

**Oxidation Coupled with Extraction to Remove Thiophene and Benzothiophene from  
Dodecane using [Mmim]DMP Ionic Liquid.**

by

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**CERTIFICATION OF APPROVAL**

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**A project dissertation submitted to the  
Chemical Engineering Programme  
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BACHELOR OF ENGINEERING (Hons)  
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**January 2009**

## CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

  
\_\_\_\_\_  
NURUL SUHAIRA ABDULLAH

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## ABSTRACT

High concentration release of sulfur from fuel to the environment can cause accumulation in the ecological system, thus posing a significant danger to human health. The available technology of for sulfur removal from fuel which is hydrodesulfurization (HDS) are rather expensive, require severe operating condition, high hydrogen consumption, and limited to aliphatic sulfur species. Therefore, vigorous studies are being conducted to develop more effective and cheaper alternatives. One of the promising alternatives that attract high attention is using ionic liquid for desulfurization due to its unique properties as a solvent and catalyst. This project is focused on removing sulfur from crude oil model by using oxidation coupling with extraction method. The ionic liquid use in this research work is methylmethylimidazolium dimethylphosphate, [Mmim]DMP. There are five main stages in this project which are preparation of ionic liquid, characterization of ionic liquid properties, model oil preparation, desulfurization and data analyzing. Two sulfur species were used: thiophene and benzothiophene. Three different amount of sulfur in model oil were employed which are 2%, 4% and 6%. The desulfurization process was conducted at ambient temperature. The percentages of sulfur removal were analyzed using X-ray fluorescence (XRF). The results showed that percentage of sulfur removal always followed the order of thiophene > benzothiophene. The significance of this finding is such that although thiophene and benzothiophene cannot be removed efficiently by HDS process, they can be easily extracted by ionic liquid. This is due to strong  $\pi$ - $\pi$  interaction between unsaturated bonds of those sulfur species and the imidazolium ring of ionic liquid.



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# CHAPTER 1

## INTRODUCTION

### 1.1 Background of Study

#### 1.1.1 Ionic Liquid

Ionic liquid is salts that have melting point below 100°C [1-3] and consist of organic cations and inorganic anions that are poorly coordinated. At least one ion has a delocalized charge and one component is organic, which prevents the formation of a stable crystal lattice [2]. Most of ionic liquid is liquid at room temperature (RTIL's). The constituents of ionic liquids are constrained by high coulombic forces, exhibiting practically no vapor pressure, and hence can emit no volatile organic compounds (VOCs) [3]. This property provides an advantage for ionic liquid, offering lower toxicity compared to the other lower boiling point solvents [1]. Both components (anion and cation) of the ionic liquids can be varied to fulfill the requirement of certain process to yield various fascinating properties including melting point, viscosity, hydrophobicity and density. This is so called "designer solvents" [4].

In general, ionic liquids consist of a salt where one or both the ions are large, and the cation has a low degree of symmetry. These factors tend to reduce the lattice energy of the crystalline form of the salt, and hence lower the melting point [5]. Ionic liquid can be classified as simple salts and binary ionic liquid [3]. Simple salts is made of single anion and cation such as  $[\text{EtNH}_3][\text{NO}_3]$ . This type of ionic liquid show simple melting behavior. On the other hand, binary ionic liquid is salt where equilibrium between ions is involved and consists of several different ionic species such as mixtures of aluminum (III) chloride and 1, 3-dialkylimidazolium chlorides. The melting point depends on the composition of each ions exist in the ionic liquid.

One of the first RTILs was a mixture of [EMIM]Cl with AlCl<sub>3</sub> forming a series of equilibrium between [EMIM][AlCl<sub>4</sub>], [EMIM][Al<sub>2</sub>Cl<sub>7</sub>], and [EMIM][Al<sub>3</sub>Cl<sub>10</sub>]. This RTIL is not water stable. The discovery of water-insoluble RTILs such as [BMIM][PF<sub>6</sub>] allowed the development of new work-up methods, including the separation of water-soluble byproducts by simple extraction. Some transition metal catalysts that are soluble in ionic liquids may be recycled together with the ionic liquid, after extraction with water and the non-polar organic solvent used for product separation. The catalyst and ionic liquid may be recycled several times.

A major drawback was their moisture sensitivity and, though to a somewhat lesser extent, their acidity/basicity, and the latter which can sometimes be used to an advantage. In 1992, Wilkes and Zawarotko reported the preparation of ionic liquids with alternative, 'neutral', weakly coordinating anions such as hexafluorophosphate ([PF<sub>6</sub>])<sup>-</sup> and tetrafluoroborate ([BF<sub>4</sub>])<sup>-</sup>, allowing a much wider range of applications for ionic liquids.[6] It was not until recently that a class of new, air- and moisture stable, neutral ionic liquids was available that the field attracted significant interest from the wider scientific community.

More recently, people have been moving away from [PF<sub>6</sub>]<sup>-</sup> and [BF<sub>4</sub>]<sup>-</sup> since they are highly toxic, and towards new anions such as bistriflimide [(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N]<sup>-</sup> or even away from halogenated compounds completely. Moves towards less toxic cations have also been growing, with compounds like ammonium salts (such as choline) being just as flexible a scaffold as imidazole.

The application of ionic liquid in petroleum industry especially in desulfurization process had gained much interest and many studies are being conducted. This is due to possibility of cost reduction as ionic liquid can be recycled as well the reaction involve is not complicated compared to molecular solvent. It also requires simple equipment and procedures.

### 1.1.2 Crude Oil

Petroleum or crude oil is a naturally occurring, flammable liquid found in rock formations in the Earth consisting of a complex mixture of hydrocarbons of various molecular weights, plus other organic compounds [7].

