OXIDATIVE DESULFURIZATION OF SIMULATED DIESEL OIL OVER COPPER AND NICKEL– LOADED SILICA CATALYST

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ABTRACT

The aim of this work was studied the desulfurization of diesel oil by oxidation reaction using hydrogen peroxide as oxidizing agent with formic acid as solvent, catalyzed by copper-loaded silica ($CuO\text{-}SiO_2$) and nickel-loaded silica ($NiO\text{-}SiO_2$). The operating variables were the metallic salt concentration (0.25,0.5,1.0 mol/l) , dosage of catalyst (0.5,1.0,2.0 %wt) , type of sulfur compound (dimethyl sulfide and dibenzothiophene) , and adding of phase transfer catalyst. The oxidized diesel oil was analyzed sulfur content and heating value. The characterization of function group of diesel oil was carried out by Fourier-Transfer Infrared Spectroscopy (FTIR) technique.

The results showed that the increasing of metallic salt concentration and catalyst dosage, the removal of sulfur compound including dimethyl sulfide and dibenzothiophene also increased. The removal of dimethyl sulfide was higher than that of dibenzothiophene when using $CuO\text{-}SiO_2$ catalyst. The removal of sulfur compound was slightly increased when adding phase transfer catalyst. In addition , the heating value of diesel oil after oxidation reaction was similar to heating value of commercial diesel oil.

Keywords : Desulfurization, Diesel oil, Copper-loaded silica, Nickel-loaded silica, Phase transfer catalyst

หัวข้อโครงงานพิเศษ การกำจัดกำมะถันในน้ำมันดีเซลหมุนเร็วด้วยปฏิกิริยาออกซิเดชัน ด้วยตัวเร่งปฏิกิริยาทองแดงและนิกเกิลบนซิลิกา

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บทคัดย่อ

งานวิจัยมีจุดประสงค์เพื่อศึกษาการกำจัดกำมะถันในน้ำมันดีเซลหมุนเร็วด้วยปฏิกิริยาออกซิเดชั่นโดยใช้ไฮโดรเจนเปอร์ออกไซต์เป็นสารออกซิไดซ์ ใช้กรดฟอร์มิกเป็นตัวทำละลาย โดยตัวเร่งปฏิกิริยาทองแดงบนซิลิกา($CuO-SiO_2$)และนิกเกิลบนซิลิกา($NiO-SiO_2$) ตัวแปรที่ทำการศึกษาได้แก่ สารละลายเกลือโลหะ (0.25, 0.5 ,1.0 โมลต่อลิตร) ปริมาณของตัวเร่งปฏิกิริยา (0.5,1.0,2.0% โดยน้ำหนัก) ชนิดของสารประกอบกำมะถัน (ไดเมทิลซัลไฟล์และไดเบนโซไทโอฟีน) และการใช้สารลดแรงตึงผิว น้ำมันดีเซลที่ผ่านการกำจัดกำมะถันแล้วจะถูกนำไปตรวจวิเคราะห์หาปริมาณกำมะถัน ค่าความร้อน รวมถึงการพิสูจน์เอกลักษณ์ทางเคมีด้วยเทคนิคอินฟาเรดสเปกโตรสโคปี

จากผลการทดลองพบว่า เมื่อปริมาณความเข้มข้นของตัวเร่งปฏิกิริยาเพิ่มมากขึ้น การกำจัดกำมะถันทั้งไดเมทิลซัลไฟล์และไดเบนโซไทโอฟีน ก็จะมีค่ามากขึ้นด้วย เปอร์เซ็นต์การกำจัดกำมะถันชนิดไดเมทิลซัลไฟล์จะมีค่าสูงกว่ากำมะถันชนิดไดเบนโซไทโอฟีน เมื่อใช้ทองแดงเป็นตัวเร่งปฏิกิริยา และเปอร์เซ็นต์การกำจัดกำมะถันก็จะเพิ่มขึ้นอีกเมื่อใส่สารลดแรงตึงผิว ขณะที่ค่าความร้อนของน้ำมันที่ผ่านการกำจัดกำมะถันแล้วมีค่าไม่แตกต่างก่อนการกำจัดกำมะถันในน้ำมันออก

คำสำคัญ : กระบวนการกำจัดกำมะถัน, น้ำมันดีเซล, ตัวเร่งปฏิกิริยาทองแดงบนซิลิกา, ตัวเร่งปฏิกิริยานิกเกิลบนซิลิกา, สารลดแรงตึงผิว

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CHAPTER 1

INTRODUCTION

1.1 Motivation

Fuel used in engines of various types of energy which important in everyday life. In addition to the benefits already but also create problems for human. The problems arising from the use of oil, but there are several key issues which are very interested in today is the problem of acid rain, the environmental problems that effect ecosystems and human health and life. When rain comes to terms with the condition can cause acid erosion construction and fell dead trees and vegetation such as wide area. Rain to soak into the soil or flows on the surface will cause soil and water conditions are acid affect plant life and the living area and the changes of ecosystem on both land and in water. Substances that caused major pollution of acid rain is Sulfur dioxide gas (so_2) caused by burning fuel with a sulfur component, especially the burning vehicle fuel. When Sulfur dioxide scattered in the atmosphere to often turn a quarter Sulfur dioxide is combined with steam in the atmosphere will become acid and supporting a full matrix in the rain and the ground agreed to become acid rain. Water conditions the acid used can be corrosive substance, including water delivery pipeline corridor made of metal materials from the decomposition of various types of contamination with water. These substances include lead metal, which affect the brain development of the brain especially for children and adults will make a state vulnerable to disease, high blood and heart disease risk. Cadmium affect the kidney damage, Aluminum affect the central nervous system also Sulfur dioxide is also directly affects the human respiratory system, especially with children and elderly woman.

The fuel must be refined to remove sulfur to reduce the problem. Two general methods of reducing the amount of sulfur have been developed. One method involves solvent extraction of the sulfur compounds and another is about decomposition of sulfur compounds using catalyst to hydrogen sulfide on silica gel. The accept method for reducing the sulfur which is contained in petroleum derived fuels is catalytic to hydrodesulfurization (HDS) which remove sulfur from the fuel molecules by transforming it to hydrogen sulfide. Catalytic hydrodesulfurization is great important in oil refining and generally in the technology of liquid fuel. The target of catalytic hydrodesulfurization is hydrogen and sulfur removal from different oil fraction.

An alternative to hydrodesulfurization, oxidative desulfurization (ODS) has received much attention as a new method for deep desulfurization of diesel fuels. The study on the oxidative desulfurization process using hydrogen peroxide H_2O_2 oxidizing agents is the most common oxidant because it is environmentally friendlier. Typical H_2O_2 is used in the present of a catalyst such as formic acid and acetic acid. However reaction safely and cost are the important concerns for the selection of oxidant, catalyst and operating conditions for oxidative desulfurization processing. High concentration of peroxy acid and hydrogen peroxide are necessary to oxidize sulfur compounds in light oil. However the use of these oxidants at high concentration should be avoid in term of safety and the loss of oil quality. Although ODS is an efficient and promising method, there are still some issues that need to be considered such as safety and economy of the process.

The ODS process consist generally of two stages: the first stage is oxidation of organic sulfur-containing compounds in fuels, and the following step is removal of oxidized sulfur-containing compounds by extraction. In previous paper [1-13], ODS process for sulfur-containing compounds in fuels employing oxidants and liquid-liquid extraction have been proposed. The extraction of oxidized sulfur-containing compounds is considered to be a useful method for removal of sulfur compounds [3,4,7,8]. Otsuki *et al.*[7] reported the thiophene and thiophene derivatives with lower electron densities on the sufur atoms could not be oxidized in the H_2O_2 / formic acid system at 50°C, while dibenzothiophenes with higher electron densities were oxidized. This is in accordance with the conventional concept that thiophene cannot be oxidized by H_2O_2 under mild conditions owing to its aromaticity. Kong *et al.*[13]

reported the thiophene could be oxidized over TS-1 catalyst slowly by H_2O_2 in water or *t*-butanol, but it could not be oxidized in methanol or acetonitrile solvent.

In this research, the oxidative desulfurization of diesel oil is studied in the H_2O_2 / formic acid system with metal oxide-loaded silica as catalyst. The influence of metal oxide type, concentration of metal-loaded on silica and addition of phase transfer catalyst on sulfur removal are studied. The research is conducted on simulated diesel oil consisted (C_2H_6S) and dibenzothiophene (DBT) as representative sulfur-containing compounds in commercial diesel oil.

1.2 Objectives

Desulfurization of high speed diesel using hydrogen peroxide as oxidants promoted by formic acid and metal oxide-loaded silica catalyzed are investigated. The main objectives of this work are as follow

1. To study the catalytic performance of metal oxide-loaded silica in the oxidative removal of sulfur compounds from high speed diesel.
2. To investigate the effect of metal oxide type, concentration of metal and phase transfer catalyst on removal of sulfur compounds and obtain the optimum condition for desulfurization of high speed diesel.
3. To study the physical properties of diesel fuel after removal of sulfur by oxidative desulfurization in the presence of metal oxide-loaded silica.

1.3 Scope of study

The sulfur compounds selected are dimethyl sulfide and dibenzothiophene that are among those found more frequently in the diesel oil. Hydrogen peroxide and formic acid are the chemicals used in oxidation system which their concentration and dosage are followed the former research [8].

In this research, the oxidative desulfurization of simulated diesel oil in the presence of metal oxide-loaded silica are studied as follow

1. Investigate of the variables that affect on percent sulfur removal including:
    - The type of catalyst such as copper loaded on silica ($CuO-SiO_2$) and nickel loaded on silica ($NiO-SiO_2$)
    - The concentration of metal salt solution (Copper (II) nitrate and Nickel nitrate) from 0.25, 0.50 and 1.0 mol/L.
    - The amount of catalysts using 0.5%, 1% and 2% by weight of diesel oil.
    - Adding of phase transfer catalyst using sodium dodecyl benzene sulfonate (SDBS).
2. Study about physical and chemical properties of diesel oil before and after oxidative desulfurization using $CuO-SiO_2$ and $NiO-SiO_2$ including :
    - Sulfur content in diesel oil measured by X-Ray Fluorescence Spectrophotometer.
    - Heating value of diesel oil measured by Bomb Calorimeter.

1.4 Expected Results

1. Can remove sulfur from high speed diesel fuel to remain the minimum value and performance of diesel oil is not decrease.
2. To know the parameters that influence amount of sulfur removal and including the suitable condition.

CHAPTER 2

FUNDAMENTALS AND RELATED WORKS

2.1 Diesel Fuel

Diesel (Diesel Fuel) is a fuel for diesel engines. As part of oil products from refineries. The oil is called transparent or Distillate Fuel oil boiling range of approximately 180-370 degrees Celsius for diesel fuel.

Diesel fuel is graded and designated by the American Society for Testing and Materials (ASTM), while its specific gravity and high and low heat values are listed by the American Petroleum Institute (API). Each individual oil refiner and supplier attempts to produce diesel fuels that comply as closely as possible with ASTM and API specifications. These grades and their general applicability for use in diesel engines are broadly indicated as follow:

Grade No. 1D comprises the class of volatile fuel oils from kerosene to the intermediate distillates. Fuels within this classification are applicable for use in high-speed engines in service involving frequent and relatively wide variations in loads and speeds. In cold weather conditions, No. 1D fuel allows the engine to start easily.

Grade No. 2D includes the class of distillate oils of lower volatility. They are applicable for use in high-speed engines in service involving relatively high loads and speeds.. Even though No. 1D fuel has better properties for cold weather operations, many still use No. 2D in the winter, using fuel heater/water separators to provide suitable starting, as well as fuel additive conditioners, which are added directly into the fuel tank.

Grade No. 4D covers the class of more viscous distillates and blends of these distillates with residual fuel oils.These fuels are applicable for use in low – and high – speed engines employed in services involving sustained loads at substantially constant speed.

A high compression engine (High Compression) and self-ignition (Self Ignition Engine) that the ignition of fuel caused by heat from the high pressure of air in the cylinder without the spark plugs. Available today can be divided into 2 types.

1. High speed diesel oil, HSD or Automotive Diesel oil, ADO

For diesel engines used on the rotation speed vehicles. The market is known as sola oil if use with the vessels are often called Marine Gas Oil. Use with the engine and heavy equipment of any kinds with the rotating speed exceeds 1,000 rpm Such as cars, trucks, fishing boats, passenger boats, tractors.

2. Low Speed Diesel, LSD

For diesel around rotation moderate or slow rotation such as diesel drive transmission installed in accordance with the factories. Working with the low around 500-1000 rpm . And the market is known that oil sludge if use with the vessels are often called Marine Diesel Oil is a mix between diesel fuel oil (Distillate Fuel) and fuel oil (Fuel Oil.,FO or Heavy Fuel Oil, HFO) in the ratio that meets the requirements of Ministry of Commerce.

2.1.1Key attributes of diesel fuel.

1.**Cetane Number**

Cetane number is a measure of the fuel oils volatility; the higher the rating, the easier the engine will start and the combustion process will be smoother within the ratings specified by the engine manufacturer. Cetane rating differs from octane rating that is used in gasoline in that the higher the number of gasoline on the octane scale, the greater the fuel resistance to self- ignition, which is a desirable property in gasoline engines with a high compression ratio. Using a low octane fuel will cause pm-ignition in high compression engines. However, the higher the cetane rating, the easier the fuel will ignite once injected into the diesel combustion chamber. If the cetane number is too low,you will have difficulty in starting.This can be accompanied by engine knock and puffs of white smoke during warm-up in cold weather. High altitudes and low temperatures require the use of diesel fuel with an increased cetane number. Low temperature starting is enhanced by high cetane fuel oil in the proportion of 1.5°F—lower starting temperature for each cetane number increase in the fuel.

2.Volatility

Fuel volatility requirements depend on the same factors as cetane number. The more volatile fuels are best for engines where rapidly changing loads and speeds are encountered. Low volatile fuels tend to give better fuel economy where their characteristics are needed for complete combustion and will produce less smoke, odor, deposits, crankcase dilution, and engine wear. The volatility of a fuel is established by a distillation test where a given volume of fuel is placed into a container that is heated gradually. The readiness with which a liquid changes to a vapor is known as the volatility of the liquid The 90 percent distillation temperature measures volatility of diesel fuel. This is the temperature at which 90 percent of a sample of the fuel has been distilled off. The lower the distillation temperature, the higher the volatility of the fuel. In small diesel engines higher fuel volatility is needed than in larger engines in order to obtain low fuel consumption, low exhaust temperature, and minimum exhaust smoke.

3.Viscosity

The viscosity is a measure of the resistance to flow of the fuel, and it will decrease as the fuel oil temperature increases. What this means is that a fluid with a high viscosity is heavier than a fluid with low viscosity. A high viscosity fuel may cause extreme pressures in the injection systems and will cause reduced atomization and vaporization of the fuel spray. The viscosity of diesel fuel must be low enough to flow freely at its lowest operational temperature, yet high enough to provide lubrication to the moving parts of the finely machined injectors. The fuel must also be sufficiently viscous so that leakage at the pump plungers and dribbling at the injectors will not occur. Viscosity also will determine the size of the fuel droplets, which, in turn, govern the atomization and penetration qualities of the fuel injector spray. Recommended fuel oil viscosity for high-speed diesel engines is generally in the region of 39 SSU (Seconds Saybolt Universal) which is derived from using a Saybolt Viscosimeter to measure the time it takes for a quantity of fuel to flow through a restricted hole in a tube. A viscosity rating of 39 SSU provides good penetration into the combustion chamber, atomization of fuel, and suitable lubrication.

