EXTRACTION OF DIBENZOTHIOPHENE FROM MODEL OIL USING IONIC LIQUIDS

KENRICK BILONG PIUS

BACHELOR OF CHEMICAL ENGINEERING (GAS TECHNOLOGY)
UNIVERSITI MALAYSIA PAHANG

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 SYAMSUL BAHARI BIN ABDULLAH

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

EXTRACTION OF DIBENZOTHIOPHENE FROM MODEL OIL USING IONIC LIQUIDS

KENRICK BILONG PIUS

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

BACHELOR OF CHEMICAL ENGINEERING (GAS TECHNOLOGY)
UNIVERSITI MALAYSIA PAHANG

JANUARY 2014

SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and in my 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 BIN ABDULLAH
Position : LECTURER
Date : JANUARY 2014

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 : KENRICK BILONG PIUS
ID Number : KC10023
Date : JANUARY 2013

Dedication

To my supervisor, lecturers, staff, parents and friends

ACKNOWLEDGEMENT

I would like to thanks the following people and organisations;

- My supervisors Dr.Syamsul Bahari bin Abdullah for his guidance through an effective well-arranged weekly meeting.
- Faculty of Chemical Engineering for helping throughout the thesis duration.

ABSTRACT

Diesel fuel in contrast has many benefits in our daily lives, which is use to power up vehicles and heavy machineries. Besides that, from the usage of diesel, it will produce sulfur when combustion is involved. Currently, Malaysia is making its effort to reach the sulfur target of 50 ppm as implemented by the Euro IV standards. Sulfur is very harmful towards humans, animals, machines and the environment. Sulfur contributes to air pollution by creating acid rains; in conjunction to machineries, it will corrode the equipment from the inside and thus reducing its effectiveness and requires a high cost to repair and maintenance. In this research, a sulfur compound called dibenzothiophene (DBT) is chosen as the study case. The objective of this research is to determine whether dibenzothiophene (DBT) can be extract or remove from model oil of n-hexane using an ionic liquid. The ionic liquid that is to be used is 1-methylpyrazolium ethyl sulphate $C_6H_{13}N_2O_4S$. The ionic liquid is to be tested on a model oil of n-hexane to check its sulfur removal efficiency. A Fourier Transform Infrared Spectroscopy (FTIR) is conducted on the ionic liquid to check its content and an Infra-Red (IR) absorptions classification according to the wavelength is obtained to determine their functional groups. Next, the ionic liquid is tested on a Carbon Hydrogen Nitrogen and Sulfur (CHNS) analysis, to check its sulfur content. From the CHNS analysis, a manual calculation is to be done to check the molecular formula and compare it with the existing molecular formula, $C_6H_{13}N_2O_4S$. On top of that, a High Performance Liquid Chromatography (HPLC) analysis is conducted. A series of concentration for standard sample and sample is prepared. The samples consist of concentration in the range of 1500ppm to 250ppm. For the standard sample, the model oil of n-hexane is mixed with dibenzothiophene (DBT) is analyse and a calibration curve is plotted. For the sample, the ionic liquid is mixed with the model oil and dibenzothiophene (DBT) is analyse. From the data obtained it is then compared with the calibration curve and the sulfur removal efficiency is calculated. A bar chart for each of the concentration was plotted. From the result, it was found out that the sulfur removal is highly efficient at concentration of 1500ppm with 90.98%. In return of this work, perhaps a further research on diesel using ionic liquid will be conducted.

Key words: ionic liquid, extraction of sulfur, model oil, DBT

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1 INTRODUCTION

1.1 Motivation and statement of problem

The implementation of the revised law of clean air in USA has brought stricter limitation on sulfur content in petroleum products. The sulfur contents in new formula gasoline and clean diesel oil are required to be no higher than 100 and 500 mg/kg, respectively. Sulphur content will be reduced from the current 3000ppm standard to a new standard of a maximum of 50ppm. The sulphur content for Euro IV has been set at 50 ppm. Euro IV is an EU emission standard that was introduced in January 2005. The standard limits car emissions to 0.25g/km of NOx (nitrogen oxides) and 0.02 g/km of PM (particulate matter). In order to meet Euro IV requirements, the country's refineries will have to upgrade their hydrotreatment units, to further remove sulphur from the fuel stream. All refineries are said to have now started the upgrading process. This shows that our country Malaysia putting an effort to reduce the emission of sulphur and help making earth a greener place to live in.

Diesel is a petroleum-based fuel that is used to empower many types of heavy vehicles and boats for transportation and many others in our daily lives. Diesel is made out of a blend of crude oil components which are hydrocarbons. Diesel are refined out of crude oil, usually by fractionate distillation. Diesel contains sulfur as part of their chemical makeup. However, sulfur is a compound that is poisonous to human. Sulfuric acid, as an example, is produced when sulfur combines with water vapor formed during the combustion process, where some of this corrosive compound is emitted into the atmosphere through the exhaust. Sulfuric acid is a major environmental pollutant, coming back to earth in contaminated rainwater. Besides that, in a study by McElroy et al. (2003), they studied that the sulfur speciation in diesel is an important task because sulphur-containing compounds create problems in poisoning of catalysts in refining; corrosion of pipelines, vessels, as well as engines.

Ionic liquid are materials that are composed solely of anions and cations. According to Yu-xin and Yong (2005), they conclude that the ionic liquids have been studied for possible applications related to green chemical processes, such as liquid/liquid extractions, gas separations, electro- chemistry and catalysis. In this research, they found out many advantages in applying an ionic liquid in their chemical process.

Besides that, they found out that ionic liquids are easy to handle because of nonvolatility, nonflammability, and high thermal stability. Hence, they pose little environmental harm which is very beneficial towards industrial processes.

In this research, the removal of sulphur compounds in model oil of n-hexane is studied using 1-methylpyrazolium ethyl sulphate $C_6H_{13}N_2O_4S$ as the ionic liquid.

1.2 Objectives

In this experiment, the objective is to determine the sulfur removal efficiency of dibenzothiophene in model oil of n-hexane using ionic liquid of 1-methylpyrazolium ethyl sulphate $C_6H_{13}N_2O_4S$.

1.3 Scope of this research

In this experiment, there are a few elements to be tested.

- To extract dibenzothiophene using ionic liquid of 1-methylpyrazolium ethyl sulphate from model oil of n-hexane.
- To extract sulfur compounds from diesel using the ionic liquid.

1.4 Main contribution of this work

The following are the contributions of this work.

- It will help decrease air pollution on the environment.
- It will provide a valuable knowledge in making an effective ionic liquid to remove sulfur containing compounds.
- The ionic liquids is energy saving, time saving, and cost saving. It can be reuse and still have the effectiveness slightly as the first time used.

1.5 Organisation of this thesis

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

Chapter 2 is the literature review section which provides a brief description of the chemicals that will be using in this experiment. This section is the literature review which all the journal and all the citation will be. This section also describes the general view on diesel composition, dibenzothiophene, ionic liquid, and n-hexane. A brief

discussion on the journal is also provided. A summary on the journal will be discussed here.

Chapter 3 is the methodology part which all the procedure is stated step by step so that it is easy to be followed. A brief description on how the material and apparatus is obtained is discussed in that section.

Chapter 4 is the result part, where the result from the analysis is available here and will be further discussed in this section. The results will be compared with the results from all the journals to check whether it is valid.

Chapter 5 is the combine of the summary of the thesis and future work that will be done. This section also discussed on what to be improved from this research.

2 LITERATURE REVIEW

2.1 Overview

This paper shows the experimental studies of ionic liquids on the removal of sulfur containing compound from diesel or model oil. From their research, the ionic liquid is made out of a myriad of ions such as chlorine, sodium, iron and so on. After the systhesis of the ionic liquid, the ionic liquid is then tested on model oil which has been premixed with a selected sulfur containing compound to observe and study the removal effectiveness of sulfur. After that, the ionic liquid is then tested on diesel to see the result, and then compare it with the model oil.

2.2 Diesel composition

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). Further study on diesel is done and a wide variety of sulfurcompunds was detected.

On the other hand, in a work presented by a number of researchers which was to determine sulfur compounds in diesel using Gas Chromatography (GC). In this work, it was known that a mixture of standard substances containing thiols, sulfides, 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 based on the removal of thiophenesulfide from diesel is done. In this research, the researchers agreed that the sulfur in the fuels are hazardous, which not only pollute environment but also corrode equipments. Therefore, sulfur removal from fuels becomes an increasing technical challenge in refinery industry. On top of that, the difficulty of sulfides removal is closed related to the sorts of sulfides. The active sulfides such as hydrogen sulfide and thiols are easy to remove, but nor to the inactive sulfides 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	**Sulfur (Max, ppm), Diesel**	**50ppm 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

Source : Asia-Pacific Petrol & Diesel Sulphur Matrix, 2012

Table 2.1 shows the sulfur content emission for selected Asia-Pacific country. It is known that some of the country has reached its target of 50ppm of sulfur content for diesel emission. The European Standard has named this target as Euro IV.

In another statement, whereby a study case done in the USA, a group of researcher found out that, a common problem that faces the refineries around the world is that the crude oils are getting worse and heavier with sulfur content getting higher. However,

sulphur emission is imposing an urgent requirement on refineries to reduce the sulfur content in the fuels they produce (Hua, et al. 2003).

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

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

* Abbreviations : MST, mercaptan, sulphide, and thiophene; BT, benzothiophene; and DBT, dibenzothiophene.

Source: Wang et al. 2003.

From Table 2-2, it is clearly stated that the sulfur compound in diesel is indeed exist. For this research, it is important to test an ionic liquid whether it is capable to remove or extract sulphur by evaluate it first on a model oil n-hexane which containing dibenzothiophene (DBT) as sulfur containing compound. By testing it on the model oil, it is to determine the effectiveness of the removal of sulfur. From the testing, it is then evaluated whether it can proceed on the real fuel such as diesel. This is to reduce the wastage of diesel because it is a non-renewable source.

2.3 1-Methylpyrazolium Ethyl Sulphate

This is the ionic liquid that will be using in this experiment. This ionic liquid is obtained from University Teknologi PETRONAS (UTP), due to the insufficient of chemical to synthesis the ionic liquid.

Table 2.3: Physical properties of 1-methylpyrazolium ethyl sulphate

Molecular formula	$C_6H_{13}N_2O_4S$
Molecular weight	209 g/mol
Physical state	Colourless Liquid
Melting point	167-169^oC
Solubility in water	Insoluble

Source: www.chemicalbook.com

From table 2.3, it shows a brief description on the physical properties of the ionic liquid. This ionic liquid is colourless liquid. It must be handle with care because the limited supply of ionic liquid.

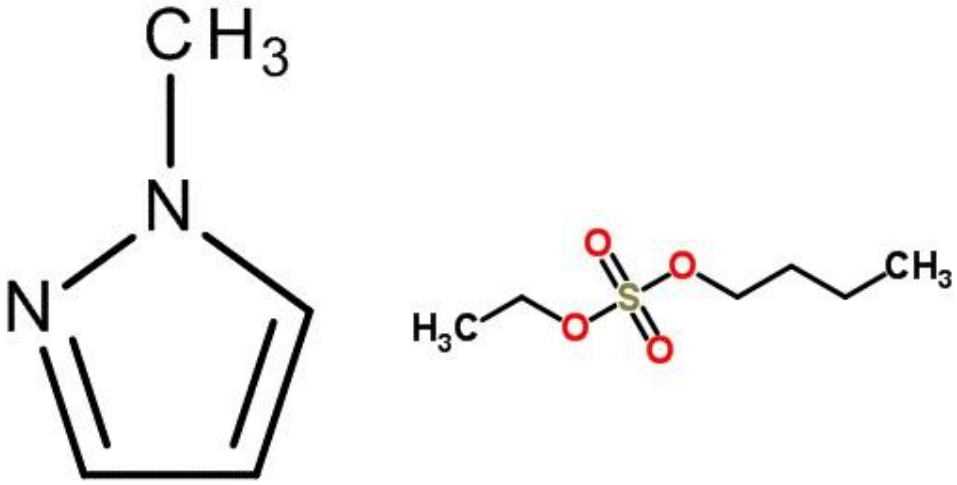


Figure 2.1: Molecular structure of 1-methylpyrazolium ethyl sulphate

2.4 Dibenzothiophene

Dibenzothiophene (DBT) is an organic sulfur compound that consists of two benzene ring and a sulfur ring in the middle. It is mostly available in a white powder form. DBT may cause eye irritation and skin irritation when handling, hence it is advisable to wear protective gear. It is also insoluble in water.

