

**DESULFURIZATION OF MODEL OIL USING
PYRIDINIUM-BASED IONIC LIQUID**

NURUL UMAIRA NISA BINTI MAZELAN

**BACHELOR OF CHEMICAL ENGINEERING (GAS TECHNOLOGY)
UNIVERSITI MALAYSIA PAHANG**

©NURUL UMAIRA NISA BINTI MAZELAN (2013)

Thesis Access Form

No _____ Location _____

Author :

Title :

Status of access OPEN / RESTRICTED / CONFIDENTIAL

Moratorium period: _____ years, ending _____ / _____ 200_____

Conditions of access proved by (CAPITALS): DR JOLIUS GIMBUN

Supervisor (Signature).....

Faculty:

Author's Declaration: *I agree the following conditions:*

OPEN access work shall be made available (in the University and externally) and reproduced as necessary at the discretion of the University Librarian or Head of Department. It may also be copied by the British Library in microfilm or other form for supply to requesting libraries or individuals, subject to an indication of intended use for non-publishing purposes in the following form, placed on the copy and on any covering document or label.

The statement itself shall apply to ALL copies:

This copy has been supplied on the understanding that it is copyright material and that no quotation from the thesis may be published without proper acknowledgement.

Restricted/confidential work: All access and any photocopying shall be strictly subject to written permission from the University Head of Department and any external sponsor, if any.

Author's signature.....**Date:**

users declaration: for signature during any Moratorium period (Not Open work):

I undertake to uphold the above conditions:

Date	Name (CAPITALS)	Signature	Address

DESULFURIZATION OF MODEL OIL USING PYRIDINIUM-BASED IONIC LIQUID

NURUL UMAIRA NISA BINTI MAZELAN

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering (Gas Technology)

**Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG**

JUNE 2013

©NURUL UMAIRA NISA BINTI MAZELAN (2013)

SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering (Gas Technology).

Signature :
Name of main supervisor : DR. SYAMSUL BAHARI ABDULLAH
Position : LECTURER
Date : 5 JULY 2013

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature :
Name : NURUL UMAIRA NISA BINTI MAZELAN
ID Number : KC09027
Date : 5 JULY 2013

Dedication

To my beloved parents, brothers and sister

ACKNOWLEDGEMENT

The highest gratitude is for Allah for giving me the strength and blesses me with abundance of people around me that have been so helpful. There are so many people that have been involved in this project directly or indirectly. I might have no chance to thank of all them, but surely I hope that their assistant would be rewarded by Allah.

Firstly, I would like to thank my supervisors, Dr Syamsul Bahari Abdullah, which has guided me along of this research. Without his continued support and interest, this thesis would not have been the same as presented here.

Besides that, I would also like to thank my friends and team mates in this research, which have been so supportive and helpful to me. Without their assistant and support, I believe I would not have the courage to finish this thesis within the time.

I am also indebted to all of my lecturers and FKKSA's laboratory staffs. With their help and assistant in my experiment, I had managed to finish my experiment although there were problem and obstacle. Last but not least, I would like to thank to my parents for supporting me all the times throughout my studies in University Malaysia Pahang (UMP)

ABSTRACT

Sulfur is the most abundant element found in crude oil. This paper contains the study on desulfurization of model oil by extraction with Pyridinium-based ionic liquids. The objective of the project is to determine the sulfur compound, dibenzothiophene (DBT) removal efficiency of pyridinium-based ionic liquids, 1-ethylpyridinium ethylsulfate, (EpyESO4) from model oil. In order to characterize the Pyridinium-based ionic liquids, the characterization process of [EpyESO4] was conducted by using fourier transform infra-red (FTIR) analyzer. Lab testing on desulfurization has been done by using different concentration of DBT (100ppm and 1000ppm) at 10 minutes of extraction time. The efficiency of the removal process has been determined using high performance liquid chromatography (HPLC). From the result, [EpyESO4] shows high efficiency in remove aromatic sulfur compound (DBT) at low concentration of sulfur content. The percentage sulfur removal from the model oil for 100ppm and 1000ppm were, 97.68% and 26.68% respectively. By considering these results, [EpyESO4] might be used as promising solvents for the extractive desulfurization of diesel.

ABSTRAK

Sulfur adalah elemen yang paling banyak terdapat dalam minyak mentah. Kertas ini mengandung kajian mengenai nyahsulfur daripada model minyak melalui pengekstrakan oleh cecair ionik berasaskan Pyridinium. Objektif projek ini adalah untuk menentukan kecekapan penyingkiran komposisi sulfur, dibenzothiophene (DBT) oleh cecair ionik berasaskan Pyridinium, 1-ethylpyridinium ethylsulfate (EpyESO4) daripada minyak model. Dalam usaha untuk menentukan ciri-ciri cecair cecair ionik berasaskan Pyridinium, proses pencirian [EpyESO4] telah dijalankan dengan menggunakan penganalisis fourier transform infra-red (FTIR). Ujian makmal pada proses nyahsulfur telah dilakukan dengan menggunakan kepekatan DBT berbeza (100ppm dan 1000ppm) dengan tempoh pengakstrakan selama 10minit. Kecekapan proses penyingkiran telah ditentukan menggunakan High Performance Liquid Chromatography (HPLC). Berdasarkan keputusan yg diperoleh, [EpyESO4] menunjukkan kecekapan yang tinggi dalam menyingkirkan kompaun aromatik sulfur (DBT) pada kepekatan sulfur yang rendah. Peratusan penyingkiran sulfur daripada model minyak untuk 100ppm dan 1000ppm adalah, masing-masing 97,68% dan 26.68%. Dengan mengambil kira keputusan ini, [EpyESO4] boleh digunakan sebagai pelarut yang menjanjikan untuk desulfurization ekstraktif diesel.

TABLE OF CONTENTS

SUPERVISOR'S DECLARATION	IV
STUDENT'S DECLARATION	V
<i>Dedication</i>	VI
ACKNOWLEDGEMENT	VII
ABSTRACT.....	VIII
ABSTRAK.....	IX
TABLE OF CONTENTS.....	X
LIST OF FIGURES	XI
LIST OF TABLES.....	XII
LIST OF ABBREVIATIONS.....	XIII
LIST OF ABBREVIATIONS.....	XIV
1 INTRODUCTION	1
1.1 Background of Study	1
1.2 Problem Statement	2
1.3 Research Objective.....	2
1.4 Scope of Study	2
1.5 Significant of the Research	3
2 LITERATURE REVIEW	4
2.1 Introduction	4
2.2 Diesel Consumption	4
2.3 Sulfur.....	8
2.4 Effect of Sulfur in Diesel and Gasoline	10
2.4.1 Environment.....	10
2.4.2 Engine Performane	10
2.4.3 Human Health	11
2.4.4 Plant	11
2.4.5 Aquatic life's.....	11
2.5 Ionic Liquid.....	11
2.6 Application of Ionic Liquid.....	13
2.7 Other Method to Remove Sulfur.....	14
3 MATERIALS AND METHODS.....	15
3.1 Material and Apparatus	15
3.2 Preparation of Model Oil	16
3.3 Desulfurization Procedure.....	16
3.4 Preparation of Mobile Phase	18
3.5 Analytical Test	19
4 RESULT AND DISCUSSION	20
4.1 Characterization of Pyridinium-based Ionic Liquid.....	21
4.2 Influence of ILs to Model Oil Volume Ratio on Extractive Sulfur Content....	22
4.3 Influence of ILs to Model Oil Volume Ratio on the Percentage of Sulfur Content Remove	24
5 CONCLUSION.....	27
5.1 Conclusion	27
5.2 Future work	27
REFERENCES.....	28
APPENDICES	31

LIST OF FIGURES

Figure 2-1: Malaysia's Oil Production and Consumption from 1991-2010	5
Figure 2-2: 2004 U.S. Diesel Fuel Sales According to Sector	5
Figure 2-3: Trends in U.S. Diesel Fuel Sales 1999-2004	6
Figure 2-4: U.S. motor gasoline and diesel fuel consumption, 2000-2035	7
Figure 2-5: Diesel Consumption based on Top 5 Gold Producers	7
Figure 2-6: Chemical Formula for certain Compound	9
Figure 3-1: Standard Curve Graphs.....	16
Figure 3-2: The Desulfurization of Dibenzothiopene.	17
Figure 3-3: Preparation of Mobile Phase	18
Figure 4-1: Molecular Structure of 1-ethylpyridinium ethylsulfate	20
Figure 4-2: FTIR Absorbance Peak for 1-ethylpyridinium ethylsulfate	21
Figure 4-3: Influence of ILs to model oil ratio on sulfur content for 100ppm sulfur.....	22
Figure 4-4: Influence of ILs to model oil ratio on sulfur content for 1000ppm sulfur...	23
Figure 4-5: Influence of ILs to model oil ratio on percentage of removal sulfur for 100ppm sulphur.....	24
Figure 4-6: Influence of ILs to model oil ratio on percentage of removal sulfur for 1000ppm sulphur.....	25
Figure 4-7: Influence of Sulfur Concentration on Percentage of Sulfur Removal	26

LIST OF TABLES

Table 2-1: Properties table of Sulfur	9
Table 2-2: Application of ionic liquid	13
Table 3-1: Properties table of n-tetradecane	15
Table 3-2: Properties table of dibenzothiopene.....	15
Table 3-3: Calibration Data.....	16
Table 4-1: Efficiency of ILs to Model Oil Volume Ratio on Sulfur Content Removal for 100ppm	25
Table 4-2: Efficiency of ILs to Model Oil Volume Ratio on Sulfur Content Removal for 1000ppm	26

LIST OF ABBREVIATIONS

$C_{12}H_{23}$	Chemical Formula
$C_{10}H_{20}$	Chemical Formula
$C_{15}H_{28}$	Chemical Formula
COS	Carbonyl Sulphide
EpyESO4	1-ethylpyridinium ethylsulfate
H_2S	Hydrogen Sulphide
H_2SO_4	Sulphuric Acid
mm	millimeter
μm	micro meter
mL	milliliter
min	minute
ppm	Part per Million
SO_2	Sulfur Dioxide
SO_3	Sulfur Trioxide

LIST OF ABBREVIATIONS

DBT	Dibenzothiène
ILs	Ionic Liquids
MECA	Manufacture of Emission Controls Association
HDS	Hydrodesulfurization
FTIR	Fourier Transform Infrared
HPLC	High Performance Liquid Chromatograph
MBPD	million barrels per day
LPG	Liquefied Petroleum Gas
EIA	Energy Information Administration
IEA	International Energy Annual
AER	Annual Energy Review
US	United State
PM	Particulate Matter
TSILs	task-specific ionic liquids

1 INTRODUCTION

1.1 Background of Study

Sulfur is an abundant and non-metal element. Numerous organic sulfur compounds are found in coal and crude oil (Yoshikazu et al, 1994). Sulfur in crude oil is organically bound and mainly in the form of condensed thiophenes where up to 70% of the sulfur found in petroleum are dibenzothiophene (DBT) and substituted DBTs (Mohammad et. al, 2010). In recent year, great attention has been paid to the deep desulfurization of fuel due its negative impact to the environment (Hongshuai et. al, 2008). Takashi et. al. (1996) identified combustion of sulfur in unprocessed fossil fuels lead to serious environmental problem of acid rain. Besides, sulfur in gasoline inhibits the emission control performance of catalyst technology (MECA, 1998).

Desulfurization is the term for process of remove sulfur compound. One of the conventional methods that widely used in industry to remove sulfur is hydrodesulfurization (HDS). Yet, this process require high temperature and pressure condition, high energy costs, and was found has difficulty to remove aromatic heterocyclic sulfur compounds such as dibenzothiophene (DBT) and its derivatives. So, the others method were proposed such as adsorption, biodesulfurization and extraction. In this research, the sulfur removal method is focusing on extraction by ionic liquid.

Ionic liquid has been said as green solvent for the future because the ionic liquid process does not require strictly anhydrous conditions or an inert atmosphere to carry out the reaction. This makes the whole reaction sequence easier, cheaper, and less time consuming to perform. According to Martyn J. and Kenneth R. (2000) by choosing the correct ionic liquid, high product yields can be obtained, and a reduced amount of waste can be produced in a given reaction. Often the ionic liquid can be recycled, and this leads to a reduction of the costs of the processes. It must be emphasized that reactions in ionic liquids are not difficult to perform and usually require no special apparatus or methodologies. The reactions are often quicker and easier to carry out than in conventional organic solvents.