4.Cloud and Pour Point

Cloud point is the temperature at which wax crystals in the fuel (paraffin base) begin to settle out with the result that the fuel filter becomes clogged. This condition exists when cold temperature are encountered and is the reason that a thermostatically controlled fuel heater is required on vehicles operating in cold weather environments. Failure to use a fuel heater will prevent fuel from flowing through the filter and the engine will not run. Cloud point generally occurs 9-14°F above the pour point. Pour point of a fuel determines the lowest temperature at which the fuel can be pumped through the fuel system. The pour point is 5°F above the level at which oil becomes a solid or refuses to flow.

5. Specific gravity

Measure the weight of oil. If heavy fuel oil, more heating value per unit weight will decrease the value cetane.Incomplete combustion occur carbon smoke stains accumulated.

6. Cleanliness and Stability

Cleanliness is an important characteristic of diesel fuel. Fuel should not contain more than a trace of foreign substances; otherwise, fuel pump and injectors difficulties will develop leading to poor performance or seizure. Because it is heavier and more viscous, diesel fuel will hold dirt particles in suspension for a longer period than gasoline. Moisture in the fuel can also damage or cause seizure of injector parts when corrosion occurs. Fuel stability is its capacity to resist chemical change caused by oxidation and heat. Good oxidation stability means that the fuel can be stored for extended periods of time without the formation of gum or sludge. Good thermal stability prevents the formation or carbon in hot parts, such as fuel injectors or turbine nozzles. Carbon deposits disrupt the spray patterns and cause inefficient combustion.

7.Flash Point

ASTM D 975 includes a flashpoint requirement.This is not related directly to engine performance.The flashpoint is controlled to meet safety requirements for fuel handling and storage. The flashpoint is the lowest fuel temperature at which the vapor above a fuel sample will momentarily ignite under the prescribed test conditions.

8. Ash

Abrasive solids or soluble metallic soaps may be present in diesel fuel. These ash-forming materials can result in injector and fuel pump wear, as well as piston and ring wear, in the case of abrasive solids, and engine deposits may also increase. The primary concern with soluble soaps is their contribution to engine deposits.

9. Corrosion Properties

A copper strip corrosion limit (under specified test conditions) is used to predict possible problems with copper, brass or bronze fuel system components.

10. Carbon Residue

A carbon residue test is performed to approximate the engine deposit-forming tendency of diesel fuels. In the ASTM speciication, this is referred to as the "Ramsbottom Carbon Residue on 10 mass percent Distillation Residue."

11. Sulfur Content

Engine wear and deposits can vary due to the sulfur content of the fuel. Today the greater concern is the impact that sulfur could have on emission control devices. As such, sulfur limits are now set by the U.S. Environmental Protection Agency (EPA), and those limits have been incorporated into ASTM D 975. For No. 2 grade low sulfur diesel, the limit is a maximum of 0.05 percent mass (500 ppm) and, for ultra-low sulfur diesel, it is 15 parts pe million (ppm) maximum.

2.1.2 High – speed diesel

At this point would be well to give a definition of diesel fuels. From the Fig.2.1,the more common designation is that portion of the distillation curve from 25 to 65% of the crude-oil barrel, or within the temperature ranges of 375 to 725 °F (150 and 400 ° C).Other properties are evaluated and characteristics determined which influence the fuel performance value in specific application.In the diesel fuel oil classification many properties are considered significant by the the American Society for Testing Materials,such as cetane number,viscosity,carbon residue,sulfur content,flash point,pourpoint,ash and copper strip corrosion.

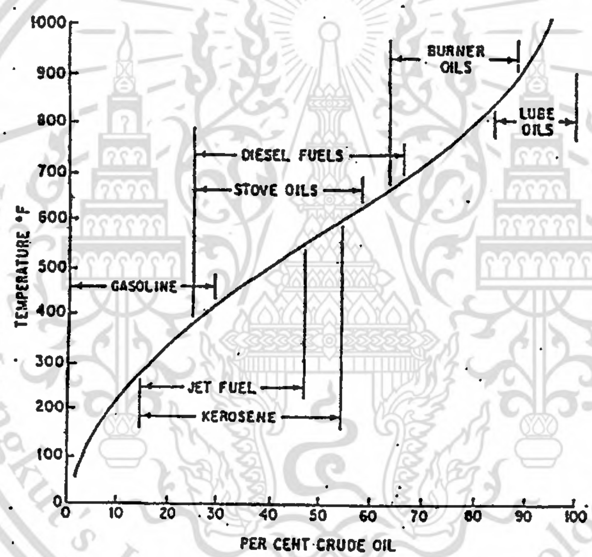


Fig.2.1 Proportion of diesel fuel and other petroleum product [9]

Properties of the commercial fuel oil depend on the method used in the refining of crude oil and natural of crude oil that used in the process. The fuel used in this trial production during the 375 and 725 °F (150 and 440 °C), the various properties such as vaporization, ignition quality , viscosity and other characteristics.

The most important properties that determine the performance value of diesel is specific gravity (API gravity), which although this is not indicated in the ASTM classification , it is evident that light fuels has a high API gravity are more volatile fuels as indicates by the ASTM data of heavy fuel will generally be at low specific gravity and high heat value which is often used as energy sources for power plants.

2.2 The Refining Process

Every refinery begins with the separation of crude oil into different fractions by distillation. The fractions are further treated to convert them into mixtures of more useful saleable products by various methods such as cracking, reforming, alkylation, polymerisation and isomerisation. These mixtures of new compounds are then separated using methods such as fractionation and solvent extraction. Impurities are removed by various methods, e.g. dehydration, desalting, sulphur removal and hydrotreating.

Refinery processes have developed in response to changing market demands for certain products. With the advent of the internal combustion engine the main task of refineries became the production of petrol.

The quantities of petrol available from distillation alone was insufficient to satisfy consumer demand. Refineries began to look for ways to produce more and better quality petrol. Two types of processes have been developed:

- Breaking down large, heavy hydrocarbon molecules
- Reshaping or rebuilding hydrocarbon molecules.

1.Distillation (Fractionation)

Because crude oil is a mixture of hydrocarbons with different boiling temperatures, it can be separated by distillation into groups of hydrocarbons that boil between two specified boiling points. Two types of distillation are performed: atmospheric and vacuum.

Atmospheric distillation takes place in a distilling column at or near atmospheric pressure. The crude oil is heated to 350 - 400°C and the vapour and liquid are piped into the distilling column. The liquid falls to the bottom and the vapour rises, passing through a series of perforated trays (sieve trays). Heavier hydrocarbons condense more quickly and settle on lower trays and lighter hydrocarbons remain as a vapour longer and condense on higher trays.

Liquid fractions are drawn from the trays and removed. In this way the light gases, methane, ethane, propane and butane pass out the top of the column, petrol is formed in the top trays, kerosene and gas oils in the middle, and fuel oils at the bottom. Residue drawn of the bottom may be burned as fuel, processed into lubricating oils, waxes and bitumen or used as feedstock for cracking units.

To recover additional heavy distillates from this residue, it may be piped to a second distillation column where the process is repeated under vacuum, called **vacuum distillation.** This allows heavy hydrocarbons with boiling points of 450°C and higher to be separated without them partly cracking into unwanted products such as coke and gas.The heavy distillates recovered by vacuum distillation can be converted into lubricating oils by a variety of processes. The most common of these is called **solvent extraction**. In one version of this process the heavy distillate is washed with a liquid which does not dissolve in it but which dissolves (and so extracts) the non-lubricating oil components out of it. Another version uses a liquid which does not dissolve in it but which causes the non-lubricating oil components to precipitate (as an extract) from it. Other processes exist which remove impurities by adsorption onto a highly porous solid or which remove any waxes that may be present by causing them to crystallise and precipitate out.

2.Reforming

Reforming is a process which uses heat, pressure and a catalyst (usually containing platinum) to bring about chemical reactions which upgrade naphthas into high octane petrol and petrochemical feedstock. The naphthas are hydrocarbon mixtures containing many paraffins and naphthenes. In Australia, this naphtha feedstock comes from the crudes oil distillation or catalytic cracking processes, but overseas it also comes from thermal cracking and hydrocracking processes. Reforming converts a portion of these compounds to isoparaffins and aromatics, which are used to blend higher octane petrol.

- paraffins are converted to isoparaffins

- paraffins are converted to naphthenes
- naphthenes are converted to aromatics

3.Cracking

Cracking processes break down heavier hydrocarbon molecules (high boiling point oils) into lighter products such as petrol and diesel. These processes include catalytic cracking, thermal cracking and hydrocracking.

Catalytic cracking is used to convert heavy hydrocarbon fractions obtained by vacuum distillation into a mixture of more useful products such as petrol and light fuel oil. In this process, the feedstock undergoes a chemical breakdown, under controlled heat (450 - 500°C) and pressure, in the presence of a catalyst - a substance which promotes the reaction without itself being chemically changed.

Fluid catalytic cracking uses a catalyst in the form of a very fine powder which flows like a liquid when agitated by steam, air or vapour. Feedstock entering the process immediately meets a stream of very hot catalyst and vaporises. The resulting vapours keep the catalyst fluidised as it passes into the reactor, where the cracking takes place and where it is fluidised by the hydrocarbon vapour. The catalyst next passes to a steam stripping section where most of the volatile hydrocarbons are removed. It then passes to a regenerator vessel where it is fluidised by a mixture of air and the products of combustion which are produced as the coke on the catalyst is burnt off. The catalyst then flows back to the reactor. The catalyst thus undergoes a continuous circulation between the reactor, stripper and regenerator sections.The catalyst is usually a mixture of aluminium oxide and silica. Most recently, the introduction of synthetic zeolite catalysts has allowed much shorter reaction times and improved yields and octane numbers of the cracked gasolines.

Thermal cracking uses heat to break down the residue from vacuum distillation. The lighter elements produced from this process can be made into distillate fuels and petrol. Cracked gases are converted to petrol blending components by alkylation or polymerisation. Naphtha is upgraded to high quality petrol by reforming. Gas oil can be used as diesel fuel or can be converted to petrol by hydrocracking. The heavy residue is converted into residual oil or coke which is used in the manufacture of electrodes, graphite and carbides.This process is the oldest technology and is not used in Australia.

Hydrocracking can increase the yield of petrol components, as well as being used to produce light distillates. It produces no residues, only light oils. Hydrocracking is catalytic cracking in the presence of hydrogen. The extra hydrogen saturates, or hydrogenates, the chemical bonds of the cracked hydrocarbons and creates isomers with the desired characteristics. Hydrocracking is also a treating process, because the hydrogen combines with contaminants such as sulphur and nitrogen, allowing them to be removed.Gas oil feed is mixed with hydrogen, heated, and sent to a reactor vessel with a fixed bed catalyst, where cracking and hydrogenation take place. Products are sent to a fractionator to be separated. The hydrogen is recycled. Residue from this reaction is mixed again with hydrogen, reheated, and sent to a second reactor for further cracking under higher temperatures and pressures.In addition to cracked naphtha for making petrol, hydrocracking yields light gases useful for refinery fuel, or alkylation as well as components for high quality fuel oils, lube oils and petrochemical feedstocks.Following the cracking processes it is necessary to build or rearrange some of the lighter hydrocarbon molecules into high quality petrol or jet fuel blending components or into petrochemicals. The former can be achieved by several chemical process such as alkylation and isomerisation.

4.Alkylation

Olefins such as propylene and butylene are produced by catalytic and thermal cracking. Alkylation refers to the chemical bonding of these light molecules with isobutane to form larger branched-chain molecules (isoparaffins) that make high octane petrol.Olefins and isobutane are mixed with an acid catalyst and cooled. They react to form alkylate, plus some normal butane, isobutane and propane. The resulting liquid is neutralised and separated in a series of distillation columns. Isobutane is recycled as feed and butane and propane sold as liquid petroleum gas (LPG).

5.Isomerisation

Isomerisation refers to chemical rearrangement of straight-chain hydrocarbons (paraffins), so that they contain branches attached to the main chain (isoparaffins). This is done for two reasons:

- They create extra isobutane feed for alkylation
- They improve the octane of straight run pentanes and hexanes and hence make them into better petrol blending components.

Isomerisation is achieved by mixing normal butane with a little hydrogen and chloride and allowed to react in the presence of a catalyst to form isobutane, plus a small amount of normal butane and some lighter gases. Products are separated in a fractionator. The lighter gases are used as refinery fuel and the butane recycled as feed. Pentanes and hexanes are the lighter components of petrol. Isomerisation can be used to improve petrol quality by converting these hydrocarbons to higher octane isomers. The process is the same as for butane isomerisation.

6.Polymerisation

Under pressure and temperature, over an acidic catalyst, light unsaturated hydrocarbon molecules react and combine with each other to form larger hydrocarbon molecules. Such process can be used to react butenes (olefin molecules with four carbon atoms) with iso-butane (branched paraffin molecules, or isoparaffins, with four carbon atoms) to obtain a high octane olefinic petrol blending component called polymer gasoline.

7.Hydrotreating and sulfur plants

A number of contaminants are found in crude oil. As the fractions travel through the refinery processing units, these impurities can damage the equipment, the catalysts and the quality of the products. There are also legal limits on the contents of some impurities like sulfur in products.

Hydrotreating is one way of removing many of the contaminants from many of the intermediate or final products. In the hydrotreating process, the entering feedstock is mixed with hydrogen and heated to 300 - 380°C. The oil combined with the hydrogen then enters a reactor loaded with a catalyst which promotes several reactions:

- hydrogen combines with sulphur to form hydrogen sulphide (H_2S)
- nitrogen compounds are converted to ammonia
- any metals contained in the oil are deposited on the catalyst
- some of the olefins, aromatics or naphthenes become saturated with hydrogen to become paraffins and some cracking takes place, causing the creation of some methane, ethane, propane and butanes.

8.Sulfur recovery plants

The hydrogen sulphide created from hydrotreating is a toxic gas that needs further treatment. The usual process involves two steps:

- the removal of the hydrogen sulphide gas from the hydrocarbon stream
- the conversion of hydrogen sulphide to elemental sulphur, a non-toxic and useful chemical.

Solvent extraction, using a solution of diethanolamine (DEA) dissolved in water, is applied to separate the hydrogen sulphide gas from the process stream. The hydrocarbon gas stream containing the hydrogen sulphide is bubbled through a solution of diethanolamine solution (DEA) under high pressure, such that· the hydrogen sulphide gas dissolves in the DEA. The DEA and hydrogen mixture is the heated at a low pressure and the dissolved hydrogen sulphide is released as a concentrated gas stream which is sent to another plant for conversion into sulphur.

Conversion of the concentrated hydrogen sulphide gas into sulphur occurs in two stages.

1. Combustion of part of the H_2S stream in a furnace, producing sulphur dioxide (SO_2) water (H_2O) and sulphur (S).

$$2H_2S + 2O_2 \rightarrow SO_2 + S + 2H_2O$$

2. Reaction of the remainder of the H_2S with the combustion products in the presence of a catalyst. The H_2S reacts with the SO_2 to form sulphur.

$$2H_2S + 2O_2 \rightarrow 3S + 2H_2O$$

As the reaction products are cooled the sulphur drops out of the reaction vessel in a molten state. Sulphur can be stored and shipped in either a molten or solid state.

2.3 Sulfur

A non-hydrocarbon substances in crude oil. Sulfur has a definite effect on the wear of the internal components of the engine, such as piston ring, pistons, valves, and cylinder liners. In addition a high sulfur content fuel requires that the engine oil and filter be changed more often. This is because the corrosive effects of hydrogen sulfide in the fuel and the sulfur dioxide or sulfur triioxide that is formed during the combustion process combines with water vapor to form acids.