Table 2.4: Physical properties of dibenzothiophene

Molecular formula	$C_{12}H_8S$
Molecular weight	184.26 g/mol
Physical state	Crystalline powder
Density	1.252 g/cm^3
Melting point	97-100^{o}C
Boiling point	332-333^{o}C
Solubility in water	Soluble

Source: apps.wku.edu

Table 2.4 shows the physical properties of dibenzothiophene. From the source, it stated that DBT is prepared by the reaction of biphenyl with sulfur dichloride in the presence of aluminium trichloride. This sulfur compound is premixed with the ionic liquid to determine the sulfur removal efficiency of the ionic liquid.

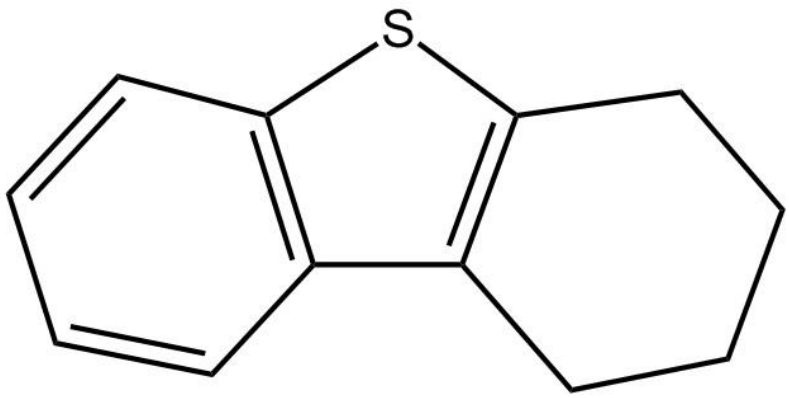


Figure 2.2: Molecular structure of dibenzothiophene

2.5 Thiophene

Thiophene, also known as thiofuran, is a cyclic compound containing four carbon atoms and one sulfur atom in the ring. Thiophene is an analog to furan and pyrrole where the sulfur atom is replaced by O and NH respectively. Thiophene is a toxic, flammable, and colorless liquid. It is also insoluble in water.

Table 2.5: Physical properties of thiophene

Molecular formula	C_4H_4S
Molecular weight	84.14
Physical state	Clear liquid
Melting point	-38^oc
Boiling point	$83\text{-}84^oc$
Specific gravity	1.06
Solubility in water	Insoluble

Source: www.chemical21.com

From table 2.5, it shows some of the physical properties of thiophene. From the source, it stated that thiophene is the simplest aromatic compound containing sulfur atom and it shares some similar chemical properties with benzene. The lone electron pairs on sulfur in the delocalized pi electron system does not exhibits the properties of thioethers but

aromaticity. The sulfur atom is unreactive but the adjacent carbons are susceptible to attack by electrophiles. It is reactive toward sulfonation. Most of the reseachers are using thiophene as their experimental sulfur compound.

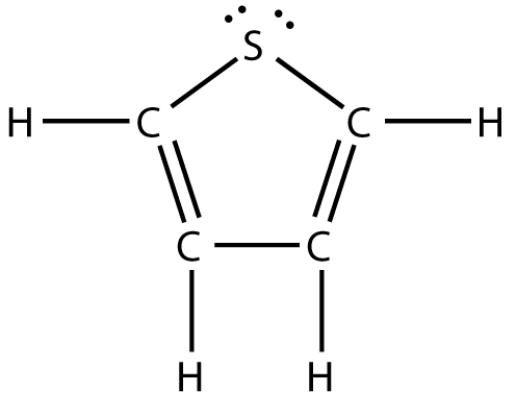


Figure 2.3: Molecular structure of thiophene

2.6 n-hexane

n-hexane is selected as the model oil in this research. This chemical, n-hexane has been chosen due to the availability and the low risk level when handling this chemical.

Table 2.6: Physical properties of n-hexane

Molecular formula	C_6H_{14}
Molecular weight	86.17536
Density	0.660 g/cm^3 at 20^{o}C
Boiling point	68.95^{o}C
Water solubility	Insoluble in water

Source: http://www.atsdr.cdc.gov

From Table 2.6, it shows some of the physical properties of n-hexane. N-hexane is a very volatile aliphatic hydrocarbon. N-hexane is colourless liquids at room temperature, odourless when pure. It is cheap, relatively safe, largely unreactive and easily evaporated.

Figure 2.4: Molecular structure of n-hexane

2.7 Ionic liquids for synthesising

Chemistry is dominated by the study of species in solution, for example, a liquid. Although any liquid may be used as a solvent, only a few of that liquid can be used. So far as we know, water is a general solvent. In a study done by a researcher, he found out that, some simple physical properties of the ionic liquids that make them interesting as potential solvents for synthesis are the following: Firstly, they are good solvents for a wide range of both inorganic and organic materials. Secondly, they are composed of poorly coordinating ions, so they have the potential to be highly polar. Thirdly, they are immiscible with some organic solvents and provide a nonaqueous, polar alternative for two-phase systems. For immiscible polar phases containing hydrophobic ionic liquids, it can also be used with water. Fourthly, they are nonvolatile, hence they may be used in

high-vacuum systems and eliminate many containment problems (Welton, 1999). Hence, it's safe to say that the synthesis ionic liquids can be used in this research.

Table 2.7: Modern ionic liquids

A salt	Cation and or anion quite large
Freezing point	Preferably below 100^{o}c
Liquid range	Often > 200^{o}c
Thermal stability	Usually high
Viscosity	Normally < 100 cP
Dielectric constant	Implied ≤ 30
Polarity	Moderate
Specific conductivity	Usually < 10mScm^{-1}, "Good"
Vapor pressure	Usually negligible

Source : Welton, 1999.

From table 2.7, shows the properties of some selected modern ionic liquids. It is known that ionic liquid exhibits a good quality and safe chemical when synthesising.

The application of ionic liquids in synthesis and catalysis are widely used nowadays. In a research done by a researcher, he found several factors that ionic liquids is better than conventional liquids which are, firstly, synthetic chemists are limited by the available molecular solvents in which they can conduct chemistry. Secondly, most of the solvents chemists like to use are banned by international protocols determined to reduce pollution, of which volatile organic compounds represent a significant part. Thirdly, the discovery of new chemistry or the ability to design a solvent that allows a specific reaction to occur (Wasserscheid and Welton, 2008). Hence, the reason he stated above

maybe because fact that ionic liquids are perceived as “green” material which do not pollute the environment.

2.8 Experimental works on ionic liquid

In this section, this paper presents a myriad of experimental works of ionic liquids on the removal of sulfur content in some compound. In a work done on sulfur removal from fuels using ionic liquids, the researchers uses 3 ionic liquids which were 1-Ethyl-3-Methylimidazolium Tetrafluoroborate ($EMIM^+$-$BF4^-$), 1-Butyl-3-Methylhexfluorophosphate ($BMIM^+$-$PF6^-$) and 1-Butyl-3-Methylimidazolium Tetrafluoroborate ($BMIM^+$-$BF4^-$). In the used ionic liquids, the molar ratio of thiophene to ionic liquid was found to be 0.86/1, 3.5/1 and 2.2/1 for $EMIM^+$-$BF4^-$, $BMIM^+$-$PF6^-$, $BMIM^+$-$BF4^-$. It was found out that for a specific aromatic compound, for example thiophene, $BMIM^+$-$PF6^-$ and $BMIM^+$-$BF4^-$ have higher absorption capacities than $EMIM^+$-$BF4^-$.The results suggest that the structure and the size of both cation and anion of an ionic liquid affect absorption. The local structure of the ionic liquids appears to have a significant effect on their interaction with the aromatic compounds (Zhang and Zhang, 2002).

In another interesting study, several researchers have conducted an experiment on the enhanced oxidative desulfurization of model fuels using a film-shear reactor. The researchers uses benzothiophene in decane, it was found out that 53% of the benzothiophene was removed from the model fuel in only 80s at 10^oc using the film-shear reactor. It was then conclude that the application of a film-shear reactor provides a remarkable enhancement in the efficiency of the ODS process compared to normal stirring. Experiments reported here demonstrate that the amount of benzothiophene in a model fuel can be rapidly reduced (Fox et al. 2011).

In another findings by some researcher on the extraction of nitrogen and sulfur containing air pollutants from model oil. They studied on do-decane and pyridine, it was found out that the effect of the ionic liquid-to-oil ratio, and the extraction capacity improved as the ratio of IL-to-oil was increased for pyridine. Besides that, the extraction of sulfur compounds from the model oil demonstrated that the concentration of the S-compound in the model oil was reduced by 99% after a completed extraction. This result demonstrated that the extraction of dibenzothiophene from the model oil, with 1-

ethyl-3-methylimidazolium chloride ([C2 mim] [Cl]) was successful (Anugwom et al. 2011).

There was also another study on desulfurization using ionic liquids by several researchers, where $FeCl_3$ [Iron (III) Chloride], was chosen to check its sulfur removal efficiency on n-dodecane. From their research, they conclude that $FeCl_3$ showed the better sulfur removal efficiency than other ionic liquids. This experiment clearly demonstrates that the extraction ability of [Bmim]Cl/FeCl3 is suitable in comparison with the other ionic liquids. It was also found that the extraction process went on quickly. It has the effectiveness of 75.6%. In general FeCl3 alone exhibited lower extraction ability than the Fe-containing ILs, signifying the important role of [Bmim]Cl (Dharaskar et al. 2013).

Besides that, in a recent study on desulfurization of fuels using ionic liquid based on $FeCl_3$ [Iron (III) Chloride], the researchers uses 10 types of Lewis acid ionic liquids. 3 of the 10 types of the ionic liquids use were [BMIM]Cl/$FeCl_3$ (BMIM: 1-Butyl-3-Methylimidazolium), [OMIM]Cl/$FeCl_3$ (OMIM: 1-Octyl-3-Methylimidazolium), T_8Cl/$FeCl_3$ (T_8Cl: Tri-Octyl Methyl Ammonium Chloride). In the study on extraction of dibenzothiophenes (DBT) in n-Octane, it was found out that [BMIM]Cl/$FeCl_3$ yield the highest extractive performance for DBT which was 67.6%. By comparing it to the other 10 types of ionic liquid, the use of $FeCl_3$ shows promising extraction rather than using $ZnCl_2$ [Zinc Chloride], $MnCl_2$ [Manganese (II) Chloride] and etc. On top of that, Fe-IL system shows considerable promise for providing a future needs for low sulfur diesel (Wang et al. 2008).

In an another research on the removal of 4,6- dimethyldibenzothiophene (DMDBT), the researchers tested the work on n-dodecane and formaldehyde vapour as reactive adsorbent. It was found that the desulfurization efficiency increased when the temperature ranged from 50°C to 80°C. The presence of formaldehyde caused 100% removal of 4,6-DMDBT in 90 min at 80°C but only 8.14% in three hours in its absence. It was concluded that the sulfur capacities of the reactive adsorbent were closely related to formaldehyde as well as the type of fuel. The presence of formaldehyde in the adsorbent makes a difference to the desulfurization capacity, which results from the polymerization degree of the sulfurs (Yu et al. 2012). Therefore, the temperature difference plays a role on how the ionic liquids behave when reacting with the solvent.

On the other hand, a recent study done by researchers, it was on the extraction of dibenzothiophene from dodecane using ionic liquids. It was found out that, among all the 18 ionic liquids that were tested, the imidazolium based ionic liquids with thiocyanate,dicyanamide and octylsulfate anions exhibited the highest extraction capabilities with 66.1%, 66.1%, and 63.6% of extraction efficiency respectively. From their observation, the π–π interaction between aromatic rings of sulfur compound and ionic liquid (IL) was not be the main extraction mechanism. A trend between specific volume and desulfurization efficiency of ILs was discovered, enabling them to predict IL's desulfurization efficiency from its specific volume. Besides that, it was found that IL can be reused in extraction without regeneration with considerable desulfurization efficiency. High energy saving can be achieved if this IL is used, instead of regenerating IL after every time of extraction (Wilfred et al. 2011). It can be said that, by recycling the IL can be time saving and energy saving because it can reduce the production of waste in conducting this experiment.

Furthermore, also there was a study done by researchers on the effect of n-containing molecules on the hydrodesulfurisation (HDS) of dibenzothiophene (DBT). It was a studied on the influence of 2-methylpyridine and 2-methylpiperidine on the HDS of dibenzothiophene (DBT) over a sulfidedNiMo/Al2O3 catalyst. It was found out that, basic N-containing compounds have been characterized among the strongest inhibitors for HDS. Their experiment showed that the presence of any amount of N-containing molecule in the feed completely blocks the hydrogenation pathway of the DBT HDS, so that the only product observed is biphenyl. 2-Methylpiperidine is a much stronger base than 2-methylpyridine. At 1:1 and 1:2 ratios of DBT to 2-methylpiperidine the conversion of DBT hardly changed. 2-Methylpiperidine did not convert to any products (Egorova and Prins, 2002). Their experimental works was not successful and maybe a further research is needed to make it work in the future.