Hydrocarbon group is the main constituent in crude oil. Crude oil consist of various hydrocarbon namely alkanes, cycloalkanes and various aromatic hydrocarbons while the other organic compounds contain nitrogen, oxygen and sulfur, and trace amounts of metals such as iron, nickel, copper and vanadium. The composition of each component is listed in the table below [8]:

**Table 1.1: Composition in crude oil**

Component	Composition (wt%)
Carbon	83-87
Hydrogen	10-14
Nitrogen	0.1-2
Oxygen	0.1-1.5
Sulfur	0.5-6%
Metal	<1000ppm

Generally, crude oil can be divided into two types which are sweet crude oil and sour crude oil. These two types are different in amount of sulfur content. Sweet crude contain <0.5 wt% sulfur [9] and usually used to produce gasoline, kerosene and high quality diesel. Sour crude consist of >1% sulfur and mainly process to produce heavy oil such as diesel and fuel oil [10].

Four different types of hydrocarbon molecules appear in crude oil. The relative percentage of each varies from oil to oil, determining the properties [11].

**Table 1.2:** Composition of Hydrocarbon Constituent in Crude Oil.

<b>Composition by Weight</b>		
<b>Hydrocarbon</b>	<b>Range</b>	<b>Average</b>
<b>Parafins</b>	<b>15-60%</b>	<b>30%</b>
<b>Naphtenes</b>	<b>30-60%</b>	<b>49%</b>
<b>Aromatics</b>	<b>3-20%</b>	<b>15%</b>
<b>Asphaltics</b>	<b>remainder</b>	<b>6%</b>

### **1.1.3 Desulfurization Process**

Sulfur exists in crude oil as elemental sulfur and hydrogen sulfide. High content of hydrogen sulfide can cause crude oil to be toxic and corrosive. At low concentrations the oil has the smell of rotten eggs, but at high concentrations the inhalation of hydrogen sulfide is instantly fatal. At higher concentrations, the hydrogen sulfide can damage the olfactory nerve, rendering the gas effectively odorless and undetectable, while paralyzing the respiratory system. If exposure is not fatal, its effects on the human body are similar to

that of Gulf War Syndrome including chronic fatigue, headaches, dizziness, skin problems, memory problems, birth defects, and a host of breathing problems such as asthma. Such sour crude oil needs to be stabilized by having hydrogen sulfide gas ( $H_2S$ ) removed from it before being transported by oil tankers for safety reasons [12].

In the petroleum refining industry, hydrodesulfurization (HDS) is the conventional process to reduce the sulfur levels of the fuels. However, in the HDS process, to achieve very low sulfur content, higher hydrogen pressure, higher reaction temperature, and more active catalysts are needed. This is because aromatic sulfur such as dibenzothiophene, benzothiophene and thiophene are very hard to remove by HDS, owing to their stereo hindrance [13].

## **1.2 Problem Statement**

### **1.2.1 Problem Identification**

Due to environmental regulation, sulfur content in transportation fuels need to be decreased to the specified amount. For example, in 2005, the maximum sulfur content will be limited to 10-50 ppm, compared to today's permitted value of 500 ppm in most western countries. This is due to formation of sulfur oxide ( $SO_x$ ) that will disperse throughout the air and inhibits pollution problem that lead to negative health and environmental impact. As the issued became a very common topic to be discussed, a lot of research had been done to solve the problem.

The conventional method applied in refinery around the world is catalytic hydrodesulfurization (HDS). Although the process is quite effective for sulfur removal,

this process required extremely high operating conditions that lead to high consumption of hydrogen at escalated cost. It also reduced the quality of the crude by decreasing the octane number. Besides that, this method also has some limitations in removing aromatic sulfur compound such as thiophene, benzothiophene and dibenzothiophene.

### **1.2.3 Significance of the Project**

To overcome those problems, a few alternatives that provide potential solutions had been studied. One of the most favorable alternatives is using ionic liquid due to its unique properties as an extractant and catalysts. This alternatives also promising lower cost of operation as ionic liquid can be regenerated for further use.

Oxidation followed by extraction using ionic liquid has found to be one of the effective techniques of removing sulfur. Investigation to synthesis ionic liquid has been broadly conducted. Furthermore, other type of ionic liquid can be produced from the available ionic liquid by the reaction of the ionic liquid with suitable salt.

## **1.3 Objectives and Scope of Study**

The objectives of this project are:

- To study the alternative for desulfurization process using ionic liquid.
- To apply technique of oxidation coupled with extraction to remove thiophene and benzothiophene from dodecane.

The scopes for this project cover all the activities listed below:

- Identifying the types of sulfur-based compound in crude oil.
- Synthesis [Mmim]DMP ionic liquid
- Applying oxidation coupling with extraction technique for desulfurization.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Preparation of Ionic Liquid

Imidazolium-based phosphoric ionic liquids were used to remove sulfur containing compound in Nie et al. [2006] [14] experimental work. [MMIM][DMP], [EMIM][DEP] and [BMIM][DBP] were prepared by reacting N-methylimidazole and the corresponding trialkyl phosphate at 423 K for 10h with a yield of 97%. The resulting yellowish viscous liquid was washed three times with diethyl ether at room temperature followed by rotary evaporation under reduced pressure for 12h to remove all volatile residues. The purity and structure of these ILs have been analyzed by NMR and electronic spray mass spectrum.

Wang et al. (2007) [15] in their research performed the desulfurization process using N-alkyl-pyridinium ionic liquids. In this experimental work, N-butyl-pyridinium bromide and N-ethyl-pyridinium bromide were synthesized by mixing pyridine (0.5 mol) and 1-bromobutane (0.5 mol). The resulting ionic liquid was found to be in form of solid with white colour. It was washed two times with ethyl acetate to avoid any contaminants and impurities. The other ionic liquids such as N-butyl-pyridinium tetrafluoroborate, N-butyl-pyridinium nitrate, N-butyl-pyridinium acetate, N-ethyl-pyridinium tetrafluoroborate, N-ethyl-pyridinium nitrate and N-ethyl-pyridinium acetate were prepared by implementing methathesis method that used N-butyl-pyridinium bromide and N-ethyl-pyridinium bromide as the starting material with appropriate solvent.



In other research, Schmidt (2008) [16] had study the ability of [BMIM][AlCl<sub>4</sub>] ionic liquid to remove sulfur. The ionic liquid was prepared by adding 200 mL of N-methylimidazolium to 500 mL of n-butyl chloride. The mixture was refluxed for 30 minutes, after which a second phase was formed. Other procedures of synthesis were done until crystallized phase was obtained after 3 days at -20°C. To 125 g of the obtained n-butyl-N-methylimidazolium chloride, 175 g of dry AlCl<sub>3</sub> was added in small portions. N-Butyl-N-methylimidazolium tetrachloroaluminate was obtained as a dark green liquid.