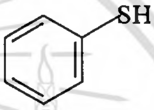
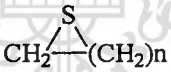
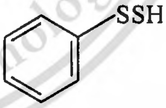
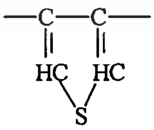
Sulfur is a soft, pale yellow, odorless, brittle solid. It is insoluble in water, but soluble in carbon disulfide, benzene, toluene. Sulfur exists in several crystalline and amorphous allotropes. The most common form is yellow, orthorhombic alpha-sulfur, which contains puckered rings of S_8. Sulfur burns with a blue flame, oxidizing to sulfur dioxide.

Sulfur's main commercial use is as a reactant in the production of sulfuric acid (H_2SO_4). Sulfuric acid is the industrialized world's number one bulk chemical, required in large quantities in lead-acid batteries for automotive use.

Sulfur is also used in the vulcanization of natural rubber, as a fungicide, in black gunpowder, in detergents and in the manufacture of phosphate fertilizers.

Sulfur is essential to life as a minor component of fats, body fluids, and skeletal minerals.

Sulfide samples are found in oil.

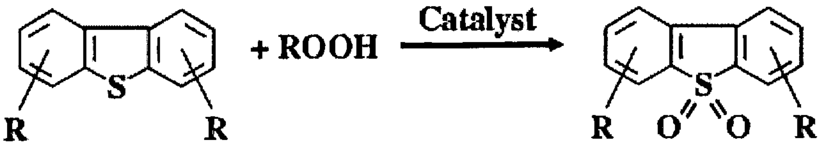
Hydrogen sulphide	H_2S
Mercaptans	
-Aliphatic	R-SH
-Aromatic	
Sulphides	
-Aliphatic	R-S-R
-Cyclic	
Diesulphide	
-Aliphatic	R-S-S-R
-Aromatic	
Polysulphide	$R\text{-}(S)_n\text{-}R$
Thiopene	

2.4 Desulfurization process

The refinery feedstocks (naphtha, kerosene, diesel oil and heavier oils) contain a wide range of organic sulfur compounds, including thiols, thiophenes, organic sulfides and disulfides, and many others. These organic sulfur compounds are products of the degradation of sulfur containing biological components, present during the natural formation of the fossil fuel, petroleum crude oil.

Hydrodesulfurization (HDS) When the HDS process is used to desulfurize a refinery naphtha, it is necessary to remove the total sulfur down to the parts per million range or lower in order to prevent poisoning the noble metal catalysts in the subsequent catalytic reforming of the naphthas.When the process is used for desulfurizing diesel oils, the latest environmental regulations in the United States and Europe, requiring what is referred to as *ultra-low sulfur diesel* (ULSD), in turn requires that very deep hydrodesulfurization is needed. In the very early 2000s, the governmental regulatory limits for highway vehicle diesel was within the range of 300 to 500 ppm by weight of total sulfur. As of 2006, the total sulfur limit for highway diesel is in the range of 15 to 30 ppm by weight.

Oxidative desulfurization (ODS) is an innovative technology that can be used to reduce the cost of producing ultra-low sulfur diesel (ULSD).Oxidative desulfurization is not a new concept and has been discussed for several years in previous publications.The advantage that oxidative desulfurization has over conventional HDS is that the difficult-to-desulfurize, refractory-substituted dibenzothiophenes (DBT) are easily oxidized under low temperature and pressure conditions to form the corresponding sulfones. This reaction is shown in this figure. The oxidant can be supplied by either hydrogen peroxide/peracid or organic peroxide. Note that there is no hydrogen consumed in this reaction. The sulfones are highly polar compounds and are easily separated from the diesel product by either extraction or adsorption.



This oxidation chemistry is complementary to hydrotreating, as other sulfur compounds such as disulfides are easy to hydrodesulfurize, but oxidize slowly. For this reason, oxidative desulfurization is best utilized as a second stage after an existing HDS unit, taking a low sulfur diesel (~500 ppm) down to ULSD (<10 ppm) levels. In this situation, the diesel product has been depleted of difficult to oxidize sulfur species and has a high concentration of the more refractory DBT constituents.

2.5 Silica

Silica is an amorphous form of silicon dioxide, which is synthetically produced in the form of hard irregular granules (having the appearance of crystals) or hard irregular beads. A microporous structure of interlocking cavities gives a very high surface area (800 square meters per gram). It is this structure that makes silica a high capacity desiccant. Water molecules adhere to the surface because it exhibits a lower vapour pressure than the surrounding air. When an equilibrium of equal pressure is reached, no more adsorption occurs. Thus the higher the humidity of the surrounding air, the greater the amount of water that is adsorbed before equilibrium is reached. It is in these higher humidity conditions (above 50% Relative Humidity) that stored or in-transit items are susceptible to damage.

The beauty of silica is the physical adsorption of water vapour into its internal pores. There is no chemical reaction, no by products or side effects. Even when saturated with water vapour, silica still has the appearance of a dry product, its shape unchanged.

In chemistry, silica is used in chromatography as a stationary phase. In column chromatography the stationary phase is most often composed of silica particles of 40-63 μm. Different particle sizes are used for achieving a desired separation of certain molecular sizes. In this application, due to silica's polarity, non-polar components tend to elute before more polar ones, hence the name normal phase chromatography. However, when hydrophobic groups (such as C_{18} groups) are attached to the silica then polar components elute first and the method is referred to as reverse phase chromatography. Silica is also applied to aluminum, glass, or plastic sheets for thin layer chromatography.

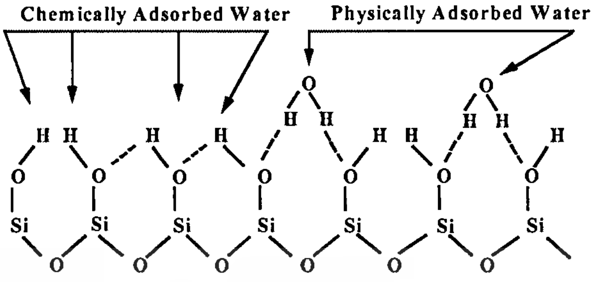
The hydroxy (OH) groups on the surface of silica can be functionalized to afford specialty silica that exhibit unique stationary phase parameters. These so-called functionalized silica are also used in organic synthesis and purification as insoluble reagents and scavengers.

Chelating groups have also been covalently bound to silica. These materials have the ability to remove metal ions selectively from aqueous media. Chelating groups can be covalently bound to polyamines that have been grafted onto a silica surface producing a material of greater mechanical integrity. Silica is also combined with alkali metals to form a M-SG reducing agent. Silica is not thought to biodegrade in either water or soil.

Silica Surface

In 1934, Hoffman postulated the existence of silanol groups (=Si-OH) on the silica surface. It is now generally accepted that surface silicon atoms tend to have a complete tetrahedral configuration and that in an aqueous medium their free valence becomes saturated with hydroxyl groups, forming silanol groups. Silanol groups in turn, may condense to form siloxane bridges (=Si-O-Si=). Therefore, the surface composition of silica is made up of physically adsorbed water, chemically bound water, and silicon dioxide (See Figure 2.2).

Silica Gel Surface



Chemically adsorbed water - 4 to 6 OH / nm^2
Physically adsorbed water - 0.1 to 0.7 fractional monolayer

Fig. 2.2

2.6 Thiophene

Thiophene is the heterocyclic compound with the formula C_4H_4S. Consisting of a flat five-membered ring, it is aromatic as indicated by its extensive substitution reactions. Related to thiophene are benzothiophene and dibenzothiophene, containing the thiophene ring fused with one and two benzene rings, respectively. Compounds analogous to thiophene include furan (C_4H_4O) and pyrrole (C_4H_4NH).

Thiophene was discovered as a contaminant in benzene. Thiophene and its derivatives occur in petroleum, sometimes in concentrations up to 1-3%. The thiophenic content of oil and coal is removed via the hydrodesulfurization (HDS) process. In HDS, the liquid or gaseous feed is passed over a form of molybdenum disulfide catalyst under a pressure of H_2. Thiophenes undergo hydrogenolysis to form hydrocarbons and hydrogen sulfide. Thus, thiophene itself is converted to butane and H_2S. More prevalent and more problematic in petroleum are benzothiophene and dibenzothiophene.

2.7 Dibenzothiophene

Dibenzothiophene is the organic compound consisting of two benzene rings fused to a central thiophene ring. This tricyclic heterocycle, and especially its alkyl substituted derivatives occur widely in heavier fractions of petroleum.

Dibenzothiophene is prepared by the reaction of biphenyl with sulfur dichloride in the presence of aluminium trichloride.

Properties 	
Molecular formula	$C_{12}H_8S$
Molar mass	184.26 g/mol
Appearance	Colourless crystals
Density	1.252 g/cm^3
Melting point	97-100 °C(lit.)
Boiling point	332-333 °C
Solubility in water	insoluble
Solubility in other solvents	benzene and related

2.8 Methods of Oxidation

The applicability of a desulfurization scheme depends on the kinetics and the selectivity of the oxidation.The oxidation should be rapid, and the oxidizer should be selective to the sulfur. The most economical oxidizer on an industrial scale, however, is oxygen. Therefore, a method is needed which uses molecular oxygen as the oxidizer. Two schemes have been used to oxidize sulfur compounds with oxygen. There are : (1) Direct application of oxygen or air : this method is suitable for thiols and is usually carried out in basic solution. (2) Indirect oxidation using an oxygen carrier. Oxygen carrier are molecules which can selectively oxidize the sulfur and which can be generates or produced using molecular oxygen. Two types of carriers were tried, regenerable and nonregenerable.

Methods with Regenerable Oxygen Carriers. The scheme of oxidation of sulfur compounds with a regenerable oxidizer UO_2 involves two steps

(1) Oxidation

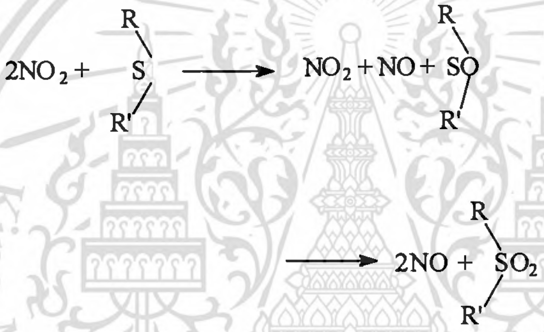
$$UO_2 + R\text{-}S\text{-}R \longrightarrow U + R\text{-}SO_2\text{-}R' \qquad (2.1)$$

(2) Regeneration of the oxidizer with molecular oxygen

$$U + O_2 \longrightarrow UO_2 \qquad (2.2)$$

Nitrogen Dioxide as a regenerable oxidizer.

(1) Oxidation

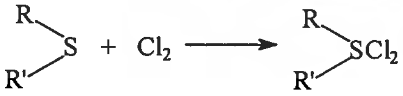


(2.3)

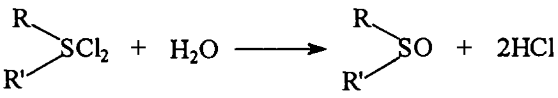
(2) Regeneration

$$2NO + O_2 \longrightarrow 2NO_2 \qquad (2.4)$$

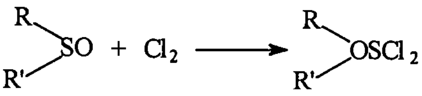
Chlorine as a regenerable oxidizer. Chlorine can be applied to desulfurization with oxidation and hydrolysis proceeding as follow :



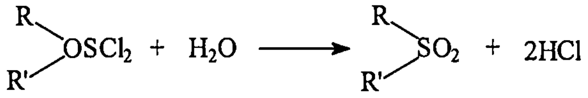
(2.5)



(2.6)



(2.7)



(2.8)

Methods without regeneration of the oxidizer. Oxidation of hydrocarbon by molecular oxygen proceeds via the intermediates of organic hydroperoxides (HP) and peroxy acids (PA). The peroxidic species can selectively oxidize sulfur compounds to the corresponding sulfides and sulfones. Much of the background material on oxidation of hydrocarbons by oxygen has also been discussed previously by numerous authors. And therefore will only briefly be discussed here.

1. Noncatalytic, liquid-phase oxidation of a hydrocarbon (RH) in the presence of excess oxygen proceeds by way of a free-radical mechanism. Initiation can occur with molecular oxygen in accord with the reaction

$$2RH + O_2 \longrightarrow 2R^\bullet + H_2O_2 \tag{2.9}$$

Or by the decomposition of intermediates, e.g., the hydrocarbon peroxides, RO_2H

$$RO_2H \longrightarrow RO^\bullet + HO^\bullet \tag{2.10}$$

The free radical $HO^\bullet$, $RO^\bullet_2$, $RO^\bullet$ denoted by $A^\bullet$,abstract a hydrogen from a hydrocarbon molecule and produce $R^\bullet$. In turn, $R^\bullet$ absorbs oxygen very rapidly, and a peroxy radical RO_2 is produced as follows

$$A^\bullet + RH \longrightarrow R^\bullet + AH \tag{2.11}$$

$$R^\bullet + O_2 \longrightarrow RO_2^\bullet \text{ (fast)} \tag{2.12}$$

Peroxy radical can abstract a hydrogen from another htdrocarbon molecule and produce a hydroperoxide

$$RO_2^\bullet + RH \longrightarrow RO_2H + R^\bullet \tag{2.13}$$

Or the peroxy radicals can terminate by the reaction

$$2RO_2^\bullet \longrightarrow RO_2R + O_2 \tag{2.14}$$

2. Hydrocarbon which contain hydrogen with lower bond energies are oxidizes more rapidly than those with higher bond energies. The hydroperoxides that result are more stable and therefore are more selective as oxidizers.

3. Hydroperoxides and peracids can selectively oxidize sulfur compounds to the corresponding sulfoxides and sulfones.

4. The protic nature of the solvent strongly affects the observed from the rate equation for the oxidation of sulfur compounds. In general , the rate equation has two terms. Once accounts for the protic aspect of the solvent, and the other accounts for the degree of association of the hydroperoxide (HP) in accord with the equation

$$d[R\text{-}S\text{-}R']/dt = k_2[R\text{-}S\text{-}R'][HP] + k_3[R\text{-}S\text{-}R'][HP]_2 \qquad (2.15)$$

All of their observation supported a mechanism of oxidation proposed in the early work of Overberger and Cummins (1953) wherein it was postulated that the sulfur was oxidized by a nucleophilic attack on a peroxidic complex which contained peroxidic and protic structures

(2.16)

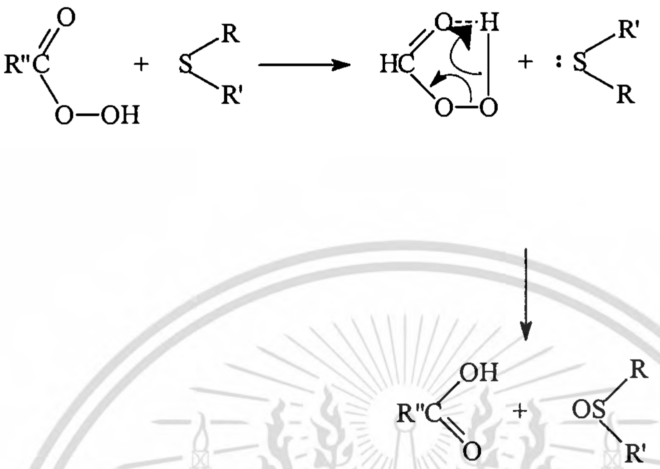
HA denotes the protic molecule, and R"O$_2$H is the peroxide.

The oxidation of the sulfoxide to the sulfone occurred by the same mechanism. In a protic solvent, the present in excess fulfills the function of HA, and the apparent rae of reaction is the first order with respect to the peroxide. In an aprotic solvent, another hydroperoxide molecule will function as HA.