In addition, a study on the complex extraction of thiophenes using room temperature ionic liquids was conducted by some researchers. Two kinds of room temperature ionic liquids (RTILs) 1-butyl-3-methyllimidazolium chloroaluminate (III) ([bmim]ClCAlCl3) and 1-butyl-3-methyl limidazoliumhexfluorophosphate ([bmim]PF6) were synthesized. The ionic liquids is then tested on the removal of thiophenes from refined diesel by the method of complex extraction. From the result obtained, it showed that under the best operational conditions, the content of thiophenes decline 46 wt% in chloroaluminate

RTIL and 69 wt% in hexfluorophosphate RTIL. The diesel was improved at the same time. The two kinds of RTILs can be used for several times through regenerating (Yuxin et al. 2007). It can be concluded that, even at room temperature the ionic liquids can performed effectively and the is no set back in this experiment.

On top of that, a study on the extractive desulfurization and denitrogenation of fuels using ionic liquids was conducted by a researcher. In the experiment, there were two types of ionic liquids, 1-alkyl-3-methylimidazolium [AMIM] tetrafluoroborate and hexafluorophosphate and trimethylamine hydrochloride ($AlCl_3$-TMAC). It was tested to see its potential for sulfur removal from transportation fuels. $EMIMBF_4$ (E = ethyl),$BMIMPF_6$ (B = butyl), $BMIMBF_4$, and $AMIMPF_6$. These four ions showed high selectivity, particularly toward aromatic sulfur and nitrogen compounds, for extractive desulfurization and denitrogenation. For $BMIMBF_4$ the highest sulfur removal percentage was 14% which was "DBT and pyridine in n-C12". $AlCl_3$-TMAC ionic liquids were found to have remarkably high absorption capacities for aromatics which were 20% sulfur removal (Zhang et al. 2004). Hence, it can be strongly agree that these ionic liquid indeed have a high percentage of sulfur removal efficiency when mixed with sulfur compounds.

On the contrary, a study on the desulfurization of gasoline by extraction with new ionic liquids was done by some researchers. In this experiment, 1-butyl-3-methylimidazolium chloride was synthesis and studied with CuCl-based ionic liquid. The structure is checked under fast atom bombardment mass spectrometry (FAB-MS). It was found out that, $CuCl_2$, Cu_2Cl_3 and Cu_3Cl_4 existed in the ionic liquid. From the result obtained in this experiment, CuCl-based ionic liquid shows remarkable desulfurization ability in the desulfurization of gasoline when used as an extraction absorbent. For $BMIMCu_2Cl_3$ the highest sulfur removal was at 37.4% with the sulfur content in oil to be treated was 196 ppmw (Huang et al. 2004) . It can be confirmed that the chlorine based ionic liquids has a higher percentage of sulfur removal efficiency.

Next, a study on the deep oxidative desulfurization of diesel fuels by acidic ionic liquids was done by some researchers. In this experiment, intensive research on the removal of thiophenicsulfur species from diesel fuels and six functional acidic ILs are studied, in which ILs are used as both extractant and catalyst. Lewis acidic species such as 1-butyl-3-methylimidazolium chloride/$2ZnCl_2$ ($[C_4mim]Cl/2ZnCl_2$ and $[C_4mim]Cl/ZnCl_2$) and

Brønsted acidic species such as 1-methyl-3-ethylcarboxylic acid imidazolium hydrogen sulfate ($[CH_2COOHmim]HSO_4$), 1-methyl-3-(butyl-4-sulfinate) imidazolium hydrogen sulfate ($[SO_3H\text{-}C_4mim]HSO_4$), $[Hmim]HSO_4$, and $[C_4mim]HSO_4$. From all these IL, it was found out that $[C_4mim]Cl/2ZnCl_2$ can reduce he sulfur content in real commercial diesel fuel from 64 to 7.9 ppm with a sulfur removal of 87.7%; however, it is not too effective for coke diesel fuel with high initial sulfur content of 5380 ppm (Yu et al. 2011). It can be concluded that, once again the chlorine type ion has a higher efficiency in helping to remove sulfur compounds.

There was also a study on the optimization of oxidative desulfurization of dibenzothiophene using acidic ionic liquid as catalytic solvent done by some researchers. In the experiment, the oxidative desulfurization of dibenzothiophene (DBT) in *n*-octane as model oil with Brönsted acidic ionic liquids (ILs) N-methyl-pyrrolidonium phosphate ($[Hnmp]H2PO_4$) as catalytic solvent. By which 99.8% of DBT in the model oil was removed under the optimal conditions. The desulfurization efficiency of actual diesel was 64.3% under the optimized conditions. From their evaluation, the desulfurization efficiency of DBT decreased when oxidation temperature > oxidation time> molar ratio of H_2O_2/sulfur (O/S) > volume ratio of ($[Hnmp]H2PO_4$) to model oil (Zhao et al. 2009). It can be say that, the temperature plays a role in the reaction with diesel by mixing with ionic liquids.

2.9 Summary of literature review

From the journal reviewed, it can be conclude that ionic liquid plays a major role in removing sulfur. It is highly effective be it in model oil, model fuel or in diesel and any other organic liquids. In one of the journal, it was also found out that the ionic liquid have a very unique characteristic, where the ionic liquid can be recycled and still performs better and consistent when reuse to remove sulfur from a model oil. This is very good because the supply of the ionic liquid in this research is very limited. On top of that, most of the ionic liquid use in their research shows the sulfur removal efficiency of more than 50%. This shows that the ionic liquid is very effective. Hence, this research on model oil of n-hexane by using ionic liquid of 1-methylpyrazolium ethyl sulphate $C_6H_{13}N_2O_4S$ should show the same result.

3 MATERIALS AND METHODS

3.1 Overview

This paper presents a process or procedure on how the extraction of dibenzothiophene from model oil will be conducted. Besides that, a total of 3 analysis will be conducted which are Fourier Transform Infrared Spectroscopy (FTIR) Analysis, Carbon Hydrogen Nitrogen Sulfur (CHNS) Analysis, High Performance Liquid Chromatography (HPLC) will be used in this experiment to assist the expected result and the result obtained later on. The ionic liquid of 1-methylpyrazolium ethyl sulphate $C_6H_{13}N_2O_4S$ is to be use and studied for its sulfur removal efficiency. On the other hand, the model oil that was chosen is n-hexane. The ionic liquid will be premixed with dibenzothiophene (DBT). Furthermore, it will be tested based on main manipulator which is the concentration.

3.2 Introduction

This section consists of a step by step procedure on how to conduct this experiment. The chemical is advised to be handling with care due to insufficient chemical to restock the chemicals. All protective gears must be worn to avoid misshaped in conducting this experiment due to all the chemical used is hazardous towards human when come in contact or exposed for a period of time.

3.3 Chemicals and Apparatus

The ionic liquid, 1-methylpyrazolium ethyl sulphate $C_6H_{13}N_2O_4S$ is obtained from University Teknologi PETRONAS (UTP), due to the insufficient supply chemicals and the unavailability of equipment in University Malaysia Pahang (UMP) laboratory that is needed to synthesis the ionic liquid.The model oil, n-hexadecane and Dibenzothiophene (DBT) are obtained from UMP laboratory.

The apparatus that will be using in this experiment are obtained from the laboratory. Some of the apparatus that will be using is conical flasks, measuring cylinder, electronic weight machine, incubating shaker; and all the other standard equipment are available in the laboratory.

3.4 Methodology

i. Preparation of n-hexane as model oil

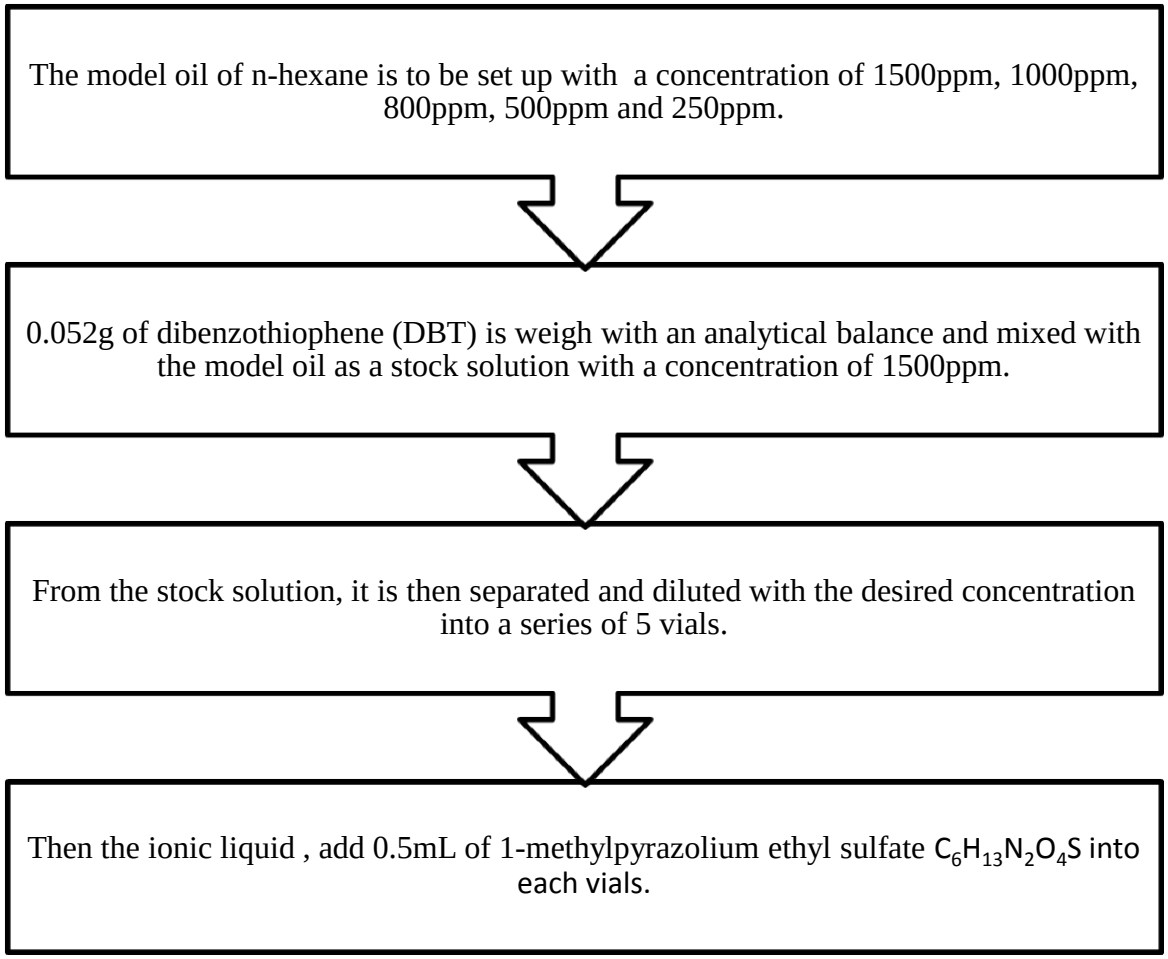


Figure 3.1: Process flow for preparation of model oil of n-hexane

Firstly, n-hexane was prepared by dissolving dibenzothiophene (DBT) in n-hexane to give solutions with sulfur contents of 1500ppm. A 0.052g of dibenzothiophene (DBT) is weigh with an analytical balance. A series of concentration of 1000ppm, 800ppm, 500ppm and 250ppm is needed to make from the stock solution of 1500ppm. Next, the concentration is put into a series of 5 vials. After that, the ionic liquid 1-methylpyrazolium ethyl sulfate $C_6H_{13}N_2O_4S$ of 0.5mL is added into each vials. Then, the vials are check with HPLC to see the sulfur removal efficiency.

