

Desulfurization of Model Oil by Extraction with Pyridinium-Based Ionic Liquids

by

Sakilah binti Mohd Rakbi

Dissertation submitted in partial fulfillment of

the requirements for the

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Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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(CHEMICAL ENGINEERING)

Approved by,



Dr. Chong Fai Kait
Project Supervisor

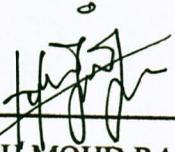
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December 2009

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.



SAKILAH MOHD RAKBI

ABSTRACT

This report contains the study on **Desulfurization of Model Oil by Extraction with Pyridinium-Based Ionic Liquids**. The objective of the project is to determine the sulfur-compound (Benzothiophene, BT) removal efficiency of pyridine-based ionic liquids ([MPy][DMP]) from model oil. The challenge in this project is preparation of pyridinium-based ionic liquid followed by characterization using Nuclear Magnetic Resonance (NMR) analyzer and Fourier Transform Infra-Red (FTIR) analyzer. Lab testing has been done by using different sulfur-containing compounds and different ionic liquids. The efficiency of the removal process has been determined using CHNS analyzer.

1-Methylpyridinium Dimethylphosphate, [MPy][DMP] can be synthesized via one-pot method with high yield, easy purification and low cost. The preparation of [MPy][DMP] was carried out in the laboratory starting from the purification of 1-Methylpyridine till drying of the ionic liquid. Then, [MPy][DMP] has been washed with diethyl ether as solvent for 2-3 times before proceeding with the drying process using rotary evaporator. The experiment went well and the ionic liquid was successfully synthesized based on the result of drying of ionic liquid. [MPy][DMP] was used to extract different percentages (2% and 6%) of sulfur compound, benzothiophene (BT) from model oil. The percentage sulfur removal from the model oil were, 33% and 47% respectively.

Commercial ionic liquid, Methylimidazolium Trimethylphosphate, [MMim][DMP] was used for comparison with the efficiency of ionic liquid prepared. The extraction results seem promising to be commercialized since the extraction performance for each sample ranging from 60% to 61% which is quite high.

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LIST OF SYMBOLS, ABBREVIATIONS AND NOMENCLATURE

[BMim][DBP]	Butyl-methyl-imidazolium Diebutylphosphate
[EMim][DEP]	Ethyl-methyl-imidazolium Diethylphosphate
[MMim][DMP]	Methyl-methyl-imidazolium Dimethylphosphate
[BPy][BF ₄]	N-butylpyridinium Tetrafluoroborate
[HPy][BF ₄]	N-hexypyridinium Tetrafluoroborate
[MPy][DMP]	1-Methylpyridinium Dimethylphosphate
[OPy][BF ₄]	N-octylpyridinium Tetrafluoroborate
[BF ₄] ⁻	Tetrafluoroborate
[PF ₆] ⁻	Hexafluorophosphate
BT	Benzothiophene
CHNS	Carbon, Hydrogen, Nitrogen, Sulfur
DBT	Dibenzothiophene
DMDBT	Dimethyldibenzothiophene
EDS	Extractive Desulfurization
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
HDS	Hydrodesulfurization
IL	Ionic Liquid
IR	Infrared
LLE	Liquid-liquid Extraction
K	Kelvin
KOH	Potassium Hydroxide
NMR	Nuclear Magnetic Resonance
NO _x	Nitrogen Oxides
SO _x	Sulfur Oxides
°C	Degree Celcius (Temperature)
atm	Atmospheric (Pressure)
g	Gram
ml	Milliliter
ppm	Parts Per Million

TABLE OF CONTENTS

CERTIFICATION OF APPROVAL	ii
CERTIFICATION OF ORIGINALITY	iii
ABSTRACT	iv
ACKNOWLEDGEMENT	v
LIST OF SYMBOLS, ABBREVIATIONS AND NOMENCLATURE	vi
LIST OF TABLES AND LIST OF FIGURES	ix
LIST OF APPENDICES	x
CHAPTER 1: INTRODUCTION		
1.1	Background of Study1
1.2	Problem Statement1
1.3	Objectives and Scope of Study2
CHAPTER 2: LITERATURE REVIEW		
2.1	Ionic Liquids3
2.1.1	<i>Ionic Liquid Systems</i>3
2.1.2	<i>Preparation of Ionic Liquid</i>6
2.2	Crude Oil Models7
2.2.1	<i>Crude Oil Components</i>7
2.3	Characterization and Measurement8
2.3.1	<i>Nuclear Magnetic Resonance (NMR) Spectroscopy</i>8
2.3.2	<i>Fourier Transform Infrared Spectroscopy (FTIR)</i>8
2.4	Partitioning Experiment9
2.4.1	<i>Condition of Extraction</i>9
2.5	CHNS Analyzer10

CHAPTER 3: METHODOLOGY

3.1	Preparation of Ionic Liquid	12
3.1.1	<i>Purification</i>	12
3.1.2	<i>Purification of Pyridine</i>	12
3.2	Synthesis of 1-Methylpyridinium Dimethylphosphate	13
3.3	Extractive Desulfurization Process	14
3.3.1	<i>Extraction of sulfur from model crude oil using 1-Methylpyridinium Dimethylphosphate [MPy][DMP]</i>	15

CHAPTER 4: RESULTS AND DISCUSSION

4.1	Purification	16
4.1.1	<i>Purification of Pyridine</i>	16
4.2	Synthesis	17
4.2.1	<i>Synthesis of 1-Methylpyridinium Dimethylphosphate [MPy][DMP]</i>	17
4.2.2	<i>Characterization</i>	19
4.3	Extractive Desulfurization Process	20
4.3.1	<i>CHNS Analysis</i>	22

CHAPTER 5: CONCLUSIONS AND RECOMMENDATION

REFERENCES

APPENDIX

LIST OF TABLES

Table 4.1	: Calculation of parameter for synthesis of 1-Methylpyridinium Dimethylphosphate	18
Table 4.2	: Percentage of Sulfur Content of the Ionic Liquid	21
Table 4.3	: Extraction Performance of [MPy][DMP]	22
Table 4.4	: Extraction performance of [MMim][DMP]	22

LIST OF FIGURES

Figure 2.1	: Chemical Structure of Seven of the Ionic Liquid Cations	4
Figure 2.2	: The Structure of the Hexfluorophosphate Anion	5
Figure 2.3	: The Structure of the Tetrafluoroborate Anion	5
Figure 2.4	: Chemical Structure of dibenzothiophene (DBT)	7
Figure 2.5	: Chemical Structure of benzothiophene (BT)	7
Figure 2.6	: CHNS Analyzer	10
Figure 3.1	: Process flow diagram of preparation, characterization, and liquid-liquid extraction of pyridinium-based ionic liquid	11
Figure 3.2	: Experiment Set-Up for purification of pyridine	12
Figure 3.3	: Experiment Set-Up for synthesis of 1-Methylpyridinium Dimethylphosphate ..	13
Figure 3.4	: Rotary Evaporator	14
Figure 3.5	: Centrifugal Separator	15
Figure 4.1	: Pyridine before purified	16
Figure 4.2	: Purified Pyridine	16
Figure 4.3	: Synthesis Equation of 1-Methylpyridinium Dimethylphosphate	17
Figure 4.4	: Mixture before the synthesis	18
Figure 4.5	: Mixture after the synthesis	18
Figure 4.6	: Fourier Transform Infrared Spectroscopy (FTIR) Analysis of [MPy][DMP] ...	19
Figure 4.7	: Two Layers Formed During Extraction	20
Figure 4.8	: Bar Chart of Sulfur Partition Coefficient, K_N for Methylpyridinium Phosphate [MPy][DMP] and Methylimidazolium Phosphate [MMim][DMP]	23

LIST OF APPENDICES

- APPENDIX A** : List of Equipments, Apparatus and Chemical Required
- APPENDIX B** : Summary Comparison of Ionic Liquid
- APPENDIX C** : FTIR Correlation Table
- APPENDIX D** : Volume Calculation to Synthesis [MPy][DMP]
- APPENDIX E** : Extraction Performance Calculation
- APPENDIX F** : Gant Chart

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Combustion of sulfur species present in transportation fuels led to sulfur oxide (SO_x) emissions into the air. These sulfur compounds could also poison the catalysts used in the engines emissions control equipment. Sulfur dioxide itself is a pollutant which causes respiratory problems, being especially irritating to the lungs. Moreover, sulfur dioxide oxidizes via several chemical pathways to sulfur trioxide which combines with water vapor or droplets to make sulfuric acid causing acid rain. Because of this dramatic environmental impact of sulfur oxides contained in engine exhaust emissions, sulfur content specifications are becoming more and more stringent worldwide.

