DESULPHURIZATION OF MODEL OIL AND DIESEL USING IONIC LIQUID

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DESULPHURIZATION OF MODEL OIL AND DIESEL USING IONIC LIQUID

MOHD RAFIQUL ZARIN BIN RAMLI

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
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27 JANUARY 2014

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).

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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.

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Dedication

I dedicate my dissertation work to my family and many friends. A special feeling of gratitude to my loving parents, Ramli Bin Hamzah and Fatimah Binti Ismail whose words of encouragement and push for tenacity ring in my ears. I also dedicate this dissertation to my many friends who have supported me throughout the process. I will appreciate all they have done, especially Abdul Hadi and Kenrick for helping me throughout during crucial moments while to settle this project. I dedicate this work and give special thanks to my supervisor, Dr. Shamsul Bahari Bin Abdullah for being very supportive and helpful while guiding me to complete this chapter successfully.

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To all my friends especially my best friends and all my course mates, thank you for believing in me and helping me to go through the difficult time. The experiences and knowledge I gained throughout the process of completing this final project would prove invaluable to better equip me for the challenges which lie ahead. Last but definitely not least to my family members, I can never thank you enough for your love, and for supporting me throughout my studies in University Malaysia Pahang.

ABSTRACT

Diesel is a multi-purpose petroleum fuel used in all kinds of vehicles. But remains one of the largest source of fine particle air pollution, which has serious health impacts. Depending on the crude oil used and the refinery configurations, sulphur levels in diesel range from below 10 ppm to as high as 1000 ppm. In fact, Europe, United States, and Japan have all put in place measures to reduce sulphur to lower levels which is below 10 ppm to 15 ppm, often along with emission standards that require advanced emission control technologies that cannot be used with higher sulphur fuels. By March of 2008, there are many countries that have switched to diesel fuel with 500 ppm or less such as Philippines, Singapore, and Thailand including our country, Malaysia. There are various methods applied in industry to obtain low-sulphur fuels such as hydrocracking processes. But, the sulphur removal using ionic liquids are gaining wide recognition as potential environmental solvents due to their very low vapour pressure, their thermal and chemical stability, their ability to act as a catalyst, and their non-flammability and non-corrosive properties. The procedures include with three sub-process which first (ILs) is analyse with Fourier transform infrared spectroscopy (FTIR). The liquid was placed on a Germanium (Ge) plate by using a dropper and the test is run until a constant reading is visible. It is then followed by a wavelength classification by referring it to a table of characteristic IR absorptions. From the classification, it was found that there is a trace of functional groups consists of amines, amides, aromatics and alkyl halides. The lower frequency, 874.55 cm^{-1} and 777.29 cm^{-1} have functional group of aromatics with bond C-H "oop". The highest frequency with 3421.96 cm^{-1} has functional group of 1^o, 2^o amines or amides with bond N-H Stretch. Besides, there are also components with functional group of aliphatic amines with bond C-N Stretch at frequency 1044.97 cm^{-1} and 1104.56 cm^{-1} respectively. Other than that, there is functional group of alkyl halides with bond C-H wag (CH_2X) at frequency 1179.15 cm^{-1}. Secondly, the ionic liquid was undergone a CHNOS testing to check the percentage of carbon (C), Nitrogen (N), Oxygen (O), and Sulphur (S) that presented within ionic liquids. The ionic liquid was sent to University Malaysia Pahang (UMP) Central Laboratory to obtain the results. Based on the result obtained, the (ILs) consists of Nitrogen by 11.37%, Carbon by 15.84%, Hydrogen by 6.729%, Sulphur by 11.185% and rest of the composition is for Oxygen by 15.84%. The result will be compared theoretically with the structure formula of (ILs).

ABSTRAK

Diesel adalah bahan api petroleum pelbagai guna yang digunakan dalam semua jenis kenderaan. Tetapi ianya juga menjadi salah satu sumber terbesar pencemaran udara zarah halus, yang mempunyai kesan kesihatan yang serius. Bergantung kepada minyak mentah yang digunakan dan konfigurasi penapisan, sulfur dalam julat diesel dari bawah 10 ppm kepada setinggi 1000 ppm. Malah, Eropah, Amerika Syarikat, dan Jepun telah semua melaksanakan langkah-langkah untuk mengurangkan sulfur ke tahap yang lebih rendah iaitu di bawah 10 ppm hingga 15 ppm, sering bersama-sama dengan standard pelepasan yang memerlukan kemajuan teknologi dalam kawalan pelepasan yang tidak boleh digunakan dengan bahan api sulfur yang lebih tinggi. Menjelang Mac 2008, terdapat banyak Negara yang telah bertukar kepada bahan api diesel dengan 500 ppm atau kurang seperti di Negara Filipina, Singapura dan Thailand termasuk juga Negara kita, Malaysia. Terdapat pelbagai kaedah yang digunakan dalam industri untuk mendapatkan bahan api rendah sulfur seperti proses pemecahan hidro. Tetapi, penyingkiran sulfur menggunakan cecair ionic semakin mendapat sambutan yang meluas sebagai pelarut yang mesra alam sekitar disebabkan oleh tekanan wap yang sangat rendah, kestabilan haba dan kimia mereka, keupayaan mereka untuk bertindak sebagai pemangkin dan sifat-sifat tidak mudah terbakar dan tidak cepat menghakis mereka. Prosedur ini termasuk dengan tiga sub-proses yang pertama adalah menganalisis cecair ionic (ILs) dengan Spektroskopi (FTIR). Cecair tersebut telah diletakkan pada satu Germanium (Ge) plat dengan menggunakan penitis dan ujian dijalankan sehingga bacaan berterusan boleh dilihat. Ia kemudian diikuti dengan klasifikasi panjang gelombang dengan merujuk kepada jadual absorptions IR. Dari klasifikasi, didapati bahawa terdapat kesan kumpulan berfungsi mengandungi amina, amides, aromatic dan alkil halida. Kedua, cecair ionic akan menjalani ujian CHNOS untuk memeriksa peratusan Karbon (C), Nitogen (N), Oksigen (O), dan Sulfur (S) yang dibentangkan dalam cecair ionic. Cecair ionic telah dihantar ke Makmal Pusat Universiti Malaysia Pahang (UMP) untuk mendapatkan keputusan. Berdasarkan keputusan yang diperolehi, (ILs) terdiri daripada Nitrogen oleh sebanyak 11.37%, Karbon sebanyak 15.84%, Hidrogen sebanyak 6.729% dan Sulfur sebanyak 11.185% dan selebihnya daripada komposisi Oksigen dengan 15.84%. Hasilnya akan dibandingkan secara teori dengan formula struktur daripada (ILs).

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LIST OF ABBREVIATIONS

DPF	Diesel particulate filter
ILs	Ionic liquids
EPA	Environmental protection agency
ULSD	Ultra-low sulfur diesel
HDS	Hydrodesulfurization
BDS	Biodesulfurization
ODS	Oxidative desulfurization
ADS	Adsorptive desulfurization
ppm	Part per millions
NMR	Nuclear magnetic resonance spectroscopy
FIA	Fluorescent indicator analysis
GC	Gas chromatography
SCTMAT	Short contact time microactivity test unit
FCC	Fluid catalytic cracking
DBT	Dibenzothiophene
BMIM	n-butyl-n-metyllimidazolium
HPLC	High Performance Liquid Chromatograph
FTIR	Fourier Transforms Infrared Spectroscopy

1 INTRODUCTION

1.1 Motivation and statement of problem

Sulphur content in fuel has become a major environmental issue worldwide. Since June of 2006, the regulations in the US have required a reduction of sulphur in transport fuel from 500 ppm to 15 ppm. Meanwhile, in Europe, the regulation on sulphur in transport fuel required it to be less than 10 ppm by 2010. In addition, there are different form of compounds within sulphur which present in diesel which about 70% are made up by thiophene and its derivatives. The sulphur content in diesel is in the range of 0.1% to 10% depending on a place of origin. The sulphur content increases as the temperature of boiling point of individual fractions increases. The most sulphur which is about 98% contained in diesel fuel is oxidized in the combustion process to sulphur dioxide which together with exhaust gas is released to the atmosphere where it can be subject to other reactions contributing to the creation of smog and acid rains. Until now, desulphurization can only be obtained via heterogeneous catalytic hydrodesulphurization (HDS) process in petroleum plants. The main drawbacks of the (HDS) process include high operating temperature of 300 ^{o}C or more, high pressure of up to 4 MPa, high energy costs and difficulty in removing aromatics heterocyclic sulphur components such as benzothiophene (BT) and its derivatives. Therefore, ionic liquids (ILs) may be potential candidates in overcoming (HDS) drawbacks in removing heterocyclic sulphur components (Syamsul et al. 2011).

In the present study, the physical property of 1-Methylpyrazolium Methylsulphate has been highlighted to gain more efficiency for desulphurization process. By using statistical approach and manipulating the data, a comparison and explanation for the physical properties of the (ILs) in the plotted data could help predict the desulphurization performance for a new emerging (ILs).

1.2 Objective

The following are the objective of this research:

- To characterize the ionic liquid, 1-Methylpyrazolium Methylsulphate

- To study the extraction process for the removal of sulphur containing compound, DBT from model oil by means of an ionic liquid.

1.3 Scopes of this research

The following are the scope of this research:

i) Study the characterization of 1-Methylpyrazolium Methylsulphate by their molecular structure and functional groups.

ii) Evaluate the performance of 1-Methylpyrazolium Methylsulphate on model oil (DBT + xylene).

iii) Test the extraction process on diesel with 1-Methylpyrazolium Methylsulphate.

1.4 Main contribution of this work

The following are the contributions of this research.

Firstly, the research will give the complete informations to the people about the effect of the sulphur content in diesel when release to the environment during combustion process. Sulphur release to the environment will lead to many serious problems such as the formation of acid rain that harmful to the human being and others living things.

Secondly, at the end of this research, the new diesels (after desulfurization process) definitely will reduce the sulphur content from the pure diesel in a certain amount. The diesel now is becoming cleaner without giving any single effect on it performance in the automobile's engines.

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides general information about the diesel properties and characteristic. The information also includes the sulphur containing compounds in diesel and the effect of sulphur containing compounds release to the environment when reacts in combustion process. Besides, this chapter also review on the status of fuel quality on Asia pacific region and their target level of sulphur content in diesel for many years to come. The lower sulphur content in diesel will achieve the clean fuel status which is demanding by the global associations. This chapter also explains about what are the ionic liquids and its properties which attract worldwide industries attention to use it as an extractants in the desulfurization process. It also includes the ionic liquids set for my later experiments on desulfurization of model oil and diesel. Lastly, the summary on the previous experiment set up by the others in their journals and articles on desulfurization process by using various types of ionic liquids on various type of model oil or fuel.

