Removal of Benzothiophene and Thiophene Using Butyl-methyl-imidazolium Dibutylphosphate [BMIM][DBP] from Crude Oil Model

by

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CERTIFICATION OF APPROVAL

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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.

MOHD ARIFF BIN ZUL-LKIFLI

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ABSTRACT

This report contains the study on desulfurization of crude oil model using butyl-methyl-imidazolium dibutylphosphate [BMIM][DBP] (ionic liquid). The classical desulfurization process involves catalytic hydrogenation of sulfur compounds (hydrodesulfurization, HDS) into hydrogen sulfide. The hydrogen sulfide which is separated from the desulfurized crude is oxidized catalytically with air into elemental sulfur. However, some S-compounds such as dibenzothiophene, methyl dibenzothiophene, and 4,6-dimethyl dibenzothiophene are less reactive to HDS. The ionic liquids gained increasing interest over the past years due to its unique properties both as extractant and also as catalyst. Therefore, extractive desulfurization using the ionic liquids has been identified as the alternative to the conventional method. The scope of this study includes preparation of [BMIM][DBP] followed by the characterization and finally the extraction of benzothiophene and thiophene (sulfur compound, S) from the crude oil model. The study is mainly done in the lab. It is include determining the sulfur content in the crude in order to create the crude oil model, characterizing the ionic liquids and testing the extraction ability of the ionic liquids. Based on the result obtained, the extraction of benzothiophene from the crude oil model using [BMIM][DBP] is ranging from 50% to 92%. The extraction performance of [BMIM][DBP] for thiophene is between 40% to 67%. This shows that the extraction performance of [BMIM][DBP] is remarkable. The extraction performance can be improved if the multiple pass extraction is done. Therefore, the extractions of sulfur compound using the ionic liquids have the bright potential to replace the conventional technique.

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LIST OF SYMBOLS, ABBREVIATIONS AND NOMENCLATURE

[BEIM][DBP]	Butyl-ethyl-imidazolium Dibutylphosphate
[BEIM][DEP]	Butyl-ethyl-imidazolium Diethylphosphate
[BMIM][DBP]	Butyl-methyl-imidazolium Dibutylphosphate
[BMIM][DMP]	Butyl-methyl-imidazolium Dimethylphosphate
[BMIM]$AlCl_4$	Butyl-methyl-imidazolium Tetrachloroaluminate
[BPy]Ac	Butyl-pyridinium Acetate
[BPy]BF_4	Butyl-pyridinium Tetrafluoroborate
[BPy]NO_3	Butyl-pyridinium Nitrate
[EEIM][DEP]	Ethyl-ethyl-imidazolium Diethylphosphate
[EMIM][DEP]	Ethyl-methyl-imidazolium Diethylphosphate
[EMIM][DMP]	Ethyl-methyl-imidazolium Dimethylphosphate
[EPy]Ac	Ethyl-pyridinium Acetate
[EPy]BF_4	Ethyl-pyridinium Tetrafluoroborate
[EPy]NO_3	Ethyl-pyridinium Nitrate
[MMIM][DMP]	Methyl-methyl-imidazolium Dimethylphosphate
°C	Celcius (Temperature)
3-MT	3-methylthiophene
$AlCl_3$-TMAC	Trichloroaluminate Trimethylamine Hydrochloride
atm	Atmospheric (Pressure)
BT	Benzothiophene
C	Carbon
DBT	Dibenzothiophene
DEGEE	Diethylene Glycol Monoethyl Ether
EDS	Extractive Desulfurization
FTIR	Fourier Transform Infrared Spectroscopy
H	Hydrogen
H_2O	Water
HDS	Hydrodesulfurization
HNMR	Proton (H^+) Nuclear Magnetic Resonance
IL	Ionic Liquid
K	Kelvin (Temperature)

K_m	Sulfur Partition Coefficient (molar basis)
K_N	Sulfur Partition Coefficient (mass basis)
kPa	Kilopascal (Pressure)
Me	Mercaptan
ml	Milliliter
N	Nitrogen
NMR	Nuclear Magnetic Resonance
ppm	Parts Per Million
S	Sulfur
SG	Specific Gravity
SO_2	Sulfur Dioxide
SO_x	Sulfur Oxides
XRF	X-Ray Fluorescence Spectrometer