Huang et al. (2004) [12] proposed extraction with new ionic liquids as an alternative for desulfurization. In this process, sulfur- containing compound which is thiophene was extracted using Cu (I) based ionic liquid namely BMimCu<sub>2</sub>Cl<sub>3</sub>. The room-temperature ionic liquid in this study was synthesized by mixing 1-butyl-3-methylimidazolim chloride (BMIC) and purified anhydrous CuCl according to a BMIC:CuCl molar ratio of 1:2, at a temperature of 80°C in heptanes. The BMIC was synthesized according to previous literature [17].

## **2.2 Factors Effecting Desulfurization Efficiency**

### **2.2.1 Water Content**

Water content of ionic liquid is a very important parameter that needs to be considered in desulfurization process. According to Nie et al. [2006] [14], even 1% of water content in ionic liquid can decrease desulfurization efficiency by 20%. It is recommended that the water content in ionic liquids to be reduced as low as possible to achieve better

desulfurization efficiency. Table 2.1 below illustrates the effect of water content on the sulfur partition coefficients.

**Table 2.1: Effect of water content in IL on Sulfur Partition Coefficients**

Dibenzothiophene		Benzothiophene		3-Methylthiophene	
Water Content in IL (wt%)	$K_N$	Water Content in IL (wt%)	$K_N$	Water Content in IL (wt%)	$K_N$
0	1.28	0	0.99	0	0.49
1.04	1.05	1.07	0.84	0.93	0.48
3	0.75	3	0.59	3.02	0.38
5.42	0.53	4.99	0.43	5.17	0.31

## 2.2.2 Chemical Properties

**Table 2.2: Desulfurization results at different mass ratio**

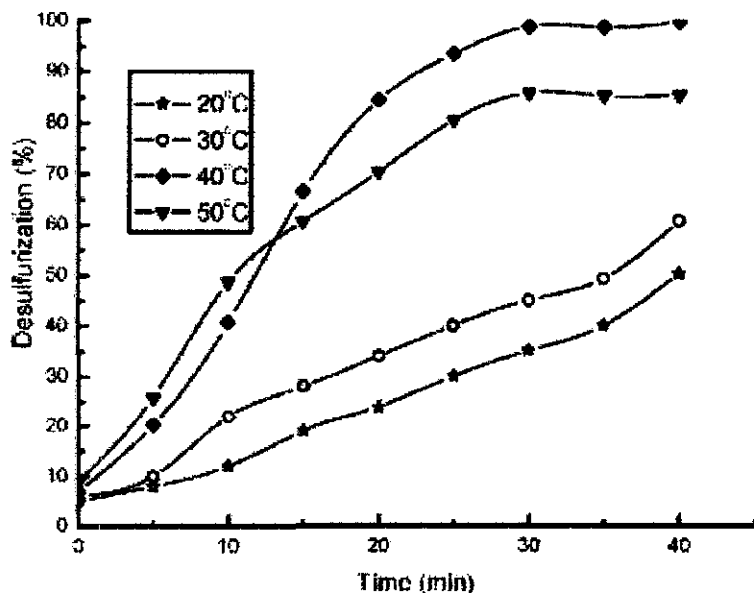
Ionic Liquids	Sulfur Removal (%)		
	Mass ratio of ILs to the model oil		
	1:1	1:2	1:3
[Bpy]BF <sub>4</sub>	45.5	28.6	16.9
[Bpy]NO <sub>3</sub>	30.1	19.1	9.4
[Bpy]Ac	32.1	20.3	10.2
[Epy]BF <sub>4</sub> <sup>a</sup>	21.8	12.6	8.9
[Epy]NO <sub>3</sub>	27.1	17.3	13.8
[Epy]Ac	23.0	15.7	9.7

Results from Wang et al. [15]. Condition: room temperature (except a: 50°C); extraction time 30-40 min.

Based on the above table, it was found that [BPy]BF<sub>4</sub> has the best extracting ability to remove thiophene from the model oil among the six ILs at the same conditions, and its extracting ability increases with the mass ratio of ILs to the model oil. The variation in anion and cation that form the ionic liquid do affect the capability of the ionic liquid. As

data shows, with the same anions ( $\text{BF}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{Ac}^-$ ), N-butyl-pyridinium based ILs with the substitution of a longer alkyl group to the pyridinium ring, have higher desulfurization ability than N-ethyl-pyridinium-based ILs. But when cations of ILs are the same (BPy, EPy), the desulfurization ability of ILs connects with the chemical property of anion. The lone pair electrons of pyridine and the electron donating ability of alkyl substitutions make the N-alkyl-pyridinium have higher polarizable aromatic  $\pi$ -electron density than pyridine. The strong affinity of the ILs for the aromatic sulfur compounds is related to the high polarity of the ILs. This is due to formation of liquid-clathrate compounds and  $\pi$ - $\pi$  interactions between aromatic structures of the extraction target and pyridinium ring system [18, 19].

### 2.2.2 Temperature



**Figure 2.1:** Effect of temperature on desulfurization.

From Zhao et al. [21]. Conditions:  $V_{\text{H}_2\text{O}_2} = 2.0\text{mL}$ , and  $0.20\text{g}$  of  $[(\text{C}_4\text{H}_9)_4\text{NBr} \cdot 2\text{C}_6\text{H}_{11}\text{NO}]$  catalyst.

Sun et al. [2008] [21] had study the effect of temperature to the desulfurization efficiency. Their result had been presented as in figure 1. Figure 1 shows the effect of the

reactive temperature on the desulfurization (%) of model oil. The reaction activity increased remarkably when the temperature increased from 20 to 40°C. 98.8% desulfurization efficiency was obtained at 40°C within 30 min. However, this is the highest percentage that can be achieved due to limitation. When the temperature increased to 50°C, the desulfurization efficiency reduced to 85.7%. This is due to the decomposition of H<sub>2</sub>O<sub>2</sub> at high temperature in the presence of an amide compound. [22].