(2.17)

Therefore, in an aprotic solvent the apparent rate of reaction 19 depends on the second power of the concentration of hydroperoxide.

5. A special case of interest is that of the peroxy acids which are formed by oxidation of the primary oxidation products, especially aldehydes. Peracids can form intermolecular, conpounds depend on the first powers of the concentrations of acids as suggested by the equation.



(2.18)

6. A larger oxidation potential is required to convert sulfoxides to sulfones than to oxidize sulfides to sulfoxides. Thus, if the oxidizer is a hydroperoxide in a protic medium the reaction may stop after sulfoxide is formed.

7. When the n electrons of the sulfur can resonate with the p electrons of the organic radical, a larger oxidation potential will be required to effect the oxidation than for cases where resonance does not exist. Therefore , it is more difficult to oxidize thiophene than aryl and alkyl sulfides.

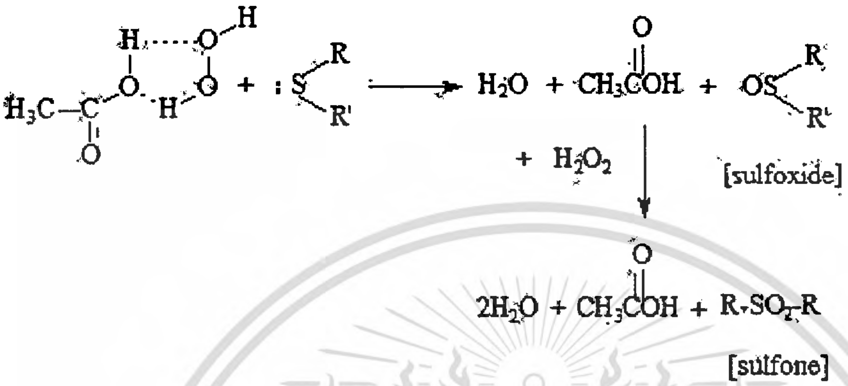
2.9 Oxidation reaction of hydrogen peroxide

In this experiment hydrogen peroxide was used as a oxidant issued by Zannikos F. and Board of Education in 1995 .The hydrogen peroxide is used as hydroperoxide agent, which the experimental results is hydrogen peroxide is appropriate to oxidize aromatic sulfur compound by solvent for oxidation reaction of sulfide are acetic acid solution and formic acid solution.

Reaction between hydrogen peroxide and sulfur compounds using acetic acid solution as solvent is the following equation.

$$2H_2O_2 + CH_3COOH + R\text{-}S\text{-}R' \longrightarrow CH_3COOH + 2H_2O + R\text{-}SO_2\text{-}R' \qquad (2.19)$$

From the reactions that occur one mole of oxidant will react with one mole of sulfide for change to sulfoxide and two oxidants will react with one mole of sulfide change to sulfone.



(2.20)

RSR '= sulfide.

From the reaction mechanism of oxidation and the process changes the structure of sulfur compounds. The free electron from the sulfur atom will react with the oxygen atom of the structure between hydrogen peroxide and an acetic acid, which called sulfoxide , so sulfoxide will be changed to sulfone.

For the mechanism of formic acid is in the same format.

2.10 Catalyst preparation

2.10.1 <u>Support preparation</u>

In the preparation of support material the precipitation is carried out in a baffled vessel by controlling the following:

a) Concentrations of solution and precipitating agents

b) Precipitation temperature and final pH

c) Mode of addition and their rate

d) Ageing time and temperature

e) Filtration and nature of washing liquid

f) Drying

g) Extrusion (shape & size)

2.10.2 Extrusion of precursor hydrate to shaped support

These extrudates are dried in an oven at 110-120 ° C for 8-12 h, preferably in flow of dry air to remove free water and acid from the surface during drying. Here, the extent of mix-mulling, the compression in extruder and the die size are important parameters which control pore size distribution, bulk density and crushing strength, etc. both at laboratory scale and commercial production.

2.10.3 Calcination / Activation

After drying the extrudates, it is subjected to calcination at 500 – 550 °C for 4-6 hours to develop surface and pore structures. The calcination in flow of dry air improves surface area and if it is done in close system like muffle furnace, a marginally lower surface area is observed and the support is subjected to some extent, hydrothermal treatment, resulting in better thermal stability of the material.

2.10.4 Impregnation with active metals

Now a days, the maximization of site II in the catalyst formulation is given the priority which gets sulfided nearly 100% giving rise highest activity of desulfurization. It depends on how we can maximize site II active sites in catalyst development.

Now, depending upon the requirement of product specifications, the composition of catalyst is chosen. The support is then impregnated with the salt solutions; a few options can be employed with any of the following technique for impregnations:

1) By dipping in excess solution
2) Incipient impregnation
3) Spraying the solutions on the support

It is also important to note that on metals impregnation, there is reduction in surface area as well as pore volume in the final catalyst (product) particularly in case of higher metals loading. Hence, care is to be taken to choose the support which on metals impregnation results in properties as targeted. A support with reasonable high surface area and pore volume may be selected to get the desired physico-chemical properties of the catalyst after impregnation and calcination.

After impregnation of the support with metals solution, the catalyst is dried at 120 ° C for 12-16 hours and then calcined at 500 ° C for 4-6 h similar to the conditions for support drying and calcination.

The catalyst with higher metals loading can also be prepared by co-precipitation of support material and metals solutions by using suitable precipitating agent.

2.11 Literature Review

Zannikos, F. et al. [1] Studied about desulfurization of petroleum fractions by oxidation and solvent extraction. The known ability of several solvents to extract sulfur compounds selectivity from petroleum fractions can be dramatically improved by oxidizing the sulfur from the divalent state (sulfur) to the hexavalent (sulfone). The oxidation process itself leads to the removal of a substantial portion of the existing sulfur and makes the remaining sulfur compounds amenable to efficient removal even by solvents such as methanol which are not effective in selective extraction of the unoxidized sulfur compounds. Thus this combination process is capable of moving up to 90% of the sulfur compounds in petroleum fractions at acceptable yields. The oxidation process has no deleterious effects on the distillation profile and the other characteristics of the middle distillate fractions that were examined.

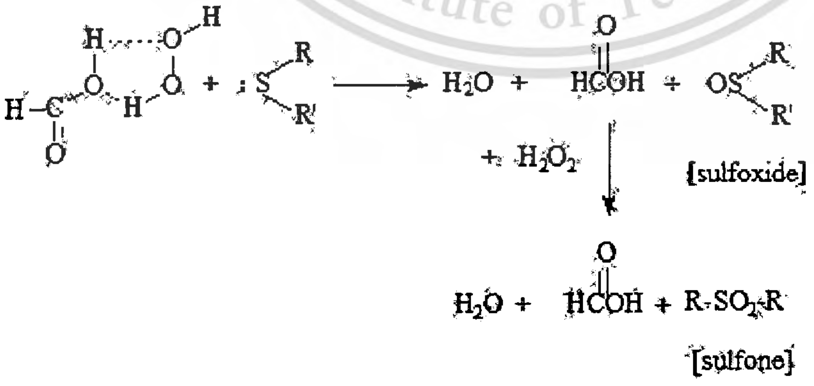
Shujiro, O. [3] Studied from the hydrodesulfurization ligth gas oil (LGO) and vacuum gas oil (VGO) using oxidation with hydrogen peroxide and formic acid at 70°C and different time follows by extracts with N,N-dimethylformamide (DMF) and actronitrile (ACN) from the trial showed that Sulfur compounds in LGO and VGO will be issued as remain only 0.01% wtSulfur by measuring the GCFPD and proven by FT / IR. Found that the LGO and VGO were issued to oxidize since sulfone will be occur. The best solvent effective to extract Sulfur compounds is DMF.

Guoxion, Y. [2] studied about the desulfurization of diesel fuels with hydrogen peroxide was studied using activated carbona as the catalysts. Adsorption and catalytic properties of activated carbons for dibenzothiophene (DBT) were investigated. The higher the adsorption capacity of the carbon is the better the catalytic activities of the activated carbon was also investigated. Oxidation of DBT is enhanced when the aqueous pH is less than 2 and addition of formic acid can promote the oxidation. The effect of carbon surface chemistry on DBT adsorption and catalytic activity was also investigated. Adsorption of DBT shows a strong dependence on carboxylic group content. The oxidative removal of DBT increases as the surface carbonyl group content increases. Oxidative desulfurization of a commercial diesel fuel(sulfur content 800 wt.ppm) with hydrogen peroxide was investigated in the presence of activated carbon and formic acid.Much lower residual sulfur content (142 wt.ppm) was found in the oxidized oil after the oxidation by using the hydrogen peroxide, activated carbon, formic acid. The resulting oil contained 16 wt.ppm of sulfur after activated carbon adsorption without any negative effect in the fuel quality. Activated carbon has high catalytic activity and can be repeatedly used following simple water washing with little change in the catalytic performance after three regeneration cycles.

Lanju, C. [4] studied about oxidation reactin of thiophene on silica gel with hydrogen peroxide is oxidizing agent and using formic acid as a solvent. Thiophene(C_4H_4S) and 3-meththiophene (3-MC_4H_4S) is a sulfur compound that found in fluid catalytic cracking (FCC) process of gasoline in oxidation reaction of C_4H_4S and 3-MC_4H_4S will be occur hydrogen peroxide and formic acid on silica gel with the metal oxide compound. Silica gel are added oxide compounds of copper and cobalt in the ratio 1:1, which found that the system is very swiftness of the hydrogen peroxide and formic acid while silica gels without filling of the metal oxides are less facile. The process of C_4H_4S and $3\text{-}MC_4H_4S$ can improved by increasing temperature but will decrease when added olefin substances.

Farhan, A. [5] studied about desulfurization diesel fuel by using hydrogen peroxide change aromatic sulfur compound to sulfone with tungstate as catalyst in oxidative desulfurization(ODS) which contains NA_2WO_{4+} 30% , hydrogen peroxide and acetic acid that suitable to remove sulfur from diesel fuel. In this system shows that dibenzothiophene and 4,6-dibenzothiophene or thiophene are the oil changes to sulfone at 70°C in less time.

Jaruprathai, C. et al. [8] Studied the desulfurization of high speed diesel by oxidation reaction using hydrogen peroxide as oxidizing agent and acid solution solvent. The experimental results showed that the sulfur compounds were oxidized to sulfone and sulfoxide. Formic acid gave higher percent of sulfur removal than acetic acid. The optimum condition for sulfur removal was found to be 30% vol. hydrogen peroxide using 10 mol/dm^3 formic acid as solvent for 60 minutes. The total sulfur was reduced by 48.91% while the heating value of diesel oil increased with the increasing of percent sulfur removal.



CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Chemicals

1) Commercial diesel oil was obtained from PTT Public Company Limited.

2) Dimethyl Sulfide (C_2H_6S, DMS), Analytical grade,from MERCK Co.,Ltd.

3) Dibenzothiophene($C_{12}H_8S$,DBT),Analytical grade,fromLAB CSAN Co.,Ltd

4) Hydrogen peroxide (H_2O_2), Analytical grade,from SR.LAB Co.,Ltd.

5) Formic acid (HCOOH), Analytical grade, from LAB CSAN Co.,Ltd

6) Silica gel powder, Analytical grade,from MERCK Co.,Ltd.

7) Sodium carbonate (Na_2CO_3), Analytical grade, from SR.LAB Co.,Ltd.

8)Anhydrous Magnesium Sulfate (anh.$MgSO_4$), Analytical grade, from SR.LAB Co.,Ltd

9) Paraffin oil, Commercial grade,from SR.LAB Co.,Ltd

10) Copper nitrate ($Cu(NO_3)_2$), Analytical grade,fr from MERCK Co.,Ltd.

11) Nickel nitrate ($Ni(NO_3)_2$), Analytical grade,from SR.LAB Co.,Ltd

12)Sodium dodecyl benzene sulfonate,Analytical grade,fromLAB CSAN Co.,Ltd

3.2 Apparatus and Instruments

1) Three necks flask	500 ml
2) Beaker	100 ml, 250 ml and 500 ml
3) Volumetric flask	250 ml
4) Conical flask	250 ml
5) Pipette	10 ml and 50 ml
6) Burette	50 ml
7) Separatory funnel	500 ml
8) Mechanical stirrer	
9) Thermometer	100°C
10) Buchner's funnel	
11) Water bath	
12) Condenser	
13) Universal indicator paper	
14) Filter paper	
15) Funnel	
16) Shaker	
17) Balance	
18) Adiabatic Bomb Calorimeter	
19) X-Ray Fluorescence Spectrophotometer (XRF)	
20) Scanning Electron Microscope (SEM)	
21) Fourier-Transform Infared Spectrophotometer (FTIR)	

3.3 Experimental Procedure

3.3.1 Catalyst preparation

Silica-supported copper and nickel catalyst ($CuO-SiO_2$ and $NiO-SiO_2$) were prepared by the incipient-wetness impregnation method. A 250 ml. beaker was charged with 50 g of silica powder and 100 ml of $Cu(NO_3)_2$ or $Ni(NO_3)_2$ solution with concentration of 0.25, 0.5 and 1.0 mol.L^{-1} (loading level of CuO and NiO on silica powder were 3 wt%, 6 wt% and 12 wt%, respectively). After the metal salts impregnation by immersing the silica support for 24 h in aqueous solution, the slurry was then dried with a vacuum rotary evaporator at 80 °C for 3 h, and then the catalyst was dried in an oven at 120 °C. The catalyst was calcined at 450 °C for 3 h.

3.3.2 Oxidative desulfurization of diesel oil

In this experiment, dimethyl sulfide and dibenzothiophene were dissolved into commercial diesel oil to make a simulated diesel solution. The concentration of hydrogen peroxide (30% by volume) and formic acid (10 mol.L^{-1}) were kept constant for all experiment runs. The detail of oxidative desulfurization of diesel oil listed as follow:

1. A 500 ml beaker was charged with 10 g of dimethyl sulfide and 200 g of diesel oil. The mixture was stirred until homogeneously. The sulfur content in diesel oil was 2.6% by weight.
2. 200 ml of diesel oil mixed with sulfur compounds 40 ml of formic acid and metal oxide-loaded silica catalyst were put in a 500 ml three-necked round bottom flask equipped with a mechanical stirrer, thermometer and a reflux condenser. The system was heated

in a paraffin oil bath until the selected reaction temperature (60°C). The experimental apparatus show as Figure 3.1

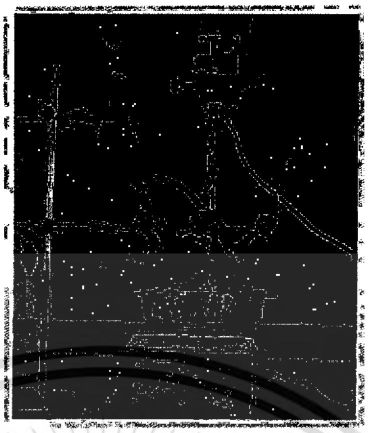


Fig.3.1 setting up apparatus

3. When the mixture reached the reaction temperature, 40 ml of hydrogen peroxide (and phase transfer catalyst) was then added and the reaction was started.
4. After complete the reaction, the three necked flask was cooled down immediately for stop the reaction.
5. The solution was filter for separate the catalyst, liquid sample was transferred into separators funnel.
6. After the liquid sample completely separate into two layers (oxidize oil and water layer), drain the water layer stored in a brown bottles.
7. Neutralized the oxidized oil by adding 1 mol.L^{-1} of sodium carbonate solution.
8. Pour the oxidized diesel oil into 250 ml beaker, then added anhydrous magnesium sulfate to absorb water remained in oxidized diesel oil.