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Crude oil is a complex mixture of hydrocarbons and other compounds (Wang & Buckley, 2003). These components can be classified as saturates, aromatics, resins and asphaltenes (SARA) (Fan & Buckley, 2002). Saturates consist of saturated hydrocarbons with straight or branched chains without ring structure (paraffins) or with one or more rings attached (cycloparaffins). It contains little or no nitrogen, sulfur, oxygen or metals. Aromatics are hydrocarbons containing one or more aromatic ring. Resins are also known as polars. It is the second heaviest fraction in crude oils. Asphaltenes are highly polar high molecular weight solids. The fraction is insoluble in low-molecular weight aliphatic hydrocarbons. It consists of highly condensed aromatic ring system with high nitrogen, sulfur, oxygen and metal content. Crude oil can be categorized into two types: sweet crude and sour crude. Sweet crude is the crude with less than 1% sulfur content and sour crude contain a substantial concentration of sulfur compounds such as hydrogen sulfide, sulfur dioxide and mercaptans (more than 1% sulfur) (Hyne, 2001). In addition to elemental sulfur and hydrogen sulfur, over 200 sulfur containing organic compounds, classified as thiols, sulfides, thiophenes and substituted benzo- and dibenzothiophenes, have been identified from crude oils (Lu et al., 1999). However, the sulfur compounds which predominate in so-called heavy fractions are primarily in the form of condensed thiophenes. For example, in some Texas oils, as much as 70% of the organic sulfur is present as dibenzothiophenes (DBTs), and in some Middle East oils, the alkyl-substituted benzo- and dibenzothiophenes contribute up to 40% of the organic sulfur present (Finnerty, 1982). The typical composition of crude oil is shown in the Table 1.1:

Table 1.1: Typical Crude Compositions (Speight, 1999)

Element	Range
Carbon	83-87%
Hydrogen	10-14%
Nitrogen	0.1-2%
Oxygen	0.1-1.5%
Sulfur	0.5-6%
Metals	<1000ppm

Four different types of hydrocarbon molecules appear in crude oil. The relative percentage of each varies from oil to oil, depends on the properties of the oil (Hyne, 2001):

Table 1.2: Typical Hydrocarbon Compositions in Crude

Hydrocarbon	Average	Range
Paraffins	30%	15-60%
Naphthenes	49%	30-60%
Aromatics	15%	3-30%
Asphaltenes	6%	remainder

Sour crude also can 'attack' the metal components of the oil well, as well as the pipelines and storage tanks which could cause corrosion of the metal components (Collins, Mestetsky, & Savaiano, 1998). The service life of the well producing sour crude is less than five years while the actuating rod and tube within the well casing may have several months of service life (Collins, Mestetsky, & Savaiano, 1998). The replacement of the equipment that is damaged does not only involve the capital, but also the downtime of the well which can affect daily production (Collins, Mestetsky, & Savaiano, 1998). Besides, the same problem with sour crude during the refining process also happens in Kuwait. The refinery equipment is exposed to risk of failure and corrosion due to the crude oil impurities problem. The most damaging impurities are inorganic salts, organic chlorides, organic acids, and sulfur compounds (Shalaby, 2005). However, that's not only the problem due to the sulfur compounds in the crude oil. The increasingly stringent limitations on SO_x emissions are imposing urgent requirement to reduce the sulfur content in the fuels. Therefore, it is preferable to reduce the sulfur content of crude oil before the oil is refined. In extractive desulfurization (EDS) process, ionic liquid is used to extract the organosulfur compounds. Therefore, the main study of this project is mainly on the ionic liquids and its potential to reduce the sulfur content in the crude oils.

1.2 Problem Statement

Ionic liquids have gained increasing interest over the past years due to its unique properties both as extractant and also as catalyst. The classical desulfurization process involves catalytic hydrogenation of sulfur compounds (hydrodesulfurization, HDS) into hydrogen sulfide. Typical reaction conditions are 300-350°C and 30-100 atm hydrogen pressure (Shafi & Hutchings, 2000). 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-dimethyl dibenzothiophene are less reactive to HDS due to the sterical hindrance adsorption of these compounds on the catalyst surface (Jian-long et al., 2007). The qualitative relationship between the type and size of sulfur molecules in various distillate fuel fractions and their relative reactivities is shown in Figure 1.1:

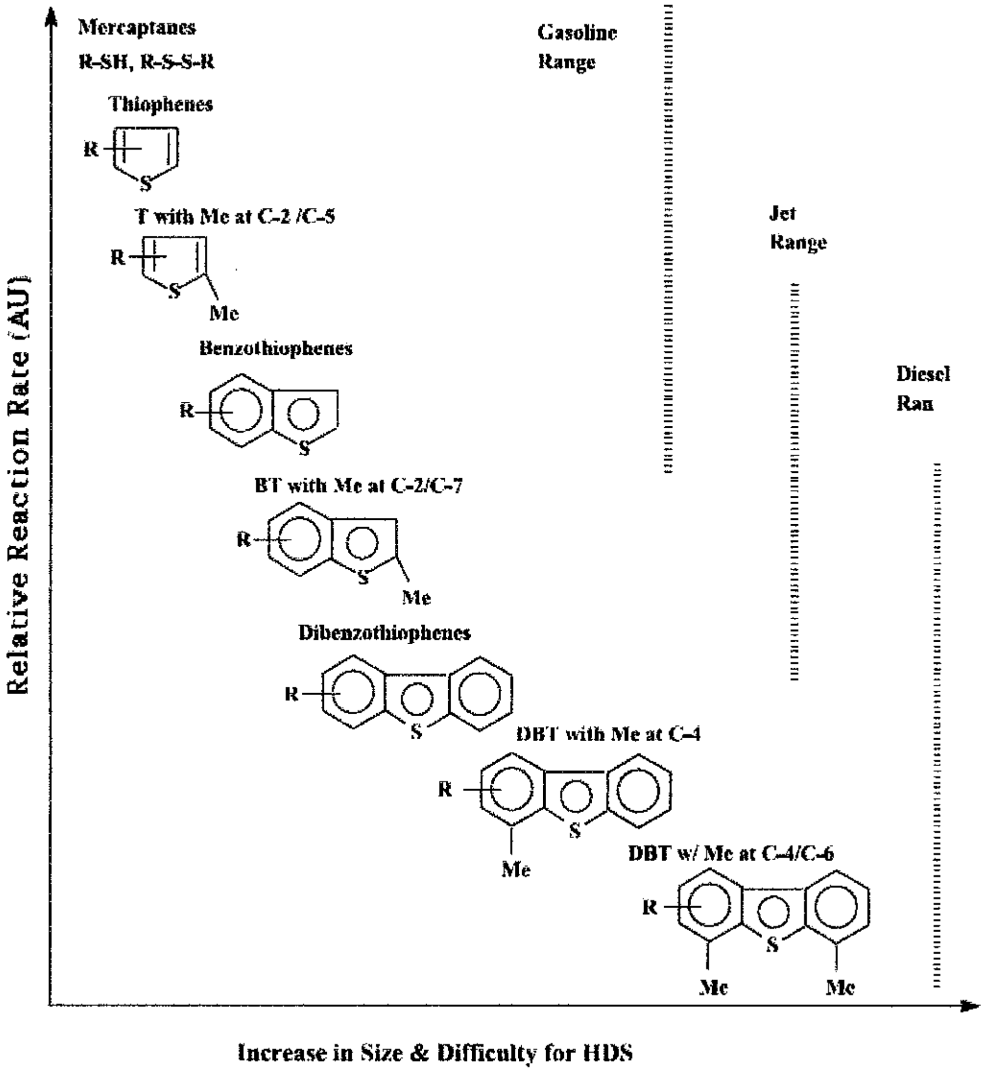


Figure 1.1: Qualitative Relationship between the Type and Size of Sulfur Molecules in Various Distillate Fuel Fractions (Song, 2002)

Besides, HDS also consume high energy and hydrogen for its process and more capital cost involved if deep HDS process is done. Thus, alternative ways without utilizing hydrogen such as oxidative desulfurization, biodesulfurization, extractive desulfurization and adsorptive extraction have been studied by the researchers (Jian-long et al., 2007). Since the main study of this project is ionic liquids, extraction or reactive extraction of S-compounds from crude oil could be one of an alternative to HDS.

1.3 Objective and Scope of Study

The objective of this study is to determine the sulfur-compounds removal efficiency of the selected ionic liquid from the crude oil models. Besides, there are many ionic liquids that can be used to extract the organosulfur compounds from the crude oil models which also have many different types of hydrocarbon such as alkanes, paraffins, aromatics and many more. Therefore, this study is mainly to determine the most suitable ionic liquid and also the method to extract the sulfur effectively.

CHAPTER 2

LITERATURE REVIEW

Basically, ionic liquids are salts with melting temperature below the boiling point of water (Wilkes, 2002). Some ionic liquids, such as ethyl ammonium nitrate are in a dynamic equilibrium where at any time more than 99.99% of the liquid is made up of ionic rather than molecular species. Ionic liquids are electrically conductive and have extremely low vapor pressure. Their other properties are diverse. Many have low combustibility, excellent thermal stability, a wide liquid range, and favorable solvating properties for diverse compounds. Ionic liquids have been studied for applications related to green chemical processes, such as liquid-liquid extractions, gas separations, electrochemistry and catalysis. The EDS is an attractive alternative for HDS because the process is applicable at ambient conditions without special equipment requirements. Besides low energy consumption, hydrogen consumption and handling is also eliminated. In general, ionic liquids have higher density than organic liquids and water. Therefore, many ionic liquids exist as a separate phase when in contact with the organic and aqueous phases. These ionic liquids also can be recycled for use of multiple extractions. Many researches have been conducted on EDS process but until now there is little known research conducted on crude oil.

