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Oxidation Desulfurization of Model Fuel by Using Nickle-Molybdenum and Nickle-Tungsten Supported on Activated Carbon

A Thesis
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2023 AD **1445 AH**

قال تعالى:

بسم الله الرحمن الرحيم

{يَرْفَعِ اللَّهُ الَّذِينَ آمَنُوا مِنْكُمْ وَالَّذِينَ أُوتُوا

الْعِلْمَ دَرَجَاتٍ وَاللَّهُ بِمَا تَعْمَلُونَ خَبِيرٌ}

صدق الله العلي العظيم

سورة المجادلة: الآية 11

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Dedicated to

To those through whom I saw my life path...
and from whom I derived my strength
and self-esteem...
To the struggle that never stops... my father
and my mother.
To my support, my strength, and my
companion...my husband,
To those who supported me with their love
and prayers...my brothers,
To my beloved and my refuge during my
academic ordeal...my sister,
To the joy of my life and the beating of my
heart, my little children (Yaman and
Shahm).

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Sura Ahmed Abdulhadi

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Abstract

This work deals with fuel desulfurization by oxidation technique, in which the fuel used here is model fuel and three types of real fuel. The model fuel is n-heptane while the dibenzothiophene represents the organic sulfur compounds, where the oxidative desulfurization of dibenzothiophene (DBT) is conducted by an oxidization system (hydrogen peroxide and acetic acid) at a temperature of 50°C and within a 60 min. The catalysts are molybdenum and tungsten oxides dispersed on activated carbon whereas nickel oxide is investigated here as catalyst promoters NiMo/Ac and NiW/Ac. The prepared catalysts were characterized by X-ray diffraction and Fourier Transform Infrared Spectroscopy (FTIR). The catalyst activity was investigated by studying the impact of three variables: catalyst dosage (0.5–1.5) g, nickel loading (2–6) wt.%, and initial sulfur concentration (400–800) ppm, while the sulfur removing efficiency is considered as the catalyst activity criteria. The experiments were designed according to the combined RSM with the Box-Behnken experimental design, and the results were analyzed and optimized by analysis variance ANOVA. Results showed that sulfur removal efficiency from model fuel ranged between 23 and 71%. These results were fitted with a second-order polynomial model with a high correlation coefficient R2 (0.9719) with optimum sulfur removing efficiency of 75% in the case of using NiMo/AC.

In comparison, the sulfur removing efficiency ranged between 26 to 81%, and the optimum removing efficiency was 84% in the case of using NiW/AC catalyst. ANOVA analysis shows that the significant effect of studied variables follows the order; initial sulfur concentration, catalyst dosage, and Ni wt.% loaded in case of using NiMo/Ac catalyst, while the more affected variables are the initial sulfur concentration followed by Ni% load and catalyst in case of using NiW/Ac catalyst. The NiW/Ac used as a catalyst for oxidative desulfurization with three real fuels (light naphtha, kerosene, and gas oil), the sulfur removing efficiency are 17.4, 61.3 and 85.7 % for light naphtha, kerosene, and gas oil respectively.

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Nomenclature

Abbreviation	Definition
AC	Activated carbon
DS	Desulfurization
ODS	Oxidative desulfurization
HDS	Hydrodesulfurization
EDS	Extractive desulfurization
BDS	Biodesulfurization
ADS	adsorptive desulfurization
ANOV	Analysis of variance
BBD	Box-Behnken design
BT	Benzothiophenes
CAC	Commercial activated carbon
DBT	Dibenzothiophene (C12H8S)
FTIR	Fourier –Transform Infrared Spectroscopy
GAC	Granular activated carbon
LHSV	Liquid hour space velocity
LPG	Liquefied petroleum gas
MAC	Modified activated carbon
min	Minute
PH	Acidity measurement
ppm	Part per million
R 2	Correlation coefficient
RSM	Response Surface Methodology
Ox/S	Oxidant/sulfur molar ratio
S%	Sulfur content percentage

SEM	Scanning Electron Microscopy
ULSD	Ultra-low sulfur diesel
XRD	X-ray Diffraction
SEC	Specific Energy Consumption
DOE	Design of Experimental
SOx	Sulfur oxides
FCC	Fluid catalytic cracking
Ni	Nickel
Ni Mo	Nickel Molybdenum
Mo	Molybdenum
W	tungsten
TNF	2,4,5,7- tetranitro-9- fluorine
SCW	supercritical water
OATS	olefinic alkylation of thiophenic sulfur
CED	Conversion - Extraction Desulfurization
NMP	N-methyl pyrrolidone
DMF	dimethylformamide
HCP	hexagonal closed packed
DFT	Density-functional theory
TMS	transition metal sulfides
NiW	Nickel tungsten
BBD	Box-Bohenken design
CCD	central-composite design

Symbol	**Definition**	**Unit**
Co	Initial sulfur concentration	mg/L
Ce	sulfur concentration at Equilibrium	mg/L
Cs	concentration of sulfur species	mg/L
Cf	final sulfur concentration	mg/L
S0	Initial sulfur content	mg/L
Sf	Final sulfur content	mg/L
S%	Sulfur removal percentage	(-)
P	Power	w
T	Time	min
T	Temperature	C
N	Reaction order	(-)
S area	Surface Area	m2 /gm
rpm	Revolution per minute	rev/min
RE %	Sulfur removal efficiency	Dimensionless

Chapter One

Introduction

Chapter One Introduction

1.1 Background

Petroleum is the primary fuel for industrialized nations. Petroleum is refined into a variety of fuels, the most common of which are diesel and gasoline. Sulfur, often in the form of organic sulfur compounds, is among these things. Sulfur content (S) is the ratio of sulfur by weight in petroleum and may range from over 5% to less than 1% **(Abid, 2015)**. Burning transportation fuel releases sulfur oxides, which contribute to acid rain and fog. Hydrocarbon fuel combustion generates air pollutants such as sulfur and nitrogen oxides. Sulfur content reduction in gasoline has positive health and environmental effects **(Mapiour, 2009).**

As the world moves toward more green fuels, new environmental rules limit the amount of sulfur in liquid hydrocarbon fuels to no more than 11 parts per million (ppm) **(de Luna et al., 2018)**.

As the economy, technology, and demand for crude oil extraction continue to advance at a rapid pace, the quality of the oil continues to deteriorate as the quantity of sulfur-containing compounds in crude oil continues to rise. Hydrocarbons make up the bulk of crude oil, although there are also a variety of sulfur, nitrogen, metals, and oxygen-containing chemicals present. Increasingly stringent environmental laws (especially regarding sulfur levels) have made it difficult for the refining sector to reduce toxic components that are derived from fuels. The main culprits behind these problems are compounds with sulfur, which may be found as impurities in several petroleum fractions **(Hantosh, 2022)**.

Refining facilities have significant difficulties because of these requirements, particularly in the elimination of organic sulfur compounds such as thiophenes and their derivatives. Hydro-desulfurization (HDS), which uses hydrogen under severe working conditions of temperature and pressure, has attracted a great deal of interest as a method for desulfurizing liquid hydrocarbons. The primary issue with this approach is that it is unable to remove resistant sulfur compounds such as Dibenzothiophene **(Bahuguna et al., 2011)**.

Since these conventional methods have their drawbacks, researchers are exploring alternatives such as extractive desulfurization (EDS), oxidative desulfurization (ODS) **(Ja'fari et al., 2018; Rahimi et al., 2017)**, and so on. ODS stands out among these techniques because of the attention it has garnered owing to its simplicity in comparison to its powerful removal effectiveness **(Sajjadifar et al., 2020).**

Owing to its ability to desulfurize petroleum fractions at ambient temperature and pressure, oxidative desulfurization (ODS) is a potential deep desulfurizing method **(Ding et al., 2011)**. The oxidative desulfurization process, in contrast to the more costly hydrodesulfurization method, operates at temperatures below 80 degrees Celsius and boasts good selectivity. **(Bagiyan et al., 2004; Caero et al., 2005)**.

ODS efficiency is a two-step process. In the first step, the sulfur that is present is oxidized to sulfoxide or sulfones in the presence of an oxidation agent. Some examples of oxidation agents include potassium ferrate, tetra-butyl hydroperoxide, hydrogen peroxide, ozone, molecular oxygen, and so on. Hydrogen peroxide, or H_2O_2, is favored among these many oxidant agents owing to its strong oxidation reactivity as well as the fact that it has a cheap cost, is safe, and has a high selectivity **(Choi et al., 2014)**. Additionally, it may be considered a green oxidant, which means that it is good for the environment. The oxidation of sulfur increased the polarity of compounds that included sulfur. The sulfoxides and sulfones may thus be readily extracted from the oil phase by using a polar solvent or adsorbents; this is the second stage in the process **(Choi et al., 2022; Zhu et al., 2012)**.

Non-acidic media may be used for the oxidation reaction if catalysts are present, such as tungsten, vanadium, or molybdenum supported on zeolite, silicates, molecular sieves, etc.**(Murata et al., 2004)**.

Clean fuels may be produced using the oxidative desulfurization process by first oxidizing sulfur compounds to forms with high polarity and then removing the oxidized sulfur compounds **(Bagiyan et al., 2004)**. Cu, Ti, Cr, Mn, Fe, Co, W, and V are all examples of transition metal oxides that have been the subject of many studies as catalysts **(Cedeño-Caero et al., 2008)**.

Furthermore, the oxidation desulfurization process has been investigated using a wide range of reactions, including hydrogen peroxide-formic acid, hydrogen peroxide-acetic acid, hydrogen peroxide-polyoxometalates, ozone, and photooxidation with molecular oxygen in the presence of sensitizers such as cyanoarenes **(Alwan et al., 2020)**.

1.2 Aims of the Study

The present study focuses on:

1. The main aim of the research is the removal of sulfur compounds from fuel using NiMo and NiW as catalysts supported on activated carbon, under some selected operating conditions. The oxidation method will be used, and NiMo and NiW catalysts will be added to facilitate the desulfurization of the model fuel.
2. Where this study is done through the preparation of the catalyst, it is prepared as a NiMo/AC catalyst by loading nickel and molybdenum

oxides on an activated carbon support and as a NiW/AC catalyst by loading nickel and tungsten oxides on an activated carbon support.

3. Investigating the effect of the influential parameters, including the initial concentration of the sulfur, the ratio of the promoter and the dose of catalyst.
4. Examine the prepared catalyst for the desulfurization of real fuels under optimum conditions.

Chapter Two

Literature Review

Chapter Two Literature Review

2.1 Introduction

The desulfurization process is the most important process found in petroleum refineries which is used for the elimination or removal of sulfur content from the different petroleum products because of harmful consequences caused by sulfur presence. The combustion of fuel may produce emission of sulfur oxides SOx that are responsible for acid rain as well as environmental pollution. There are too many technologies used to remove sulfur from petroleum refineries such as Hydrodesulfurization (HDS), oxidative desulfurization ODS, adsorptive desulfurization, etc. The ODS may be considered a promising process because it can be done in moderate conditions **(Mohammed et al., 2020).**

Sulfur organic compounds may take many forms such as thiol (RS-H), sulfides (R-S-R), thiophene (C4H4S) and thiophene derivatives e.g. benzothiophene (C8H6S) and dibenzothiophene ($C_{12}H_8S$). fig 2-1 shows the different sulfur organic compounds **(Alwan et al., 2021)**.

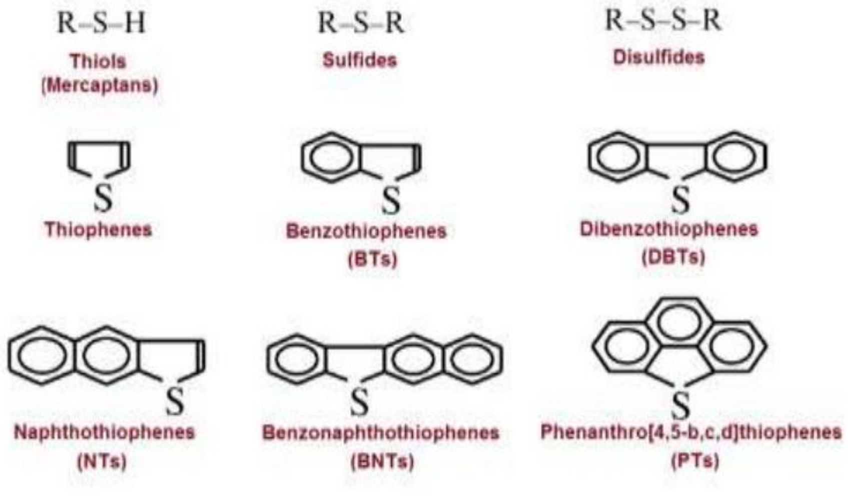

Figure 2.1. Illustrates the sulfur compounds found in the crude oil (C. Song, 2003)

According to the organic theory for the creation of natural petroleum, in addition to hydrocarbons, natural petroleum also had many organic metal compounds, such as organic sulfur, which came from the breakdown of living parts. Organosulfur compounds like organic sulfides and disulfides, thiols, and thiophene are found in the different parts of petroleum. Sulfur was found in crude oils in concentrations between 0.1 and 8% wt.%. This percentage is related to the gravity of the crude oil, so it can be categorized as light or heavy. Organosulfur compounds found in petroleum crude or petroleum fractions range from thiols to thiophene and their derivatives. Figure 2-1 shows some of the sulfur compounds found in petroleum products **(Shafi and Hutchings, 2000)**.

2.2 Desulfurization Methods

There are many technologies used to remove sulfur from different petroleum products, in general. The desulfurization methods can be classified into two major techniques according to using hydrogen, Figure 2.2 summarizes these techniques: HDS based and non-HDS-based categories.

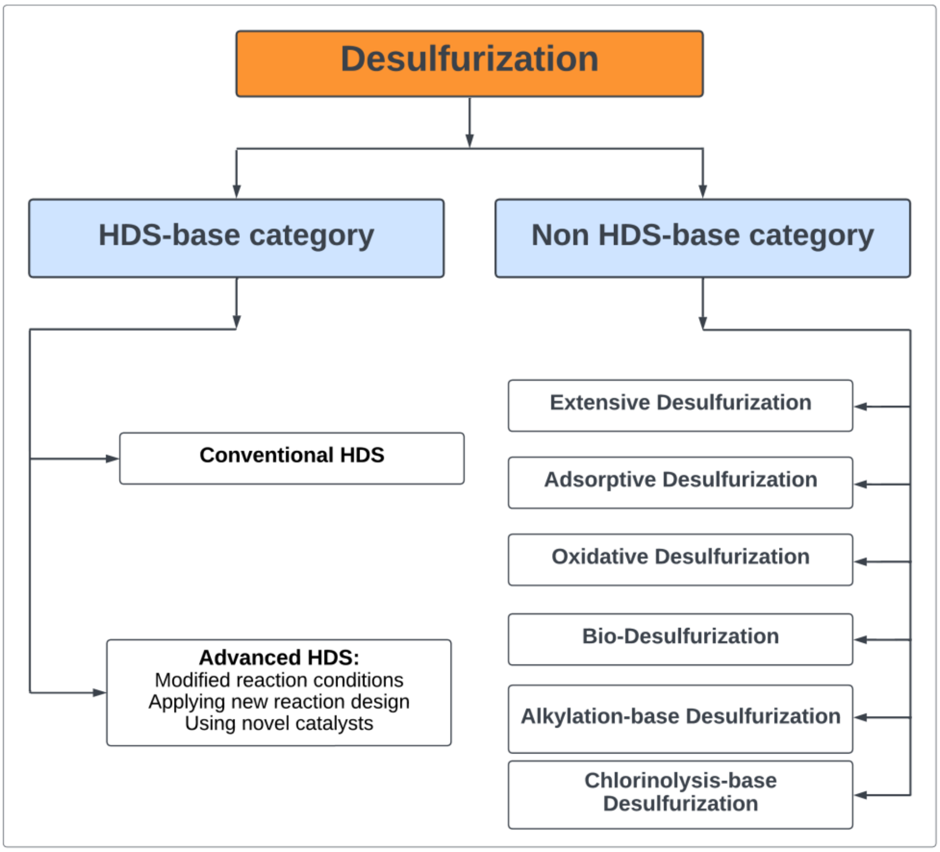

Figure 2.2. Classification of desulfurization technologies by hydrogen role (Babich and Moulijn, 2003)

2.2.1 Hydrodesulfurization (HDS)

Hydrodesulfurization is the most used method in the petroleum industry to reduce the sulfur content of crude oil. In most cases, HDS is performed by co-feeding oil and H_2 to a fixed-bed reactor packed with an appropriate HDS catalyst. The standard HDS catalysts are $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$, but there are many more types available. During HDS, the sulfur in the organosulfur compounds is converted to H_2S. **(Javadli and de Klerk, 2012)**.

Hydrodesulfurization (HDS) in combination with carbon rejection technologies, such as coking and fluid catalytic cracking (FCC), are the main technologies industrially employed for the desulfurization of heavy oil **(Rana et al., 2007)**. Although these technologies are quite capable of desulfurizing heavy oil, their carbon footprints are substantial. All of these technologies, including the production of hydrogen that is needed for HDS, involve high-temperature processing. The refining cost (financial and environmental) increases as heavier, and more sulfur-rich crude oils are being processed. Alternative desulfurization pathways are therefore of interest.**(Javadli and de Klerk, 2012)**.

2.2.2 Adsorptive Desulfurization (ADS)

Adsorptive Desulfurization is recognized as an efficient and economical way to remove OSCs from diesel fuel due to its low energy consumption, its operation at ambient temperature and pressure without the need for using pressurized hydrogen gas, the ability to regenerate the spent adsorbent, and the broad availability of adsorbents **(Nunthaprechachan et al., 2013)**

This method includes adsorptive and reactive adsorption desulfurization. Adsorptive desulfurization involves the physical adsorption of organic sulfur compounds on the solid sorbent surface, whereas reactive adsorption involves chemical interaction. Sulfide bonds sulfur to the sorbent. Flushing spent sorbent with adsorbent removes sulfur as H2S, S, or SOx, depending on the feedstock and procedure. This method's effectiveness relies on the sorbent's selectivity to OSCs, adsorption capacity, durability, and renewability **(Javadli, 2011; Khalfalla et al., 2008; Sulaymon et al., 2009)**.