Chapter 3 gives a review of the chemicals and the apparatus needed to set up the experiment. There are several chemicals that we need to purchase it from the supplier such as ionic liquids, xylene, DBT and Methanol because it will not be supply by the University's laboratory. In addition, the apparatus such as thermometer, test tube, magnetic stirrer and the rest are mostly available from the laboratory. Then, this chapter explains about the methodology. The methodology divides into three parts which are preparation of ionic liquids, extraction on model oil and lastly, it will be the extraction on diesel.

Chapter 4 is supposed to be the extraction on model oil with ionic liquid. The experiment is set up by preparing the model oil with DBT and xylene to give certain volume of the solutions with sulphur content. The expected result from this experiment is the selected ionic liquid 1-Methypyrazolium Methylsulphate be able to remove the sulphur content, DBT from the model oil and the early aim for utmost objective is achieve.

Chapter 6 draws together a summary of the thesis and outlines the future work which might be derived from the model developed in this work.

2 LITERATURE REVIEW

2.1 Introduction

This paper presents the experimental studies on desulfurization of diesel and model oil by using ionic liquids. Firstly, the preferred ionic liquids must be able to use as an extractant for desulfurization of model oil before it will be tested with diesel. The good extractant will exhibits a better extractive performance for removal of selected sulphur compounds. The ionic liquids is prepared and tested on model oil. Then, the ionic liquid is tested on diesel to compare the results.

2.2 Overview of Diesel

Diesel is a complex mixture of hydrocarbons with a boiling range from about 400 to 670°F. Besides that, it is also composed of hydrocarbons of three major classes: paraffinic, naphthenic, and aromatic hydrocarbons. In an analysis of diesel done by some researcher, the biggest setback is the separation and identification of pure compounds or classes of compounds from the complex hydrocarbon mixtures in diesel. The analysis uses the fluorescent indicator analysis method (FIA; ASTM D-1319) to separate and quantify saturates, olefins and aromatic hydrocarbons in diesel fuels. Another approach is to determine aromatic content by nuclear magnetic resonance spectroscopy, (NMR). These methods do not give the same result because they do not measure the same properties (Thomas, et al. 1991).

On the other hand, in a work presented by a number of researchers which was to determine sulphur compounds in diesel using Gas Chromatography (GC). In this work, it was known that a mixture of standard substances containing thiols, sulphides, thiophenes, benzothiophenes, dibenzothiophenes and benzonaphthothiophenes was present in diesel. Besides that, by using a one-dimensional chromatography it requires a very high column efficiency and stability in retention time of substances to avoid errors of the identification. On the flipside, by using a two-dimensional chromatography it easier and more reliable be identified due to the substance can be determined by both X- and Y-axis (Wei et al. 2003).

Furthermore, a study done by a researcher on the removal of thiophene sulphide from diesel. In this research, the researchers agreed that the sulphur in the fuels are hazardous, which not only pollute environment but also corrode equipment. Therefore, sulphur removal from fuels becomes an increasing technical challenge in refinery industry. On top of that, the difficulty of sulphides removal is closed related to the sorts of sulphides. The active sulphides such as hydrogen sulphide and thiols are easy to remove, but nor to the inactive sulphides with aromatic rings such as thiophene and its derivatives (Xin and Yong, 2005).

Table 2-1: Status of Fuel Quality on Asia-Pacific Region

Country	**Sulphur (Max, ppm), Diesel**	**50 ppm Target Date**
China	2,000	2016
India	500	No Date
Indonesia	3,500	No date
Malaysia	500	2016
Philippines	500	2010
Republic of Korea	50	2012
Singapore	50	2012
Thailand	500	2012
Vietnam	500	2016

Table 1 shows the sulphur content emission for selected Asia-Pacific country. It is known that some of the country has reached its target of 50 ppm of sulphur content for diesel emission. The European Standard has named this target as Euro IV.

Table 2-2: Analysis of Sulphurs-Containing Compounds of Diesel Samples (Wang et al., 2003).

Name	**7000 ppm**	**1200 ppm**	**120 ppm**
MST	1099	19	0
BT	0	0	0
C1BT	9	0	0
C2BT	88	3	0
C3BT	391	17	0
C4BT	477	24	0
C5BT	468	29	0
C6BT	457	35	0
C7BT	470	41	0
C8BT	457	44	0
C9BT	364	43	0
C10BT	328	41	0
C11BT	247	33	0
C11+BT	152	25	0
C0DBT	83	7	1
C1DBT	306	91	3
C2DBT	503	234	23
C3DBT	484	250	34

C4DBT	315	156	23
C5DBT	222	103	16
C6+DBT	164	81	12
Total	7085	1277	111

From Table 2, it is clearly stated that the sulphur compounds in diesel have different kind of various form and structure. From this research perspective, it is important to test an ionic liquid whether it is capable to remove or extract sulphur from diesel by evaluate it first on a model oil xylene which containing DBT as sulphur containing compound. By testing it on the model oil, it is to determine the effectiveness of the removal of sulphur before conducting it on diesel.

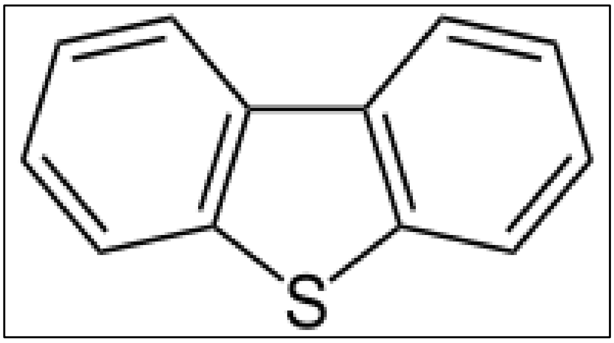


Figure 2-1: The structure of selective sulphur component in diesel DBT.

Table 2-3: The properties of the selective sulphur component in diesel DBT.

Solubility in water	**Insoluble in water**
Molar mass	**184.26 g/mol**
Appearance	**Colourless crystals**

Boiling point	**323-333 °C(lit.)**
Melting point	**97-100 °C(lit.)**
Density	**1.252 g/mL at 25 °C(lit.)**

2.3 Ionic Liquids

The Room temperature ionic liquids (RTIL) are liquids that are composed entirely of ions. In fact, ionic liquids can now be produced which remain liquid at room temperature and below (even as low as -90 ^{o}C) and appear to be undemanding and inexpensive to manufacture. Ionic liquids offer an attractive alternative to conventional organic liquids for clean synthesis, as they are easy to recycle, lack flammability, and effectively possess no vapour pressure. Compared with classical molecular solvents, the ionic liquids are environmentally benign reaction media (Hou[a], R. S. et al., 2006).

The 1-Methylpyrazolium Methylsulphate is one of the example (RTIL) which is known as a viscous, colourless, and hydrophobic and non-water soluble ionic liquids. It has a capability to absorb a little amount for paraffins and olefins, but absorbed a small amount of aromatics and a larger amount of thiophene and methylthiophene.

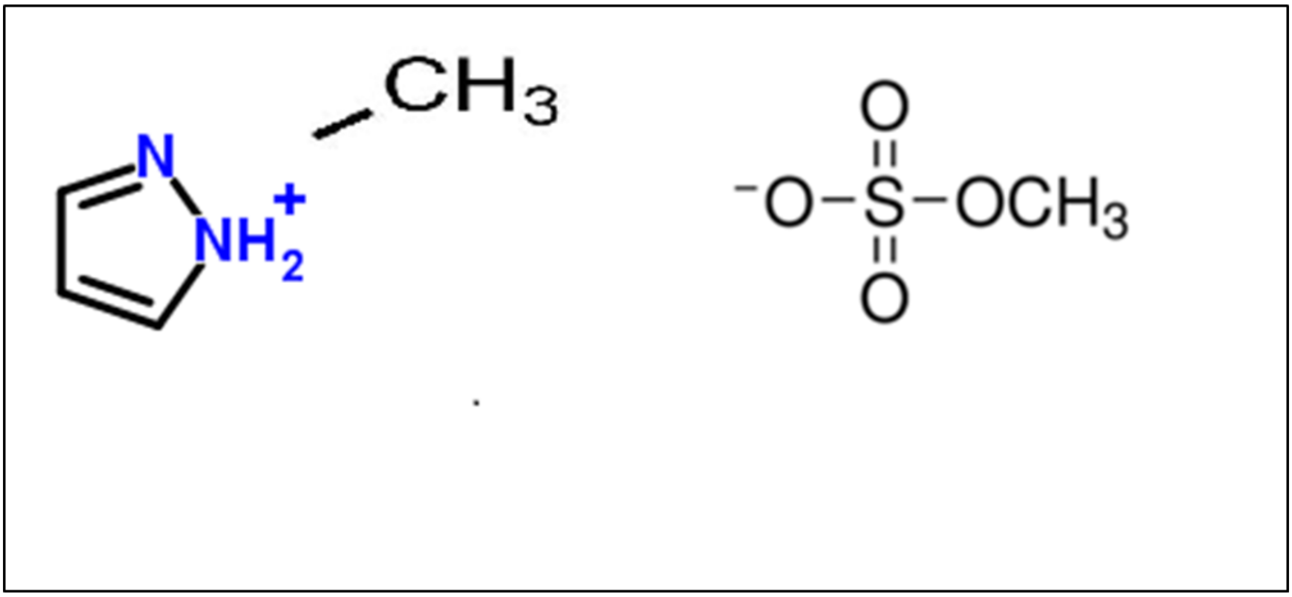


Figure 2-2: The structure of selected ionic liquid 1-Methylpyrazolium Methylsulphate

2.4 Usage of Ionic Liquids

The following chart summarizes important properties of ionic liquids and their potential with current applications:

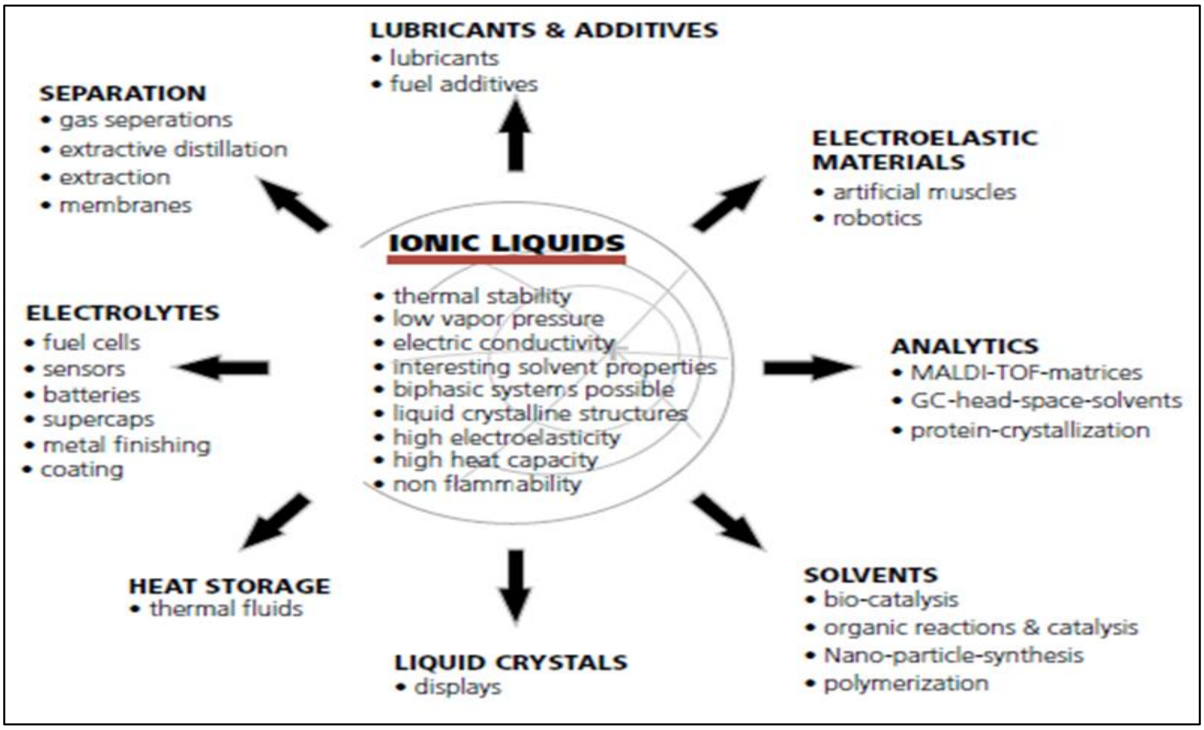


Figure 2-3: The important properties of Ionic Liquids (ILs) and their potential and current applications.

2.5 Experimental Work on Ionic Liquids

Kowsari et al., (2013) discussed about the effect of diesel fuel which is one of the largest sources of fine particle air pollution, that lead to serious health impacts. In the beginning of 2001, Environmental Protection Agency (EPA) passed the rules requiring use of ultra-low sulphur diesel (ULSD). The benefit from the usage of (ULSD) is it lowers the level of released sulphur and hydrocarbon to almost zero. Thus, the technology for reduction of sulphur in diesel fuel up to 15 part per million (ppm) which is currently available and the new technologies are under development that could reduce the cost of desulfurization. It also mentioned chemical oxidation in conjunction with ionic liquid extraction can increase the removal of sulphur sharply. Besides, ionic liquids have the ability of extracting aromatic sulphur compounds at ambient condition without consumption of hydrogen, H_2. The cations, anions structure, and size of ionic liquids are important parameters affecting the extracting ability. In addition, ionic liquids are immiscible with fuel, and the used ionic liquids can be regenerated and recycled by solvent washing or distillation process.

Valla et al., (2007) exhibit a research about the effect of heavy aromatic compounds on sulphur. There are five different model of sulphur compounds were studied, like benzothiophene, 2-methyl-benzothiophene, 3-decyl-thiophene, dibenzothiophene, and 4,6-dimethyl-dibenzothiophene. Each one of them was diluted in conventional gas oil in order to maintain a realistic hydrocarbon environment. After that, their cracking behaviour was studied using a steamed deactivated FCC catalyst, while the run tests were performed in an automated Short Contact Time Microactivity Test Unit (SCT-MAT). The result obtained at the end of the experiment showed the long chain alkyl-thiophene, 3-decyl-thiophene is mainly responsible for the increase of sulphur amount in diesel during cracking. That sulphur compound was also the most reactive one with respect to desulfurization, since it was highly cracked to H_2S and decomposed to S. The reactive order of the five heavy sulphur compounds during the FCC process is 3-decyl-thiophene > benzothiophene > dibenzothiophene > 4,6-dimethyl-dibenzothiophene > 2-methyl-benzothiophene.

Fox et al., (2010) prepared the experiment to enhance the desulfurization of model fuels using a film-shear reactor. The application of a film-shear reactor provides a remarkable enhancement in the efficiency of the ODS process compared to normal stirring. If the flow rate and all parameters were held constant, the extent of thiophene removal increased as the residence time increased. The results from the experiments showed that an increase in oxidant concentration did not lead to increased thiophene removal.

Zhao et al., (2009) prepared the desulfurization of fuel oil by pyridinium-based ionic liquids. The ionic liquid $[BPy]BF_4$ was found to be very effective for the extraction of sulphur components, thiophene and dibenzothiophene (DBT) in model oils and diesel at room temperature. The effects of extraction desulfurization on model oil with sulphur components were tested. The desulfurization process was achieved after H_2O_2 was utilized for oxidizing the sulphur components to the corresponding sulfones which were extracted by ionic liquid. The desulfurization of thiophene and DBT by the extraction-oxidation system can reach maximum value, 78.5% and 84.3% which are higher than those achieved by extractive desulfurization. The used ionic liquid was regenerated through re-extraction in tetracholromethane, and can be recycled four times without any obvious decrease in activity.

Wang et al., (2006) presented competitive extraction capacity of different ionic liquids for model fuel. The ionic liquids used for the experiment were based on $FeCl_3$, $ZnCl_2$, $SnCl_2$, $MnCl_2$, and lastly $CoCl_2$. From the result obtained, the ionic liquids based on $FeCl_3$ showed the better extraction capacity of dibenzothiophene (DBT) from diesel than other ionic liquids. The sulphur removal of DBT-containing model oil can reach 67.6% with single extraction under mild condition while the extraction capacities for the other ionic liquids were below than 50.0%. The extraction process went on quickly, and it could reach extraction equilibrium in a short period. Furthermore, Fe-based ionic liquids system shows considerable promise for providing a technology to meet future needs for low sulphur diesel.

Zhang & Zhang (2002) presented selective sulphur removal from fuels by using ionic liquids at room temperature. In their work, three ionic liquids, [BMIM] [PF_6], [BMIM] [BF_4] and [EMIM] [BF_4] were found to have distinctive absorption for sulphur containing compounds, allowing the removal of sulphur from fuels at room temperature. The model compounds used were 2-methylpentane, 1-hexane, methylcyclopentane, toluene, trimethylbenzene, thiophene, 2-methylthiophene, and isobutyl mercaptan to represent typical molecules in diesel fuels. The absorption capacity of an ionic liquid for a specified compound was measured at room temperature by the weight gain in the ionic liquid phase at saturated absorption. The ionic liquid [BMIM] [PF_6] and [BMIM] [BF_4] when applied to a mixture of thiophene and toluene showed there was stronger absorption for thiophene rather than toluene. For a specific aromatic compound such as thiophene [BMIM] [PF_6] and [BMIM] [BF_4] have higher absorption capacity than [EMIM] [BF_4]. It is because of the structure and the size of both cation and anion of ionic liquid that affect the absorption capacity. Besides, it was found that high level of aromatics does not significantly affect the absorption of ionic liquids for sulphur compounds.

Xuemei et al., (2008) presented the desulfurization of diesel fuel by extraction with [BF_4]-based ionic liquids. The results show that the absorption capacity of an ionic liquid for the S-compound in diesel fuels relies on its structure and its size. In the cased of the two examined diesel fuels, both elongating the cation tail length and increasing the mass ratio of ionic liquid/ diesel fuel promote the desulfurization ability of the examined ionic liquids. Besides, the results show that imidazolium-based ionic liquids displays higher extraction efficiencies than pyridinium-based ionic liquids, presumably owing to the fact that the rings of the S-compounds are similar to the imidazolium head ring. The rates of the first desulfurization of diesel using [C_8mim] [BF_4] suggest that that ionic liquid is a promising extractant for desulfurization of the diesel fuels. The rate of desulfurization can reach up to 39.76%.

Wang et al., (2010) developed the extractive desulfurization of fuels using ionic liquids based on $FeCl_3$. Six Lewis acid ionic liquids were synthesized and employed as extractants for desulfurization of the model oil containing dibenzothiophene (DBT). The ionic liquids based on $FeCl_3$ showed the better extraction capacity than other based ionic liquids such as Zn, Sn, Mn and Co. At the end, it shows that 1-butyl-3-methylimidazolium chloride was very promising ionic liquid, which performed perfectly in the studied ionic liquids under the same operating conditions. It can remove DBT from model oil after continuous extraction for four steps, and the desulfurization efficiency can reach maximum value under mild reaction conditions. The used ionic liquid could be regenerated six times without a significant decrease in activity.

Dharaskar et al., (2009) prepared eleven Lewis acid based ionic liquids were screened to investigate the desulfurization efficiency. $FeCl_3$ based ionic liquid used as an effective extractant for removing DBT from liquid fuel. [BMIM]Cl/ $FeCl_3$ found to be the best ionic liquid as a kind of novel extractant for desulfurization of ionic liquid fuel, which exhibits a better extractive performance for DBT. The used ionic liquid, $FeCl_3$ was able to extract DBT from model liquid fuel even without regeneration. Furthermore, Fe based ionic liquids system shows considerable promise for providing a technology to meet future needs for low sulphur fuel or clean fuels.

3 MATERIALS AND METHODS

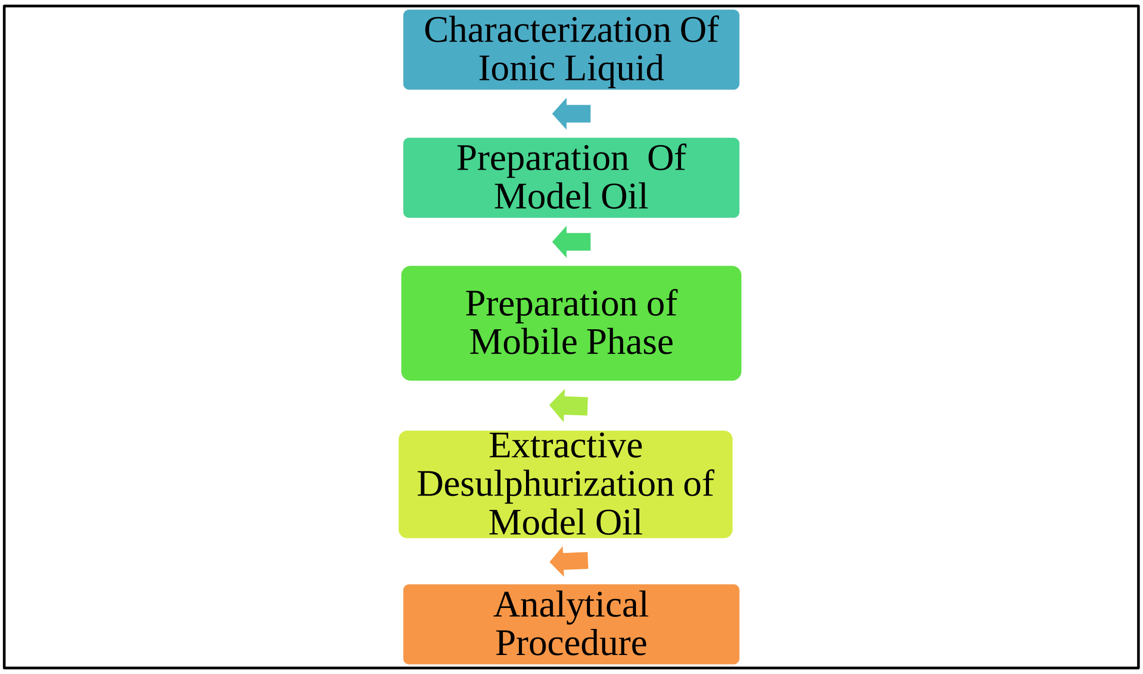
3.1 Overview

This paper presents the preparation to set up the experiment of desulfurization. The chemicals and the apparatus need during the experiment are listed down based on the procedures. The rare chemicals are usually not available in the laboratory, so those chemicals need to be purchased from the supplier. Besides, this chapter also focused on how the ionic liquids and model oil are being prepared in the laboratory. The procedure continue with the extraction on model oil, the ionic liquid is tested on the model oil first to observe the ability of its absorption capacity on DBT before tested it with diesel.