9. Separate the magnesium sulfate by filtration, the desulfurized diesel oil was keep in brown bottles in order to further analyze sulfur content and its properties.

Characterization of desulfurized diesel oil

Diesel oil before and after the oxidative desulfurization reaction were determined the sulfur content and other properties show as Table 3.1

Table 3.1 List of desulfurized diesel oil characterization and testing instruments.

Properties	**Instrument**
Sulfur content	X-Ray Fluorescence Spectrophotometer (XRF)
Heating value	Adiabatic Bomb Calorimeter
Chemical identification	Fourier-Transform Infared Spectrophotometer (FTIR)

3.4 Experimental design

The univariate experiment was designed for study the effect of process variables on sulfur removal. The concentration of metallic salts, dosage of catalyst and type of metal oxide were firstly studied. The optimum condition of oxidative desulfurization reaction was used for study the effect of phase transfer catalyst on sulfur removal.

The experimental condition were shown in table 3.3-3.4

Table 3.2 Experimental conditions for study the effect of the metallic salt concentration on sulfur removal

Type of sulfur compound	**Catalyst**	**Metallic salt Concentration (mol.L^{-1})**	**Dosage of catalyst (wt%)**	**Reaction time (h)**
Dimethyl sulfide (DMS)	$CuO-SiO_2$	0.25	3	2
		0.5	3	2
		1.0	3	2
	$NiO-SiO_2$	0.25	3	2
		0.5	3	2
		1.0	3	2
Dibenzothiophene (DBT)	$CuO-SiO_2$	0.25	3	2
		0.5	3	2
		1.0	3	2

Table 3.3 Experimental conditions for study the effect of catalyst amount on sulfur removal

Type of sulfur compound	**Catalyst**	**Dosage of catalyst (wt%)**	**Metallic salt Concentration ($mol.L^{-1}$)**	**Reaction time (h)**
Dimethyl sulfide (DMS)	$CuO-SiO_2$	0.5	0.5	2
		1	0.5	2
		2	0.5	2
	$NiO-SiO_2$	0.5	0.5	2
		1	0.5	2
		2	0.5	2
Dibenzothiophene (DBT)	$CuO-SiO_2$	0.5	0.5	2
		1	0.5	2
		2	0.5	2

Table 3.4 Experimental conditions for study the effect of phase transfer catalyst on sulfur removal

Type of sulfur compound	**Catalyst type**	**Metallic salt Concentration (mol.L^{-1})**	**Dosage of catalyst (wt%)**	**Phase transfer catalyst**
Dimethyl sulfide (DMS)	CuO-SiO$_2$	0.5	3	Sodium dodecyl benzene sulfonate 1%
	NiO-SiO$_2$	0.5	3	Sodium dodecyl benzene sulfonate 1%

CHAPTER 4

RESULTS AND DISCUSSION

In the present work, the oxidative desulfurization of simulated diesel oil was studied in the H_2O_2 /formic acid system over metal-loaded silica catalyst. The effect of oxidative system , metal-loaded silica and the addition of phase transfer catalyst on the removal of sulfur compounds of dimethyl sulfide (DMS) and dibenzothiophene (DBT) were investigated in details.

4.1 Effect of metallic salt concentration on the oxidation of sulfur compound

4.1.1 Removal of dimethyl sulfide (DMS)

The $CuO-SiO_2$ and $NiO-SiO_2$ catalyst were prepared by impregnation method. The SiO_2 were impregnated with an aqueous solution of $Cu(NO_3)_2$ with concentration of 0.25,0.5 and 1.0 $mol.L^{-1}$. In the same manner, $NiO-SiO_2$ were prepared by SiO_2 immersed in the solution of $Ni(NO_3)_2$. The influence of metallic salt concentration or metal content of catalyst to the sulfur content remaining and percentage of sulfur removal was shown in Table 4.1.

The sulfur content remaining in the diesel oil and percentage of sulfur removal that catalyzed by $CuO-SiO_2$ and $NiO-SiO_2$ were shown in Figure 4.1-4.4.

Table 4.1 : Effect of metallic salt concentration on the oxidation of sulfur compound.

Type of sulfur compound	**Catalyst**	**Metallic salt Concentration (mol.L^{-1})**	**Dosage of Catalyst (wt%)**	**Sulfur remaining in diesel oil (wt%)**	**Sulfur Removal (%)**
Dimethyl sulfide (DMS)	CuO-SiO_2	0.25	3	0.1566	93.98
		0.5	3	0.0361	98.61
		1.0	3	0.0232	99.11
Dimethyl sulfide (DMS)	NiO-SiO_2	0.25	3	0.0507	98.05
		0.5	3	0.0366	98.59
		1.0	3	0.0189	99.27
Dibenzothiophene (DBT)	CuO-SiO_2	0.25	3	0.5023	49.77
		0.5	3	0.4325	56.75
		1.0	3	0.4129	58.71

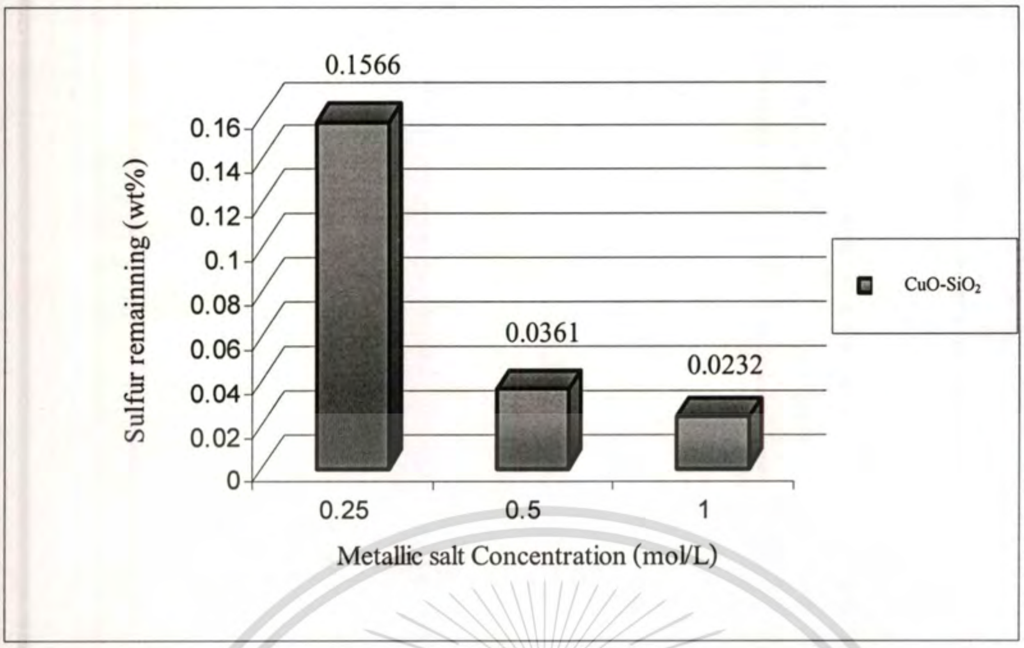


Figure 4.1: Effect of metallic salt concentration of catalyst on sulfur content remaining in diesel oil over CuO-SiO$_2$ catalyst

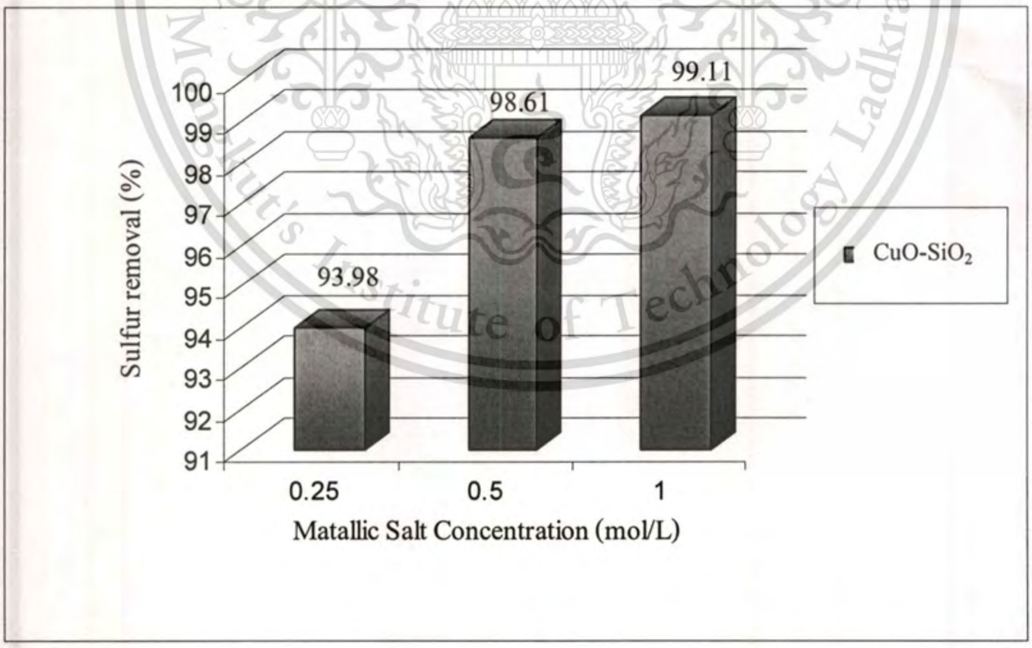


Figure 4.2 : Effect of metallic salt concentration of catalyst on percent sulfur removal over CuO-SiO$_2$ catalyst.

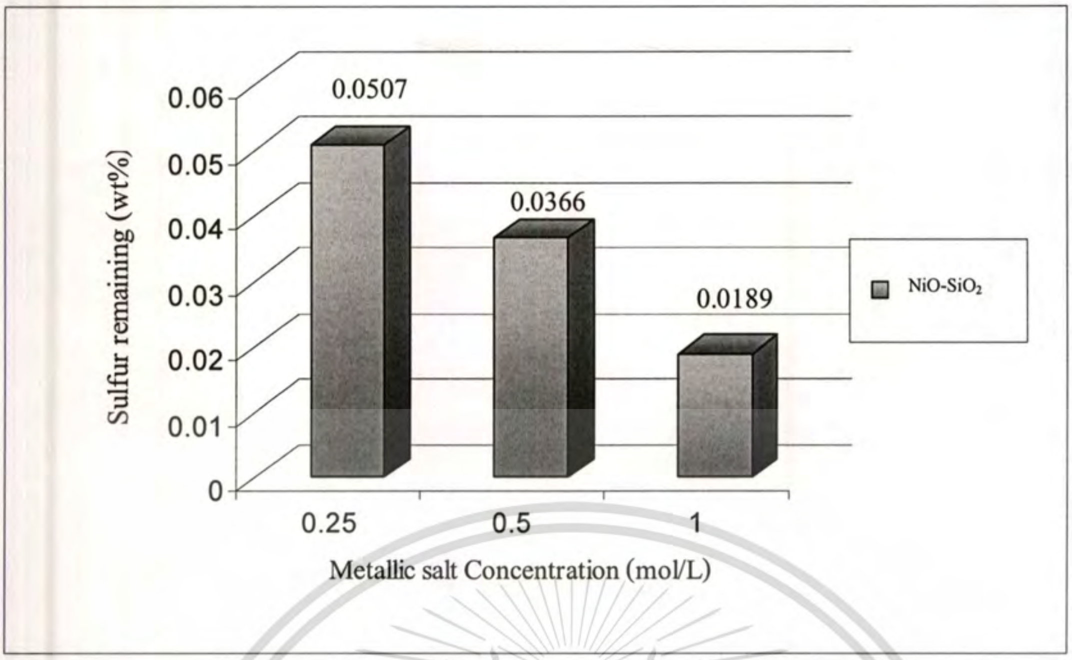


Figure 4. 3 : Effect of metallic salt concentration of catalyst on sulfur content remaining in diesel oil over NiO-SiO$_2$ catalyst

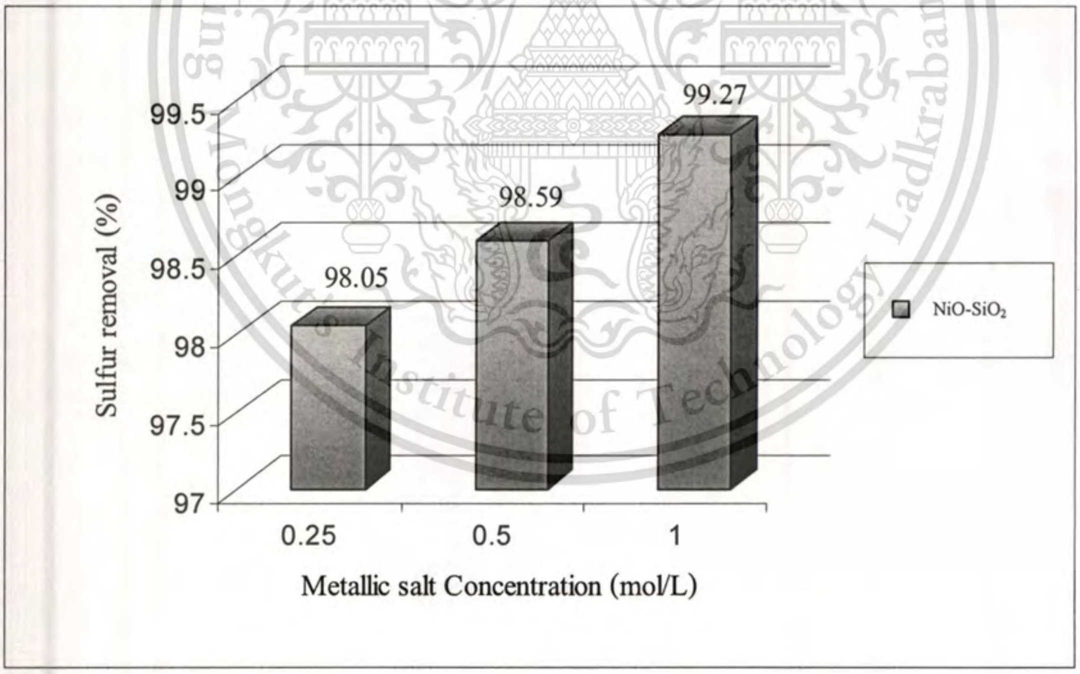


Figure 4.4 : Effect of metallic salt concentration of catalyst on percent sulfur removal over NiO-SiO$_2$ catalyst.

As seen from figure 4.1 to 4.4 ,when the metallic salt concentration or amount of loaded metal increased, the sulfur removal was increased due to the decreasing of sulfur content remaining in diesel oil after oxidation reaction.

However, over $CuO\text{-}SiO_2$ catalyst ,with increase in the amount of loaded copper from 0.25 to 0.05 mol/l , the sulfur removal increased from 93.98% to 98.61% (Figure 4.2). At the copper salt concentration over 0.5 mol/l, the percentage of sulfur removal was slightly increased from 98.61% to 99.11%. It can be implied that the optimum copper salt concentration for preparing of $CuO\text{-}SiO_2$ was 0.5 mol/l because at this concentration ,the higher percentage of sulfur removal was observed.