2.2.3 Extractive Desulfurization

Liquid-liquid extraction is an important kind of separation method that is based on the distribution of chemicals between two different liquid phases. Compared to other separation methods, liquid-liquid extraction often has unique advantages for the separation of chemicals that have high or similar boiling points, with relatively large capacity and low consumption of material and energy **(Qilong et al., 2011)**.

Extractive desulfurization depends on the fact that OSCs are more soluble in a suitable solvent than hydrocarbons. Low temperature and low-pressure applicability is the most attractive aspect of extractive desulfurization. Extractive desulfurization is primarily constrained by the solubility of organic sulfur compounds in the solvent. Enhanced solubility can be achieved by selecting an appropriate solvent in consideration of the sulfur compounds to be removed. Typically, this is accomplished by producing a " solvent cocktail " consisting of acetone and ethanol or tetramethylene glycol and methoxy tri glycol. Preparation of such a " solvent concoction " is relatively challenging and intrinsically inefficient, as its composition is highly dependent on the OSC spectrum present in the input stream **(Babich and Moulijn, 2003)**.

2.2.4 Biodesulfurization (BDS)

BDS, an enzymatic process involving the use of bacteria as biocatalysts to remove OSCs in fuels, is an innovative technology, which uses bacteria as the catalyst to remove sulfur from the feedstock **(Chan, 2010)**. Theoretically, BDS can be conducted in aerobic or anaerobic conditions. In aerobic conditions, OSCs are stepwise oxidized and eventually form sulfate salts in the presence of sulfur-specific desulfurization microbes such as R. Rhodochrous, R. erythropolis D-1, Gordona CYKS1, and Rhodococcus UM3. OSCs are first oxidized to the corresponding sulfoxide, and then to sulfone, followed by sulfinate, and finally to desulfurized organic portion and inorganic sulfate ions **(McFarland, 1999)**.

2.2.5 Desulfurization by Precipitation

This method depended on the formation of complex insoluble charge-transfer materials by contacting complex organic sulfur compounds like; (4,6-DMDBT, referred to as DBT) with 2,4,5,7- tetranitro-9- fluorine (TNF) usually in a batch reactor followed by filtration to remove these complex materials and, the remaining p- acceptor will adsorbate using suitable adsorbent material **(Babich and Moulijn, 2003)**

2.2.6 Chlorinolysis-based desulfurization

Chlorinolysis involves the scission of C–S and sulfur-sulfur (S–S) bonds through the action of chlorine (Eqs. 2.1, 2.2).

R-S-R´ + Cl_2-------------- R-S-Cl + R´-Cl (Eq. 2.1)

R-S-S-R´+ Cl_2------------ R-S-Cl + R´-S-C (Eq. 2.2)

The process is performed at low temperatures (25–80 ºC) and near-atmospheric pressure and requires a short residence time. It requires good mixing of oil and chlorine gas and it requires equipment having adequate corrosion resistance to chlorine. At moderate temperatures and in the presence of water, chlorinolysis can be followed by hydrolysis and oxidation of the sulfur to produce sulfates. A 3:10 volumetric ratio of water to oil works best. This is followed by aqueous and caustic washes to remove the sulfur and chlorine-containing by-products. Around 75–90% of total sulfur can be removed in an hour.

Although the chlorinolysis-based desulfurization method has not been tested with heavy oil or oil sands-derived bitumen, in theory, it has some potential to be applied to bitumen production at steam-assisted gravity drainage (SAGD) sites. In this way the reaction is conducted within the oil sands formation, avoiding much of the cost associated with chlorine-resistant materials. However, there is a safety risk associated with such an operation and the volume of chlorine required is considerable **(Javadli and de Klerk, 2012)**.

2.2.7 Supercritical water-based desulfurization

The effect of supercritical water (SCW) on the desulfurization of oil is marginal **(Vogelaar et al., 1999)**. (11) The purpose of using SCW (critical point of water: 374 °C and 22.1 MPa) as a reaction medium is to break C–S bonds. According to experiments that were carried out at 400 °C and 25 MPa, aromatic sulfur compounds do not react in SCW, but SCW can convert non-aromatic sulfur compounds. Similar findings were reported **(Katritzky et al., 1992; Katritzky et al., 1994; Katritzky et al., 1997; Katritzky et al., 1990)**, who conducted an extensive study on the conversion of sulfur-containing compounds in sub- and supercritical water. It was found that thermal free radical-based conversion dominated and not converted by aqueous ionic pathways.

Some benefit of using SCW was reported for the in situ generation of H2, as well as using SCW as a medium for hydrotreating Athabasca bitumen. These are indirect benefits. The best desulfurization results with SCW were achieved when conventional hydrotreating catalysts were added to the system, which facilitated HDS. The experimental results show that SCW alone cannot remove sulfur appreciably, but in combination with H2 and conventional HDS catalysts; sulfur and metal impurities can be removed. **(Javadli and de Klerk, 2012)**

2.2.8 Alkylation-based desulfurization

There are two types of Alkylation-based desulfurization:

C-alkylation and S-alkylation. The C-alkylation-based desulfurization has been tested with thiophilic sulfur compounds at a small scale, and it is commercially applied for light oil at a large scale as the olefinic alkylation of thiophilic sulfur (OATS) process developed by British Petroleum **(Arias et al., 2008)**. It exploits the aromaticity of the thiophilic compounds to selectively perform acid-catalyzed aromatic alkylation with olefins. This causes the molecular mass and boiling point of the alkylated thiophene compounds to increase, enabling their separation by distillation (Figure 2.3).

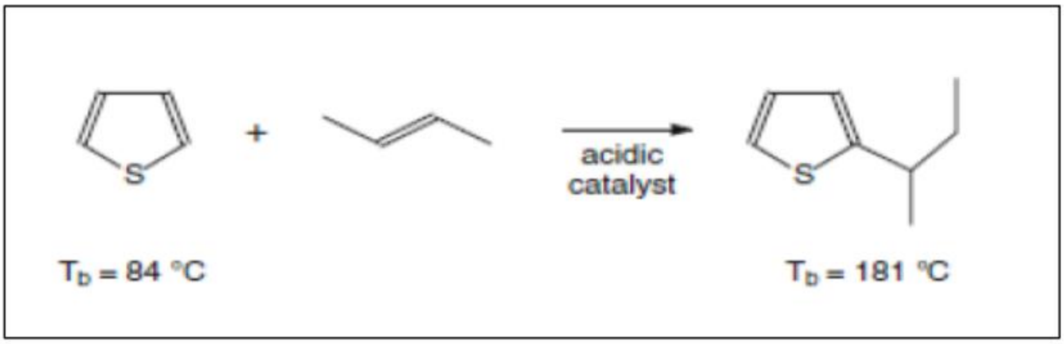

Figure 2.3. Alkylation-based desulfurization illustrated by the acid catalyzed alkylation of thiophene with 2-butene to increase the boiling point temperature (Tb) of the product (Javadli, 2011)

In the S-alkylation-based desulfurization, the alkylated sulfur compounds can then be removed from the oil as precipitates, thereby effectively desulfurizing the oil. It does not require separation by distillation as in the case of C-alkylation, which simplifies the separation. However, alkylation takes place competitively with aromatic hydrocarbons, eroding its applicability to oils that are aromatic rich Since heavy oils tend to be aromatic, this technology is not suitable for the desulfurization of heavy oils (Figure 2.4) . **(Javadli and de Klerk, 2012)**.

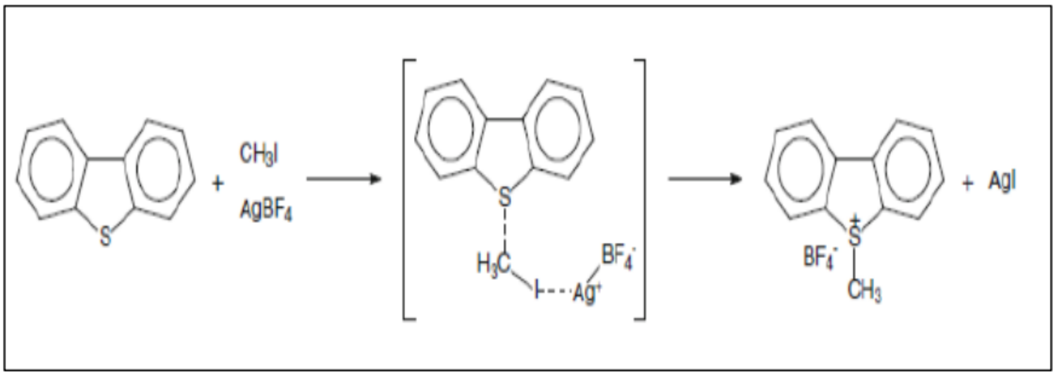

Figure 2.4. Thiophene compounds S-Alkylation by idomethane and sliver tetrafluoroborate to produce S-alkylsulfonion salts (Shiraishi et al., 1998)

2.2.10 Oxidative Desulfurization (ODS)

Oxidative desulfurization has been widely recognized as one of the promising methods for the production of low-sulfur fuels. ODS offers several advantages as compared with traditional HDS, such as milder reaction conditions (ambient pressure and low temperatures), no need for so expensive hydrogen gas, and a high potential for desulfurization of sterically hindered Sulfur compounds, like thiophenes and their derivatives (Figure 2.5). **(Al-Shahrani et al., 2007)**

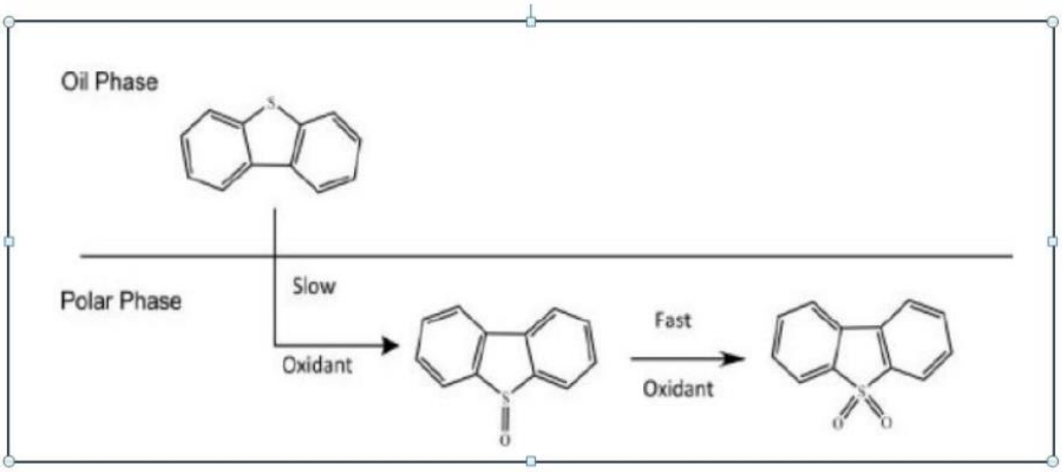

Figure 2.5. Simultaneous oxidation/ extraction ODS process (Campos-Martin et al., 2010)

2.3 History of Oxidative Desulfurization

Oxidative desulfurization is not new. It is believed that the earliest study in oxidative desulfurization area was carried out in 1893 by Kayser using nitric acid as an oxidant **(Mei, 2003)**. UOP made a lot of research since the sixth decade of the last century concerning air oxidation of mercaptans and then developed industrial units using activated carbon-supported phthalocyanine metals as catalysts and sodium hydroxide as co-catalyst. The process has gained a trade mark of MEROX **(Leitão and Rodrigues, 1991)**.

Also, many other companies developed new commercial units depending on an oxidative desulfurization technique by chemical oxidation in the liquid phase, such as oxidative desulfurization process (ASR-2) by Unipure; oxidative desulfurization process by SulphCo using Hydrogen peroxide (H_2O_2) under ultrasound radiation; and Conversion - Extraction Desulfurization (CED) by Petrostar using peroxyacetic acid, but most of these faced economical difficulty due to high cost of construction and operation .

Among these methods, ODS has been frequently suggested as the best technique due to the mild operation conditions and the ease of separation of oxidized sulfur compounds (sulfones). Since the first report of ODS was published in 1967,10, a lot of attempts have been made at ODS. Significantly, the number of reports on ODS has steadily increased over the years with the motive of satisfying the needs of environmental protection agencies regarding the sulfur level in liquid fuels.

A comprehensive review on oxidative desulfurization catalysts targeting clean energy and environment Antony **(Rajendran et al., 2020)**.

2.4 Oxidative Desulfurization Processes

Catalytic oxidative desulfurization (ODS) is one of the promising new desulfurization technologies for decreasing sulfur in different distillates (less than 10 ppm)**(Collins et al., 2003).** Moreover, ODS is one of the most effective ways to remove residual aromatic compounds containing sulfur reaming after hydrotreating processes. The oxidation reactivity seems to increase when the electron density of the sulfur species is higher, dibenzothiophene > 4,6-dimethyl dibenzothiophene> benzothiophene thiophene in the reverse reactivity order of HDS **(Otsuki et al., 2000)**.

ODS consists of two stages; (1) oxidation of aromatic containing sulfur- compounds in distillates, (2) the removal of sulfoxides or sulfones (oxidized sulfur-containing compounds) by either extraction or adsorption **(Campos-Martin et al., 2010)**.

In the oxidation process, the divalent sulfur atom (e,g., thiophene condensate) is oxidized by the addition of the oxygen atoms to form hexavalent sulfur (sulfones) according to the electrophilic addition reaction. The chemical and physical properties of sulfones differ significantly from those of hydrocarbons in fuel oil (increasing relative polarity, which increases solubility in polar solvents) **(Maciuca et al., 2008)**. The oxidized sulfur (sulfone) compounds are more polarized compounds that are removed using a polar solvent like methanol, N-methyl pyrrolidone (NMP), dimethylformamide (DMF), and acetonitrile as shown in Figure (2.6). N-methyl pyrrolidone and dimethylformamide are good solvents for the extraction of sulfone compounds, but they have a boiling point close to sulfones (300 C), making the separation process very difficult and costly. On the contrary, acetonitrile has good physical properties such as low boiling point (82 C), which facilitates separation of sulfones by distillation for further extraction.

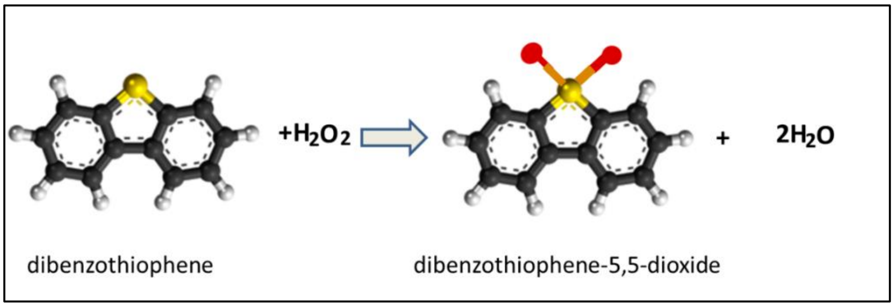

Figure 2.6. Oxidization desulfurization process of DBT (Murata et al., 2004)

2.5 Types of Oxidative Desulfurization

Can be classified into five categories. The first is a two-phase liquid system using H_2O_2 as the oxidant. Next are single-phase liquid systems with organic hydroperoxides as oxidants. The third is a gas–liquid system oxidized using ozone, NO_2, or O_2. Next are biological oxidation systems via O2 and bacteria. A final category is a miscellaneous group of unconventional methods that also cause desulfurization.**(Hebert, 2007)**.

2.5.1. Two liquid phase oxidation system (ODS with aqueous hydrogen peroxide).

Hydrogen peroxide (H_2O_2) is the main oxidizing agent due to its high chemical reactivity and its availability. Also, produces water only as a by-product after performing the ODS process so H_2O_2 can be a green oxidizing agent for liquid-phase organic reactions. The first study in the ODS process is associated with photosensitizer **(Hirai et al., 1996; Hirai et al., 1997)**. The H_2O_2 is the favorable oxidant owing to its high active oxygen content (47%), and acceptable safety in storage and operation. so there is no environmental risk. Consequently, the oxidation of Sulfer-containing aromatic compound was intensely discussed using H_2O_2. The decomposition of H_2O_2 is shown below:

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad \text{(Eq. 2.3)}$$

2.5.2 Single-Phase Liquid System (Organic Peracid)

Hydrogen peroxide with a carboxylic acid, e.g., formic acid and acetic acid is considered as an efficient oxidative-desulfurization system. Firstly, H_2O_2 reacts with the carboxylic group quickly, forming peracid, which reacts with the sulfur atom in aromatic compounds forming sulfoxide and further oxidation for sulfoxide forming sulfones. The oxidation proceeds can perform at a temperature below 70 °C for less than 6 h **(Campos-Martin et al., 2010)**.

The organic peracids are very reactive and highly corrosive **(Otsuki et al., 2000)**. Therefore, it is difficult to be economically feasible because it will need to change the reactors, especially when used at high temperatures. Peracids are difficult to feasible economically because the amount of oxidizing agent is very high in comparison to the sulfur removed. The most common option is the use of transition metal salts, specifically, tungsten salts which have a high catalytic activity and high selectivity **(Al-Shahrani et al., 2007; Kazumasa et al., 2003)** In addition, modified activated carbon was also used, which showed more than 95% sulfur oxidation in the model fuel **(G. Yu et al., 2005)**. Some metals like Co **(Hao et al., 2020)** or Fe **(de Souza et al., 2009)** showed a high ability to perform the oxidation desulfurization process with high yield **(Campos-Martin et al., 2010)**.

2.5.3 Gas-liquid Oxidation System

In this process, oxygen in the air is used to oxidize the refractory sulfur compounds in the presence of catalysts such as MnO_2/Al_2O_3 and Co_3O_4/Al_2O_3 130–200 °C and pressure of 10 bars **(Sampanthar et al., 2006)**. Moreover, $FeBr_3$ stabilized in cyclodextrin can effectively catalyze sulfide oxidation to their corresponding sulfoxides **(Rossi and de Rossi, 2004)**. Air (O_2 in air) can be an ideal oxidant in the ODS process of oil because it is free, readily available, portable, and environmentally friendly. However, the temperature of this process is high and requires different types of solvents, catalysts, and advanced instrumentation, for this reason, it is not as selective as oxidization methods **(Kadijani et al., 2014)**.