ii. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

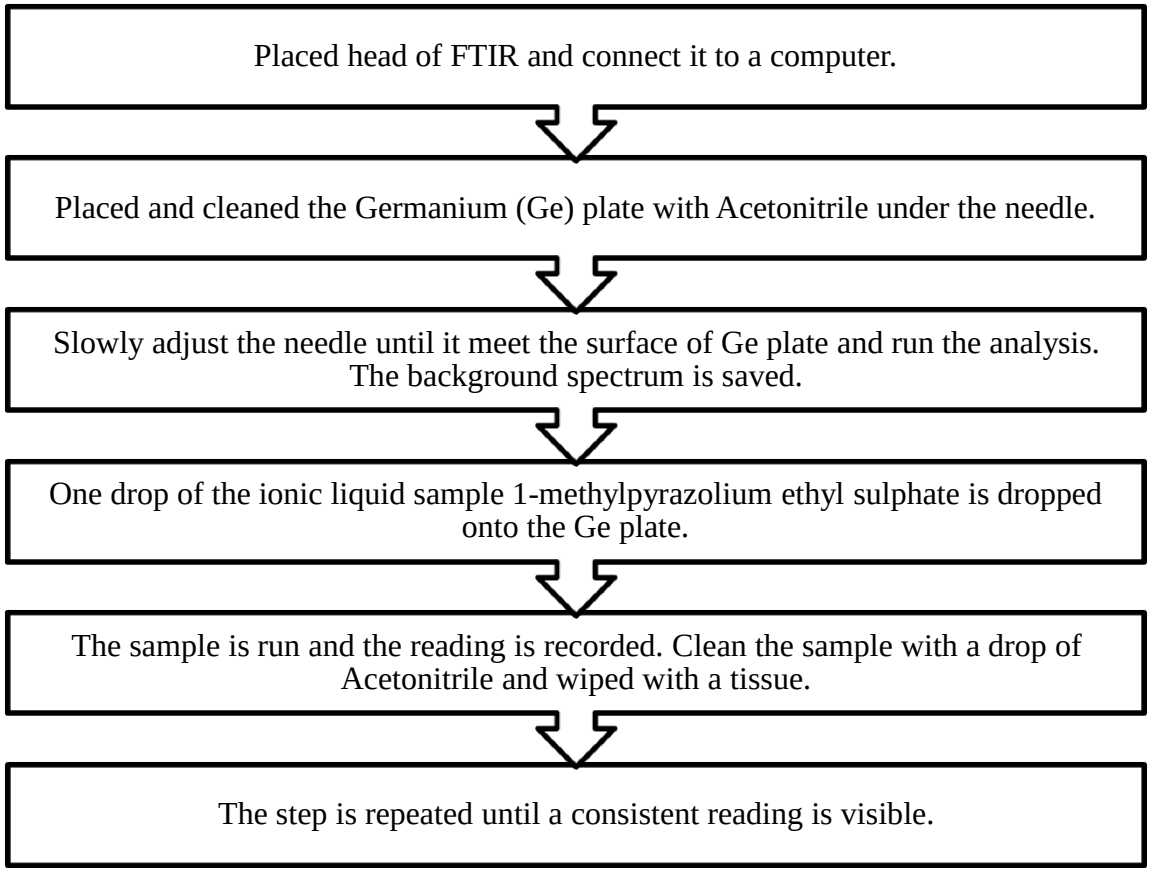


Figure 3.2: Process flow for FTIR analysis of ionic liquid

For this analysis, the head of the FTIR is placed and connected to a computer. Next, a Germanium (Ge) plate is cleaned with Acetonitrile, wiped with tissue and placed under the needle. Then, the needle is slowly adjusted until it meets the surface of the Ge plate and run the analysis. The background spectrum is saved. By using a dropper, one drop of the ionic liquid sample 1-methylpyrazolium ethyl sulphate is dropped onto the Ge plate. Next, the sample is run and the reading is recorded. The sample is cleaned with a drop of Acetonitrile and wiped with a tissue. Finally, the step is repeated until a consistent reading is visible.

iii. Carbon Hydrogen Nitrogen Sulfur (CHNS) Analysis

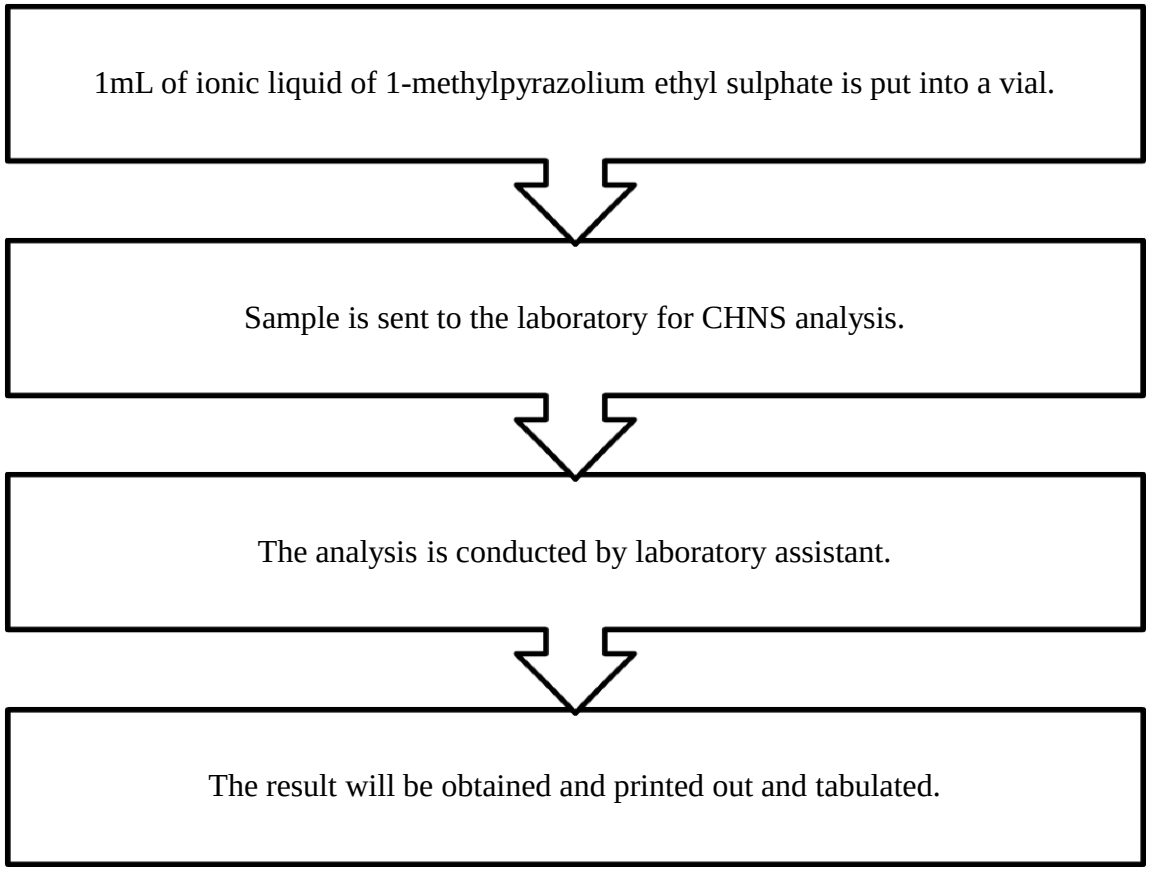


Figure 3.3: Process flow for CHNS analysis of ionic liquid

For this analysis, a 1 mL of ionic liquid of 1-methylpyrazolium ethyl sulphate is put into a vial. Next, the sample is sent to the laboratory for CHNS analysis. Then, the analysis is conducted by the laboratory assistant. Finally, the result will be obtained, printed out and tabulated.

iv. High Performance Liquid Chromatography (HPLC) Analysis

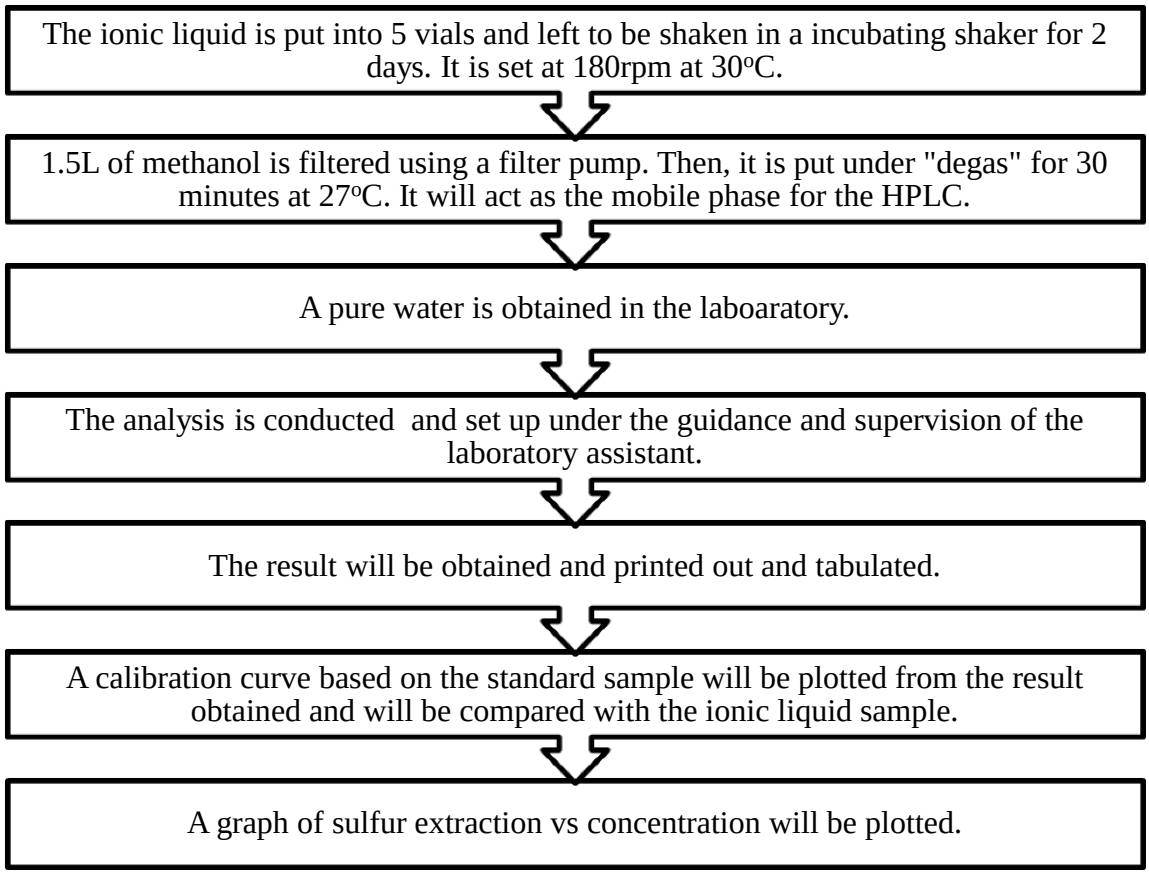


Figure 3.4: Process flow for HPLC analysis of ionic liquid

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 n-hexane will be separated and put into a series of 5 vials. The vials are then go through a incubating shaker for 2 days at 180 rpm and at 30^{o}C. After that, 1.5L 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.

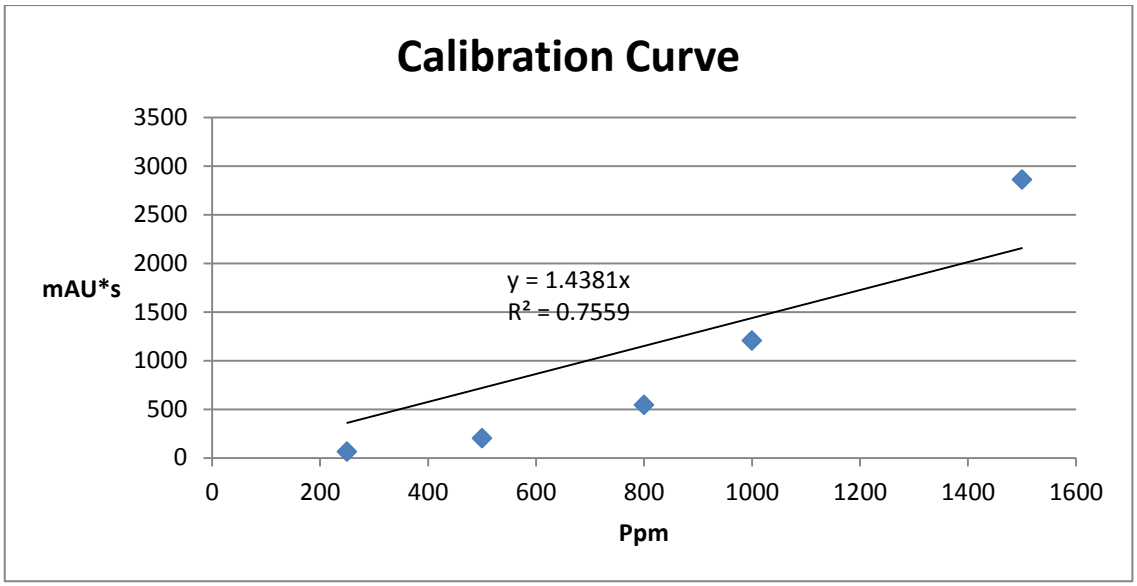


Figure 3.5: Calibration curve for standard sample

4 EXTRACTION OF SULFUR COMPOUNDS

4.1 Overview

This section shows what will be the expected result when conducting this experiment. A detailed discussion on the results will be discussed here and opinion upon conducting this experiment. The results obtained will be compared with the journal results upon completion of the analysis. From the analysis, it will be observed on the effectiveness of the sulfur removal efficiency.

4.2 Introduction

This part will be the results obtained from the analysis that has been done. A further discussion on the result will be done in the next part.

4.3 Results and Discussion

4.4 Fourier Transform Infrared Spectroscopy (FTIR) Results

For the Fourier Transform Infrared Spectroscopy (FTIR) analysis on the ionic liquid. The result from the analysis is shown in Figure 4.1. It is then classified using a table of characteristics for Infra-Red (IR) absorptions according to the wavelength obtained.