2.1 Desulfurization of fuel oils using N,N-dialkylimidazolium dialkylphosphate

The research is done on the various structures of N,N-dialkylimidazolium dialkylphosphate (Nie et al., 2008) ionic liquids structure as shown in Figure 2.1.

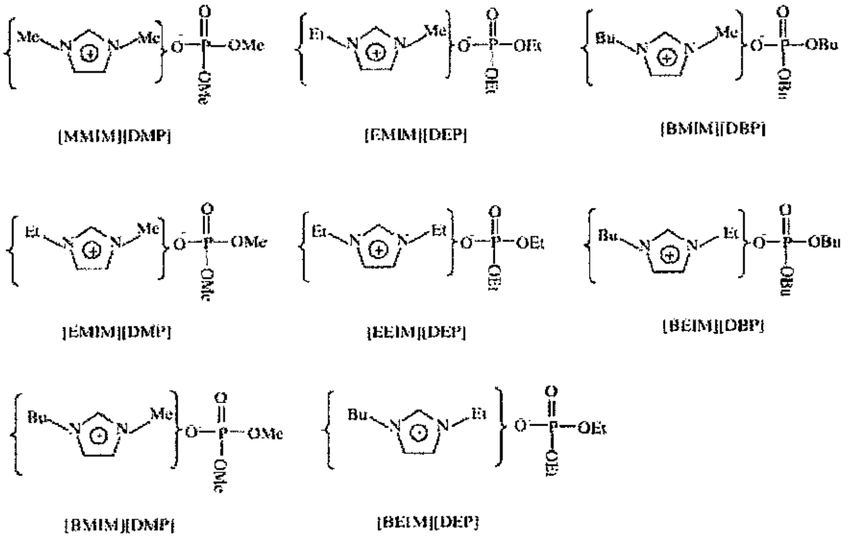


Figure 2.1: Structures of N,N-dialkylimidazolium dialkylphosphate ionic liquids (Nie et al., 2008)

The ionic liquids used in this study are butyl methyl imidazolium dimethylphosphate, [BMIM][DMP] and butyl ethyl imidazolium diethylphosphate, [BEIM][DEP]. The ionic liquids are prepared by mixing the N-butylimidazole and corresponding trialkylphosphate equimolarly via one-pot reaction. The resulting yellowish viscous liquid is washed several times with diethyl ether at room temperature followed by rotary evaporation for 12h. The ionic liquid is identified by using proton nuclear magnetic resonance (HNMR). The sulfur partition coefficient on mass basis, K_N is an important parameter for EDS process and the higher the K_N, the better the desulfurization process. Table 2.1 shows the value of K_N and K_m between selected ionic liquids and fuel oil at 298.15 K. The fuel oil used in this study is gasoline and the GC-MS of the gasoline is shown in Figure 2.2:

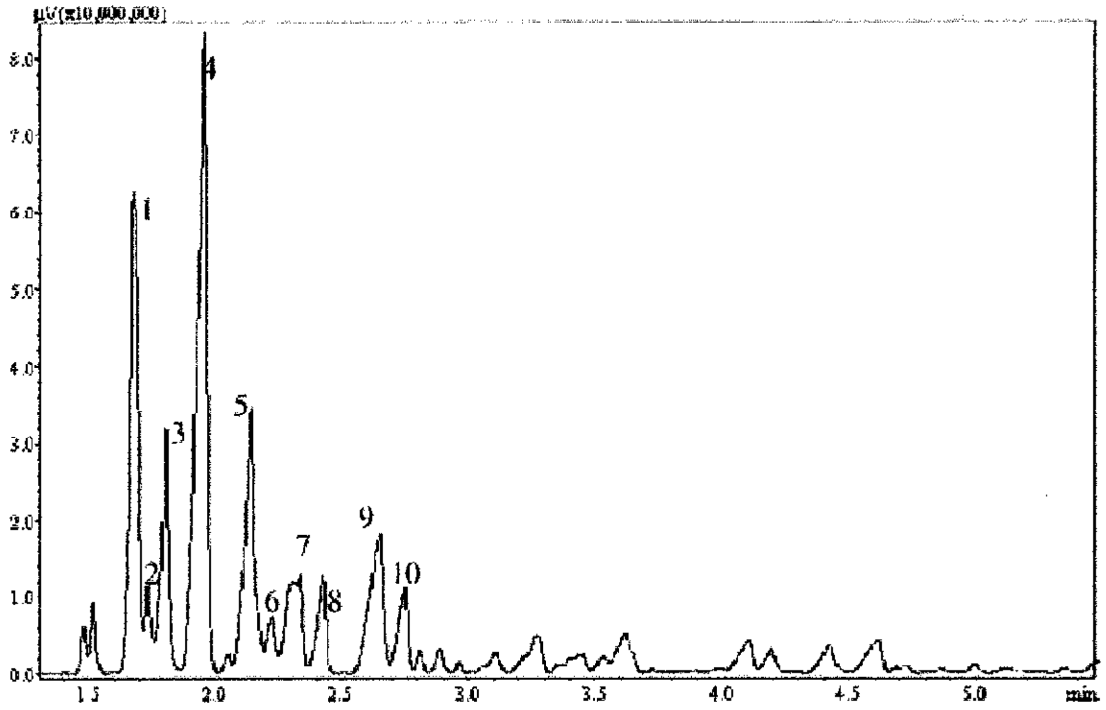


Figure 2.2: GC-MS of the Fuel Oil (Gasoline) (Nie et al., 2008)

Table 2.1: Value of K_N and K_m between Selected Ionic Liquids and Fuel Oil at 298.15K (Nie et al., 2008)

IL	Cn	3-MT		BT		DBT	
		K_N	K_m	K_N	K_m	K_N	K_m
[MMIM][DMP]	2	0.059	0.11	0.47	0.92	0.46	0.90
[EMIM][DMP]	3	0.50	1.04	0.92	1.90	1.17	2.42
[BMIM][DMP]	5	0.58	1.34	1.26	2.92	1.57	3.64
[EMIM][DEP]	3	0.47	1.09	0.94	2.18	1.27	2.94
[EEIM][DEP]	4	0.78	1.90	1.39	3.39	1.61	3.93
[BEIM][DEP]	6	0.88	2.36	1.53	4.11	1.79	4.81
[BMIM][DBP]	5	0.59	1.80	1.37	4.18	1.59	4.85
[BEIM][DBP]	6	0.91	2.89	1.49	4.73	1.72	5.46

**Cn: Carbon number of alkyl substitutes in imidazole ring; Average molecular weight of straight run gasoline is 114 based on the component distribution shown in Figure 2.2;* K_N *on a mass basis;* K_m *on a molar basis.*

Besides the K_N and K_m value, the mutual solubility also become an important factor to evaluate the ionic liquids applicability as an extractant, because solubility of imidazolium based ionic liquids in oil may contaminate the fuel and cause NO_x pollution and high solubility in oil results in higher separation cost. Table 2.2 shows the solubility of gasoline in selected ionic liquids at 298.15 K.

Table 2.2: Solubility of Gasoline in Ionic Liquids at 298.15K (Nie et al., 2008)

IL	Solubility of gasoline, mg(fuel)/g(IL)
[MMIM][DMP]	11.2
[EMIM][DMP]	20.6
[BMIM][DMP]	35.3
[EMIM][DEP]	42.5
[EEIM][DEP]	58.1
[BEIM][DEP]	102.6
[BMIM][DBP]	206.4
[BEIM][DBP]	266.9

From the experiment on the ionic liquids above, it shows that [BMIM][DMP] shows remarkable selectivity for extraction of aromatic S-compounds; 3-methylthiophene and dibenzothiophene from the gasoline. It is attributed to the formation of complex between π-electrons of aromatic S-compound and the charged imidazolium ring of the ionic liquids, which is largely affecting the size of the alkyl substitutes via steric effect and dispersion interaction involved.

2.2 Desulfurization of fuel oils using trimethylamine hydrochloride ($AlCl_3$-TMAC)

The other ionic liquid that studied by the researcher is trimethylamine hydrochloride ($AlCl_3$-TMAC) (Zhang, Zhang, & Zhang, 2003). The ionic liquid is prepared by preparing two acidic trimethylammonium chloroaluminate ionic liquids with Al-TMAC with ratio of 1.5 and 2.0, respectively.

a) 2.0:1.0 $AlCl_3$ – TMAC ionic liquid

Aluminum trichloride (2 mol) was added slowly to trimethylammonium chloride salt (TMAC, 1 mol) in a glovebox under dry nitrogen the reaction between the two solids was exothermic. A light brownish liquid was formed. The liquid was stirred for 5h. It has density of 1.4 - 1.5 g/cm^3 at room temperature. The product was stable as a liquid at room temperature under dry atmosphere.

b) 1.5:1.0 $AlCl_3$ – TMAC ionic liquid

The same procedure as described above for preparation of 2.0:1.0 $AlCl_3$ – TMAC ionic liquid was applied, except the molar ratio of 1.5 for $AlCl_3$-TMAC was used. A light yellow liquid was formed.

The quantitative analysis of sulfur content was conducted using X-Ray Fluorescence (XRF) Spectrometer. The HNMR is used to determine the ionic liquids structure. Some ionic liquids with absorbed sulfur compounds were analyzed using Fourier Transform Infrared (FTIR). In this experiment, they studied the absorption capacity of $AlCl_3$-TMAC ionic liquids for the model compounds (fuel oil). The results of the experiment are shown in Figure 2.3.