1.2 Problem Statement

Ionic liquids have gained increasing interest over the past years due to its unique properties both as an extractant and also as a catalyst. The classical desulfurization process involves catalytic hydrogenation of sulfur compounds (hydrodesulfurization, HDS) into hydrogen sulfide by reacting crude oil fractions with hydrogen at high temperatures and pressures. Typical reaction conditions are 350°C and 30-100 bar hydrogen pressure. The hydrogen sulfide which is separated from the desulfurized oil is oxidized catalytically with air into elemental sulfur. However, some S-compounds such as dibenzothiophene, methyl dibenzothiophene, and 4, 6-di methyl dibenzothiophene are less reactive to HDS making the attainment of ultra low sulfur fuels very expensive process. Therefore, liquid- liquid extraction of S-compounds from crude oil using ionic liquid could be an alternative to HDS.

1.3 Objectives and Scope of Study

The main objectives of this research are:

- Development of pyridinium-based ionic liquids for sulfur removal from model oil
- Determination of extraction performance of the ionic liquid prepared

The scope of work for this project is to investigate ionic liquid synthesis and to determine the efficiency of the pyridinium-based ionic liquids for sulfur removal from model oil. Once the ionic liquid was prepared, they will be tested by using different sulfur-containing compounds in the model oil and different ionic liquids. The efficiency of the sulfur removal will be determined using CHNS analyzer.

CHAPTER 2

LITERATURE REVIEW

2.1 Ionic Liquids

Ionic liquids (ILs) are salts that are liquid at ambient or near ambient temperatures (melt below 100°C) [Alonso and Arc, 2008]. They have many attractive properties which make them ideal solvents for liquid-liquid extraction (LLE). Their properties can be tuned by altering their ionic structures to meet specific demands. Ionic liquids can be tuned or controlled by tailoring their cationic and anionic structures to optimize their physicochemical properties [Chu, et al., 2007]. Most ionic liquids have negligible vapor pressure, for this reason they are called ‘green’ solvents; chemically and thermally stable, non-flammable and adjustable miscibility and polarity.

The main reasons for the employment of ionic liquids as an alternative to remove sulfur-containing compounds can be summarized as follows [Nie, et al., 2006]:

- 1) It is environmentally benign and designable
- 2) It is virtually immiscible with fuels and hence free of cross-contamination
- 3) It is nonvolatile and thermally stable over a wide range of temperature, as a result the used ionic liquids can be regenerated by distillation
- 4) Many ionic liquids display desulfurization ability to a varying degree

2.1.1 Ionic Liquid Systems

From literature, there are many types of ionic liquid systems that have been tested as solvent for the removal of sulfur compounds (S-compounds) from the sample crude oils. Ionic liquids basically have only anions and cations. Anions are negatively charged ions, formed when an atom gains electrons in a reaction. Anions are negatively charged because there are more electrons associated with them than there are protons in their nuclei while cations are positively charged ions, formed when an atom loses electrons in

a reaction, forming an 'electron hole'. Based on the literature [Holbrey, et al., 2007], they used a range of ionic liquids with varying cation classes such as imidazolium, pyridinium and pyrrolodinium and a range of anion types.

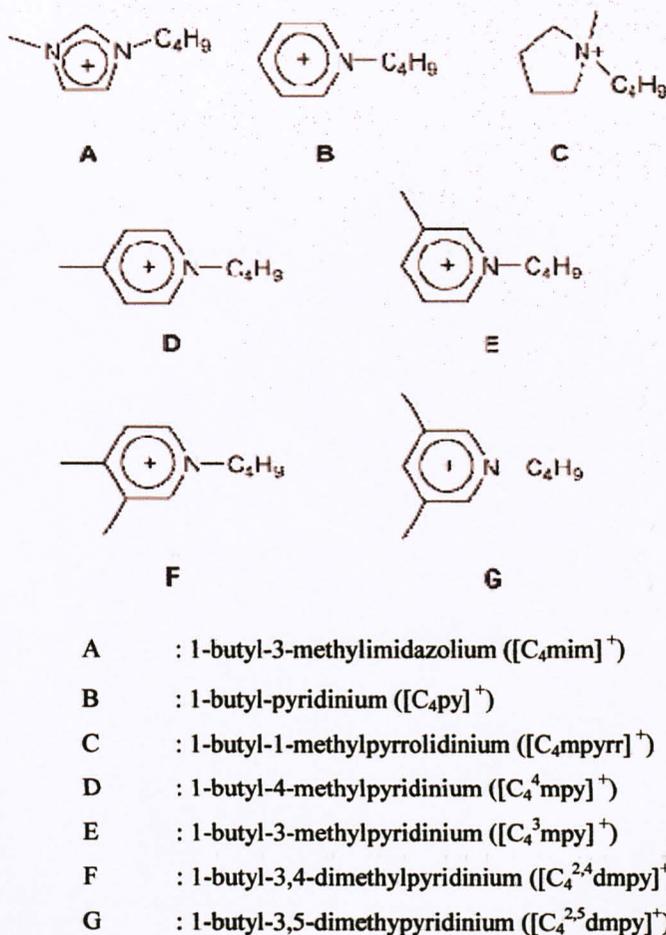


Figure 2.1: Chemical Structure of Seven of the Ionic Liquid Cations [Holbrey, et al., 2007]

For extractive desulfurization (EDS) process, the key to success is to find an effective IL that is nontoxic, chemically stable to moisture and air, and not expensive for commercial application. There has been a lot of focus on using the imidazolium-based phosphoric ionic liquids for extraction such as *N*-methyl-*N*-methylimidazolium diethyl phosphate, [MMim][DMP]; *N*-ethyl-*N*-methylimidazolium diethyl phosphate, [EMim][DEP]; and *N*-butyl-*N*-methylimidazolium dibutyl phosphate, [BMim][DBP] which are advantageous as they are easy to manufacture in a commercial scale with very high yield. [Nie, et al., 2006].

More recently, people have been moving away from using hexafluorophosphate, $[\text{PF}_6]^-$ (Figure 2.2) and tetrafluoroborate, $[\text{BF}_4]^-$ (Figure 2.3) since they are toxic [Chu, et al., 2007]. These anions are less nucleophilic and basic than nitrates and halides. Thus, when using these salts, one can usually assume that the cation is the reactive agent and this anion is inert. $[\text{BF}_4]^-$ owes its inertness to two factors:

- (i) It is symmetrical so that the negative charge is distributed equally over several (four) atoms
- (ii) It is composed of highly electronegative fluorine atoms, which diminished the basicity of the anion.

Hexafluorophosphate, $[\text{PF}_6]^-$ is more stable toward hydrolysis and whose salts tend to be lipophilic.

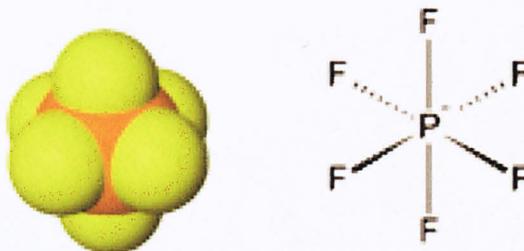


Figure 2.2: The structure of the hexafluorophosphate anion, PF_6^-

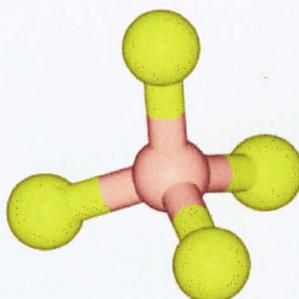


Figure 2.3: The structure of the tetrafluoroborate anion, BF_4^-

The pyridinium-based ionic liquids N-butylpyridinium tetrafluoroborate ([BPy][BF₄]), N-hexylpyridinium tetrafluoroborate ([HPy][BF₄]), an N-octylpyridinium tetrafluoroborate ([OPy][BF₄]) were found to be effective for the selective removal of aromatic heterocyclic sulfur compounds from diesel at room temperature [Gao, et al., 2008]. The results suggested that the structure and size of the cation greatly affect the extractive performance of ionic liquids. The extractive performance using pyridinium-based ILs followed the order [BPy][BF₄] < [HPy][BF₄] < [OPy][BF₄], and for ILs, the sulfur removal selectivity of sulfur compounds followed the order benzotheophene (BT) < dibenzotheophene (DBT) under the same conditions. The pyridinium-based ILs would not contaminate the diesel due to their insolubility. On the other hand, diesel has certain solubility in pyridinium-based ILs. [Gao, et al., 2008].

2.1.2 Preparation of Ionic Liquids

The synthesis of ionic liquids involves several techniques. One of the techniques is by in-situ process which is normally used for synthesis of imidazole-based ionic liquids. Most ionic liquids involves reflux for a designated time. [Gao, et al., 2008].