For the oxidative reaction over $NiO\text{-}SiO_2$ (Figure 4.4), the percentage of sulfur removal was slightly increased with the nickel salt concentration that varied from 0.25 to 0.1 mol/l. Then, the optimum nickel salt concentration for preparing of $NiO\text{-}SiO_2$ was 0.25 mol/l. The sulfur removal range was 98.05% to 99.27% that obtained by using 0.25 to 0.1 mol/l of $Ni(NO_3)_2$ solution

4.1.2 Removal of dibenzothiophene (DBT)

In this study, the $CuO\text{-}SiO_2$ catalyst was catalyzed the oxidative reaction of DBT in diesel oil. The effect of metallic salt concentration on sulfur remaining and percent salt removal was shown in Table 4.1 and plotted in Figure 4.5 and 4.6 , respectively. As seen in the Figure 4.5 and 4.6, the sulfur remaining content in diesel oil after oxidative reaction was 0.4129 %wt to 0.5023wt%, that corresponding to the percentage of sulfur removal 49.77 %wt to 58.71wt% . Compare with DMS removal , it can be discussed that $CuO\text{-}SiO_2$ had the efficiency for remove DBT less than DMS. Dimethyl sulfide is an organosulfur compound that boils at 37°C , it could be oxidized easily because the dimethyl sulfide had high electron densities on the sulfur atom , then it could be oxidized in the H_2O_2/formic acid and $CuO\text{-}SiO_2$ system at mind condition, while dibenzothiophenes with lower electron densities than dimethylsulfide , then it was difficult to oxidize sulfur atom of dibenzothiophene to sulfone.

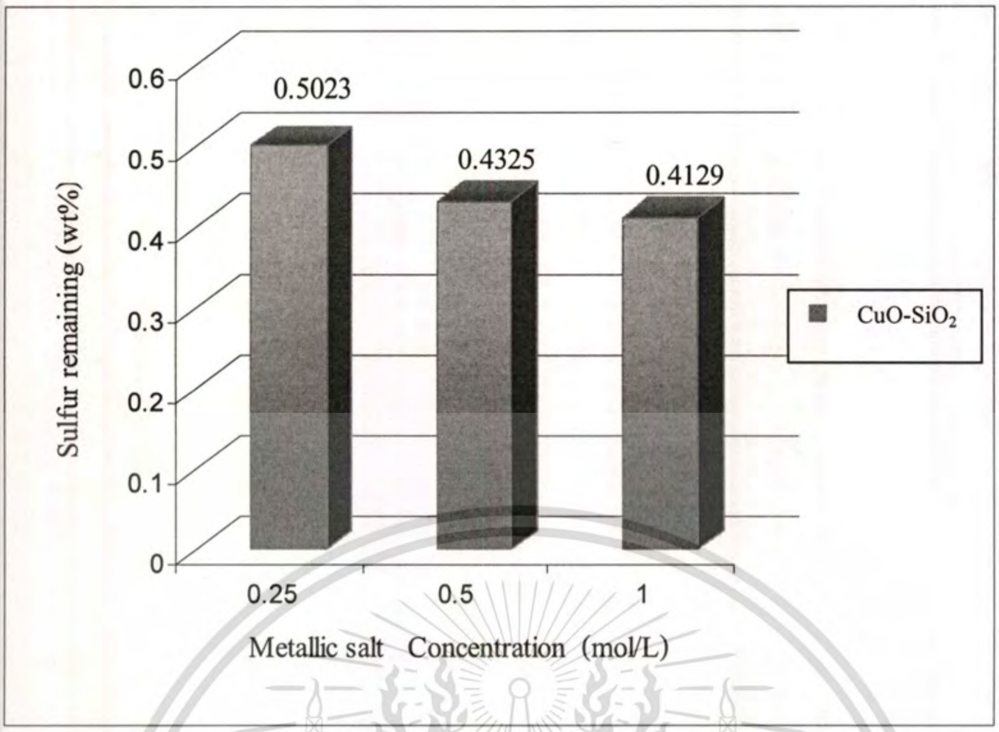


Figure 4.5 : Effect of metallic salt concentration on remaining sulfur over CuO-SiO_2 catalyst

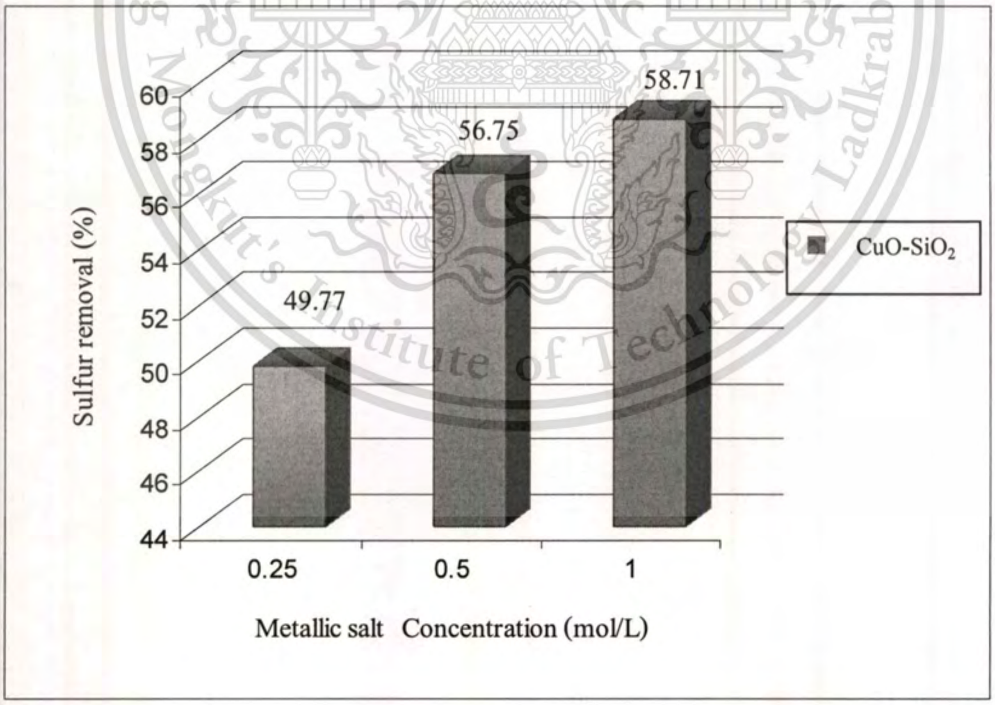


Figure 4.6 : Effect of metallic salt concentration on the sulfur removal over CuO-SiO_2 catalyst

4.2 Effect of dosage of catalyst on the oxidation of sulfur compound

In this study $CuO\text{-}SiO_2$ and $NiO\text{-}SiO_2$ prepared by loaded metallic salt concentration of 0.5 mol.L^{-1} on silica support were used in the reaction.The amount of catalyst were varied from 0.5,1.0 and 2.0 wt%.

The effect of catalyst amount on sulfur remaining and sulfur removal was shown in Table 4.2 and plotted in Figure 4.7-4.10.

Table 4.2 Effect of dosage of catalyst on sulfur remaining and sulfur removal

Type of sulfur compound	**Catalyst**	**Dosage of catalyst (wt%)**	**Metallic salt Concentration (mol.L^{-1})**	**Sulfur remaining in diesel oil (wt%)**	**Sulfur Removal (%)**
DMS	$CuO\text{-}SiO_2$	0.5	0.5	0.8443	67.53
		1	0.5	0.6228	76.05
		2	0.5	0.1025	96.06
	$NiO\text{-}SiO_2$	0.5	0.5	0.1090	95.81
		1	0.5	0.0760	97.08
		2	0.5	0.0519	98.00
DBT	$CuO\text{-}SiO_2$	0.5	0.5	0.8667	13.33
		1	0.5	0.6419	35.81
		2	0.5	0.5621	43.79

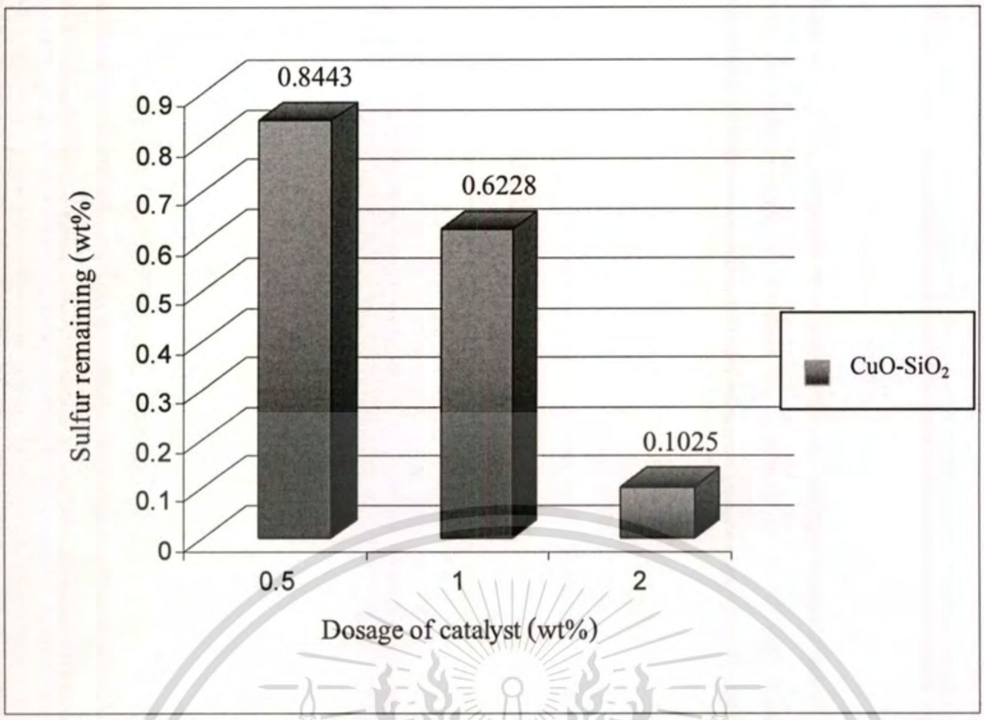


Figure 4.7 : Effect of dosage of catalyst CuO-SiO_2 on sulfur remaining (DMS) in diesel oil

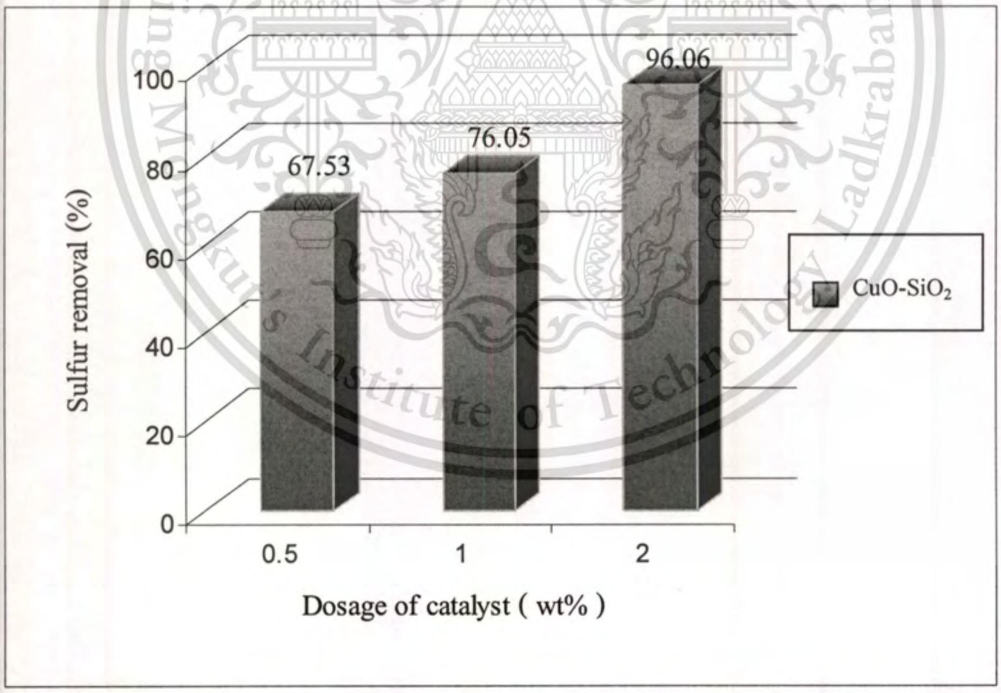


Figure 4.8 : Effect of dosage of catalyst CuO-SiO_2 on the percentage of sulfur removal (DMS) in diesel oil

Fig 4.7 and 4.8 explains if the catalyst is predetermined to have the same kind or richness but comparatively used in different amounts effects the amount of remaining sulfur and amount of sulfur removal. The amount of sulfur remaining had a steady decrease according to the steady increase concentration or richness of the catalyst. Thus, effecting the percentage of sulfur removal to increase in efficiency with the highest amount at 2.0 %wt.

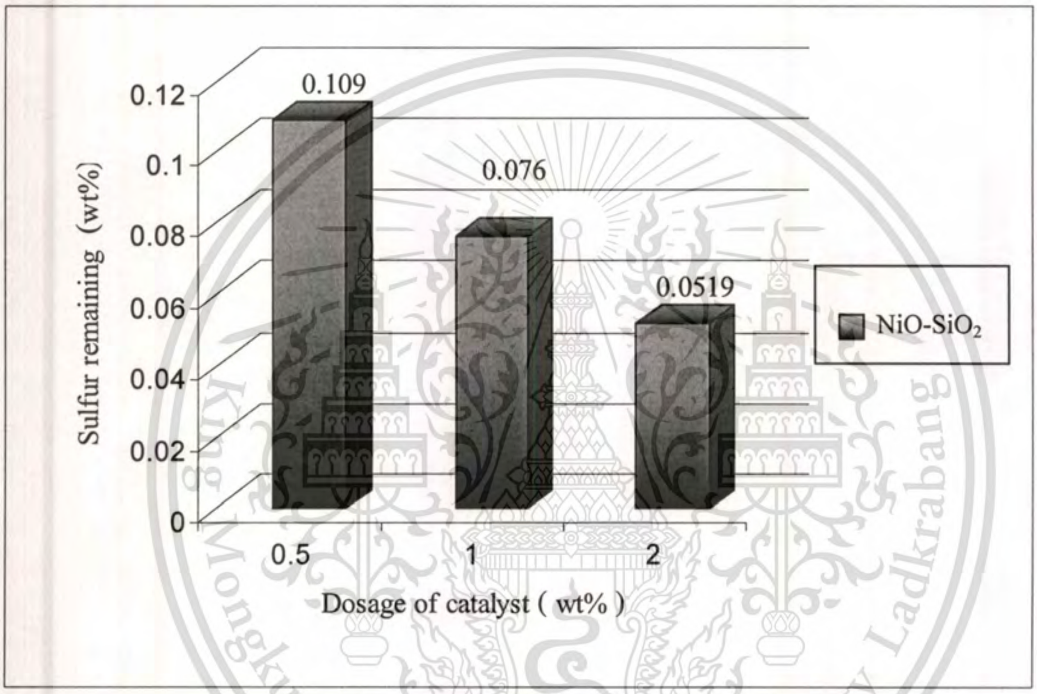


Figure 4. 9 : Effect of dosage of catalyst (NiO-SiO$_2$)on sulfur remaining in diesel oil (DBT)

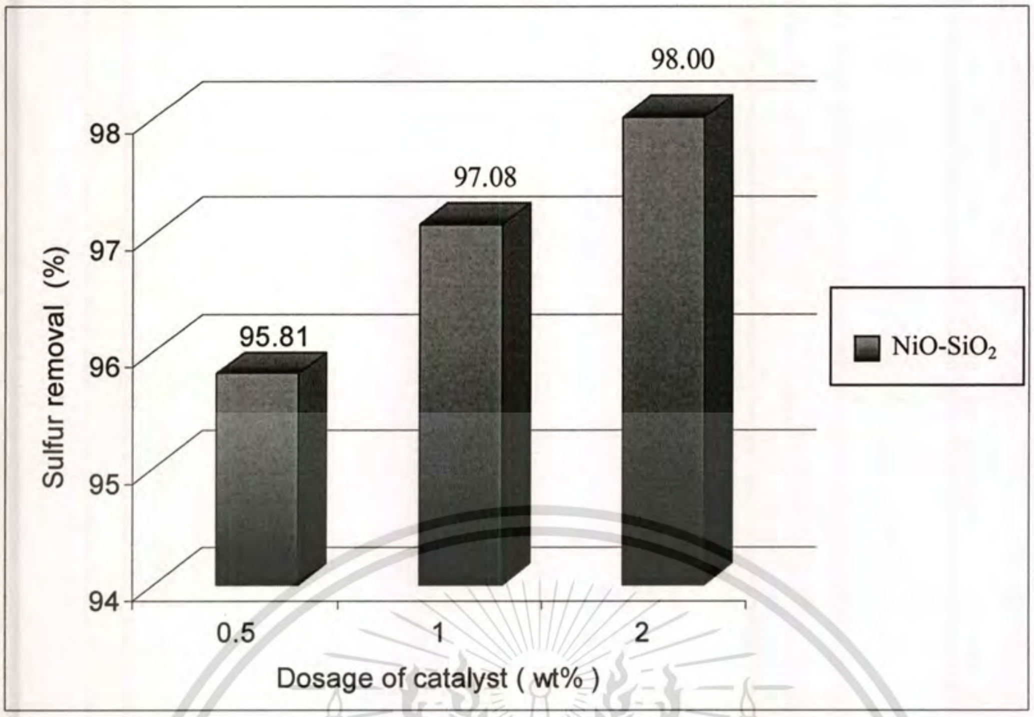


Figure 4.10 : Effect of dosage of catalyst NiO-SiO_2 on the percentage of sulfur removal (DBT)

From Fig. 4.9 and 4.10 explained that the percentage when used with a catalyst of the same kind and richness. From the results, it was determined that an increase in catalyst caused ever greater efficiency with steady increase and better removal of sulfur with the most optimal amount at 2.0%wt.