1.2 Problem Statement

Sulphur has been claimed as one of the component in crude oil and was found in both gasoline and diesel. When those fuels are burned, sulfur is emitted as sulfur dioxide (SO₂) or sulfate particulate matter. Particulate matter in open air can cause serious air pollution if there is no prevention. In addition, SO₂ in engine can affect on the vehicle emission. According to Miłosław K. and Jerzy M. (2005) in their research, about 98% sulfur contained in diesel fuel is oxidized in the combustion process to SO₂ which together with exhaust gas is released to the atmosphere where it can be subject to other reactions contributing to the creation of London-type smog and acid rains. Acid rain or acid precipitation is defined as rainfall with a pH lower than 5.6. Acid rain can cause such big impact to the environment, plant, aquatic life and human as well. Then, United States, Europe and some Asian countries limit sulfur emissions for on-road diesel to 500 parts per million (ppm). In less developed areas of the world the maximum sulfur ranges from 2000 ppm to above 5000 ppm. According to Katherine (2009) in Sweden, concentration of sulfur in diesel should be 10 ppm sulfur has been commercially available for several years.

1.3 Research Objectives

The main objective of this study is to remove sulfur compound (DBT) from model oil by study the aromatic compound of the sulfur and ionic liquid used in the extraction process.

1.4 Scope of Research

The following are the scope of this research:

- i) To characterized ionic liquid, ILs using Fourier Transform Infrared (FTIR) analyzer
- ii) To remove sulphur compound, DBT from model oil by extraction at volume ratio of 1:1, 1:2, 1:3 and 1:4.
- iii) To study the effect of pyridinium-based ionic liquid on the percentage of sulfur removed by using High Performance Liquid Chromatography (HPLC).

1.5 Significant and Rationale

There are several significant of this study:

- Lower operating cost.
 - ILs can be prepared without required any modern technology and it can done using common chemical solution.
 - The energy cost for sulfur removal is less compare conventional HDS since it does not required high condition of temperature and pressure.
- Effective.
 - ILs can remove sulfur and has high ability to extract aromatic compound.
 - Easy to conduct.
 - Less time for sulfur removal process.
- Environmental friendly.
 - . ILs can be re-use again by purified the ILs by rotary evaporation.

2 LITERATURE REVIEW

2.1 Introduction

Petroleum diesel fuel commonly has chemical formula of $C_{12}H_{23}$, ranging approximately from $C_{10}H_{20}$ to $C_{15}H_{28}$. Composed from 75% of saturated hydrocarbon (primarily paraffins including n, iso and cyclo) and 25% of aromatic hydrocarbons (including naphthalenes and alkylbenzenes). The first refined product was kerosene which has been discovered in Pennsylvania in 1859. The development of the internal combustion engine began in the late eighteenth century by Rudolf Diesel on 1892 came out with a patent for a compression ignition reciprocating engine which used coal dust as fuel but it was useless. Later on, he found that diesel (byproduct liquid petroleum) might be better engine fuels than coal dust. Once fuel change, his mechanical design also changes and succeeds with his prototype engine in 1895. Until now, both engine and fuel used his name.

The demand for transportation fuels has been increasing in most countries for the past three decades (Chunshan, 2003). The total world petroleum consumption increased from 49.42 million barrels per day (MBPD) in 1971 to 77.12MBPD in 2001, representing a 56% increase (EIA/IEA, 2002). The total US consumption of petroleum products reached 19.59MBPD in 2001, about 39% increase from 1971 (14.11 MBPD). Of the petroleum products consumed in US in 2001, 8.59MBPD was supplied as motor gasoline, 3.82MBPD as distillate fuels, including 2.56MBPD as high-way diesel fuels and 1.26MBPD as off-road fuels and industrial fuels, 1.65MBPD as jet fuel, 0.93MBPD as residual fuel oil, and 1.13MBPD as liquefied petroleum gas (LPG), and 3.47MBPD for other uses in the US (EIA/AER, 2001).

2.2 Diesel Consumption

At first, diesels were used to power ships, trains and industrial plants. The uses began to increase from year to year until nowadays, diesel are widely used for many sector all over the world such as transportation, manufacturing, construction, farming and power generation (John et. Al., 2007).

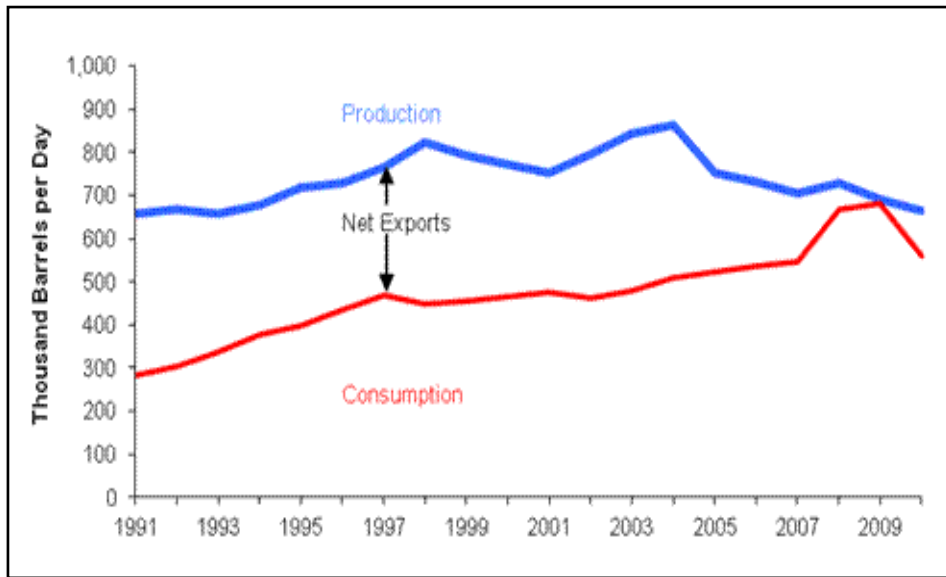


Figure 2-1: Malaysia’s Oil Production and Consumption from 1991-2010
(Source: EIA)

From figure 2-1 we can see that the trend of oil consumption, increase from year 1991 to 2009 and a little bit decline on 2010.

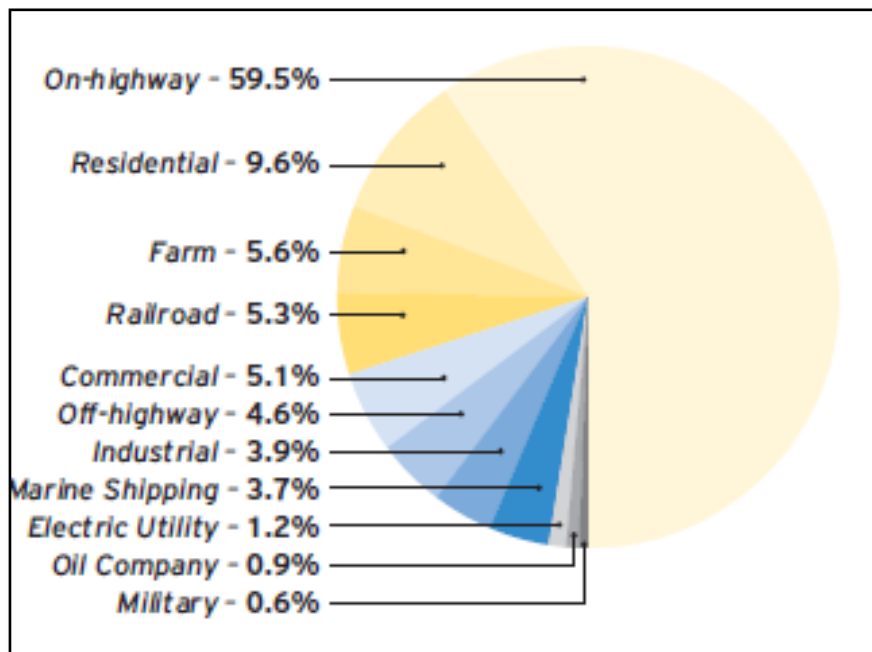


Figure 2-2: 2004 U.S. Diesel Fuel Sales According to Sector
(John et. Al, 2007)

Based on figure 2-2, on-highway transportation, primarily trucks, accounted for nearly 60 percent of the diesel fuel consumed in 2004 In the United States. Because diesel fuel is used to move goods from manufacturer to consumer, its sales are linked to the strength of the economy.

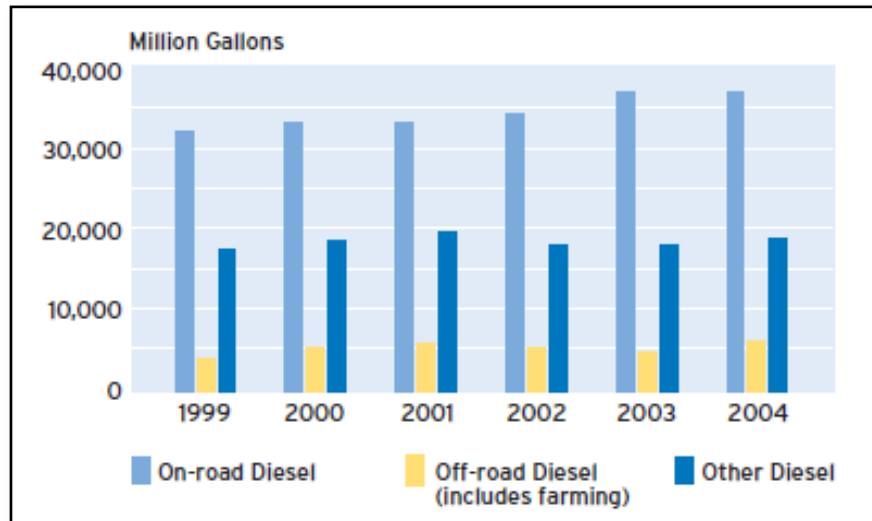


Figure 2-3: Trends in U.S. Diesel Fuel Sales 1999-2004
(Source: John et. al., 2007)

Figure 2-3 shows that sales of on-road diesel fuel in the U.S. raised from 32 billion gallons in 1999 to over 37 billion gallons in 2004, an increase of nearly three percent annually. By comparison, U.S. gasoline sales in 2003 were 136 billion gallons and jet fuel sales were 24 billion gallons. Most of the diesel fuel sold in the U.S. is refined in the U.S. Relatively small volumes are imported and exported in response to market conditions in coastal or border locations. The Energy Information Administration estimates that worldwide production of diesel fuel in 2002 was nearly 197 billion gallons.⁴ In Europe and Asia, where there is a significant population of diesel-powered automobiles the amount of diesel fuel produced exceeded the production of gasoline by just over 1.7 billion gallons.

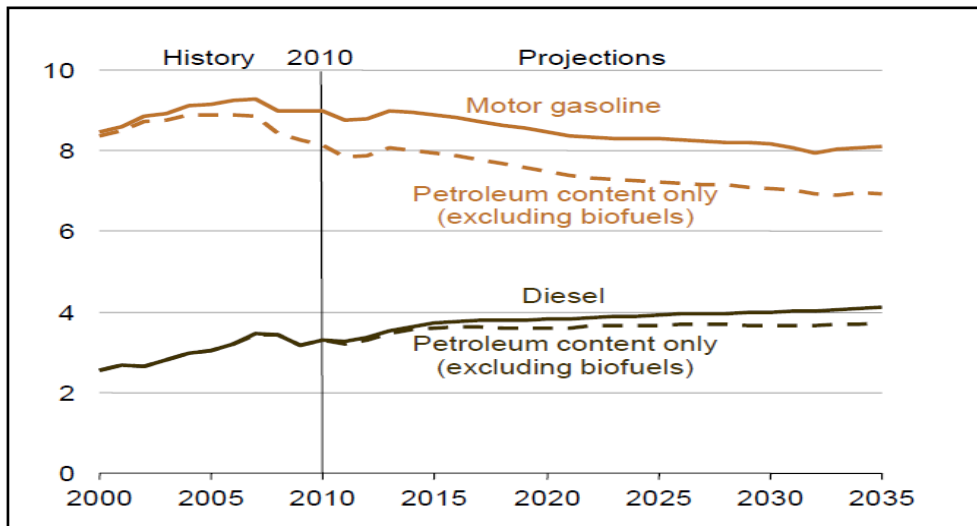


Figure 2-4: U.S. motor gasoline and diesel fuel consumption, 2000-2035 (MBPD)
(Source: EIA 2012)

From figure 2-4, we can observe that the consumption of diesel fuel in U.S. increases by approximately 0.8 million barrels per day from 2010 to 2035, while motor gasoline consumption falls by 0.9 million barrels per day.