**Table 2.3:** Desulfurization results of [BPy]BF<sub>4</sub> at different temperatures.

Temperature (°C)	25	32	40	50	60
Sulfur removal (%)	45.5	45.8	46	46.9	48.3

Results from Wang et al. [14]. Condition: BPy]BF<sub>4</sub>, mass ratio of ILs/model gasoline = 1:1; extraction time 30-40 min.

Another research on effect of temperature to the percentage of sulfur removal had been done by Wang et al. [2007] [14]. From the table, it is clearly show that the % of sulfur removal is directly proportional to the temperature increment. This is due to reduction of viscosity of the ILs molecule and sulfur-containing compound in the oil have higher chance to contact with each other, resulting in high sulfur removal. However, the effect of temperature on the desulfurization is limited to certain level of temperature. Extreme temperature will cause the ILs to decompose.

#### 2.2.4 Amount of Hydrogenperoxide (H<sub>2</sub>O<sub>2</sub>)

Besides effect of temperature, Sun et al. [2008] [21] also studied the effect of the mount of H<sub>2</sub>O<sub>2</sub> on desulfurization. It is found that, desulfurization efficiency increase with increment of H<sub>2</sub>O<sub>2</sub> amount. With the increase of H<sub>2</sub>O<sub>2</sub>, the oxidant and sulfur compound

had more opportunity to react, thus increase desulfurization (%). However, due to cost limitation, the optimal amount of H<sub>2</sub>O<sub>2</sub> is 2mL in the present study.

### 2.3 Regeneration of Used ILs

Rotary evaporation at 100°C and re-extraction in tetrachloro-methane was suggested by Wang et al. (2007) [14] in their paper work to be apply as a technique to regenerate the used ILs. They also identified that re-extraction method is better than rotary evaporation. Their findings are presented in table 5 below:

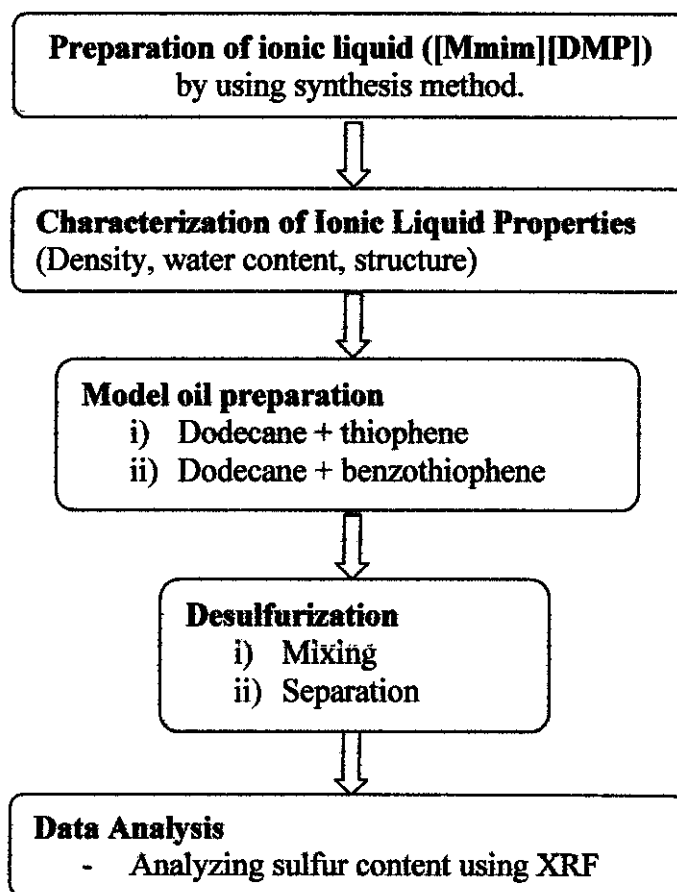
**Table 2.4:** Desulfurization of regenerated [BPy]BF<sub>4</sub>

Regeneration method	Sulfur removal (%)	
	Fresh ILs	Regenerated ILs
Rotary evaporation	45.5	39.4
Re-extraction using tetrachloro-methane	45.5	43.8

## CHAPTER 3

### METHODOLOGY

The methodology of this project can be divided into five main stages as illustrated by flowchart below:



**Figure 3.1: Experiment Flow Chart**

### 3.1 Preparation of Ionic Liquid

#### 3.1.1 Distillation of 1-methylimidazole

1. 1-methylimidazole was distilled to remove impurities. Distillation apparatus was set up as in appendix A-1.
2. 100ml of 1-methylimidazole was poured in tri-neck round flask at room temperature.
3. The Potassium Hydroxide (KOH) was added to 1-methylimidazole to avoid the production of moisture in the flask.
4. The solvent was being heated in vacuum pressure condition until it reached its boiling point ( $\approx 140^{\circ}\text{C}$ ) and the product produced in the round flask is the pure 1-methylimidazole.

#### 3.1.2 Mixing of 1-methylimidazole and Tri-methylphosphate

1. Purified 1-methylimidazole (0.5 mol) and trimethyl phosphate (0.5 mol) were mixed in a tri-neck round-bottom flask fitted with a reflux condenser and a drying tube. Reflux apparatus is set up as in appendix A-2.
2. The temperature was maintained between the ranges  $55 - 65^{\circ}\text{C}$  with continuous flow of nitrogen gas and the reaction was left for 3 days.

**Table 3.1: Volume for Mixing**

Solutions	Mol	Molecular Weight (gmol)	Density ( $\text{g}/\text{cm}^3$ )	Volume ( $\text{cm}^3$ )
MIM	0.5	82.11	1.03	39.86
$\text{M}_3\text{PO}_4$	0.5	140.08	1.21	57.88

### **3.1.3 Washing**

1. After 3 days, the [Mmim][DMP] ionic liquid was washed by using diethyl ether.
2. The equivolume of diethyl ether was added into [Mmim][DMP] ionic liquid and two layer was formed. This step was repeated for 3 times.

### **3.1.4 Solvent Removal and Drying**

1. Diethyl ether was remove from the [Mmim][DMP] solution by using rotary evaporator at 50°C for 3 hours.
2. The pure IL was then dried in the vacuum line to remove moisture. (Please refer to appendix A-5 for the arrangement of vacuum line).