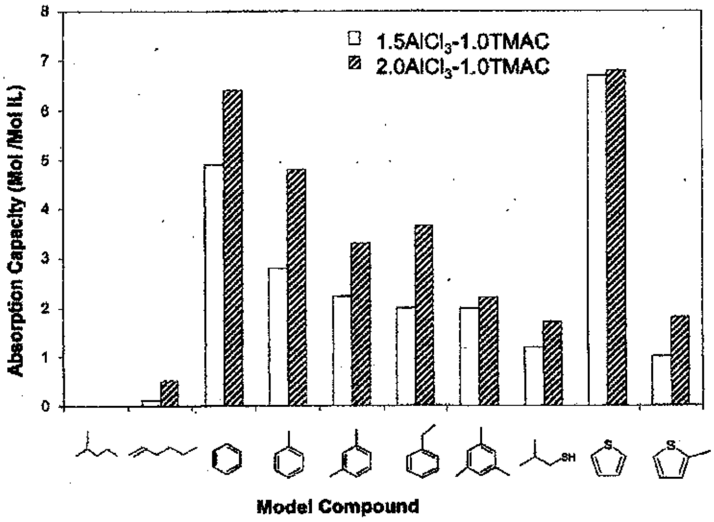


Figure 2.3: Absorption capacity of $AlCl_3$ – TMAC ionic liquids for model compounds (Zhang, Zhang, & Zhang, 2003)

From the result obtained, $AlCl_3$-TMAC ionic liquids were found to have remarkably high absorption capacities for aromatics, but their regeneration is quite problematic. A methyl group on the aromatic rings was found significantly reduce the absorption capacity because of the steric effect.

2.3 Desulfurization of oil fuels using butyl-methyl-imidazolium tetrachloroaluminate [BMIM]AlCl$_4$

Besides, butyl-methyl-imidazolium tetrachloroaluminate, [BMIM]AlCl$_4$ also can be done to remove more sulfur (Schmidt, 2008),. [BMIM]AlCl$_4$ is prepared by adding 200ml of N-methylimidazolium to 500ml of n-butyl chloride in a 1L three-neck flask under nitrogen. The mixture was refluxed for 30 min, after which a second phase formed. The mixture was continuously refluxed for 7h in order to complete the reaction. Excess n-butyl chloride was distilled off in vacuum at elevated temperature. From the studies, this ionic liquid can significantly lower the sulfur content in oil fuels (gasoline and diesel).

2.4 Desulfurization of gasoline using N-alkyl-pyridinium based ionic liquids

The ionic liquids used in this research are N-butyl-pyridinium tetrafluoroborate, [BPy]BF$_4$, N-butyl-pyridinium nitrate, [BPy]NO$_3$, N-butyl-pyridinium acetate, [BPy]Ac, N-ethyl-pyridinium tetrafluoroborate, [EPy]BF$_4$, N-ethyl-pyridinium nitrate and [EPy]NO$_3$, N-ethyl-pyridinium acetate, [EPy]Ac (Jian-long et al., 2007). The ionic liquids are prepared by adding pyridine (0.5 mol) and 1-bromobutane (0.5 mol) into a magnetic stirred slurry of cyclohexane (50ml) in round-bottom flask fitted with a reflux condenser and drying tube. The mixtures was stirred at 64°C for 24h until no further precipitation. The white precipitate was filtrated off, then the resulting solid was washed two times with ethyl acetate. The resulting N-butyl-pyridinium bromide was evaporated in a vacuum drying oven to remove the remaining ethyl acetate, raw material and solvent. N-ethyl-pyridinium bromide was prepared as the same procedure as N-butyl-pyridinium bromide. Ionic liquid N-butyl-pyridinium tetrafluoroborate was prepared by adding N-butyl-pyridinium bromide (0.3 mol) and sodium fluoroborate (0.35 mol) to acetone (300 ml), and then the mixture was agitated at room temperature for 24 hours. Then the resulting precipitate was filtered off, and the solvent was removed by rotary evaporation to leave a yellowish liquid. The trace quantity of acetone was removed by vacuum evaporation. N-ethyl-pyridinium tetrafluoroborate was prepared as the same procedure as N-butyl-pyridinium tetrafluoroborate. Ionic liquid N-butyl-pyridinium nitrate was prepared by adding equal amount (mole) of N-butyl-pyridinium bromide and ammonium nitrate to methyl alcohol, and then the mixture was agitated at room temperature for 48 hours. Then the resulting precipitate was filtered off, and the solvent was removed by rotary evaporation to leave a brown liquid. The trace quantity of methyl alcohol was removed by vacuum evaporation. N-ethyl-pyridinium nitrate, N-butyl-pyridinium acetate, N-ethyl-pyridinium acetate were prepared as the same procedure as N-butyl-pyridinium nitrate. The extraction effect of various types of ionic liquids can be summarized as in the Table 2.3.

