection.

3.2. Materials

3.2.1. Chemical compounds

1. Sample is Fuel oil: is used for the chemical experiments for the decreasing of sulphur.
2. HCOOH: is used as a catalyst .
3. H₂O₂: is used as an oxidant .
4. H₃C=N: is used as a solvent for the departure .
5. CH₃COOH: is used as a catalyst .

3.2.2. Instruments used in this experiment

Water bath, Thermometer, Heater, Beaker, Stirrer, Test tube, Puar, Digital Balance , XRF device model RX-360SH

Act as the catalyst. Under various temperatures ranging from 35 to 75 C° for 60 minutes to deduce the optimal heat for the reactions, the samples were stirred with 1500 RPM to increase the reaction speed, which resulted in an environment for the samples that are similar to a reactor.



Figure 3.1. Postion of field petroleum.



Figure 3.2. Laboratory collocate.

3.3. Method

This study was conducted to evaluate the oxidative desulfurization process, which is used to reduce the sulfur content of oil, over the Zakho refinery heavy fuels. The test equipment were the usual assortment of glass elements like the batch reactor, and heater and stirrer, along with a thermometer to measure the optimal reaction temperature.

ODS has two distinctive steps, namely the reaction and separation phases. To start the tests, various amounts of H_2O_2 were introduced to fuel samples to act as an oxidant. Following that, test subjects were separated into two groups where one group was processed with formic acid and the other with acetic acid, again in various amounts, to

The aqueous and oil phases were then separated and 25 ml of each sample were taken into decanters for the extraction step.

With that, the second step of ODS began, where the samples were processed with selective liquid-liquid solvents. The choice of solvent is rather important as the best properties for a suitable solvent are high polarity and being non-dissolvable inside the fuel. Since the boiling point (BP) of a solvent is also important, acetonitrile was chosen for this study, as it has a low BP, and it is rather easy to separate from the sulfones by straight distillation.

Each decanter was introduced a proper amount of acetonitrile – based on their initial oxidant volumes – and the decanters were then shaken for 20 minutes to increase reaction speed of the solvent. This resulted in two clearly separate phases for the liquids inside the decanters. The fuel oil was heavier than the solvent agent so it sank to the bottom of the decanters. To prevent disturbances and re-mixing, the lids of the decanters were opened slowly and carefully. The oil was removed, 15 mL portions of each of them were analyzed for their sulfur content using the X-Ray fluorescence test (XRF device model RX-360SH) ASTM-D 4294.

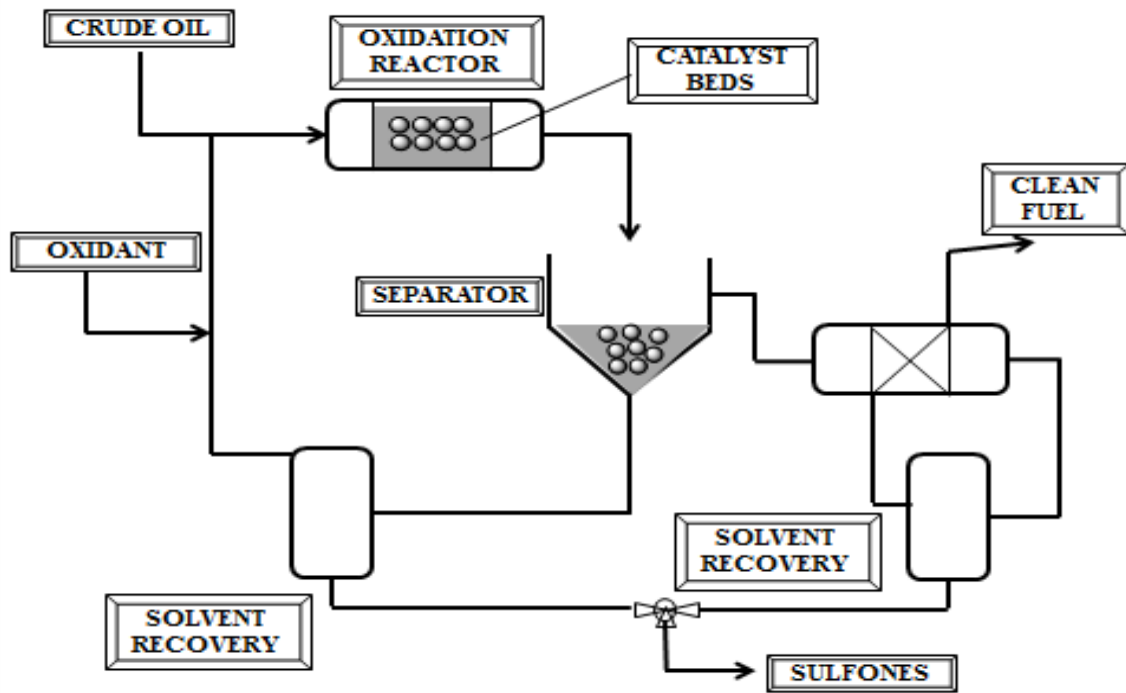


Figure 3.3. Schematics of oxidative-desulfurization ODS process.

4. RESULTS AND DISCUSSION

4.1. Introduction

This study conducted the oxidative desulfurization method on various samples of Zakho refinery heavy fuels, with various agents and temperature levels to observe their effects on the reaction. This chapter presents the results attained.

One of the major interests of our study was to evaluate the performances of acetic and formic acids when used with hydrogen peroxide in terms of sulfur removal. Initial sulfur content from Zakho refinery was 4.7% (w).



Figure 4.1. Sulfur measurement device.

4.2. Using Formic Acid and Hydrogen Peroxide Together

Sulfur Removal Performance

Table 4.1. Sulfur removal performance of formic acid when used in conjunction with hydrogen peroxide

Sample No	RPM (Stirrer)	Degree of Temperature (°C)	Sample Weight (gram)	Weight of HCOOH acid(gram)	Hydrogen Peroxide Weight (gram)	Sulfur percentage in sample %wt
1	1500	65	100	15	20	3.56
2	1500	65	100	25	30	3.26
3	1500	65	100	35	35	3.0
4	1500	65	100	50	45	2.7

The data above displays the sulfur content, which was reduced from 4.7% (w) to 3.56, 3.26, 3.0, and 2.7% (w) respectively under various parameters. The best result was, as can be seen from the figure, reduction from 4.7% to 2.7% (w). During the test, higher formic acid and hydrogen peroxide concentrations resulted in a higher amount of sulfur reduced. However, utilization of the formic acid caused the formation of a sticky substance in the samples, which was something undesirable out of this reaction. As a result, even though the formic acid was actually a formidable catalyst, this sticky polymer formation presented a strong argument against it.