## **3.2 Characterization of Ionic Liquid Properties.**

### **3.2.1 Analyzing Density using density meter**

1. The density meter was warmed-up by pushing the light button.
2. 5 cc syringe full of Mili-Q water was took up. The syringe was kept on the cell.
3. The 5 cc syringe was then filled with Acetone. Air bubble was removed, then 3-4 mL of acetone was injected into the inside slide of the cell.
4. The air pump tube was inserted into the inlet side of the cell and then the pump key was pressed.
5. The pump was automatically turned off after 3 minutes.



6. The 5 cc syringe was then filled with [Mmim]DMP. Air bubble was removed, then 3-4 mL of [Mmim]DMP was injected into the inside slide of the cell.
7. The readings were taken at temperature 25°C, 35°C, 45°C, 55°C, and 65°C.

### **3.2.2 Analyzing Water Content using Karl Fisher**

1. The main switch was switch on.
2. RUN button was ten pressed.
3. Method 1 (H<sub>2</sub>O standard) was chosen.
4. Pretitration took places.
5. The system go to standby mode after pre-titration was compleed. (Drift must less than 20).
6. Sample button was pressed.
7. Analysis of sample came out (max weight 5g).
8. OK button was pressed.
9. [Mmim][DMP] was added into the titration cell.
10. Weight value was entered.
11. Readings were taken for 3 times.

### **3.2.3 Analyzing Structure Using FTIR**

1. The power of the instrument was turned on.
2. The sample holder was cleaned up with acetone.
3. The “spectrum” software on the desktop was launched.
4. [Mmim]DMP was placed on the sample holder. As the sample is liquid, the procedure was proceeded to collect the spectrum by pressing the “Apply” and “Start” button.
5. The software was then turn off after the result was obtained.

### **3.3 Model Oil Preparation**

#### **3.3.1 Dodecane with Thiophene**

1. Sulfur content in 99% of liquid thiophene was determined.
2. Amount of thiophene that represents 2%, 4% and 6% of sulfur content in dodecane was determined.
3. The calculated amounts of thiophene were added to dodecane with basis of 100 mL solution of model oil.
4. 1mL H<sub>2</sub>O<sub>2</sub> was then added to each of the model oil.

#### **3.3.1 Dodecane with Benzothiophene**

1. Sulfur content in 97% of benzothiophene was determined.
  2. Amount of benzothiophene that represents 2%, 4% and 6% of sulfur content in dodecane was determined.
  3. The calculated amounts of thiophene were added to dodecane with basis of 100 g solution of model oil.
  4. 1mL H<sub>2</sub>O<sub>2</sub> was then added to each of the model oil.
- *Please refer to appendix C for the sample calculation.*

### **3.4 Desulfurization**

1. Model oils prepared were added to ionic liquid in a syringe with 1:1 volume ratio (2ml each).
2. Each sample was mixed using vortex mixer for 5 minutes with speed of 2500 rpm (please refer to appendix B-1 for the illustration). Desulfurization process occurred during the mixing.
3. The well mixed mixtures were separated in centrifugal for 1 minute. Two clear layers of liquid were formed (appendix B-4).
4. The two layers which represent ionic liquid and model oil were then separated and put in vial.

### **3.5 Data Analysis**

1. The sulfur content in ionic liquid and model oil were analyzed using XRF.

## CHAPTER 4

### RESULTS AND DISCUSSIONS

#### 4.1 Preparation of Ionic Liquid

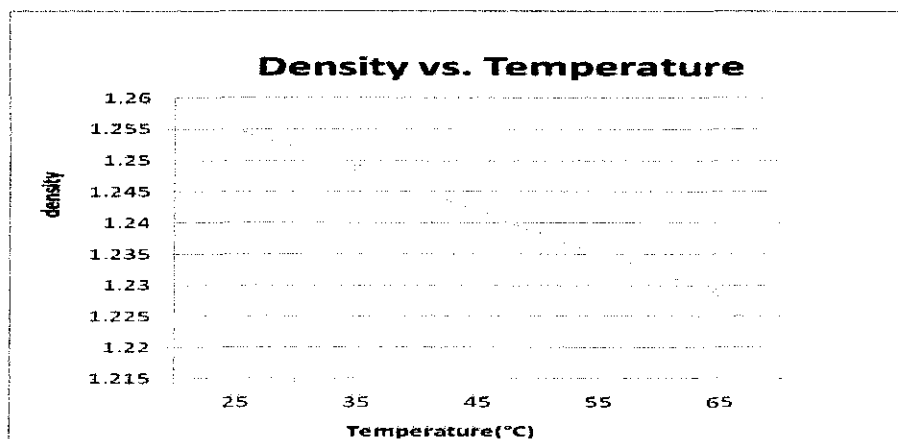
There are five main steps involved in the preparation of [Mmim]DMP ionic liquid which are distillation, mixing, washing, solvent removal and drying. During the distillation process, potassium hydroxide (KOH) was added to absorb moisture and impurities from 1-methylimidazole. Nitrogen gas was continuously purge throughout the mixing process to avoid moisture content from contaminating the ionic liquid. The reaction temperature was maintained between 55-65°C. This is because, if reaction temperature is below 55°C, the reaction will not occur. On the other hand, if the temperature exceeds 65°C, the ionic liquid will decomposed. The reaction was completely done when the ionic liquid become viscous and in reddish color. The optimal period of reaction had been found to be 72 hours.

#### 4.2 Ionic Liquid Properties

##### 4.2.1 Density

**Table 4.1 : Density of [Mmim][DMP]**

Temperature (°C)	Density (g/cm <sup>3</sup> )	SG
25	1.255	1.259
35	1.249	1.256
45	1.242	1.254
55	1.235	1.253
65	1.229	1.253



**Figure 4.1 :** Graph of density vs. temperature.

The density of [Mmim]DMP ionic liquid was determined using Anton Paar, DMA 5000 density meter. From the graph plotted, it can be seen the density of [Mmim][DMP] is inversely proportional with temperature. The results also show that the density of [Mmim][DMP] is greater than the density of water which is  $1\text{g/cm}^3$ .