2.5.4 ODS Using Miscellaneous Oxidizing Agents

There are different methods of oxidation of organic sulfur compounds using various oxidants such as nitrogen dioxide, chlorine oxide, etc. that can provide molecular oxygen atoms for the S-containing compounds **(Javadli and de Klerk, 2012)**. Photochemical oxidation and ultrasound oxidation are two less-known oxidization methods investigated in several research papers **(Ibrahim et al., 2003)**. The oxidation mechanisms are similar to other oxidation methods, but energy is provided by the use of light or ultrasound instead of heat. The first method is just viable for light oil and the second one cannot be scaled up to use on industrial scales **(Javadli and de Klerk, 2012)**.

- Advantages of ODS

the oxidative desulfurization does not need to build large reactors (inexpensive capital cost). Low operating costs where desulfurization works at moderate reaction conditions (due to low supplied temperatures and no need for hydrogen gas). High selective, especially in the removal of alkylated thiophene. Short stay time due to high-efficiency catalyst **(S. S. Cheng, 2008)**.

2.6 Catalytic Oxidation Desulfurization:

Catalytic ODS Oxidants may use ODS without a catalyst, but the results are poor, and the circumstances are severe. Thus, the initial ODS study by J. F. Ford et al. stressed the necessity for a catalyst for efficient and fast ODS **(J. F. Ford et al., 1967)**. In the same patent, the catalyst promotes selective sulfur compound oxidation. However, research on ODS catalysts shows that catalytic designing is crucial for the selective oxidation of sulfur compounds.**(Hao et al., 2020)**.

Catalysts generate reactive oxygen species (metal peroxo species) from the most desired oxidants, such as H_2O_2 and O2, which speeds up the ODS process. A polyoxometalate (POM) with intrinsic metal peroxo groups may induce ODS utilizing its catalytic oxygen without an oxidant, but an oxidant is required to replenish the POM's metal peroxo species. ODS catalysts reduce ODS's energy barrier and speed up ODS, according to the standard catalytic technique. The gentle operating conditions (low temperature and ambient pressure) and higher efficiency provided by a catalyst that follows green chemistry principle nine make catalytic ODS practicable **(Houda et al., 2018)**. From simple acids to solid composites, a literature review shows a broad spectrum of catalysts used in ODS. In the following sections, ODS catalysts are categorized and evaluated.

2.7 Catalyst

2.7.1 Definition

A catalyst is a substance which used to increase the rate of the chemical reaction or approach the chemical reaction to equilibrium without changing the equilibrium constant, equilibrium conversion, ΔH, and ΔG. It just decreases activation energy which is due to an increase in the number of molecules colliding in a chemical reaction leading to a reaction without change in the involved catalyst. There are three types of catalysts: homogeneous catalysts, heterogeneous catalysts, and enzyme catalysts **(Richardson et al., 1989)**.

The activity of the catalyst depended on the surface area. If a catalyst had more surface area due to more places for other chemical agents to bind, interact, and react. Also, the particle size decreasing causes the surface area to increase with the total mass of the material as same. The particle size in the nanoscale materials has the maximum possible surface area, and the maximum possible reactivity, which is the aim of the catalyst **(Bing Zhou, 2007)**.

2.7.2 Active Components

Active components are the first step in catalyst design which is responsible for the principal chemical reaction **(Richardson et al., 1989)**. The active components were metal (like Pt, Ni, and Fe), oxides and sulfides (like NiO, ZnO, Cr_2O_3, MoS_2, and CuO), and high melting point oxides (like Al_2O_3, SiO_2, MgO, Zeolites, and SiO-Al_2O_3) which helped directly in achieving objectives of the catalyst. The activity, selectivity, and lifetime of the catalyst depended on the proportions of active components loaded on the catalyst **(Voskanyan, 2010)**.

2.7.3 Support

Is providing a large surface area for the dispersion of a small amount of catalytically active agent. This is particularly important when expensive metals, such as platinum, ruthenium, palladium, or silver are used as the active agent. Supports give the catalysts their physical form, texture, mechanical resistance, and certain activity, particularly for bifunctional catalysts. The area of the support can range from 1 - 1000 m^2 /gm. Common supports are alumina, silica, silica-alumina, molecular sieves, etc. The surface area of α - alumina is in the range of 1-10 m2 /gm whereas the surface area for γ or η - alumina can be in the range of 100 – 300 m^2 /gm. Support may be inert or interact with the active component. This interaction may result in a change in the surface structure of the active agent and thereby affect the catalyst activity and selectivity. The support may also exhibit the ability to adsorb reactants and contribute to the reaction process.

2.7.4 Promoter

Promoter (chemistry) was a substance added to a solid catalyst to improve it was given more activity in a chemical reaction with little or no catalytic effect. Some promoters interact with active components of catalysts and thereby change their chemical effect on the catalyzed substance. The interaction may be due to the change in the electronic or crystal structures of the active solid component. More common promoters used in hydrodesulfurization are (Pd–Co–Mo/Al_2O_3), cobalt, and nickel (Ni, promoted, Mo/Al_2O_3 and CoMo/Al_2O_3) **(Akia et al., 2010).** Co-Mo-S catalyst can give higher activity in HDS by the addition of promoters such as (Ni, W). The metal (Co, Ni) had different modulation abilities to S-metal bonding energy. This was the metal increase activity of HDS **(Atta, 2016).**

2.8 Principles of Catalyst Development

The support material was a calcined, amorphous refractory oxide that doesn't have solid molecular sieves. The amorphous, porous refractory oxide support was calcined at a temperature higher than 560 °C. Porous refractory oxide supports include alumina, silica-alumina, silica, gamma-alumina, theta-alumina, zirconia, titania, and magnesia. Amorphous was better because it was more open. The most used support was -Al_2O_3, which had a surface area of more than 100 m2/g **(Kokayeff P., 1990)**.

2.9 Catalyst Preparation

The standard catalyst comprises at least one catalytically active component supported by a catalyst support. The catalytically active components consisted of metals and/or compounds containing metal. In general, the support materials had particular pore volumes and distributions with a high surface area **(Plotkin, 2007)**.

There were different ways to get catalytically active components to stick to catalyst supports. A water solution of the catalytically active parts was soaked into the catalyst base. The support that had been soaked was dried and baked. By precipitation, the catalyst-active component also forms on the catalyst support. A catalyst base that was first soaked with a noble metal solution in water. The metal was then formed on the support by putting a water solution of an alkali metal salt in touch with the saturated support **(O'Brien et al., 1986).**

Preparing a catalyst depends on a lot of things, like the percentage of the solution, how long it stays in contact with the material, the temperature, how it is washed, and how it is reduced.

Mochida and Choi (2006) found that the metal was spread out on a support and that it had an effect as well as a relationship with the support.

The choice of metal salt must be based on its solubility in water, preferred solvent, and dispersibility across the support. The catalyst was impregnated by filling the support's apertures with a solution of metal salt's active species and then evaporating the solvent.

Babich and Moulijn (2003) report that successive impregnation with intermediate precipitation and thermal activation to in solubilize the supported species can increase the metal content concentration. At the time of hydration, impregnation with interaction occurs when the solute to be deposited forms a bond with the surface of the support. This interaction results in an almost atomic dispersion of the precursor of the active species. The interaction may be an ion exchange, an adsorption, or a chemical reaction, although ion exchanges occur significantly more frequently than the other two.

For the salt to precipitate on the surface of the pores, drying was required. This phase can result in an irregular and dissimilar concentration distribution if not conducted adequately. If the rate of drying is too sluggish, the meniscus will evacuate and retreat down the pore. There is some salt deposition, but the majority of the solute simply concentrates deeper within the pore. The salt was deposited at the bottom of a pore or the particle center when it ultimately precipitated. When the drying rate is excessively rapid, a temperature gradient develops. Vaporization deep within the pore forces the solution toward the exterior, where the majority of deposition occurs. When crystallization was sluggish enough to produce homogenous deposits, this was the optimal situation. Because the support has a variety of capillary sizes, it was impossible to satisfy optimal conditions for each. Only through experimentation can the most effective procedures be determined, but some degree of nonuniformity must always be anticipated. These effects can be utilized advantageously when concentration profiles are desired for process purposes **(Magee et al., 1998).**

Calcination is any heat treatment done to break down precursor compounds (generally with the release of gas) and/or allow solid-state reactions to happen between different catalyst components and/or make the catalyst sinter **(Richardson et al., 1989)**. In most cases, the calcination temperature was not lower than the temperature at the industrial building where the process took place.

2.10 The oxidation Reaction by H_2O_2

The oxidative desulfurization method is regarded as a two-step reaction. In the first step, sulfur-containing compounds are oxidized by an oxidizing agent such as hydrogen peroxide to their corresponding sulfones or sulfoxides which are comprised of the addition of two oxygen atoms to the sulfur but without breaking any carbon–sulfur bonds. In the second stage, these highly polarized products are removed from the fuels by adsorption, liquid-liquid extraction, and emulsification as shown in Figure 2.5 **(Zeng et al., 2014)**. The first reaction (2.4) is considered fast while the second reaction (2.5) is slow. The formula for the oxidation desulfurization mechanism is such as:

$$H_2O_2 + HCO_2H \rightarrow HCO_3H \qquad (2.4)$$

$$1,2 + 2HCO_3H \rightarrow 1,2\text{--}O_2 + 2HCO_2H \qquad (2.5)$$

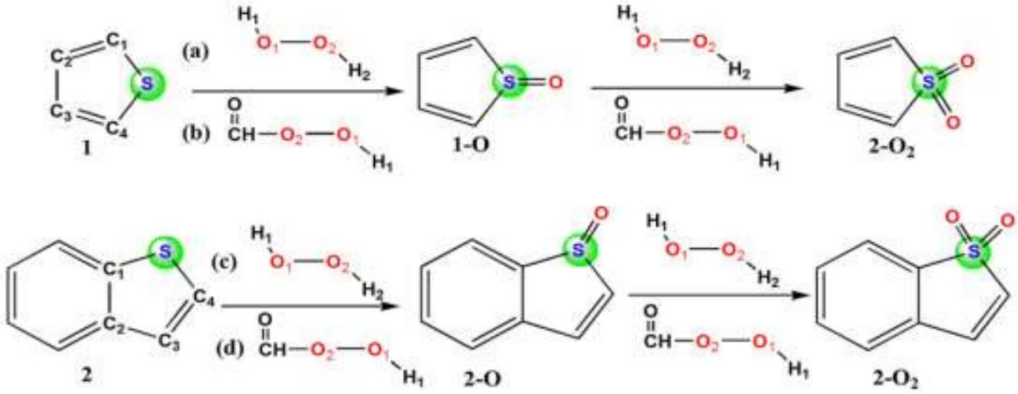

Figure 2.7. Oxidization utilizing (1) (H_2O_2) and (2) HCO_3 H as oxidants (Zeng et al., 2014)

Following that, a purification step is undergone during oxidized sulfur compounds are separated from oils due to their different physical and chemical properties from the original sulfur compounds.

When choosing oxidizers, the following factors should be considered.

- Price
- Reaction products.
- the amount of active oxygen.
- The capacity for displaying selectivity during application.

There are many oxidizing factors, but hydrogen peroxide is the primary factor in the desulfurization reaction because water and oxygen are the only byproducts of the reactions or degradation that are harmless to the environment, as demonstrated by the equation (2.6) below. It is a chemical compound whose formula, H_2O_2, has a very faint blue hue.

Its natural environment is most often used to remove oxidized sulfur compounds with the assistance of catalysts under normal conditions (Zhang et al., 2009; Chan, 2010

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (2.6)$$

Hydrogen peroxide is agitated under the photosensitizer due to its instability, and light radiation is used to oxidize the sulfur compounds excited by hydrogen peroxide, particularly BT. However, this procedure is not industrially applicable due to its lengthy reaction time **(Campos-Martin et al., 2010)**. Ultrasound-assisted oxidative desulfurization (UAODS) can be utilized to improve the efficiency of oxidation desulfurization. **(Duarte et al., 2011)** combined ultrasound irradiation with H_2O_2 and CH_3COOH for sulfur removal on sulfur-containing gas oil and hydrocarbon fraction feedstock (BT, DBT, and di-methyl DBT).

2.11 Activated Carbon Modifications

Recently, many studies have focused on applications of activated carbons for ultra-deep desulfurization. The results showed an improvement in the capacity and selectivity upon oxidation. The latter is an important factor since on the surface of unmodified activated carbons other aromatic components of liquid fuels are also adsorbed in significant quantities. Oxidation increases the selectivity of DBT adsorption via an increase in the number of specific adsorption centers, whereas the adsorption of aromatic hydrocarbons decreases with an increase in the extent of oxidation. Moreover, it was also shown that selectivity can be improved when metals, such as copper are present on the surface of activated carbons **(Mykola and Teresa, 2010)**.

Activated carbons due to their low cost, high surface area, thermal and chemical stability under anoxic conditions, receptivity for modification, and high affinity toward adsorption of aromatic and refractory sulfur compounds have been extensively studied for the removal of TC from different fuels. Activated carbon pores have a slit shape geometry that is more suitable for adsorbing planar aromatic compounds (e.g., TC), compared to the cylindrical zeolite pores that are more suitable for the adsorption of non-planar molecules **(Moosavi et al., 2012)**.

The surface of activated carbons consists of hydrophobic graphene layers and hydrophilic functional groups. Organic compounds are adsorbed on the former, whereas polar species are adsorbed on the latter. The treatment with an oxidizing agent, either in the gas phase or in solution, introduces a large amount of oxygen-containing surface complexes on the surface of AC, which makes the activated carbon more hydrophilic and acidic. Although chemical oxidation results in the fixation of both oxygen and nitrogen functional groups on the surface of activated carbon, it does not significantly modify the textural properties of activated carbon. This treatment enhances its adsorption and modifies its selectivity to aqueous metal cation species.

The oxygen functional groups on activated carbon can act as acids or bases, showing properties of ion exchange and coordination. For the oxidation treatment, various reagents including concentrated nitric or sulfuric acid, sodium hypochlorite, permanganate, bichromate, hydrogen peroxide, transition metals, and ozone-based gas mixtures have been used as oxidizers **(X. Song et al., 2010)**.

Dispersion of oxides on high area supports is carried out by one of four methods: precipitation, adsorption, ion exchange, and impregnation. Depositing active components on the internal surface of porous particles requires special attention to avoid pore-diffusional limitations that give uneven distributions **(Richardson et al., 1989)**.

2.12 Previous Works

G. Yu et al. (2005) studied the desulfurization of diesel using activated carbons for dibenzothiophene (DBT). In the presence of activated carbon and formic acid, hydrogen peroxide was studied for the oxidative desulfurization of a commercial diesel fuel containing 800 ppm sulfur. The residual sulfur content of the oxidized oil was significantly lower (142 ppm). Sulfur was extracted from diesel oil with 82 % oil recovery

Shakirullah et al. (2010) examined the desulfurization of kerosene, diesel oil, heavy residue, and commercial furnace oil via extraction with aqueous sodium hydroxide solutions. The sulfur content of kerosene, diesel oil, heavy residue, and commercial furnace oil can be decreased to 59, 62, 67, and 62 %, respectively, at 40 °C, a 10 % sodium hydroxide concentration, in 30 minutes.

Yazu et al. (2010) naphtha/acetic acid (AcOH) biphasic system was investigated for oxidative desulfurization using H_2O_2 in the presence of H_2SO_4 (313 K, 1 ml H_2O_2). In the octane/AcOH biphasic system, the organosulfur compounds were oxidized with H_2O_2 in the presence of H_2SO_4. Since most of the oxidized sulfur compounds were found in the AcOH phase, it was this phase that was used to gradually purge the octane phase of sulfur compounds. Adsorption with silica gel further decreased the sulfur content of the naphtha to below 0.5 mass ppm after it had been treated with an oxidative process.

Jiang et al. (2011) studied the use of H2O2/organic acids, H2O2/heteropolyacids, H2O2/Ti-containing zeolites, and other non-hydrogen peroxide systems (such as t-butyl hydroperoxide) for the oxidative desulfurization of fuel oils (6000 ppm). The purpose of this research was to determine whether, under moderate circumstances, H2O2 could be used to selectively oxidize the sulfur-containing compounds contained in diesel to their corresponding sulfones in the presence of amphiphilic emulsion catalysts. Using a polar extractant, the sulfones in the oxidized fuel oils may be extracted. After oxidation and extraction (under 100 C, 30% oxidant, 70 minutes), the sulfur content of prehydrotreated diesel was reduced from a few hundred g/g to 0.1 g/g. In contrast, the sulfur content of straight-run diesel was reduced from 6,000 g/g to 30 g/g.

Shen et al. (2016) aimed at ultra-deep oxidative desulfurization (ODS) of dibenzothiophene (DBT) and 4,6-dimethyl dibenzothiophene (4,6-DMDBT) to control air pollution. Hydrogen peroxide which is considered the “green” oxidant was used, and for the extreme liquid−liquid phase ratio (usually larger than 1500) reaction system, the pore volume of 0.19 mL/g of the catalyst provides enough space for storage of hydrogen peroxide. The as-prepared catalyst offers a high interfacial surface area of 116.9 m2/g and enhances the reaction by facilitating mass transfer. The mono-dispersed TiO2 exhibited good crystallinity. The catalyst showed high activity and good stability for producing ultra-clean fuels: 100% conversion was obtained within 2 min and the conversion decreased from 100.0±1.0 % to 94.3±0.6 % after 5 cycles.

Mojaverian Kermani et al. (2018) the Keplerate nanoball iso-polyoxomolybdate supported on activated carbon (AC) has been synthesized and evaluated as a new, green, and cost-effective catalyst inoxidative Its purpose desulfurization of the model fuel containing dibenzothiophene (DBT). Studies showed that the catalyst was highly efficient in the removal of DBT using hydrogen peroxide (H_2O_2) as the oxidant, which could result in a sulfur removal of up to 99.5% (or even more than that) under optimum reaction conditions.

Kayedi et al. (2021) has been surveyed desulfurization with particular attention to the effect of temperature, Fe^{+2}/H_2O_2 (650 ppm) molar ratio, residence time, fluid viscosity, and agitation speed. In this research reduction of sulfur content of understudy fuel from 650 to 800 ppm to 185.7 ppm during 45 min of oxidative reaction. The sulfur removal efficiency predicted by the software was 86.47% and the value from the experiment was 89.39% while it was arranged based on the severity index for more accuracy of results through 45 minutes,35 ^{o}C, 2.98% oxidant. As a result, removal efficiency with Fenton reactions as a strong economic process under a pseudo-first-order kinetics model was approved.