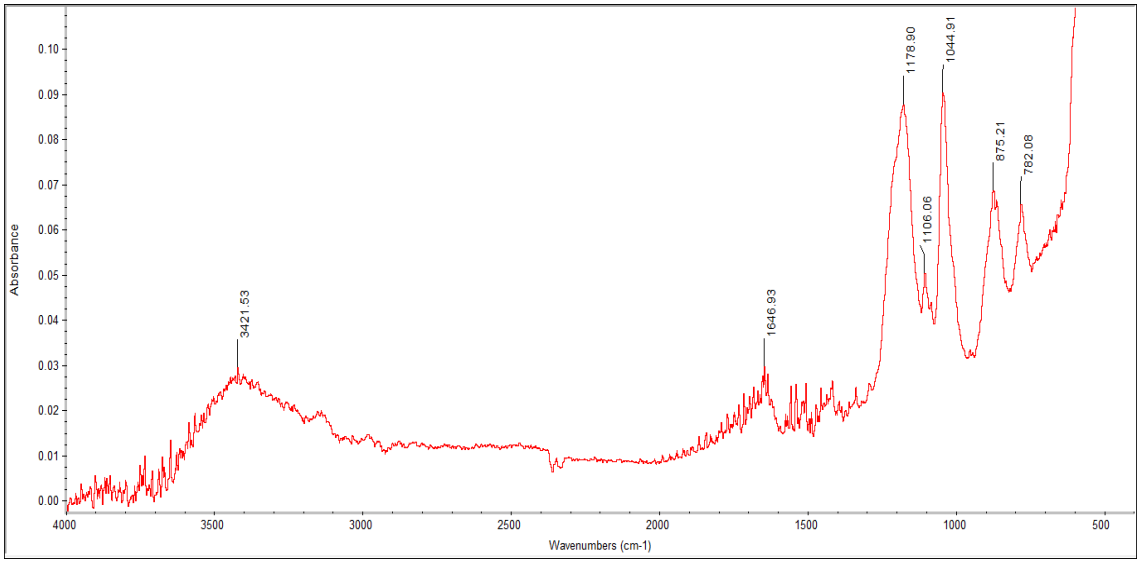


Figure 4.1: FTIR results

For the FTIR analysis on the ionic liquid, the wavelengths (see Table 4.1), were classified by referring it to a table of characteristics for (Infra-Red) IR absorptions. From the analysis, it was found out that there were a trace of functional groups consists of amines, amides, aromatics and alkyl halides. The highest frequency recorded was 3421.53 cm^{-1}. The possible functional group was 1^o,2^o amines, amides which has a N-H stretch of bond present in this ionic liquid. The lowest frequency recorded was 875.21 cm^{-1} and 782.08 cm^{-1}. The functional group for this frequency was aromatics and it consists of C-H "oop" bond. On the other hand, another group of aromatics was also identified at the frequency of 1646.93cm^{-1} with the C-C stretch (in ring) bonding. For the frequency of 1106.06cm^{-1} and 1044.91cm^{-1}, the possible functional group was aliphatic amines and shares the C-N stretch bonding. The last frequency identified was at 1178.90cm^{-1} with a functional group of alkyl halides, C-H wag (-CH_2X) bonding. This FTIR analysis is done because to determine the molecule that exists in this ionic liquid but this FTIR has some limitations. The limitation was the FTIR cannot identify the sulfur compound and thus a further analysis must be done.

Table 4.1: IR absorptions classification

Frequency, cm-1	Bond	Functional group
3421.53	N-H Stretch	1',2' amines, amides
1646.93	C-C Stretch (in-ring)	aromatics
1178.90	C-H wag (-CH2X)	alkyl halides
1106.06	C-N Stretch	aliphatic amines
1044.91	C-N Stretch	aliphatic amines
875.21	C-H "oop"	aromatics
782.08	C-H "oop"	aromatics

4.5 Carbon Hydrogen Nitrogen and Sulfur (CHNS) Results

For the Carbon Hydrogen Nitrogen and Sulfur (CHNS) analysis, to further support that all the 5 molecules exists in the ionic liquid. A further manual calculation will be done to check the molecular formula from the ratio of the percentage. From the CHNS analysis, it was found out that the nitrogen content was 9.88%, carbon was 21.52%, hydrogen 7.55%, sulfur 11.25% and the rest is oxygen at 49.8%. A manual calculation based on the percentage of the molecular weight on each molecule is done. A detailed calculation for each element is available in the *Appendices* section. For example, nitrogen yield a 9.88%, it will be divided with its molecular weight which is 14.0067 g/mol. The value obtained will be 0.7054. Then, it will be done the same for each of the elements to get the ratios. Lastly, from the ratio, a simplest ratio will be calculated and it will be compared with the molecular formula to check if the ionic liquid has the same molecular formula. From the calculation, it was found out that the value varies from the CHNS analysis. The actual molecular formula for the ionic liquid, 1-methylpyrazolium ethyl sulphate is $C_6H_{13}N_2O_4S$. However, from the manual calculation the molecular formula obtained was $C_5H_{21}N_2O_9S$ (see Table 4.1). The reason the value was different is because, a mishandling of vials, or the vials is contaminated or the ionic liquid itself have some impurities. Another main reason is probably the present of water in the vials; this may alter the results when the CHNS analysis is run. The purpose of conducting this CHNS analysis is from this analysis and manual calculation, it can be concluded that sulfur exists in this ionic liquid.

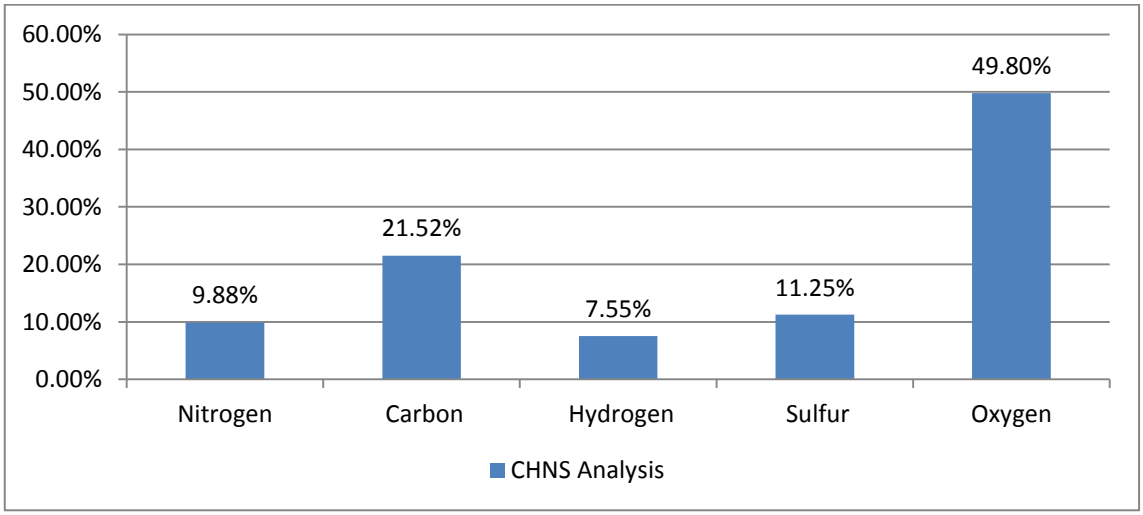


Figure 4.1: CHNS results

Table 4.1: Manual molecular formula calculation

Elements	Percentage Yield,%	Molecular Weight, g/mol	Value	Ratio	Simplest Ratio
Nitrogen	9.88%	14.0067	0.7054	2.0108	2
Carbon	21.52%	12.01	1.7918	5.1078	5
Hydrogen	7.55%	1.008	7.4900	21.3512	21
Sulfur	11.25%	32.065	0.3508	1.0000	1
Oxygen	49.80%	16	3.1125	8.8726	9

4.6 High Performance Liquid Chromatography (HPLC) Results

For the High Performance Liquid Chromatography (HPLC) analysis was done to measure the sulfur content in the model oil. From the analysis a calibration curve of the standard sample was plotted. From the result on the standard sample, at concentration of 250 ppm, the area is 61.47274. At concentration of 500 ppm, the area is 201.191. At concentration of 800 ppm, the area is 542.5143. At concentration of 1000 ppm, the area is 1203.643 and lastly at concentration of 1500 ppm, the area is 2860.044. From figure 3.5, it can be conclude that the higher the concentration, the higher the DBT content. Hence, the sulfur content in the model oil will be higher as the concentration increases.

After the calibration curve was plotted using Microsoft Excel, a further analysis was done. From the graph plotted, a linear function ($y = mx + c$) is to be constructed. The c (y –intercept) is to be set at zero. From this linear function it will be used to calculate the sulfur removal efficiency in each concentration for the sample of the ionic liquids.

Next, the analysis was done based on 1:3 ratios (1 part ionic liquid: 3 part model oil). From the analysis, it is to check how effective the ionic liquid in extracting the sulfur from the model oil. From the HPLC analysis, at concentration of 250 ppm, the area is 250.3286. Next, concentration at 500 ppm, the area is 190.8506. Then, concentration at 800 ppm, the area is 175.3801. For concentration at 1000 ppm, the area is 177.9929. Lastly, for concentration at 1500 ppm, the area is 194.6738. From this area, it is then compared using the linear function to get the remaining concentration. Next, a calculation is done to get the sulfur extraction efficiency. Then, a graph of extraction of sulfur versus concentration is plotted. From the calculation, at 250 ppm the extraction efficiency is 30.46%. For 500 ppm, it was 73.45%. For 800 ppm, it was 84.75%. For 1000 ppm, it was 87.62% and lastly for 1500 ppm it was 90.08%. From the results, it

shows that the higher the concentration, the higher the sulfur removal efficiency. The highest efficiency was at 1500 ppm with 90.98%.

From the result done by (Zhao et.al. 2009), this experiment was to study the oxidative desulfurization of dibenzothiophene (DBT) in *n*-octane as model oil with Brönsted acidic ionic liquids (ILs) N-methyl-pyrrolidonium phosphate ([Hnmp]H_2PO_4) as catalytic solvent and H_2O_2 as oxidant was optimized by orthogonal experiments. Form their research, it was found out that 99.8% of DBT in the model oil was removed under the optimal conditions. When compared with the result on model oil of n-hexane, the removal efficiency was 90.98%. This shows that the ionic liquid can perform in any model oil and still can have a high or almost perfect removal efficiency.

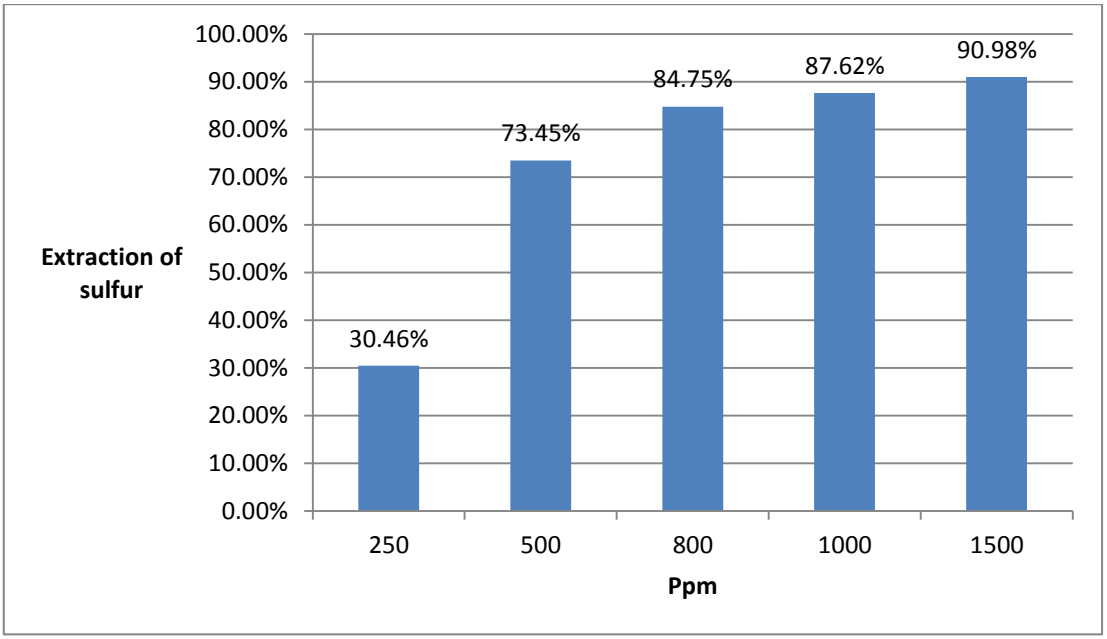


Figure 4.2: Sulfur extraction efficiency

5 CONCLUSION

5.1 Conclusion

This project focuses on the extraction of dibenzothiophene (DBT) from diesel using ionic liquids by testing it on model oil which is n-hexane. The ionic liquid 1-methylpyrazolium ethyl sulphate $C_6H_{13}N_2O_4S$ was studied on model oil. The ionic liquid contains N-H Stretch, C-C Stretch (in-ring), C-H wag (-CH2X), C-N Stretch, C-N Stretch, C-H "oop". Extraction of dibenzothiophene (DBT) from model oil is highly efficient in concentration of 1500 ppm with 90.98%.