#### 4.2.2 Water Content

**Table 4.2: Water Content in [Mmim][DMP]**

	Weight (g)	Water Content(ppm)	Water Content(wt%)
Sample 1	0.4978	17149.16	1.7149
Sample 2	0.6505	12973.21	1.2973
Sample 3	0.4064	20784.36	2.0784
Total		50870.73	5.0871
Average		16956.91	1.6957

Table 4.2 show the water content of 3 samples of [Mmim]DMP. The equipment used is Karl Fisher titrations Coulometer (Mettler Toledo DL39). From the results obtained, it clearly indicate that [Mmim]DMP ionic liquid appears to be hygroscopic at ambient temperature as it exceed 1%.

Water content is an essential property that needs to be determined in ensuring the performance of the IL. It had proved that even 1% of water content in IL can decrease the extracting ability by 20% [14].

### 4.2.3 Structure Analyzation.

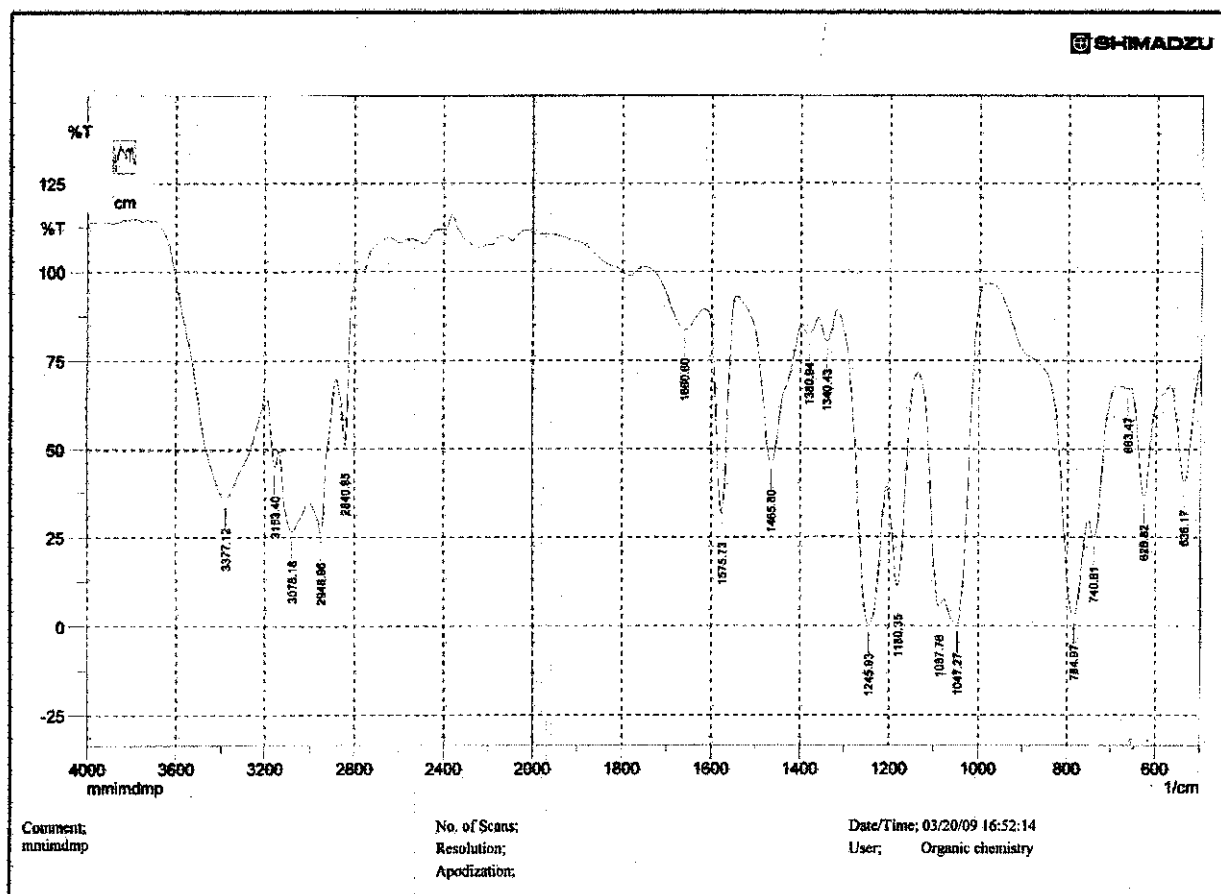
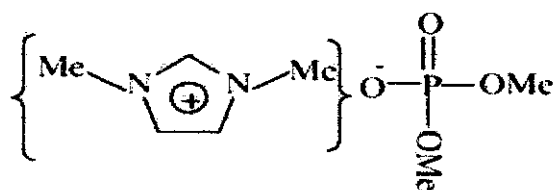


Figure 4.2: FTIR spectrum of MMIM[DMP]

**Table 4.3:** Identified structure of the sample

Functional Group	Molecular Motion	Wavcnumber (cm <sup>-1</sup> )
Alcohol	O-H bond	3650-3300
Alkanes	C-H stretch	2950-2800
Amines	C-N stretch	1200-1025
Phosphine Oxides	P=O	1210-1140



**Figure 4.3:** Molecular Structure of [Mmim]DMP

The types of functional group of a sample can be identified by referring to the value of the wavenumber at each peak occurred. By analyzing to the spectrum of IL in *figure 4.2*, the IL contains the functional group of alcohols (O-H bond with wavenumber range between 3650–3300cm<sup>-1</sup>), alkanes (wavenumber range between 2950–2800cm<sup>-1</sup>), amines with C-N stretch (wavenumber range between 1200–1025cm<sup>-1</sup>) and phosphine oxides (wavenumber range between 1210–1140cm<sup>-1</sup>). Thus, by comparing the results with the structure in *figure 4.3*, the sample tested is verified as MMIM[DMP] ionic liquid.