The preparation of phosphoric ionic liquids, [MMim][DMP], [EMim][DEP], and [BMim][DBP] were prepared by reacting n-methylimidazole and the corresponding trialkyl phosphate at 423K for 10 hours 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 12 hours to remove all volatile residues (e.g, the reactants unreacted and diethyl ether). The purity and structure of these ILs have been analyzed by NMR and electronic spray mass spectrum [Nie, et al, 2006].

2.2 Crude Oil Models

2.2.1 Crude Oil Components

There are lots of components present in crude oils. The typical molecules in gasoline and diesel fuels consists of 2-methylpentane, 1-hexane, methylcyclopentane, benzene, toluene, trimethylbenzene, thiophene, 2-methylthiophene, isobutyl mercaptan, dibenzothiophene (DBT), and 4,6-dimethyldibenzothiophene (DMDBT) [Zhang, 2004].

Simple hydrocarbons are insoluble in many ionic liquids, aromatic compounds, such as benzene and toluene, can be highly soluble, with interactions between ionic liquids and aromatic solutes leading to liquid clathrate and solid-state inclusion complexes [Holbrey, et al., 2007]. Mutual solubility is an important factor to be considered in choosing suitable extractant. Noticeable solubility of imidazolium-based ionic liquid in gasoline may on one hand contaminate the fuel and on the other hand lead to NO_x pollution while we intend to reduce SO_x pollution [Nie, et al., 2006].

The amount of sulfur in fuels depends on the source of the crude feedstock, methods of refining and the type of blending. Refineries remove organic sulfur from crude oil-derived fuels by hydrodesulfurization (HDS). HDS is a catalytic process that converts organic sulfur to hydrogen at high pressures and temperatures. Nonetheless some sulfur compounds of the fuels, such as benzothiophenes (BT) and dibenzothiophenes (DBT) have great resistance to HDS making the attainment of ultra low-sulfur fuels a very expensive process [Alonso and Arce, 2008]. Dibenzothiophene (Figure 2.4) is the organic compound heterocycle, and especially its alkyl substituted derivatives occur widely in heavier fractions of petroleum.

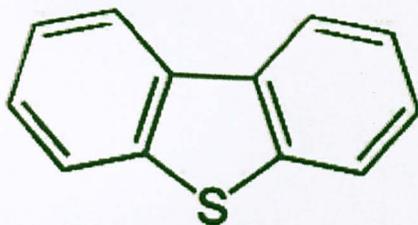


Figure 2.4: Chemical structure of dibenzothiophene (DBT)

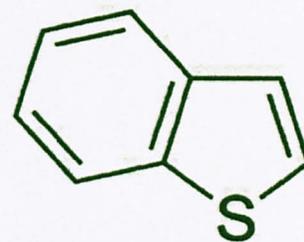


Figure 2.5: Chemical structure of benzothiophene (BT)

2.3 Characterization and Measurement

2.3.1 *Nuclear Magnetic Resonance (NMR) Spectroscopy*

From the literature [Holbrey, et al., 2007], the ionic liquids were characterized by proton Nuclear Magnetic Resonance (NMR) spectroscopy. In principle, NMR is applicable to any nucleus possessing spin. Structure information of compounds can be obtained from an NMR spectrum. Much like using infrared (IR) spectroscopy to identify functional groups, analysis of a 1D NMR spectrum provides information on the number and type of chemical entities in a molecule. However, NMR provides much more information than IR.

2.3.2 *Fourier Transform Infrared Spectroscopy (FTIR)*

FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitate some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. The term Fourier Transform Infrared Spectroscopy (FTIR) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. [Service, 2009]

2.4 Partitioning Experiment

2.4.1 *Condition of Extraction*

From the literature, the extraction experiment was performed under standard conditions of equal volumes of sample crude oils and ionic liquid [Holbrey, et al., 2007; Chu, et al., 2007]. There are also several literatures with the experiments conducted using different volume ratio between sample crude oil and ionic liquids, [Zhang, 2004; Huang, et al., 2004]. For example, the experiments using ionic liquids $\text{AlCl}_3\text{-TMAC}$, EMIMBF_4 , MOIMBF_4 , BMIMPF_6 , and HMIMPF_6 , the weight ratio of organic phase over ionic liquid was 5:1 [Zhang, 2004]. Basically, the experiments were carried out at room temperature and atmospheric pressure.

2.5 CHNS Analyzer

CHNS Analyzer is a scientific instrument which can determine the elemental composition of a sample. The names derives from the four primary elements measured by the device which are carbon (C), hydrogen (H), nitrogen (N) and sulfur (S). Oxygen can also be measured. The CHNS Analyzer find utility in determining the percentages of C, H, N, S and O of organic compounds based on the principle of “Dumas method” which involves the complete and instantaneous oxidation of the sample by ‘flash combustion’. The combustion products are separated by a chromatographic column and detected by the thermal conductivity detector (T.C.D.), which gives an output signal proportional to the concentration of the individual components of the mixture.

The instrument is calibrated with the analysis of standard compounds using the K-factors calculations. Thus the instrument ensures maximum reliability of the results because the combustion gases are not split or diluted but directly carried to build in GC system simultaneous determination of CHNS can be done in fewer 10 minutes. This method finds greatest utility in finding out percentages of C, H, N, S, (O) in organic compounds which are generally combustible at 1800°C.

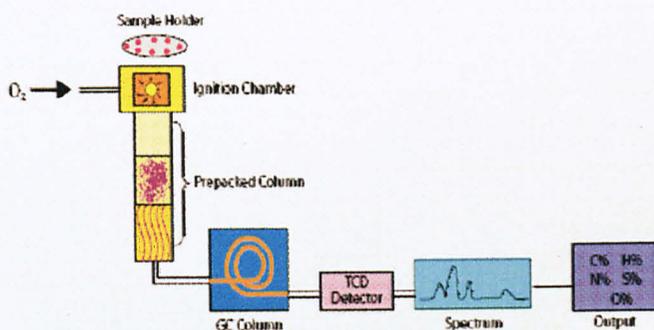


Figure 2.6: CHNS Analyzer

CHAPTER 3

METHODOLOGY

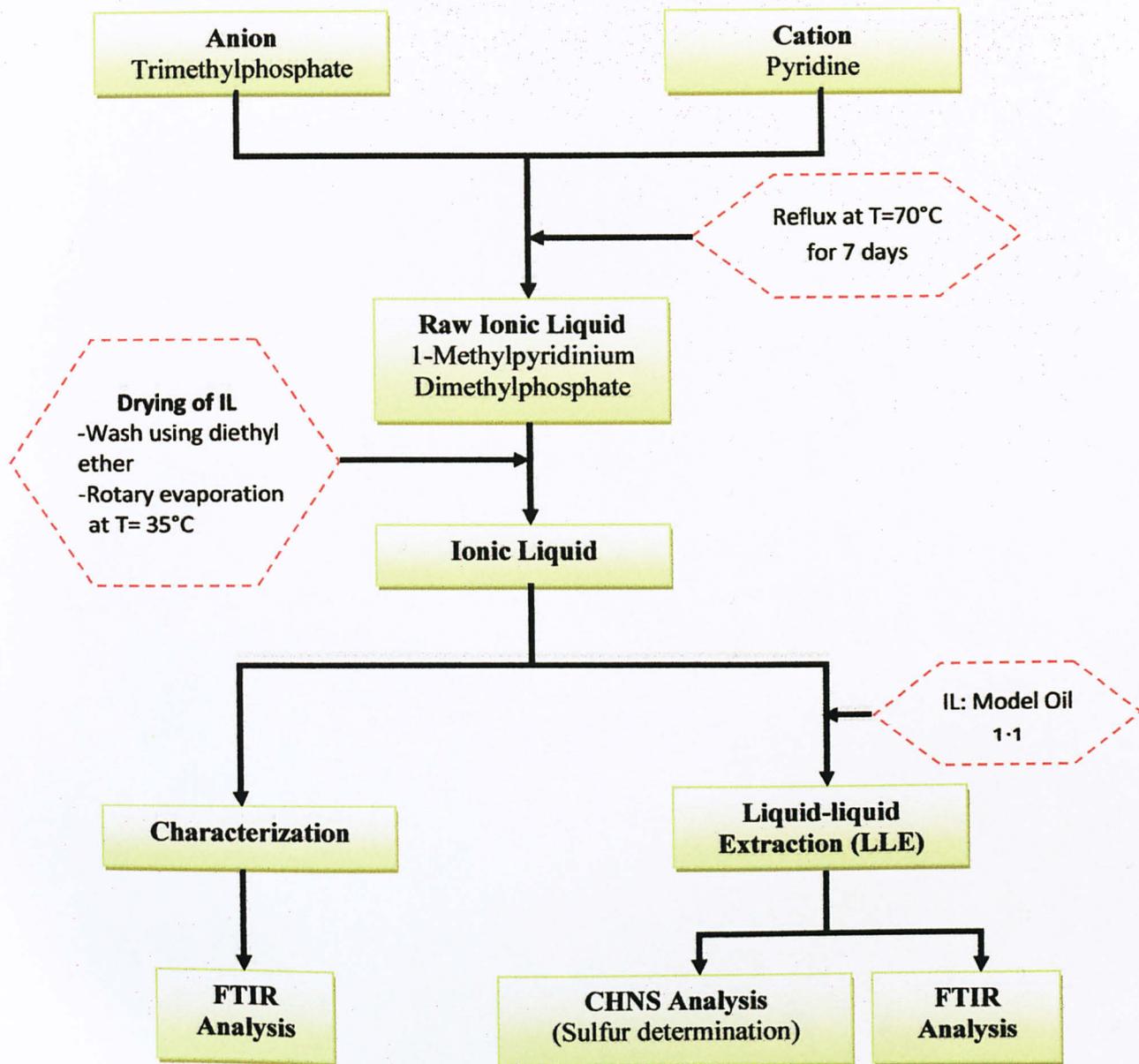


Figure 3.1: Process flow diagram of preparation, characterization, and liquid-liquid extraction of pyridinium-based ionic liquid