Chapter Three

Experimental Procedures

Chapter Three Experimental Procedures

3.1 Introduction

The experimental work for this work included the following:

a) Using activated carbon (AC) purchased from the local market as a support for the catalyst.

b) The catalyst was prepared by wet impregnation AC with nickel molybdenum and tungsten precursors.

c) Molybdenum and tungsten act as active components in the catalyst, while nickel act as promoter components.

d) Characterization of prepared two catalysts *x*NiMo/AC and x NiW/AC, in which x represented the loaded nickel percent.

e) The catalyst activity was investigated for oxidative desulfurization reaction ODS from model fuel and as follows:

   i. The catalyst dosage (weight), sulfur initial concentration, and Nickel loaded percent are chosen as studied variables for ODS for both catalysts.
   ii. The effect of these variables is managed by using the Box-Behnken design experimental for both catalysts.
   iii. The results were analyzed with Minitab software version 17.

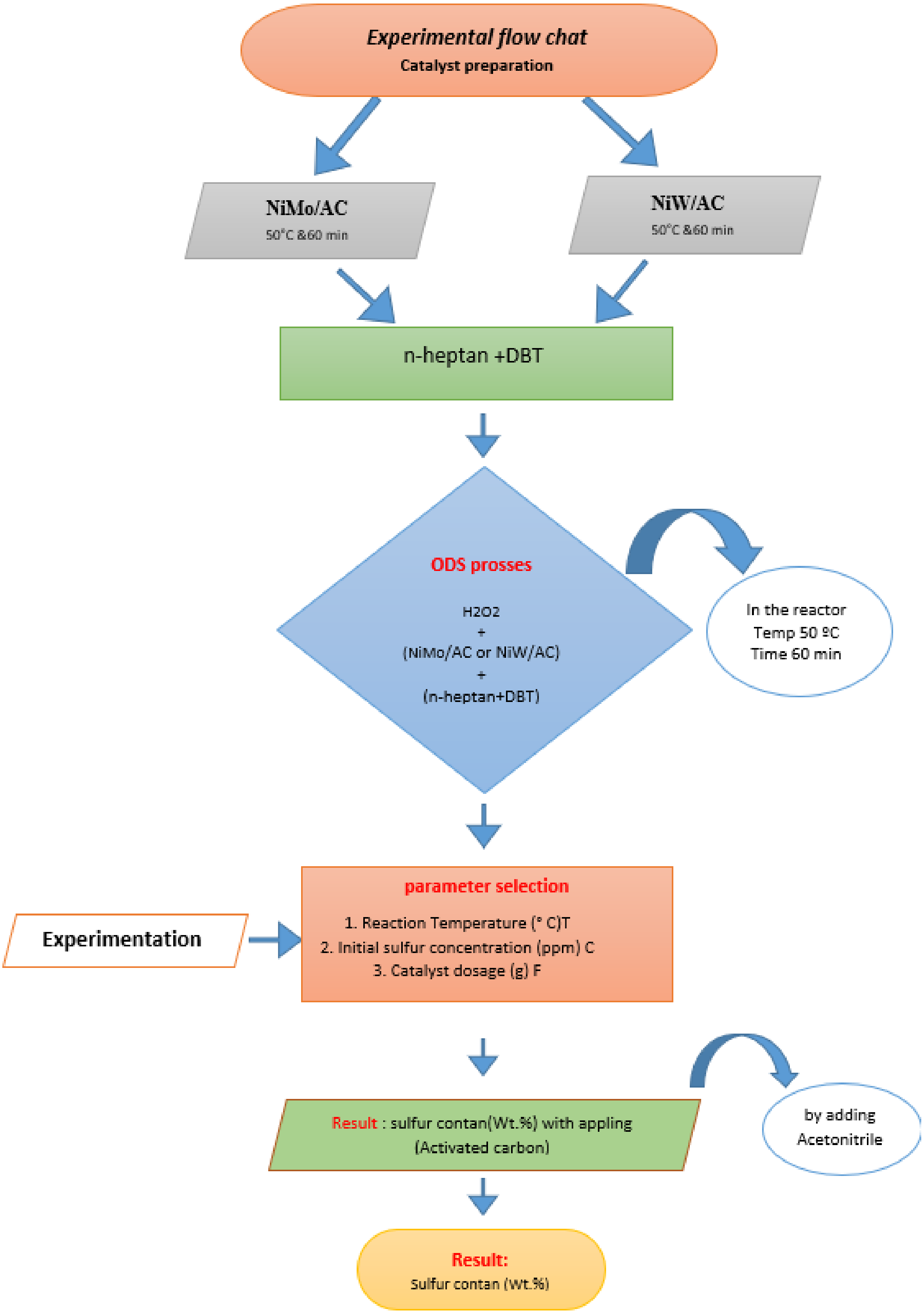

Figure 3.1. Flow chart of the experimental work.

3.2 Materials

The chemical materials used are shown in Table 3.1.

Table 3.1. The chemical materials used in the work.

No.	Material	State	Chemical formula	company	Purity
1	Activated Carbon AC	Solid	C		
5	Nickel nitrate hexa hydrate	Solid	$Ni(NO_3)_2.6H_2O$	AAG	99%
5	Ammonium Penta tungstate AMT	Solid	$(NH_4)_{10}W_{12}O_{41}.5H_2O$		
	Hydrogen peroxide	Liquid	H_2O_2		
6	Ammonium heptamolybdate tetra hydrate AHM	Solid	$(NH_4)_6Mo_7O_2.4H_2O$	HOPKIN & WILLIAMS	99%
7	Heptane	Liquid	C_7H_{16}	J.T. Baker	99%
8	Dibenzothiophene	Solid	$C_{12}H_8S$	Riedel-de Haen	99%
9	Distilled water DW	Liquid	H_2O		
10	Glacial acetic acid	Liquid	CH_3COOH	GCC	10%

3.3 Laboratory equipment

Table 3.2 lists the laboratory equipment utilized.

Table 3.2. Listed laboratory equipment used in this work.

No.	Equipment	Specifications	Model
1	Electrical oven	300ºC	DHG-9055A
2	Electric furnace	300ºC / <=133 Pa	DZF-6020
3	4 digits Balance	Max 210g, D=0.1 Sartorius	BL 210S
4	Water bath	-	-

3.4 Catalyst Preparation

1. The activated carbon AC purchased from the local market was chosen as catalyst support. The AC has a surface area is 568.8 m^2/ g, with pore volume is 0.0062 cm^3/g.
2. There are two catalysts prepared by wet impregnation for AC; the first catalyst is nickel oxide – molybdenum oxide (NiO_2-MoO_3) and, the second one is nickel oxide -tungsten oxide (NiO_2-WO_3), in which the NiO_2 acted as the catalyst promotor, while MoO_3 and WO_3 as an active phase for catalyst
3. The MoO_3 was loaded at about 15 wt.% and the NiO_2 loading percent was chosen as the operation variable to investigate the effect of NiO_2 loading as a catalyst promotor. The preparation procedure is as follows.

a. 10 g of AC was weighed and poured into a three-neck flask.

b. The associated moisture and trapped air in AC were evacuated by using a vacuum pump.

c. 2 g of Ammonium heptamolybdate tetra hydrate AHM salt (molybdenum oxide source) was dissolved in DW.

d. 1.0289, 2.0594, and 3.0891 g of nickel nitrate hexahydrate salt Ni (NO3)2.6H2O (as NiO2 source) were dissolved in DW to get loading percent for nickel oxide weight percent; 2%,4%, and 6% respectively and they symbolized as %NiMo/AC, 4%NiMo/AC, and 6%NiMo/AC.

e. The solution prepared in insteps c and d was dropped co-precipitation on the AC surface to precipitate nickel and molybdenum oxides.

f. The impregnated AC was dried at 110 °C for two hours.

g. After drying the calcination step was done at 400°C for four hours.

h. The prepared catalyst was symbolized according to nickel oxide loading percent.

4. Step 3, was repeated to prepare the second catalyst in the same manner with different nickel loading amounts and symbolized as2%NiW/AC, 4%NiW/AC, and 6%NiW/AC for 2%,4%, and 6% nickel loading respectively, while the W loading is 10%, in which the tungsten source is Ammonium Penta tungstate AMT.

3.5 Catalyst Characterizations

The prepared catalysts were characterized by:

3.5.1 X-Ray diffraction:

XRD is the most important test which is used for identifying the prepared materials. XRD device used here, Shimadzu Model XRD- 6000 – Japan. The investigation was done with Cu wavelength radiation in the range (2θ =5-60 °) and a power source. XRD device located in the College of Materials / University of Babylon.

Figure 3.2. Shimadzu XRD device model XRD 6000.

3.5.2 Energy Dispersive X-ray Spectrometry (EDS)

Energy Dispersive Spectrometry EDS (BRUKER Model X Flash 6l10 Germany) was used to analyze elements found in prepared catalysts. EDS located in the Petroleum Research and Development Center / Ministry of Oil

3.5.3 Surface area and pore volume

Brunauer, Emmett, and Teller BET method were conducted at Thermo Analyzer to measure surface area and pore volume, these tests were conducted at the Petroleum Research and Development Center / Ministry of Oil. Using Brunauer, Emmett, and Teller (BET) method with Thermo Analyzer/USA shown in Figure 3.4 according to ASTM D1993.

Figure 3.3. BRUKER EDS device model X Flash 6-10.

Figure 3.4. BET device.

3.5.4 Catalyst activity investigation

The catalyst activity was investigated by applying oxidative desulfurization reaction ODS for model fuel,

1. The model fuel (DBT dissolved in n-heptane) was prepared by three different DBT concentrations (400, 600, and 800) ppm where the required DBT concentrations were specified according to Box-Behnken experimental design BBD.

2. ODS reaction was done in reaction vessel set up as shown in Figure 3.5 and the reaction was conducted as follows:

a. The model fuel was poured into the reactor with continuous mixing.
b. The reactor content was heated to 50°C by pumping hot water into the reactor jacket.
c. At the temperature reached the required temperature, the specified catalyst dosage and 10 ml oxidation agent (hydrogen peroxide) H2O2 with 5 ml of acetic acid CH_3COOH were added with continuous mixing by a magnetic stirrer.
d. The reaction was stopped after 60 minutes.

e. Subsequently, OSCs were converted into polar compounds e.g., sulfides converted to sulfoxide and/or sulfones which can be easily separated from fuel by adding acetonitrile (solvent extraction). The separation by extraction was done by using a separation funnel where the upper phase is the low sulfur fuel content while the lower layer is the mixture of oxidative products and solvent (acetonitrile).
f. The final sulfur content was measured by X-ray fluorescence (sulfur meter model RX-620SA / Tanka Scientific) as shown in Figure 3.6.
g. The DBT conversion (sulfur percentage removal) R% is related to initial (S_i) and final (S_f) concentrations according to the following equation:

$$DBT\ conversion(R\%) = \frac{Si-So}{Si} \times 100 \qquad (3.1)$$

h. The results were analyzed with Minitab software version 17. and for both catalysts % x NiMo/AC and % x NiW/AC where x represents the nickel percentage loading.
i. After the optimization conditions were determined during the analysis of the results, these conditions were used for the application of ODS reaction on real fuel (light naphtha, kerosene, and gas oil).

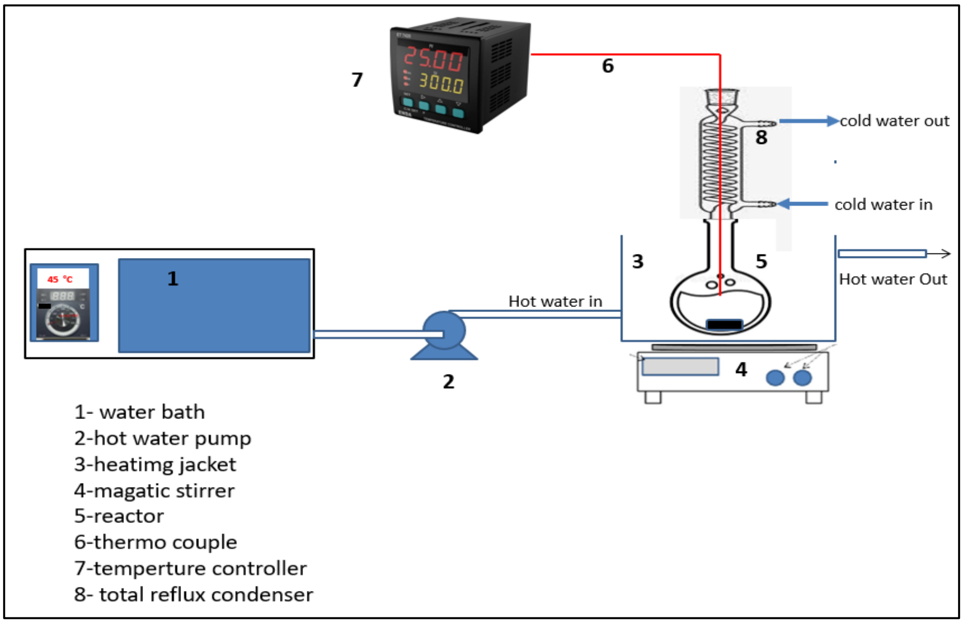

Figure 3.5. Experimental scheme of the oxidation process.

Figure 3.6. Experimental setup.

Figure 3.7. Sulfur content meter device.

3.4 Experimental Design

3.4.1 The Box-Behnken of Experimental DOE

The Box-Behnken experimental design can be used to study experiments with a low possible number of experiments with high accuracy compared to classic methods. The Box- Behnken was designed to remove the sulfur component from gas oil are investigating the relationship between experimental factors and responses. The independent factors chosen in the design of Box-Behnken are **(Lal et al., 2019)**.

3.4.2 Using Box-Behnken design with response surface methodology RSM

RSM is a practical procedure used for evaluating the relation between actual experimental results (response) with studied variables (control variables), and this is usually done by combining RSM with factorial design techniques such as central-composite design CCD and Box-Bohenken design BBD **(Alwan et al., 2021)**.

BBD technique can reduce the required number of experiments without decreasing the accuracy of the optimization in comparison with other factorial design methods **(Alwan et al., 2021)**.

The required experiments number to cover the studied variables system according to using BBD is:

$$N = 2k(k-1) + r \qquad \text{(Eq. 3.2)}$$

Where N is the number of experiments, k is the number of variables, and r is the replicate number of central points (3-6). BBD stated that the levels of the studied variables were adjusted to only three levels (-1.0, 1) with equal values for the interval between each level, thus for three variables with three levels, the number of experiments was 15 -18 depending on the number of replicated experiments number (r in the equation). The catalyst dosage, Ni% loaded in the catalyst, and initial sulfur concentration is chosen as studied (controlled) variables on DBT conversion (Table 3-3), and the experimental design using design expert version 13 as shown in Table 3-4.

Table 3.3. Independent (controllable) variables and their levels.

variables, unit	**symbol**		**levels**		
	coded	**Actual**	**-1**	**0**	**1**
Catalyst dosage, g.	x_1	X_1	0.5	1.0	1.5

Ni% loaded	x_2	X_2	2	4	6
Sulfur initial concentration ppm	x_3	X_3	400	600	800

Table 3.4. Box-Behnken design matrixes.

Design Parameters				**Design Parameters**				**Design Parameters**			
Run	$\mathbf{x_1}$	$\mathbf{x_2}$	$\mathbf{x_3}$	**Run**	$\mathbf{x_1}$	$\mathbf{x_2}$	$\mathbf{x_3}$	**Run**	$\mathbf{x_1}$	$\mathbf{x_2}$	$\mathbf{x_3}$
1	1	0	-1	6	0	1	1	11	0	0	0
2	-1	0	1	7	0	-1	-1	12	-1	0	-1
3	1	-1	0	8	0	0	0	13	0	1	0
4	1	1	0	9	0	0	0	14	-1	1	0
5	0	-1	1	10	1	0	1	15	-1	-1	0

The experiment results for the effects of catalyst dosage (x_1), Ni wt. % loaded on the catalyst (x_2) and, sulfur initial concentration (x_3) on oxidative desulfurization were fitted as second-order polynomials, and it can be used to estimate predict values and optimization the system, for three variables where the second-order polynomial represented by equation.

$$R\% = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j + \varepsilon \qquad (2)$$

Where R% is predicated response, β_0 is the intercept coefficient, β_i is the linear effect (slope) of input variable x_i, β_{ij} is the interaction effect of linear by linear between two input variables x_i, and B_{ii} is the squared effect.

Chapter Four

Result and Discussion

Chapter Four Result and Discussion

4.1 Characterization of the prepared catalyst

4.1.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR test was done for the 6 wt.% NiMo and 6 wt.% NiW, which is shown in figures 4-1 and, 4-2, the FTIR spectra in the range 400-4000 cm^{-1}, and the peak in the band range (400 – about 900) correspond to MoO3 **(Latoof and Hassan, 2022).**

The spectrum for carbon when it's used as support shows the main band at 1100 ±1050 cm^{-1}, but in the molybdenum-based catalyst, this band disappeared because of impregnation of the support with different active component solutions via interaction between precursor and support **(Vázquez et al., 1999)**. The band associated at range 1114-1180 cm^{-1} was assigned as the interaction between carbon and tungsten or WC stretching vibration mode of isotropic cubic phase **(Hoffmann et al., 2003)**.

