OXIDATIVE DESULFURIZATION OF DIBENZOTHIOPHENE IN DIESEL OIL WITH ALDEHYDE/MOLECULAR OXYGEN AND THE PRESENCE OF COBALT AND COPPER CATALYSTS

MR. PASUTA POEIAM
MR. PORNPISSANU THOME
MR. WEERANUT JITVITTHAYAPORN

A SPECIAL PROJECT SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIRMENT FOR THE DEGREE OF BACHELOR OF SCIENCE
IN PETROCHEMICAL TECHNOLOGY
FACULTY OF SCIENCE
KING MONGKUT'S INSTITUTE OF TECHNOLOGY LADKRABANG
ACADEMIC YEAR 2010

Title of Special Project : Oxidative Desulfurization of Dibenzothiophene in Diesel Oil with Aldehyde / Molecular Oxygen and the Presence of Cobalt and Copper Oxide Catalysts

Students : Mr. Pasuta Poeim
Mr. Pornpissanu Thome
Mr. Weeranut Jitvitthayaporn

Deegree : Bachelor of Science

Program : Petrochemical Technology (International Program)

Acedemic year : 2010

Advisor : Dr.Amnat Permsubscul

ABTRACT

The aim of this work was studied the desulfurization of dibenzothiophene dissolved in diesel oil by oxidation reaction in aldehyde and molecular oxygen system over metal oxide-loaded silica catalyst. The effects of the oxidative system, type of aldehydes (isobutyraldehyde and 3-methylbtyraldehyde), type of catalysts (Cu/SiO_2 and Co/SiO_2), metal salt concentration (0.33, 0.50 ,and 0.67 mol/L) , and reaction time on sulfur removal were investigated in details. The oxidized diesel oil was analyzed sulfur content to determine the sulfur remaining by X-Ray Fluorescence Spectroscopy (XRF) technique. The characterization of functional group of diesel oil was analyzed by Fourier-Transfer Infrared Spectroscopy (FTIR) technique.The results showed the sulfur removal rate of simulated diesel oil in aldehyde/molecular oxygen/ metal oxide-loaded silica catalyst was higher than in non-catalytic oxidative system. The copper oxide-loaded silica (CuO/SiO_2) was found very active catalyst for oxidation of simulated diesel oil in this system. The sulfur removal rate of dibenzothiophene was enhanced when adding of 3-methlybutyraldehyde. Moreover, the sulfur removal increasing with metal salt concentration and reaction time.

Keywords : Oxidative desulfurization, Diesel oil, Isobutyraldehyde , 3-methylbutyraldehyde Cobalt-loaded silica, Copper-loaded silica.

หัวข้อโครงงานพิเศษ : การกำจัดกำมะถันในน้ำมันดีเซลโดยปฏิกิริยาออกซิเดชันด้วยอัลดิไฮด์ / โมเลกุลออกซิเจน และตัวเร่งปฏิกิริยาโคบอลและคอปเปอร์ออกไซด์

ชื่อนักศึกษา : นาย พสุธา โพธิ์เอี่ยม
นาย พรพิศณุ ทอม
นาย วีรณัฐ จิตวิทยาภรณ์

ปริญญา : วิทยาศาสตร์บัณฑิต

สาขาวิชา : เทคโนโลยีปิโตรเคมี (หลักสูตรนานาชาติ)

ปีการศึกษา : 2553

อาจารย์ที่ปรึกษา : ดร.อำนาจ เพิ่มทรัพย์สกุล

บทคัดย่อ

งานวิจัยมีจุดประสงค์เพื่อศึกษาการกำจัดกำมะถัน ของ ไดเบนโซไทโอฟีนที่ ละลายในน้ำมันดีเซลโดย การทำปฏิกิริยาออกซิเดชันในแอลดีไฮด์และระบบออกซิเจนโมเลกุลบนตัวเร่งปฏิกิริยาคอปเปอร์ออกไซด์โหลดบนตัวซิลิกา (CuO/SiO_2) และโคบอลล์ออกไซด์โหลดบนตัวซิลิกา (CoO/SiO_2) ผลกระทบของระบบออกซิเดชัน ประเภทของแอลดีไฮด์ (ไอโซบิวทิลาดีไฮด์ และ 3-เมทิลบิวทิลาดีไฮด์), ชนิดของตัวเร่งปฏิกิริยา (CuO/SiO_2 และ CoO/SiO_2), ความเข้มข้นของเกลือโลหะ (0.33, 0.50, และ 0.67 โมลต่อลิตร) และช่วงเวลาทำปฏิกิริยาต่อการกำจัดกำมะถันทำการศึกษาในรายละเอียด น้ำมันดีเซลออกซิไดซ์ได้จากการวิเคราะห์ปริมาณกำมะถันเพื่อกำหนดกำมะถันที่เหลืออยู่โดย เทคนิคของ X - Ray Fluorescence Spectroscopy (XRF) ลักษณะของหมู่ฟังค์ชันของกำมะถันของน้ำมันดีเซลได้จากการวิเคราะห์โดยเทคนิคฟูเรียร์ ทรานเฟอร์ อินฟราเรดสเปกโทรสโกปี (FTIR) ผลการศึกษาพบอัตราการกำจัดกำมะถันของน้ำมันดีเซลจำลองในแอลดีไฮด์และออกซิเจนโมเลกุล ตัวเร่งปฏิกิริยาโลหะออกไซค์บนซิลิกาโหลดมีค่าสูงกว่าในระบบที่ไม่ใช้ตัวเร่งในปฏิกิริยาออกซิเดชัน คอปเปอร์ออกไซด์โหลดบนซิลิกา (CuO/SiO2) พบตัวเร่งปฏิกิริยาที่ใช้งานมากสำหรับออกซิเดชันของน้ำมันดีเซลจำลองในระบบนี้อัตราการกำจัดกำมะถันของ ไดเบนโซไทโอฟีน ได้เพิ่มขึ้นเมื่อเติม 3-เมทิลบิวทิลาดีไฮด์ นอกจากนี้ยังมีการเพิ่มความเข้มข้นของโลหะออกไซด์เพื่อเพิ่มการกำจัดกำมะถันในน้ำมันดีเซลและเพิ่มเวลาในการทำปฏิกิริยา

คำสำคัญ : กระบวนการกำจัดกำมะถัน, น้ำมันดีเซล, ไอโซบิวทิลาดีไฮด์, 3-เมทิลบิวทิลาดีไฮด์ โคบอลล์ออกไซด์โหลดบนซิลิกา, คอปเปอร์ออกไซด์โหลดบนซิลิกา

Acknowledgement

This special project was carried out and completed with a reasonable suggestion for solving riddles and all hints are given us the right direction.

We would right to thank our respect adviser, Dr.Amnat Permsubscul for all suggestions and answering all questions. And thank tou very much for helping us until we finished this Special Project.

We would like to thank Asst. Prof. Dr.Vanchat Chuenchom and Asst. Prof. Dr.Chonlada Ritvirulh for all comments and suggestions.

We would like to thank staffs of the Department of Chemistry, KMITL for equipments and helping us to find all items.

We would like thank staffs of PTT Pulblic Company Limited (Phrakanong Office and Oil Terminal) for equipments and teaching us how to used the equipments.

Finally, we would like to thank our family for giving us a wisdom to pass on all questions.

Mr. Pasuta Poeiam
Mr. Pornpissanu Thome
Mr.Weeranut Jitvitthayaporn

Table of Contents

CHAPTER 1 INTRODUCTION

CHAPTER 2 THEORY AND LITERATURE REVIEWS

CHAPTER 3 EXPERIMENTAL DETAILS

CHAPTER 4 RESULTS AND DISCUSSION

CHAPTER 5 CONCLUSION AND RECOMMENDATION

List of Tables

List of Figures

Figure Page

CHAPTER 1

INTRODUCTION

1.1 Motivation

Sulfur in fuels causes pollution by emitting SO_x and particulate matter (PM) from internal combustion engines. It adversely affects the performance of emission control systems as well as causes corrosion of engines and process equipment. Because of the inherent benefits of diesel fuel, its consumption in automotives is increasing throughout the world. In view of environmental concerns more stringent specifications for sulfur in diesel fuel are being implemented by developed countries. The United States Environmental Protection Agency (USEPA) recommended reduction of sulfur level to 15 ppm by June 2006 in on road diesel. Developed countries throughout the world put regulations to reduce sulfur to 15/10 ppm by 2009 in diesel fuel. Similar directives were followed by developing countries with later date of implementation. In India, sulfur in diesel fuel is to be reduced to 50 ppm in 11 major cities and to 350 ppm in rest of the country by 2010. [1] Hydrodesulfurization has been an integral part of refinery operations. It can easily remove sulfur compounds, such as sulfides, disulfides, thiols, thiophenes, benzothiophenes, and dibenzothiophenes from middle distillates. On moderate operation with Mo/Al_2O_3 catalyst, hydrodesulfurization in diesel fuel reduces sulfur to the order of 350–500 ppm. However, alkylsubstituted dibenzothiophenes like 4,6-dimethyldibenzothiophene are refractive to hydrodesulfurization due to steric hindrance and are difficult to remove to a great extent. In order to produce ultralow sulfur diesel (ULSD) fuel with this process, the deep HDS technique is to be adopted. This technique requires severe conditions and has negative effects like decrease in catalyst life, higher hydrogen consumption, and higher yield losses resulting in higher costs. It also causes global warming by raising CO_2 emissions. Owing to these difficulties, alternative methods are being investigated worldwide. Among those methods, oxidative desulfurization of diesel has attracted worldwide attention due to inherent advantages like mild reaction conditions and low cost. [2]

The oxidative desulfurization process consists generally of two stages: The first is oxidation of organic sulfur-containing compounds in fuels, and the following step is removal of oxidized sulfur-containing compounds by solvent extraction.

In oxidative desulfurization, various oxidation systems have been reported in the literature before, such as acetic acid/H_2O_2 [3], formic acid/H_2O_2 [4], heteropolyacid/H_2O_2 [5], polyoxometalates/H_2O_2 and TS-1/H_2O_2 [6]. Obviously H_2O_2 has become a popular oxidant as it does not pollute the environment and the only byproduct is water, making the process promising for future application.Other oxidants like *tert*-butyl hypochlorite and *tert*butyl hydroperoxide have also been reported in the literature for oxidation of sulfur compounds. Among these oxidants, peracids produced *in situ* from organic acids and H_2O_2 are reported to be very effective for rapid oxidation of sulfur compounds present in diesel under mild conditions.[3]

Nowadays, the catalyst-making companies have developed high performance catalysts, which can reduce the sulfur level in diesel fuels to around 50 wt ppm. The ODS of thiophene(Th), benzothiophene(BT), dibenzothiophene(DBT) and their derivatives with t-butyl hydroperoxide were studied by using different solid catalysts such as Mo–Al_2O_3 , Cobalt–aluminium phosphate, Copper zeolites . The polyaromatic sulfur compounds were oxidized into their corresponding sulfoxides and sulfones which were then removed by simple liquid–liquid separation. [4]

Molecular oxygen is an environment-friendly and abundantly available cheap oxidant. The peracids generated *in situ* from aldehyde and molecular oxygen form a powerful oxidation system which has been used for a variety of oxygenation reactions. Oxidation of DBT and alkyl DBTs with aldehyde/molecular oxygen in the presence of various catalysts extended these studies for oxidative desulfurization of diesel. The presence work investigate the oxidation reaction of dibenzothiophene (DBT) in diesel fuels using the aldehyde/molecular oxygen system in the presence of Cobalt and Copper catalyst for the removal of oxidized sulfur compounds from diesel fuels. [5]

1.2 Objectives

Desulfurization of high speed diesel using aldehyde/molecular oxygen system in the presence of metal catalyst are investigated. The main objectives of this work are as follow

1. To study the effect of metal loaded catalyst in the oxidative removal of sulfur compounds from diesel oil.
2. To investigate the effect of the metal types, aldehyde types, metal loading, amount of catalyst and reaction time on the sulfur removal.