3.1 Preparation of Ionic Liquid

3.1.1 Purification

The experiment was begun with purification of pyridine. Distillation is the best choice to purify the liquids. The impurities can be left behind by boiling off the compound and collecting it into a different container. If the impurities are liquid this complicates the distillation process as both boil off at the same time but in different proportions.

3.1.2 Purification of Pyridine

Boiling point of pyridine : 115.2°C

Chemicals : Pyridine, Potassium hydroxide, Silicon Oil

Experimental procedure:



Figure 3.2: Experiment Set-Up for purification of pyridine

1. The experiment was set up as in Figure 3.2.
2. Transfer the aqueous solution containing 150 ml pyridine to a 250 ml round bottom flask.
3. Add about 100 g Potassium Hydroxide (KOH) pellet into the flask.
(Addition of KOH is to absorb the water in the Pyridine).

4. Place the flask containing the mixture into silicon oil bath to avoid direct heating of pyridine.
5. Vacuum distillation is conducted at 103 °C up to 110 °C. The temperature should be monitored during the experiment to avoid the thermometer from damage.
6. Stop the experiment when all the pyridine has been collected in the other flask.

3.2 Synthesis of 1-Methylpyridinium Dimethylphosphate [MPy][DMP]

Chemicals : Purified pyridine, Trimethyl phosphate, Nitrogen Gas

Experimental procedure:

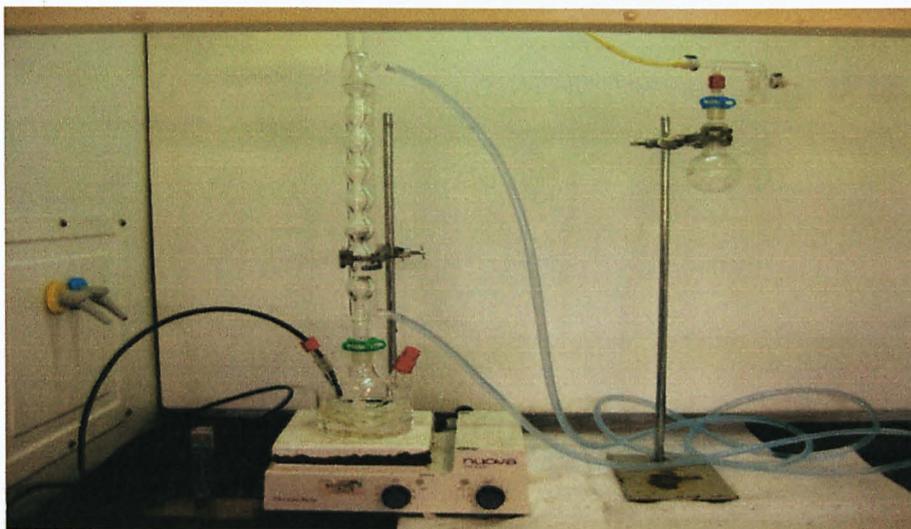


Figure 3.3: Experiment Set-Up for synthesis of 1-Methylpyridinium Phosphate

1. The experiment was set up as in Figure 3.3.
2. Make sure the nitrogen gas flows throughout the experiment.
3. First, add 0.1 mol of Pyridine to a 250 ml 3 neck round bottom flask fitted with a reflux condenser.
4. Stir the pyridine in the flask for about 5 to 10 minutes.
5. Set the flask containing the mixture into silicon oil bath (heated by a hot plate stirrer). Silicon oil is used as a medium to avoid direct heating of pyridine.

6. By using a syringe, inject 0.1 mol of Trimethyl Phosphate into the flask.
7. Next, the mixture is heated to 70°C. The temperature should be monitored during the experiment.
8. Then, mixture was reflux at 70°C for seven days. Yellowish liquid forms at the end of the reaction.
9. Then, wash the yellowish liquid with diethyl ether (solvent) to remove contaminants.
10. Finally, the solvent was removed by rotary evaporation.

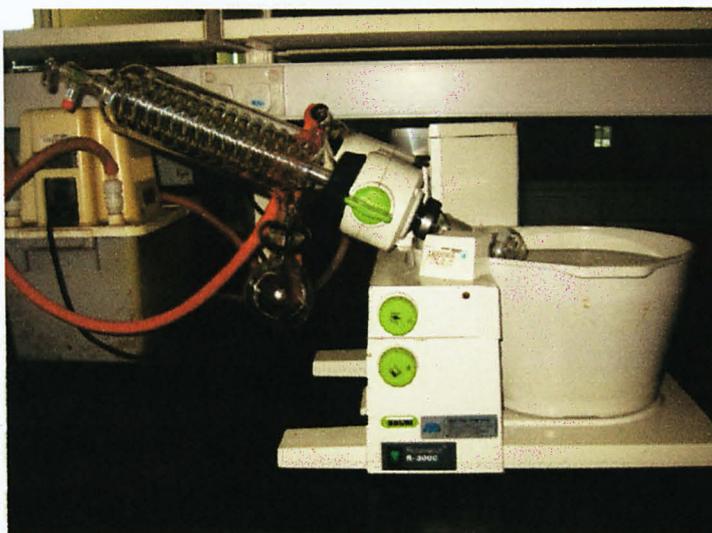


Figure 3.4: Rotary Evaporator

3.3 Extractive Desulfurization Process

The next step of this project is the extraction of the sulfur compound from crude oil model. The experiment is carried out by using the synthesized ionic liquid, 1-Methylpyridinium Dimethylphosphate, ([MPy][DMP]) and also commercial ionic liquid, 1-3- Dimethylimidazolium Dimethylphosphate, (Mmim)[DMP]. All the extractive desulfurization experiments were conducted in 12 ml centrifuge tube with cap. The mass ratios of ILs to crude oil model were 1:1.

3.3.1 Extraction of sulfur from model crude oil using 1-Methylpyridinium Dimethylphosphate [MPy][DMP]

Chemicals : [MPy][DMP], Dodecane contains of 2% Benzothiophene (BT), Dodecane contains of 6 % Benzothiophene (BT)

Experimental procedure:

1. First, add 2 ml of [MPy][DMP] into a 12 ml centrifuge tube with cap followed by 2 ml of Dodecane contains 2% Benzothiophene (BT).
2. The mixture is mixed by using vortex mixer for 1 minute.
3. Next, the mixture is separated by using centrifugal separator (centrifuge). The centrifuge is set for 1 minute with 25 000 ppm. Two layers are formed.
4. Separate the layers and stored them into 2 different vinyls. Repeat step 1 to 4 by using dodecane containing 6% benzothiophene (BT).
5. The same procedure is repeated by using different ionic liquid, [MMim][DMP].



Figure 3.5: Centrifugal Separator

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Purification

4.1.1 Purification of Pyridine

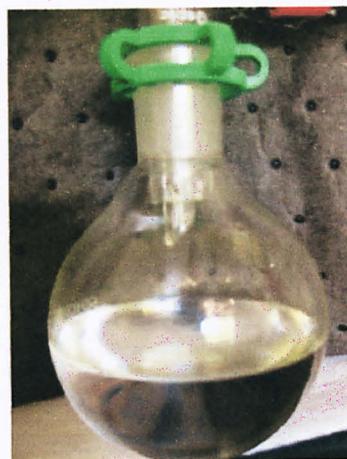
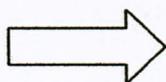


Figure 4.1: Pyridine before purified

Figure 4.2: Purified Pyridine

Based on the experiment, the only physical change that can be observed is the color of pyridine. Before purification process, the color of pyridine is yellowish. After purification process is carried out, pyridine became colorless. Throughout the experiment, the temperature of the pyridine is always be monitored. This is because; very high temperature will oxidize the pyridine. Besides, the pump also should be attached during the experiment to create a vacuum condition in the apparatus set-up. This will reduce the boiling point of pyridine to 103°C and hence make the process faster. The pyridine was also mixed with potassium hydroxide to absorb the water and impurities in pyridine solution. Purification of pyridine took about 3 hours to complete.