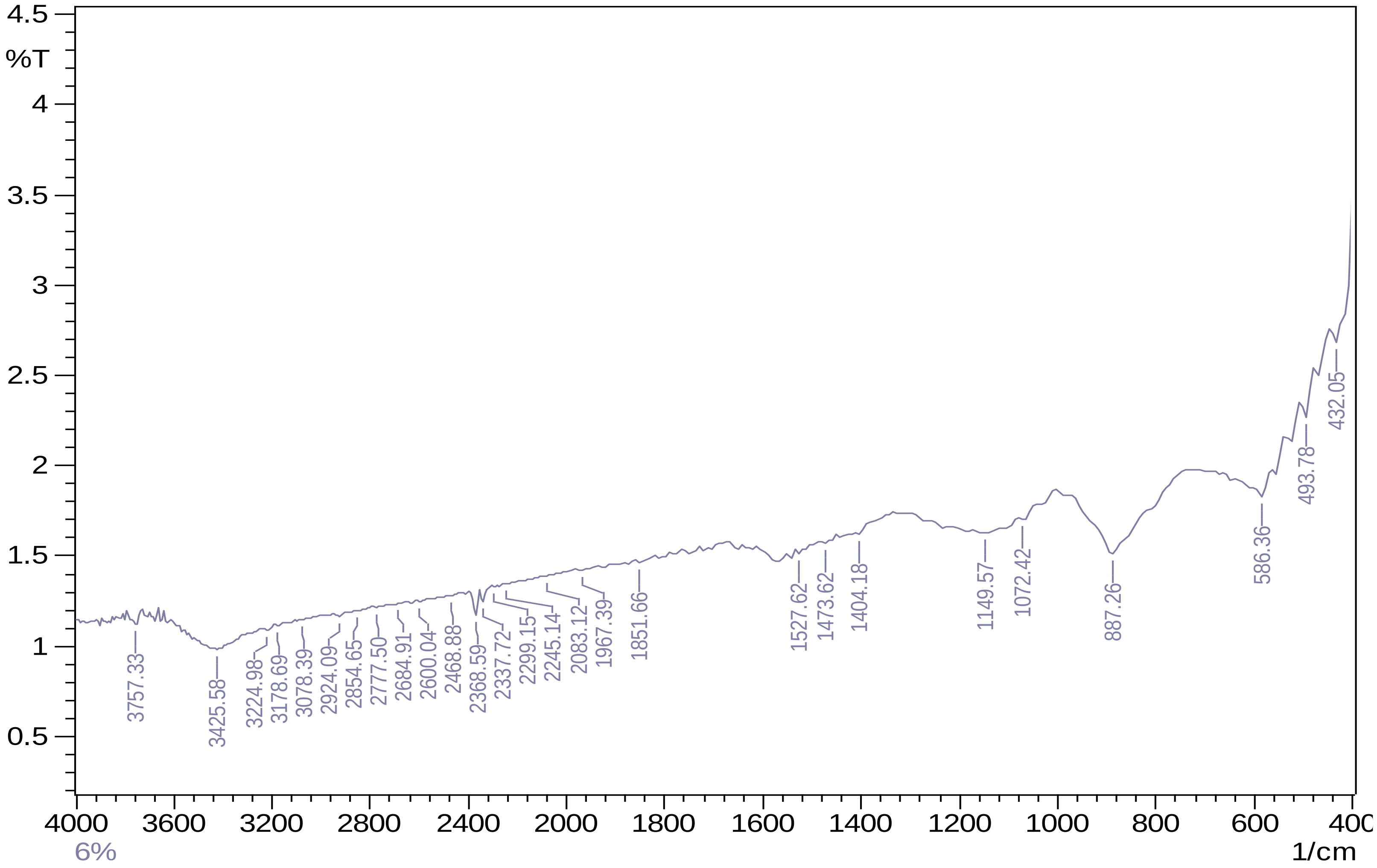

Figure 4.1. FTIR spectra 6 wt.% NiMo catalyst.

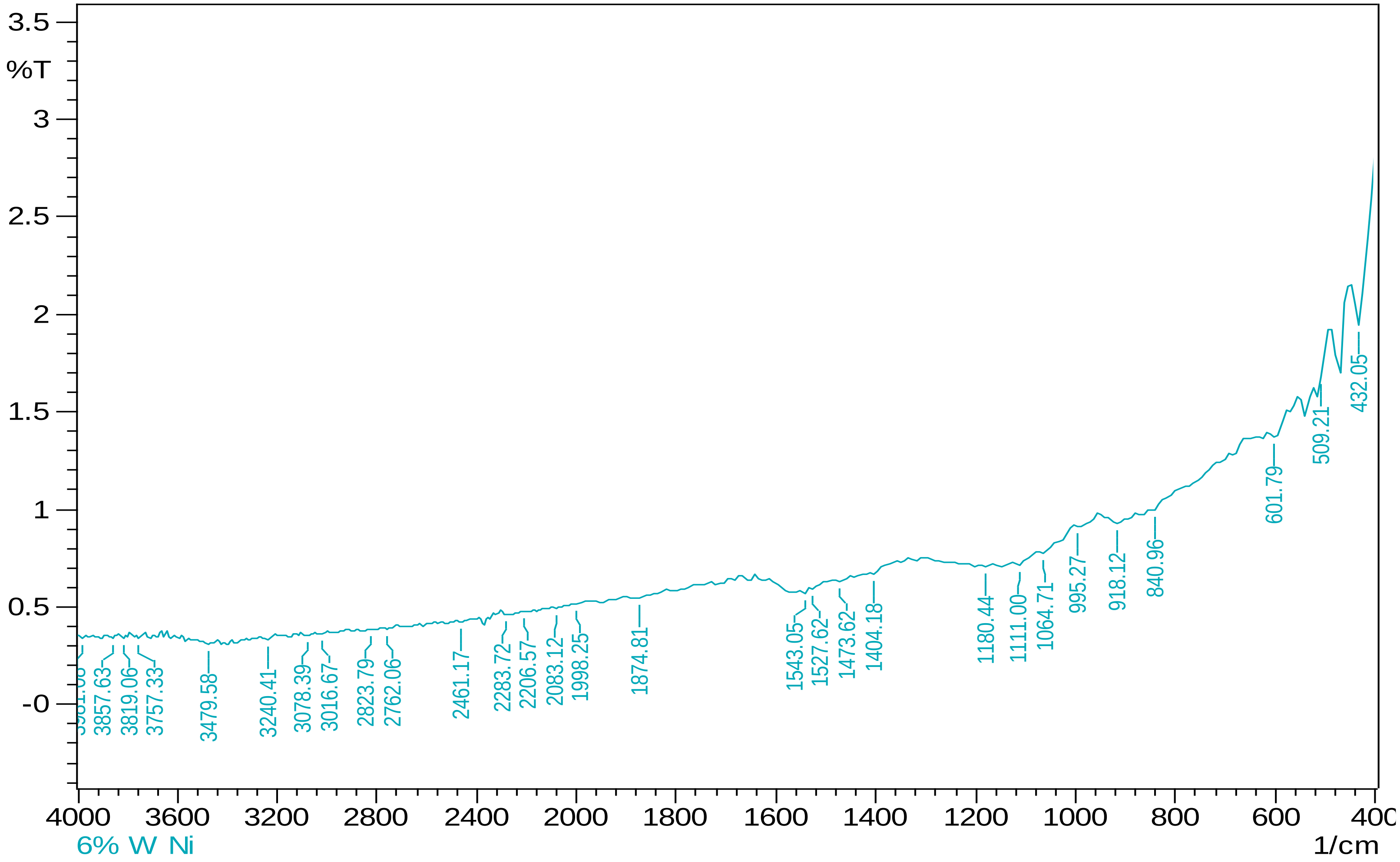

Figure 4.2. FTIR spectra 6 wt.% NiW catalyst.

4.1.2 X-Ray diffraction (XRD)

Scherer`s equation is used to measure particle size according to this formula **(Alrubaye, 2013)**, **(Alrubaye 2013)**:

$$D_P = \frac{0.94\,\lambda}{\beta.\cos(\theta)} \quad \text{(Eq. 4.1)}$$

Where:

DP = Crystalline size (nm).

λ = X-ray wave length = 1.5406 Å.

θ = Bragg angle (deg.).

β = Line width at half maximum FWHM.

While Bragg's law is the basis of XRD principles for materials stated below :(Cullity 1978)

$$n\lambda = 2d_{(hkl)}\,sin\,(\theta) \quad \text{(Eq. 4.2)}$$

Where:

n = an integer representing the order of different peaks.

d = spacing distance.

hkl = Miller indices.

Figure 4.3 displays the XRD (X-ray diffraction) patterns illustrating the characteristics of two nickel-molybdenum/activated carbon (NiMo/AC) catalysts. The red curve corresponds to the 6 wt.% NiMo/AC catalyst, whereas the blue curve represents the 2 wt.% NiMo/AC catalyst. The peaks observed at approximately 28.9° and 28.77° in the 2θ range indicate the presence of graphite (carbon) in the 6% NiMo/AC and 2% NiMo/AC samples, respectively. This information aligns with the findings reported by **Wang et al. (2020).** Additionally, the XRD pattern reveals a peak at approximately 27.38° for molybdenum trioxide (MoO3) in the 2% NiMo/AC catalyst. In comparison, peaks at 32.72° and 39.26° are observed in the 6% NiMo/AC catalyst, as characterized by JCPDS No. 05-0508. The well-defined nature of these peaks suggests that MoO3 possesses favorable crystalline properties, corroborating the observations made by Juehan and supported by the works of **Dedual et al. (2014)**, **Jang and Park (2012)**, and **Alwan et al. (2021)**.

The X-ray diffraction (XRD) analysis revealed the presence of the diffraction of the NiMoO4 phase in both the 6% NiMo/AC and 2% NiMo/AC samples, as evidenced by diffraction peaks at approximately 23.94° and 23.46°, respectively. These observations align with the standard reference card JCPDS No. 86-0361 **(Ghosh et al., 2013)**.

Additionally, the nickel oxide diffraction pattern displayed peaks at approximately 43.26° and 54.34°, which corresponded well with the findings reported by **Jang and Park (2012)**.

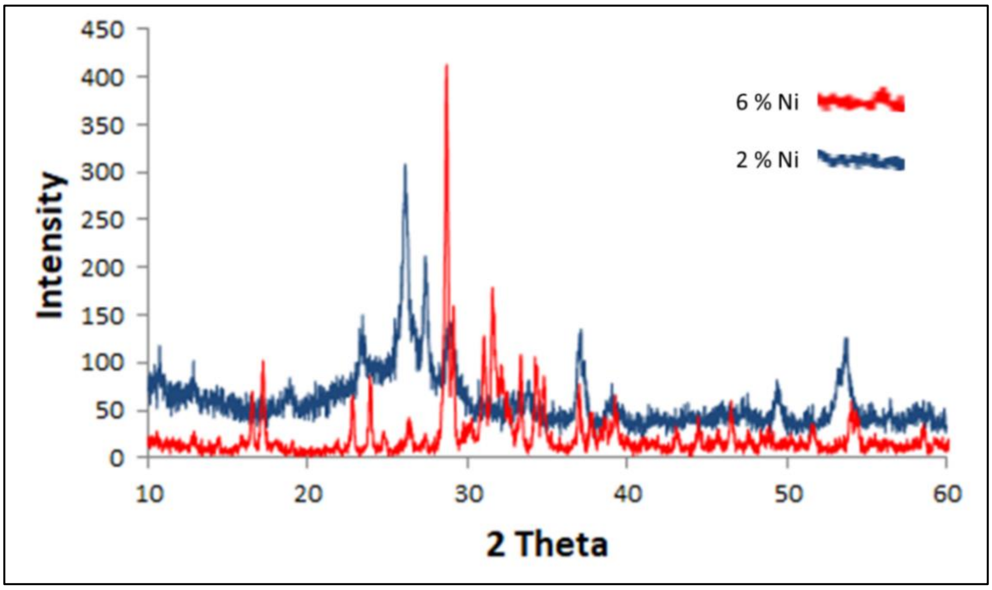

Figure 4.3. XRD pattern for 2% NiMo/Ac, and 6% NiMo/Ac catalysts.

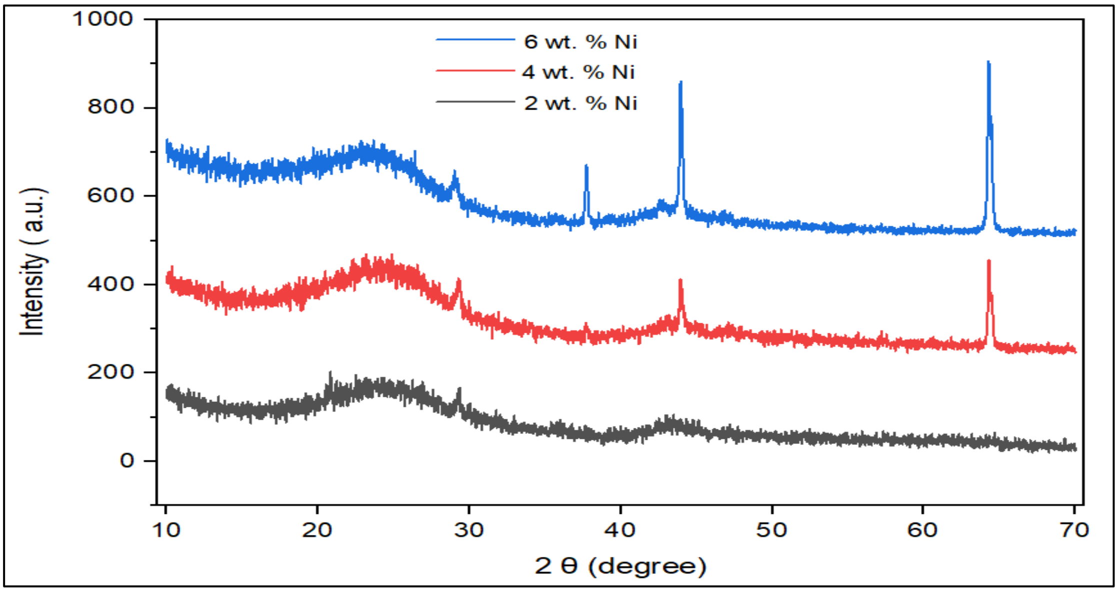

Figure 4.4. XRD pattern for x% NiW/AC catalysts.

The XRD pattern for the NiW/AC catalyst is shown in Figure 4.4, As seen in the figure the peaks around 2θ equal 37.7 which is attributed to the Ni_3C phase **(Xiong et al., 2015)**. The diffraction of the $NiWO_4$ phase was shown at peaks of about 57.1 and 64.3°, and this is agreed with **Mancheva et al. (2007)**, **Mani et al. (2016)**, and **Oliveira et al. (2020)** while the nickel oxide phase showed diffraction peaks at about 43.9 ° which agreed with Dong et al. **(Jang and Park, 2012)**.

Figure 4-5 shows the EDS analysis of the elemental composition of the 6 wt.% NiMo/AC catalyst sample. The results confirm the successful loading of molybdenum (Mo) and nickel (Ni) into the activated carbon surface, with a low variation from the expected theoretical loads of 15 wt. 15 wt. % for Mo and 6 wt.% for nickel. The measured Mo content was determined to be 9.42 %, while the Ni content was detected to be 5.85%. The difference between the expected theoretical loads and the detected percentages can be attributed to various factors. This slight deviation can be attributed to the fact that the detected percentages reflect the surface composition of the catalyst, which may differ slightly from its bulk composition. Surface oxidation, contamination, or adsorption of other elements may contribute to the observed differences between the theoretical values and the detected values. Operating conditions during catalyst preparation such as pH of solution and temperature both greatly affect solubility and precipitation.

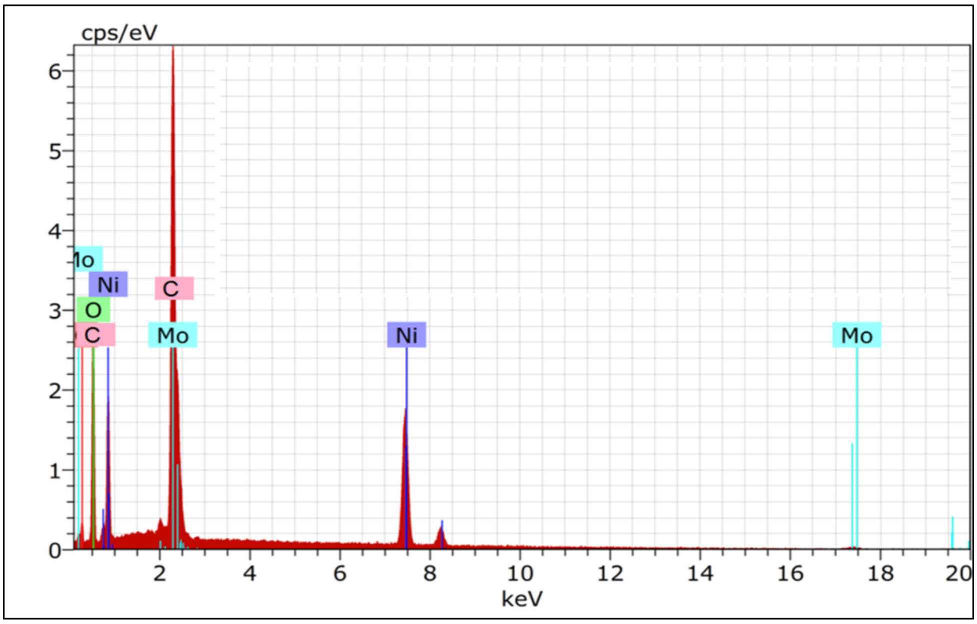

Figure 4.5. EDX spectrum for 6% NiMo/Ac catalyst, the analysis confirms the presence of carbon about 82 %, nickel 5.7 %, and molybdenum 14.5 %.

4.2 Catalyst Activity Results

4.2.1. Activity investigation for NiMo/AC catalyst

Table 4-1 provides a comprehensive overview of the DBT (dibenzothiophene) conversion achieved in all experiments conducted using the Box-Behnken design (BBD). The conversion rates of DBT ranged between 23% and 71%. Notably, these outcomes were successfully suited to a 2nd order polynomial model, specifically a quadratic model. This equation establishes a relationship between the DBT conversion rate

(R%) and the independent parameters: Ni% loaded, sulfur initial concentration, and catalyst dosage. The equation accurately represents the actual values, as indicated below:

$$R\% = -1.516 + 0.989X_1 - 0.1557X_2 + 0.00555X_3 - 0.0121X_1X_2 - 0.0011X_1X_3 + 0.00132X_2X_3 - 0.043X_1^2 + 0.01018X_2^2 - 0.000003X_3^2 \quad \text{(Eq. 4.3)}$$

Table 4-2 presents the results of the ANOVA (analysis of variance) conducted on the predicted models. The ANOVA was performed using Minitab Ver.17. The expected model demonstrates a highly satisfactory fit to the actual data, as evidenced by the 0.9719 significant coefficient R^2 and the 0.9213 closely aligned value of the adjusted R^2. These values indicate that the presumed model aligns well with the observed outcomes. The regression model's F-value was 16.77, surpassing the listed values ($F_{95,5,0,05}$=4.77). The findings suggest that the initial sulfur concentration has the greatest influence on DBT conversion, signifying its significant impact on sulfur removal efficiency. The catalyst dosage and Ni% loaded also contribute to the overall conversion. This assertion is supported by the corresponding F-values obtained for each variable, with initial sulfur concentration exhibiting the highest F-value of 89.45, followed by catalyst dosage with 8.07, and Ni% loaded with 0.61. These F-values validate the anticipated order of their effects as predicted in the analysis. Consequently, the optimal DBT conversion rate of 75.74% is attained when using a catalyst dosage of 0.5 g, a Ni loading of 6%, and an initial sulfur concentration of 700 ppm.