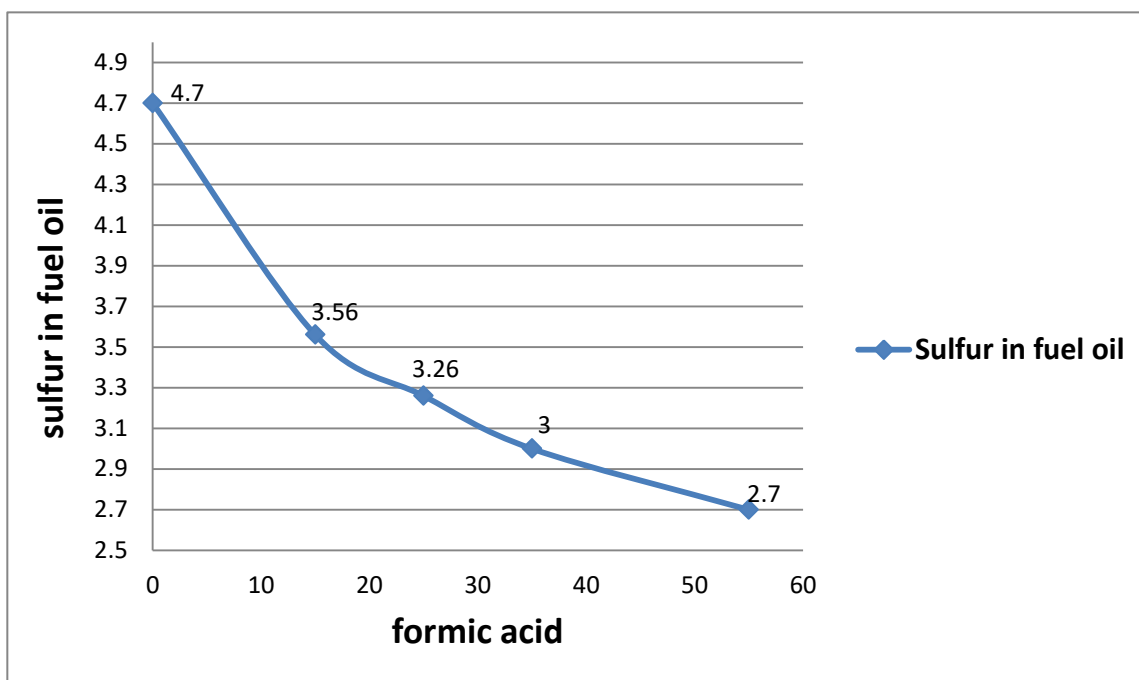


Figure 4.2. The amount of formic acid used plotted against sulfur removal performance.



Figure 4.3. Sticky substance forming on the fuel sample after sulfur removal with formic acid.

4.3. Using Acetic Acid and Hydrogen Peroxide Together

Sulfur Removal Performance.

Table 4.2. Sulfur removal performance of acetic acid when used in conjunction with hydrogen peroxide

Sample No	RPM (Stirrer)	Dgree of Temperature (°C)	Sample Weight (gram)	Weight of CH ₃ COOH (gram)	Weightof Hydrogen Peroxide (gram)	Sulfur percentage in sample %wt
1	1500	65	100	15	20	3.17
2	1500	65	100	25	30	2.97
3	1500	65	100	35	35	2.80
4	1500	65	100	50	45	2.56

The same reactions were repeated with acetic acid for some of the samples as well, and its performance was compared to that of formic acid.

The table clearly indicates that increasing amounts of catalyst again has positive impact on the sulfur removal performance, and the effects of acetic acid is significantly stronger compared to that of formic acid. Besides, acetic acid did not cause any unwelcome substances to form during or after the reaction either.

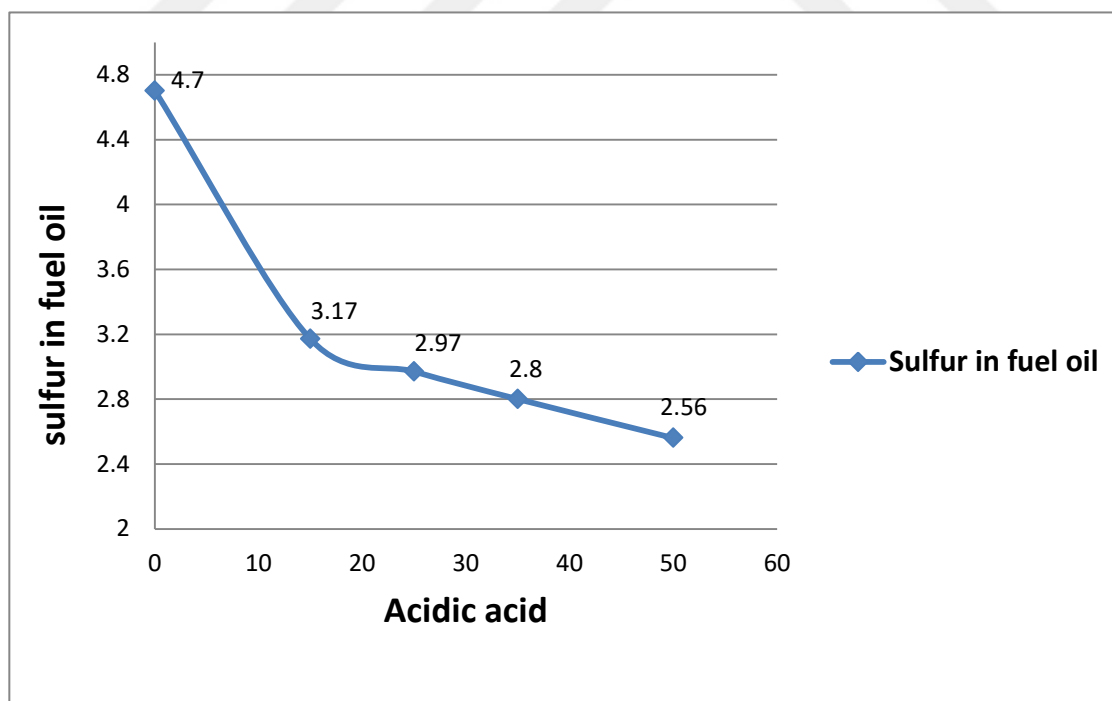


Figure 4.4. The amount of formic acid used plotted against sulfur removal performance.