5.2 Future Works and Recommendation

The research carried in this paperwork will be continued on again if given the time and space and the materials to do the experimental works in the laboratory again. The aim was to synthesis the ionic liquids and be carried out on the diesel to support the hypothesis which the ionic liquid will remove the sulfur containing compound which is dibenzothiophene in diesel. In the future works of this ionic liquid it is hoping that, to have a chance to synthesis the ionic liquid itself. In this research, it was clearly seen that mishandling or impurities has been the enemy, where the result should had been near perfect but the fact that error is always there, the result is prone to abnormalities. As for the future research, the current experiment could be done in a larger scale because the small scale experiment might not be up to par as the large scale experiment.

REFRENCES

[1] Anugwom, I., Arvela, P., M., Salmi, T., Mikkola, J-P.,*(2011). Ionic Liquid Assisted Extraction of Nitrogen and Sulphur-Containing Air Pollutants from Model Oil and Regeneration of the Spent Ionic Liquid*. Journal of Environmental Protection, 2, pp. 796-802.

[2] Dharaskar, S., A., Wasewar, K., L., Varma, M., N., Shende, D., Z., (2013). *Extractive Deep-desulfurization of liquid Fuels Using Lewis based Ionic Liquids*. Visvesvaraya National Institute of Technology, Department of Chemical Engineering.

[3] Egorova, M., &Prins, R. (2002). Effect of N-Containing Molecules on the Hydrodesulfurisation of Dibenzothiophene.In *Prepr.Symp. Am. Chem. Soc., Div. Fuel Chem* (Vol. 47, No. 2, p. 445).

[4] Fox, B., R., Sun, A., W., Dauer, H., B., Male, J., L., Stewart, M., L., (2011).*Enhanced oxidative desulfurization of model fuels using a film-shear reactor*.University of Oregon, Department of Chemistry USA. Fuel 90, pp. 898-901.

[5] Hua, R., Li, Y., Liu, W., Zheng, J., Wei, H., Wang, J., et al.,(2003) *Determination of sulfur-containing compunds in diesel oils by comprehensive two-dimensional gas chromatography with a sulfur chemiluminescence detector.* Journal of Chromatography. pp. 101-109.

[6] Huang, C., Chen, B., Zhang, J., Liu, Z., & Li, Y. (2004). Desulfurization of gasoline by extraction with new ionic liquids. *Energy & Fuels*, *18*(6), 1862-1864.

[7] "Material Safety Data Sheet Dibenzothiophene, 99%". (1997). Retrieved December 30, 2013, from http://www.apps.wku.edu

[8] "n-Alkane Category: decane, undecane, dodecane", (2004). Retrieved April 27 2013, from http://www.tera.org/peer/vccep/n-alkanes/vccep%20n alkanes%20submission%20jun%2017%202004%20-%20revised.pdf

[9] "*Physical Properties of Thiophene*", (n.d.). Retrieved May 3 2013, from http://www.chemicalland21.com/lifescience/phar/THIOPHENE.htm

[10] Shepard, A. F., Henne, A. L., &Midgley, T. (1931). *Physical properties of the normal paraffin hydrocarbons, pentane to dodecane*. Journal of the American Chemical Society, 53(5), 1948-1958.

[11] Thomas, S.G., Kleiman, J.P., Brandt, V.O., (1991). *Analysis of Commercial Diesel Fuels by Preparative High Performance Liquid Chromatography and Gas Chromatography – Mass Spectrometry*. Ethyl Corporation.

[12] “Toxic profile n-Hexane”. (2013). Retrieved December 30, 2013, from http://www.atsdr.cdc.gov

[13] Wang, F.C-Y., Robbins, W.K., Sanzo, F.P.D., McElroy, F.C.,(2003). *Speciation of Sulfur-Containing Compounds in Diesel by Comprehensive Two-Dimensional Gas Chromatography*.Journal of Chromatographic Science, Vol 41.

[14] Wang, S., Wang, R., Yu, H., (2012). *Deep Removal of 4,6-Dimethyldibenzothiophene from Model Transportation Diesel Fuels over Reactive Adsorbent*. Brazilian Journal of Chemical Engineering. Vol 29, No.02, pp. 421-428.

[15] Wang, Y., Li, H., Zhu, W., Jiang, X., et al. (2008). *Deep Desulfurization of Fuels Using Ionic Liquid Based on $FeCl_3$*. National Nature Science Foundation of China.

[16] Wasserscheid, P., &Welton, T. (Eds.). (2008). *Ionic liquids in synthesis* (Vol. 1).Weinheim, Germany: Wiley-Vch.

[17] Welton, T. (1999). Room-temperature ionic liquids.Solvents for synthesis and catalysis. *Chemical reviews*, *99*, 2071-2084.

[18] “*What does 'Euro IV' mean*?”, (2007). Retrieved May 1, 2013, from http://www.whatcar.com/car-news/what-car-q-and-a/what-does--euro-iv--mean/225420

[19] Wilfred, C. D., Kiat, C. F., Man, Z., Bustam, M. A., Mutalib, M. I. M., &Phak, C. Z. (2012). Extraction of dibenzothiophene from dodecane using ionic liquids.*Fuel Processing Technology*, *93*(1), 85-89.

[20] Xin, W.Y., Yong, L.X.,(2005). *Extractive Removal of Thiophene Sulfide from Diesel using Ionic Liquids*. The Proceedings of the 3rd International Conference on Functional Molecules.

[21] Yu, G., Zhao, J., Song, D., Asumana, C., Zhang, X., & Chen, X. (2011). Deep oxidative desulfurization of diesel fuels by acidic ionic liquids. *Industrial & Engineering Chemistry Research*, *50*(20), 11690-11697.

[22] Yuxin, W., Zubin, C., Dandong, L., &Shuyun, M. (2007). Complex Extraction of Thiophenes Using Room Temperature Ionic Liquids. *Petroleum Science and Technology*, *25*(8), 1073-1080.

[23] Zhang, S., Zhang, Q., & Zhang, Z. C. (2004). Extractive desulfurization and denitrogenation of fuels using ionic liquids. *Industrial & engineering chemistry research*, *43*(2), 614-622.

[24] Zhang, S., Zhang, Z.C., *Selective Sulfur Removal from Fuels Using Ionic Liquids at Room Temperature.* Fuel Chemistry Division Preprints. 47(2), pp.449, 2002.

[25] Zhao, D. S., Sun, Z. M., Li, F. T., & Shan, H. D. (2009). Optimization of oxidative desulfurization of dibenzothiophene using acidic ionic liquid as catalytic solvent. *Journal of fuel chemistry and technology*, *37*(2), 194-198.

APPENDICES

1.CHNS

analysis manual calculation.

C = 12.01 g/mol

H = 1.008 g/mol

N = 14.0067 g/mol

S = 32.065 g/mol

O = 16.00 g/mol

The value for N = $\frac{9.88}{14.0067}$

= 0.7054

For C = $\frac{21.52}{12.01}$

= 1.7918

For H = $\frac{7.55}{1.008}$

= 7.4900

For S = $\frac{11.25}{32.065}$

= 0.3508

For O = $\frac{49.80}{16.00}$

= 3.1125

For the simplest ratio, the smallest value is taken

For N = $\frac{0.7054}{0.3508}$

= 12.108

For C = $\frac{1.7918}{0.3508}$

= 5.1078

For H = $\frac{7.4900}{0.3508}$

= 21.3512

For S = $\frac{0.3508}{0.3508}$

= 1.000

For O = $\frac{3.1125}{0.3508}$

= 8.8726

CENLAB/F/007

Universiti Malaysia PAHANG

CENTRAL LABORATORY
Universiti Malaysia Pahang, Lebuhraya Tun Razak,
26300 Kuantan, Pahang Darul Makmur.
Tel: 09-5493344/8097 Fax: 09-5493353
E-mail: ucl@ump.edu.my

CERTIFICATE OF ANALYSIS (COA)

To :	MOHD RAFIQUL ZARIN RAMLI	Attn :	
Address :	UNIVERSITI MALAYSIA PAHANG		
c.c. :		Page :	1 of 1
Fax No :	Tel No :		Sample Lab No: 2013/563

Sample description : 3 samples in glass beaker

Sample marking : MS04 (PICO), MS04 (HADI), MS04(KEN)

Date of sample received : 12/11/2013

Date reported : 19/01/2013

RESULTS:

No	Sample	N [%]	C [%]	H [%]	S [%]	Method
1.	MS04 (PICO)	11.37	15.84	6.729	11.185	In House-Method
2.	MS04 (HADI)	14.97	29.71	5.463	16.107	In House-Method
3.	MS 04 (KEN)	9.88	21.52	7.551	11.247	In House-Method

The above analysis is based on the sample submitted by the customer.

FADHLULLAH BIN RAHMAN
PEGAWAI SAINS
MAKMAL BERPUSAT
UNIVERSITI MALAYSIA PAHANG
LEBUHRAYA TUN RAZAK
26300 GAMBANG KUANTAN, PAHANG
TEL: [illegible]

2.HPLC

Calculation for the extraction sulfur efficiency

From the linear function, y = 1.4381x. It is then compared with the ionic liquid sample result.

The area of the sample is to be y, and x is to be calculated

For 250 ppm,

250.3286 = 1.4381x

x = 173.84 ppm

For 500 ppm,

190.8506 = 1.4381x

x = 132.71 ppm

For 800 ppm,

175.3801 = 1.4381x

x = 121.95 ppm

For 1000 ppm,

177.9929 = 1.4381x

x = 123.77 ppm

For 1500 ppm

194.6738 = 1.4381x

x = 135.37 ppm

From this value, the extraction sulfur efficiency is calculated by

For 250 ppm,

$\frac{250-173.84}{250}$ x 100% = 30.46%

For 500 ppm,

$\frac{500-132.71}{500}$ x 100% = 73.45%

For 800 ppm,

$\frac{800-121.95}{800}$ x 100% = 84.75%

For 1000 ppm,

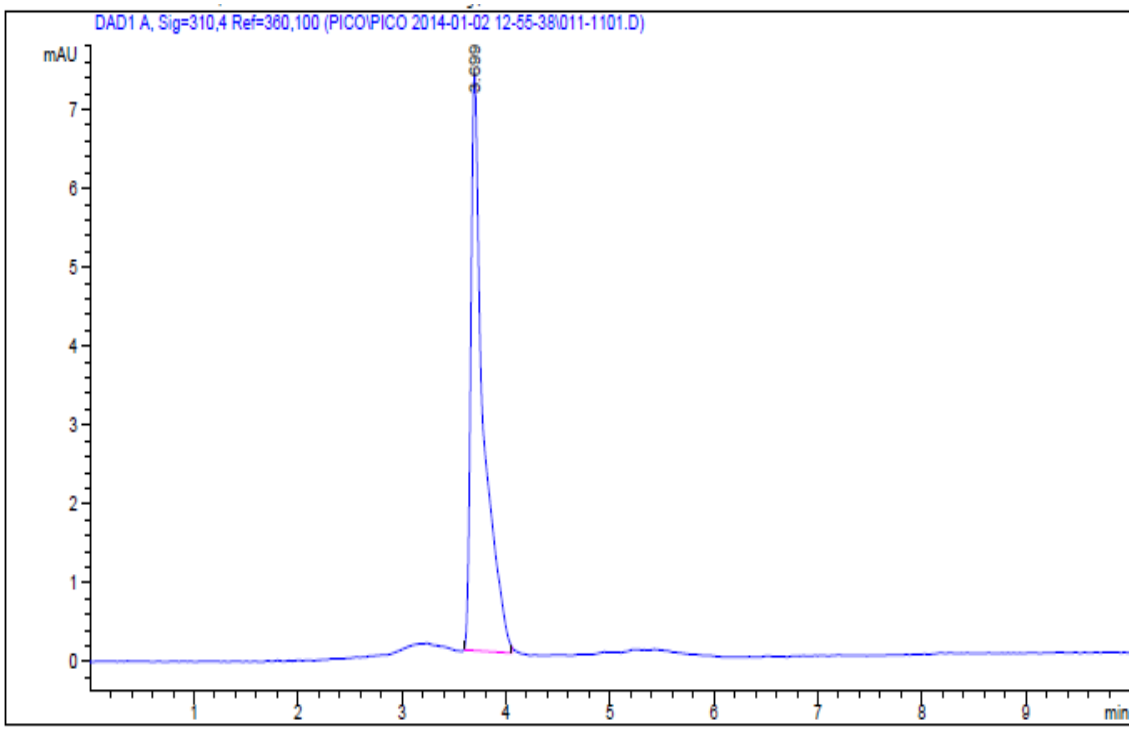
$\frac{1000-123.77}{1000}$ x 100% = 87.62%