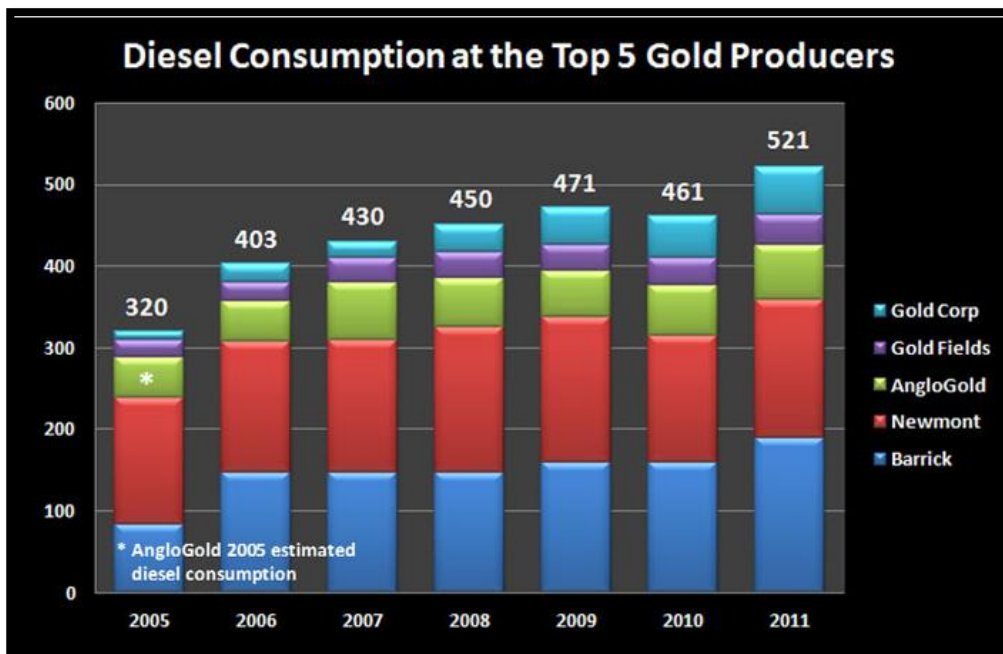


Figure 2-5: Diesel Consumption based on Top 5 Gold Producers
(Source: <http://www.silverbearcafe.com>)

Figure 2-5 shows the relationship between head grades and diesel consumption in these gold producers. Here we can see that the lower the head grade in the mining companies

reserves, the higher the amount of diesel is consumed. Newmont (shown in red in both charts) has the lowest head grade of the bunch, and it consumes the highest amount of diesel. On the other hand, Gold Fields (purple) has the highest average head grade and consumes the least amount of diesel. If we assume that GoldCorp's reserve head grade is similar to Newmonts, and it was producing the same amount of gold as Newmont, its overall diesel consumption would be more than twice of what it is currently.

According to their 2011 Annual Report, GoldCorp forecasts a 70% increase in gold production (1.75 million oz) in the next five years. If they are successful in bringing on this new production, it will increase in their diesel consumption from 58 million gallons in 2011, to nearly 100 million gallons by 2016. As ore grades decline more diesel is consumed in the mining process. Furthermore as open-pit mines age, it takes more energy (diesel) to extract the same or even less metal. In the past five years, the top 5 gold companies have increased their diesel consumption 72% per ounce of gold produced.

Based on the entire figure above, the consumption of diesel increases as time passes. It shows that if the diesel used contained a high amount of sulfur, the possibility of bad impact increases.

2.3 Sulfur

Sulfur is present in petroleum in a form of different compounds of which about 70% are made up by thiophene and its derivatives. The range of the sulfur is between 0.1 to 10% depending on a place of origin. (Miloslaw et. al, 2005). As the temperature of boiling point of individual fractions increases, the sulfur content in diesel fuel fraction increases.

Table 2-1: Properties table of Sulfur

Physical Properties	Description
Atomic number	16
Atomic Mass	32.06 g.mol ⁻¹
Density	2.07g.cm ⁻³ at 20°C
Melting Point	113°C
Boiling Point	445°C
Specific Gravity	2.07 at 70°F
Solubility in Water	Insoluble


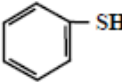
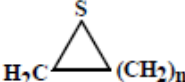
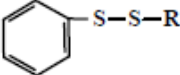
Compound	Chemical formula
Hydrogen sulphide	H ₂ S
Thiophen and its derivates	
Aliphatic mercaptans	RSH
Aromatic mercaptans	
Aliphatic sulphides	R-S-R
Cyclic sulphides	
Aliphatic disulphides	R-S-S-R
Aromatic disulphides	
Polysulphides	R-S _n -R

Figure 2-6: Chemical Formula for certain Compound

(Source: Miloslaw et. al., 2005)

Formation of hydrogen sulphide H_2S is only occur when the rich air-fuel mixture is burned, whereas carbonyl sulphide COS appears at the exhaust gas temperature higher than $700^\circ C$. Certain Part of SO_2 in the presence of oxygen contained in exhaust gas can be oxidized to SO_3 . The high exhaust gas temperature causes that SO_3 remains in its vapour state and easily combines with water formed during the combustion process.

In the exothermic reaction the aerosol of sulphuric acid is formed, which with the chemically bonded water makes up one of the components of the particulate emission (PM). Certain amount of SO_3 being formed during the combustion process combines also with hydrocarbons or metals forming sulphates (chemical compounds containing SO_4^{2-} group, are called sulphates, including sulphuric acid H_2SO_4). Metals can come from the products of abrasive wear of the engine elements, from lubricating oil, fuel (catalyst residue) or erosion of exhaust system. In general, forming the sulphates requires SO_2 present in exhaust gas to be oxidized to SO_3 . However, under normal conditions (lack of catalyst) such a process proceeds very slowly and as a result of that only approx. 1% of SO_2 is oxidized before leaving the engine exhaust system (Kozak, 2000).

2.4 Effect of Sulfur in Diesel and Gasoline

2.4.1 Environment

According to Patrick et al., (1990) sulfur oxide contributed to environmental pollution problem such as acid rain. Takashi et al., (1996) also claimed that environmental problem of acid rain was cause by the combustion of sulfur compound in unprocessed fossil fuels. More researchers also claimed that those sulfur emission release to the environment contribute to acid rain and air pollution. Mohammad et al., (2010) highlight in their research that sulfur dioxide emission trough fossil fuel combustion isa major contributor to the generation of acid rain and air pollution.

2.4.2 Engine Performance

Sulfur compound in fuel indicate corrosion to the parts of internal combustion engines due to the formation of oxyacid of sulfur from the product of combustion (Patrick et al., 1990). Thus, it will affect the performance of engine.

2.4.3 Human Health

Acid rain harms human through atmospheric and soil pollution. Acid rain causes formation of toxic compounds by reacting with naturally occurring chemical compounds. This toxic compound can be found in drinking water when the acid rain seeps into the soil and spreads to the source of drinking water and also the food chain. This contaminated food can damage nerves in children or result in severe brain damage and even worse can cause death. Scientists suspect that aluminium, one of the metals affected by acid rain, has a connection with Alzheimer's disease. The emissions of sulfur compounds cause serious human health and environmental concerns (Katherine et al, 2009). Sulfur dioxide can affect the breathing capacity of lungs and cause permanent damage to the lung.

2.4.4 Plant

When it rains, the water will absorb into the earth. The plant will be poisonous since it absorbs the toxic water from the soil which highly contains sulfur dioxide. This rain also dissolves the beneficial minerals and nutrients in the soil which are then washed away, before the plant has a chance of using them in order to grow. When there is frequent acid rain, it corrodes the waxy coating of the leaves. When the protective coating is lost, the plant will be easier to get diseased and can cause its death.

2.4.5 Aquatic life's

A high amount of sulfuric acid in the seawater will interfere with the ability of fish and other aquatic life to take nutrients, salt, and oxygen. Same as human, they need a balance amount of minerals and salts in their tissues. The molecules of acid result in mucus forming in their gills which prevents them from absorbing oxygen. Besides that, the acidity which results in reduced pH levels will cause an imbalance of salt in the tissues of fish body.

2.5 Ionic Liquids (ILs)

Ionic liquid is a liquid mainly consists of positively charged cation and a negatively charged anion. ILs is a class of ionic compounds in liquid state at room temperature. By having such great properties of thermal stability, negligible vapour pressure, miscibility, high conductivity and high capacity, ILs gave good perception among the

researcher for their research since it has wide range applications in industry and give such no environmental effect.

The cation's structural factors are important in determining the physiochemical properties of the ionic liquid. These factors include symmetry, polarity or charge density, cyclic and branched structures, and the functional tail groups where any of these factors can be changed either singularly or in conjunction with other changes to vary the properties of the ionic liquid. The ability to change various factors of the cation and the selection of various anions allows for the variability of ionic liquids causing them to be deemed task-specific ionic liquids (TSILs), since they can be tuned and varied to meet the application's needs.

Advantages of ionic liquid:

- Easy separation
- Liquid over wide range of temperature
- Very low pressure
- Non-flammable substance
- High thermally stable
- High mechanically stable
- Electrochemically stable
- Low toxicity
- Non-volatility

2.6 Application of Ionic Liquids (ILs)

Ionic liquids have many uses for industrial and research usages. Table 2-2 summarized applications of ionic liquid.

Table 2-2: Application of ionic liquid

application	description
Process technology	<ul style="list-style-type: none">• Deep desulfurization• Gas separation• Extractive distillation• Liquid-liquid extraction
Functional fluids	<ul style="list-style-type: none">• Hydraulics oil• Storage media for gases• Lubricants• Surfactant
Synthesis and catalyst	<ul style="list-style-type: none">• Enzyme reaction• Immobilization of catalyst• Nanoparticle synthesis• Solvent for organic reaction
Thermodynamic application	<ul style="list-style-type: none">• Thermal fluids• Phase changing material• Sorption cooling media
Electrochemical applications	<ul style="list-style-type: none">• Fuel cells• Metal deposition and metal finishing• Batteries• Dye sensitized solar cells• Sensor• Super capacitors
Analytics	<ul style="list-style-type: none">• Electrophoresis• Solvent for GC head space• Solvents for Karl-Fisher titration• Solvent for GC head space• Solvent for protein crystallization• Materials for GC column

2.7 Other Method to Remove Sulfur

- ❖ Hydrodesulfurization
 - Remove sulfur by convert organic sulfur in the feed to hydrogen sulfide in the presence of a transition metal catalyst and hydrogen (Mohammad et. al., 2010). This technique is high in cost and energy intensive since it required high hydrogen pressure and temperature for greater efficiencies sulfur removal but this technique is not effective at removing polycyclic sulfur compound (Rhee et. al., 1998).
- ❖ Oxidative desulfurization
- ❖ Bio-desulfurization
- ❖ adsorptive desulfurization
- ❖ ultra deep desulfurization

3 MATERIALS AND METHODS

3.1 Material and Apparatus

The model oil used for this experiment is n-tetradecane since carbon chain of model oil should be enough to be like as a diesel and the sulfur representative is dibenzothiophene (DBT). All of the materials are provided by Chemical Engineering Laboratory of University Malaysia Pahang. The main equipments for this experiment are Fourier Transform Infrared Spectroscopy (FTIR) and High Performance Liquid Chromatography (HPLC).

Table 3-1: Properties table of n-tetradecane

Physical Properties	Description
Molecular Formula	$C_{14}H_{30}$
Molar Mass	$198.39 \text{ g.mol}^{-1}$
Density	0.767 g.cm^{-3}
Melting Point	42.6°F
Boiling Point	488.7°F at 760mmHg
Specific Gravity	0.7628 at 68°F
Solubility in Water	Insoluble

Table 3-2: Properties table of dibenzothiophene

Physical Properties	Description
Molecular Formula	$C_{12}H_8S$
Molar Mass	$184.26 \text{ g.mol}^{-1}$
Density	1.252 g.cm^{-3}
Melting Point	$97\text{-}100^{\circ}\text{C}$
Boiling Point	332°C
Solubility in Water	Insoluble

3.2 Preparation of Model Oil

Model oil was prepared by dissolved 402mg of Dibenzothiopene (DBT) in 70mL n-tetradecane to form 1000ppm sulfur content in the model oil. Then it was diluted to 750ppm, 500ppm, 400ppm, 300ppm, 200ppm and 100ppm. The entire sample has been analyzed for calibration standard of this research and calibration data was summarized in table 3-3.