Table 4.1. Experimental (observed) and predicted DBT conversion at NiMo/AC catalyst.

Run	**Catalyst dosage, g.**	**Ni% loaded**	**Sulfur initial concentration ppm**	**DBT conversion R%**	**Run**	**Catalyst dosage, g.**	**Ni% loaded**	**Sulfur initial concentration ppm**	**DBT conversion R%**
1	1.5	4	400	0.468	9	1	4	600	0.623
2	0.5	4	800	0.624	10	1.5	4	800	0.571
3	1.5	2	600	0.662	11	1	4	600	0.615
4	1.5	6	600	0.605	12	0.5	4	400	0.230
5	1	2	800	0.629	13	1	6	400	0.240
6	1	6	800	0.710	14	0.5	6	600	0.590
7	1	2	400	0.370	15	0.5	2	600	0.598
8	1	4	600	0.595					

Table 4.2. ANOVA analysis results for RSM for a quadratic model for using NiMo/AC catalyst.

Source	DF	Adj. SS	Adj. MS	F-value	p-value
Model	9	0.39941	0.04438	16.77	0.003
Linear	3	0.25973	0.086577	32.71	0.001
Catalyst dosage (X_1)	1	0.02135	0.021356	8.07	0.036
Ni% loaded (X_2)	1	0.001617	0.001617	0.61	0.470
Initial sulfur conc. (X_3)	1	0.23675	0.236758	89.45	0.000
Square	3	0.079546	0.026515	10.02	0.015
(Catalyst dosage)^2 (X_1^2)	1	0.000435	0.000435	0.16	0.702
(Ni% loaded)^2 (X_2^2)	1	0.006120	0.006120	2.31	0.702
(Initial sulfur conc.)^2 (X_3^2)	1	0.069720	0.069720	26.34	0.004
2-way Interaction	3	0.060141	0.020047	7.57	0.026
Catalyst dosage* Ni% loaded (X_1X_2)	1	0.000584	0.000584	0.22	0.658
Catalyst dosage* Initial sulfur conc.(X_1X_3)	1	0.048400	0.048400	18.29	0.008
Ni% loaded * Initial sulfur conc. (X_2X_3)	1	0.11157	0.11157	4.22	0.095
Error	5	0.013234	0.002647		
Lack–of–Fit	3	0.009093	0.003031	1.46	0.430
Pure Error	2	0.004141			
Total	14	0.412651			

Figure 4-6 depicts the variables' individual impacts and the investigated system's optimization. The DBT (dibenzothiophene) conversion rate exhibited an upward trend with a rise in the initial sulfur loading from 400 ppm to approximately 700 ppm. However, additional increments in the initial sulfur loading resulted in a decline in DBT conversion. This may be because of the presence of the limited number of active sites in a fixed amount of catalyst, in which these limited active sites are insufficient for conversion of DBT **(Gosu et al., 2018)**.

The DBT conversion rate was found to increase by augmenting the dosage or amount of catalyst employed. This increase in catalyst dosage leads to the generation of a larger quantity of catalytic intermediates through their reaction with the oxidant agent (H_2O_2). In essence, the amplified catalyst dosage provides a greater number of active sites, thereby enhancing the likelihood of surface interactions between the active sites of the catalyst and the DBT molecule. Several studies, including those by **Chu et al. (2010)**, **K. P. Cheng et al. (2015)**, and **F. Yu and Wang (2013)**, support this observation.

The influence of the nickel loading on DBT conversion demonstrated a diminishing effect as the nickel weight percentage increased. This decrease in the impact of nickel loading could be associated with the formation of less activated surface sites resulting from the higher nickel loading. This phenomenon could potentially obstruct certain active sites due to the presence of nickel species, as noted by **Kim et al. (1996)**. Furthermore, **Zhang et al. (2008)** stated that an increase in nickel loading resulted in a lower nickel dispersion, providing additional evidence of the diminishing impact of higher nickel loading on DBT conversion.

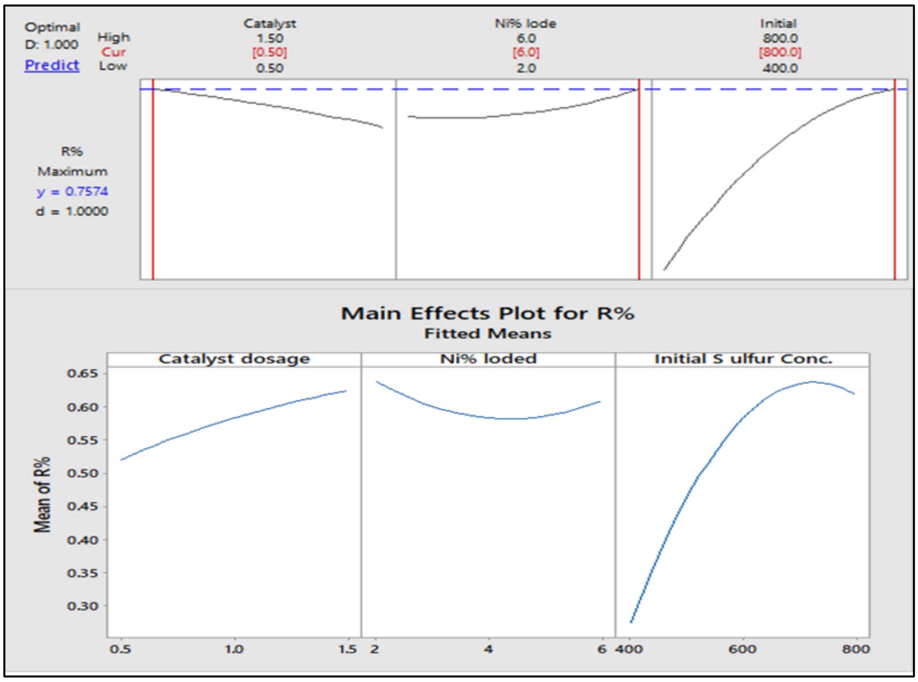

Figure 4.6. Effect of studied variables on DBT conversion.

The conversion increased with catalyst dosage and initial sulfur concentration and decreased with Ni load increasing (lower graph). The optimum DBT conversion is 75.74% at 0.5 g, 6%, and 700 ppm for catalyst dosage, Ni loaded and initial sulfur concentration respectively (upper graph).

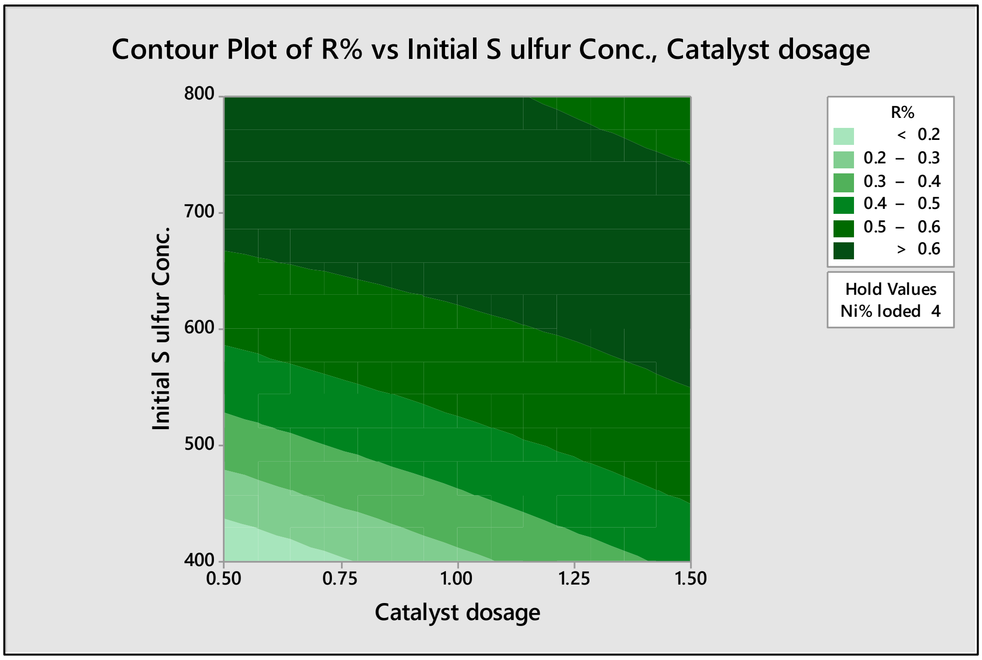

Figure 4.7. The interaction effect of initial sulfur concentration and catalyst dosage on DBT conversion while holding Ni% loaded at 4%.

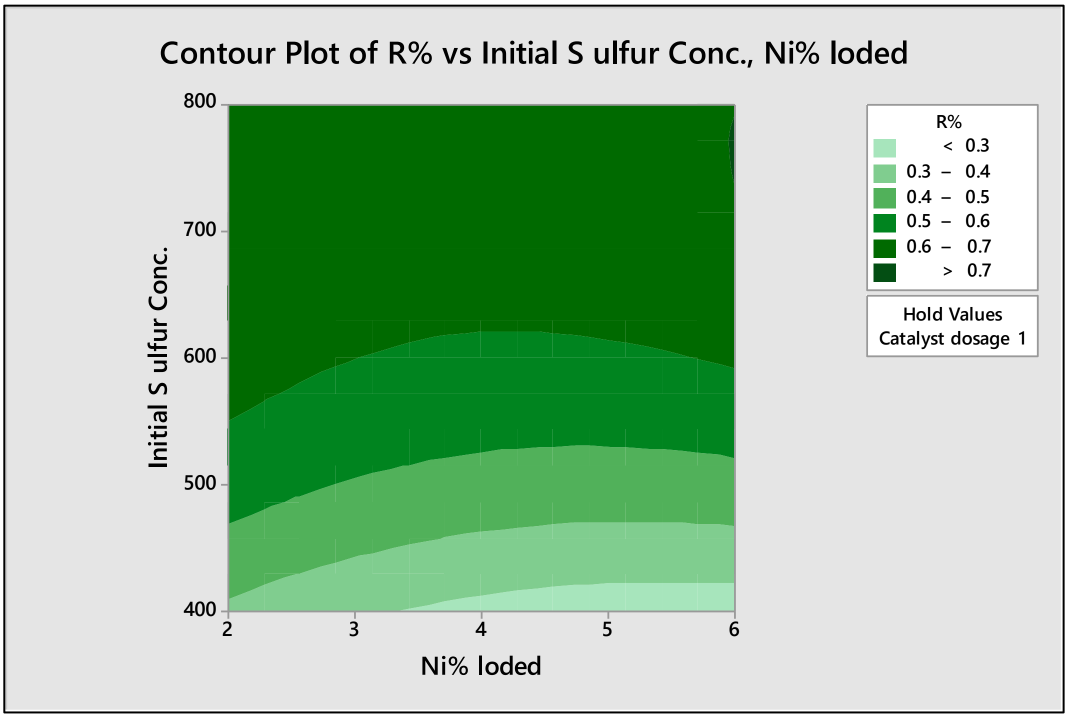

Figure 4.8. The interaction effect of initial sulfur concentration and Ni% loaded on DBT conversion while holding catalyst dosage at 1g.

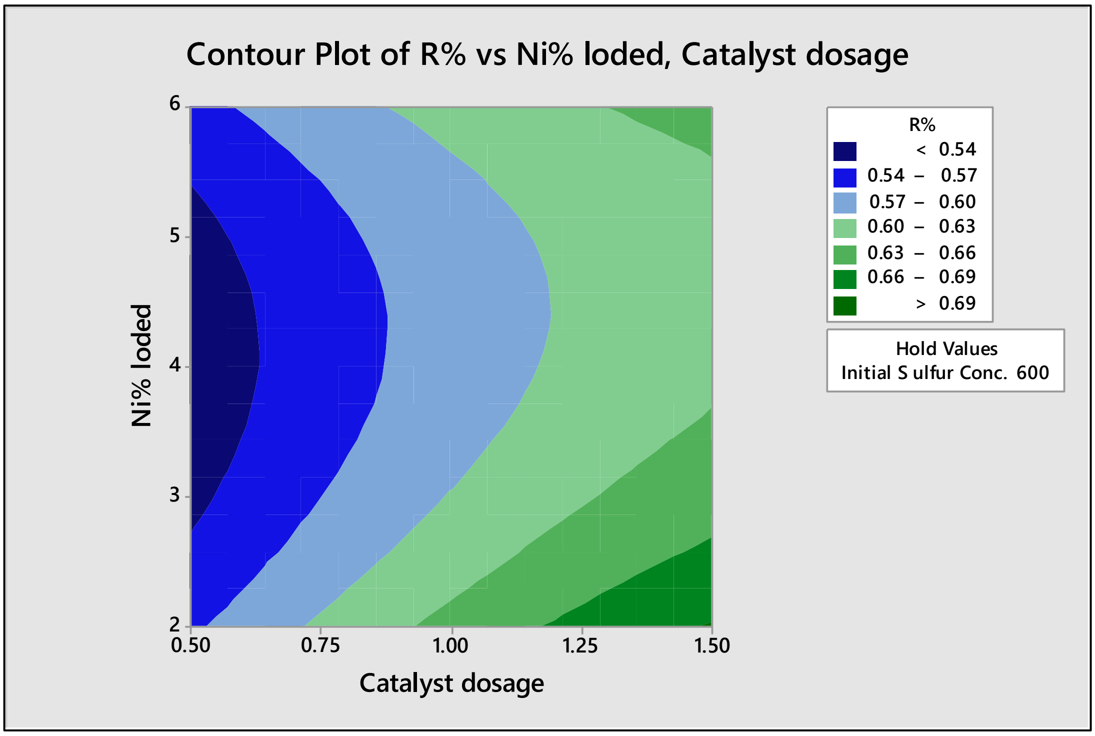

Figure 4.9. The interaction effect of catalyst dosage and Ni% loaded on DBT conversion while holding initial sulfur concentration at 600 ppm.

4.2.2 Activity investigation for NiW/AC catalyst

Table 4-3 lists the result for all experiments designed according to BBD; the DBT conversion ranged between. The DBT conversion for all experiments done according to BBD. The DBT conversion ranged between 26 to 81% and results fitting with a second-order polynomial (quadratic model) are:

$$R\% = 16.8 + 73.8X_1 - 2.2X_2 + 0.143X_3 - 1.17X_1X_2 + 0.0628X_1X_3 + 0.0255X_2X_3 + 24.2X_1^2 - 1.11X_2^2 - 0.000194X_3^2$$

(Eq. 4.2)

Table 4.3. Experimental (observed) and predicted DBT conversion at NiW/AC catalyst.

Run	Catalyst dosage, g.	Ni% loaded	Sulfur initial concentration ppm	DBT conversion R%	Run	Catalyst dosage, g.	Ni% loaded	Sulfur initial concentration ppm	DBT conversion R%
1	1.5	4	400	0.305	9	1	4	600	0.533
2	0.5	4	800	0.546	10	1.5	4	800	0.812
3	1.5	2	600	0.532	11	1	4	600	0.5
4	1.5	6	600	0.522	12	0.5	4	400	0.29
5	1	2	800	0.276	13	1	6	400	0.288
6	1	6	800	0.709	14	0.5	6	600	0.535
7	1	2	400	0.263	15	0.5	2	600	0.498
8	1	4	600	0.483					

Table 4.4. ANOVA analysis results for RSM for a quadratic model for using NiW/AC catalyst.