3.2 Chemicals & Apparatus

The materials involved in this experiment are DBT, 1-Methypyrazolium Methylsulphate, Methanol (standard for HPLC), water, Xylene and diesel needed to purchase from the supplier. The basic apparatus for this experiment such as beaker, test tube with rack, round bottomed flask, vials, Fourier transforms infrared spectroscopy (FTIR), (HPLC), magnetic stirrer, syringe, dropper, and others are obtained from the laboratory.

3.3 General methodology



3.4 Characterization of ionic liquid

The method for synthesis of ionic liquids was neglected because of several problems while purchasing the chemicals from outsiders. The chemicals needed were expected cannot be delivering on time. Thus, the initial ionic liquid was replaced with 1-Methylpyrazolium Methylsulphate. Then, the procedure was proceeding with characterization (CHNOS test) of new ionic liquid by sending it to UMP Central Lab and to determine the probability of its functional groups by Fourier transform infrared spectroscopy (FTIR) test.

3.4.1 Sample preparations

The (ILs) is obtained from Universiti Teknologi Petronas (UTP) via our course lecturer. The amount of (ILs) is very limited but enough for almost all of the usage in the experiments.

3.4.2 Fourier transforms infrared spectroscopy (FTIR)

This equipment is a measurement technique whereby spectra are collected based on measurements of the coherence of a radiative source, using time.

The ionic liquid, 1-Methylpyrazolium Methylsulphate was tested with a FTIR to check the functional groups. It is then followed by a wavelength classification by referring it to a table of characteristic IR absorptions (see Table 4-1). The procedure start with by placed the head of FTIR and connected to a host. Then, place a (Ge) plate. Approach the needle with the (Ge) plate and save the background spectrum. The liquid was placed on a Germanium (Ge) plate by using a dropper and the test is run until a constant reading is visible. For cleaning (Ge) plate purpose, a drop of acetone is used. From the classification, it was found that there is a trace of functional groups consists of amines, amides, aromatics and alkyl halides. The wavelength can be observed from the absorptions data.

3.4.3 Elemental analysis using CHNS

The ionic liquid was undergone a CHNOS testing to check the percentage of Carbon, Nitrogen, Oxygen and Sulphur that is present in the ionic liquid. The ionic liquid was sent to University Malaysia Pahang (UMP) Central Laboratory to obtain the results. The time duration was one week for the result before any other experiment can be conducted. From the data obtained, it was found out that there was presence of sulphur in the ionic liquid.

3.4.4 High Performance Liquid Chromatograph (HPLC) test

This equipment is a measurement technique to separate a mixture of compounds in analytical chemistry and biochemistry with the purposes of identifying of purifying the individual component mixture.

Before the High Performance Liquid Chromatography (HPLC) analysis can be done several steps will be prepared. Firstly, the ionic liquid that has been premixed with DBT and the model oil of xylene will be separated and put into a series of 5 vials. The vials are then going through an incubating shaker for 2 days at 180 rpm and at 30^{o}C. After that, 1.5 L methanol obtained and filtered using a filter pump. It is then put under "degas" treatment for 30 minutes at 27^{o}C and this will be the mobile phase for the HPLC analysis. Next, pure water is obtained in the laboratory. The analysis is conducted and set up under the guidance and supervision of the laboratory assistant. The result will be obtained and printed out and tabulated to be used in the discussion part in the result section. From the results, a calibration curve based on the standard sample will be plotted and will be compared with the ionic liquid sample.

3.5 Preparation of model oil

For this investigation, a solution of sulphur compound, Dibenzothiophene (DBT) in xylene was employed as a model fuel.

0.06 mg of DBT was dissolved in 73 mL xylene to form 1421 ppm DBT content in the model oil. From 2000ppm DBT, it was diluted to 1421 ppm, 1000 ppm, 800 ppm, 500 ppm and 250 ppm of DBT. The sample was used to be analysed for standard calibration curve in this research.

Table 3-1: Concentration and Area for Standard Calibration Curve.

Concentration (ppm)	Area (mAU*s)
250	501.15227
500	299.59027
800	703.91636
1000	1327.12846
1421	3303.06999

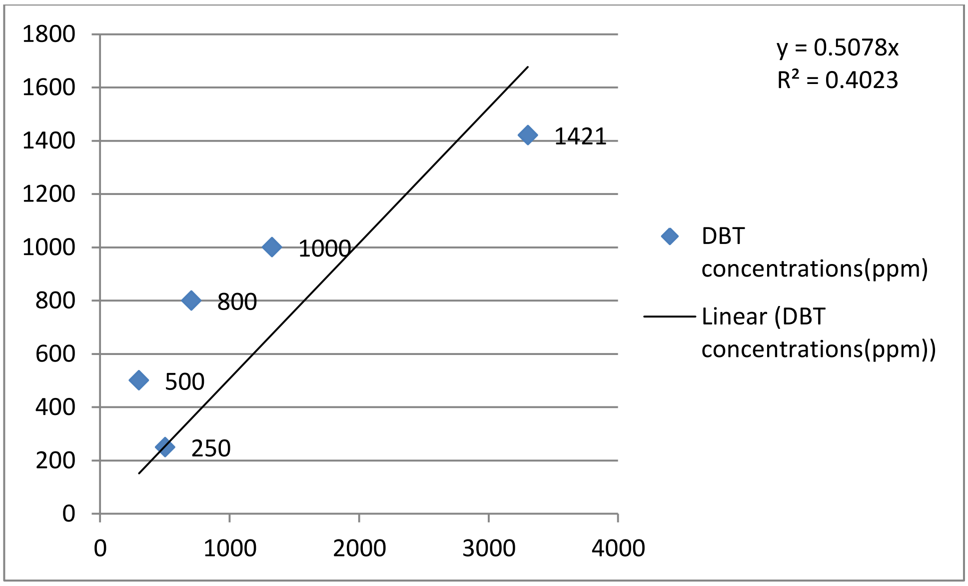


Figure 3-1: Area versus DBT Concentration.

3.6 Preparation of mobile phase

The selection of mobile phase is based on the desired retention behaviour and the physiochemical properties of the analyte. For this analysis, methanol and ultra-pure water as a mobile phase with ratio 90:10 (900 mL of methanol and 100 mL of ultra-pure water) was mixed in the scotch bottle. The mobile phase then was filtered with membrane-type filter with a porosity of 0.45μm to remove mechanical particle by pumping it using a vacuum pump. After all the mobile phase was already filtered, then the mobile phase was degassed by sonification to avoid the formation of bubbles in the detector cell.

3.7 Extractive desulphurization of model oil

The experiment was conducted by using model oil with 1421 ppm, 1000 ppm, 800 ppm, 500 ppm, and 250 ppm of DBT. The ionic liquid and model oil were mixed at 1:1 volume ratio which is 0.5 mL 0f IL and 0.5 mL model oil in the universal bottle. The mixture in the bottle was heated in water bath at 30 ºC with 185 rpm stirring for 30 minutes. The mixture then allowed settling for 5 to 10 minutes to obtain the splitting.

After that, the sample from xylene layer was taken from the mixture by using needle syringe 6 mL. Before transfer the sample to the vial bottle, the needle was change by nylon filter. So that, the sample was filter before enter the 3 mL vial bottle. The procedures were repeated for different ionic liquids model oil mixing ratio (1:1).

4 RESULTS AND DISCUSSIONS

4.1 Overview

This chapter review the results from characterization of ionic liquids by using FTIR and CHNS respectively. The data obtain will be analysed to determine the structure, functional groups and molecular structure. Then, the efficiency of sulphur removal of different volume ratios of DBT is calculated and graphed based on the results from HPLC. The discussions will explained some of the errors occurs while undergo the experimental work and provided the recommendation for future work.

4.2 Characterization of pyrazolium-based ionic liquids by using FTIR

The ionic liquid, 1-Methylpyrazolium Methylsulphate was tested with a FTIR to check the functional groups. It is then followed by a wavelength classification by referring it to a table of characteristic IR absorptions (see Table 4-1). The liquid was placed on a Germanium (Ge) plate by using a dropper and the test is run until a constant reading is visible. From the classification, it was found that there is a trace of functional groups consists of amines, amides, aromatics and alkyl halides. The wavelength can be observed from the absorptions data which is available in Figure 4-1.

Table 4-1: Table of Characteristic IR Absorptions.

Peak number	**Frequency, cm^{-1}**	**Bond**	**Functional group**
01	3421.96	N-H Stretch	1^o, 2^o amines
02	1179.15	C-H wag (-CH_2X)	alkyl halides
03	1104.56	C-N Stretch	aliphatic amines
04	1044.97	C-N Stretch	aliphatic amines
05	874.55	C-H "oop"	Aromatics
06	777.29	C-H "oop"	Aromatics

There are several possibilities of characteristics based on frequency (cm^{-1}), bond and functional group in 1-Methylpyrazolium Methylsulphate. From Figure 4-1, the lower frequency, 874.55 cm^{-1} and 777.29 cm^{-1} have functional group of aromatics with bond C-H "oop". The highest frequency with 3421.96 cm^{-1} has functional group of 1^{o}, 2^{o} amines or amides with bond N-H Stretch. Besides, there are also components with functional group of aliphatic amines with bond C-N Stretch at frequency 1044.97 cm^{-1} and 1104.56 cm^{-1} respectively. Other than that, there is functional group of alkyl halides with bond C-H wag (CH_2X) at frequency 1179.15 cm^{-1}.