4.2.1 Removal of DMS by CuO-SiO_2 and NiO-SiO_2

From Figure 4.8 and 4.10 , this can be explained that the percentage sulfur removal increasing from 67.53% to 96.06% when using CuO-SiO_2 of 0.5wt% to 2wt% , while the slightly increasing of sulfur removal was observed when using NiO-SiO_2 as catalyst. It is well know that increasing catalyst amount can increase the concentration of metal active site. A larger amount of active metal implies a higher removal of sulfur. However, using 1%wt of NiO-SiO_2 loading gave the percentage of sulfur removal same as using 2wt% of CuO-SiO_2 (%sulfur removal 96-97%).

Then, it can be implied that NiO-SiO_2 was the active catalyst than CuO-SiO_2 for oxidative desulfurization due to Ni has smaller in atomic size, therefore the surface of NiO-SiO_2 catalyst gave higher surface area. For this reason , higher surface area, the better in active site for force the reaction. Less dosage of NiO-SiO_2 but the high sulfur removal was obtained.

4.2.2 Removal of dibenzothiophene (DBT)

The effect of dosage of CuO-SiO_2 on sulfur remaining and percentage of sulfur removal were shown in Table 4.2 , Figure 4.11 and 4.12

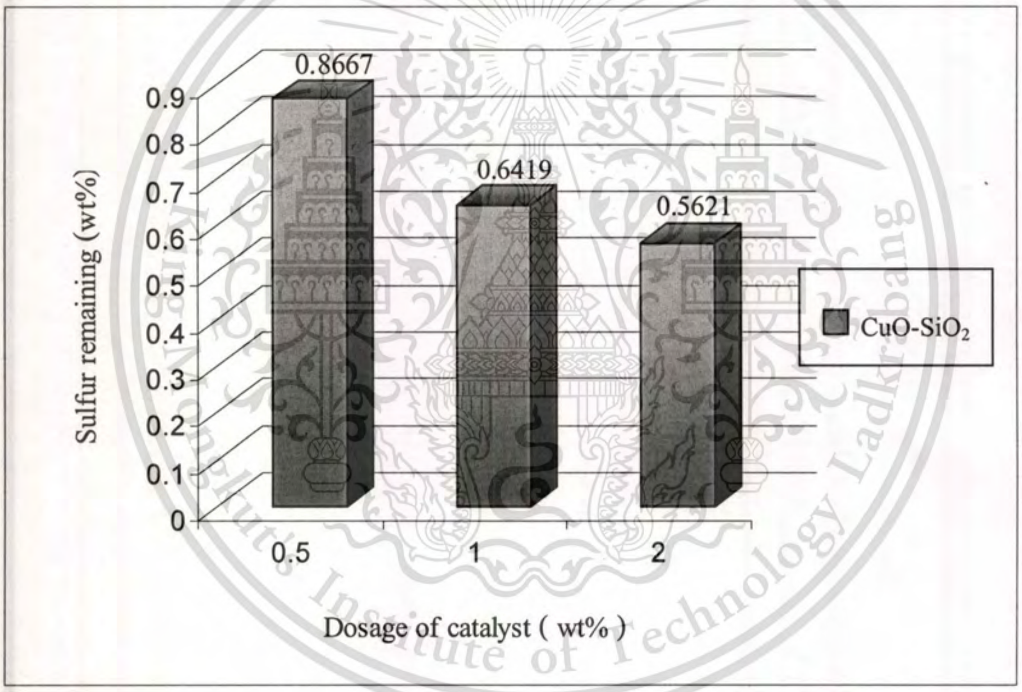


Figure 4.11 : Effect of dosage of catalyst (CuO-SiO_2)on sulfur remaining in diesel oil (DBT)

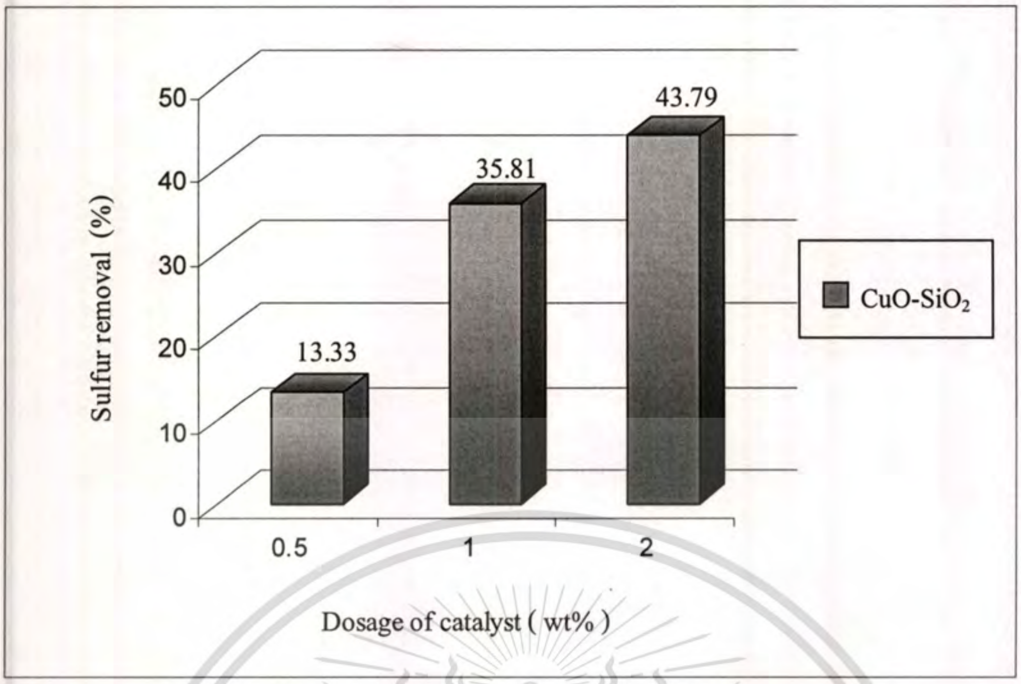


Figure 4.12 : Effect of dosage of catalyst (CuO-SiO$_2$) on the percentage of sulfur removal (DBT)

From Figure 4.12 , the percentage of DBT removal also increased with the increasing of CuO-SiO$_2$ loading. It can be concluded that a larger amount of metal active site of catalyst implies a higher removal of DBT. Because of dibenzothiophene was the sulfur compound that difficult to oxidized, from the experimental data shown that the reduction of DBT amount can be achieve when using larger amount of catalyst.

4.3 Effect of phase transfer catalyst

Since the reaction system was heterogeneous with three (oil phase, water phase, and solid phase). The oxidation reaction could be improved by phase transfer catalyst (PTC). The oxidation of DMS in the H_2O_2/formic system when PTC was added. In this experiment, sodium dodecyl benzene sulfonate was used as phase transfer catalyst. The chemical structure of sodium dodecyl benzene sulfonate was shown in Figure 4.13

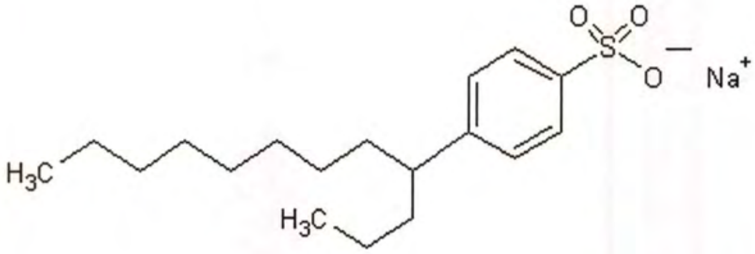


Figure 4.13 Chemical structure of Sodium dodecylbenzene sulfonate

Table 4.3 The results of the experiment in use of phase transfer catalyst to the sulfur remaining in diesel oil with metallic salt concentration 0.5 mol/L and dosages of catalyst 3 wt%.

Type of sulfur compound	**Catalyst**	**Metallic salt Concentration ($mol.L^{-1}$)**	**Dosage of catalyst (wt%)**	**Sulfur remaining in diesel oil (wt%)**	**Sulfur removal (%)**
DMS	$CuO-SiO_2$	0.5	3	0.0201	99.23
	$NiO-SiO_2$	0.5	3	0.0240	99.08

The effect of phase transfer catalyst on the sulfur remaining (DMS) and percentage of sulfur removal were shown in Figure 4.14 and 4.15,respectively compare with the reaction without phase transfer catalyst. The operating condition in this experiment were metallic salt concentration of $CuO-SiO_2$ 0.5 mol/l, dosage of catalyst 3wt%, and reaction time 2 hrs.

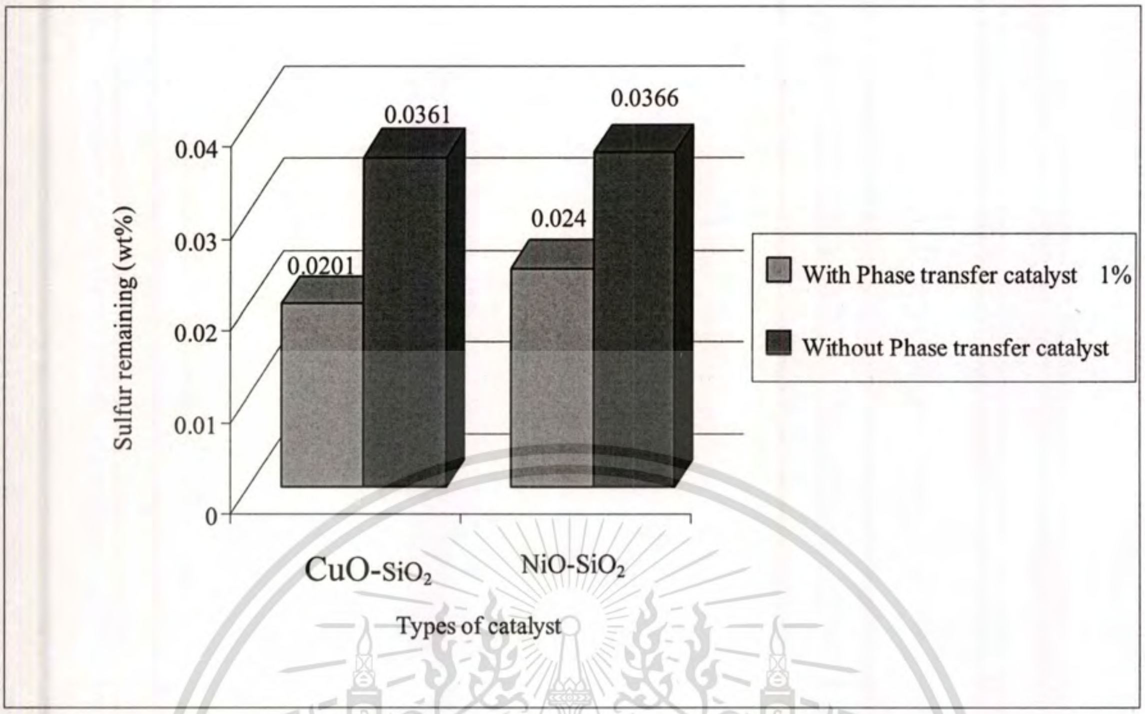


Figure 4.14 : The comparison of the sulfur remaining in diesel oil over $CuO\text{-}SiO_2$, $NiO\text{-}SiO_2$ with and without phase transfer catalyst.

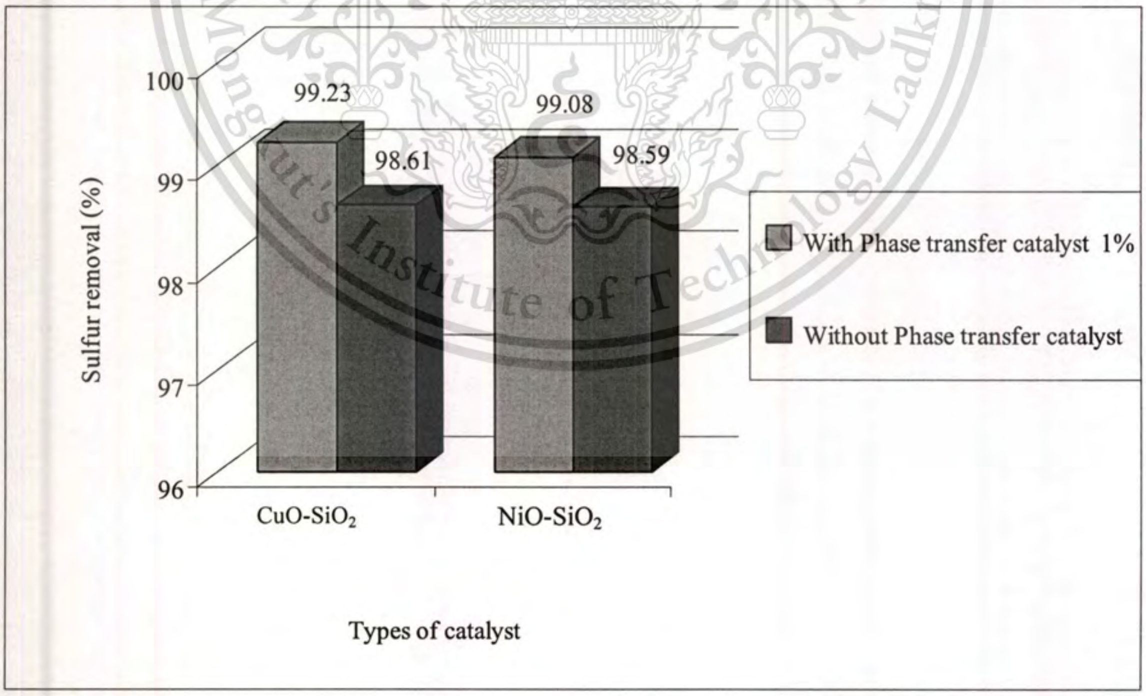


Figure 4.15 : The comparison of the percentage of sulfur removal over $CuO\text{-}SiO_2$, $NiO\text{-}SiO_2$ with and without phase transfer catalyst.