1.3 Scope of study

The sulfur compound selected is dibenzothiophene(DBT) that is among those more amount in the diesel oil. Oxygen from the air pump with the constant flow rate of 1.082 L/min is used in oxidation system. In this research, the oxidative desulfurization of simulated diesel oil in the presence of metal loaded silica are studied as follow

1. Investigate of the variables that affect on percent sulfur removal including:
    - The type of aldehyde are Isobutyraldehyde and Methylbutyraldehyde.
    - The type of catalysts are cobalt oxide loaded on silica (CoO/SiO_2) and Copper oxide loaded on silica (CuO/SiO_2).
    - Mole ratio of aldehyde to sulfur are 5:1, 10:1, 15:1, 20:1 , 25:1 and 30:1.
    - The amount of metal oxide on catalyst ; CuO are 7.80, 12.83 and 13.74 wt% and CoO are 8.15, 10.89 and 13.74 wt%
    - Reaction times are 30, 60, 90 and 120 minutes.
2. Study about chemical properties of diesel oil before and after oxidative desulfurization using CoO/SiO_2 and CuO/SiO_2.
    - Sulfur content in diesel oil measured by X-Ray Fluorescence Spectrophotometer.
    - Functional group in diesel oil measured by Fourier-Transform Infrared Spectrophotometer.
    - Characterization of catalyst by using X-Ray Fluorescence Spectrophotometer.

1.4 Expected Results

1. Can remove sulfur from diesel fuel to remain the minimum value.
2. To know the parameters that influence amount of sulfur removal and including the suitable condition.

CHAPTER 2

THEORY AND LITERATURE REVIEWS

2.1 Diesel Fuel [7]

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 possiblewith 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 kind 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.

2.1.1 Key attributes of diesel fuel. [8,9]

2.1.1.1 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.

2.1.1.2 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 isestablished 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.

2.1.1.3 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.

2.1.1.4 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 temperatures 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.

2.1.1.5 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.

2.1.1.6 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 difficultie wil 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.

2.1.1.7 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.

2.1.1.8 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.

2.1.1.9 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.

2.1.1.10 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."

2.1.1.11 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 distillatation 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.

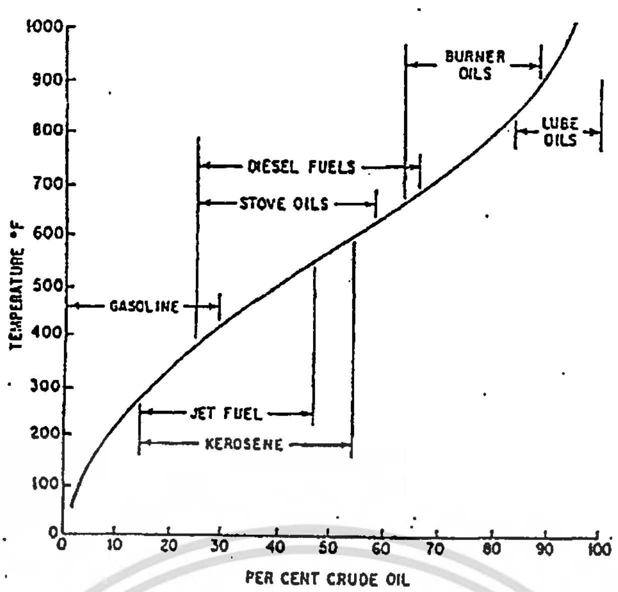


Figure 2.1 : Proportion of diesel fuel and other petroleum product

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 [10,11]

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.

2.2.1 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.

2.2.2 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

2.2.3 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.

2.2.4 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).

2.2.5 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.

2.2.6 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.

2.2.7 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 sulphur, 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.

2.2.8 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).

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

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.

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

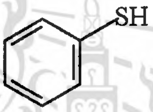
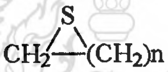
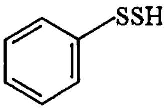
As the reaction products are cooled the sulphur drops out of the reaction vessel in a molten state. Sulphur can be stored and shipped in either a molten or solid state.

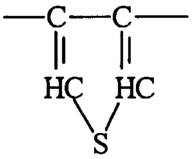
2.3 Sulfur [12]

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-
-Cyclic	
Disulphides	
-Aliphatic	R-S-S-R
-Aromatic	
Polysulphides	$R\text{-}(S)_n\text{-}R$



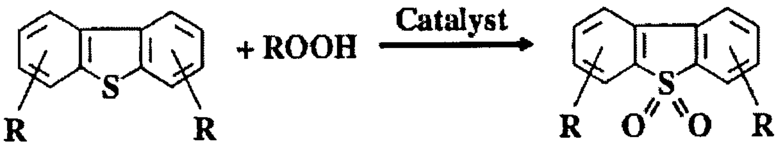
Thiophene

2.4 Desulfurization process[13]

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 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 [14]

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.

<u>Silica surface</u> [14]

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).

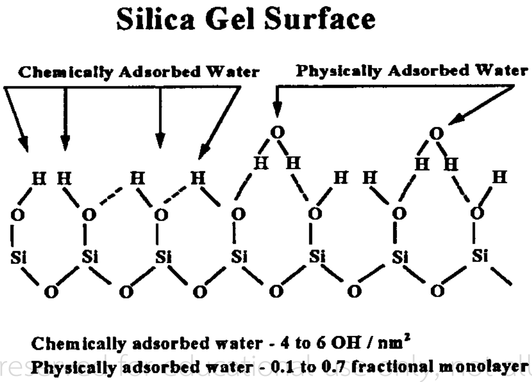


Figure 2.2 : The surface composition of silica [15]

2.6 Thiophene [16]

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).

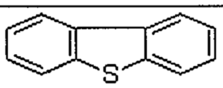
Thiophene was discovered as a contaminant in benzene. Thiophene and its derivatives occur in petroleum, sometimes in concentrations up to 1-3%. The thiophenic content of oil and coal is removed via the hydrodesulfurization (HDS) process. In HDS, the liquid or gaseous feed is passed over a form of molybdenum 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 [17]

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.

Table 2.1 : Properties of Dibenzothiophene

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 [18]

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

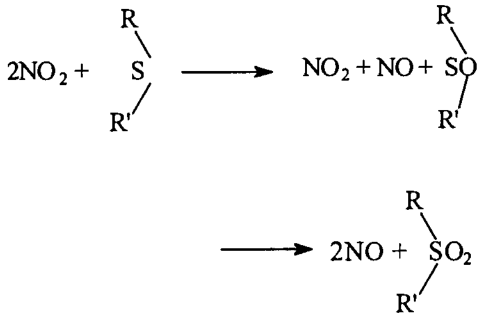
$$UO_2 + R\text{-}S\text{-}R \longrightarrow U + R\text{-}SO_2\text{-}R' \tag{2.1}$$

(2) Regeneration of the oxidizer with molecular oxygen

$$U + O_2 \longrightarrow UO_2 \tag{2.2}$$

Nitrogen Dioxide as a regenerable oxidizer.

(1) Oxidation



(2.3)

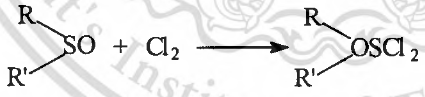
(2) Regeneration

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

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

$$2RH + O_2 \longrightarrow 2R^{\bullet} + H_2O_2 \qquad (2.9)$$

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

$$RO_2H \longrightarrow RO^{\bullet} + HO^{\bullet} \qquad (2.10)$$

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

$$A^{\bullet} + RH \longrightarrow R^{\bullet} + AH \qquad (2.11)$$

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

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

$$RO_2^{\bullet} + RH \longrightarrow RO_2H + R^{\bullet} \qquad (2.13)$$

Or the peroxy radicals can terminate by the reaction

$$2RO_2^{\bullet} \longrightarrow RO_2R + O_2 \qquad (2.14)$$

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.

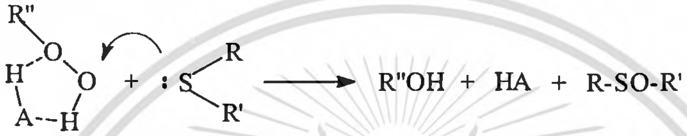
3. Hydroperoxides and peracids can selectively oxidize sulfur compounds to the corresponding sulfoxides and sulfones.

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)

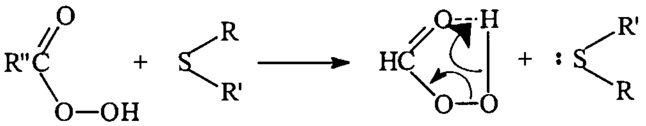
HA denotes the protic molecule, and R"O_2H is the peroxide.

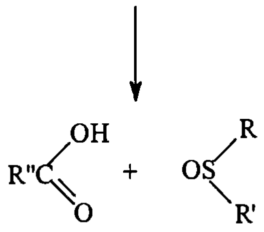
The oxidation of the sulfoxide to the sulfone occurred by the same mechanism. In a protic solvent, the present in excess fulfills the function of HA, and the apparent rae of reaction is the first order with respect to the peroxide. In an aprotic solvent, another hydroperoxide molecule will function as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

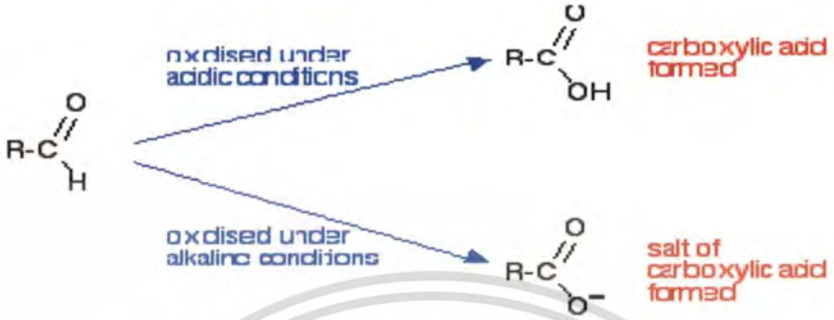
2.9 Oxidation of aldehydes [19]

The formyl group readily oxidizes to the corresponding carboxylic acid (-COOH). The preferred oxidant in industry is oxygen or air. In the laboratory, popular oxidizing agents include potassium permanganate, nitric acid, chromium(VI) oxide, and chromic acid. The combination of manganese dioxide, acetic acid and methanol will convert the aldehyde to a methyl ester.