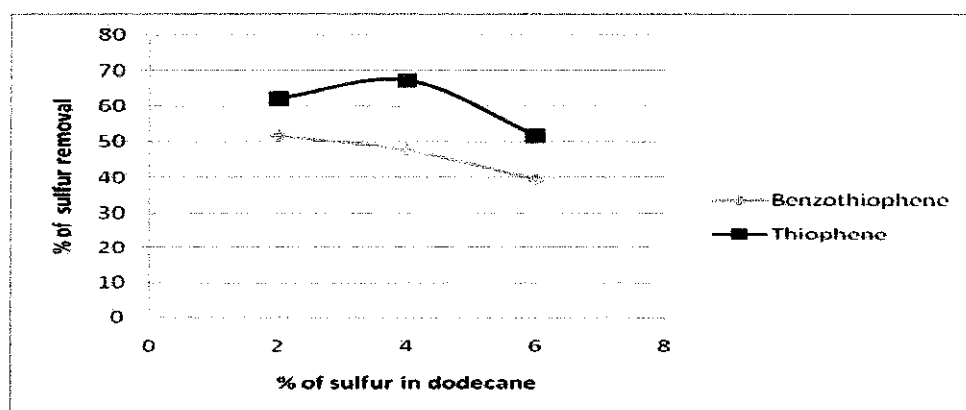
### 4.3 Data Analysis

**Table 4.4: Desulfurization of Model Oil with benzothiophene as the sulfur species**

MODEL OIL	Sulfur Content (%)			Sulfur Removal (%)
	BEFORE	AFTER		
	Model Oil	Model Oil	IL	
2% BT in Dodecane	1.781	0.862	0.164	51.60
4% BT in Dodecane	3.348	1.753	0.381	47.64
6% BT in Dodecane	4.587	2.783	0.59	39.33

**Table 4.5: Desulfurization of Model Oil with Thiophene as the sulfur species**

MODEL OIL	Sulfur Content (%)			Sulfur Removal (%)
	BEFORE	AFTER		
	Model Oil	Model Oil	IL	
2% Thiophene in Dodecane	0.208	0.079	0.022	62.02
4% Thiophene in Dodecane	3.997	1.315	0.408	67.10
6% Thiophene in Dodecane	3.912	1.895	0.383	51.56



**Figure 4.4: Comparison of percentage of sulfur removal for different sulfur species.**

Table 4.4 and 4.5 listed the results of desulfurization with [Mmim]DMP ionic liquid.

[Mmim]DMP ionic liquid shows remarkable ability for removing sulfur. After oxidation/extraction with the ionic liquid, more than 67% of the sulfur compounds have been removed from the model oil.

For each S-component studied, the percentage of sulfur removal always followed the order of Thiophene > Benzothiophene. The significance of this finding is such that although Thiophene and Dibenzothiophene cannot be removed efficiently by HDS process, they can be easily extracted by ionic liquid. This is due to strong  $\pi$ - $\pi$  interaction between unsaturated bonds of those sulfur species and the imidazolium ring of ionic liquid [14].

The rate of sulfur removal can be improved by repeating the extraction process for several times instead of using single extraction.

## **CHAPTER 5**

### **CONCLUSION AND RECOMMENDATIONS**

#### **5.1 Conclusion**

In conclusion, [Mmim]DMP show remarkable ability in extracting oxidative thiophene and benzothiophene sulfur species which are difficult to remove using HDS process. The desulfurization (%) of thiophene-containing model oil and benzothiophene-containing model oil can reach 67.1% and 51.6% respectively. This is due to strong  $\pi$ - $\pi$  interaction between unsaturated bonds of those sulfur species and the imidazolium ring of ionic liquid.

The [Mmim]DMP ionic liquid is an advantageous ionic liquid because it is not expensive for commercial application. Consequently, the [Mmim]DMP is a promising ionic liquid in oxidation/extraction process.

#### **5.2 Recommendations**

Based on the project, there are several recommendations that can be done to improve the outcome of the research:

1. Apply the desulfurization technique in this project to the crude oil.
2. Use ionic liquid that can be synthesis using natural and widely available resource such as glucose.