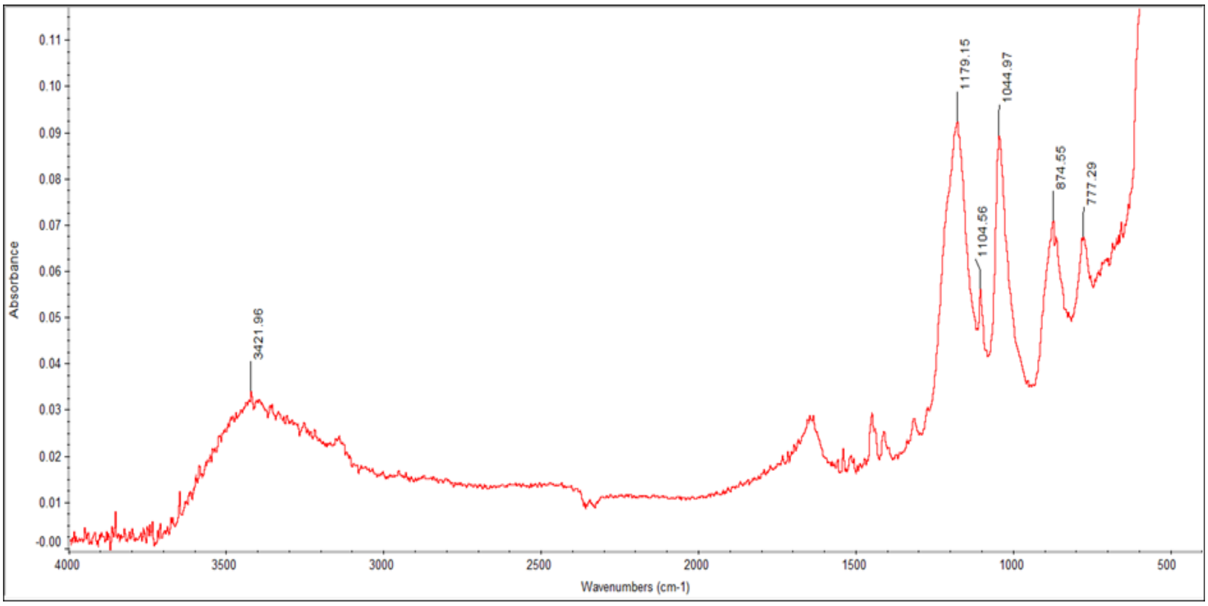


Figure 4-1: FTIR Transmittance Peak for 1-Methylpyrazolium Methylsulphate.

4.3 Characterization of pyrazolium-based ionic liquid by using CHNOS

The ionic liquid was undergone a CNOS testing to check the percentage of Carbon, Nitrogen, Oxygen and Sulphur that is present in the ionic liquid. The ionic liquid was sent to University Malaysia Pahang (UMP) Central Laboratory to obtain the results. The time duration was 1 week for the result. From the data obtained it was found out that there was presence of sulphur in the ionic liquid. The (ILs) consists of Nitrogen by 11.37%, Carbon by 15.84%, Hydrogen by 6.729%, Sulphur by 11.185% and rest of the composition is Oxygen by 54.876%. The result obtained will be comparing theoretically with the structure formula of (ILs) as shown in Table 4-2. The pyrazolium structure consists of C_3H_5 N_2 and Methyl with CH_3. While, the Methylsulphate consists of

CH_3SO_4. From the calculation, the percentage composition of Nitrogen, Carbon, Hydrogen, Sulphur and Oxygen are 14.36%, 30.77%, 5.64%, 16.41% and 32.82% respectively. There is nothing differences between the both experimental and theoretically calculated results. It shows that the experimental results obtained from the UMP Central Laboratory is fare and no other impurities in the (ILs). The percentage from both results can be seen in Table 4-2.

Table 4-2: The data for calculated component's ratio in the ionic liquid (ILs) molecular structure.

Components	MW (g/mol)	Percentage Yield (%)	Percentage Yield/MW	Ratio	Simplest ratio
Carbon	12.0107	30.77	2.5619	5.0057	5
Nitrogen	14.0067	14.36	1.0252	2.0031	2
Hydrogen	1.00794	5.64	5.5956	10.9332	11
Sulphur	32.065	16.41	0.5118	1.0000	1
Oxygen	15.9994	32.82	2.0513	4.0080	4

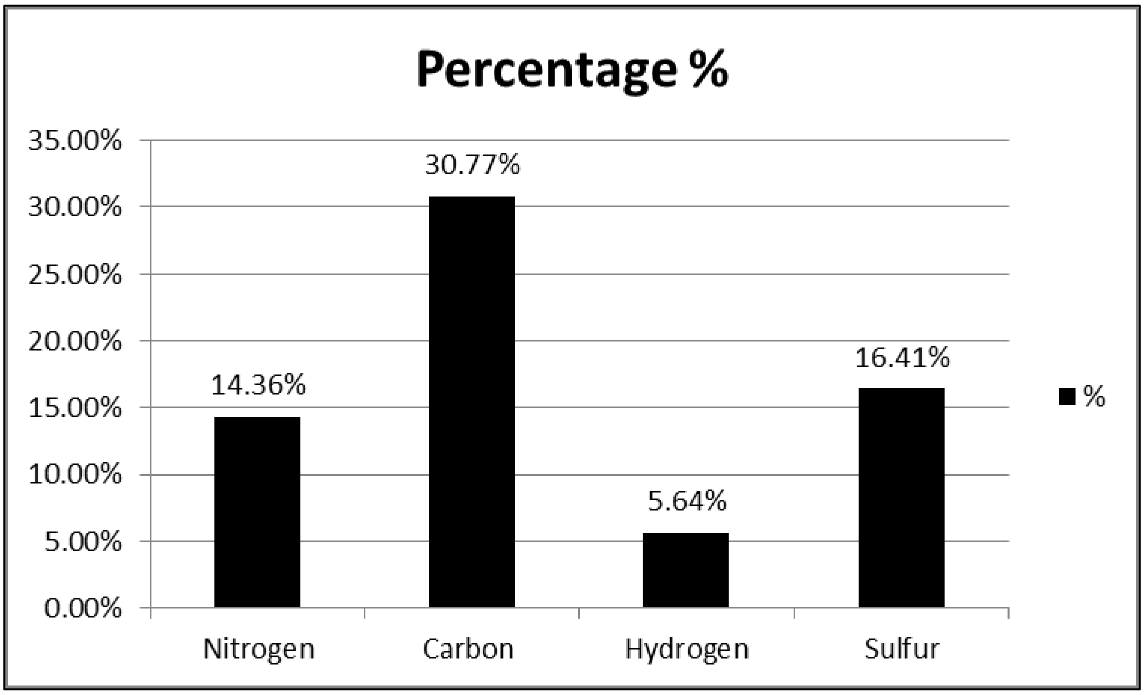


Figure 4-2: From CHNS result, percentages yield (%) for each component in the 1-Methylpyrazolium Methylsulphate.

4.4 Influence of (ILs) to Model Oil Volume Ratio on the Percentage of DBT Content Remover

The percentage of DBT removal can be calculated and illustrated in the below figure.

Table 4-3: Efficiency of ionic liquid (ILs) to Model Oil Volume Ratio on DBT Content Removal with DBT concentrations.

DBT concentrations (ppm)	**Sulphur removal (%)**
250	-56.8425
500	95.9942
800	96.8542
1000	97.5670
1421	66.3264

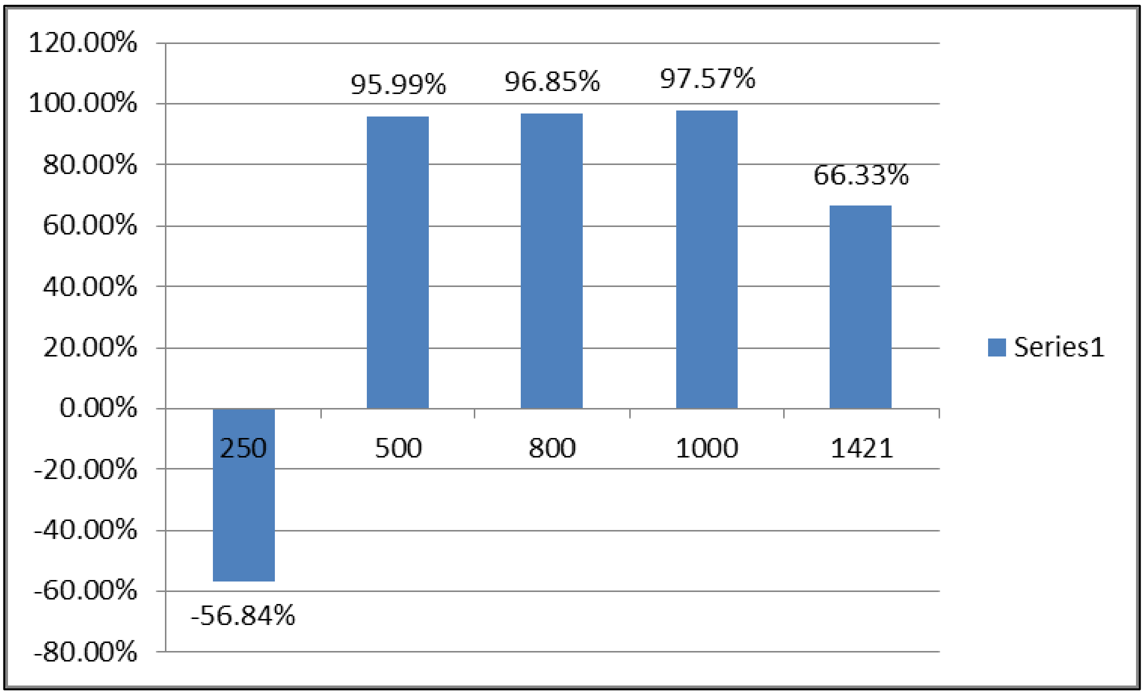


Figure 4-3: Influence of ionic liquid (ILs) to model oil ratio on percentage removal of DBT.

Based on figure 4-3, the relationship between (ILs) to model oil volume ratio is directly proportional at DBT concentrations are 500 ppm, 800 ppm and 1000 ppm respectively. For the initial DBT concentrations give the negative result which means that at 250 ppm of DBT concentrations there was no removal of sulphur content. While, at 1421 ppm give the decreasing value about 67% and clearly out from the Sulphur removal increasing order. It shows that, the highest percent DBT removal at 1:1 which is 97.5670 % and almost reaches 100 % for completely removed from the process. It also not good for commercial desulfurization process because of the ratio is 1:1 that same volume of the IL and model oil. The investment was very high as many as volumes ionic liquid (ILs) were used. It was deemed uneconomic for practical application in the industry. Similar experimental result were published by other researchers, where increasing the ionic liquid (ILs) model oil volume ratio would result in the increasing of desulfurization efficiency (Chu. X.M et al, 2008).