Another oxidation reaction is the basis of the *silver mirror test*. In this test, an aldehyde is treated with Tollens' reagent, which is prepared by adding a drop of sodium hydroxide solution into silver nitrate solution to give a precipitate of silver(I) oxide, and then adding just enough dilute ammonia solution to redissolve the precipitate in aqueous ammonia to produce $[Ag(NH_3)_2]^+$ complex. This reagent will convert aldehydes to carboxylic acids without attacking carbon-carbon double-bonds. The name *silver mirror test* arises because this reaction will produce a precipitate of silver whose presence can be used to test for the presence of an aldehyde.

If the aldehyde cannot form an enolate (e.g., benzaldehyde), addition of strong base induces the Cannizzaro reaction. This reaction results in disproportionation, producing a mixture of alcohol and carboxylic acid.

It depends on whether the reaction is done under acidic or alkaline conditions. Under acidic conditions, the aldehyde is oxidised to a carboxylic acid. Under alkaline conditions, this couldn't form because it would react with the alkali. A salt is formed instead.



2.10 Catalyst preparation [20]

2.10.1 Support preparation

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 Reviews

Venkateshwar Rao, T. [1] studied the Oxidation of dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT), and 4,6-dimethyldibenzothiophene (4,6-DMDBT) was studied using the isobutyraldehyde/molecular oxygen oxidation system in the absence of metal catalyst as the sulfur present in hydrodesulfurized (HDS) diesel is mostly in the form of substituted dibenzothiophenes. This oxidation system was found to oxidize these sulfur compounds to their respective sulfones, and oxidation reactivity was found to decrease in the order 4,6-DMDBT > 4-MDBT > DBT. Further, the study was extended to oxidation of sulfur compounds present in HDS diesel in a two-phase system using the aldehyde/molecular oxygen oxidation system. The oxidized HDS diesel on extraction with polar solvents showed remarkable reduction in total sulfur. Acetonitrile was found to be the most effective among solvents studied, and isobutyraldehyde was observed to be the best among aldehydes studied. In HDS diesel, total sulfur could be reduced from 448 to 77 ppm by oxidation followed by solvent extraction, and it could be further reduced to 31 ppm by passing through a silica gel column.

Oliviero, L. [21] studied the oxidation of dibenzothiophene by an oxygen/aldehyde system, using heterogeneous (unsupported and alumina-supported oxides) and homogeneous (acetate salts) catalytic systems based on Mn, Co and Ni, was examined. In all instances, Co- and Mn-based systems were the most active catalysts. In contrast, a markedly lower activity was measured for Ni(II) acetate whereas NiO and the alumina-supported NiO were inactive. The study indicates that involvement of homogeneous catalysis cannot be excluded when using the supported catalysts.

Murata, S. [5] studied the Oxidative desulfurization of diesel fuels with molecular oxygen was examined by using cobalt salts and aldehydes as catalysts and sacrificial materials, respectively. At first, the authors conducted desulfurization of model oils consisting of benzene and dibenzothiophene. A mixture of benzene, dibenzothiophene, *n*-octanal, and an appropriate cobalt salt (acetate or chloride) was stirred at 40 °C under atmospheric pressure of oxygen to afford dibenzothiophene sulfone in almost quantitative yield within 15 min. Dibenzothiophene sulfone produced could be easily removed from the model oils by silica or alumina adsorption. Several organic sulfides including thioanisole, diphenyl sulfide, benzothiophene, and 4,6-dimethyldibenzothiophene also could be converted to the corresponding sulfones in almost quantitative yields. Then, the authors examined ultra deep desulfurization of a commercial diesel fuel, which contains 193 wt ppm of sulfur. By using the system consisting of cobalt acetate, aldehyde, and molecular oxygen, sulfur-containing compounds in the diesel fuel were oxidized, and then removed by alumina adsorption and/or solvent extraction. The resulting oil contained less than 5 wt ppm of sulfur; this corresponds to the result that more than 97% of sulfur in the oil could be removed. These results may indicate that this brand-new oxidative desulfurization process has a potential to meet a future regulation of sulfur in the diesel fuel.

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Chemicals

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

2) Dibenzothiophene [$C_{12}H_6S$], Analytical grade, from ALDRICH Co.,Ltd

3) Isobutyraldehyde [$(CH_3)_2CHCHO$] ,Analytical grade, from Fluka Co.,Ltd

4) 3- methylbutyraldehyde [$(CH_3)_2CHCH_2CHO$] , Analytical grade, from ALDRICH Co.,Ltd

5) Acetonitrile [C_2H_3N], Analytical grade, from Fisher scientific Co.,Ltd

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

8) Paraffin oil, Commerial grade, from SR.LAB Co.,Ltd

9) Cobalt nitrate [$Co(NO_3)_2$], Analytical grade, from ALDRICH Co.,Ltd

10) Copper nitrate [$Cu(NO_3)_2$], Analytical grade, from ALDRICH Co.,Ltd

3.2 Apparatus and Instruments

1)	Three necks round-bottome flask	500 ml
2)	Beaker	100 ml,250 ml and 500 ml
3)	Pipette	10 ml
4)	Burette	50 ml
5)	Separatory funnel	500 ml
6)	Volumetric flask	50 ml
7)	Thermometer	100 °C
8)	Water bath	
9)	Reflux condenser	
10)	Universal indicator paper	
11)	Filter paper	
12)	Funnel	
13)	Crucible	
14)	Ring	
15)	Oxygen Pump	
16)	X-Ray Fluorescence Spectrophotometer (XRF); Model X-1000 Oxford Instrument	
17)	Fourier-Transform Spectrophotometer (FT-IR); Model FT-IR spectrum GX,Perkin Elmer	

3.3 Experimental Procedure

3.3.1 Catalyst preparation

Silica-supported cobalt and copper catalyst (Co/SiO_2 and Cu/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 $Co(NO_3)_2$ or $Cu(NO_3)_2$ solution with concentration 0.33, 0.50 and 0.67 mol/L. After the metal salts impregnation by immersing the silica support for 24 h in aqueous solution, the slurry was then dried with an oven at 110°C for 24 h, and then the catalyst was calcined 550°C for 5 h.

3.3.2 Simulated diesel oil preparation

Commercial Diesel oil from the gas station mixed with DBT to produce the simulated diesel oil. Each experiment need the approximate 0.5 wt% of sulfur content, so simulated diesel oil 100 g consist of diesel oil 99.5 g and DBT 0.5 g. The mixture was stirred and heated until homogeneously. The sulfur content in diesel oil was measured by XRF.

3.3.3 oxidative desulfurization of diesel oil

In this experiment, Dibenzothiophene were dissolved into commercial diesel oil to make a simulated diesel solution. The detail of oxidative desulfurization of diesel oil listed as follow:

1. The three-necked round bottom flask was connected with thermometer, reflux condenser and oxygen pump. The system was heated in a paraffin oil bath until the reaction temperature rise to 40°C.
2. Acetonitrile 50 ml and aldehyde (In appendix B) (Isobutyraldehyde or 3-methylbutyraldehyde) were taken in the reaction assembly, then blow oxygen gas at constant flow rate 0.2 L/min and kept the temperature of 40°C for 30 minutes.
3. After 30 minute, the mixture 99.5 g of diesel oil and 0.5 g of DBT, 2 wt% of catalyst were introduced into three-necked flask and control the temperature of 40°C at desired reaction times.
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 out by vacuum pump, the liquid sample was transferred into separatory funnel.
6. 50 ml of Acetonitrile was added into the liquid mixture 2 times for separate two layers and then keep the bottom layer (oil after oxidative).

3.3.4 Characterization of desulfurized diesel oil and catalyst

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

Table 3.1 List of samples characterization and testing instruments.

Samples	Properties	Instrument
Diesel oil	Sulfur content	X-ray Fluorescence Spectrophotometer (XRF)
Diesel oil	Functional group	Fourier transform infrared spectroscopy (FTIR)
Catalyst	Metal content	X-ray Fluorescence Spectrophotometer (XRF)

3.4 Experimental design

The experiment was designed for study the effect of process variables on sulfur removal. The aldehyde, metal type, and metal loaded were firstly studied. The mole ratio of aldehyde to sulfur and reaction time were also studied by using the best type of aldehyde and catalyst that affected on the percent of sulfur removal. Moreover, the best condition from Part 1 to Part 3 was chosen for removing sulfur in non-desulfurized diesel oil.

Table 3.2 : Experimental conditions fot study the effect of aldehydes, catalysts, and Amount of metal oxide catalyst on the percentage of sulfur removal

Type of Aldehyde	Type of Catalyst	Amount of metal oxide catalyst (wt%)	Dosage of Catalyst (wt%)	Reaction time (min.)
Isobutyraldehyde	non-catalyst	-	-	60
	SiO_2	-	2	
	CoO/SiO_2	8.15 10.89 13.74		
	CuO/SiO_2	7.80 12.83 13.28		
3-Methlybutyraldehyde	non-catalyst	-	-	60
	SiO_2	-	2	
	CoO/SiO_2	8.15 10.89 13.74		
	CuO/SiO_2	7.80 12.83 13.28		

Table 3.3 : Experimental conditions for study effect of mole ratio of aldehyde to sulfur on percent sulfur removal

Type of Aldehyde	Type of Catalyst	Mole ratio of aldehyde to Sulfur	Dosage of Catalyst (wt%)	Reaction time (min)
Choose the optimum aldehyde type	Choose the optimum catalyst type	5:1	2	60
		10:1		
		15:1		
		20:1		
		25:1		
		30:1		

Table 3.4 : Experimental conditions for study effect reaction time on percent removal

Type of Aldehyde	Type of Catalyst	Mole ratio of aldehyde to Sulfur	Dosage of Catalyst (wt%)	Reaction time (min)
Choose the optimum aldehyde type	Choose the optimum catalyst type	Choose the optimum ratio	2	30
				60
				90
				120

CHAPTER 4

RESULTS AND DISCUSSION

The oxidation of dibenzothiophene in simulated diesel oil by an aldehyde/oxygen system, using silica-supported oxide based Cu and Co, was examined. The aim of the present study was to investigate the effect of oxidative reaction variables such as type of aldehyde, type and concentration of catalyst, mole ratio of aldehyde to sulfur, and reaction time on percentage of sulfur removal. The optimum condition that found in oxidative reaction of simulated diesel oil was used for non-desulfurization diesel oil.

4.1 Determination of sulfur content in diesel oil.

The sulfur content in commercial diesel oil and simulated diesel (diesel oil + DBT) that analyzed by XRF technique were reported in Table 4.1

Table 4.1 : Sulfur content in commercial and simulated oil

Sample	Sulfur content (wt%)
Commercial diesel oil	0.0193
Simulated diesel oil (diesel oil + DBT)	0.0275

From the result in Table 4.1, the commercial diesel oil from the gas station has sulfur content about 0.0193 wt%. After the commercial diesel oil was mixed with DBT, the sulfur content increased to approximate 0.0275 wt%.