Table 3-3: Calibration Data

Concentration (ppm)	Area (mAU*s)
100	6305.6
200	12914.2
300	19008.0
400	24500.1
500	28689.0
750	37122.8
1000	41814.8

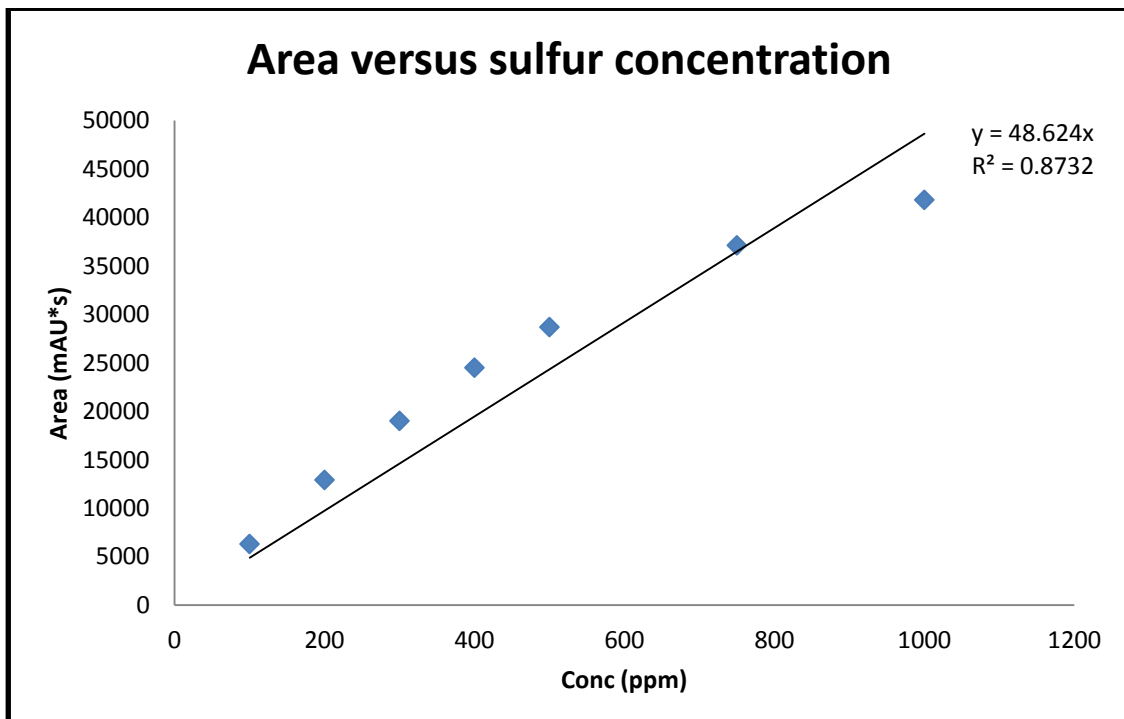


Figure 3-1: Standard Curve Graphs

3.3 Desulfurization Procedure

All the extractive desulfurization experiment was conducted by using model oil with 1000ppm, and 100ppm of sulfur because limited amount of ionic liquid. The volume ratios of ionic liquids (ILs) to the model oil are 1:1, 1:2, 1:3 and 1:4. The ionic liquid was added to the model oil and stirred for 10 minutes to reach thermodynamic equilibrium, and then allowed to settle for 5 minutes to obtain phase splitting and settling. This procedure has been done in the fume hood because model oil used is easy to vaporize at room temperature.

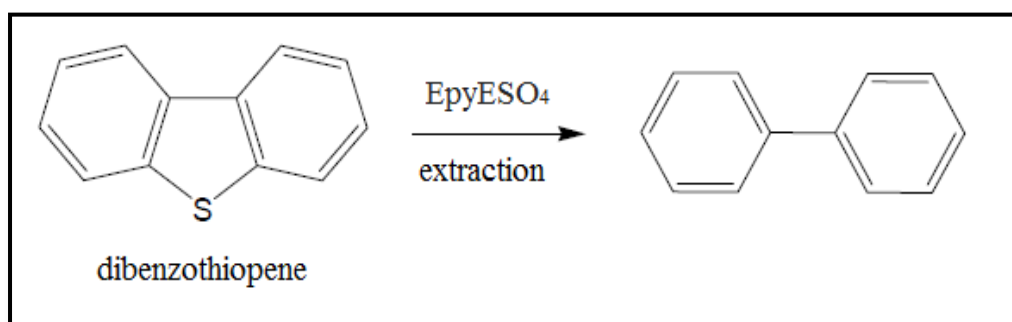


Figure 3-2: The Desulfurization of Dibenzothiophene.

(Source: Diego et. al., 2010)

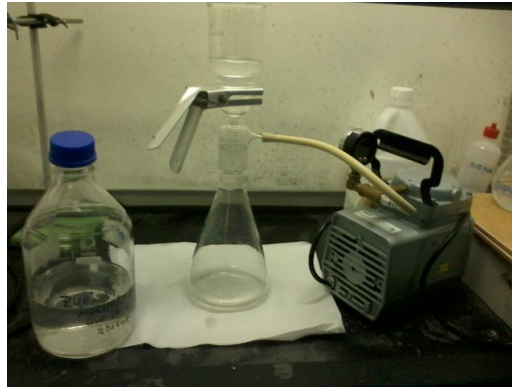
3.4 Preparation of Mobile Phase

Mobile phase is required for analytical test of sample. Figure 3-3 describe the preparation process of model oil.

Firstly, 900mL of methanol HPLC grade was added to 100mL of ultra pure water.



The mobile phase solution is then filtered using membrane filter (size: 4.0microns) by pumping it using a vacuum pump.



Lastly, the mobile phase is de-gas using sonicator to remove bubble.



Figure 3-3: Preparation of Model oil Process

3.5 Analytical Test

HPLC was used for the quantitative assay of DBT in the model oil phase. HPLC was performed on a Agilent 1200 (HP1200, Agilent, USA) liquid chromatograph equipped with an autosampler, a Zorbax Eclipse Plus C18 column (4.6 mm × 250 mm; 5.0 μm), and a diode array detector. The mobile phase was 90% methanol in 10% of ultra pure water (v/v, %) with a flow rate of 1.0 mL/min. For the quantification DBT, the external standard method was used at 280 nm with the time set 10 minutes for each sample.

4 RESULT AND DISCUSSION

4.1 Characterization of Pyridinium-based Ionic Liquid

In this research, FTIR analysis was used to determine the functional group of ionic liquid, 1-ethylpyridinium ethylsulfate in order to characterize it. FTIR analysis is a success analysis technique that provides information about the chemical bonding or molecular structure of a ionic liquid use for sulfur extraction in this research. Figure 4-2 shows the absorbance peak for 1-ethylpyridinium ethylsulfate. From figure 4-2, the spectrum reveals the occurrence of interaction between the characteristic groups of 1-ethylpyridinium and ethylsulfate. The characteristic IR absorption bands for ethylsulfate are at the five first peaks where the wavelengths are 1488.79 cm^{-1} , 1225.91 cm^{-1} , 1174.13 cm^{-1} , 1060.48 cm^{-1} and 1017.30 cm^{-1} . The alkanes group C-H₂ bend and C-H₃ bend indicates the peak with wavelength of 1488.79 cm^{-1} and 1225.91 cm^{-1} . The S=O stretch and S-O stretch indicates the peak with wavelength of 1174.13 cm^{-1} and 1060.48 cm^{-1} respectively. The wavelength of 1017.30 cm^{-1} is representing the C-O stretch of anhydride in the chemical bonding of ethylsulfate. The peak region between 619.62 cm^{-1} and 914.45 cm^{-1} is the fingerprint region and indicative of aromatic functional groups consist of C-H bend, C=C stretch and heterocyclic amine that characterize the 1-ethylpyridinium.

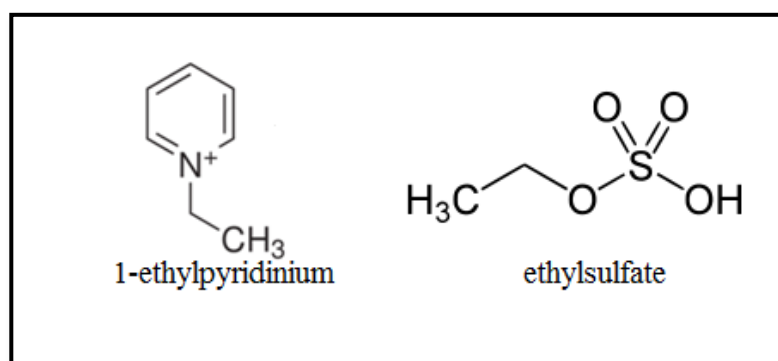


Figure 4-1: Molecular Structure of 1-ethylpyridinium ethylsulfate

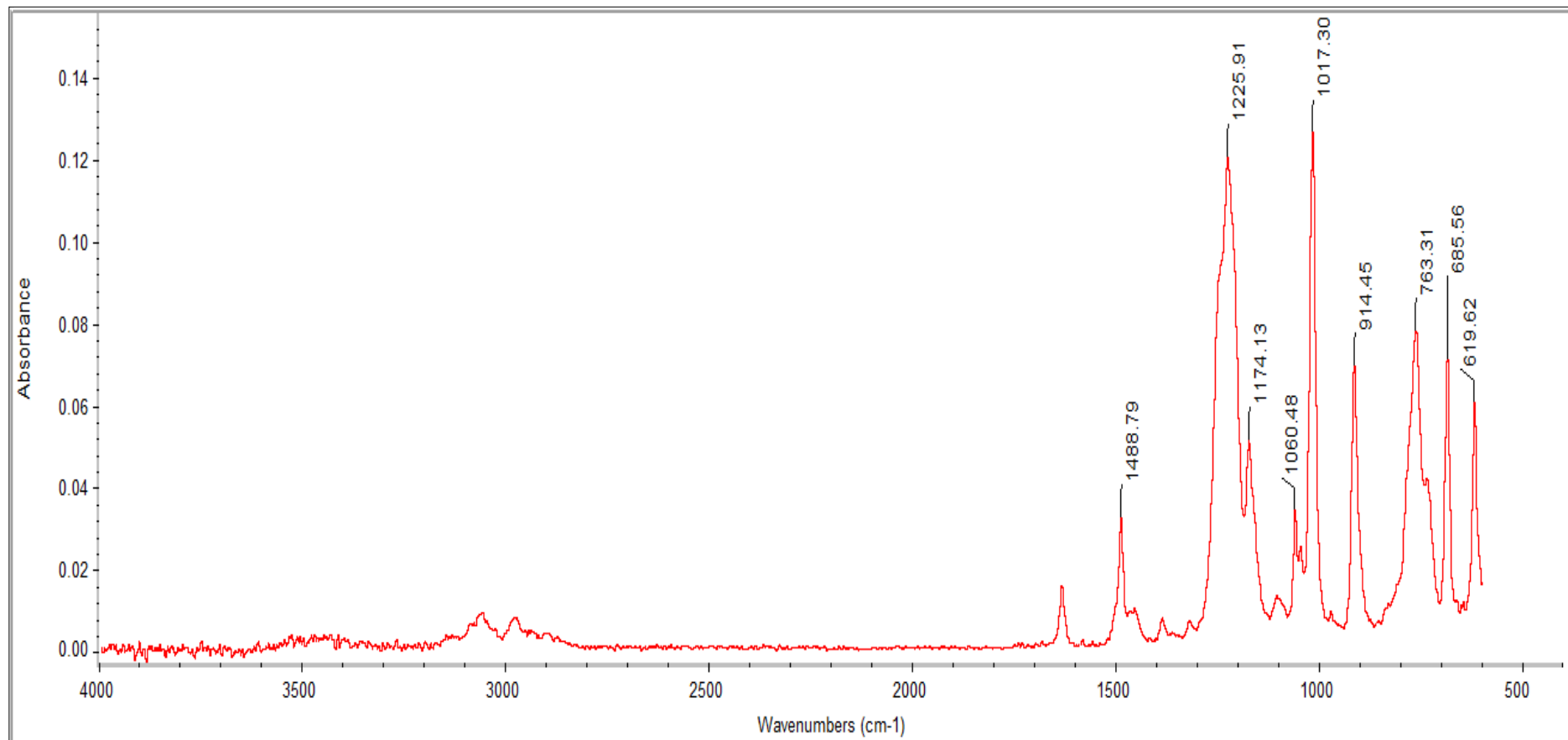


Figure 4-2: FTIR Absorbance Peak for 1-ethylpyridinium ethylsulfate

4.2 Influence of ILs to Model Oil Volume Ratio on Extractive Sulfur Content

To investigate the effect of volume ratio of ILs to model oil on the extraction of sulfur content, the extraction of sulfur compounds (DBT) in n-tetradecane by 1-ethylpyridinium ethylsulfate ionic liquid under various volume ratio of ILs to model oil, experiment was carried out at room temperature. This is because, ionic liquid is in liquid state at room temperature due to its unique properties. Figure 4-3 and 4-4 shows influence of ILs to model oil ratio on sulfur content for 100 ppm and 1000 ppm sulfur. It also shows at once that then volume ratio of ILs to model oil has strong influence on the sulfur content after extraction using ILs.