4.2 Synthesis

4.2.1 Synthesis of 1-Methylpyridinium Dimethylphosphate [MPy][DMP]

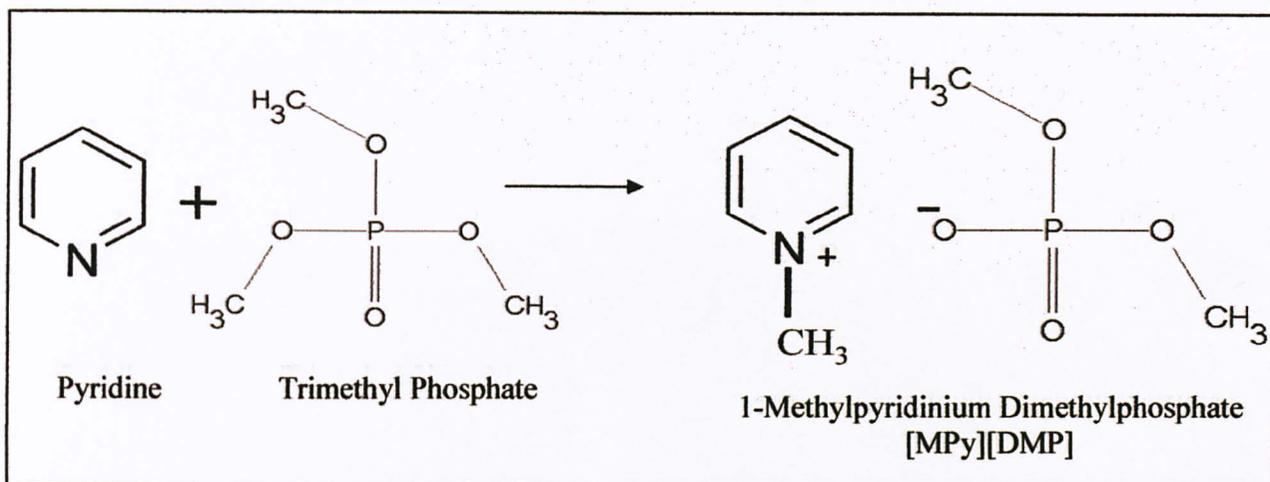


Figure 4.3: Synthesis Equation of 1-Methylpyridinium Dimethylphosphate

Before the synthesis of Ionic Liquid can be done, several parameters need to be determined.

$$\text{Mol} = \frac{\text{Mass}}{\text{Molecular Weight}}$$

$$\text{Density, } \rho = \frac{\text{Mass}}{\text{Volume}}$$

$$\text{Mass} = \text{Mol} (\text{Molecular Weight})$$

Therefore,

$$\text{Volume, } V = \frac{\text{Mol}(\text{Molecular Weight})}{\text{Density}}$$

Table 4.1: Calculation of parameter for synthesis of 1-Methylpyridinium Dimethylphosphate

Chemicals	Mol	Molecular Weight	Density, ρ (g/cm ³)	Volume
Pyridine	0.1	79.10	0.9819	8.0558
Trimethylphosphate	0.1	140.076	1.210	11.5765



Figure 4.4: Mixture before the synthesis

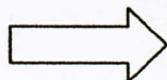


Figure 4.5: Mixture after the synthesis

After the purification has completed, pyridine was refluxed with trimethylphosphate in the nitrogen atmosphere for 7 days. Nitrogen gas was used in this process in order to avoid oxidation during the process since the ionic liquid is sensitive to oxidation. The temperature and pressure used in this process was 70°C and 1 atm respectively. There is physical change that can be observed during synthesis in which the mixture became yellowish (Figure 4.5) and more viscous indicating formation of [MPy][DMP]. In order to monitor the completion of synthesis, diethyl ether is used. If there are no two layers when diethyl ether is added to the mixture, the reaction has not completed. Therefore, the mixture must be continued to reflux until two layers can be formed.

4.2.2 Characterization

Chemical compound can be determined using FTIR analysis. The sample will be exposed to electromagnetic radiation and the response is monitored as shown in the Figure 4.6.

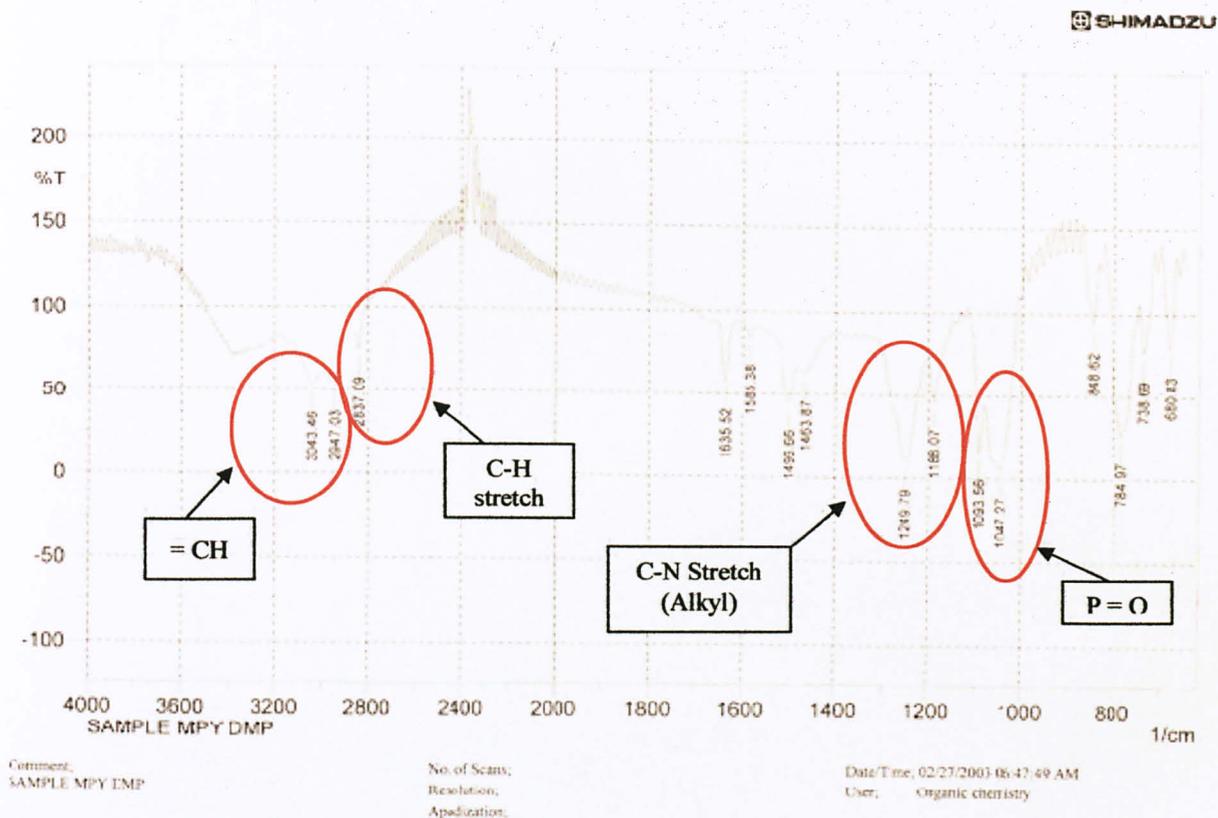


Figure 4.6: Fourier Transform Infrared Spectroscopy (FTIR) Analysis of [MPy][DMP]

**Equipment Model Shimadzu FTIR 8400S*

The peaks of wave number indicate the types of the functional group in the ionic liquid. The types of functional group can be determined through the correlation table in **Appendix C**. Based on the analysis of Figure 4.6, the ionic liquid (Figure 4.3) contains of amines with alkyl group (C-N bond) with wave number: 1200-1025 cm^{-1} ; phosphine oxides group (P = O bond) with wave number: 1210-1140 cm^{-1} ; alkenes group (=CH bond) with wave number: 3100-3010 cm^{-1} and alkanes group (C-H bond) with wave number: 2950-2800 cm^{-1} . Therefore, the analysis illustrate that the [MPy][DMP] is verified.