Figure 4.1 : Simulated diesel oil (diesel oil + DBT)

4.2 Characterization of metal oxide content on catalysts.

The CuO/SiO_2 and CoO/SiO_2 catalyst were prepared by impregnation method. The silica support was impregnated in constant volume of aqueous solution of $Cu(NO_3)_2$ and $Co(NO_3)_2$ with concentration 0.33, 0.50, and 0.67 mol/L. The amount of metal oxide loaded on silica support catalyst obtained from XRF technique is shown in Table 4.2

Table 4.2 : Metal oxide content on silica-supported catalyst

Concentration of metal nitrate (mol/L)	Amount of metal oxide on catalyst (wt%)	
	CuO	CoO
0.33	7.80	8.15
0.50	12.83	10.89
0.67	13.28	13.74

As seen from the result in Table 4.2, the amount of metal oxied (CuO and CoO) was increased with the increasing of metal nitrate concentration in the aqua solution.

4.3 Oxidation of DBT in simulated diesel oil

In this study, Isobutyraldehyde and 3-Methylbutyraldehyde were taken in this experiment to study the effect of aldehydes type on sulfur removal. The influence of catalyst and amount of metal oxide loading on catalyst were also studied. The results are reported in Table 4.3.

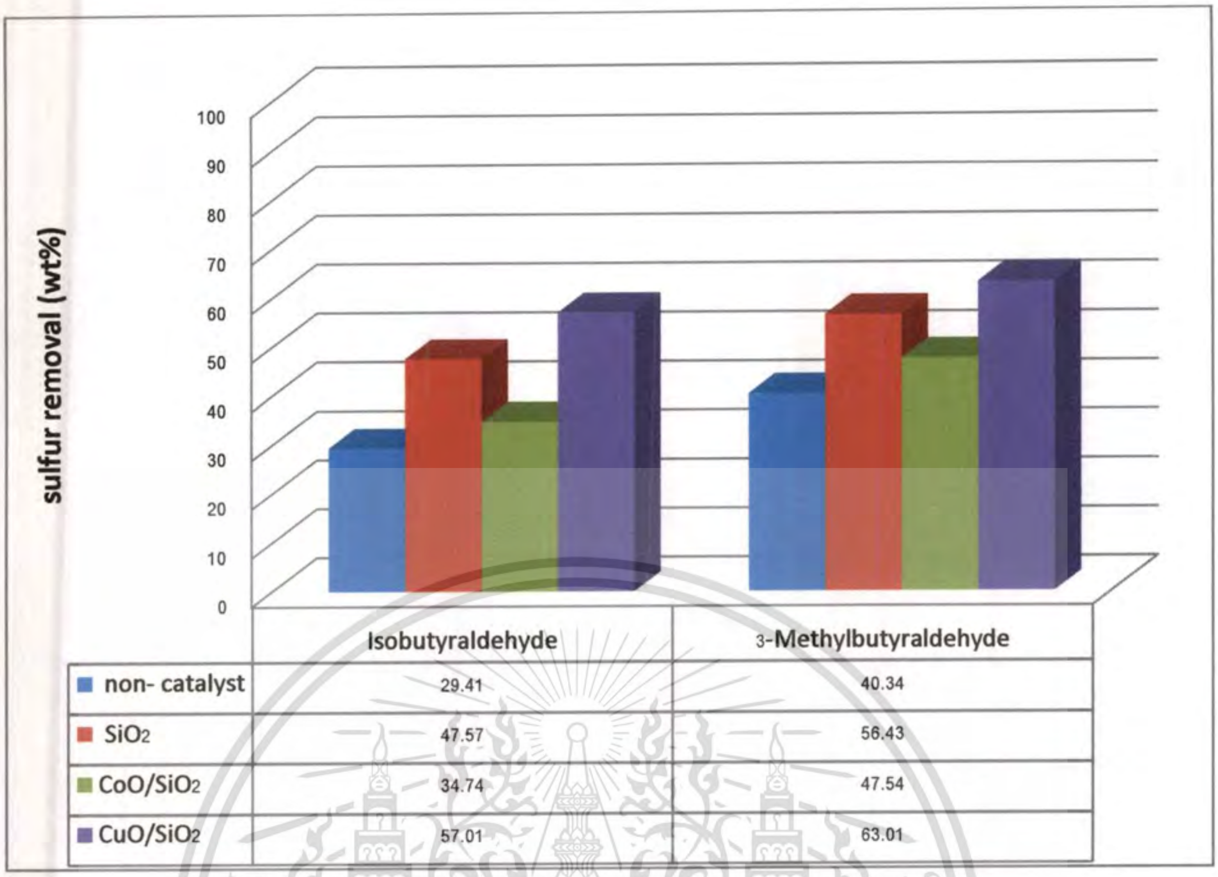
Table 4.3 : The effect of aldehyde , catalyst , and metal salt concentration on the percentage of sulfur removal

Type of Aldehyde	Type of Catalyst	Amount of metal oxide on catalyst (wt%)	Dosage of Catalyst (wt%)	Reaction time (min.)	Sulfur removal (wt%)
Isobutyraldehyde	non-catalyst	—	—	60	29.41
	SiO_2	—	2		47.57
	CoO/SiO_2	8.15			25.63
		10.89			29.34
		13.74			34.74
	CuO/SiO_2	7.80			38.36
		12.83			47.70
		13.28			57.01

3-Methlybutyraldehyde	non-catalyst	—	—	60	40.37
	SiO_2	—	2		56.43
	CoO/SiO_2	8.15			40.89
		10.89			45.55
		13.74			47.54
	CuO/SiO_2	7.80			60.88
		12.83			62.36
		13.28			63.01

4.3.1 The effect of aldehyde type

To investigate the effect of aldehyde types, the experiment carried out the oxidation of dibenzothiophene using isobutyraldehyde and 3-methylbutyraldehyde in the non-catalyst and catalyst systems. The catalysts were used in the oxidation reaction such as CoO/SiO_2, CuO/SiO_2 and SiO_2 without metal oxide loading. The effect of aldehyde types on the percentage of sulfur removal is shown in Figure 4.2.

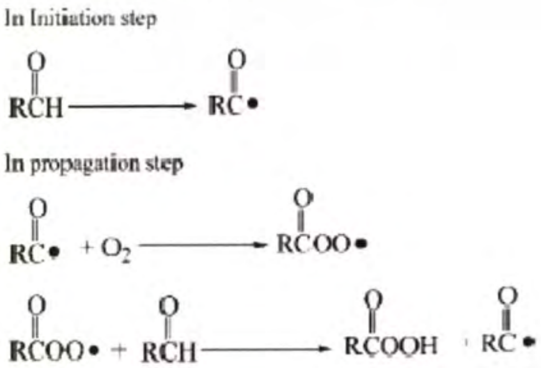


	Isobutyraldehyde	3-Methylbutyraldehyde
■ non- catalyst	29.41	40.34
■ SiO_2	47.57	56.43
■ CoO/SiO_2	34.74	47.54
■ CuO/SiO_2	57.01	63.01

Figure 4.2 : The effect of aldehyde type on the percentage of sulfur removal

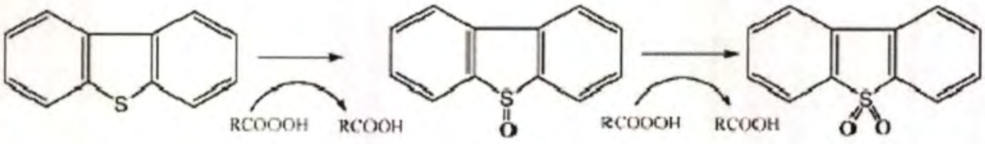
The oxidation reaction using aldehyde/molecular oxygen/metal oxide supported catalyst proceed through autooxidation of aldehyde, forming an acyl radical. Acyl radical on reaction with molecular oxygen forms a peroxy radical. Peroxy radical abtracts a hydrogen atom from the other aldehyde molecule, forming peracid and another acyl radical in the chain propagation step (Scheme 1) [1]

Scheme 1. Peracid Formation



Peracid converts sulfur compound to sulfoxide by trasfering an oxygen atom. As a result, the peracid molecule itself transforms to the corresponding carboxylic acid. Another peracid molecule converts sulfoxide to sulfones on transfer of oxygen atom (Sheme 2) [1]

Scheme 2. Oxidation of DBT



DBT DBT Sulfoxide DBT Sulfone

The oxidation reaction proposed in Scheme 1 and 2 proceed in oil phase, then the highly dissolved between diesel oil and aldehyde, resulting in more efficiency of the DBT oxidation.

From the results are presented in Figure 4.1. The simulated diesel oil after solvent extraction by acetonitrile without oxidative reaction can remove sulfur about 21.05 %wt. So between the two types of aldehyde, 3-methylbutyraldehyde was the most suitable aldehyde in every condition. It is due to the polarity of 3-methlybutyraldehyde is lower than isobutyraldehyde because 3-methlybutyraldehyde has longer hydrocarbon chain which is attracted to C=O group of aldehyde, so 3-methlybutyraldehyde can dissolve easier in diesel oil which is non-polar compound and the oxidative reaction with DBT was higher efficiency.

4.3.2 The effect of catalyst type

The oxidation of dibenzothiophene by an oxygen/aldehyde system, using heterogeneous catalytic systems based on CuO and CoO over silica was examined(Figure 4.3 and 4.4). To compare the sulfur removal by non-catalytic system and SiO_2, the oxidation test under the using of 3-Methylbutyraldehyde is shown the result in figure 4.3.