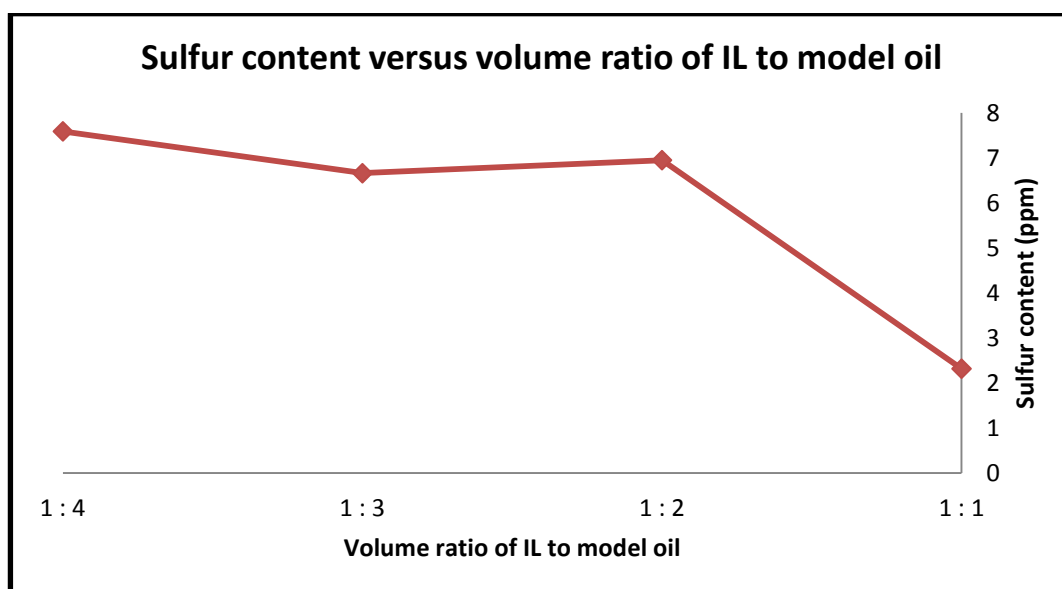


Figure 4-3: Influence of ILs to model oil ratio on sulfur content for 100ppm sulfur

Based on figure 4-3, the sulfur content in the model oil reduces as the volume ratio goes to 1:1. As in early experiment, the sulfur content is 100ppm. When the model oil is extract with ILs to model oil volume ratio of 1:4, 1:3, 1:2 and 1:1, the sulfur content were reduced to 7.59ppm, 6.66ppm, 6.95ppm and 2.32ppm respectively. From the past research on extraction of sulfur compound by using ILs, the graph produced should be directly proportional but, in this experiment, data collected shows some error on the volume ratio of 1:2. This may be due to error while conducting the experiment. However, the results shown still satisfy for this research.

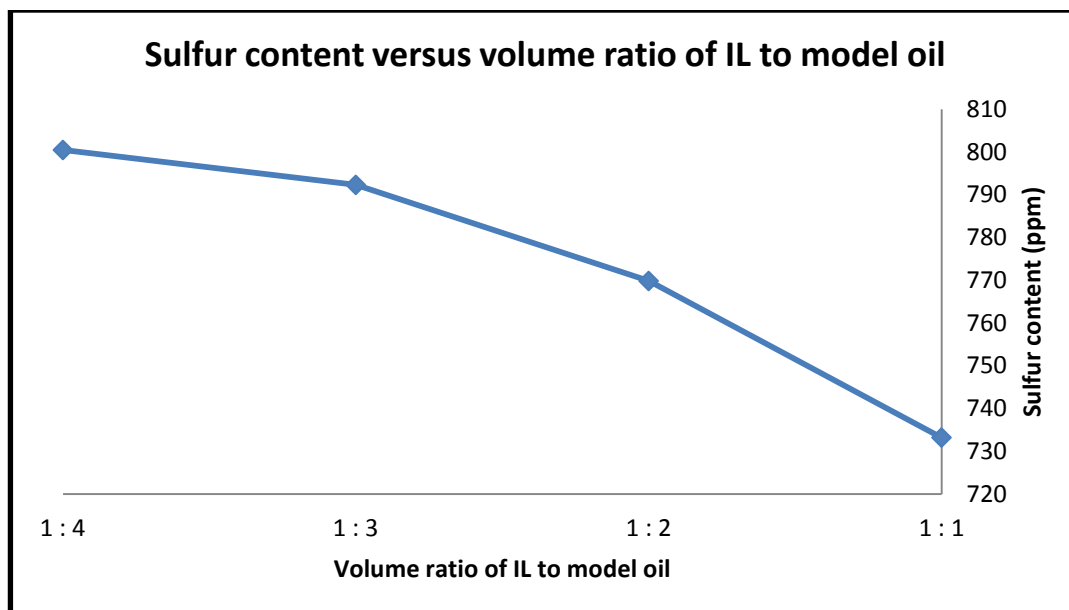


Figure 4-4: Influence of ILs to model oil ratio on sulfur content for 1000ppm sulfur

Figure 4-4 also shows the same trend as figure 4.3 where as the volume ratio up to 1:1, the sulfur content remove shows the lowest sulfur content compare to 1:2, 1:3 and 1:4 volume ratio of ILs to model oil. This mechanism for the extraction of sulfur compound with 1-ethylpyridinium ethylsulfate can be understand as the interaction of π - π between aromatic sulfur compound of DBT and the pyridinium rings of 1-ethylpyridinium ethylsulfate. This is due to the effect of cation and anion interaction of ionic liquid to the DBT. These result has been confirm by the Hollbrey (2003) in his research, which indicate the same reason of π - π interaction between ILs and sulfur compound. As calculated by Otsuki et al., the electron density for sulfur atom in DBT is 5.758 and prove that 1-ethylpyridinium ethylsulfate is highly polarizable aromatic π –electron in extract aromatic sulfur compound of DBT which has higher density of aromatic π -electron.

4.3 Influence of ILs to Model Oil Volume Ratio on the Percentage of Sulfur Content Remove

Based on the figure 4-3 and 4-4, percentage of sulfur removal can be obtained and illustrated in figure 4-5 and figure 4-6. Figure 4-5 shows influence of ILs to model oil ratio on percentage of removal sulfur for 100ppm sulfur and figure 4-6 shows influence of ILs to model oil ratio on percentage of removal sulfur for 1000ppm sulfur.

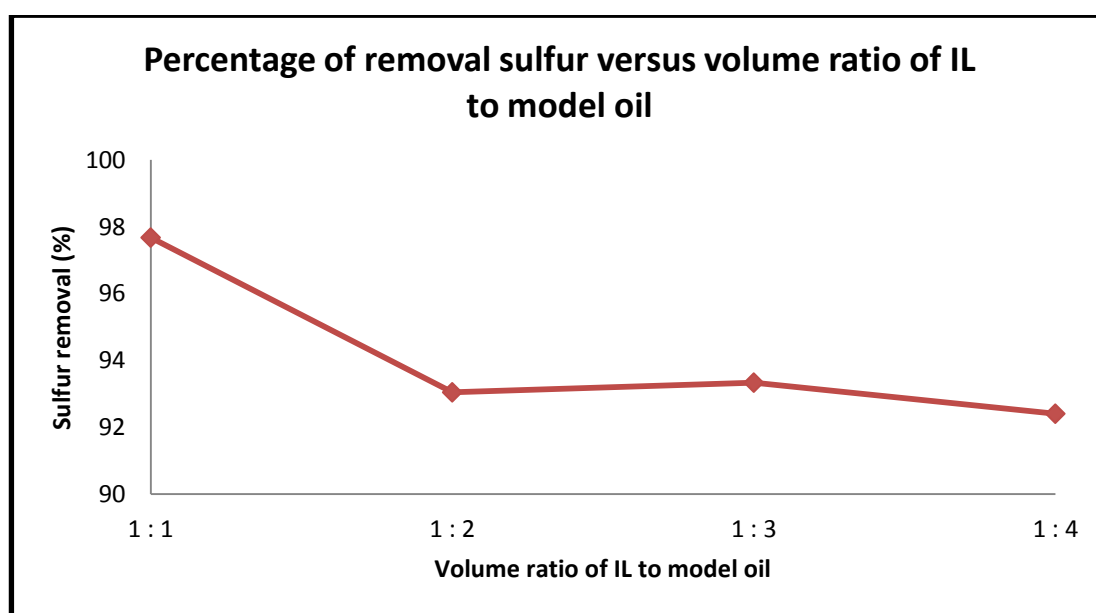


Figure 4-5: Influence of ILs to model oil ratio on percentage of removal sulfur for 100ppm sulphur

From calculation, percentage of sulfur removal shows the performance of 1-ethylpyridinium ethylsulfate is quite good for commercial desulfurization process. Figure 4-5 shows the relation between volume ratio of ILs and model oil and the percentage of sulfur removal is directly proportional. The efficiency of ILs to model oil ratio for 100ppm was concluded as in table 4-1.

Table 4-1: Efficiency of ILs to Model Oil Volume Ratio on Sulfur Content Removal For 100 ppm

ILs to model oil ratio	Sulfur removal (%)
1:1	97.68
1:2	93.05
1:3	93.34
1:4	92.41

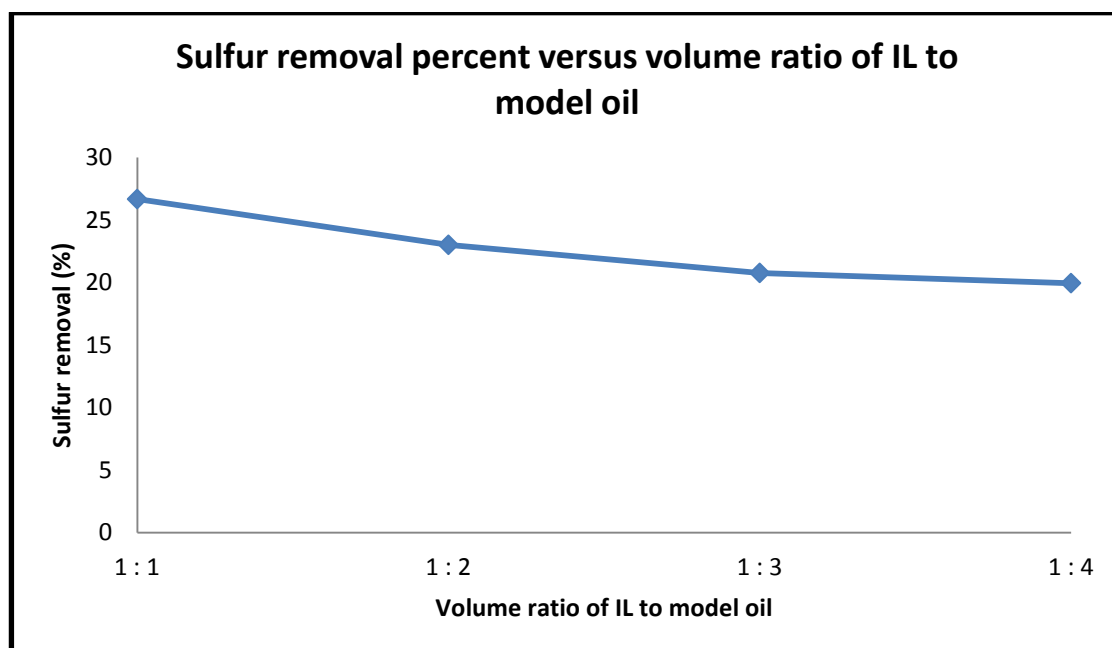


Figure 4-6: Influence of ILs to Model Oil Ratio on the Percentage of Removal Sulfur For 1000ppm Sulfur

Based on figure 4-6, the relation between ILs to model oil volume ratio also is seen as directly proportional. Percentage different between one to the other of ILs to model oil ratio is seen not slightly different where it contribute 1 to 7 % percentage different. The efficiency of ILs to model oil ratio for 1000ppm was concluded as in table 4-2.

Table 4-2: Efficiency of ILs to Model Oil Volume Ratio on Sulfur Content Removal for 1000ppm

ILs to model oil ratio	Sulfur removal (%)
1:1	26.68
1:2	23.02
1:3	20.77
1:4	19.95

Study on different concentration of sulfur content on the percentage of sulfur removal efficiency has been determined in figure 4-7 where it shows comparison on the efficiency of sulfur removal between 100ppm and 1000ppm.