6 CONCLUSION

6.1 Conclusion

The ionic liquid has a unique characteristic that has been seen as one of the potential method to remove sulphur compound in the model oil. Before the ionic liquid was used in this research, it must undergo a characterization process by FTIR and CHNOS testing. It is to know the chemical compound or the functional group that present in the ionic liquid. By this research, 1-Methylpyrazolium Methylsulphate was used as an ionic liquid to removed sulphur content in the model oil. From the FTIR analysis, it show that the aimed product 1-Methylpyrazolium Methylsulphate. From the result of HPLC analysis, we could assume that the desulfurization efficiency increase when its volume ratio was increased, however the increasing of desulphurization of efficiency was decreasing at high ratio of (ILs) to volume of model oil. Therefore, it was obviously less efficient if we tried to increased desulphurization efficiency by increasing the (ILs) to model oil volume ratio. The higher efficiency of removal sulphur by using 1:1 volume ratio was at 1000 ppm of DBT which is almost 98% then 800 ppm of DBT which is almost 97%, 500ppm of DBT which is almost 96%. While at 250 ppm there is no completely removal of sulphur. This problem occurs due to the activity shaking the vial's samples in an incubator shaker for long duration of time. The samples maybe evaporated to the atmosphere and affect the results.

6.2 Future work

For the similar research, some modifications and recommendations will be suggested. Firstly, the right selection of ionic liquid that used for extraction. In the future, the ionic liquids can reusability without regeneration. The selected ionic liquids was able to extract dibenzothiophene, DBT from the model oil even without regeneration, however, at lower efficiency. The desulfurization efficiency of selected ionic liquids could also be calculated from its partition coefficient (Man Zakaria et al, 2012). The effectiveness of the ionic liquid also could be improved by increasing the extraction time and also the rpm stirring effect in order to ensure sulphur is highly extracted from the model oil. The experimental works should also be done in the fume chamber due to the properties of the xylene. Xylene was easy to evaporate to the atmosphere when exposed. This problem will affect the sulphur removal efficiency results.

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6.5 APPENDICES

APPENDIX A

1. Calculation for total sulphur in DBT content

$$ppm = \frac{mass\ of\ solute\ (g)}{mass\ of\ solute\ \&\ Solvent\ (g)}$$

$$= \frac{1mg}{L}$$

Molecular Weight (g/mol)	
DBT	184.26
Sulphur	32.065

$$\frac{x\ ppm\ \ S}{250ppm\ DBT} = \frac{32.065\ g/mol}{184.26\ g/mol}$$

$$\frac{x\ ppm\ \ S}{500ppm\ DBT} = \frac{32.065\,\frac{g}{mol}}{184.26\,\frac{g}{mol}}$$

$$\frac{x\ ppm\ \ S}{800ppm\ DBT} = \frac{32.065\ g/mol}{184.26\ g/mol}$$

$$\frac{x\ ppm\ \ S}{1000ppm\ DBT} = \frac{32.065\ g/mol}{184.26\ g/mol}$$

$$\frac{x\ ppm\ \ S}{1421ppm\ DBT} = \frac{32.065\ g/mol}{184.26\ g/mol}$$

DBT (ppm)	Total Sulfur (ppm)
250	43.5
500	87.0
800	139.2
1000	174.0
1421	247.254

2. Calculation for dilution

   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

a) $M_1V_1 = M_2V_2$

$$(1421\ ppm)(20\ mL) = (1000\ ppm)V_2$$

$$V_2 = 28.42\ mL$$

b) $(1000\ ppm)(15\ mL) = (800\ ppm)V_2$

$$V_2 = 18.75\ mL$$

c) $(800\ ppm)(10\ mL) = (500\ ppm)V_2$

$$V_2 = 16.00\ mL$$

d) $(500\ ppm)(5\ mL) = (250\ ppm)V_2$

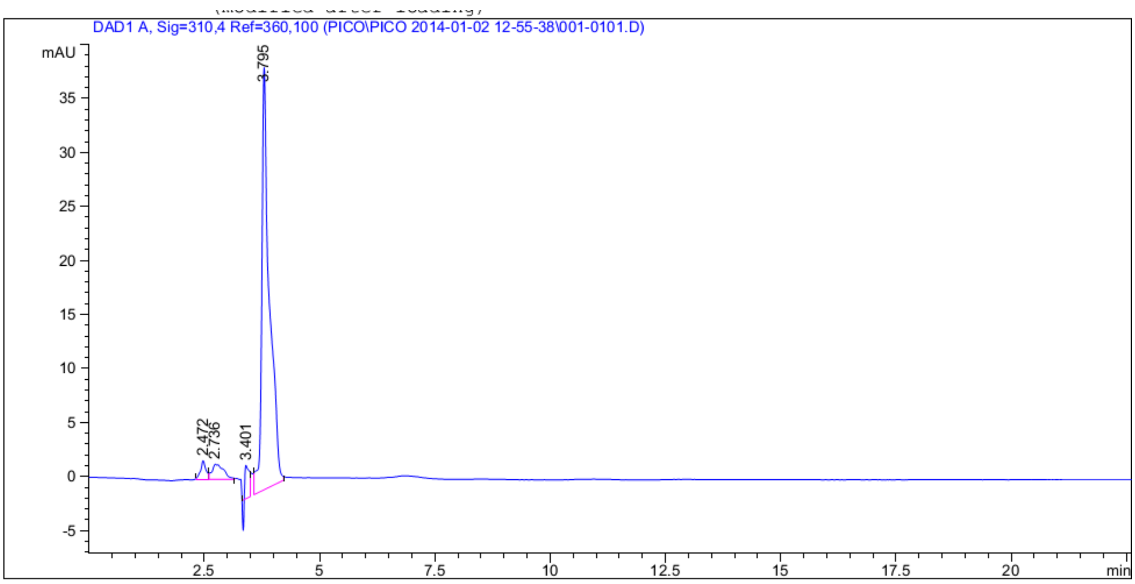
$$V_2 = 10.00\ mL$$

1) $30\ ml\ feedstock$
2) $28.42\ ml(DBT + xylene) + 20\ ml(Ionic\ LIquid) = 48.42\ ml$
3) $18.75\ ml(DBT + xylene) + 15\ ml(Ionic\ Liquid) = 33.75\ ml$
4) $16\ ml(DBT + xylene) + 10\ ml(Ionic\ Liquid) = 26.00\ ml$
5) $10\ ml(DBT + xylene) + 5\ ml(Ionic\ Liquid) = 15\ ml$

APPENDIX B

1. Analysis data from HPLC (Standard Calibration Curve)

   a) Standard for 250 ppm



Area Percent Report

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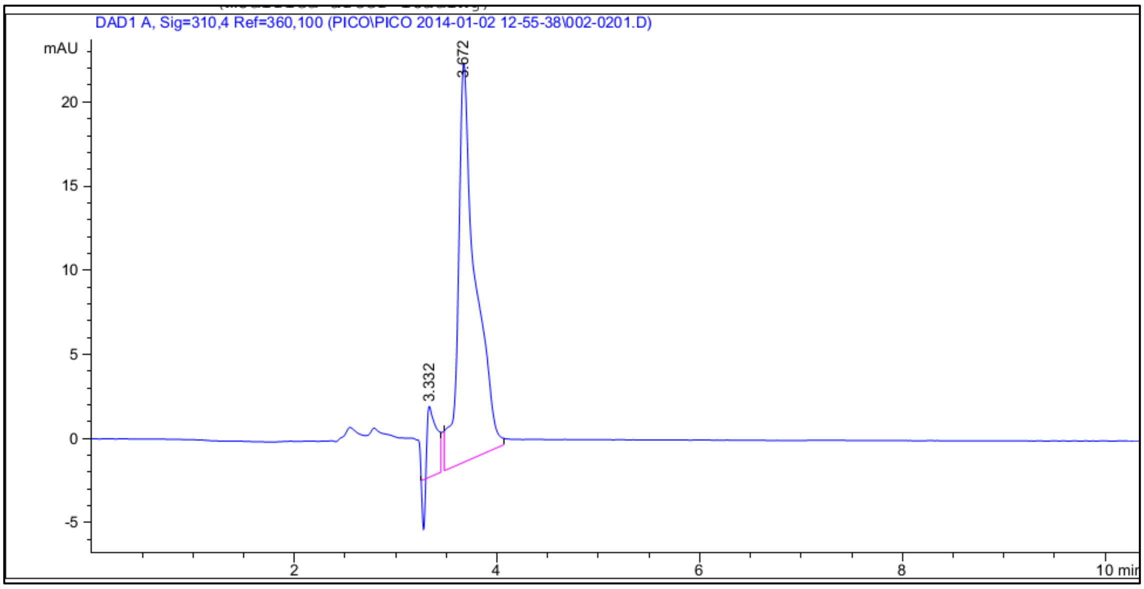
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=310,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	2.472	BV	0.1099	14.09901	2.8133	?
2	2.736	VB	0.2266	25.04290	4.9971	?
3	3.401	BB	0.0676	14.24592	2.8426	
4	3.663		0.0000	0.00000	0.0000	
5	3.795	BB	0.1576	447.76443	89.3470	?

Totals : 501.15227

b) Standard for 500 ppm

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                         Area Percent Report
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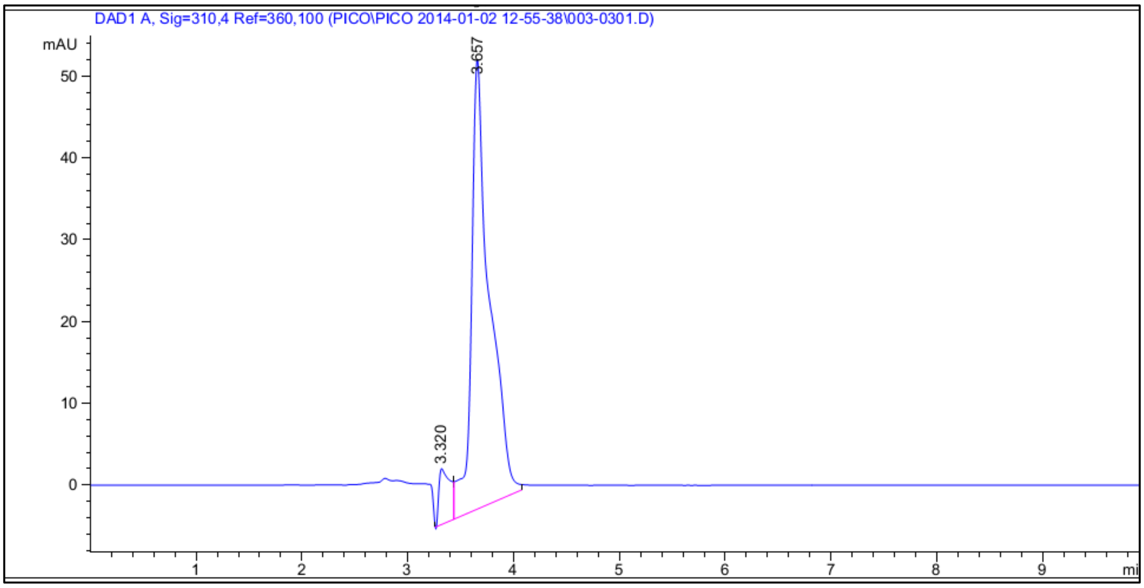
Multiplier:                          :        1.0000
Dilution:                            :        1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=310,4 Ref=360,100