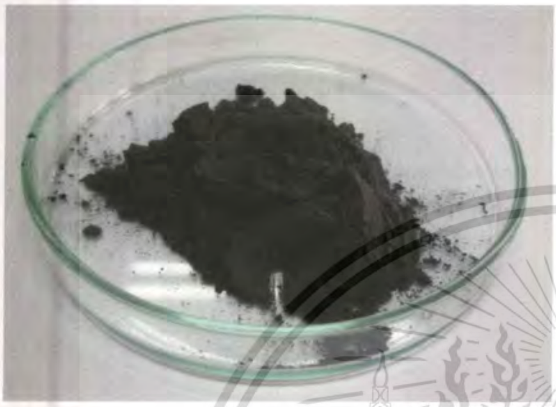


Figure 4.3 : Cobalt oxide loaded on silica

Figure 4.4 : Copper oxide loaded on silica

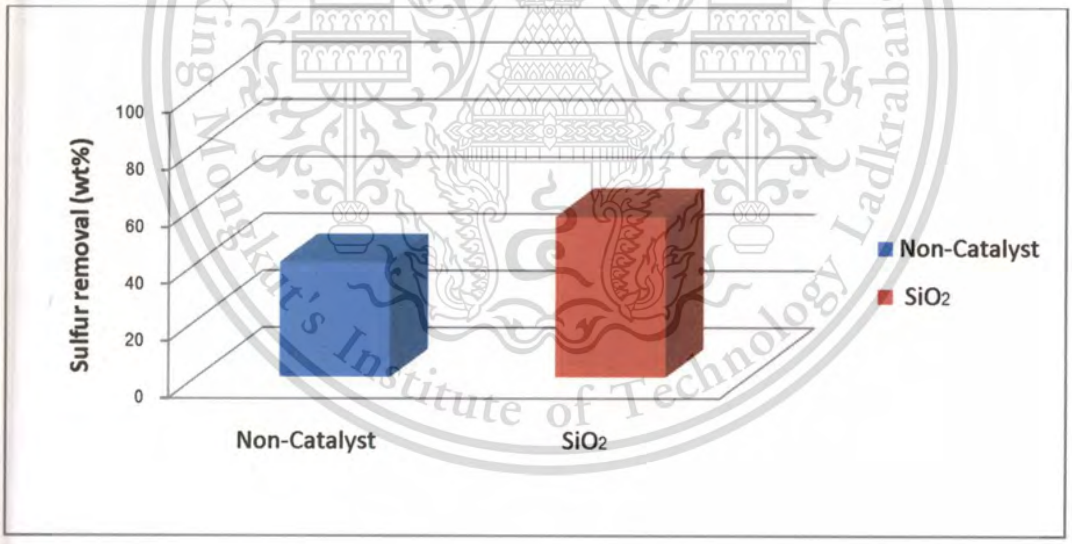


Figure 4.5 : Comparison of sulfur removal percentage in the DBT oxidation with SiO_2 and without catalyst.

As seen from the figure 4.5, SiO_2 showed higher oxidation activity than non-catalyst system. The sulfur removal difference between the reaction using SiO_2 and non-catalytic system was 16% because SiO_2 have surface area that can adsorb oxygen gas on the surface itself, So it is the oxidative well.

The result from this experiment SiO_2 is removal sulfur better than CoO/ SiO_2 because there are calcite CoO/SiO_2 , it may be not good, organic still on SiO2 , it don't make good oxidative but CuO/SiO_2 are good calcite therefore removal sulfur better than SiO_2.

For comparison, DBT was oxidized under the same conditions over CoO/SiO_2 and CuO/SiO_2 in the range of 7.80-13.28 wt% of CoO and 8.15-13.74 wt% of CoO solutions. The results are shown in Figure 4.6.

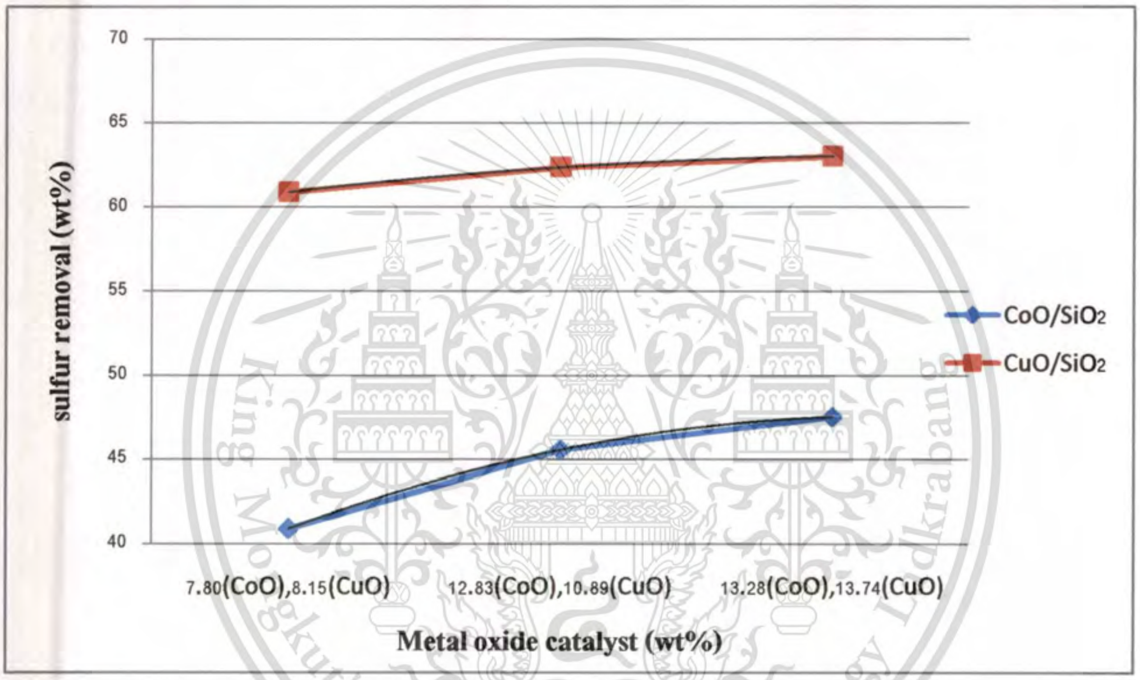


Figure 4.6 : Comparison in oxidation reactivity of DBT over CoO/SiO_2 and CuO/SiO_2 at various percent weight of metal oxide.

From the Figure 4.6, an increase of the metal salt concentration led to a slightly increase in the DBT removal. When increase concentration of $Cu(NO_3)_2$ from 0.33 to 0.67, the DBT removal by CuO/SiO_2 catalyst was slightly increased from 60.88% to 63.01% for the using of CoO/SiO_2; the DBT removal was increased from 40.89% to 47.54%.

The results shown that the increasing of both metal oxide catalyst insignificantly improve the DBT removal in the diesel oil.

Moreover, CuO/SiO_2 showed the more oxidation performance for DBT removal than CoO/SiO_2, probably due to the adsorption of oxygen gas over the CoO supported on silica. The oxidation of DBT proceeds through autooxidation of aldehyde with molecular oxygen. that adsorbed over metal oxide on silica support. Copper can adsorb oxygen gas better than Cobalt, and then oxidative desulfurization of DBT over CuO/SiO_2 can be easily occurred and higher amount of oxidized DBT than those of CoO/SiO_2.

4.3.3 The effect of mole ratio of aldehyde to sulfur

This experiment carried out the oxidation reaction of DBT in diesel oil under various mole ratio of 3-methylbutyraldehyde to sulfur with 2 wt% of Cu/SiO_2 which prepared from 0.67 mol/L of $Cu(NO_3)_2$. The effect of mole ratio of aldehyde to sulfur on sulfur removal is shown in Table 4.4 and Figure 4.5

Table 4.4 : The effect of mole ratio of 3-methylbutyraldehyde to sulfur on sulfur removal

Type of Aldehyde	Amount of metal oxide on catalyst (wt%)	Mole ratio of aldehyde to Sulfur	Dosage of Catalyst (wt%)	Reaction time (min.)	Sulfur removal (wt%)
3-Methlybutyraldehyde	13.28 CuO/SiO_2	5 : 1	2	60	54.38
		10 : 1			63.01
		15 : 1			71.19
		20 : 1			70.44
		25 : 1			70.78
		30 : 1			69.87

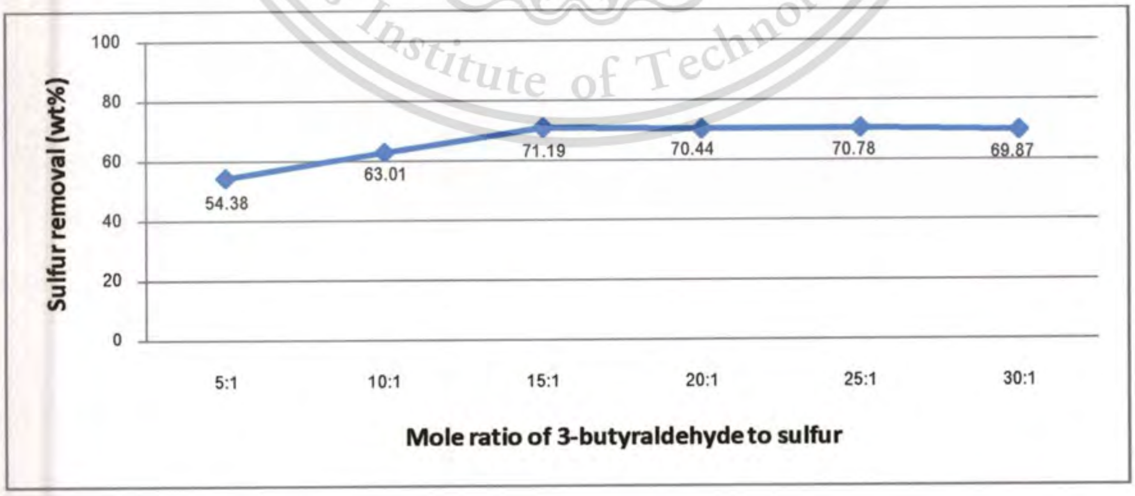


Figure 4.7 : DBT removal over CuO/SiO_2 with difference mole ratio of 3-methylbutyraldehyde and sulfur.

As shown in Figure 4.4, the sulfur removal increased with the mole ratio of 3-methylbutyraldehyde/sulfur, at the mole ratio of 15:1, the maximum DBT removal was achieved.This ratio could be came from the peracid converts sulfur compound to sulfoxide by transferring an oxygen atom. As a result , the peracid molecule itself transforms to the corresponding carboxylic acid. Another peracid molecule convert sulfoxide to sulfones on transfer of oxygen atom. Therefore, stoichiometrically two molecules of aldehyde and two molecules are required to oxidize a sulfide molecule to its sulfone and form two molecules of the corresponding acid molecules without participating in oxidation of sulfide. Because of this, more than a stoichiometric amount of aldehyde is required.