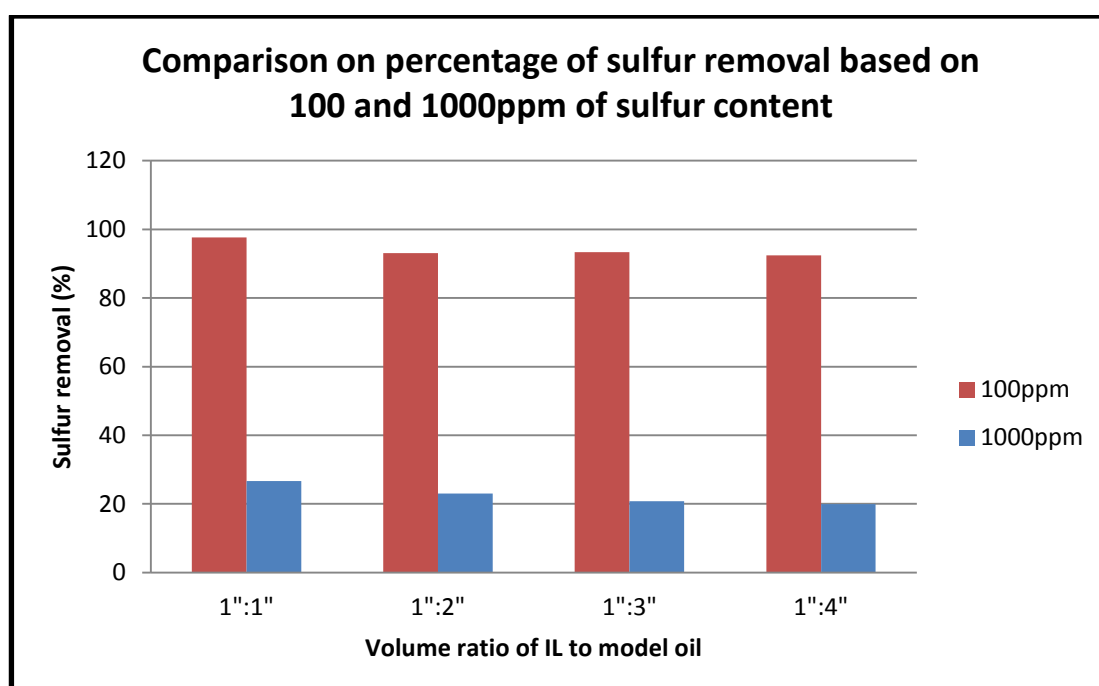


Figure 4-7: Influence of Sulfur Concentration on Percentage of Sulfur Removal

From Figure 4-7, it shows that 1-ethylpyridinium ethylsulfate has high efficiency to remove sulfur at lower concentration of sulfur where in this experiment, lower concentration of sulfur which is 100ppm used and higher concentration, 1000ppm of sulfur. Although the percentage for 1000ppm sulfur removal is not as good as 100ppm, but 1-ethylpyridinium ethylsulfate still can be seen as high potential material that can be used to remove sulfur in oil industry.

5 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Ionic liquid has been seen as one potential method to remove sulfur compound. From this research, ionic liquid used in this research is successfully characterized by using FTIR. Through the experiment, 1-ethylpyridinium ethylsulfate ionic liquid was found to be effective ionic liquid for the selective removal of aromatic heterocyclic sulfur compound from diesel at room temperature. The results shows different volume ratio of ILs to the model is able to remove sulfur compound in the relation of directly proportional. 1:1 volume ratio of ILs to model oil shows the higher efficiency of removal sulfur using 1-ethylpyridinium ethylsulfate ionic liquid where it can remove 97.68% of sulfur content from 100ppm sulfur and 26.68% of sulfur content from 1000ppm sulfur. By considering these results, [EpyESO4] might be used as promising solvents for the extractive desulfurization of diesel.

5.2 Recommendation

In this research, there are many recommendation can be suggested. In order to obtain such a good results in the near future, first is regarding to the right selection of ionic liquid to be used for extraction. In the future, the ionic liquid potential can be renew by doing such a good research on the properties of the ionic liquid to be used which is suitable to the sulfur compound that should be extract. The effectiveness of the ionic liquid also can be improved by increase a little bit the extraction time in order to ensure sulfur is highly extracted from the oil. On industrial point of view, this extraction process should be done in continuous process since extraction is a batch process. By able to run in continuous process will be great opportunity of using ionic liquid as medium for desulfurization in refineries industry.

REFERENCES

- Mohammad, R. A., Ayeh, A., Behnam, R., Fatemah, Y., Behrouz, Z., Mohammad, Z., and Hasein, N. (2010). Biodesulfurization of Dibenzothiophene by a Newly Isolated, *Stenotrophomonas maltophilia* Strain Khol. *World Applied Science Journal* 10 (3): 272-278.
- Takashi O., Teruki H., Ichiro H., and Yoshikazu I. (1996). Characterization of Dibenzothiophene Desulfurization Reaction by Whole Cells of *Rhodococcus Erythropolis H-2* In The Presence Of Hydrocarbon. *Journal of Fermentation and Bioengineering* Vol. 82, No. 6, 610-612.
- SRS Rocco (n.d.). Huge Downward Revision of Shale Gas Reserves: Its Impact on Gold and Silver. Retrieved from <http://www.silverbearcafe.com/private/09.12/shalegas.html>.
- John B., John F., Andy G., Lew G., Greg H., Kent H., Jerry H., Michael I., Larry J., David K., David L., Jim M., Manuch N., Eric O., Roger O., Bill S., Mark S., Andrea T., Chuck W., John L., Jacqueline J., Deborah S., and Jennifer M. (2007). Diesel Fuels Technical Review. Chevron Corporation.
- Patrick S. T., James R. Kittrell, and John W. Eldridge (1990). Desulfurization of Fuel Oil by Oxidation and Extraction. Enhancement of Extraction Oil Yield. *Ind. Eng. Chem. Res.* 1990,29, 321-324
- Hongshuai G., Mingfang L., Jianmin X., Yong W., Yuguang L., Wangliang L., Qingfen L., and Huizhou L., (2008). Desulfurization of Fuel by Extraction with Pyridinium-Based Ionic Liquids. *Ind. Eng. Chem. Res.* 2008, 47, 8384–8388
- Wang J. L., Zhao D. S., Zhou E. P., and Dong Z. (2007). Desulfurization of gasoline by extraction with *N*-alkyl-pyridinium-based ionic liquids. *J Fuel Chem Technol*, 2007, 35(3), 293–296

- Chunshan Song (2003). An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel Catalysis.
- Manufacturers of Emission Controls Association (1998). The Impact of Gasoline Fuel Sulfur on Catalytic Emission Control Systems.
- Diego P. M., Alexander S. T., and Steven C. F. (2010). Desulfurization of Dibenzothiophene and Oxidized Dibenzothiophene Ring Systems
- Jinlin X., Tony E. G, and, Alan C. H. (1998). Effect of biodiesel on engine performances and emissions
- J. Neil Capea, David F., and Alan D. (2003). Ecological effects of sulfur dioxide, fluorides, and minor air pollutants: recent trends and research needs. *Environment International* 29 (2003) 201– 211
- D. W. Schindler (2005). Effect of acid rain on freshwater ecosystem.
- Katherine O. B., Michael P. W., and Charlotte P. (2009). Low-Sulfur Gasoline & Diesel: The Key To Lower Vehicle Emissions
- Yoshikazu I., Takashi O., Hiroshi O., Yoshimitsu H., and Masayuki S. (1994). Selective Desulfurization Of Dibenzothiophene By *Rhodococcus Erythropolis* D-1. *Applied and Environmental Microbiology*, Jan. 1994, P. 223-226
- Holbrey J. D., Reichert W. M., Nieuwenhuryzen M., Sheppard O., Hardocre C., and Rogers R. D. Liquid Clathrate Formation in Ionic Liquid-Aromatic Mixtures. *Chem. Commun.* **2003**, 4, 476.
- Manufacture of Emission Controls Association, MECA (1998). The Impact of Gasoline Fuel Sulfur on Catalytic Emission Control Systems.
- EIA/AER, Annual Energy Review 2001, Energy Information Administration, US Department of Energy, Washington, DC, 2002.

EIA/IEA, International Energy Annual 2001, Energy Information Administration,
US Department of Energy, Washington, DC, 2002.

Rhee S.K., J.H. Chang, Y.K. Chang and H.N. Chang (1998). Desulfurization of
Dibenzothopene and Diesel Oil by a Newly Isolated Gordona Strain, CYKSI.
Applied and Environmental Microbiol., 154 : 2169-2183.

APPENDICES

Appendix A: Calculation on dilution

$$\begin{aligned} \text{Ppm} &= \frac{\text{mass of solute (g)}}{\text{Mass of solute \& solvent (g)}} \\ &= \frac{1\text{mg}}{\text{L}} \end{aligned}$$

Molecular weight (g/mol)	
DBT	184.26
Sulphur	32.065

$$\begin{aligned} \frac{1000\text{ppm } S}{x \text{ DBT}} &= \frac{32.065 \text{ g/mol}}{184.26 \text{ g/mol}} \\ x &= 5746.45 \text{ ppm DBT} \end{aligned}$$

$$\begin{aligned} \frac{750\text{ppm } S}{x \text{ DBT}} &= \frac{32.065 \text{ g/mol}}{184.26 \text{ g/mol}} \\ x &= 4309.84 \text{ ppm DBT} \end{aligned}$$

$$\begin{aligned} \frac{500\text{ppm } S}{x \text{ DBT}} &= \frac{32.065 \text{ g/mol}}{184.26 \text{ g/mol}} \\ x &= 2873.23 \text{ ppm DBT} \end{aligned}$$

$$\begin{aligned} \frac{400\text{ppm } S}{x \text{ DBT}} &= \frac{32.065 \text{ g/mol}}{184.26 \text{ g/mol}} \\ x &= 2298.58 \text{ ppm DBT} \end{aligned}$$

$$\begin{aligned} \frac{300\text{ppm } S}{x \text{ DBT}} &= \frac{32.065 \text{ g/mol}}{184.26 \text{ g/mol}} \\ x &= 1723.94 \text{ ppm DBT} \end{aligned}$$

$$\begin{aligned} \frac{200\text{ppm } S}{x \text{ DBT}} &= \frac{32.065 \text{ g/mol}}{184.26 \text{ g/mol}} \\ x &= 1149.29 \text{ ppm DBT} \end{aligned}$$

$$\begin{aligned} \frac{100\text{ppm } S}{x \text{ DBT}} &= \frac{32.065 \text{ g/mol}}{184.26 \text{ g/mol}} \\ x &= 574.65 \text{ ppm DBT} \end{aligned}$$

Sulphur (ppm)	DBT (ppm)
1000	5746.45
750	4309.84
500	2873.23
400	2298.58
300	1723.94
200	1149.29
100	574.65

Dilution formula,

$$M_1V_1 = M_2V_2$$

Where,

M_1 = initial concentration

M_2 = final concentration

V_1 = initial volume

V_2 = final volume

$$5746.45 \text{ ppm} = \frac{\text{DBT mg}}{0.07\text{L model oil}}$$

$$\begin{aligned} \text{DBT} &= 402.2515 \text{ mg} \\ &= 0.40225 \text{ g} \end{aligned}$$

Calculation to dilute 5746.45ppm to 4309.84ppm

$$M_1V_1 = M_2V_2$$

$$(5746.45\text{ppm})(0.015\text{L}) = (4309.84\text{ppm})V_2$$

$$V_2 = 0.0199\text{L}$$

$$= 19.9\text{ml}$$

Calculation to dilute 5746.45ppm to 2873.23ppm

$$M_1V_1 = M_2V_2$$

$$(5746.45\text{ppm})(0.01\text{L}) = (2873.23\text{ppm})V_2$$

$$V_2 = 0.0199\text{L}$$

$$= 19.9\text{ml}$$

Calculation to dilute 5746.45ppm to 2298.58ppm

$$M_1V_1 = M_2V_2$$

$$(5746.45\text{ppm})(0.008\text{L}) = (2298.58\text{ppm})V_2$$

$$V_2 = 0.02\text{L}$$

$$= 20\text{ml}$$

Calculation to dilute 5746.45ppm to 1723.94ppm

$$M_1V_1 = M_2V_2$$

$$(5746.45\text{ppm})(0.006\text{L}) = (1723.94\text{ppm})V_2$$

$$V_2 = 0.0199\text{L}$$

$$= 19.9\text{ml}$$

Calculation to dilute 5746.45ppm to 1149.29ppm

$$M_1V_1 = M_2V_2$$

$$(5746.45\text{ppm})(0.004\text{L}) = (1149.29\text{ppm})V_2$$

$$V_2 = 0.02\text{L}$$

$$= 20\text{ml}$$

Calculation to dilute 5746.45ppm to 574.65ppm

$$M_1V_1 = M_2V_2$$

$$(5746.45\text{ppm})(0.002\text{L}) = (574.65\text{ppm})V_2$$

$$V_2 = 0.0199\text{L}$$

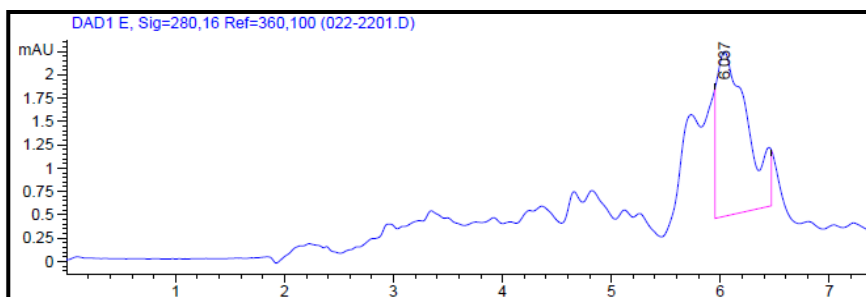
$$= 19.9\text{ml}$$



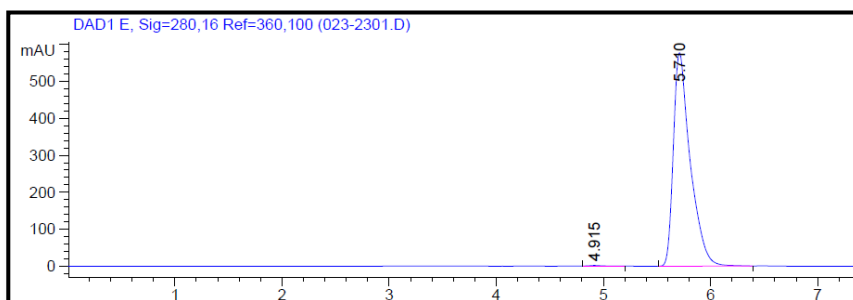
Appendix B Column Zorbax Eclipse Plus C18