Table 2.3: Desulfurization Results of ILs at Different Mass Ratio of ILs to Model Oil (Jian-long et al., 2007)

Ionic Liquids	**Sulfur Removal (%)**		
	Mass ratio ILs to Model Oil		
	1:1	**1:2**	**1:3**
[BPy]BF_4	45.5	28.6	16.9
[BPy]NO_3	30.1	19.1	9.4
[BPy]Ac	32.1	20.3	10.2
[EPy]BF_4	21.8	12.6	8.9
[EPy]NO_3	27.1	17.3	13.8
[EPy]Ac	23.0	15.7	9.7

From the table above, it is shown that [BPy]BF_4 has the best extraction ability to remove sulfur component among the other pyridinium based ionic liquid and its extracting ability increase with the mass ratio of ILs to the model oil. However, the application of tetrafluoroborate and hexaflourophosphate anion for ionic liquids in the industry is not favorable because these types of ionic liquids will produce hydrofluoric acid, which is very corrosive to the equipment with the presence of water (Seddon, 2004).

2.5 Desulfurization of Fuel Using N-ethyl-N-ethyl-imidazolium diethylphosphate, [EEIM][DEP]

The ionic liquids used in this study are N-ethyl-N-methyl-imidazolium dimethylphosphate, [EMIM][DMP], N-ethyl-N-ethyl-imidazolium diethylphosphate, [EEIM][DEP] and N-butyl-N-ethyl-imidazolium dibutylphosphate, [BEIM][DBP] (Jiang et al., 2006). These ionic liquids are prepared by adding equimolar quantities of N-ethyl-imidazole and the corresponding trialkylphosphate to a round-bottom flask fitted with a reflux condenser and then reacting them at 423 K for 10 h with a yield of 98%. The resulting yellowish viscous liquid was cooled to room temperature and then washed several times with diethyl ether followed by rotary evaporation under reduced pressure of about 1 kPa for 12 hours to remove all volatile residues, e.g., the reactants remained and diethyl ether. The structures of these ionic liquids are determined by using the HNMR. The results of the desulfurization are shown in Table 2.4.

Table 2.4: K_N Values at 298.15K for Extraction of S-compounds with Different Phosphate ILs (Jiang et al., 2006)

IL	Cn	K_N		
		3-MT	BT	DBT
[MMIM][DMP]	2	0.059	0.47	0.46
[EMIM][DMP]	3	0.50	0.92	1.17
[EMIM][DEP]	3	0.47	0.94	1.27
[EEIM][DEP]	4	0.78	1.39	1.61
[BMIM][DBP]	5	0.59	1.37	1.59
[BEIM][DBP]	6	0.91	1.49	1.72

**Cn: Carbon number at alkyl-substitutes in imidazolium ring*

Based on the Table 2.4, [EEIM][DEP] has shown remarkable extraction ability which is measured by sulfur partition coefficients, K_N (higher the K_N, higher the extraction effect). [EEIM][DEP] also less soluble in the fuel (Table 2.2). Besides, [EEIM][DEP] also can be recovered by dissolution with water followed by simple distillation for clear separation of IL and water.

The literature review above can be summarized as in the Table 2.5:

Table 2.5: Summary of the Literature Review

IL(s)	**Preparation IL**	**Characterization**	**Performance**	**Remarks**
[BMIM][DMP], [BEIM][DEP]	IL is prepared by mixing equal moles of N-butylimidazole and the corresponding trialkylphosphate (the purity >99%) via one-pot reaction with a yield of above 97%.	Sulfur partition coefficient on mass basis (K_N) [ratio of sulfur concentration (S-concentration) in IL to the S-concentration in fuel oil] of IL increase due to increasing size of alkyl group in the imidazolium ring.	[BMIM][DMP] show strong preferential extraction for DBT and 3-MT vs. toluene. Selectivity factor of DBT versus toluene for IL [BMIM][DMP] is above 12.	[BMIM][DMP] shows remarkable selectivity for the extraction of aromatic compounds 3-MT and DBT
$AlCl_3$-TMAC	Aluminum trichloride (2 mol) was added slowly to trimethylammonium chloride salt (TMAC, 1 mol), in a glovebox under dry nitrogen the reaction between the two solids was exothermic. A light brownish liquid was formed. The liquid was stirred for 5h. it has density of 1.4 - 1.5 g/cm^3 at room temperature. The	In this experiment, the absorption capacity of $AlCl_3$-TMAC ionic liquids for the model compounds (fuel oil) was determined	$AlCl_3$-TMAC ionic liquids were found to have remarkably high absorption capacities for aromatics. A methyl group on the aromatic rings was found significantly reduce the absorption capacity because of the steric effect	Regeneration of IL is quite problematic