4.3.4 The effect of reaction time

The effect of reaction time on sulfur removal under the optimum condition is shown in Table 4.5 and plotted in Figure 4.5

Table 4.5 : The effect of various reaction times to sulfur removal

Type of Aldehyde	Amount of metal oxide on catalyst (wt%)	Mole ratio of aldehyde to Sulfur	Dosage of catalyst (%wt)	Reaction time (min)	Sulfur removal (wt%)
3-Methylbutyraldehyde	13.28 CuO/SiO_2	15:1	2	30	69.88
				60	71.18
				90	72.48
				120	74.06

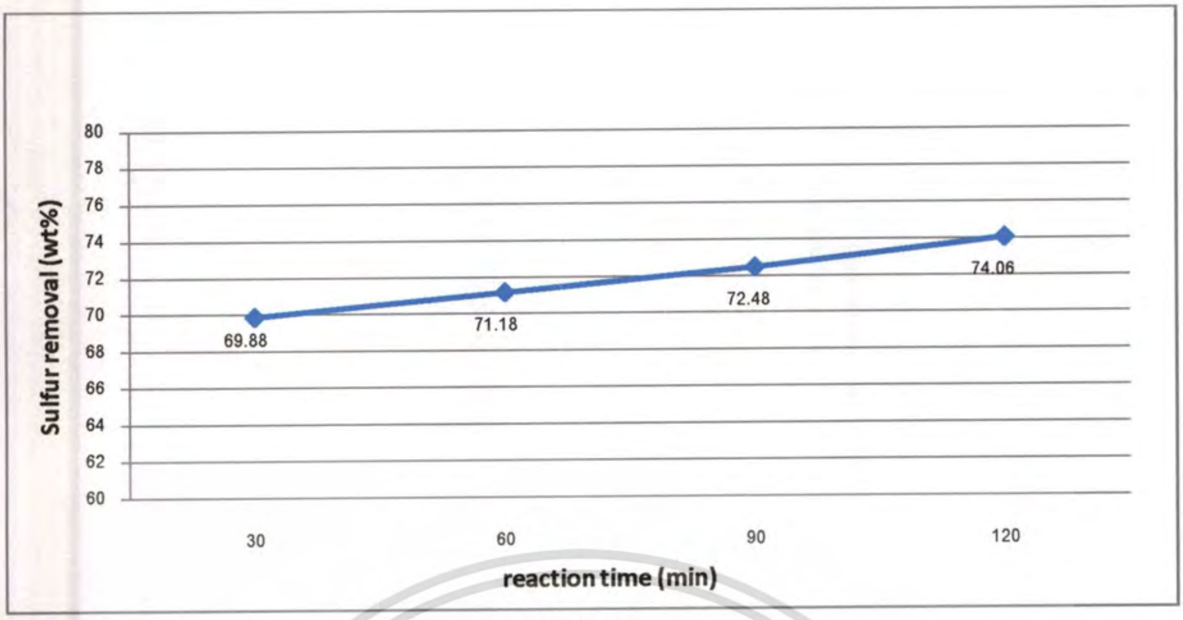


Figure 4.8 : Variation of sulfur removal with different reaction time

From the Figure 4.5, it was found that the DBT removal increased slightly when the reaction time was increased from 30 to 120 minutes under the system of 3-methylbutyraldehyde, molecular oxygen, and CuO/SiO_2. This result clearly shown that higher removal of sulfur can be achieved in a longer reaction time. Then, the reaction time of 120 minute was the best condition of experiment for the oxidation of DBT over CuO/SiO_2.

4.4 The oxidative desulfurization test with non-desulfurized diesel oil

The oxidation desulfurization of non-desulfurized diesel oil supplied from PTT Public Company Limited, Thailand by using the optimum reaction condition that determined from the oxidation of DBT in simulated diesel oil. The dosage of 2 wt% of CuO/SiO_2 catalyst with impregnated concentration 0.67 mol/L, the mole ratio of 3-methylbutyraldehyde to sulfur was 15:1 and the reaction time of 120 minute were the optimum condition for this experiment. The comparison of sulfur removal of non-desulfurized diesel oil before and after pass the oxidation reaction is shown in Figure 4.6

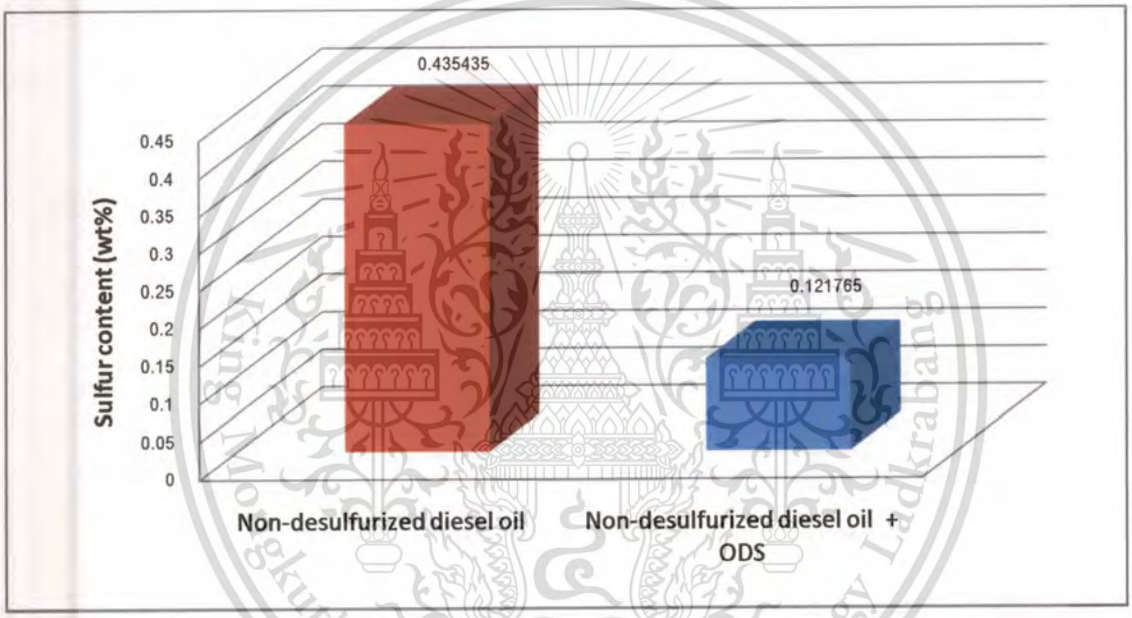


Figure 4.9 : The comparison of sulfur removal of non-desulfurized diesel oil before and after pass the oxidation reaction

As seen from Figure 4.6, the sulfur content in non-desulfurized diesel oil was 0.4 wt%. After treated non-desulfurized diesel oil by oxidation with best condition aldehyde/molecular oxygen/CuO supported on SiO2 catalyst system, the sulfur content of desulfurized diesel oil was reduced to 0.122 wt% that correspond to the sulfur removal of 72.03%. The percentage sulfur content of non-desulfurized diesel oil more than of simulated diesel oil because have some sulfur compound is not DBT consisted in non-desulfurized diesel oil was less to removed.

4.5 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 Facuity of King Mongkut's Institute of Technology Ladkrabang. The FTIR spectrum were shown in Figure 4.10-4.14.

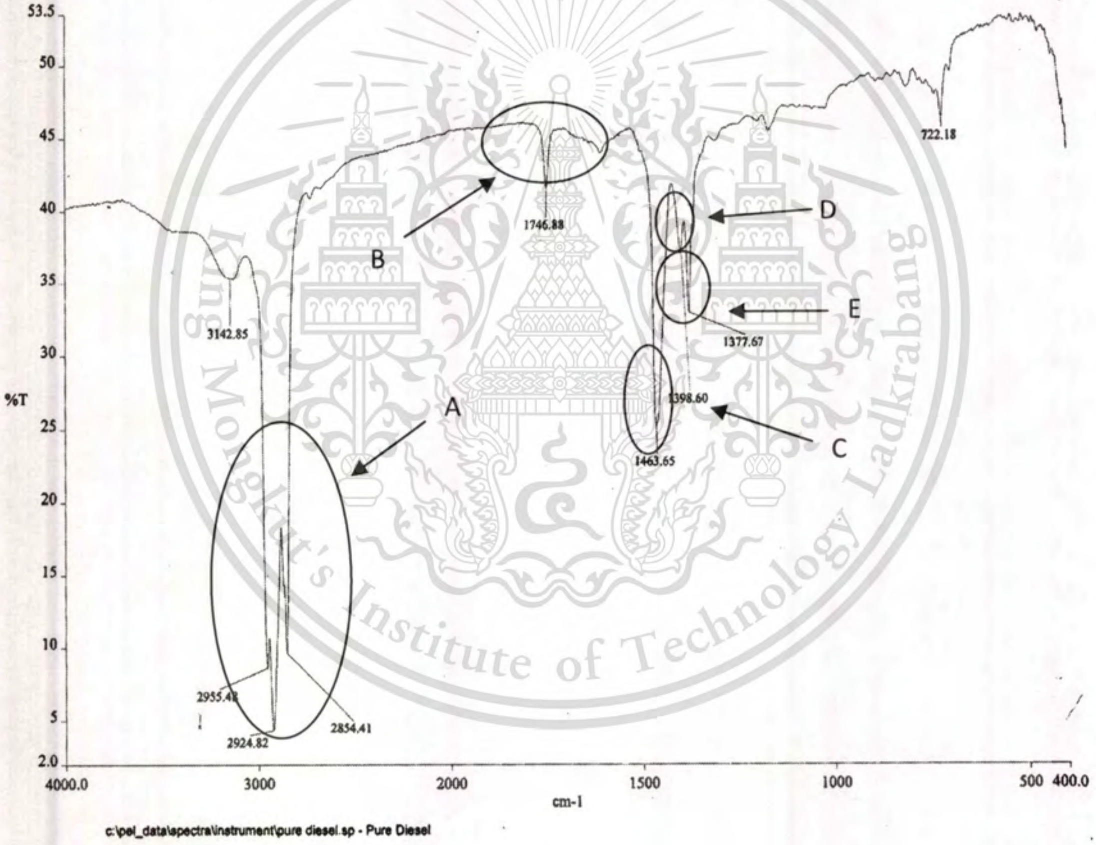


Figure 4.10 : FTIR spectrum of commercial diesel oil

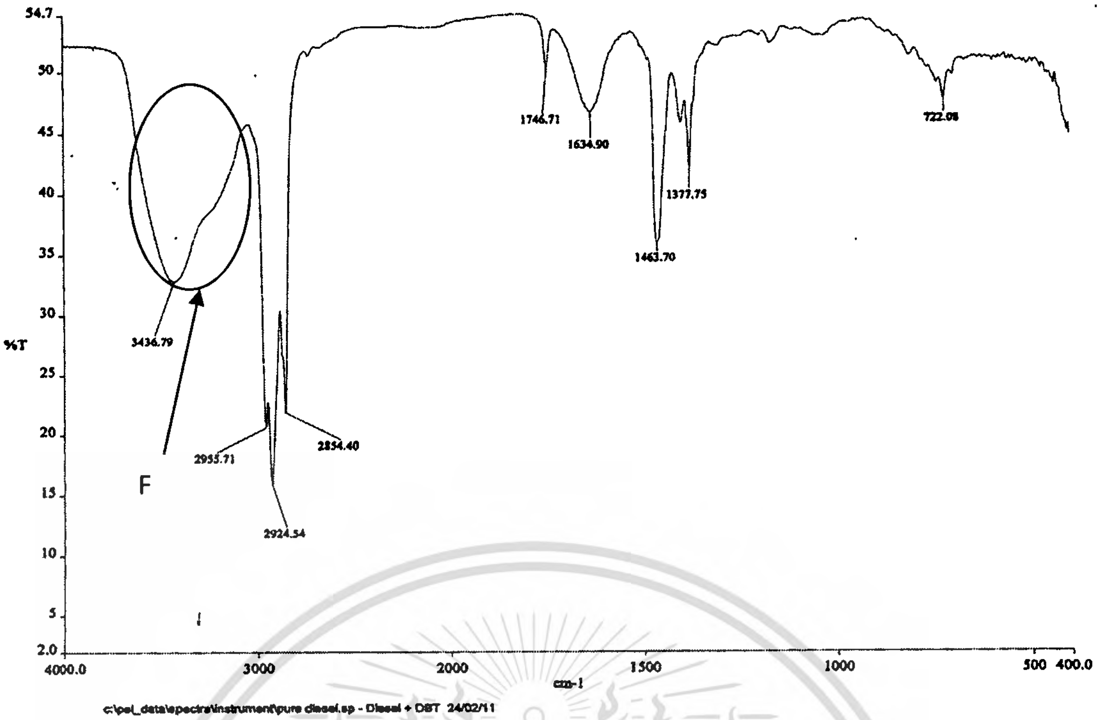


Figure 4.11 : FTIR spectrum of simulated diesel oil (commercial oil + DBT)