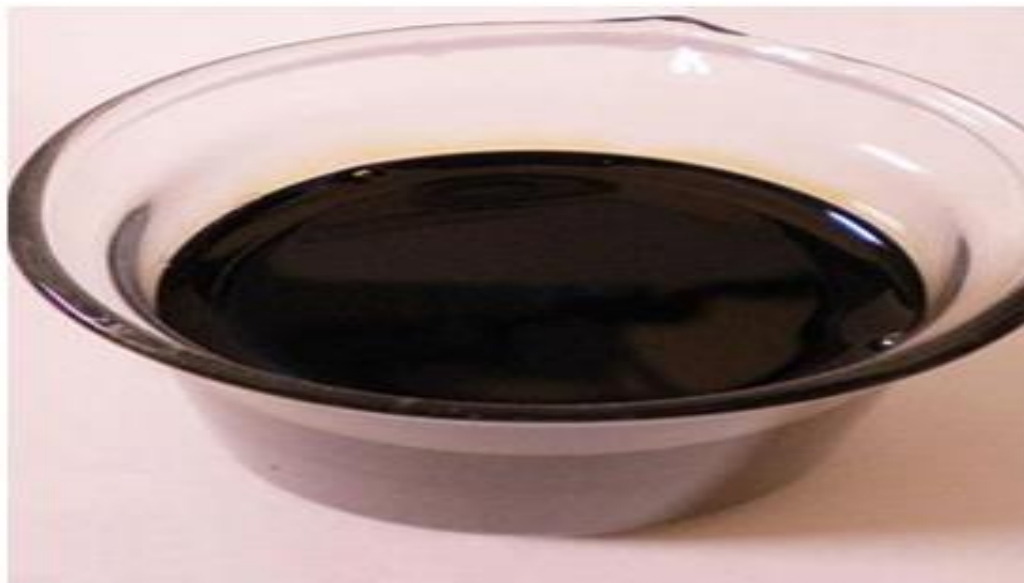


Figure 4.5. Sample of fuel oil after sulfur reduction with acetic acid.

4.4. Oxidative Desulfurization: The effects of temperature

The study also inspected the effects of various temperature levels on the performance of oxidative desulfurization (ODS) process. Different test samples were subjected to the ODS process in temperature levels varying between 35 and 75 °C, and hydrogen peroxide and formic acid levels were kept constant to isolate the effects of temperature change. The results clearly indicate that the optimum reaction performance was achieved at 65 °C, and the performance began to decrease again as it was increased to up to 75 °C. Table 4.3 below summarizes the results of temperature test.

Table 4.3. The effects of temperature level on the sulfur removal performance of hydrogen peroxide in conjunction with formic acid

Sample No	RPM (Stirrer)	Dgree of Temperature (°C)	Sample Weight (gram)	Weight of HCOOH (gram)	Hydrogen Peroxide Weight (gram)	Sulfur percentage in sample %wt
1	1500	35	100	50	45	3.22
2	1500	45	100	50	45	3.13
3	1500	55	100	50	45	3.01
4	1500	65	100	50	45	2.70
5	1500	75	100	50	45	2.73

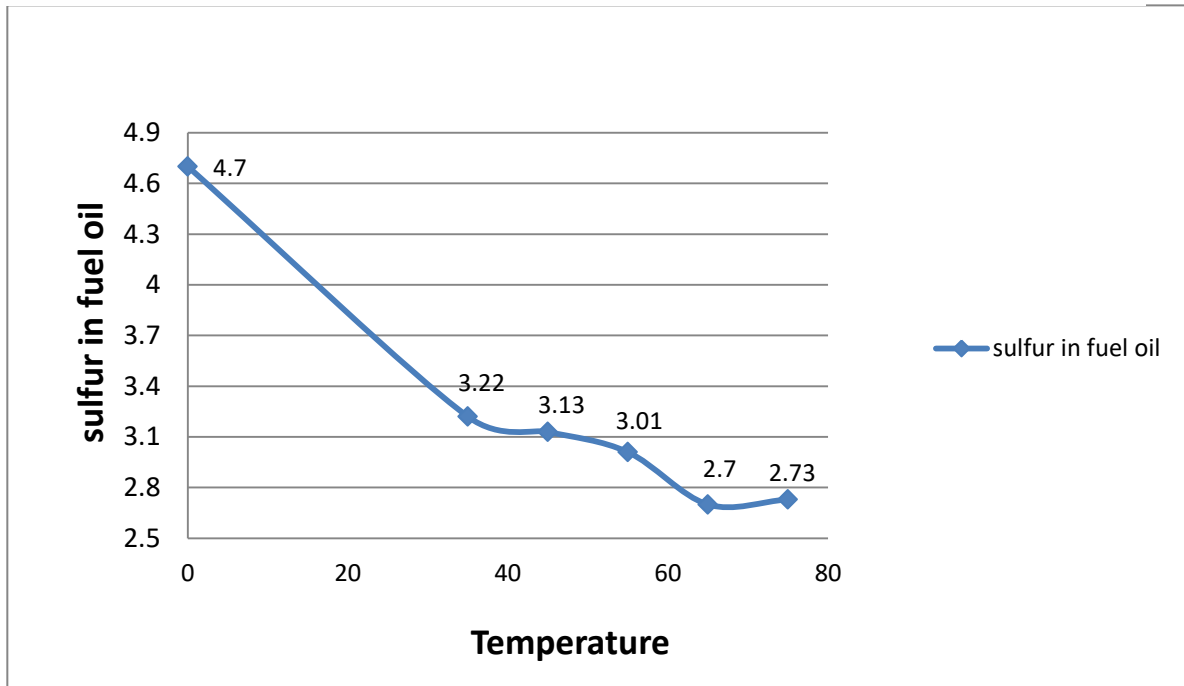


Figure 4.6. ODS process test temperature plotted against remaining sulfur content within the sample.