4.3 Extractive Desulfurization Process

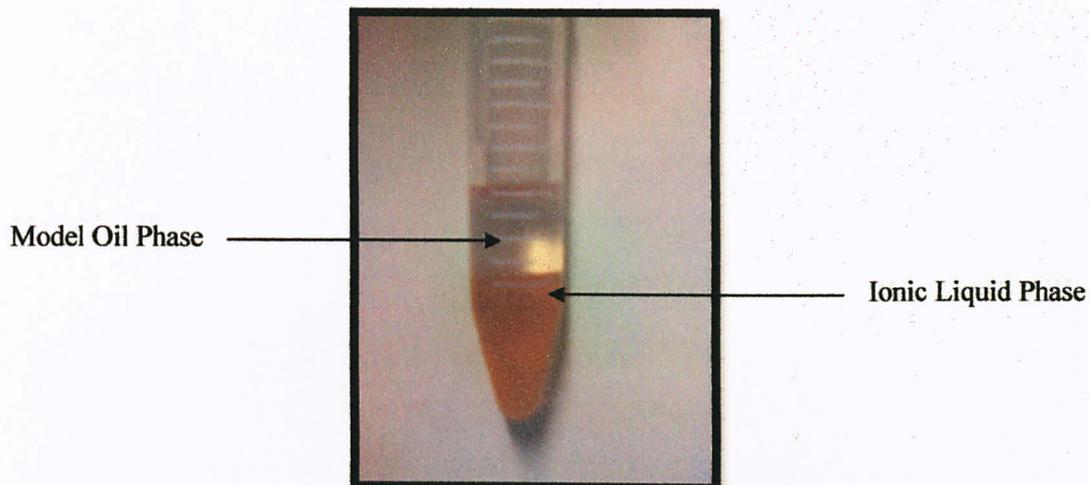


Figure 4.7: Two Layers Formed During Extraction

In the extraction process, the model oil and ionic liquid were mixed by 1:1 ratio. The mixture was mixed using the vortex mixer in order to have higher mass transfer area which can increase the extraction of the sulfur content. As the model oil was added and mixed into ionic liquid, there were two layers formed as shows in Figure 4.7. The upper layer was model oil phase while the bottom layer was ionic liquid phase. The removal of benzothiophene, BT from model oil is believed to happen during this extraction stage whereas the ionic liquid and model oil containing BT were mixed followed by centrifugal separation. The mixture was transferred into vials for analysis using CHNS elemental analyzer.

4.3.1 CHNS Analysis

CHNS analysis was carried out in order to determine the percentage of benzothiophene, BT, presents in the ionic liquid and also model oil. The sample of pure ionic liquid and model oil with different percentage of BT was first to be analyzed to find out the initial percentage of sulfur content followed by the sample of ionic liquid and model oil after extraction process. The data were summarized in the Table 4.2 and Figure 4.10 as follows:

Table 4.2: Percentage of Sulfur Content of the Ionic Liquid

No.	Solution	Sample Reference Number	Sulfur Content (%)
1.	Model Oil after extraction, 2% BT	U 2001	0.4230
2.	[MPy][DMP] after extraction, 2% BT	U 2002	0.2099
3.	Model Oil after extraction, 6% BT	U 2003	2.2900
4.	[MPy][DMP] after extraction, 6% BT	U 2004	2.0226
5.	Model Oil after extraction, 2% BT	U 2005	0.2519
6.	[MMim][DMP] after extraction, 2% BT	U 2006	0.3810
7.	Model Oil after extraction, 6% BT	U 2007	1.6791
8.	[MMim][DMP] after extraction, 6% BT	U 2008	2.6335
9.	[MPy][DMP] before extraction	U 2009	0.0000
10.	[MMim][DMP] before extraction	U 2010	0.0000
11.	Dodecane	U 2011	0.0000
12.	Dodecane + 2% BT before extraction	U 2012	0.6329
13.	Dodecane + 6% BT before extraction	U 2013	4.3126

Efficiency of the ionic liquid is defined by the percentage of sulfur removal in model oil. It has been determined as follows:

$$\text{Extraction performance} = \frac{\text{Initial sulfur content (\%)} - \text{Final sulfur content (\%)}}{\text{Initial sulfur content (\%)}} \times 100$$

Table 4.3: Extraction performance of [MPy][DMP]

No.	Solution	Percentage of sulfur contains in model oil (%)		Extraction performance (%)
		Before Extraction	After Extraction	
1.	Model Oil (Dodecane + 2% BT)	0.6329	0.4230	33.0
2.	Model Oil (Dodecane + 6% BT)	4.3126	2.2099	47.0

Table 4.4: Extraction performance of [MMim][DMP]

No.	Solution	Percentage of sulfur contains in model oil (%)		Extraction performance (%)
		Before Extraction	After Extraction	
1.	Model Oil (Dodecane + 2% BT)	0.6329	0.2519	60.2
2.	Model Oil (Dodecane + 6% BT)	4.3126	0.3810	61.0

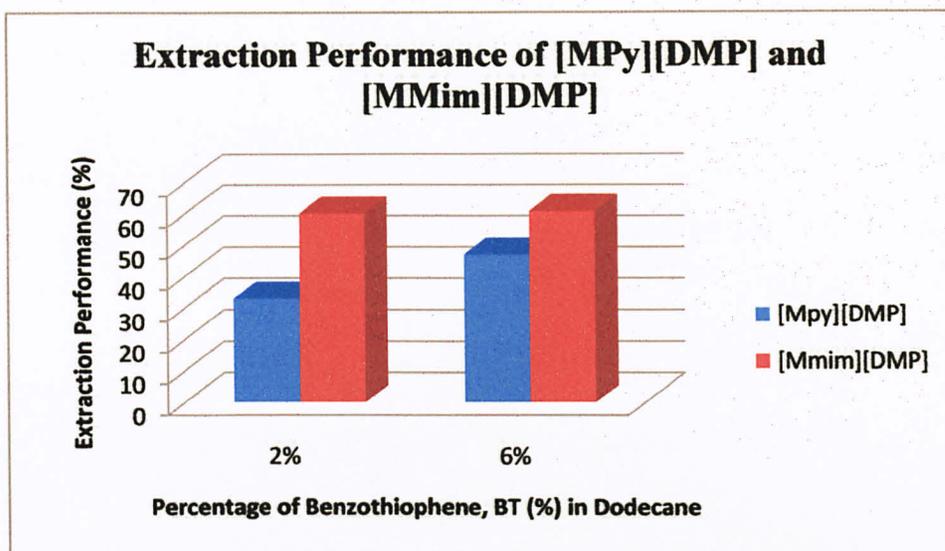


Figure 4.8: Bar Chart of Extraction Performance for Methylpyridinium Dimethylphosphate [MPy][DMP] and Methylimidazolium Dimethylphosphate [MMim][DMP]

Based on results in Table 4.3, Table 4.4 and Figure 4.8 it shows that, the extraction performances for both type of ionic liquids increases with the percentage of sulfur content in dodecane. The performance of [MMim][DMP] is better compared to [MPy][DMP] which are 33% and 60.2% respectively for test with 2% of BT in dodecane while 47% and 61% respectively for test using 6% of BT in dodecane. Factor for low performance may be due to water content in the synthesized ionic liquid, [Gao, et al., 2008]. Future work should include the determination of water content in the synthesized ionic liquid. Although the performance of [MPy][DMP] is not impressive, other contributing factors should be looked into (water content, equilibrium time, purity of the product, etc.).

CHAPTER 5

CONCLUSIONS AND RECOMMENDATION

Purification of the starting material (pyridine) was conducted in order to prepare [MPy][DMP] ionic liquid. However, the [MPy][DMP] produced is still not pure based on the FTIR spectroscopic result. The factor for the impurity may be due to existence of contaminants in the trimethylphosphate used since the purification was only conducted for pyridine. The purity of [MPy][DMP] can be improved if the purification is conducted for all starting materials.

Based on the result obtained, the extraction of sulfur from model oil using [MPy][DMP] is ranging from 33% to 47% while the extraction performance for [MMim][DMP] is about 61%. It shows that the extraction performance of [MMim][DMP] is remarkable. However, although the performance of [MPy][DMP] is not impressive, other contributing factors should be looked into (water content, equilibrium time, purity of the product, etc.).

As the conclusion, 1-Methylpyridinium Phosphate [MPy][DMP] has a good extraction performance for aromatic sulfur compounds and promising to be commercialized. It is encourage to use [MPy][DMP] for higher percentage of benzothiophene.