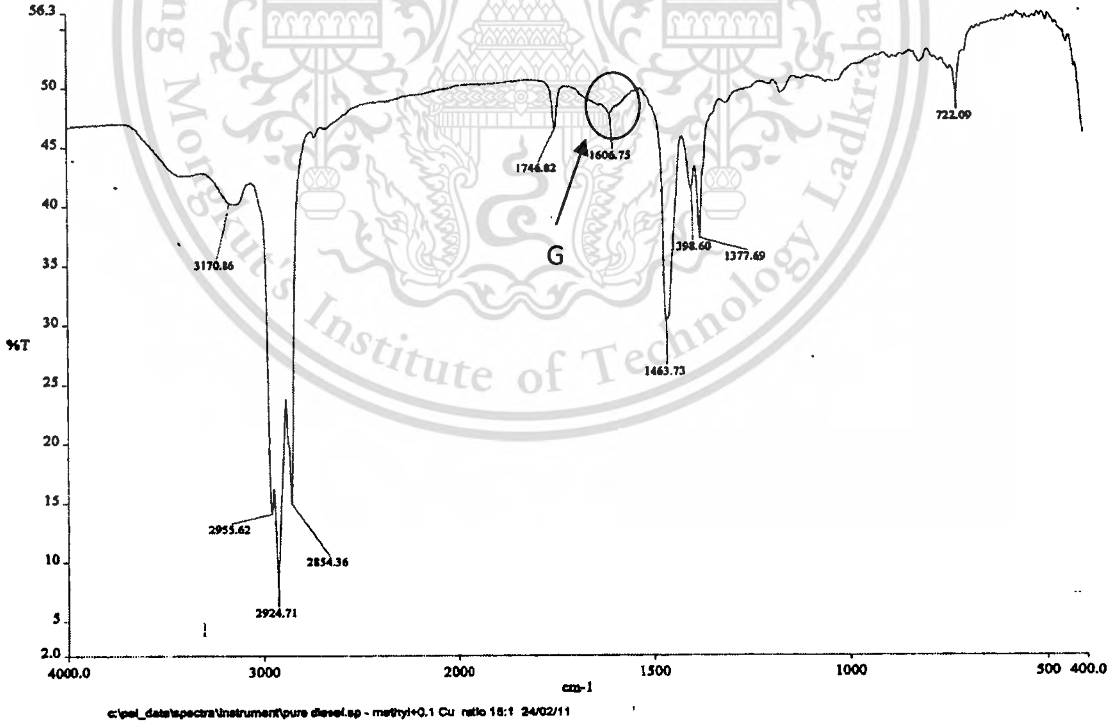


Figure 4.12 :FTIR spectrum of simulated diesel oil after the oxidation with 3-methybutyraldehyde catalytzed by CuO/SiO_2

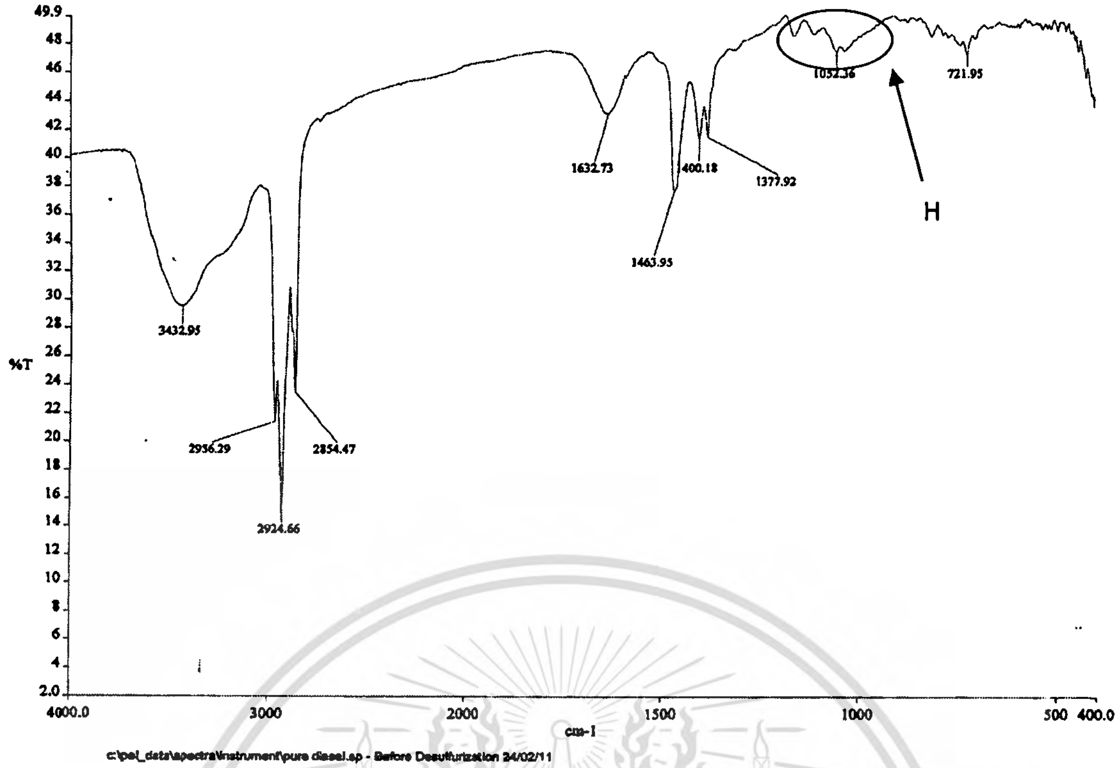


Figure 4.13 : FTIR spectrum of non-desulfurization oil before oxidative desulfurization

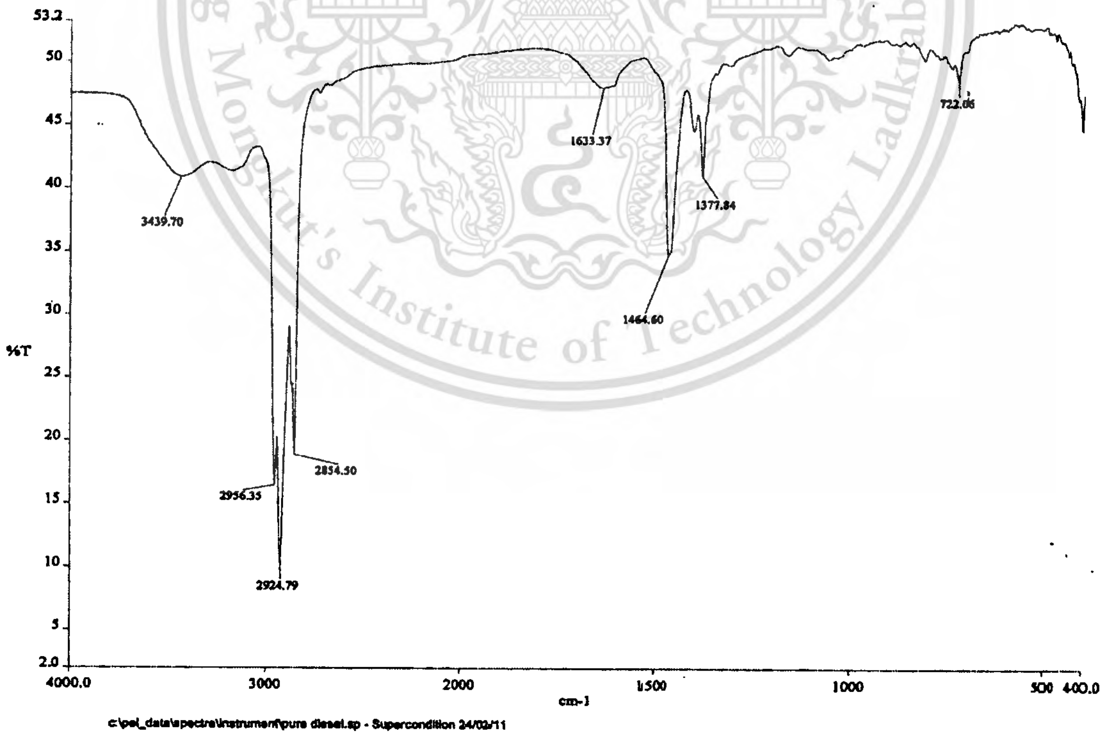


Figure 4.14 : FTIR spectrum of diesel oil after oxidative desulfurization

The analysis of the chemical identity of the 5 FTIR spectrum in Figure 4.7-4.11. Observed that the peak will vary with each different functional groups.

A. C-H Streaching 3000-2800 cm-1

B. Carbonyl 1720-1740 cm-1

C. CH2(scissoring) 1458 cm-1

D. CH Bending 1400 cm-1

E. Sulfone 1300-1070 , 1160-1140 cm-1

F. Alcohol 3500-3200 cm-1

G. Aromatic 1615 cm-1

H. Sulphoxides 1070-1030 cm-1

The results of the measured by Fourier transform Infrared spectroscopy (FTIR) showed that after added the DBT into the Pure Diesel can be observed at 4.5.2 FTIR graph has a new peak is an alcohol because added DBT to increase more impurity and sulfur.

At 4.5.3 FTIR graph can be observed on the alcohol peak is more decreased and has a new peak(peak G) is a Carbonyl Aldehyde peak because added Methylbutyraldehyde

At 4.5.4 FTIR graph is showed all of peaks are not Desulfurization process. This FTIR graph shows some impurity substances if compared with diesel has Desulfurization are alcohol peak(peak F) and sulphoxide peak(peak H)

At 4.5.5 FTIR graph has Desulfurization by best condition will observed that when compare with the 4.5.4 FTIR graph(before desulfurization) the Alcohol peak is more decreased(peak F) and sulphoxide peak(peak H) is disappear. So, The best condition have affects to help reduce the sulfur content and impurity substances.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

This special project was intented to defulfurizatied of dibenzothiophene (DBT) in diesel oil by using aldehyde consist of isobutyraldehyde and 3-methylbutyraldehyde with molecular oxygen and the presence of cobalt and copper catalysts. From the results , it can be summarized as the following.

5.1 Conclusion

The goal of this research was to study the effectiveness type of aldehyde such as iosbutyraldehyde and 3-methlybutyraldehyde, and the mole ration of aldehyde to sulfur. Also to study the effectiveness type of catalyst such as cobalt loaded on silica (CoO/SiO_2) and copper loaded on silica (CuO/SiO_2) , and various percentage of metal oxide loaded on catalyst. The reaction time was varied to increase every 30 minutes.