Source	**DF**	**Adj. SS**	**Adj. MS**	**F-value**	**p-value**
Model	9	3235.80	359.53	3.86	0.075
Linear	3	2202.1	734.24	7.89	0.024
Catalyst dosage (X_1)	1	113.44	113.44	1.22	0.320
Ni% loaded (X_2)	1	293.02	293.02	3.15	0.136
Initial sulfur conc. (X_3)	1	1796.25	1796.25	19.30	0.007
Square	3	454.68	151.56	1.63	0.295
(Catalyst dosage)^2 (X_1^2)	1	134.70	124.70	1.45	0.283
(Ni% loaded)^2 (X_2^2)	1	72.42	72.42	0.78	0.418
(Initial sulfur conc.)^2 (X_3^2)	1	221.87	221.87	2.38	0.183
2-way Interaction	3	578.40	192.80	2.07	0.223
Catalyst dosage* Ni% loaded (X_1X_2)	1	5.44	5.44	0.06	0.819
Catalyst dosage* Initial sulfur conc.(X_1X_3)	1	157.82	157.82	1.70	0.250
Ni% loaded * Initial sulfur conc. (X_2X_3)	1	415.14	415.14	4.46	0.088
Error	5	465.39	93.08		
Lack–of–Fit	3	452.43	150.81	23.81	.0.041
Pure Error	2	0.1296	0.0648		
Total	14	3701.19			

Again, the ANOVA analysis for the experiments results in the case of using NiW/AC catalyst are shown in Table 4-4, in which the predicted model shows good fitting for real results as high R^2 (87.3%). The f-value is equal to 3.86 and it is greater than the tabulated value ($F_{95,\ 5,0,05} = 4.77$). According to F-values, the most affected variables is the initial sulfur concentration followed by Ni% load and catalyst; 19.3, 3.15, and 1.2 respectively, whereas the optimum DBT conversion is 84% at 1.5 g, 6%, and 800 ppm for catalyst dosage, Ni loaded and initial sulfur concentration respectively (figure 4-10)

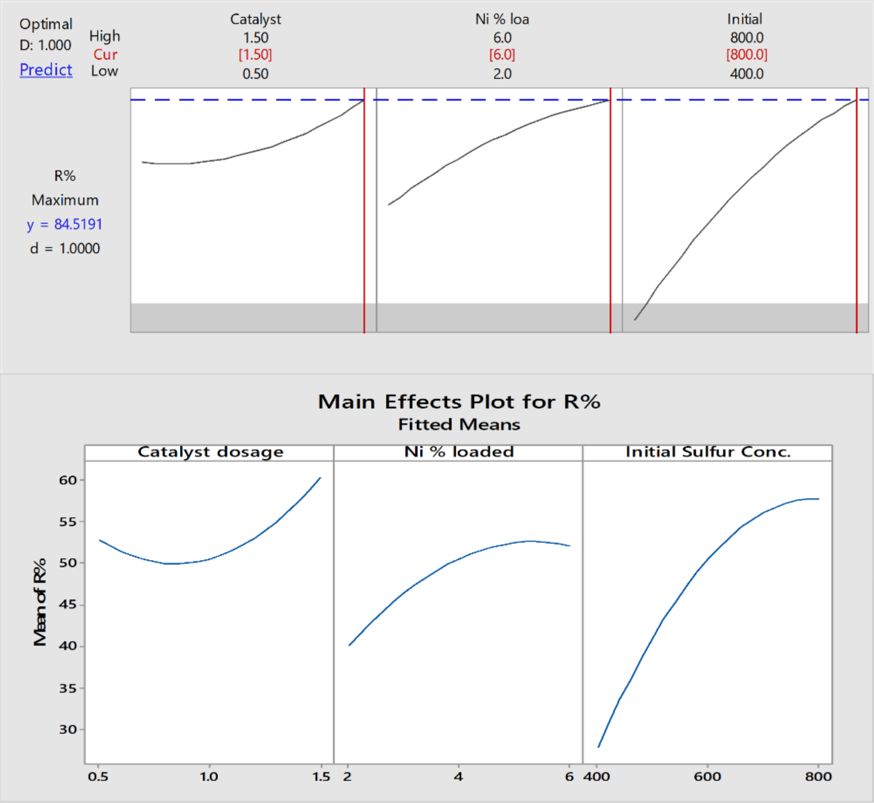

Figure 4.10. Effect of studied variables on DBT conversion.

The conversion increased with catalyst dosage and initial sulfur concentration and decreased with Ni load increasing (lower graph). The optimum DBT conversion is 84.5% at 1.5 g, 6%, and 700 ppm for catalyst dosage, Ni loaded and initial sulfur concentration respectively (upper graph).

The effect of the studied variable individually on DBT conversion at NiW/AC catalyst and optimization of the studied system was shown in Figure 7, as seen in the same behavior as in the case of using NiMo/AC catalyst. DB conversion increases with the increase in the initial concentration, and it was noted that the rate of increase is high until the initial concentration reached about 700 ppm, after which the increase continues with the rate, but at a lower rate of increase, and the explanation for this is the occupation of the active sites in catalyst surface. (V.Subbaramaiah 2018) , also DBT conversion was increasing with increasing dosage (amount) of the catalyst and this is agreed **F. Yu and Wang (2013)**, **K. P. Cheng et al. (2015)**, and **Chu et al. (2010)**. The effect of increasing nickel weight percent loaded as a promotor on DBT conversion was decreased because any addition of dosage of nickel may lead to less-active surface species formation which caused blockage of some active cites by Ni species (Kim et al. 1996). The extra nickel amount prevents or eliminates nickel dispersion which means lowering DBT conversion **(Zhang et al., 2008).**

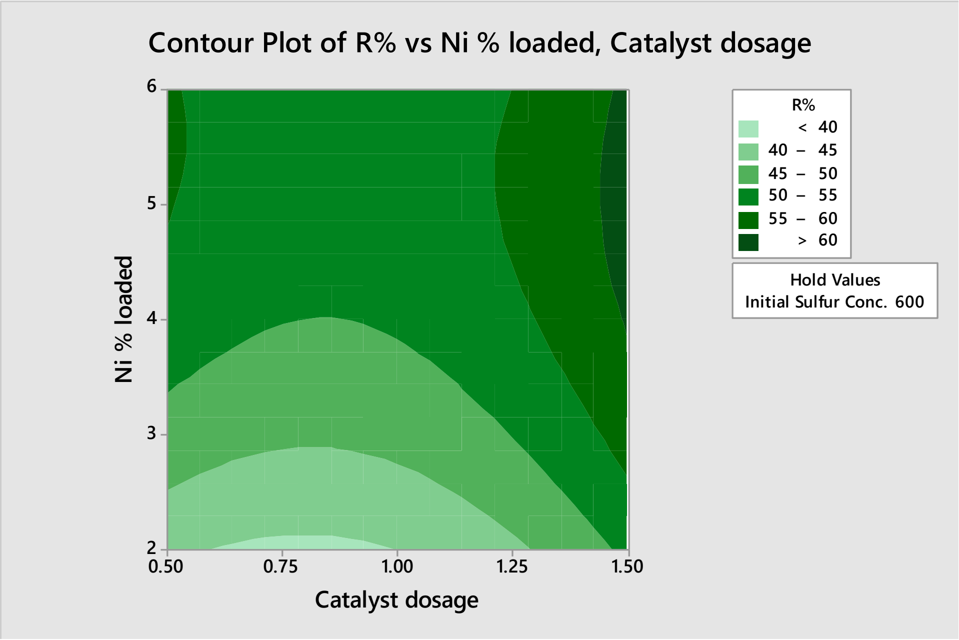

Figure 4.11. The interaction impact of catalyst dosage and Ni % loaded on sulfur removing efficiency while holding the Nickel % loaded constant.

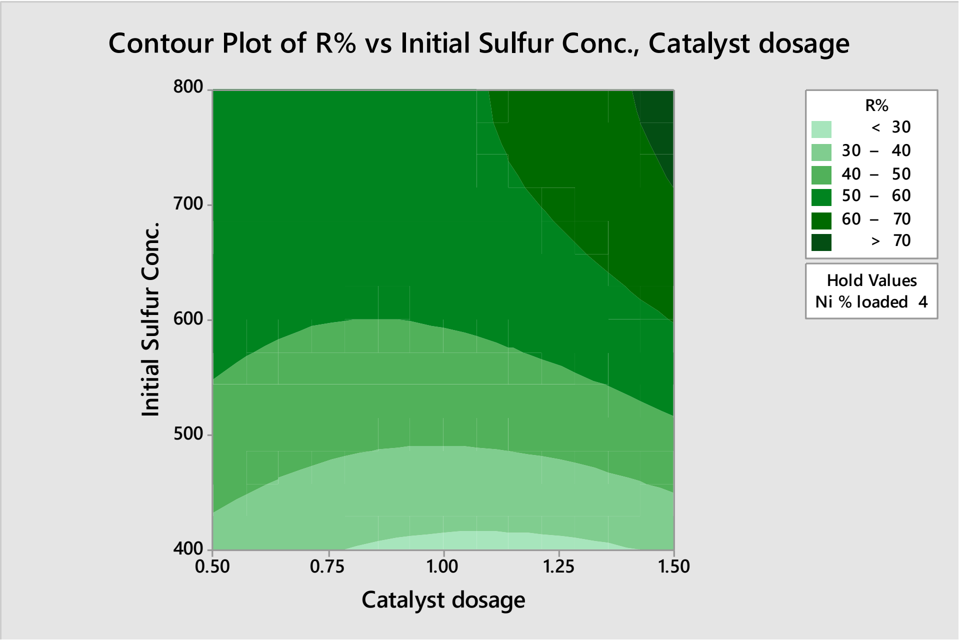

Figure 4.4.12. The interaction impact of catalyst dosage and initial sulfur concentration on sulfur removing efficiency while holding the Nickel % loaded constant.

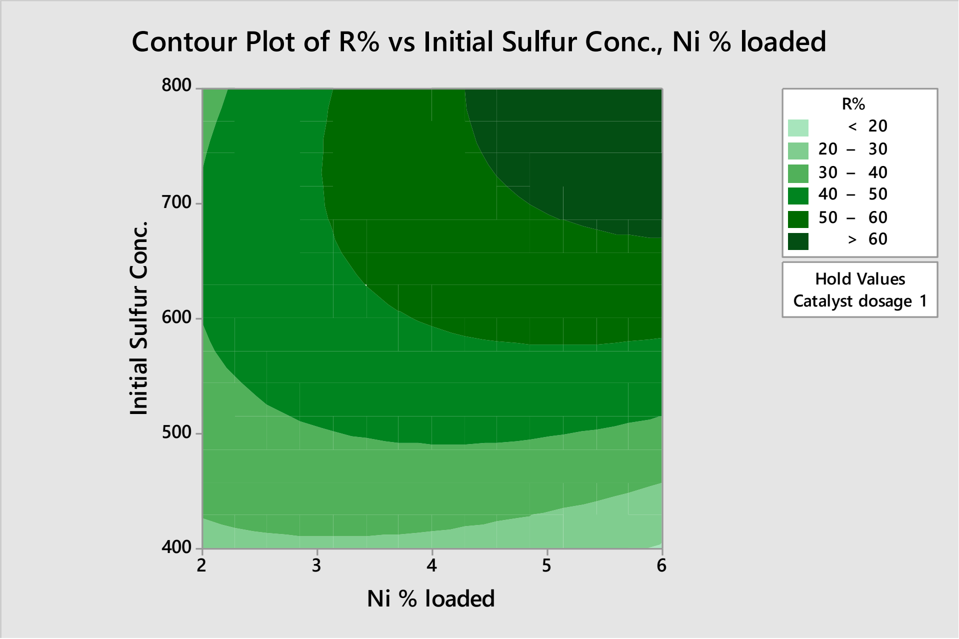

Figure 4.13. The interaction impact of Ni % loaded and initial sulfur concentration on sulfur removing efficiency while holding the Nickel % loaded constant.

4.3 Proposed mechanism

To gain a deeper comprehension of the oxidative desulfurization (ODS) mechanism facilitated by the H_2O_2/CH_3COOH in the NiO-MoO3/Ac catalyst existence, a theoretical framework assumes the NiO existence as a catalyst booster and MoO3 as the activated phase. The initiated MoO3 reaction involves the hydrolytic cleavage of hydrogen peroxides, resulting in the generation of potent oxidation agents, specifically active hydroxyl radicals (OH•). These highly reactive radicals then proceed to attack acetic acid, leading to the formation of peracetic acid. Peracetic acid, in turn, serves as an oxygen source for the oxidation of DBT (dibenzothiophene), resulting in the formation of DBTO (sulfoxide, containing S=O). Subsequent attacks on DBTO produce DBTO2 (sulfones containing O=S=O). The proposed reaction pathway is depicted in Figure 4.14 **(Ahmadi et al., 2017).**

$$DBT \overset{[O]}{\rightarrow} DBTO \overset{[O]}{\rightarrow} DBTO_2 \qquad \text{(Eq.4.5)}$$

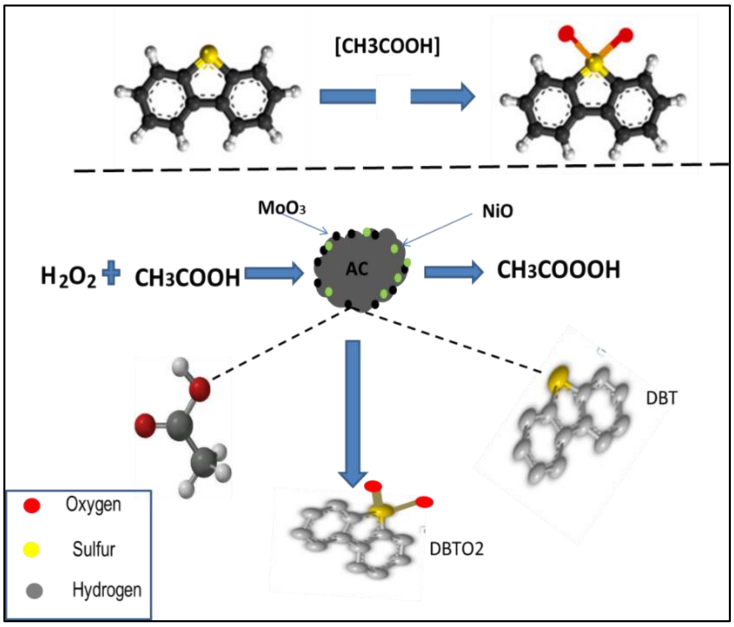

Figure 4.14. Mechanism of ODS for DBT with H_2O_2/CH_3COOH oxidation system in presence of $NiO-MoO_3/Ac$ catalyst.

4.4 ODS Reaction with Real Fuel

The ODS process was repeated with three real fuels; light naphtha, kerosene, and gas oil with initial sulfur content of 700, 4000, and 15000 ppm respectively. The comparison study uses a 6%NiW/AC catalyst, and the experiments were done at optimum values for all operation conditions. The results show sulfur removing efficiencies as shown in table 4-5.

Table 4.5 the sulfur removal efficiency by using a 6% Ni W/AC catalyst for oxidation reaction real fuel (light naphtha, kerosene, and gas oil), the operation condition at the optimum values.

Table 4.5. the sulfur removal efficiency by using 2 wt. % Ni W/AC catalyst for oxidation reaction real fuel (light naphtha, kerosene, and gas oil), the operation condition at the optimum values.

Product	**Initial sulfur concentration**	**Final sulfur concentration**	**Sulfur removing efficiency (%)**
Light naphtha	776	578	25
Kerosene	4000	1550	61.3
Gas oil	15000	2150	85.6

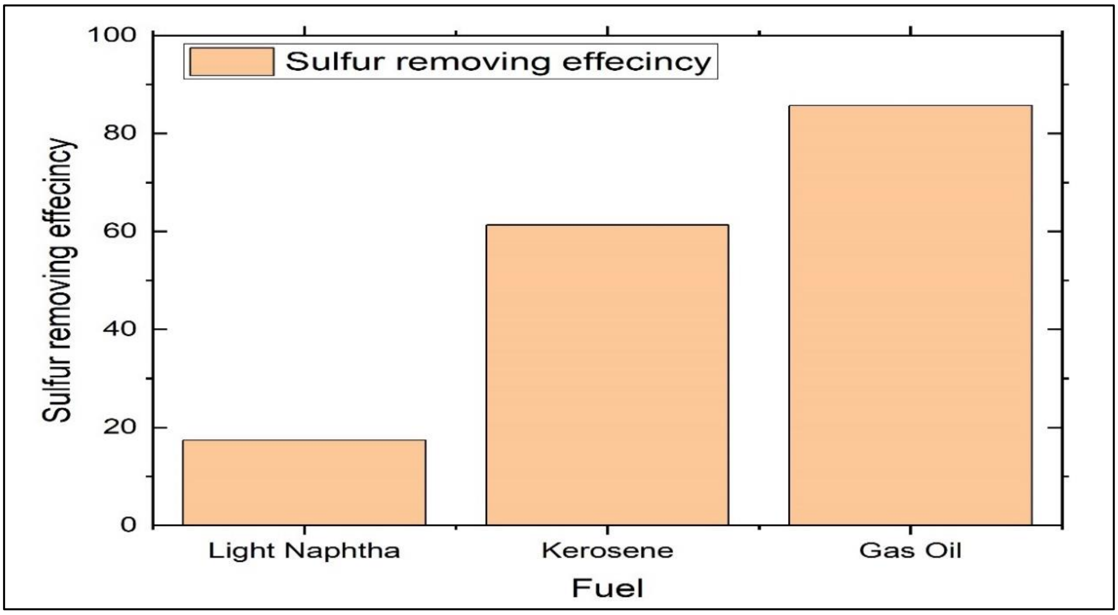

Figure 4.15. Sulfur removing efficiency for real fuels (light naphtha, Kerosene, and gas oil) by using 1.2 grams from (2 wt.%) Ni W/AC at 50°C under stirring rate 600 rpm

It is well known that the organic sulfur compounds are distributed in different petroleum product, and this distribution may affect the selection of desulfurization technique, for example, the sulfur organic components light is concentrated in light fraction while the concentration of heavy sulfur organic components is high in heavy fraction especially thiophene and its derivatives. **(C. Song et al)** reported that it can be virtually infinitely reactive in practical high-conversion processes (HDS), Similarly, the reactivities of 4-methyl dibenzothiophene and 4,6-dimethyl dibenzothiophene (4,6-DMDBT) are much lower than those for other organic sulfur compounds presence in crude oil and its products **(C. Song, 2003)**, while the ODS is one of the most effective ways to remove residual aromatic compounds containing sulfur reaming after the hydrotreating process. The oxidation reactivity seems to increase when the electron density of the sulfur species is higher, dibenzothiophene > 4,6-dimethyl dibenzothiophene> benzothiophene > thiophene in the reverse reactivity order of HD. (JMCampos 2010). The results show that the desulfurization of three real fuel is ordered as follow: gas oil > kerosene > light naphtha and this means that a heavy fraction (gas oil) is desulfurized easily compared to a light fraction (light naphtha) via the presence of a relatively higher concentration of high electron density on sulfur atoms and this is agreed with **Shiraishi and Hirai (2004)** and **(Campos-Martin et al., 2010)**.

The results shown in Table 4-5 can be considered agree with the above as well as good proof for the effectivity ODS process to remove sulfur aromatic compounds in HDS**.**

Chapter Five

Conclusion and Recommendations

Chapter Five Conclusion and Recommendations

5.1 Conclusions

The oxidative desulfurization of model fuel (n-heptane contain dibensozthionphene DBT) by oxidation system (H2O2 + acetic acid) on two catalyst surface; NiMo and NiW supported on activated carbon was studied and there is an effect of three variables was investigated (catalyst dosage , nickel weight percent loading and initial sulfur concentration).