For 1500 ppm,

$\frac{1500-135.37}{1500}$ x 100% = 90.98%

HPLC

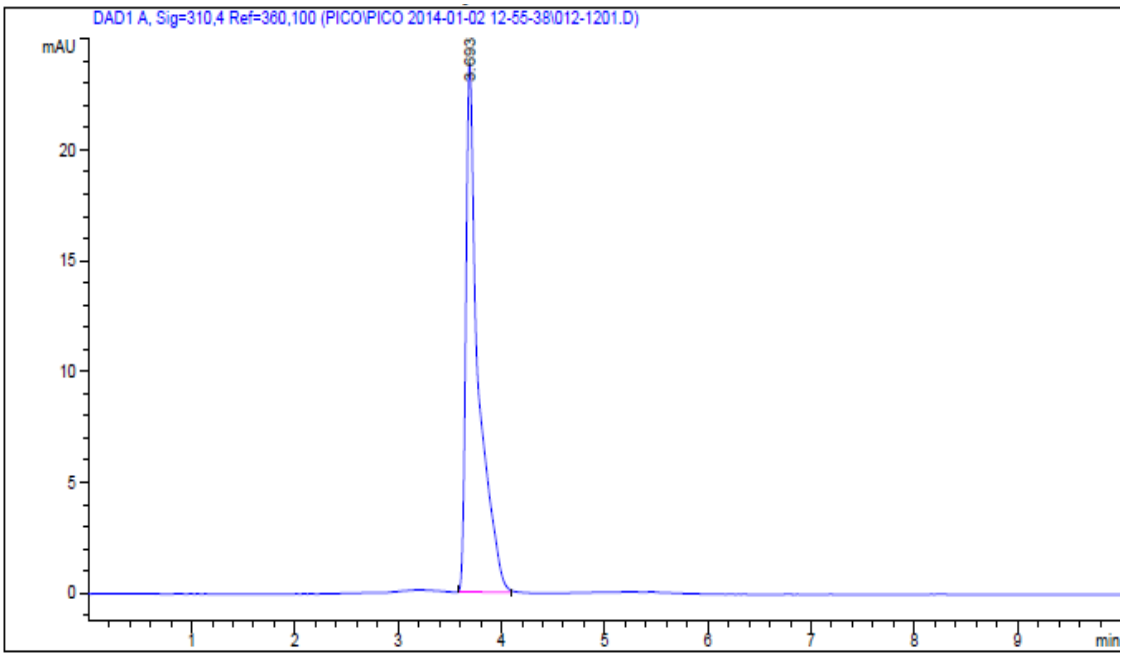
Standard sample 250ppm



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	3.326		0.0000	0.00000	0.0000	
2	3.699	BB	0.1159	61.47274	100.0000	
Totals :				61.47274		

HPLC

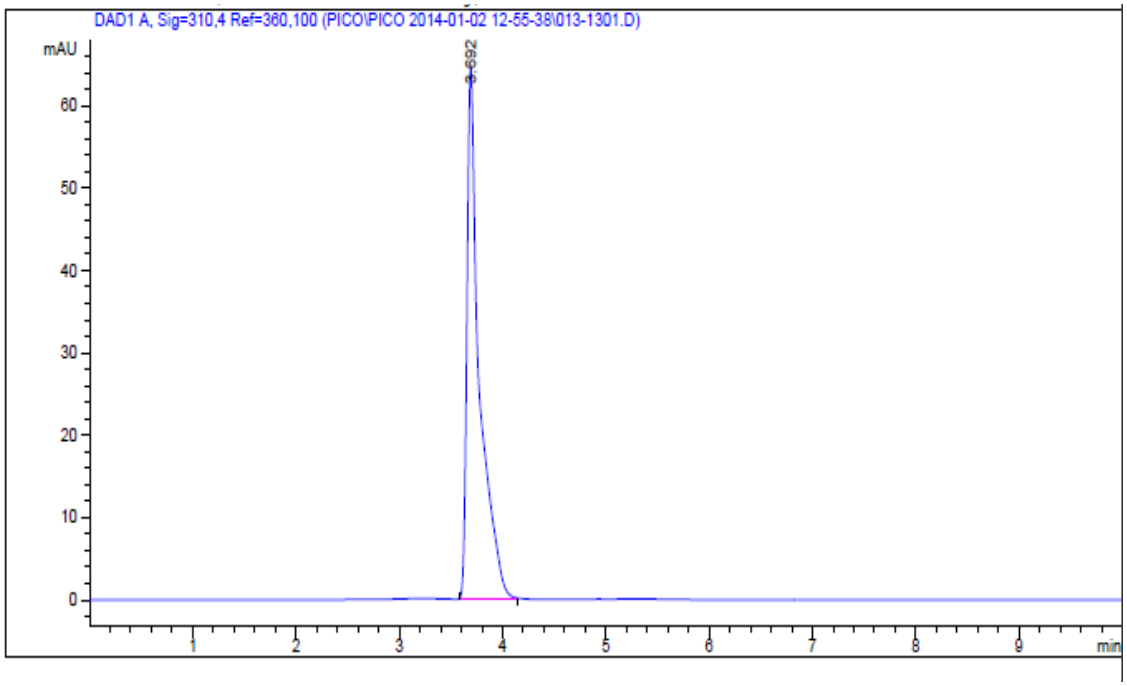
Standard sample 500ppm



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	3.326		0.0000	0.00000	0.0000	
2	3.693	BB	0.1185	201.19101	100.0000	
Totals :				201.19101		

HPLC

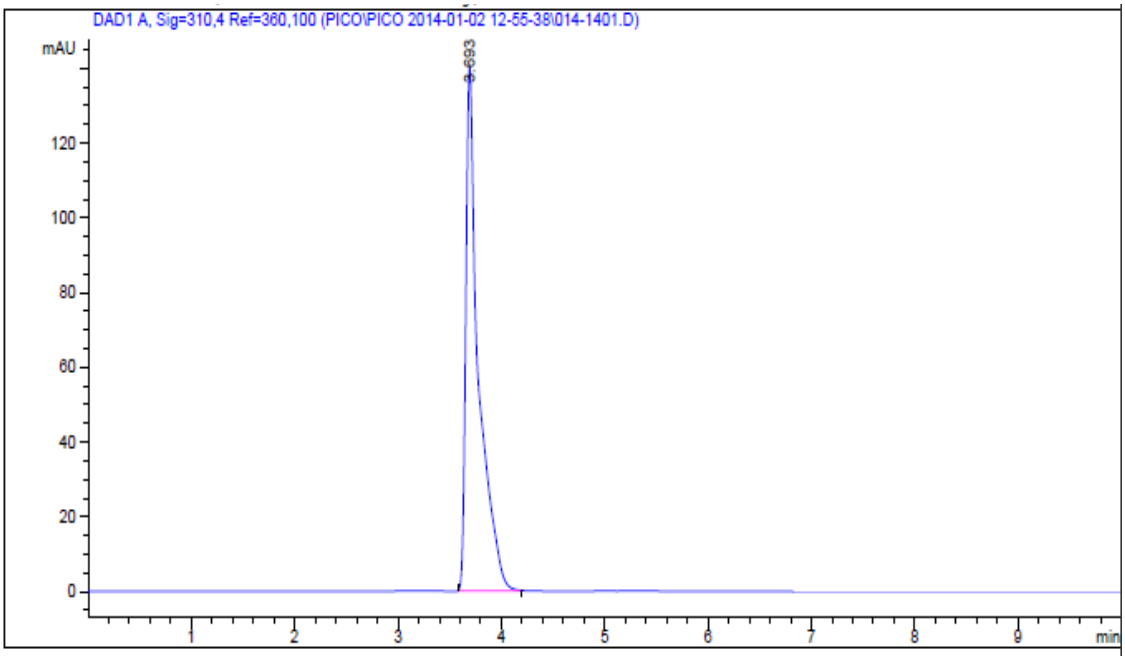
Standard sample 800ppm



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	3.326		0.0000	0.00000	0.0000	
2	3.692	BB	0.1179	542.51434	100.0000	
Totals :				542.51434		

HPLC

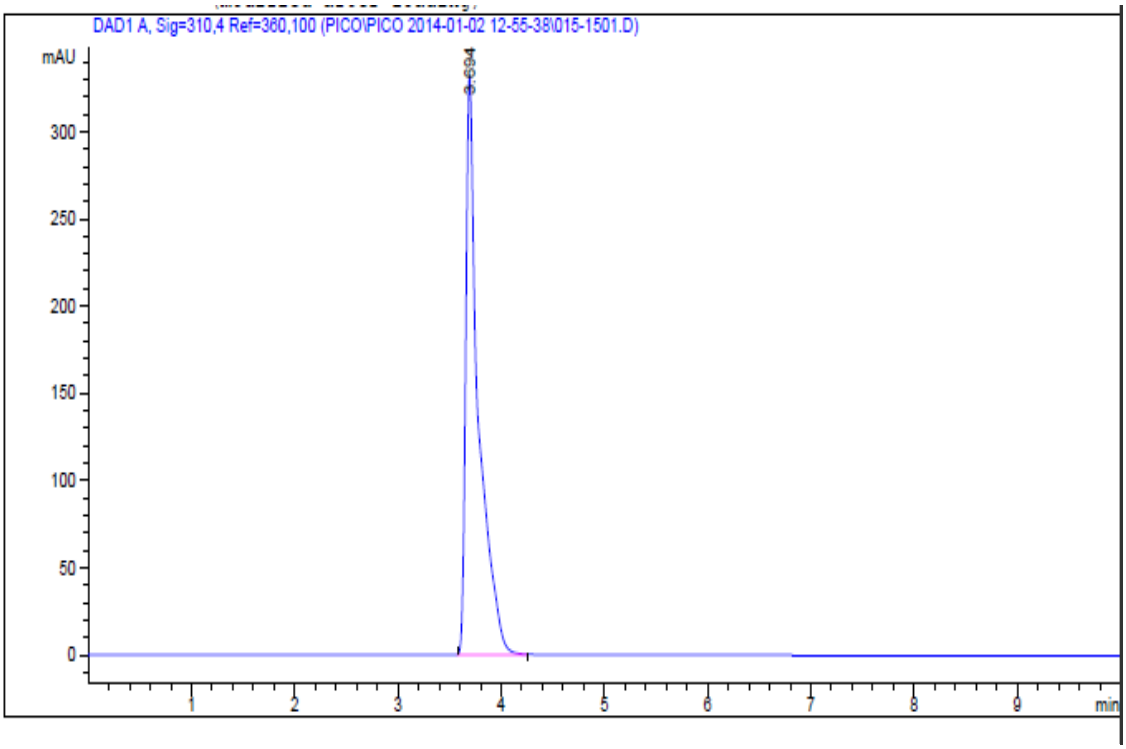
Standard sample 1000ppm



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	3.326		0.0000	0.00000	0.0000	
2	3.693	BB	0.1199	1203.64331	100.0000	
Totals :				1203.64331		

HPLC

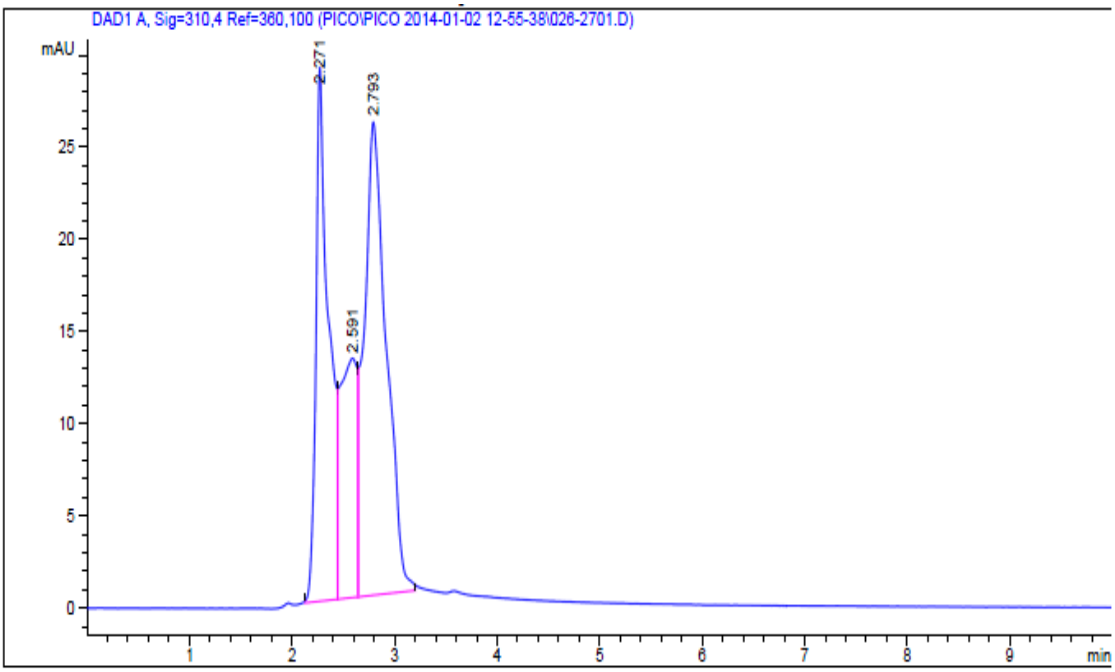
Standard sample 1500ppm



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	3.326		0.0000	0.00000	0.0000	
2	3.694	BB	0.1205	2860.04443	100.0000	
Totals :				2860.04443		