Figure 4.7. Measurement of sulfur in the fuel sample via sulfur measurement device.

4.5. Oxidative Desulfurization

The Impact of Stirrer Dimension on the Reaction Performance

The study also inspected the effects of the stirrer size on the ODS reaction. When the stirrer size was increased from no.4 to no.6, the sulfur content in the final sample was reduced from 2.94 to 2.54% (wt). This test was conducted using formic acid, and the stick substance was present again. Table 4.4 and Figure 4.8 represents the findings of this test.

Table 4.4. The stirrer size ODS performance in conjunction of formic acid and hydrogen peroxide

Sample No	RPM (Stirrer)	Degree of Temperature (°C)	Sample Weight (gram)	Weight of HCOOH (gram)	Hydrogen Peroxide Weight (gram)	Sulfur percentage in sample %wt
1	1500	65	100	25	30	2.94
2	1500	65	100	50	45	2.54

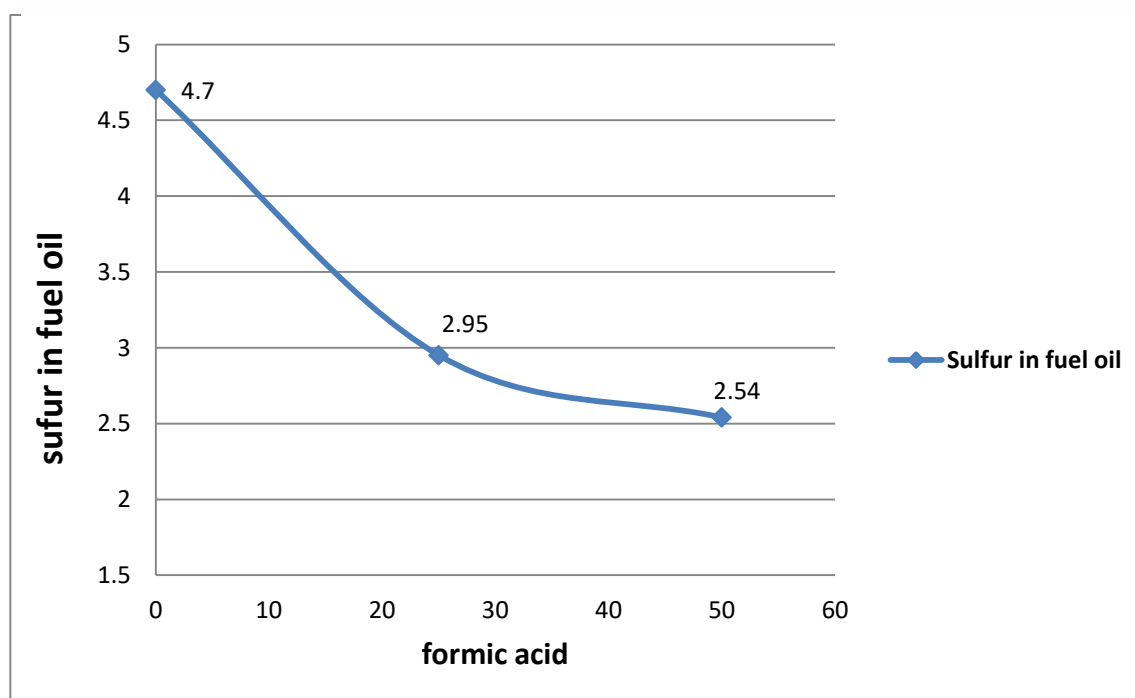


Figure.4.8. Sample under stirring effect.



Figure 4.9. Stirrer size No 6.

5. CONCLUSION

This study inspected the effects of acetic and formic acid in conjunction of hydrogen peroxide in ODS process, along with some other parameters like the temperature and stirrer size. The non-temperature tests were conducted at 55 °C, while the temperature test was conducted in temperatures between 35 and 75 °C. The results were evaluated using X-Ray technique.

The results indicate that the best reaction performance was attained in 65 °C. The acetic acid was found to be a better reactant compared to formic acid, because the latter caused the formation of a sticky substance at the end of the reaction. All that being said, the ODS method tested in the fuel samples of the Zakho refinery was able to reduce sulfur content from 4.7% (weight) to 2.54% (weight). Furthermore, the larger stirrer size was found to be helpful for the performance of the ODS reaction. Above the temperatures of 65 °C, the reaction performance began to decline.



REFERENCES

- Abubakar, A., Mohammed-Dabo, I. A., Ahmed, A. S. 2016. Reduction of sulphur content of urals crude oil prior to processing using oxidative desulphurization. *Nigerian Journal of Basic and Applied Sciences*, **24**(1): 19-24.
- Afsanepurak, S.A., Bahram, A., Dana, A., Abdi, J. 2012. The effect of self-talk and mental imagery on self-efficacy in throwing darts in adolescents. *International Research Journal of Applied and Basic Science*, **3** (3): 594-600.
- Aida, T., & Yamamoto, D. 1994. Annual book of ASTM standards. Standard test method for determination of sulfur compounds in natural gas and gaseous fuels by gas chromatography and chemiluminescence. *Prepr. Pap. Am. Chem. Soc., Div. Fuel Chem*, **39**: 623.
- Al-Shahrani, F., Xiao, T., Llewellyn, S. A., Barri, S., Jiang, Z., Shi, H., Green, M. L. 2007. Desulfurization of diesel via the H₂O₂ oxidation of aromatic sulfides to sulfones using a tungstate catalyst. *Applied Catalysis B: Environmental*, **73**(3-4): 311-316.
- Booth, M., Buglass, J. G., Unsworth, J. F. 2001. Tailoring fuels for the new millennium. *Topics in Catalysis*, **16**(1-4): 39-46.
- Bordoloi, N. K., Rai, S. K., Chaudhuri, M. K., Mukherjee, A. K. 2014. Deep-desulfurization of dibenzothiophene and its derivatives present in diesel oil by a newly isolated bacterium *Achromobacter* sp. to reduce the environmental pollution from fossil fuel combustion. *Fuel Processing Technology*, **119**: 236-244.
- Campos-Martin, J. M., Capel-Sanchez, M. D. C., Perez-Presas, P., Fierro, J. L. G. 2010. Oxidative processes of desulfurization of liquid fuels. *Journal of chemical technology and biotechnology*, **85**(7): 879-890.
- Chambliss, S., Miller, J., Façanha, C., Minjares, R., Blumberg, K. 2013. The impact of stringent fuel and vehicle standards on premature mortality and emissions. *The International Council on Clean Transportation*, www.theicct.org/global-healthroadmap.
- Chen, H., Zhang, W. J., Chen, J. M., Cai, Y. B., & Li, W. 2008. Desulfurization of various organic sulfur compounds and the mixture of DBT+ 4, 6-DMDBT by mycobacterium sp. ZD-19. *Bioresource technology*, **99**(9): 3630-3634.
- Chica, A., Corma, A., Dómine, M. E. 2006. Catalytic oxidative desulfurization (ODS) of diesel fuel on a continuous fixed-bed reactor. *Journal of Catalysis*, **242**(2): 299-308.
- De Filippis, P., Scarsella, M. 2003. Oxidative desulfurization: oxidation reactivity of sulfur compounds in different organic matrixes. *Energy and Fuels*, **17**(6): 1452-1455.
- De Rosa, M., Lamberti, M., Pellicchia, C., Scettri, A., Villano, R., Soriente, A. 2006. An efficient solvent free catalytic oxidation of sulfides to sulfoxides with hydrogen peroxide catalyzed by a binaphthyl-bridged Schiff base titanium complex. *Tetrahedron letters*, **47**(40): 7233-7235.
- Desouky, S., Betiha, M., Badawi, A., Ghanem, A., Khalil, S. 2013. Catalytic aquathermolysis of Egyptian heavy crude oil. *World Academy of Science*,