1. The oxidation process effectively oxidized sulfur compounds to the corresponding sulfone compounds. Acetic acid achieves proper oxidation and desulfurization of model fuel(DBT dissolved in n-heptane) The maximum sulfur content of 1.0875% was achieved using the following conditions:(temperature 50 C, oxidant 10%, and reaction time 60 min)
2. Addition of NiMo and NiW catalysts enhancing oxidation process. The study consists of the investigation of the effect of three parameters which are arranged by combined RSM and Box-Behnken design. the studied variables were catalyst dosage, Ni% loaded, and initial sulfur concentration
3. Results show that DBT conversion (sulfur removal efficiency) ranged between 23 and 71%, and they were fitted with seconds–order polynomial (high correlation coefficient R2 = 0.9719) with regard to a catalyst NiMo.These results agreed with many previous studies but the most point considered is the use of nickel oxide for enhancement of the molybdenum-based catalysis activity. In contrast, using nickel oxide caused a decrease in sulfur removal efficiency, which may mean that the catalyst's deactivation

happened rapidly. The optimum DBT conversion is 75.74% at 0.5 g, 6%, and 700 ppm for catalyst dosage, Ni loaded, and initial sulfur concentration respectively.

4. In the case of using a NiW/Ac catalyst, it can be concluded that the catalyst, is prepared by incorporating Ni and W metals onto Activated carbon (AC) support. The effects of catalyst dosage, initial sulfur concentration, and Nickel weight percent loading on sulfur removal were systematically evaluated. The increase in studied variables on sulfur removal shows that increasing sulfur removal till reached specified values (optimum point for each variable) after, the sulfur removal starts to incline. The catalyst's performance was verified at the optimal point, achieving a remarkable desulfurization efficacy of 83.4 %. The predicted model shows good fitting for real results as high R2 (84.3%). According to F-values, the most affected variables are the initial sulfur concentration followed by Ni% load and catalyst dosage; 19.30, 3.15, and 1.22 respectively. The optimum DBT conversion is 84 % at 1.5 g, 6%, and 800 ppm for catalyst dosage, Ni% loaded, and initial sulfur concentration respectively. These results demonstrate the superior performance of the NiW/AC catalyst in comparison with other reported catalysts. This study provides valuable insights into the ODS process and offers a foundation for the advancement of highly efficient catalysts for sulfur removal in the petroleum industry.
5. The catalyst activity was investigated by using three real fuels (light naphtha, kerosene and gas oil); in which the investigation show sulfur removal efficiency 24.54 % , 61.25 % and 82.08 %.

5.2 Recommendations for Future Work

1. Examine and develop a catalyst to overcome the delayed oxidation reaction barrier of the sulfur component.
2. Using different petroleum products.
3. The model fuel had more than one sulfur component, such as thiophene, bemzothiophene, mercaptans, etc.
4. Using different oxidation system or oxidation agents such as atmospheric oxygen, ozone etc.
5. Changing the solvent used in the separation step or the volume ratio of fuel to solvent.
6. Putting a process into continuous mode.

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Appendices

Appendices

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وزارة الصناعة والمعادن
هيأة البحث والتطوير الصناعي
مركز البحوث الكيمياوية والبتروكيمياوية

تقرير الفحص

رقم تقرير النتائج (Report No.):- 2
تاريخ الاصدار (Date of Issue) :- 2023/3/22
اسم الشعبة الفاحصة :- فحوصات الزيوت والوقود

نتائج الفحص

طريقة الفحص		تمت الفحوصات حسب المواصفة ASTM D4294			اللاتاكدية ± U	حدود المواصفة	مواصفة الفحص
ت	رمز العينة	نوع الفحص	الاجهزة المستخدمة بالفحص	القراءات المقاسة			ASTM D4294
1	1	محتوى الكبريت	X-ray sulfur meter	0.150 wt%			
2	2			0.155 wt%			
3	3			0.031 wt%			
4	4			0.0579 wt%			
5	5			0.0281wt%			
6	6			0.0295 wt%			
7	7			0.0287 wt%			
8							
9							

Environmental conditions :- Temp.: 22 °c Humidity: 30 %

تم حساب اللاتاكدية بدرجة وثوقية 95% و K=2 ، تم الاعتماد على دليل الجودة UKAS M3003

سلسلة القياس : تم حساب النتائج وتتبعها مع المراجع القياسية المعتمدة الدولية والوطنية (PHT984/CC12237154/CC12237152/UME(G1K-0248

تم الفحص بتاريخ 22 / 3 / 2023 من قبل :
1-قريش عباس
-2

النتيجة: النتائج تخص العينة المفحوصة.

الأراء والتفسيرات:

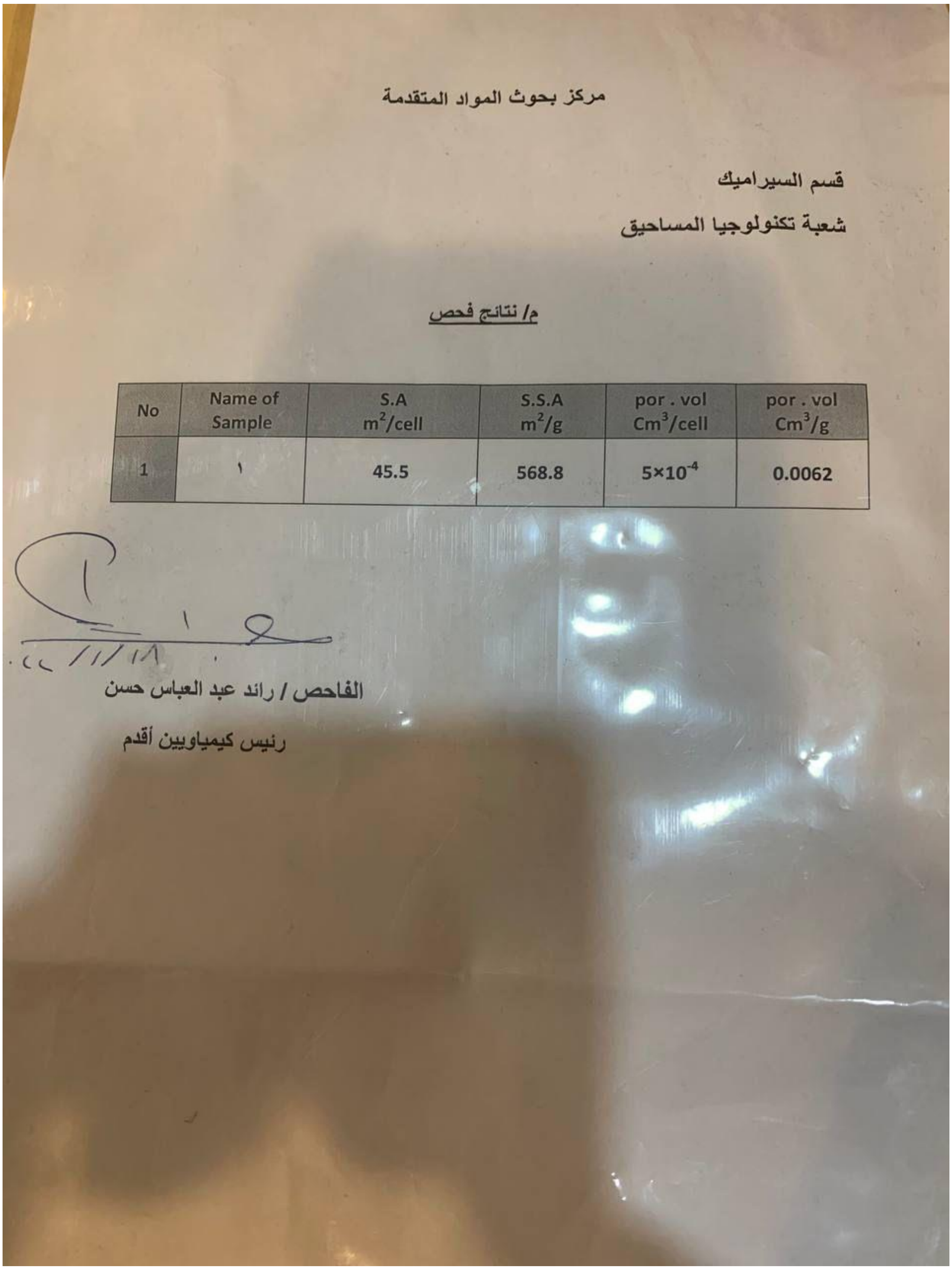
التدقيق من قبل : انوار شاكر
المصادقة من قبل :

مدير الشعبة
قريش عباس كاظم

مدير المركز
د. محمد جابر ياس

بغداد – الجادرية – مجمع وزارة العلوم والتكنلوجيا – بناية مركز البحوث الكيمياوية والبتروكيمياوية
هذه الوثيقة خاصة بمركز البحوث الكيمياوية والبتروكيمياوية لذا غير مسموح تعديلها او نسخ محتوياتها بدون موافقة مدير المركز

Page 2 of 2



مركز بحوث المواد المتقدمة

قسم السيراميك

شعبة تكنولوجيا المساحيق

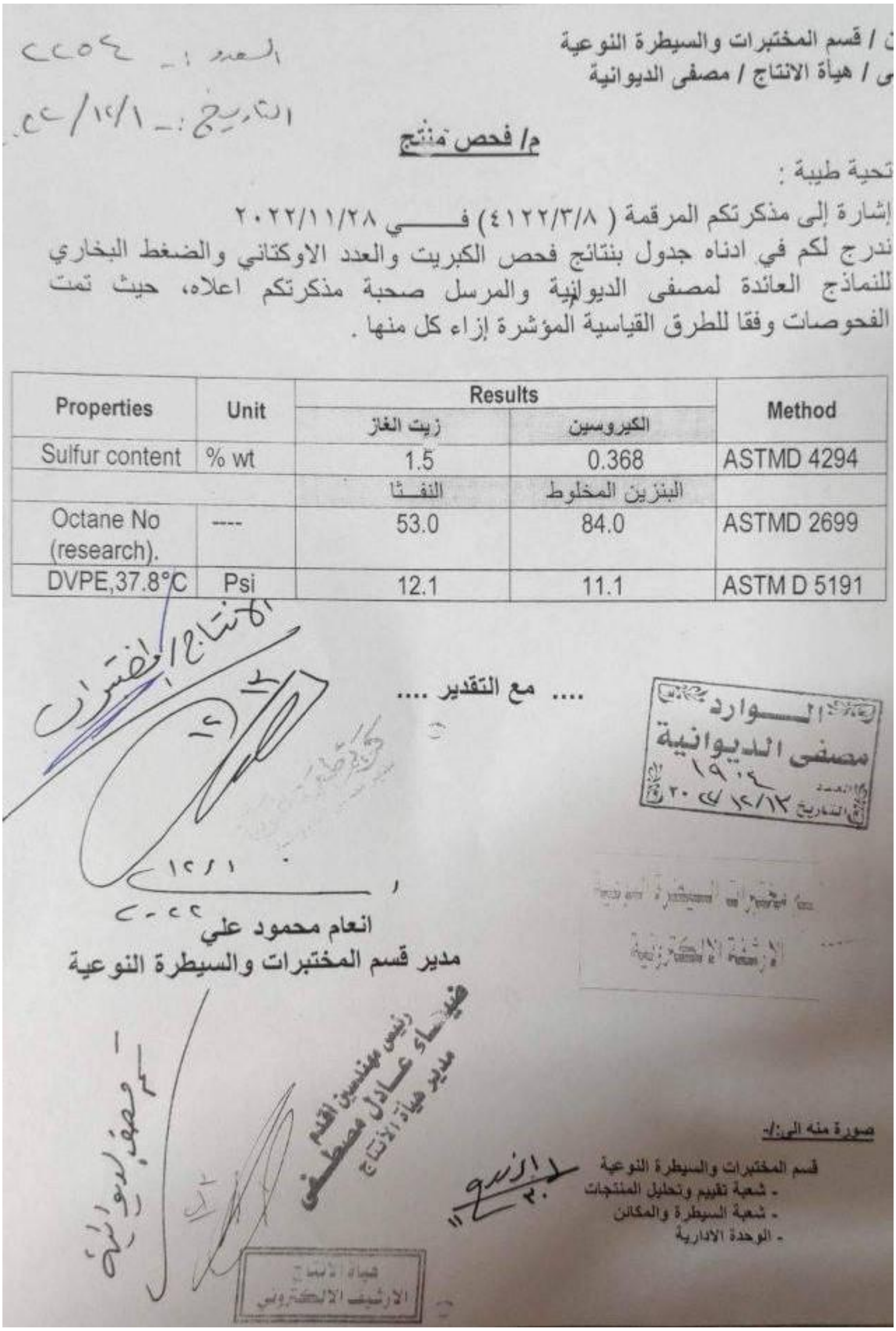
م/ نتائج فحص

No	Name of Sample	S.A m^2/cell	S.S.A m^2/g	por . vol Cm^3/cell	por . vol Cm^3/g
1	١	45.5	568.8	5×10^{-4}	0.0062

١٨/١١/٠٢٢

الفاحص / رائد عبد العباس حسن

رئيس كيمياويين أقدم



العدد :- ٢٢٥٤
التاريخ :- ١/١٢/٢٠٢٢

ن / قسم المختبرات والسيطرة النوعية
ى / هيأة الانتاج / مصفى الديوانية

م/ فحص منتج

تحية طيبة :

إشارة إلى مذكرتكم المرقمة (٤١٢٢/٣/٨) فـــــي ٢٠٢٢/١١/٢٨
ندرج لكم في ادناه جدول بنتائج فحص الكبريت والعدد الاوكتاني والضغط البخاري للنماذج العائدة لمصفى الديوانية والمرسل صحبة مذكرتكم اعلاه، حيث تمت الفحوصات وفقا للطرق القياسية المؤشرة إزاء كل منها .

Properties	Unit	Results		Method
		زيت الغاز	الكيروسين	
Sulfur content	% wt	1.5	0.368	ASTMD 4294
		النفـثا	البنزين المخلوط	
Octane No (research).	----	53.0	84.0	ASTMD 2699
DVPE,37.8°C	Psi	12.1	11.1	ASTM D 5191

الانتاج / المختبرات

.... مع التقدير ....

الـــوارد
مصفى الديوانية
العدد ١٩٠٩
التاريخ ١٢/١٢/٢٠٢٢

١٢/١
٢٠٢٢

انعام محمود علي
مدير قسم المختبرات والسيطرة النوعية

المختبرات والسيطرة النوعية
الارشفة الالكترونية

رئيس مهندسين اقدم
ضياء عادل مصطفى
مدير هيأة الانتاج

مصفى الديوانية

صورة منه الى:/-

قسم المختبرات والسيطرة النوعية
- شعبة تقييم وتحليل المنتجات
- شعبة السيطرة والمكائن
- الوحدة الادارية

الارشيف
٢٠

هيأة الانتاج
الارشيف الالكتروني

إزالة الكبريت بطريقة الاكسدة لوقود افتراضي باستخدام اوكسيد النيكل -المولبيديوم و أوكسيد النيكل- التنكستن المحملين على الكاربون المفعل

اعداد

سرى احمد عبد الهادي

إشراف

أ.د. حميد حسين علوان

الخلاصة

يتناول هذا العمل إزالة الكبريت من الوقود بتقنية الأكسدة، حيث يكون الوقود المستخدم هنا هو الوقود النموذجي وثلاثة أنواع من الوقود الحقيقي. الوقود النموذجي هو ن–هيبتان بينما يمثل ثنائي بنزوثيوفين (DBT) مركبات الكبريت العضوية، حيث تتم عملية إزالة الكبريت التأكسدية للثنائي بنزوثيوفين DBT) بواسطة نظام أكسدة (بيروكسيد الهيدروجين وحمض الأسيتيك) عند درجة حرارة 50 درجة مئوية وخلال 60 دقيقة. العوامل المساعده هي أكاسيد الموليبدينوم والتنغستن المشتتة على الكربون المنشط بينما يتم فحص أكسيد النيكل هنا كعوامل مساعده محضره NiMo/Acو NiW/Ac.

تم فحص العوامل المساعده المحضرة بواسطة حيود الأشعة السينية جهاز "فورييه" لتحويل طيف الأشعة تحت الحمراء (FTIR) تم دراسة نشاط المحفز من خلال دراسة تأثير ثلاثة متغيرات: جرعة المحفز (0.5–1.5) جم، تحميل النيكل (2–6) بالوزن٪، وتركيز الكبريت الأولي (400–800) جزء في المليون، في حين أن كفاءة إزالة الكبريت هي تعتبر معايير النشاط المحفز.

تم تصميم التجارب وفقًا لـ RSM المدمج مع التصميم التجريبيBox–Behnken ، وتم تحليل النتائج وتحسينها من خلال تحليل التباين.ANOVA

أظهرت النتائج أن كفاءة إزالة الكبريت من الوقود النموذجي تراوحت بين 23 و 71%، وتم تزويد هذه النتائج بنموذج متعدد الحدود من الدرجة الثانية مع معامل ارتباط مرتفع (0.9719) R2 مع كفاءة إزالة الكبريت المثلى 75% في حالة استخدامNiMo/ Ac ، بينما تراوحت كفاءة إزالة الكبريت بين 26 إلى 81% وكفاءة الإزالة المثلى 84% في حالة استخدام محفز .NiW/Ac

ويبين تحليل ANOVA أن التأثير الكبير للمتغيرات المدروسة يتبع الترتيب؛ تركيز الكبريت الأولي وجرعة المحفز ونسبة Ni% المحملة في حالة استخدام محفز NiMo/Ac ، بينما المتغيرات الأكثر تأثراً هي تركيز الكبريت الأولي يليه حمل Ni% والمحفز في حالة استخدام محفز NiW/Ac.

يستخدم NiW/Ac كعامل محفز لإزالة الكبريت التأكسدي مع ثلاثة أنواع من الوقود الحقيقي (النفثا الخفيفة، الكيروسين، وزيت الغاز)، وكفاءة إزالة الكبريت هي 17.4، 61.3 و85.7% للنافتا الخفيفة، الكيروسين، وزيت الغاز على التوالي.

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة بابل
كلية الهندسة
قسم الهندسة الكيمياوية

إزالة الكبريت بطريقة الاكسدة لوقود افتراضي باستخدام اوكسيد النيكل -المولبيديوم وأوكسيد النيكل- التنكستن المحملين على الكاربون المفعل

رسالة

مقدمة الى قسم الهندسة الكيمياوية، كلية الهندسة في جامعة بابل كجزء من
متطلبات نيل درجة ماجستير علوم في الهندسة الكيمياوية

من قبل

سرى احمد عبد الهادي

(بكالوريوس هندسة كيمياوية ,2018)

إشـراف

أ.د. حميد حسين علوان

2023
1445