HPLC

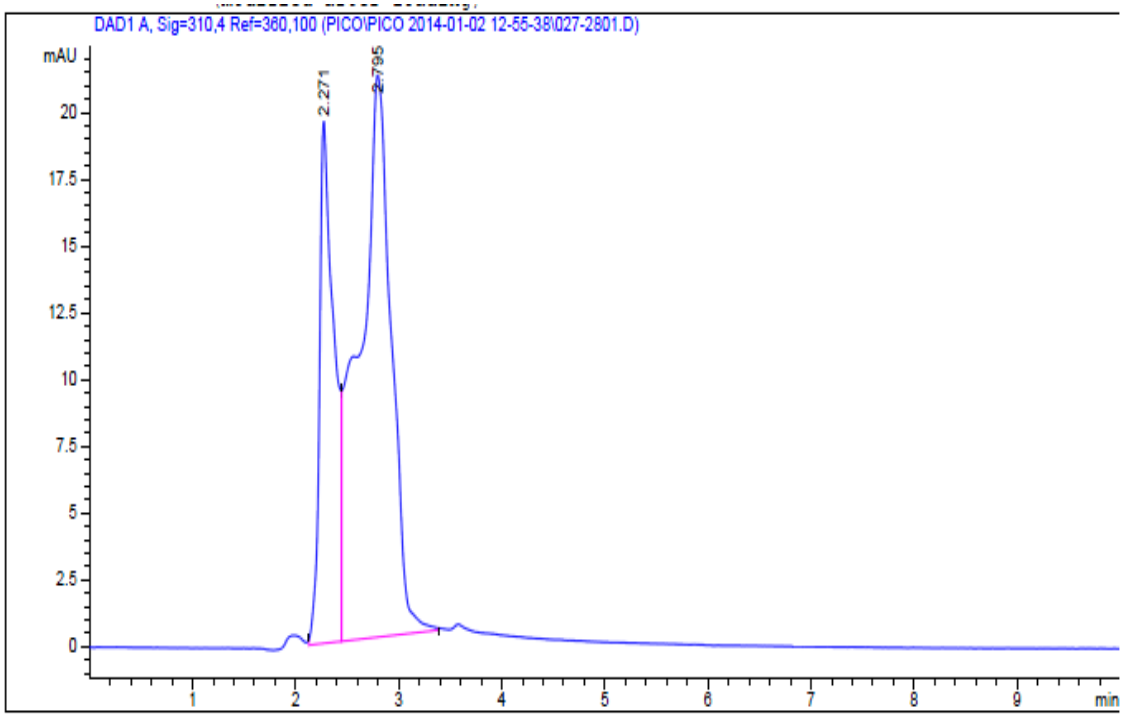
Sample 250ppm



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	2.271	BV	0.1146	250.32864	32.0176	?
2	2.591	VV	0.1565	147.33490	18.8445	?
3	2.793	VB	0.2084	384.18384	49.1380	?
4	3.326		0.0000	0.00000	0.0000	
5	3.663		0.0000	0.00000	0.0000	
Totals :				781.84738		

HPLC

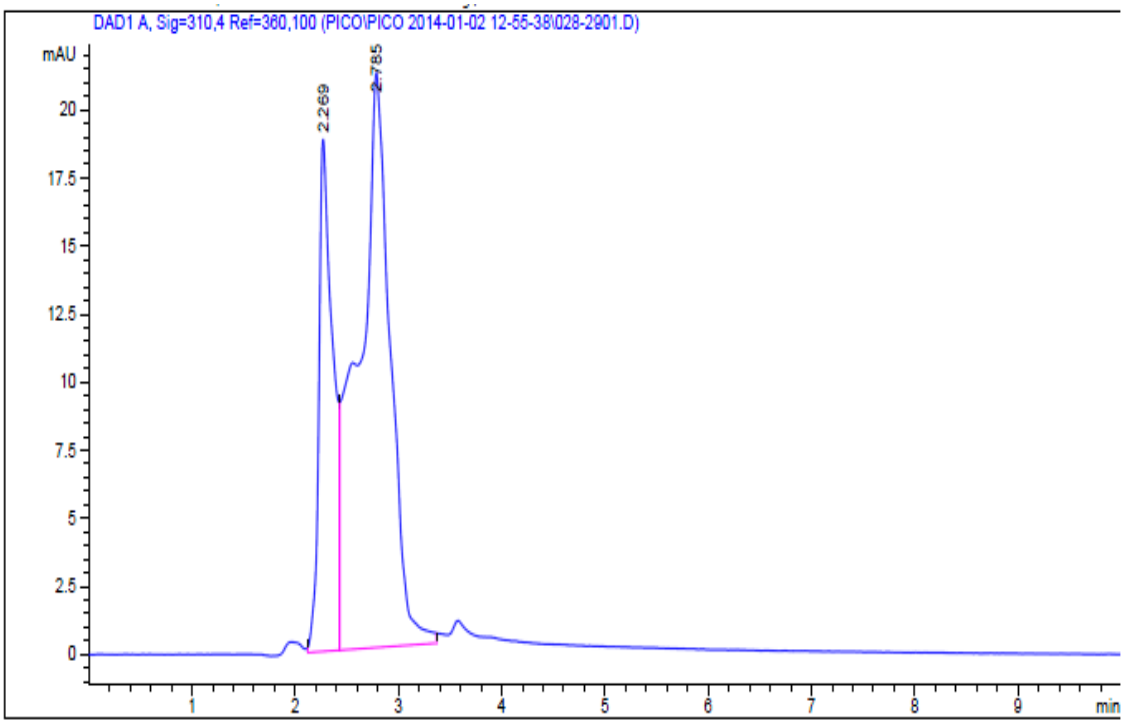
Sample 500ppm



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	2.271	BV	0.1319	190.85060	29.4573	?
2	2.795	VB	0.2891	457.03760	70.5427	?
3	3.326		0.0000	0.00000	0.0000	
4	3.663		0.0000	0.00000	0.0000	
Totals :				647.88820		

HPLC

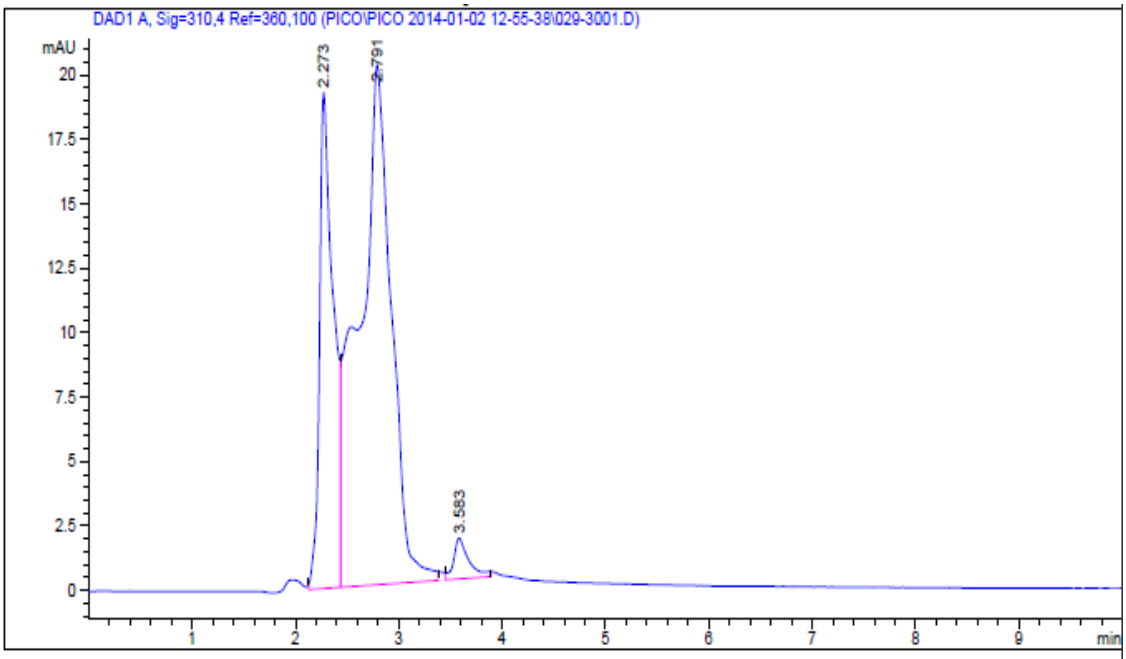
Sample 800ppm



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	2.269	BV	0.1286	175.38011	27.7036	?
2	2.785	VB	0.2730	457.67892	72.2964	?
3	3.326		0.0000	0.00000	0.0000	
4	3.663		0.0000	0.00000	0.0000	
Totals :				633.05904		

HPLC

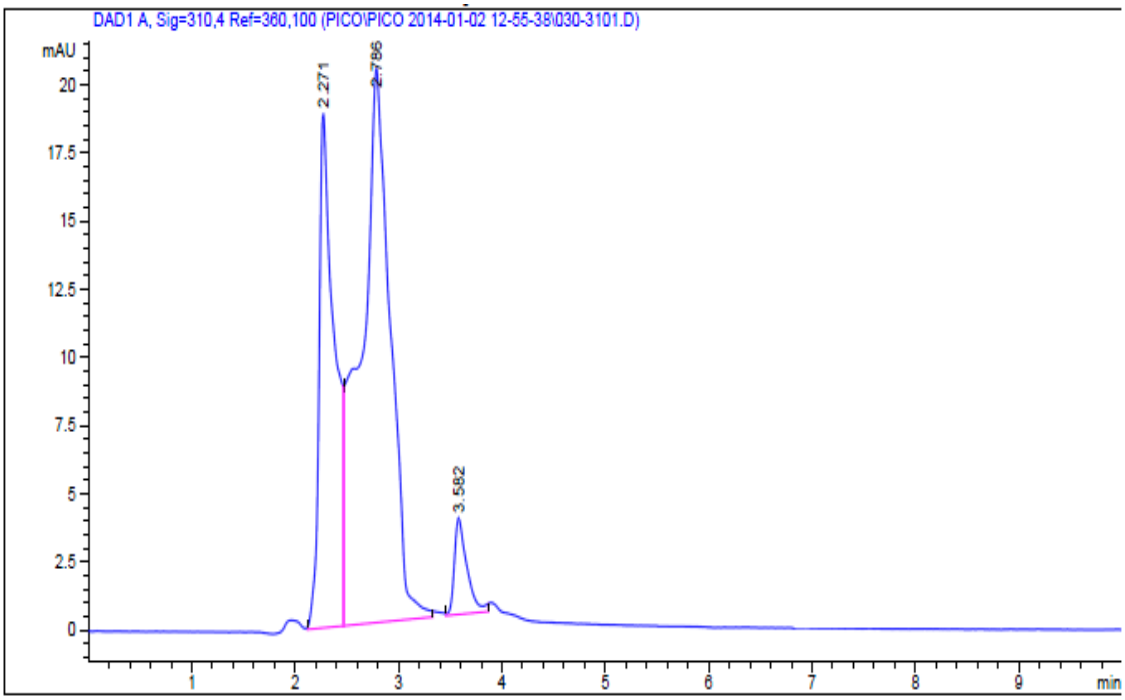
Sample 1000ppm



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	2.273	BV	0.1279	177.99292	27.9795	?
2	2.791	VB	0.2795	441.91846	69.4671	?
3	3.326		0.0000	0.00000	0.0000	
4	3.583	BB	0.1417	16.24336	2.5534	
Totals :				636.15474		

HPLC

Sample 1500ppm



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Area %	Name
1	2.271	BV	0.1382	194.67380	30.7034	?
2	2.786	VB	0.2573	409.56491	64.5954	?
3	3.326		0.0000	0.00000	0.0000	
4	3.582	BB	0.1208	29.80796	4.7012	
Totals :				634.04667		

FTIR Results