- Engineering and Technology, International Journal of Chemical and Molecular Engineering*, 7(8): 638-643.
- Duissenov, D. 2013. *Production And Processing Of Sour Crude And Natural Gas-Challenges Due To Increasing Stringent Regulations*, (Master's thesis, Institutt for petroleumsteknologi og anvendt geofysikk).
- Dysard, J. M., Hou, Z., McConnachie, J. M., Malek, A., Gupta, R., Lewis, W. E. 2009. *U.S. Patent No. 7,507,327*. Washington, DC: U.S. Patent and trademark office.
- Fallah, R. N., Azizian, S., Dwivedi, A. D., Sillanpää, M. 2015. Adsorptive desulfurization using different passivated carbon nanoparticles by PEG-200. *Fuel Processing Technology*, 130: 214-223.
- Gao, J., Chen, X., Ren, N., Wu, W., Li, C., Meng, H., & Lu, Y. 2013. Acylation desulfurization of oil via reactive adsorption. *AIChE Journal*, 59(8): 2966-2976.
- Girgis, M. J., & Gates, B. C. 1991. Reactivities, reaction networks, and kinetics in high-pressure catalytic hydroprocessing. *Industrial Engineering Chemistry Research*, 30(9): 2021-2058.
- Gore, W., Bonde, S., Dolbear, G. E., Skov, E. R. 2003. *U.S. Patent No. 6,596,914*. Washington, DC: U.S. Patent and trademark office.
- Haghighat Mamaghani, A., Fatemi, S., Asgari, M. 2013. Investigation of influential parameters in deep oxidative desulfurization of dibenzothiophene with hydrogen peroxide and formic acid. *International Journal of Chemical Engineering*, 1-11. <http://dx.doi.org/10.1155/2013/951045>.
- Hanni, V. D., Mustafa, H. D. 2004. Innovative refining technology-crude oil quality improvement (COQI). Real Innovators Group. *Chemical Engineering Division, Santaeruz E, Mumbai, India*, 330-335.
- Haruna, S. Y., Faruq, U. Z., Zubairu, A. Y., Liman, M. G., Riskuwa, M. L. 2018. Comparative studies on reduction of sulphur content of heavy crude oil using $\text{KMnO}_4 + \text{H}_2\text{O}_2/\text{CH}_3\text{COOH}$ and $\text{KMnO}_4 + \text{H}_2\text{O}_2/\text{HCOOH}$ via oxidative desulphurization (ODS). *American Journal of Applied Chemistry*, 6(1): 15-24.
- Hosseini, H., Hamidi, A. 2014. Sulfur removal of crude oil by ultrasound assisted oxidative method. *In Proceedings of The International Conference on Biological, Civil and Environmental Engineering (BCEE-2014), Dubai, United Arab Emirates*, 17-18.
- Huang, D., Wang, Y. J., Yang, L. M., Luo, G. S. 2006. Chemical oxidation of dibenzothiophene with a directly combined amphiphilic catalyst for deep desulfurization. *Industrial And Engineering Chemistry Research*, 45(6): 1880-1885.
- Jarullah, A. T., Mujtaba, I. M., Wood, A. S. 2011. Kinetic parameter estimation and simulation of trickle-bed reactor for hydrodesulfurization of crude oil. *Chemical Engineering Science*, 66(5): 859-871.
- Jones, J. A. 2010. Deep desulfurization of diesel fuel using a single phase photochemical microreactor. *Green Chemistry*, 12: 1139-1149.
- Kahl, J. 2006. Effect of acid rain on building material of the El Tajín archaeological zone in Veracruz, Mexico. *Environmental Pollution*, 144(2): 655-660.
- Kumar, S., Srivastava, V. C., Badoni, R. P. 2012. Oxidative desulfurization by chromium promoted sulfated zirconia. *Fuel Processing Technology*, 93(1):18-25.