Peak RetTime  Type   Width      Area       Area     Name
  #   [min]          [min]    [mAU*s]       %
----|-------|------|-------|----------|--------|---------------
   1    3.332 BB      0.0755   22.26496   7.4318
   2    3.672 BB      0.1584  277.32532  92.5682

Totals :                      299.59027
```

c) Standard for 800 ppm

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Sorted By              :      Signal
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Multiplier:                       :       1.0000
Dilution:                         :       1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=310,4 Ref=360,100

Peak RetTime  Type   Width     Area       Area     Name
  #    [min]          [min]    [mAU*s]      %
----|-------|------|-------|----------|--------|--------------
   1   3.320 BV      0.0988   49.75163   7.0678
   2   3.657 VB      0.1627  654.16473  92.9322

Totals :                     703.91636
```
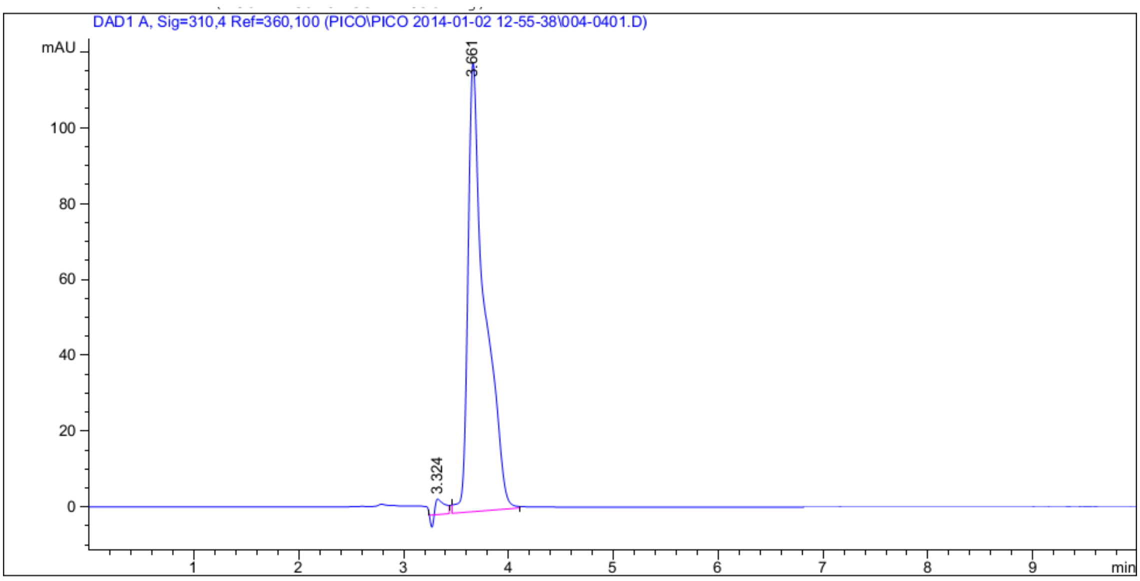

d) Standard for 1000 ppm

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=====================================================================
                        Area Percent Report
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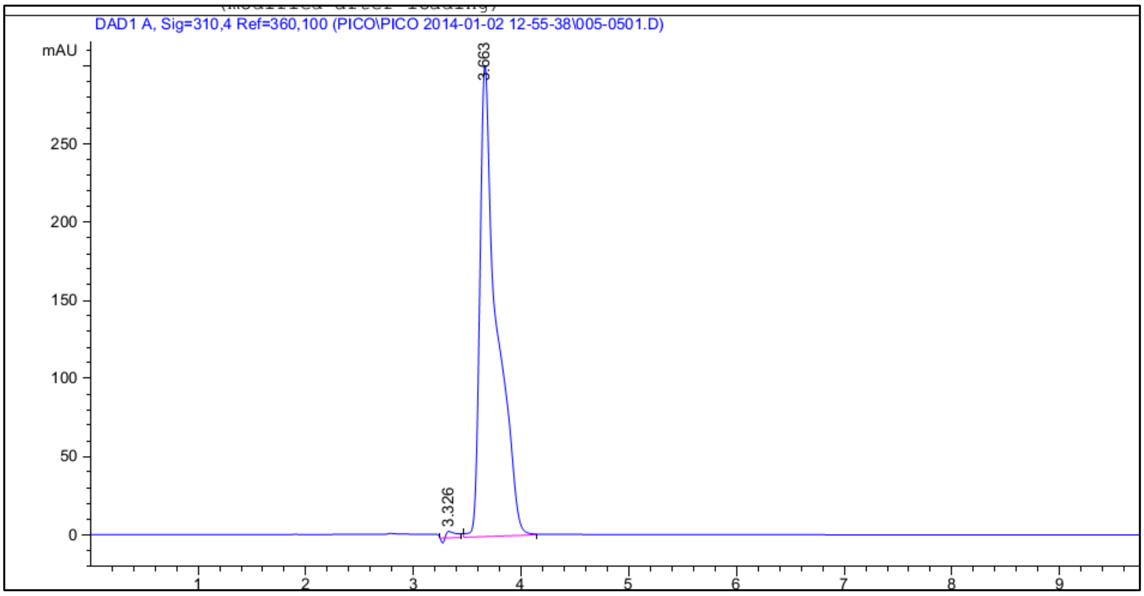
Sorted By             :      Signal
Calib. Data Modified  :      1/3/2014 4:20:52 PM
Multiplier:                    :       1.0000
Dilution:                      :       1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=310,4 Ref=360,100

Peak RetTime  Type   Width     Area      Area    Name
  #    [min]         [min]   [mAU*s]       %
----|-------|------|-------|----------|--------|--------------
   1   3.324 BB      0.0686   19.24443   1.4501
   2   3.661 BB      0.1528 1307.88403  98.5499

Totals :                    1327.12846
```

e) Standard for 1421 ppm

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                         Area Percent Report
=====================================================================

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Multiplier:                    :       1.0000
Dilution:                      :       1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=310,4 Ref=360,100

Peak RetTime  Type   Width     Area      Area    Name
  #   [min]          [min]   [mAU*s]      %
----|-------|------|-------|----------|--------|----------------
   1   3.326 BB      0.0741   20.67863   0.6260
   2   3.663 BB      0.1506 3282.39136  99.3740

Totals :                    3303.06999
```
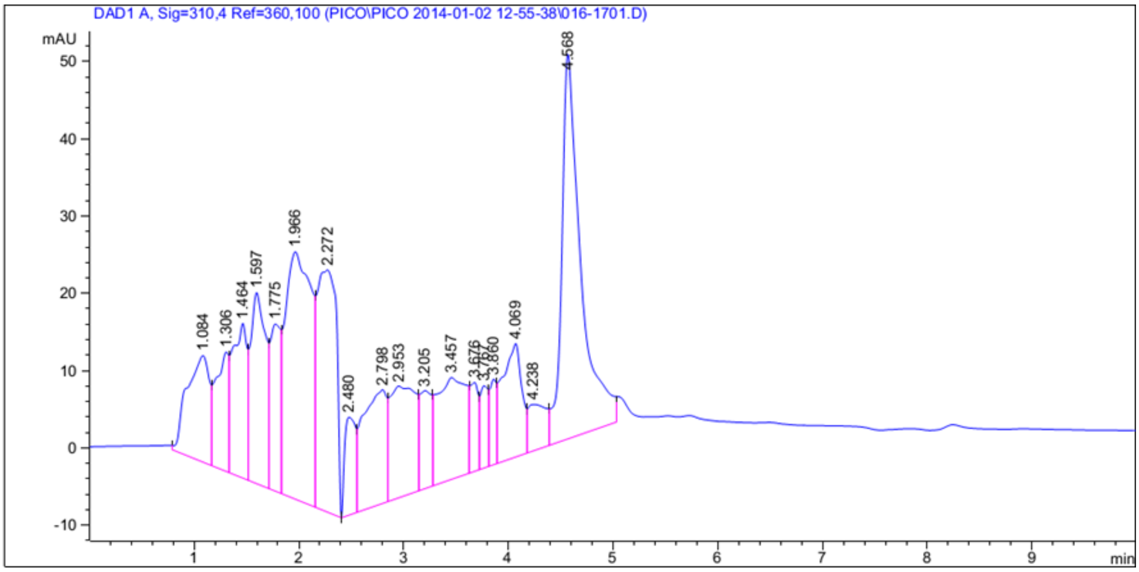

2. Ionic liquid (ILs) : Model oil volume ratio (1:1)

a) 250 ppm



Area Percent Report

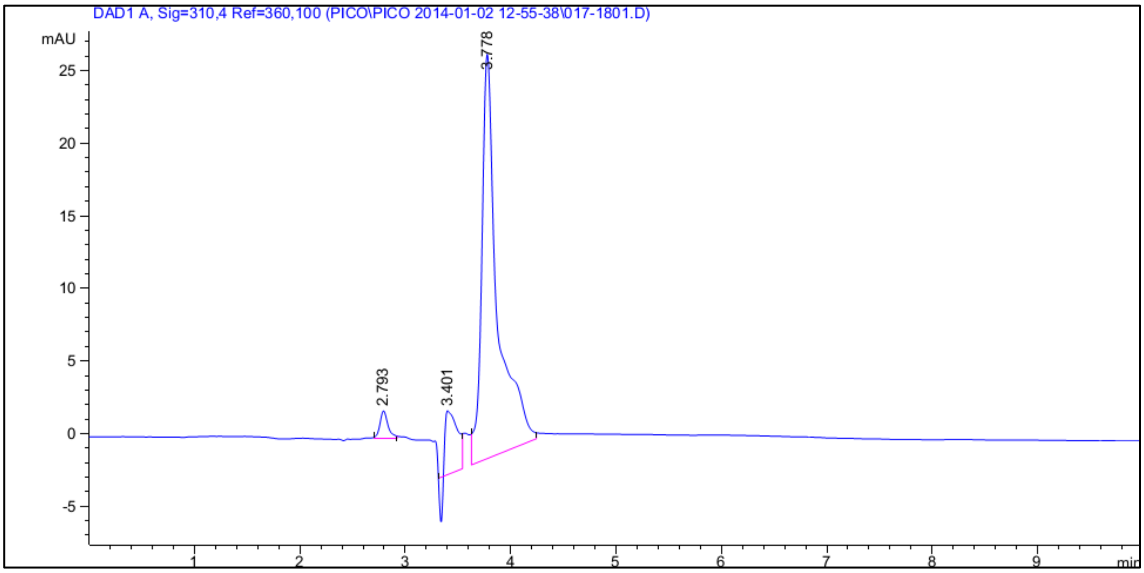
Sorted By : Signal
Calib. Data Modified : 1/3/2014 4:20:52 PM
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=310,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	1.084	BV	0.1947	199.11159	5.1782	?
2	1.306	VV	0.1120	129.90892	3.3785	?
3	1.464	VV	0.1250	190.57625	4.9562	?
4	1.597	VV	0.1359	249.88441	6.4986	?
5	1.775	VV	0.1004	149.06306	3.8766	?
6	1.966	VV	0.2368	551.24872	14.3360	?
7	2.272	VV	0.1669	394.76724	10.2664	?
8	2.480	VV	0.1078	90.86802	2.3631	?
9	2.798	VV	0.1981	234.95145	6.1102	?
10	2.953	VV	0.2138	242.42694	6.3046	?
11	3.205	VV	0.1059	99.84532	2.5966	?