From Figure 4.15 , it can be seen that the sulfur removal of DMS in the oxidized oil larger with PTC was higher than the reaction with out PTC approximately 1%. Phase transfer catalyst was improved the miscibility of oil, water, and solid phase. Then, the oxidized sulfur compound was also improved. The slightly increase in percentage of sulfur removal between adding and non-adding PTC. It can be suggested that, the mixture solution in reaction system was strongly stirred with mechanical stirrer, then the three phase was well mixed to form homogeneous phase.

4.4 Properties of diesel oil before and after oxidative desulfurization

Desulfurized diesel oil was measured the properties that is heating value. The results of heating value of diesel oil before and after oxidative desulfurization was shown in Table4.4, Table 4.5 and Table 4.6.

Table 4.4 Heating value of diesel oil was identified by Bomb-calorimeter

Type of sulfur compound	**Catalyst**	**Metallic salt Concentration (mol.L^{-1})**	**Dosage of catalyst (wt%)**	**Heat capacity of oxidized diesel oil (cal/g)**
DMS	$CuO-SiO_2$	0.25	3	10908
		0.5	3	10769
		1.0	3	10759
	$NiO-SiO_2$	0.25	3	10714
		0.5	3	10720
		1.0	3	10631
DBT	$CuO-SiO_2$	0.25	3	10521
		0.5	3	10519
		1.0	3	10508

Table 4.5 Heating value of diesel oil with varied dosages of catalyst

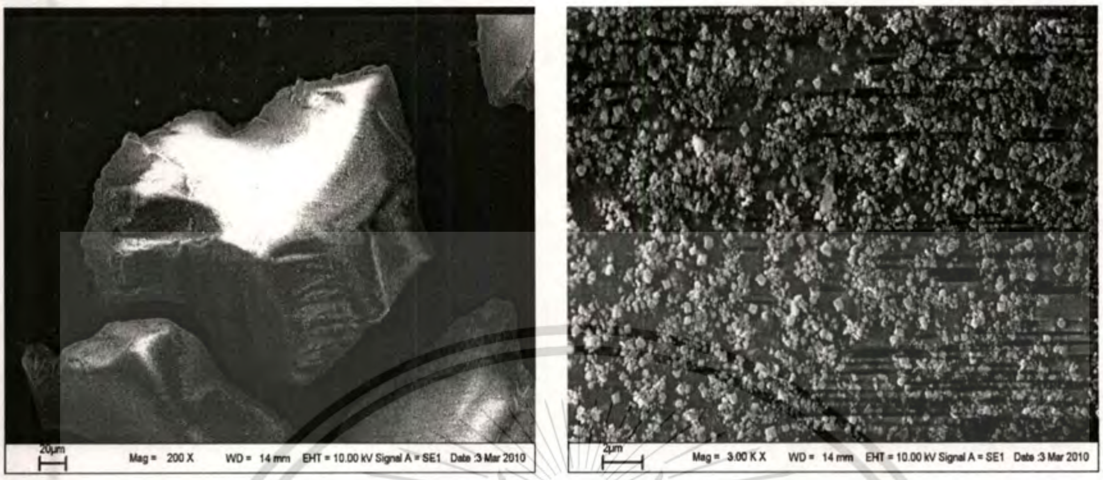
Type of sulfur compound	**Catalyst**	**Dosage of catalyst (wt%)**	**Metallic salt Concentration (mol.L^{-1})**	**Heat capacity of oxidized diesel oil (cal/g)**
DMS	CuO-SiO$_2$	0.5	0.5	10817
		1	0.5	10740
		2	0.5	10726
	NiO-SiO$_2$	0.5	0.5	10566
		1	0.5	10576
		2	0.5	10513
DBT	CuO-SiO$_2$	0.5	0.5	10311
		1	0.5	10354
		2	0.5	10328

Table 4.6_ Heating value of diesel oil with phase transfer catalyst.

Type of sulfur compound	**Catalyst**	**Metallic salt Concentration (mol.L^{-1})**	**Dosage of catalyst (wt%)**	**Heat capacity of oxidized diesel oil (cal/g)**
DMS	CuO-SiO$_2$	0.5	3	10286
	NiO-SiO$_2$	0.5	3	10211
Commercial diesel oil				10800

From Table 4.4 , 4.5 and 4.6 ,heating value diesel oil after desulfurization and commercial diesel oil not significantly different by which the heating value lie between 10200 and 10900 cal/g. It can be concluded that the heating value of the desulfurized diesel oil are not negatively affected by the oxidative desulfurization process.

4.5 Surface structure of NiO-SiO_2 and CuO-SiO_2 catalysts by Scanning electron microscope (SEM)



(a) (b)

Figure 4.16 : Scanning electron micrograph of NiO-SiO_2 (concentration of metal salt solution 1.0 mol/L.) (a) magnitude of 300 (b) magnitude of 3000

(a) (b)

Figure 4.17 : Scanning electron micrograph of CuO-SiO_2 (concentration of metal salt solution 1.0 mol/L.(a) magnitude of 300 (b) magnitude of 2000

4.6 Characterization of diesel oil before and after desulfurization by FTIR

The diesel oil before and after oxidative desulfurization were analyzed the functional group by Fourier-Transfer Infrared Spectrophotometer ,model thermo 470 generation at Science Faculty of King Mongkut's Institute of Technology Ladkrabang. The FTIR spectrum were shown in Figure 4.17 and 4.18.

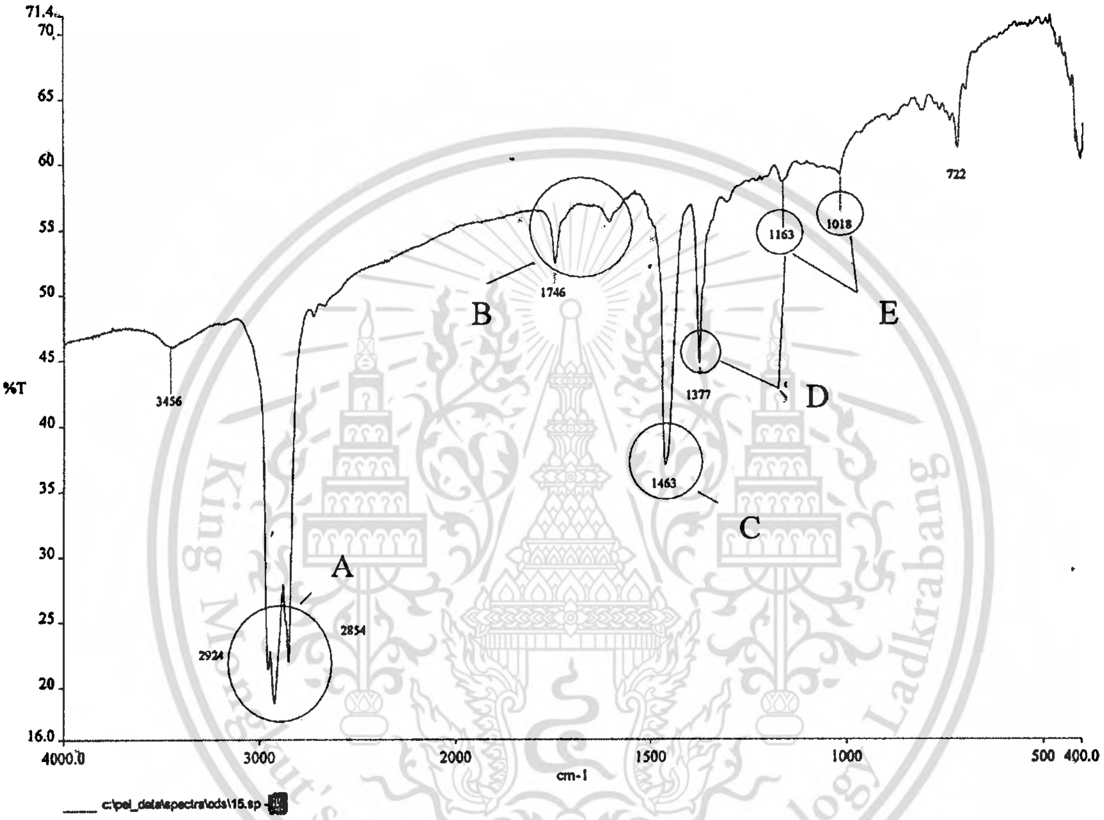


Figure 4.18 FTIR spectrum of diesel oil before desulfurization

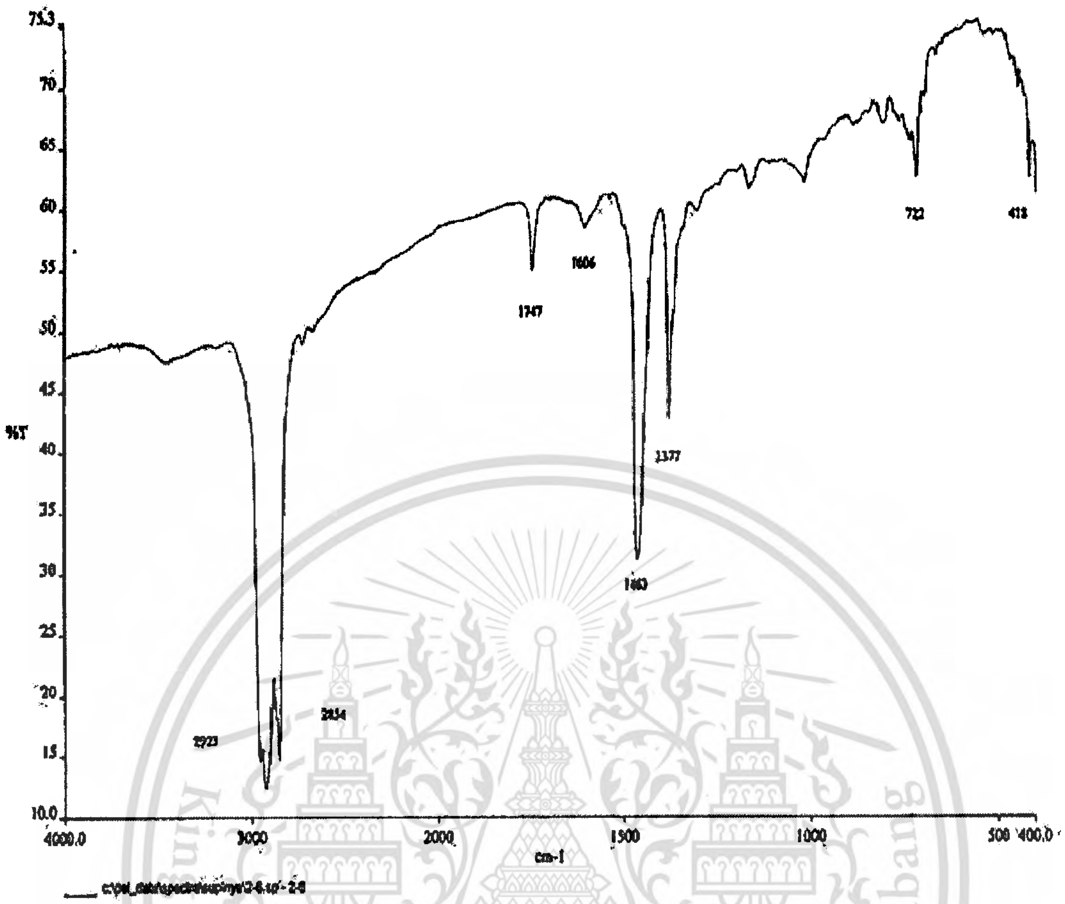


Figure 4.19 FTIR spectrum of diesel oil after desulfurization reaction.

From FTIR spectrum diesel oil in Figure 4.17 and 4.18, the result was reported from spectrum were similar in which :

A. C-H stretching at 3000-2800 cm^{-1}

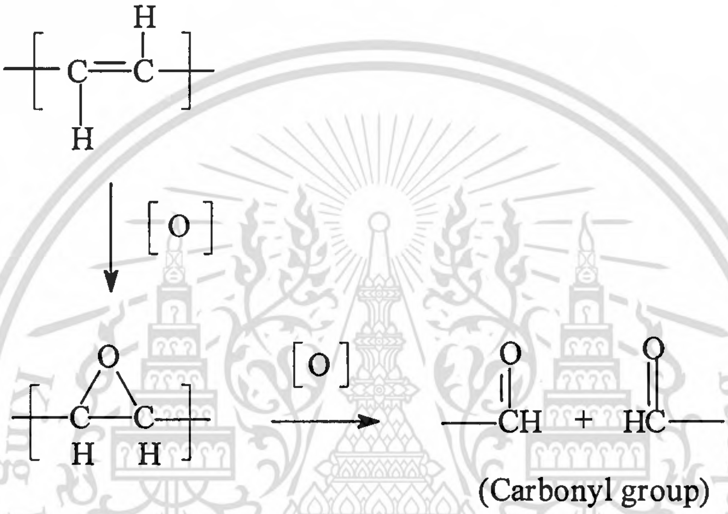
B. Carbonyl group of Aldehyde at 1720-1740 cm^{-1}

C. CH_2 (scissoring) at 1458 cm^{-1}

D. Sulphone at 1300-1070 cm^{-1} , 1140-1160 cm^{-1}

E. Sulphoxide at 1030-1070 cm^{-1}

The resulted from detecting by Fourier Transform Infrared spectroscopy (FTIR) give the information before desulfurization that the peak of sulfoxide at 1030-1070 cm^{-1} and then will be changed to sulfone in range of 1150 to 1300 cm^{-1}. Because of oxidative desulfurization with hydrogen peroxide can change sulphide to sulfone as shown in the equation (4.1) and found that the peak in range of 1700 cm^{-1} was the peak of carbonyl group due to oxidation reaction on double bond of hydrogen in Diesel oil was carbonyl group (C=O) as shown in (4.2)



CHAPTER 5

CONCLUSION AND RECOMMENDATION

This special project was intended to desulfurized the simulated diesel oil in the presence of metal oxide-loaded silica by using oxidation reaction of hydrogen peroxide and formic acid by comparing the types of sulfur compound in diesel oil (DMA and DBT) and comparing by with and without phase transfer catalyst. From the results , it can be summarized that as the following.

5.1 Conclusion

The goal of this research was to study the type of catalyst such as copper loaded on silica ($CuO-SiO_2$) and nickel loaded on silica ($NiO-SiO_2$) using in oxidation that affect on percent sulfur removal. The studying in the concentration of metal salt solution (Copper (II) nitrate and Nickel nitrate) are 0.25 mol/L, 0.50 mol/L, and 1.0 mol/L. The studying in the amount of catalysts that affect to percent sulfur removal of 0.5 wt%, 1.0 wt% and 2.0 wt% .

The studying in adding of phase transfer catalyst using sodium dodecyl benzene sulfonate (SDBS).

The increasing of concentration of metal salt solution (Copper (II) nitrate and Nickel nitrate) , the increasing of percentage sulfur removal.

The amount of catalyst used in the desulfurization process is affect to percent sulfur removal ,when increase amount of catalyst the amount of sulfur remaining in diesel oil is decreased and percent sulfur removal increased. The amount of catalyst as 3.0 wt% gave the lowest amount of sulfur remaining and highest percent sulfur removal.

Adding phase transfer catalyst to the desulfurization process affect in decreasing amount of sulfur remaining but increasing percent sulfur removal. However, it is not significantly different from the desulfurization process without phase transfer catalyst.

5.2 Recommendations

1. Study the effect of phase transfer catalyst on sulfur removal such as other type of phase transfer catalyst and using in NiO-SiO_2 catalyst reaction system.

2. Study the other type of sulfur compound that contaminated in diesel oil such as mercaptan and thiophene derivatives.

3. Study the other type of catalyst composition such as Co, Mo, V.

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