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APPENDIX A
LIST OF EQUIPMENTS, APPARATUS
AND CHEMICALS REQUIRED

APPENDIX A: List of Equipments, Apparatus and Chemical Required

No.	Equipment	Quantity
1.	Distillation apparatus with tube	1 set
2.	Reflux condenser	1 set
3.	Gas bubbler	1 set
4.	Rotary evaporator (Rotavap with 100ml flask)	1 set
5.	Hot plate stirrer	1 set
6.	Air pump	1
7.	Centrifuge	1
8.	Mixer	1
	Apparatus	Quantity
1.	Magnetic stirrer	1
2.	Thermometer (max T: 250°C)	1
3.	Basin	1
4.	Measuring cylinder (100 ml)	2
5.	Round bottom 1 neck flask	3
6.	Round bottom 3 neck flask	3
7.	Beaker	3
8.	Storage bottle (250 ml)	5
9.	Syringe (12 ml)	10
10.	Test tube with cap	10
11.	Pipette (10 ml)	10
12.	Centrifuge tube with cap (12 ml)	10
	Chemicals	Amount
1.	1-Methylpyridine	250 ml
2.	Trimethylphosphate	100 ml
3.	1-Methylimidazolium Dimethylphosphate	100 ml
4.	Dodecane (with 2% and 6% BT)	50 ml
5.	Silicon Oil	100 ml
6.	Potassium hydroxide (KOH)	100 g

APPENDIX B
SUMMARY COMPARISON OF IONIC LIQUID

Journal	Ionic Liquid System	Preparation of Ionic liquid	Condition of Extraction	Characterization	Remarks
Desulfurisation of oils using ionic liquids: selection of cationic and ionic components to enhance extraction efficiency	<p>Cations:</p> <p>1-Methylimidazole, pyridine, 4-methylpyridine, 3-methylpyridine, 3,4-methylpyridine, 3,5-dimethylpyridine</p> <p>Anions:</p> <p>Hexafluorophosphate, Octylsulfate, Trifluoromethanesulfonate, Tetrafluoraborate, Triocynate, Ethanoate</p> <p>Crude:</p> <p>Dodecane containing 500ppm sulfur as DBT</p>	Cations was synthesized by alkylation followed by anion metathesis.	<ul style="list-style-type: none"> standardize condition equals V of dodecane & IL (2cm³:2cm³) Time mixing = 1hour (950ppm) Time Eq.= 15 mins T=25, 40, and 60°C 	Characterized by proton NMR spectroscopy, ion-chromotography and Karl Fisher titration.	$K_D = [DBT]_{IL} / [DBT]_{dodecane}$ $K_D = [I_{initial} - I_{dodecane}] / I_{dodecane}$ <p>(I indicates the highest peak in the data)</p> <p>The higher coefficient (K_D) is, the better desulphurization performance of an IL.</p>

<p>Extractive Desulfurization of Gasoline Using Imidazolium-Based Phosphoric Ionic Liquids</p>	<p>Phosphoric IL:</p> <ul style="list-style-type: none"> • N-Methyl-N-Methylimidazolium diethyl phosphate, [MMIM][DMP] • N-ethyl-N-methylimidazolium diethyl phosphate, [EMIM][DEP] • N-butyl-N-methylimidazolium dibutyl phosphate, [BMIM][DBP] <p>Sulfur Component:</p> <ul style="list-style-type: none"> • DBT • BT • 3-MT <p>Crude:</p> <ul style="list-style-type: none"> • Gasoline 	<p>Reacting the N-methylimidazole and the corresponding trialkyl phosphate at T=423K</p> <p>Time = 10hour</p> <p>Yield = 97%</p> <p>The resulting yellowish viscous liquid was washed 3 times with diethyl ether at room T followed by rotary evaporation under reduced pressure for 12 hour to remove all volatile residues</p> <p>e.g. the reactants unreacted and diethyl ether. The purity and structure of these ILs have been analyzed by NMR and electronic spray mass spectrum.</p>	<ul style="list-style-type: none"> • Using gravimetric method by dissolving a definite amount of 3-MT, BT or DBT in known quantities of IL • Dissolving 0.174g of DBT in 17.734g of [BMIM][DBP]= 1689.8ppm S-content IL sample was obtained • A known weight of S-free IL and gasoline was mixed. A known amount of S-concentrated IL was added, stirred to the above biphasic mixture at room T. 	<p>The qualitative composition using GC.</p> <p>The S-content in gasoline phase was measured by liquid chromatograph using external standard method.</p> <p>S-content in IL phase was calculated via mass balance as such the sulfur partition coefficient was calculated.</p>	<p>Mutual solubility of IL and gasoline- Solubility of Imidazolium-based IL in gasoline may on one hand contaminate the fuel and on the hand lead to NO_x pollution while we are intending to remove SO₂ pollution.</p> <p><i>This ILs are negligible solubility in gasoline.</i></p> <p>Effect of water content in IL on the extractive desulphurization performance. Removal S-component by water dilution. (Diluting the S-concentrated IL with water. In the process, the BT/DBT precipitated or crystallized gradually in the solution).</p> <p>The precipitates was removed by centrifugation.</p>
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<p>Extractive Desulfurization and Denitrogenation of Fuels Using Ionic Liquids</p>	<p>Ionic Liquids</p> <ul style="list-style-type: none"> 1-alkyl-3-methylimidazolium [AMIM]tetrafluoroborate Hexafluorophosphate and trimethylamine hydrochloride, [AlCl₃-TMAC] <p>Gasoline and diesel fuel</p> <ul style="list-style-type: none"> 2-methylpentene 1-hexane Methylcyclopentene Benzene Toluene Trimethylbenzene Thiophene 2-methylthiophene Isobutyl mercaptan Dibenzothiophene (DBT) 4,6-dimethyldibenzothiophene (DMDBT) 	<p>EMIMBF₄ ionic liquid:</p> <ul style="list-style-type: none"> Mix equal moles of 1-ethyl-3-methyl-1 H-imidazolium chloride [BMIM]Cl and lithium tetrafluoroborate [LiPF₄] in acetonitrile followed by filtration to remove LiCl precipitate and distillation to remove acetonitrile. [BMIM]Cl was obtained by refluxing equal molar amounts of 1-methylimidazole and 1-chlorobutene at 70°C for 48hrs. <p>BMIMBF₄ ionic liquid:</p> <ul style="list-style-type: none"> Mix 1-butyl-3-methylimidazolium chloride [LiPF₄] in acetonitrile followed by filtration to remove LiCl precipitate and distillation to remove acetonitrile. [BMIM]Cl was obtained by refluxing equal molar amounts of 1-methylimidazole and 1-chlorobutene at 70°C for 48hrs. <p>Trimethylammonium Chloroaluminate ionic liquid:</p> <ul style="list-style-type: none"> 2 acidic trimethylammonium chloroaluminate IL were prepared with Al-TMAC ratios of 1.5 and 2.0 respectively. 	<ul style="list-style-type: none"> The model compounds represent typical types of molecules in gasoline & diesel was selected. A model fuels with about 100ppm sulfur were prepared by dissolving a certain amount of DBT/DMDBT in n-dodecane (n-C12) Amount of absorbed model compound in the IL phase was measured by the weight gain The concentrations of absorbed toluene and thiophene in the IL phase were measured by NMR spectroscopy after equal absorption. All single extraction were conducted for 30mins with a weight ratio (organic phase/ionic liquid) of 5:1, except where otherwise indicated at room temperature 	<p>Gas chromatograph (GC) and mass spectrometer (MS) was used to carry out the aromatics analysis and to obtain S-compound and N-compound contents in the model fuels containing both.</p> <p>NMR spectrometer was used to verify the structures of the ionic liquids.</p> <p>NMR analysis was conducted to obtain the sulfur content in the IL phase after absorption.</p> <p>Some IL with absorbed compounds were characterized using Fourier Transform Infrared (FTIR).</p>	<p>Equal. was reached after 10mins of contact between the model fuel phase and the IL phase.</p>
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<p>Desulfurization of Gasoline by Extraction with new ionic liquid</p>	<p>Ionic Liquids:</p> <ul style="list-style-type: none"> 1-butyl-3-methylimidazolium tetrachloroaluminate (BMImAlCl₄) 1-butyl-3-methylimidazolium tetrafluoroborate <p>Anion:</p> <ul style="list-style-type: none"> CuCl₂⁻ Cu₂Cl₃⁻ Cu₃Cl₄⁻ <p>Crude Oil:</p> <ul style="list-style-type: none"> Gasoline 	<p>Mixing 1-butyle-3-methylimidazolium chloride (BMIC) and purified anhydrous CuCl in heptane</p> <p>BMIC:CuCl = 1:2</p> <p>T= 80°C</p>	<ul style="list-style-type: none"> All the desulfurization exp.were conducted IN A 100ml glass vial. The IL was added into model oil or gasoline at room temperature. The mass ratios of IL to model oil/gasoline = 1:5 The obtained biphasic mixture was then stirred for 30mins. The model oil used was prepared by adding 680ppm thiophene and 20% toluene into heptane 	<p>Structure of anions in ionic liquid was detected via fast atom bombardment mass spectrometry (FAB-MS) in characterizing the structure of ions in ionic liquids.</p> <p>The sulfur content in fuel was analyzed by using wavelength dispersive X-ray fluorescence spectrometer</p>	<p>The experiment has been tested using different ionic liquid (not different based)</p> <p>This journal to prove CuCl-based ionic liquid as alternative and more efficient.</p>
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<p>Deep Oxidative Desulfurization of Fuels Catalyzed by Ionic Liquid in the Presence of H₂O₂</p>	<p>Ionic Liquids:</p> <ul style="list-style-type: none"> • [HMIm]BF₄ <p>Crude:</p> <ul style="list-style-type: none"> • DBT 	<p>The ionic liquid [HMIm]BF₄ was synthesized by the published procedure</p> <p>DBT was dissolved in iso-octane (2,2,4-trimethylpentane) to simulate the model oil</p>	<ul style="list-style-type: none"> • Sulfur content = 1000ug/mL 	<p>The oxidation reaction was carried out in a 100mL flask containing 3.2mL of model oil, a 30% aqueous solution of H₂O₂ [n(H₂O₂)/n(DBT)=10], and 5mL of [HMIm]BF₄.</p> <p>The mixture was stirred at 90°C for 6hrs.</p> <p>The resulting mixture was cooled to room temperature.</p> <p>The sulfur content of the organic layer was detected by microcoulometry</p>	<p>Oxidation Desulfurization.</p> <p>Difference??</p> <p>Not using Liquid-Liquid Extraction. Instead of using Ionic Liquid to extract sulfur, this journal explains how to oxidize the sulfur.</p>
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<p>Desulfurization of Diesel Fuel by Extraction with [BF4-] based Ionic Liquid</p>	<p>Anion: [BF4]-</p>	<p>The chloride salts were prepared by reacting N-methylimidazole or pyridine with RCL, where R=Benzy, nC4H11 or n-C8H17.</p> <p>The product were purified by repeated extractions of the remaining starting materials with ethyl acetate</p> <p>After the last extraction, the remaining starting materials ethyl acetate was removed at 343.15K under vacuum.</p> <p>Equimolar amounts of [1-alkyl-mim][Cl] and NaBF4 were dissolved in acetone separately.</p> <p>The 2 solutions were gradually mixed together with stirring.</p> <p>The precipitated sodium chloride was separated from the liquid by filtration.</p>	<p>• T= 298.15K</p>	<p>The desulfurization experiments were carried out in glass vials placed in a water bath controlled at T(left)</p> <p>The mass ratio IL:diesel fuel were conducted at 1:5, 1:2, 1:1 respectively</p> <p>LLE can be achieved after biphasic mixtures were stirred for 10mins.</p> <p>The sulfur content in diesel fuels before and after extraction exp.were analyzed using quantitative elemental analysis conducted on an NS analytical apparatus.</p>	<p>Its not good of using [BF4-] based ionic liquid because the reaction will produce HF which is very reactive and corrosive.</p> <p>NOT Recommended!!!</p>
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APPENDIX C
FTIR CORRELATION TABLE