- Lanju, C. H. E. N., Shaohui, G. U. O., Dishun, Z. H. A. O. 2007. Oxidative desulfurization of simulated gasoline over metal oxide-loaded molecular sieve1. *Chinese Journal of Chemical Engineering*, **15**(4): 520-523.
- Leadbeater, N. E., Khan, M. R. 2008. Microwave-promoted desulfurization of heavy and sulfur-containing crude oil. *Energy and Fuels*, **22**(3): 1836-1839.
- Lin, T. B., Huang, H. Y., Hwang, J. H., Shen, H. C., Chuang, K. T. T. 2007. *U.S. Patent No. 7,276,152*. Washington, DC: U.S. Patent and trademark office.
- Ma, X., Turaga, U., Watanabe, S., Velu, S., Song, C. 2004. *Deep Desulfurization of Diesel Fuels By A Novel Integrated Approach*. Pennsylvania State University (US).
- McClellan, R. O., Hesterberg, T. W., Wall, J. C. 2012. Evaluation of carcinogenic hazard of diesel engine exhaust needs to consider revolutionary changes in diesel technology. *Regulatory Toxicology and Pharmacology*, **63**(2): 225-258.
- Muhammad, A. B. 2015. Thermal evolution of aliphatic and aromatic moieties of asphaltenes from coals of different rank: possible implication to the molecular architecture of asphaltenes. *Chinese Journal of Geochemistry*, **34**(3): 422-430.
- Murata, S., Murata, K., Kiden, K., Nomura, M. 2004. A novel oxidative desulfurization system for diesel fuels with molecular oxygen in the presence of cobalt catalysts and aldehydes. *Energy And Fuels*, **18**(1): 116-121.
- Ojinnaka, C., Osuji, L., Achugasim, O. 2012. Remediation of hydrocarbons in crude oil-contaminated soils using Fenton's reagent. *Environmental Monitoring And Assessment*, **184**(11): 6527-6540.
- Paniv, P. M., Pysh'ev, S. V., Gaivanovich, V. I., Lazorko, O. I. 2006. Noncatalytic oxidation desulfurization of the kerosene cut. *Chemistry And Technology of Fuels And Oils*, **42**(3): 159-166.
- Pawelec, B., Navarro, R. M., Campos-Martin, J. M., & Fierro, J. L. 2011. Retracted article: towards near zero-sulfur liquid fuels: a perspective review. *Catalysis Science Technology*, **1**(1): 23-42.
- Sadare, O. O., Obasu, F., Daramola, M. O. 2017. Biodesulfurization of Petroleum Distillates Current Status, Opportunities and Future Challenges. *Environments*, **4**(4): 85.
- Schulz, H., Böhringer, W., Waller, P., Ousmanov, F. 1999. Gas oil deep hydrodesulfurization: refractory compounds and retarded kinetics. *Catalysis Today*, **49**(1-3): 87-97.
- Sharaf, J. 2013. Exhaust emissions and its control technology for an internal combustion engine. *International Journal of Engineering Research and Applications*, **3**(5): 947-960
- Shen, H., Shen, B., Ling, H. 2013. Desulfurization of fluid catalytic cracking gasoline by extractive distillation coupled with hydrodesulfurization of heavy fraction. *Energy And Fuels*, **27**(9): 5153-5160.
- Song, C. 2002. New approaches to deep desulfurization for ultra-clean gasoline and diesel fuels: an overview. *Prepr Paper Am Chem Soc Div Fuel Chem*, **47**: 438-444.
- Tam, P. S., Kittrell, J. R., Eldridge, J. W. 1990. Desulfurization of fuel oil by oxidation and extraction. 1. Enhancement of extraction oil yield. *Industrial And Engineering Chemistry Research*, **29**(3): 321-324.

- Tam, P. S., Kittrell, J. R., Eldridge, J. W. 1990. Desulfurization of fuel oil by oxidation and extraction. 1. Enhancement of extraction oil yield. *Industrial And Engineering Chemistry Research*, **29**(3): 321-324.
- Venturello, C., Alneri, E., Ricci, M. 1983. A new, effective catalytic system for epoxidation of olefins by hydrogen peroxide under phase-transfer conditions. *The Journal of Organic Chemistry*, **48**(21): 3831-3833.
- Whitehurst, D. D., Farag, H., Nagamatsu, T., Sakanishi, K., Mochida, I. 1998. Assessment of limitations and potentials for improvement in deep desulfurization through detailed kinetic analysis of mechanistic pathways. *Catalysis Today*, **45**(1-4): 299-305.
- Yu, H. L., Chien, L. C. 2016. Short-term population-based non-linear concentration–response associations between fine particulate matter and respiratory diseases in Taipei (Taiwan): a spatiotemporal analysis. *Journal of Exposure Science And Environmental Epidemiology*, **26**(2): 197.
- Zapata, B., Pedraza, F., Valenzuela, M. A. 2005. Catalyst screening for oxidative desulfurization using hydrogen peroxide. *Catalysis Today*, **106**(1-4): 219-221.
- Zeelani, G. G., Ashrafi, A., Dhakad, A., Gupta, G., Pal, S. L. 2016. Catalytic Oxidative desulfurization of liquid fuels: *International Research Journal Engineering and Technology*, **3**(5): 331-336.
- Zhang, G., Yu, F., Wang, R. 2009. Research advances in oxidative desulfurization technologies for the production of low sulfur fuel oils. *Petroleum And Coal*, **51**(3): 196-207.
- Zhu, W., Xu, Y., Li, H., Dai, B., Xu, H., Wang, C., Liu, H. 2014. Photocatalytic oxidative desulfurization of dibenzothiophene catalyzed by amorphous TiO₂ in ionic liquid. *Korean Journal of Chemical Engineering*, **31**(2): 211-217.

EXTENDED TURKISH SUMMARY (GENİŞLETİLMİŞ TÜRKÇE ÖZET)

1. ÖZET

Normal şartlarda ağır yakıtlar önemli miktarda Kükürt içermektedir. Yakıt, eliminasyon sürecinde problemlere sebep olan ağır karbon katmanlarından oluştuğu için bu kükürtün tasfiye edilmesi oldukça zordur. Bu çalışmada akaryakıtlardan kükürt oranının azaltılmasında sıklıkla kullanılan Oksidatif Kükürt Giderme tekniği (ODS) incelenecektir.

ODS İki adımlı bir tekniktir: birinci adım sülfonları oluşturmak için yakıtın , kimyasal maddelerin ve katalizatörün birbiriyle etkileşime geçtiği adımdır. İkinci adım ise çözücü bir madde kullanarak bu sülfon kombinasyonunun ortadan kaldırıldığı adımdır. Bu reaksiyonlar doğal olarak çok yavaştır ancak bu reaksiyonların hızını arttırmak için süreçte bazı ek önlemler bulunmaktadır. Bu çalışmada, reaksiyonu hızlandırmak amacıyla karışımlar 1500 RPM ile karıştırılmıştır.