12	3.326		0.0000	0.00000	0.0000	
13	3.457	VV	0.2407	251.74063	6.5469	?
14	3.676	VV	0.0771	64.25382	1.6710	
15	3.767	VV	0.0788	55.54115	1.4444	?
16	3.860	VV	0.0614	48.74500	1.2677	?
17	4.069	VV	0.1684	192.12447	4.9965	?
18	4.238	VV	0.1747	70.37602	1.8302	?
19	4.568	VB	0.1714	629.78394	16.3784	?
Totals :				3845.21695		

b) 500 ppm



Area Percent Report

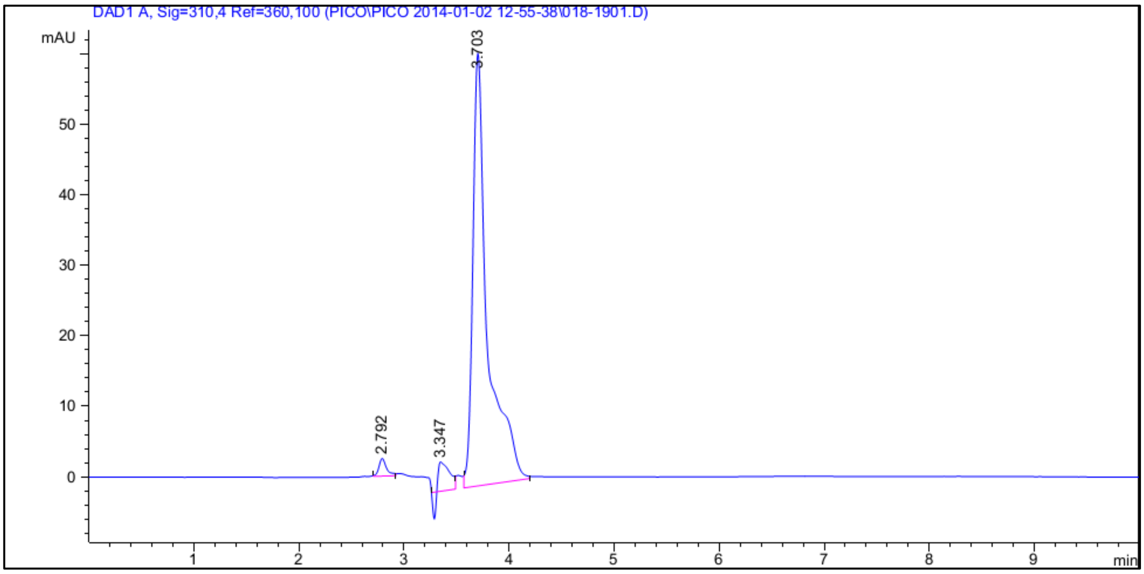
Sorted By : Signal
Calib. Data Modified : 1/3/2014 4:20:52 PM
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=310,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	2.793	BB	0.0785	10.17060	3.0828	?
2	3.401	BB	0.0956	30.02704	9.1013	
3	3.663		0.0000	0.00000	0.0000	
4	3.778	BB	0.1473	289.72159	87.8159	?

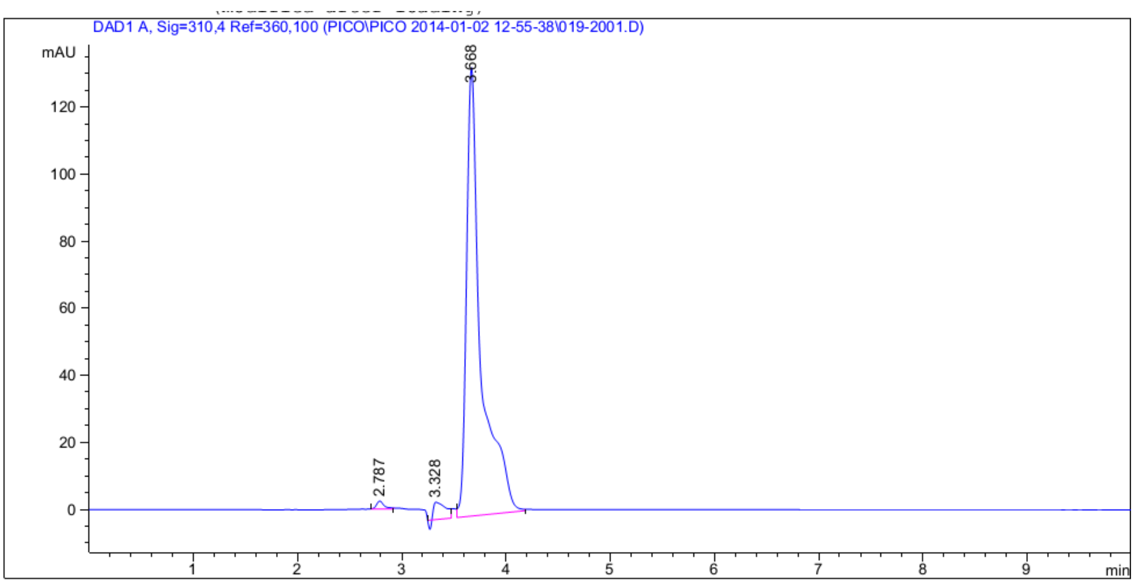
Totals : 329.91924

c) 800 ppm



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By                   :      Signal
Calib. Data Modified        :      1/3/2014 4:20:52 PM
Multiplier:                         :       1.0000
Dilution:                           :       1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=310,4 Ref=360,100

Peak RetTime  Type   Width      Area       Area     Name
  #    [min]         [min]    [mAU*s]        %
----|-------|------|-------|----------|--------|------
   1   2.792 BB      0.0755   12.77940   2.0065 ?
   2   3.347 BB      0.0800   23.56490   3.7000
   3   3.703 BB      0.1400  600.55103  94.2935

Totals :                     636.89532
```

d) 1000 ppm



Area Percent Report

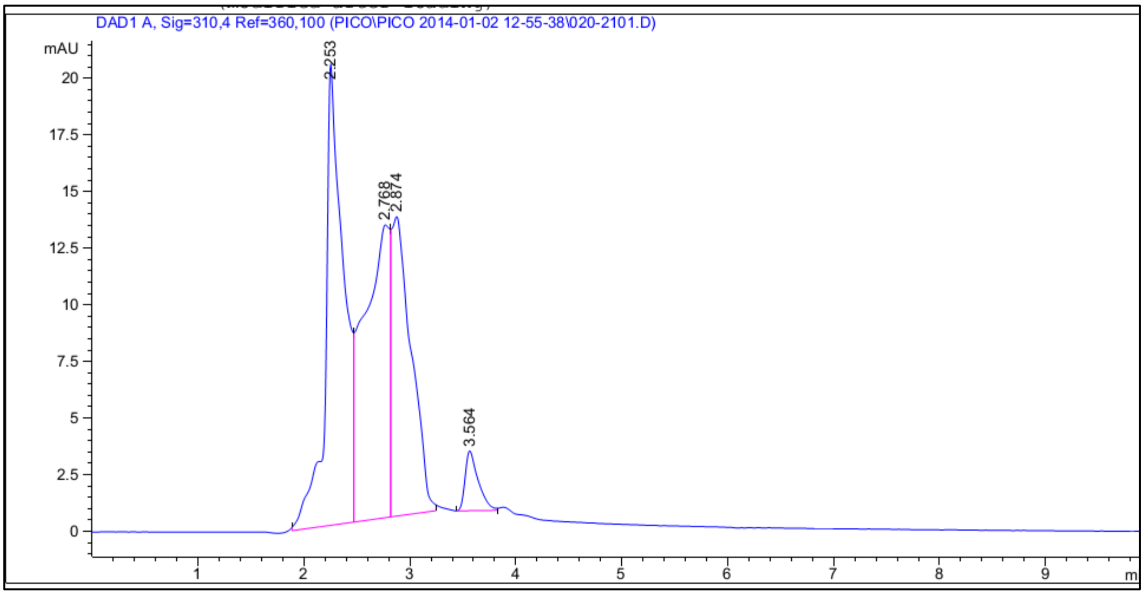
Sorted By : Signal
Calib. Data Modified : 1/3/2014 4:20:52 PM
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=310,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	2.787	BB	0.0761	12.35471	0.9203	?
2	3.328	BB	0.0983	37.71119	2.8092	
3	3.668	BB	0.1367	1292.34570	96.2705	

Totals : 1342.41160

e) 1421 ppm



Area Percent Report

Sorted By : Signal
Calib. Data Modified : 1/3/2014 4:20:52 PM
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=310,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	2.253	BV	0.1531	242.98294	37.1538	?
2	2.768	VV	0.2162	217.38414	33.2395	?
3	2.874	VB	0.1667	170.88319	26.1292	?
4	3.326		0.0000	0.00000	0.0000	
5	3.564	BB	0.1245	22.74264	3.4775	?
6	3.663		0.0000	0.00000	0.0000	
Totals :				653.99291		

APPENDIX C

a) CHNOS calculation

Molecular formula of (ILs): C5H11N2SO4

Molecular weight of components:

Components	MW (g/mol)	Percentage Yield (%)	Percentage Yield/MW	Ratio	Simplest ratio
Carbon	12.0107	30.77	2.5619	5.0057	5
Nitrogen	14.0067	14.36	1.0252	2.0031	2
Hydrogen	1.00794	5.64	5.5956	10.9332	11
Sulphur	32.065	16.41	0.5118	1.0000	1
Oxygen	15.9994	32.82	2.0513	4.0080	4

Percentage Yield/ MW: The calculation to be done and select the lowest value among these 5 components to find their simplest ratio. After that, the stoichiometry of each component in the ionic liquid is compared with the stoichiometry calculated.

Example: Carbon

$$= \frac{percentage\ yield\ (\%)}{Molecular\ weight\ (\frac{g}{mol})}$$

$$= \frac{30.77}{12.0107\ (\frac{g}{mol})}$$

$$= 2.5619$$

From the calculation, Sulphur has the lowest value (Percentage yield/ MW) with 0.5518

$$\frac{2.5619}{0.5518}$$

$$= 5.0057$$

$$The\ simplest\ ratio : 5$$