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## APPENDICES

### Appendix A: Preparation of Ionic Liquid

#### 1. Distillation of 1-methylimidazole

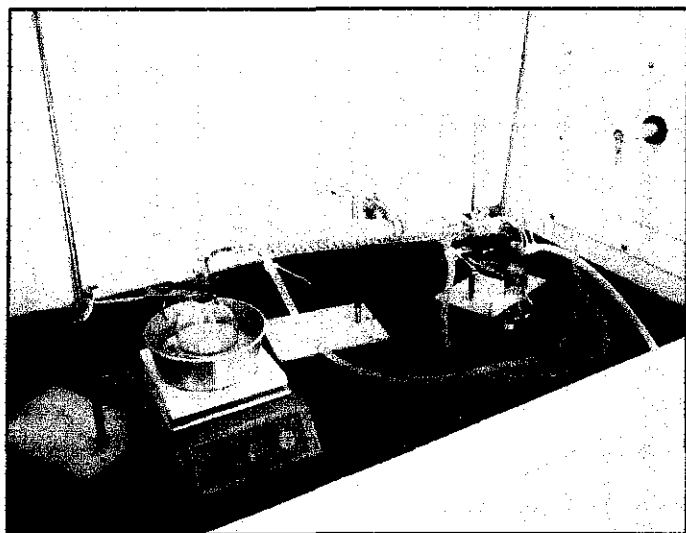


Figure A-1: Set up of distillation apparatus

#### 2. Preparation of MMIM DMP ionic liquid (Reflux)

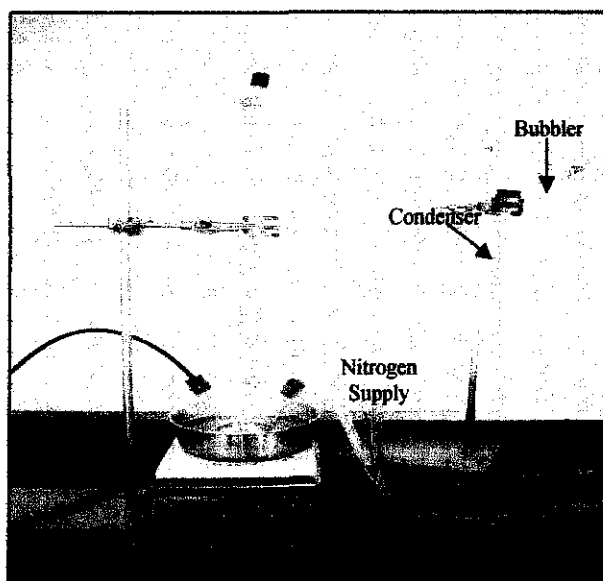


Figure A-2: Reflux Set

3. Washing ionic liquid with diethyl ether & Rotary evaporator used to remove residue in ionic liquid.

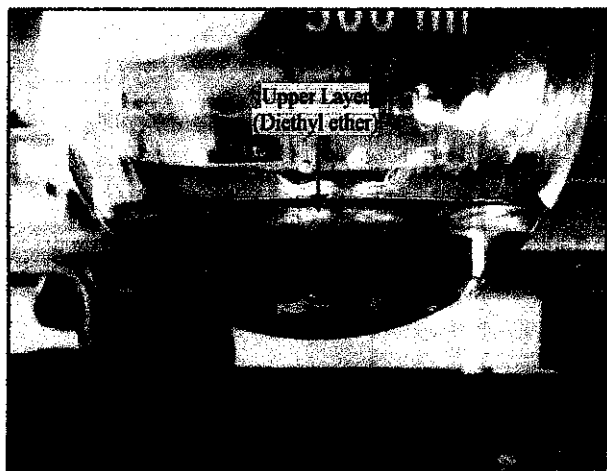


Figure A-3: Two layer of diethyl ether and ionic liquid



Figure A-4: Rotary evaporator set

4. Drying of ionic liquid

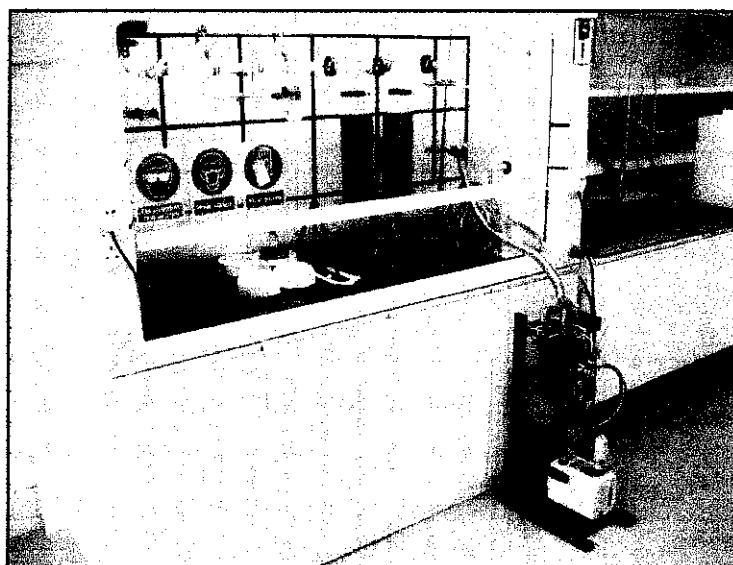


Figure A-5: Vacuum Line

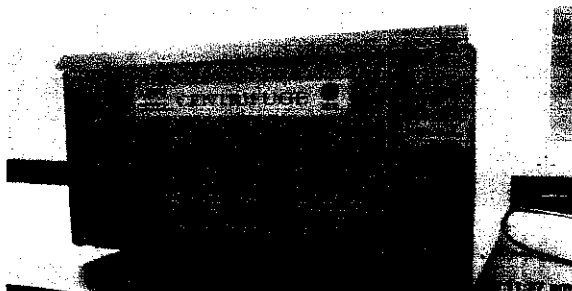
## Appendix B: Desulfurization

### 1) Mixing



**Figure B-1: Mixing of Ionic Liquid and Model Oil Using Vortex Mixer**

### 2) Separation

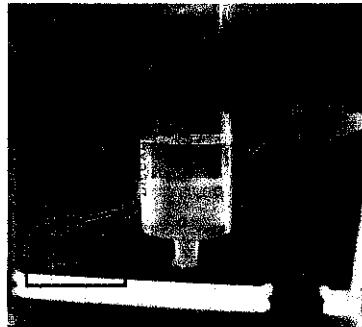


**Figure B-2: Centrifuge equipment**



**Figure B-3: Inside centrifuge**





**Figure B-4: After separation**

### **Appendix C: Example of Calculation for Model Oil Preparation**

#### **1) Dodecane + 2% Thiophene**

For thiophene (99.5% purity),

Molecular formula = C<sub>4</sub>H<sub>4</sub>S

Molar Mass = 84.14 g/mol

Density = 1.05 g/cm<sup>3</sup>

Molar mass of sulfur = 32.06g/mol

$$\begin{aligned} \% \text{ of sulfur in thiophene} &= \frac{\text{Molar mass of sulfur in thiophene}}{\text{Molar mass of thiophene}} \\ &= \frac{32.06 \text{ g/mol}}{84.14 \text{ g/mol}} \times 100 \\ &= 38.1\% \end{aligned}$$

38.1% sulfur = 99.5% thiophene

$$\begin{aligned} 2\% \text{ sulfur} &= \frac{2 \times 99.5}{38.1} \\ &= 5.22\% \text{ thiophene.} \end{aligned}$$

→ 100mL model oil requires 94.8 mL dodecane and 5.2mL thiophene.

#### **2) Dodecane + 2% Benzothiophene**

For benzothiophene (97% purity),

Molar Mass = 134.2 g/mol

Molar mass of sulfur = 32.06g/mol

$$\% \text{ of sulfur in thiophene} = \frac{\text{Molar mass of sulfur in benzothiophene}}{\text{Molar mass of benzothiophene}}$$

$$= \frac{32.06 \text{ g/mol}}{134.2 \text{ g/mol}} \times 100$$

$$= 23.17\%$$

23.17% sulfur = 97% benzothiophene

$$2\% \text{ sulfur} = \frac{2 \times 97}{23.17}$$

$$= 8.37\% \text{ benzothiophene.}$$

→ 100g model oil requires 91.63 g dodecane and 8.37g benzothiophene.