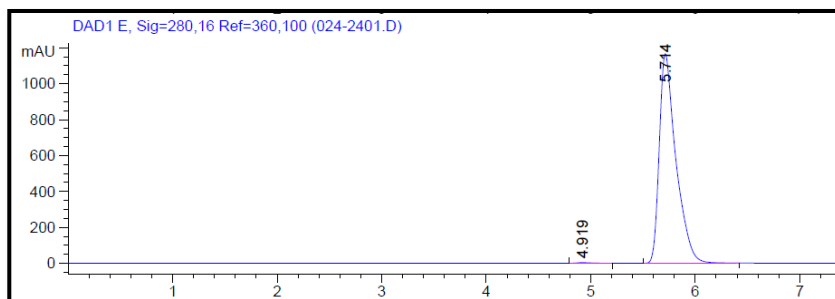
Appendix C HPLC Agilent 1200 Series



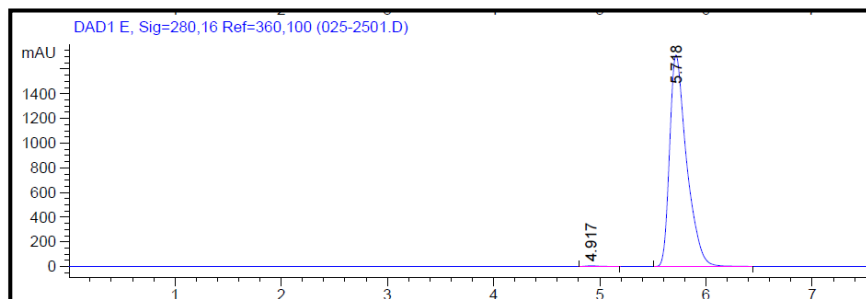
Appendix D Model Oil Sample without Sulfur Content



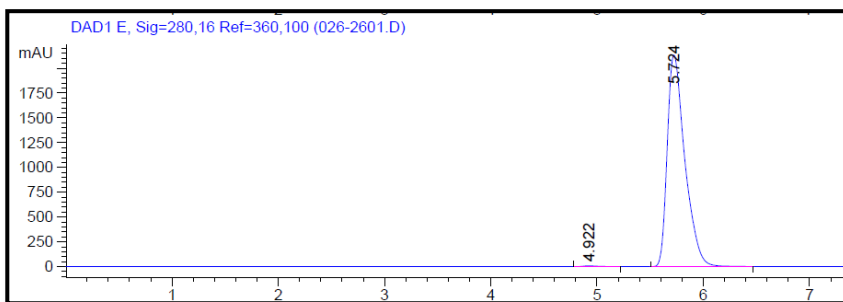
Appendix E Model Oil Sample with 100ppm Sulfur Content



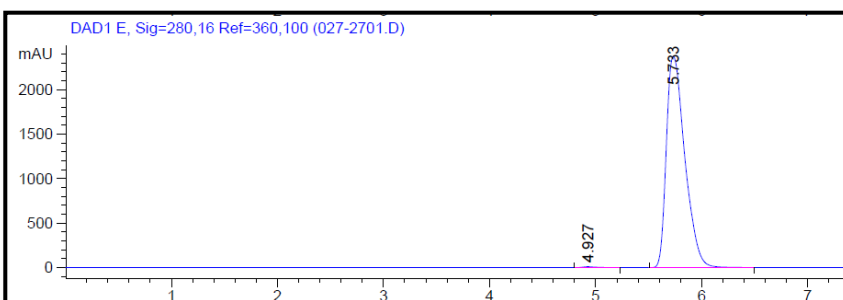
Appendix F Model Oil Sample With 200ppm Sulfur Content



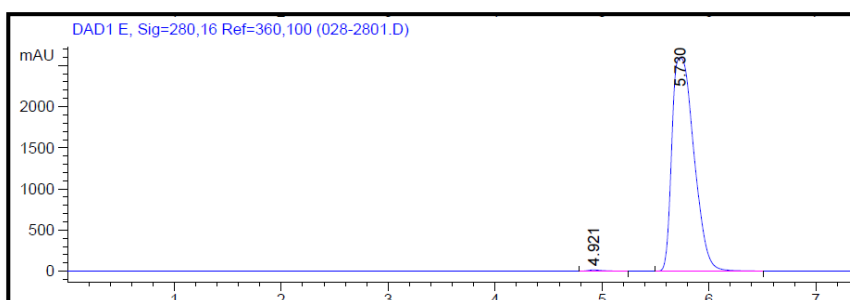
Appendix G Model Oil Sample With 300ppm Sulfur Content



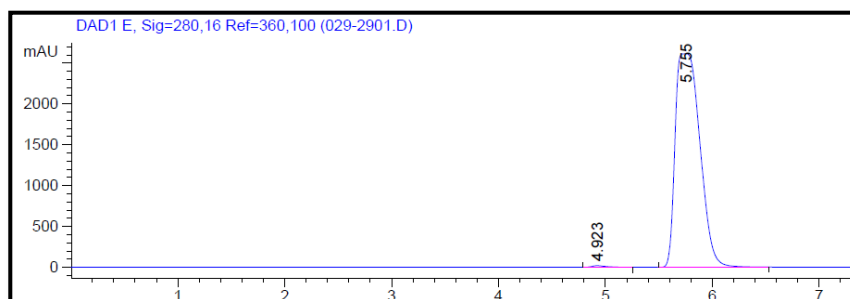
Appendix H Model Oil Sample With 400ppm Sulfur Content



Appendix I Model Oil Sample With 500ppm Sulfur Content



Appendix J Model Oil Sample With 750ppm Sulfur Content



Appendix K Model Oil Sample With 1000ppm Sulfur Content

Appendix L Calculation on Sulfur Content After Extraction

Step 1: find out the equation of calibration curve

Equation obtained from calibration curve,

$$y = 48.624x$$

$$y = mx$$

Where,

y = area under the graph (mAU*s)

m = gradient (48.624)

x = sulfur concentration (ppm)

Step 2: find area from HPLC analysis data sample

Volume ratio of ILs to model oil	Area (mAU*s)	
	For 100ppm	For 1000ppm
1:4	369.04352	3.89×10^4
1:3	323.84711	3.85×10^4
1:2	337.94052	3.74×10^4
1:1	112.82615	3.57×10^4

Step 3: calculate sulfur concentration after extraction using equation $y = 48.624x$

When $y = 369.04352$

$$369.04352 = 48.624x$$

$$x = 7.59\text{ppm}$$

Volume ratio of ILs to model oil	Sulfur concentration (ppm)	
	For 100ppm	For 1000ppm
1:4	7.59	800.471
1:3	6.66	792.308
1:2	6.95	769.836
1:1	2.32	733.224

Appendix M Calculation on Percentage of Sulfur Removal

$$\text{Sulfur removal (\%)} = \frac{(x_i - x_f)}{x_i} \times 100\%$$

Where,

x_i = Initial concentration of sulfur (ppm)

x_f = final concentration of sulfur (ppm)

Volume ratio of ILs to model oil	Sulfur removal (%)	
	For 100ppm	For 1000ppm
1:4	92.41	19.95
1:3	93.34	20.77
1:2	93.05	23.02
1:1	97.68	26.68

Appendix N

Desulfurization of Model Oil Using Pyridinium-based Ionic Liquid

Nurul Umaira Nisa binti Mazelan

Faculty of Chemical & Natural Engineering
Universiti Malaysia Pahang, Tun Razak Highway, 26300 Kuantan, Pahang, MALAYSIA.
*Correspondence: syamsul@ump.edu.my, Tel: 09-5492393

ABSTRACT: Sulfur is the most abundant element found in crude oil. This paper contains the study on desulfurization of model oil by extraction with Pyridinium-based ionic liquids. The objective of the project is to determine the sulfur compound, dibenzothiophene (DBT) removal efficiency of Pyridinium-based ionic liquids, 1-ethylpyridinium ethylsulfate (EpyESO4) from model oil. In order to characterize the Pyridinium-based ionic liquids, characterization process of EpyESO4 was conducted by using fourier transform infra-red (FTIR) analyzer. Lab testing on desulfurization has been done by using different DBT concentration (100ppm and 1000ppm) at 10 minutes of extraction time. The efficiency of the removal process has been determined using high performance liquid chromatography (HPLC). From the result, EpyESO4 shows high efficiency in remove aromatic sulfur compound (DBT) at low concentration of sulfur content. The percentage sulfur removal from the model oil for 100ppm and 1000ppm were, 97.68% and 26.68% respectively. By considering these results, EpyESO4 might be used as promising solvents for the extractive desulfurization of diesel.

Key words: Dibenzothiophene, Desulfurization, Model oil

1. INTRODUCTION

Sulfur is an abundant and non-metal element. Numerous organic sulfur compounds are found in coal and crude oil [1]. Sulfur in crude oil is organically bound and mainly in the form of condensed thiophenes where up to 70% of the sulfur found in petroleum are dibenzothiophene (DBT) and substituted DBTs [2]. In recent year, great attention has been paid to the deep desulfurization of fuel due its negative impact to the environment [3]. Combustion of sulfur in unprocessed fossil fuels lead to serious environmental problem of acid rain [4]. Besides, sulfur in gasoline inhibits the emission control performance of catalyst technology [5].

Desulfurization is the term for process of remove sulfur compound. One of the conventional methods that widely used in industry to remove sulfur is hydrodesulfurization (HDS). Yet, this process require high temperature and pressure condition, high energy costs, and was found has difficulty to remove aromatic heterocyclic sulfur compounds

such as dibenzothiophene (DBT) and its derivatives. So, the others method were proposed such as adsorption, biodesulfurization and extraction. In this research, the sulfur removal method is focusing on extraction by ionic liquid.

Ionic liquid has been said as green solvent for the future because the ionic liquid process does not require strictly anhydrous conditions or an inert atmosphere to carry out the reaction. This makes the whole reaction sequence easier, cheaper, and less time consuming to perform. By choosing the correct ionic liquid, high product yields can be obtained, and a reduced amount of waste can be produced in a given reaction [6]. Often the ionic liquid can be recycled, and this leads to a reduction of the costs of the processes. It must be emphasized that reactions in ionic liquids are not difficult to perform and usually require no special apparatus or methodologies. The reactions are often quicker and easier to carry out than in conventional organic solvents.

2. EXPERIMENTAL

2.1 Materials

The model oil used for this experiment is n-tetradecane since carbon chain of model oil should be enough to be like as a diesel and the sulfur representative is dibenzothiophene (DBT). All of the materials are provided by Chemical Engineering Laboratory of University Malaysia Pahang.

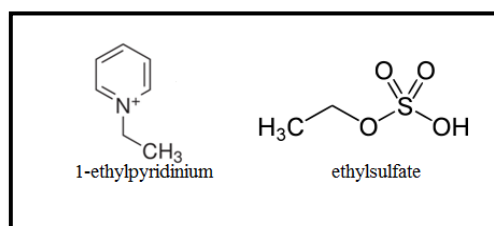


Fig.1. Molecular Structure of 1-ethylpyridinium ethylsulfate

2.2 Preparation of Model Oil

Model oil was prepared by dissolved 402mg of Dibenzothiophene (DBT) in 70mL n-tetradecane to form 1000ppm sulfur content in the model oil. Then it was diluted to 750ppm, 500ppm, 400ppm, 300ppm, 200ppm and 100ppm. The entire sample has been analyzed for calibration standard of this research.