ODS yoluyla ağır yakıttan kükürtün neredeyse tamamen ayrıştırıldığı reaksiyonun çeşitli faktörleri ve parametreleri incelendikten sonra sonuç belirgin olmuştur: %4.7 oranındaki kükürt içeriği %2.54'e indirilmiştir. Ayrıca asetik asitli H₂O₂ , formik asitli H₂O₂'den daha iyi sonuçlar kazandırmıştır.

Performans üzerindeki etkileri bağlamında katalizator miktarı, oksidan miktarı ve sıcaklık gibi diğer faktörler de değerlendirilmiştir. Bu incelemelerden ortaya çıkan ilginç biri bulgu şudur ki reaksiyonu sıcaklığını 65°C'ye kadar arttırmak daha iyi sonuçlar doğurmaktadır ki bu Duhok rafinerisinde ODS tekniğiyle kükürtün ayrıştırılması işleminde görülmüştür.

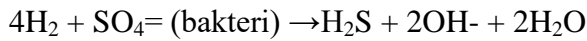
Anahtar kelimeler: Akaryakıt, Asetik Asit, Formik Asit, Hidrojen Kükürtsüzleştirme, Katalizator, Kükürt, Oksidatif Kükürtsüzleştirme, Peroksit.

2.GİRİŞ

Akaryakıtlarda çok çeşitli kükürt içeriği bulunmaktadır ve bu, SO₂ ve sülfür, disülfür tiyofen, tiyol gibi uçuşan partiküllerin oluşumuna sebep olmaktadır. Bundan dolayı akaryakıt kükürtsüzleştirilmesi, petrol ve gaz işletim endüstrisinde oldukça önemlidir. Geçmiş yıllarda akaryakıttan bu içeriklerin tasfiye edilmesi konusunda çeşitli çalışmalar yapılmıştır. Hidrojenle beraber yüksek basınç ve yüksek sıcaklık ile petrolün işlenmesi en yaygın ve en önemli endüstriyel işlemdir. Bu işlem Hidrojen Kükürtsüzleştirme (HDS) olarak adlandırılmıştır. 1930'larda ortaya çıkmasından itibaren büyük dikkat çekmiştir. Bu çalışmayla ilgili binlerce literatür çalışması, patent ve bilimsel mühendislik belgesi bulunmaktadır (Song ve Ma, 2003). Hidrojen Kükürtsüzleştirme; hafif petrolünün sıcaklığının yükseltildiği, hidrojen ile kombine edildiği ve bir reaktöre takviye edildiği bir süreçtir. Organik kükürt bileşimleri iki gruba ayrılmaktadır. İlk gruptaki bileşimler HDS gibi maliyetli işlemler tarafından ayrıştırılmaktadır. İkinci gruptaki bileşimler ise zor ayrışabilen bileşimlerdir. Hafif petrolün kükürtsüzleştirilmesinde, oksidatif kükürtsüzleştirme (ODS) yeni bir teknoloji olarak değerlendirilmektedir. Bu işlem iki adımdan oluşmaktadır. İlk adım oksidasyon adımıdır. Ayrıştırma işlemi ise ikinci adımda bulunmaktadır. Düşük reaksiyon sıcaklığı ve basınç ile maliyetli hidrojenin kullanılmaması ODS işleminin belirgin avantajlarından biridir.

3. LİTERATÜR BİLDİRİŞLERİ

Akaryakıttaki kükürtün organik maddenin çökmesiyle meydana geldiği ve kükürtün akaryakıttan Hidrojen Sülfür (H₂S) şeklinde ayrıldığı bilinmektedir. Başka bir iddia ise sülfat iyonlarının desülfobibrio desülfürikanların bakteriyel hareketi yoluyla depo sıvısından gelen hidrojen tarafından azaltıldığıdır.



Kükürt karışımlarının ayrıştırılması için H₂S aynı zamanda hidrokarbonlarla etkileşime geçebilir (Wauquier, 1995).



Genellikle yüksek yoğunluktaki akaryakıt daha az bir API'ye ve daha yüksek bir kükürt içeriğine sahiptir. Akaryakıttaki kükürt oranı hafif akaryakıt için %0.04'den ağır yakıt için %5'e kadar dalgalanabilir. Akaryakıttaki kükürt oranı aynı zamanda başta farklı jeolojik yerler arasındakiler olmak üzere halen keşfedilmemiş alanların kimyasal yapısına bağlı olarak da değişebilmektedir (Speight, 2007).

Akaryakıtta meydana gelen kükürt kombinasyonları sıklıkla altı kimyasal grupta kategorize edilmektedir: Serbest elemental kükürt (S), Hidrojen Sülfid (H_2S), Tiyol, Sülfid, Disülfid, Tiyofen ve değişkenleri.

4. MATERYAL VE METOT

4.1 Giriş

Bu çalışma akaryakıttan kükürtün ayrıştırılması işlemini incelemek üzere gerçekleştirilmiştir. Bu bölümde deneysel çalışma ve bilgi toplama üzerinde durulacaktır.

4.2 Materyaller

4.2.1 Kimyasal Bileşikler

- 1.Akaryakıt: Kükürtün azaltılması için kimyasal deneylerde kullanılmıştır.
- 2.Hidrojen Peroksit: Bir oksidan olarak kullanılmıştır.
- 3.Formik Asit: Bir katalizatör olarak kullanılmıştır.
- 4.Asetik Asit: Bir katalizatör olarak kullanılmıştır.
- 5.Asetonitril: Bir çözücü olarak kullanılmıştır.