APPENDIX C: INFRARED SPECTROSCOPY -IR Absorption for Representative Functional Groups

Functional Group	Molecular Motion	Wavenumber (cm⁻¹)
alkanes	C-H stretch	2950-2800
	CH ₂ bend	~1465
	CH ₃ bend	~1375
	CH ₂ bend (4 or more)	~720
alkenes	=CH stretch	3100-3010
	C=C stretch (isolated)	1690-1630
	C=C stretch (conjugated)	1640-1610
	C-H in-plane bend	1430-1290
	C-H bend (monosubstituted)	~990 & ~910
	C-H bend (disubstituted - E)	~970
	C-H bend (disubstituted - 1,1)	~890
	C-H bend (disubstituted - Z)	~700
alkynes	acetylenic C-H stretch	~3300
	C ₂ C triple bond stretch	~2150
	acetylenic C-H bend	650-600
aromatics	C-H stretch	3020-3000
	C=C stretch	~1600 & ~1475
	C-H bend (mono)	770-730 & 715-685
	C-H bend (ortho)	770-735
	C-H bend (meta)	~880 & ~780 & ~690
	C-H bend (para)	850-800
alcohols	O-H stretch	~3650 or 3400-3300
	C-O stretch	1260-1000
ethers	C-O-C stretch (dialkyl)	1300-1000
	C-O-C stretch (diaryl)	~1250 & ~1120
aldehydes	C-H aldehyde stretch	~2850 & ~2750
	C=O stretch	~1725
ketones	C=O stretch	~1715
	C-C stretch	1300-1100
carboxylic acids	O-H stretch	3400-2400
	C=O stretch	1730-1700
	C-O stretch	1320-1210
	O-H bend	1440-1400
esters	C=O stretch	1750-1735
	C-C(O)-C stretch (acetates)	1260-1230
	C-C(O)-C stretch (all others)	1210-1160
acid chlorides	C=O stretch	1810-1775
	C-Cl stretch	730-550

anhydrides	C=O stretch	1830-1800 & 1775-1740
	C-O stretch	1300-900
amines	N-H stretch (1 per N-H bond)	3500-3300
	N-H bend	1640-1500
	C-N Stretch (alkyl)	1200-1025
	C-N Stretch (aryl)	1360-1250
	N-H bend (oop)	~800
amides	N-H stretch	3500-3180
	C=O stretch	1680-1630
	N-H bend	1640-1550
	N-H bend (1°)	1570-1515
alkyl halides	C-F stretch	1400-1000
	C-Cl stretch	785-540
	C-Br stretch	650-510
	C-I stretch	600-485
nitriles	C,N triple bond stretch	~2250
isocyanates	-N=C=O stretch	~2270
isothiocyanates	-N=C=S stretch	~2125
imines	R ₂ C=N-R stretch	1690-1640
nitro groups	-NO ₂ (aliphatic)	1600-1530 & 1390-1300
	-NO ₂ (aromatic)	1550-1490 & 1355-1315
mercaptans	S-H stretch	~2550
sulfoxides	S=O stretch	~1050
sulfones	S=O stretch	~1300 & ~1150
sulfonates	S=O stretch	~1350 & ~1750
	S-O stretch	1000-750
phosphines	P-H stretch	2320-2270
	PH bend	1090-810
phosphine oxides	P=O	1210-1140

APPENDIX D
VOLUME CALCULATION TO
SYNTHESIS [MPy][DMP]

APPENDIX D: Volume Calculation to Synthesis [MPy][DMP]

Equal mol of pyridine and trimethylphosphate has been used;

$$\text{Mol} = \frac{\text{Mass}}{\text{Molecular Weight}}$$

$$\text{Density, } \rho = \frac{\text{Mass}}{\text{Volume}}$$

$$\text{Mass} = \text{Mol} (\text{Molecular Weight})$$

Therefore,

$$\text{Volume, } V = \frac{\text{Mol}(\text{Molecular Weight})}{\text{Density}}$$

Chemicals	Mol	Molecular Weight	Density, ρ (g/cm ³)
Pyridine	0.1	79.10	0.9819
Trimethylphosphate	0.1	140.076	1.210

$$\text{Volume : Pyridine} = \frac{0.1 (79.10)}{0.9819}$$

$$= 8.0558 \text{ ml}$$

$$\text{: Trimethylphosphate} = \frac{0.1 (140.076)}{1.210}$$

$$= 11.5765 \text{ ml}$$

APPENDIX E
EXTRACTION PERFORMANCE
CALCULATION

APPENDIX E: Extraction Performance Calculation

$$\text{Extraction Performance} = \frac{\text{Initial sulfur content (\%)} - \text{Final sulfur content (\%)}}{\text{Initial sulfur content (\%)}} \times 100$$

- **Solution** : Model Oil (Dodecane + 2% Benzothiophene) extraction with [MPy][DMP]:

$$\text{Extraction performance (\%)} = \frac{0.6329 - 0.4230}{0.6329} \times 100 = 33.0\%$$

- **Solution** : Model Oil (Dodecane + 6% Benzothiophene) extraction with [MPy][DMP]:

$$\text{Extraction performance (\%)} = \frac{4.3126 - 2.2099}{4.3126} \times 100 = 47.0\%$$

- **Solution** : Model Oil (Dodecane + 2% Benzothiophene) extraction with [MMim][DMP]:

$$\text{Extraction performance (\%)} = \frac{0.6329 - 0.2519}{0.6329} \times 100 = 60.2\%$$

- **Solution** : Model Oil (Dodecane + 6% Benzothiophene) extraction with [MMim][DMP]:

$$\text{Extraction performance (\%)} = \frac{4.3126 - 0.3810}{4.3126} \times 100 = 61.0\%$$

APPENDIX F
GANTT CHART

APPENDIX F: Gant Chart

No.	Detail / Week	01	02	03	04	05	06	07		08	09	10	11	12	13	14	
1	Project Work Continue								MID TERM BREAK								
2	Submission of Progress Report 1				●												
3	Project Work Continue																
4	Submission of Progress Report 2									●							
5	Seminar (Compulsory)																
6	Project Work Continue																
7	Poster Exhibition												●				
8	Submission of Dissertation (soft bound)														●		
9	Oral Presentation															●	
10	Submission of Project Dissertation (hard bound)																●



Process



Suggested milestone