2.3 Desulfurization Procedure

All the extractive desulfurization experiment was conducted by using model oil with 1000ppm, and 100ppm of sulfur because limited amount of ionic liquid. The volume ratios of ionic liquids (ILs) to the model oil are 1:1, 1:2, 1:3 and 1:4. The ionic liquid was added to the model oil and stirred for 10 minutes to reach thermodynamic equilibrium, and then allowed to settle for 5 minutes to obtain phase splitting and settling. This procedure has been done in the fume hood because model oil used is easy to vaporize at room temperature.

2.4 Analytical Test

HPLC was used for the quantitative assay of DBT in the model oil phase. HPLC was performed on a Agilent 1200 (HP1200, Agilent, USA) liquid chromatograph equipped with an autosampler, a Zorbax Eclipse Plus C18 column (4.6 mm × 250 mm; 5.0 μm), and a diode array detector. The mobile phase was 90% methanol in 10% of ultra pure water (v/v, %) with a flow rate of 1.0 mL/min. For the quantification DBT, the external standard method was used at 280

nm with the time set 10 minutes for each sample.

3. RESULT AND DISCUSSION

3.1 Characterization of Pyridinium-based Ionic Liquid

In this research, FTIR analysis was used to determine the functional group of ionic liquid, 1-ethylpyridinium ethylsulfate in order to characterize it. FTIR analysis is a success analysis technique that provides information about the chemical bonding or molecular structure of a ionic liquid use for sulfur extraction in this research. Fig. 2 shows the absorbance peak for 1-ethylpyridinium ethylsulfate. From fig. 2, the spectrum reveals the occurrence of interaction between the characteristic groups of 1-ethylpyridinium and ethylsulfate. The characteristic IR absorption bands for ethylsulfate are at the five first peaks where the wavelengths are 1488.79 cm⁻¹, 1225.91 cm⁻¹, 1174.13 cm⁻¹, 1060.48 cm⁻¹ and 1017.30 cm⁻¹. The alkanes group C-H₂ bend and C-H₃ bend indicates the peak with wavelength of 1488.79 cm⁻¹ and 1225.91 cm⁻¹. The S=O stretch and S-O stretch indicates the peak with wavelength of 1174.13 cm⁻¹ and 1060.48 cm⁻¹ respectively. The wavelength of 1017.30 cm⁻¹ is representing the C-O stretch of anhydride in the chemical bonding of ethylsulfate. The peak region between 619.62 cm⁻¹ and 914.45 cm⁻¹ is the fingerprint region and indicative of aromatic functional groups consist of C-H bend, C=C stretch and heterocyclic amine that characterize the 1-ethylpyridinium.

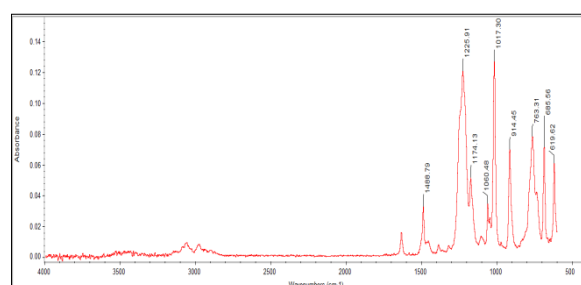


Fig. 2. FTIR Absorbance Peak for 1-ethylpyridinium ethylsulfate

3.2 Influence of ILs to Model Oil Volume Ratio on Extractive Sulfur Content

To investigate the effect of volume ratio of ILs to model oil on the extraction of sulfur content, the extraction of sulfur compounds (DBT) in n-tetradecane by 1-ethylpyridinium ethylsulfate ionic liquid under various volume ratio of ILs to model oil, experiment was carried out at room temperature. This is because, ionic liquid is in liquid state at room temperature due to its

unique properties. Fig. 3 and 4 shows influence of ILs to model oil ratio on sulfur content for 100 ppm and 1000 ppm sulfur. It also shows at once that then volume ratio of ILs to model oil has strong influence on the sulfur content after extraction using ILs.

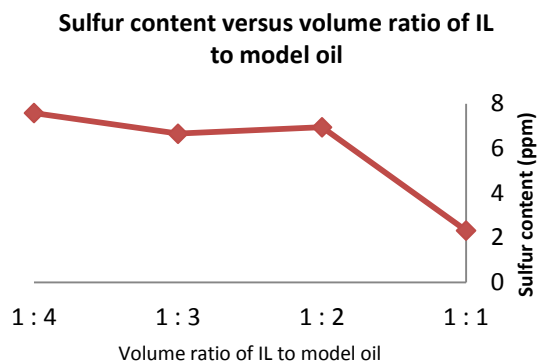


Fig. 3. Influence of ILs to Model Oil Ratio on sulfur Content for 100ppm Sulfur

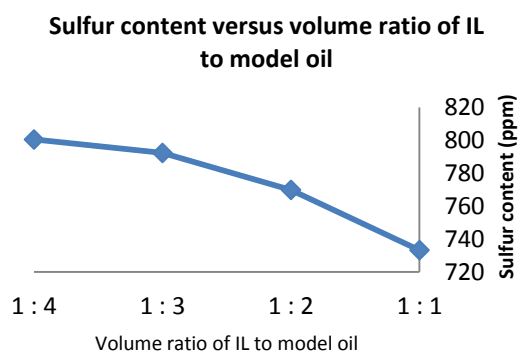


Fig. 4. Influence of ILs to Model Oil Ratio on sulfur Content for 1000ppm Sulfur

Based on figure 3 and 4, the sulfur content in the model oil reduces as the volume ratio goes to 1:1. As in early experiment, the sulfur content is 100ppm. When the model oil is extract with ILs to model oil volume ratio of 1:4, 1:3, 1:2 and 1:1, the sulfur content were reduced to 7.59ppm, 6.66ppm, 6.95ppm and 2.32ppm for 100ppm sulphur and 800.47ppm, 792.31ppm, 769.84ppm and 733.22ppm respectively. From the past research on extraction of sulfur compound by using ILs, the graph is directly proportional.

This mechanism for the extraction of sulfur compound with 1-ethylpyridinium ethylsulfate can be understand as the interaction of π - π between aromatic sulfur compound of DBT and the pyridinium rings of 1-ethylpyridinium ethylsulfate. This is due to the effect of cation and anion interaction of ionic liquid to the DBT. These result has been confirm by the Hollbrey

(2003) in his research, which indicate the same reason of π - π interaction between ILs and sulfur compound. Electron density for sulfur atom in DBT is 5.758 and so that 1-ethylpyridinium ethylsulfate is highly polarizable aromatic π -electron in extract aromatic sulfur compound of DBT which has higher density of aromatic π -electron.

3.2 Influence of ILs to Model Oil Volume Ratio on the Percentage of Sulfur Content Remove

Based on the figure 3 and 4, percentage of sulfur removal can be obtained and illustrated in figure 5 and 6. Figure 5 shows influence of ILs to model oil ratio on percentage of removal sulfur for 100ppm sulfur and figure 6 shows influence of ILs to model oil ratio on percentage of removal sulfur for 1000ppm sulfur.

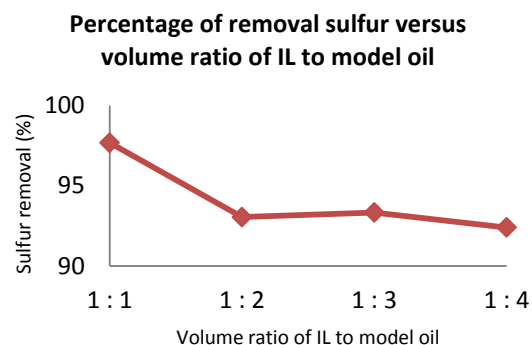


Fig.5 influence of ILs to model oil ratio on percentage of removal sulfur for 100ppm sulphur

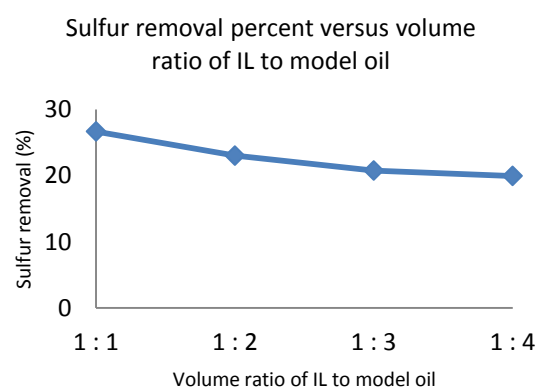


Fig.6. influence of ILs to model oil ratio on percentage of removal sulfur for 1000ppm sulphur

Figure 5 and 6 shows the relation between volume ratio of ILs and model oil and the percentage of sulfur removal is directly proportional. The efficiency of ILs to model oil ratio for 100ppm and 1000ppm was concluded as in table 1 and 2.

Based on figure 6, the relation between ILs to model oil volume ratio also is seen as directly proportional. Percentage different between one to the other of ILs to model oil ratio is seen not slightly different where it contribute 1 to7 % percentage different.

Table 1: Efficiency of ILs to Model Oil Volume Ratio on Sulfur Content Removal for 100 ppm

ILs to model oil ratio	Sulfur removal (%)
1:1	97.68
1:2	93.05
1:3	93.34
1:4	92.41

Table 4-2: Efficiency of ILs to Model Oil Volume Ratio on Sulfur Content Removal for 1000ppm

ILs to model oil ratio	Sulfur removal (%)
1:1	26.68
1:2	23.02
1:3	20.77
1:4	19.95

4. CONCLUSION

Ionic liquid has been seen as one potential method to remove sulfur compound. From this research, ionic liquid used in this research is successfully characterized by using FTIR. Through the experiment, 1-ethylpyridinium ethylsulfate ionic liquid was found to be effective ionic liquid for the selective removal of aromatic heterocyclic sulfur compound from diesel at room temperature. The results shows different volume ratio of ILs to the model is able to remove sulfur compound in the relation of directly proportional. 1:1 volume ratio of ILs to model oil shows the higher efficiency of removal sulfur using 1-ethylpyridinium ethylsulfate ionic liquid where it can remove 97.68% of sulfur content from 100ppm sulfur and 26.68% of sulfur content from 1000ppm sulfur. By considering these results, [EpyESO4] might be used as promising solvents for the extractive desulfurization of diesel.

ACKNOWLEDGEMENT

I would like to thanks my supervisors Dr. Syamsul Bahari Abdullah his guidance and FKKSA Laboratory's staff for being helpful on my research.

REFERENCES

- [1] Yoshikazu I., Takashi O., Hiroshi O., Yoshimitsu H., and Masayuki S. (1994). Selective Desulfurization Of Dibenzothiophene By Rhodococcus Erythropolis D-1. Applied and Environmental Microbiology, Jan. 1994, P. 223-226
- [2] Mohammad, R. A., Ayeh, A., Behnam, R., Fatemah, Y., Behrouz, Z., Mohammad, Z., and Hasein, N. (2010). Biodesulfurization of Dibenzothiophene by a Newly Isolated, Stenotrophomonas maltophilia Strain Khol. World Applied Science Journal 10 (3): 272-278.
- [3] Hongshuai G., Mingfang L., Jianmin X., Yong W., Yuguang L., Wangliang L., Qingfen L., and Huizhou L., (2008). Desulfurization of Fuel by Extraction with Pyridinium-Based Ionic Liquids. *Ind. Eng. Chem. Res.* 2008, 47, 8384–8388
- [4] Takashi O., Teruki H., Ichiro H., and Yoshikazu I. (1996). Characterization of Dibenzothiophene Desulfurization Reaction by Whole Cells of *Rhodococcus Erythropolis H-2* In The Presence Of Hydrocarbon. Journal of Fermentation and Bioengineering Vol. 82, No. 6, 610-612.
- [5] Manufacture of Emission Controls Association, MECA (1998). The Impact of Gasoline Fuel Sulfur on Catalytic Emission Control Systems.
- [6] Wang J. L., Zhao D. S., Zhou E. P., and Dong Z. (2007). Desulfurization of gasoline by extraction with *N*-alkylpyridinium-based ionic liquids. *J Fuel Chem Technol*, 2007, 35(3), 293–296
- [7] Holbrey J. D., Reichert W. M., Nieuwenhuryzen M., Sheppard O., Hardacre C., and Rogers R. D. Liquid Clathrate Formation in Ionic Liquid-Aromatic Mixtures. *Chem. Commun.* 2003, 4, 476.
- [8] Katherine O. B., Michael P. W., and Charlotte P. (2009). Low-Sulfur Gasoline & Diesel: The Key To Lower Vehicle Emissions
- [9] Chunshan Song (2003). An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel Catalysis.
- [10] Diego P. M., Alexander S. T., and Steven C. F. (2010). Desulfurization of Dibenzothiophene and Oxidized Dibenzothiophene Ring Systems.