4.3 Metot

Bu çalışma, Duhok petrol rafinerisinde akaryakıttan kükürt içeriğinin azaltılması için kullanılan oksidatif kükürtsüzleştirme tekniğini değerlendirmek üzere yapılmıştır. Test ekipmanları optimal reaksiyon sıcaklığını ölçmek için kullanılan termometrenin yanısıra kesikli reaktör, ısıtıcı ve karıştırıcı gibi çeşitli araçlardan oluşmuştur. ODS'nin biri reaksiyon biri de ayrıştırma adımı olarak iki farklı adımı bulunmaktadır. Deneyle başlanınca bir oksidan olarak eylemde bulunmaları için yakıt örneklerine çeşitli miktarlarda H₂O₂ eklenmiştir. Daha sonra denekler iki gruba ayrılmış ve katalizator olarak eylemde bulunmaları ilk grup formik asit ile diğer grup ise asetik asit ile işleme tabi tutulmuştur. Bunun devamında reaksiyon hızını artırmak amacıyla 60 dakika boyunca 35-75°C sıcaklık arasında karışımlar 1500 RPM ile karıştırılmıştır. Ayrıştırma işlemi için yukarıda ifade edilen fazların her birinden 25 ml kaplara alınmış ve bununla beraber deneklerin seçici sıvı-sıvı çözeltilerle işlendiği ODS'nin ikinci adımı başlamıştır. Çözücünün seçimi oldukça önemlidir. Uygun bir çözücünün en iyi özellikleri yüksek polaritesi ve yakıt içerisinde çözülebilir olmamasıdır. Bir çözücünün kaynama noktası da (BP) önemli olduğu için düşük bir kaynama noktasına sahip olan ve düz distilasyon yoluyla sülfonlardan ayrıştırılması oldukça kolay olan asetonitril seçilmiştir. Baştaki oksidan yoğunluklarına bağlı olarak her bir kaba uygun miktarda asetonitril eklenmiş ve çözücünün reaksiyon hızını arttırmak amacıyla kaplar 20 dakika boyunca çalkalanmıştır. Bu işlem, iki ayrı fazın ortaya çıkmasıyla sonuçlanmıştır. Akaryakıt çözücü maddeden daha ağırdı ve bu yüzden kapların dibine batmıştır. Çalkalanmasını ve yeniden karıştırılmasını önlemek amacıyla kapların kapakları yavaş ve dikkatli bir şekilde açılmıştır. Her bir kaptan 15 ml alınmış ve X-Ray floresan testi (XRF) kullanılarak kükürt içerikleri analiz edilmiştir (RX-360SH/ ASTM-D 4294).

5. SONUÇ VE TARTIŞMA

5.1 Giriş

Bu çalışmada çeşitli faktörler ve parametreler göz önünde bulundurularak Duhok petrol rafinerisinde ağır yakıtlardan örneklerin alınıp oksidatif kükürtsüzleştirme tekniği yoluyla işlenmesi üzerinde durulmuştur. Bu bölüm, elde edilen sonuçları sunmaktadır. Bizim çalışmamızın en önemli amaçlarından biri de kükürtün ayrıştırılması bağlamında hidrojen peroksit ile kullanıldığında asetik ve formik asitin performanslarını değerlendirmek olmuştur. Duhok rafinerisinde başta gözlediğimiz kükürt oranı %4.7 idi.

ODS Süreci Üzerinde Sıcaklığın Etkisi

Oksidatif kükürtsüzleştirme (ODS) yoluyla akaryakıttan kükürtün ayrıştırılması işlemi üzerinde sıcaklığın etkisi de değerlendirilmiştir. Birçok örnek için sıcaklık 35 ile 75°C arasında tutulmuştur. Ve sonuçlar şunu göstermiştir ki reaksiyon için en iyi sıcaklık 65°C olup bundan sonrası reaksiyon üzerinde ters etki yaratmaya başlamıştır.

ODS Süreci Üzerinde Karıştırma Etkisi

Karıştırıcıda 4 ile 6 boyutları kullanıldığında elde edilen kükürt oranı sırasıyla %2.94 ve %2.54 olmuştur. Bu oranlar düşük olmakla beraber ODS reaksiyonunun önemini göstermiştir.

6. SONUÇ

Bu çalışmada Oksidatif Kükürtsüzleştirme (ODS) tekniđi kullanılarak akaryakıttan kükürtün ayrıştırılması incelenmiş ve değerlendirilmiştir. Deneklerdeki reaksiyonlar 55°C sıcaklıkta ve reaktörlerin uyguladığı basınç seviyelerinde yapılmıştır. Her bir denek 80 dakika boyunca işleme tabi tutulmuş ve daha sonra sülfonların ayrıştırılması için asetonitril ile işlenmiştir. Bunun devamında denekler X-Ray tekniđi kullanılarak değerlendirilmiştir. Karıştırmanın sülfür oranının azaltılması üzerinde pozitif bir etkisi olmuştur. ODS tekniđi kükürt oranını %4.7'den %2.54'e düşürebilmiştir.

Aynı şartlar altında gözlendiğinde kükürt oranının azaltılmasında asetik asit formik asitten daha etkili olmuştur.

Reaksiyon en iyi tepkimesini 65° C sıcaklıkta vermiştir. 65°C üzerindeki sıcaklıkta ise ters etkiler oluşmaya başlamıştır.

CURRICULUM VITAE

He was born in Shaqlawa of Hawler - Iraq, 1983. He has completed his primary and secondary education in Hawler. During the period of 2006-2010 He had studied in University of Salahaddin, the college of education, Department of Chemistry. At the February of 2014 He started his master study in Van Yuzuncu Yıl University.



UNIVERSITY OF VAN YUZUNCU YIL
THE INSTITUTE OF NATURAL AND APPLIED SCIENCES
THESIS ORIGINALITY REPORT

Date: 26/04/2018

Thesis Title: Implementing of Decreasing Sulphur From Heavy Fuel Oil Of Zakho By Oxidation Desulphuriation (Ods) Method. The title of the mentioned thesis, above having total 47 pages with cover page, introduction, main parts and conclusion, has been checked for originality by..... computer program on the date of 11/04/2018 and its detected similar rate was 0% according to the following specified filtering

Originality report rules:

- Excluding the Cover page,
- Excluding the Thanks,
- Excluding the Contents,
- Excluding the Symbols and Abbreviations,
- Excluding the Materials and Methods
- Excluding the Bibliography,
- Excluding the Citations,
- Excluding the publications obtained from the thesis,
- Excluding the text parts less than 7 words (Limit match size to 7 words)

I read the Thesis Originality Report Guidelines University of Van Yuzuncu Yil for Obtaining and Using Similarity Rate for the thesis, and I declare the accuracy of the information I have given above and my thesis does not contain any plagiarism; otherwise I accept legal responsibility for any dispute arising in situations which are likely to be detected.

Sincerely yours,


26/04/2018

Name and Surname: Rebeen Ramzi ALI

Student ID#: 149101335

Science: Chemical Engineering

Program: Chemical Engineering

Statute: M. Sc. Ph.D.

APPROVAL OF SUPERVISOR
SUITABLE

Prof. Dr. Nahit AKTAS



APPROVAL OF THE INSTITUTE
SUITABLE