From the results, it can conclude that the most effectiveness type of aldehyde to the reduction percentage of sulfur is 3-methlybutyraldehyde because the longer of hydrocarbon chain the lower polarity will react easily with diesel oil which is non-polar compound. In addition, the mole ratio of aldehyde to sulfur also play the important role to sulfur removal in diesel oil, the result show that 15:1 is the best for remove DBT.

The studying in type of catalyst observed that CuO/SiO_2 is better than CoO/SiO_2 for oxidative desulfurization in mind condition in atmospheric pressure with low temperature at 40 °c. Copper can adsorb oxygen gas better than Cobalt, then oxidative desulfurization of DBT over CuO/SiO_2 can be easily occur and higher amount of oxidized DBT than using of CoO/SiO_2. Moreover, the increasing of concentration of metal salt solution (Copper(II), nitrate) , the increasing of percentage sulfur removal and from the studied shows that the higher removal of sulfur can be achieved in a longer reaction time.

5.2 Recommendations

1. Study the other type of aldehyde which is has lower polarity such as octanal and benzaldehyde.

2. Change air pump to pure oxygen pump to increase the amount of oxygen .

3. Change support type to be high surface area.

Reference

[1] Oxidative Desulfurization of HDS Diesel Using the Aldehyde/Molecular Oxygen Oxidation System Tumula Venkateshwar Rao,* Bir Sain,* Sudha Kafola, Bhagat Ram Nautiyal,Yogendra Kumar Sharma, Shrikant Madhusudan Nanoti, and Madhukar Omkarnath Garg *Indian Institute of Petroleum, Dehradun 248005, India*

[2] Zannikos, F., Lois, E., Stouranas, S. Desulfurization of Petroleum Fractions by Oxidation and Solvent Extraction. *Fuel Processing technology*. 1995, 42, 35-45.

[3] Shuujiro, O., Takeshi, N., Noriko, T., Weihua,Q.,Atsushi,I.,Tomatsu,I.,Toshiaki, K. Oxidative Desulfurization of Light Gas Oil and Vacuum Gas oil by Oxidative and Solvent Extraction. Energy and Fuels. 2000, 14, 1232-1239

[4] Oxidation of dibenzothiophene to dibenzothiophene-sulfone using silica gel
Karina Castillo a,*, J.G. Parsons b, David Chavez a, Russell R. Chianelli
Department of Chemistry, University of Texas at El Paso, 500 W University Ave.,
El Paso, TX 79968, United States

[5] A Novel Oxidative Desulfurization System for Diesel Fuels with Molecular Oxygen in the Presence of Cobalt Catalysts and Aldehyde. Satoru Murata, *Kazautaka Murata, and Masakatsu Nomura. Department of Applied Chemistry, Faculty of Engineering, Osaka University.

[6] Wonglumsum, P Desulfurization of High speed diesel using hydrogenperoxide and peroxy as oxidants and solvent extraction, Master Thesis, Program of Petrochemistry, Chulalongkorn University, 2001.

[7] [Online].Available http://en.wikipedia.org/wiki/Diesel_fuel#Refining

[8] [Online].Available http://www.thaigoodview.com/library/studentshow/2549/m6-6/no11

[9] [Online].Available http://en.wikipedia.org/wiki/Cetane_number

[10] [Online].Available http://earthsci.org/mineral/energy/gasexpl/refine.html

[11] [Online].Available www.emtindia.net/process/petrochemical/pdf/refiningofpetroleum.pdf

[12] [Online].Available http://en.wikipedia.org/wiki/Sulfur

[13] [Online].Available http://en.wikipedia.org/wiki/Hydrodesulfurization

[14] Colloid Chemistry of Silica Horacio E. Bergna DuPont, Wilmington, DE 19880-0228

[15] Silicon-29 NMR study of the surface of silica gel by cross polarization and magic-angle spinning Gary E. Maciel, Dean W. Sindorf *J. Am. Chem. Soc.*, 1980, *102* (25), pp 7606–7607

[16] [Online].Available http://en.wikipedia.org/wiki/Thiophene

[17] [Online].Available http://www.chemeurope.com/en/encyclopedia/Dibenzothiophene.html

[18] [Online].Available http://www.chemguide.co.uk/organicprops/carbonyls/oxidation.html

[19] [Online].Available http://en.wikipedia.org/wiki/Aldehyde

[20] GENERAL ARTICLE -*What we need to consider for a successful development of catalysts? R.P. Mehrotra S□d-Chemie India Pvt.Ltd New Delhi*

[21] Oxidation of dibenzothiophene by a metal–oxygen–aldehyde system V. Dumonta, L. Oliviero, a, , F. Maugéa and M. Houallaa Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen, CNRS, 6, Bd Maréchal Juin, F-14050 Caen, France

Appendix A

Calculation of Catalyst Compositon

In this experiment, $Cu(NO_3)_2$ and $Co(NO_3)_2$ were used as the impregnated solution for synthesis of CuO/SiO_2 and CoO/SiO_2 catalysts. The composition of CuO and CoO on supported catalyst was calculated by this formula;

$$\boxed{\frac{\text{grams of sample} \times 100}{\text{amount of SiO2}} = \text{wt\% of catalyst}}$$

For example;

0.05 CuO/SiO_2	**0.05 CoO/SiO_2**
Assume 100 g of SiO_2 = 0.1 mol CuO if 50 g of SiO_2 = 0.05 mol CuO 0.05 mol × 79.5 M.W. of CuO = 3.975 g $\frac{3.975 \times 100}{50}$ = 7.95 wt% of CuO	Assume 100 g of SiO_2 = 0.1 mol CuO If 50 g of SiO_2 = 0. 05 mol CuO 0.05 mol × 74.9 M.W. of CoO = 3.745 g $\frac{3.745 \times 100}{50}$ = 7.49 wt% of CoO

The compositon of CuO and CoO show as this table.

Sample	Compositon (wt%)	
	CuO	CoO
0.050 mol	7.95	7.49
0.075 mol	11.92	11.23
0.100 mol	15.90	14.98

Appendix B

Calculation of Mole Ratio of Aldehyde to Sulfur

Molecular weight of Isobutyraldehyde = 72.11 g

Molecular weight of 3-Methylbutyraldehyde = 86.13 g

Molecular weight of Dibenzothiophene = 184.26 g

Using this formula for calculate mole ratio of aldehyde to sulfur

$$\text{Amount of aldehyde} = \frac{\text{weight of DBT} \times \text{mole ratio of aldehyde} \times \text{M.W.of aldehyde}}{\text{M.W.of DBT}}$$

For example;

Mole ratio of Isobutyraldehyde to sulfur	Mole ratio of 3-methylbutyraldehyde to sulfur
10:1 mol ratio of Isobutyraldehyde $\frac{0.5 \times 10 \times 72.11}{184.26}$ = 1.956 g of aldehyde Then, Using 1.956 g = 10:1 mol ratio	10:1 mol ratio 3-methylbutyraldehyde $\frac{0.5 \times 10 \times 86.13}{184.26}$ = 2.34 g of aldehyde Then, Using 2.34 g = 10:1 mol ratio

Appendix C

The Experimental Data

Table C-1 The experimental data for study the effect of aldehyde and catalyst type.

Entry	Aldehyde	Catalyst (mol)	Aldehyde: Sulfur Mole ratio	Amount of catalyst	Reaction time (min)	Sulfur content (wt%)	Sulfur removal (%)
1	Diesel oil	-	-	-	-	0.019290	-
2	Diesel + DBT	-	-	-	-	0.027543	-
3	Isobutyraldehyde	-	10:1	-	60	0.021745	29.4107%
4	3-Methylbutyraldehyde	-	10:1	-	60	0.016433	40.3369%
5	Isobutyraldehyde	SiO_2	10:1	2%	60	0.014440	47.5728%
6	3-Methylbutyraldehyde	SiO_2	10:1	2%	60	0.012001	56.4289%
7	Isobutyraldehyde	0.050CuO/SiO_2	10:1	2%	60	0.016978	38.3582%
8	Isobutyraldehyde	0.075CuO/SiO_2	10:1	2%	60	0.014405	47.6999%
9	Isobutyraldehyde	0.100CuO/SiO_2	10:1	2%	60	0.011840	57.0126%
10	Isobutyraldehyde	0.050CoO/SiO_2	10:1	2%	60	0.016281	25.6326%
11	Isobutyraldehyde	0.075CoO/SiO_2	10:1	2%	60	0.014996	29.3395%
12	Isobutyraldehyde	0.100CoO/SiO_2	10:1	2%	60	0.014448	34.7420%
13	3-Methylbutyraldehyde	0.050CuO/SiO_2	10:1	2%	60	0.010774	60.8829%
14	3-Methylbutyraldehyde	0.075CuO/SiO_2	10:1	2%	60	0.010366	62.3643%
15	3-Methylbutyraldehyde	0.100CuO/SiO_2	10:1	2%	60	0.010187	63.0141%
16	3-Methylbutyraldehyde	0.050CoO/SiO_2	10:1	2%	60	0.021745	40.8887%
17	3-Methylbutyraldehyde	0.075CoO/SiO_2	10:1	2%	60	0.019462	45.5542%
18	3-Methylbutyraldehyde	0.100CoO/SiO_2	10:1	2%	60	0.017974	47.5438%

Table C-2 The experimental data for study the effect of mole ratio of aldehyde to sulfur

Entry	Aldehyde	Catalyst (mol)	Mole ratio of aldehyde to Sulfur	Amount of catalyst	Reaction time (min)	Sulfur content (Wt%)	Percent of Sulfur remove (Wt%)
1	3-Methylbutyraldehyde	0.100CuO/SiO_2	5:1	2%	60	0.012565	54.38
2	3-Methylbutyraldehyde	0.100CuO/SiO_2	10:1	2%	60	0.010187	63.01
3	3-Methylbutyraldehyde	0.100CuO/SiO_2	15:1	2%	60	0.007936	71.19
4	3-Methylbutyraldehyde	0.100CuO/SiO_2	20:1	2%	60	0.008472	70.44
5	3-Methylbutyraldehyde	0.100CuO/SiO_2	25:1	2%	60	0.008647	70.78
6	3-Methylbutyraldehyde	0.100CuO/SiO_2	30:1	2%	60	0.008826	69.87

Table C-3 The experimental data for study the effect of reaction time

Entry	Aldehyde	Catalyst (mol)	Mole ratio of aldehyde to Sulfur	Amount of catalyst	Reaction time (min)	Sulfur content (Wt%)	Percent of Sulfur remove (Wt%)
1	3-Methylbutyraldehyde	0.100CuO/SiO_2	15:1	2%	30	0.008296	69.88
2	3-Methylbutyraldehyde	0.100CuO/SiO_2	15:1	2%	60	0.007936	71.18
3	3-Methylbutyraldehyde	0.100CuO/SiO_2	15:1	2%	90	0.007578	72.48
4	3-Methylbutyraldehyde	0.100CuO/SiO_2	15:1	2%	120	0.007144	74.06