<table>
<tr><th>IL(s)</th><th>Preparation IL</th><th>Characterization</th><th>Performance</th><th>Remarks</th></tr>
<tr><td></td><td>product was stable as a liquid at room temperature under dry atmosphere.</td><td></td><td></td><td></td></tr>
<tr><td>[BPy] BF_4</td><td>N-butyl-pyridinium tetrafluoroborate was prepared by adding N-butyl-pyridinium bromide (0.3 mol) and sodium fluoroborate (0.35 mol) to acetone (300 ml), and then the mixture was agitated at room temperature for 24 h. Then the resulting precipitate was filtered off, and the solvent was removed by rotary evaporation to leave a yellowish liquid. The trace quantity of acetone was removed by vacuum evaporation.</td><td>The lone pair electrons of pyridine and the electron-donating ability of alkyl substitutions make the N-alkyl-pyridinium have higher polarizable aromatic π-electron density than pyridine.</td><td>Desulfurization results of IL at different mass ratios of IL to model gasoline
<table>
<tr><th rowspan="3">IL</th><th colspan="3">Sulfur removal η / %</th></tr>
<tr><th colspan="3">mass ratio of IL to the model oil</th></tr>
<tr><th>1:1</th><th>1:2</th><th>1:3</th></tr>
<tr><td>[BPy] BF_4</td><td>45.5</td><td>28.6</td><td>16.9</td></tr>
</table></td><td>BF_4 and PF_6 anion for ionic liquids in the industry is not favorable because these types of ionic liquids will produce HF, which is very corrosive to the equipment with the presence of water</td></tr>
</table>

IL(s)	Preparation IL	Characterization	Performance	Remarks
[BEIM][DBP], [EEIM][DEP], [EMIM][DMP]	IL were prepared by adding equimolar quantities of N-ethylimidazole and the corresponding trialkylphosphate to a round-bottom flask fitted with a reflux condenser and then reacting them at 423 K for 10 h with a yield of 98%. The resulting yellowish viscous liquid was cooled to room temperature and then washed several times with diethyl ether followed by rotary evaporation under reduced pressure of about 1 kPa for 12 h to remove all volatile residues, e.g., the reactants remained and diethyl ether.	The extractive ability of the alkylphosphate ILs was dominated by the structure of the cation and followed the order [BEIM][DBP] > [EEIM][DEP] > [EMIM][DMP] for each S-compound studied	K_N-value being [BEIM][DBP] = 1.72, [EEIM][DEP] = 1.61 and [EMIM][DMP] = 1.17, respectively for DBT.	[EEIM][DEP] also can be recovered by dissolution with water followed by simple distillation for clear separation of IL and water

Based on the literature review done on various types of ionic liquids, this project will be using the [EEIM][DEP] because the yield in the desulfurization is high, lower solubility for fuel and thus negligible influence on the constituent of fuel and ease of regeneration via water dilution process. However, due to some unforeseen circumstances, the ionic liquid used for this research is [BMIM][DBP]. Even though [BMIM][DBP] have high solubility in gasoline, but there are no evidence to support that [BMIM][DBP] is soluble in crude oil.

CHAPTER 3

METHODOLOGY

Based on the literature review, these projects will mainly involve laboratory experiments. The experiments will be conducted by using suitable ionic liquids in order to extract the sulfur content from the crude oil model. The duration of this experiment will be approximately 20 hours per week. The detailed method is described below:

3.1 Preparation of Alkylphosphate Ionic Liquid

100ml of 1-methylimidazole is purified by distillation. Butyl-methyl-imidazole dibutylphosphate [BMIM][DBP] (Figure 3.1) was prepared by adding equimolar (0.2mol) quantities of 1-methylimidazole and the tributylphosphate to a round-bottom flask fitted with reflux condenser and then reacting them at 363K for 3 days (yield of 98%) with nitrogen gas. The detail calculations of the volume used to make ionic liquids are shown in Appendix A. Resulting yellowish viscous liquid was cooled to room temperature and then washed several times with diethyl ether followed by rotary evaporation under reduced pressure of about 1 kPa for 3 hours to remove all volatile residues (the reactant remained and diethyl ether). Finally, the ionic liquid is dried using the vacuum line connected to liquid nitrogen. After drying, the ionic liquid was verified by NMR and FTIR. The photographs showing the sequence of the ionic liquid synthesis process are shown in the Appendix B.

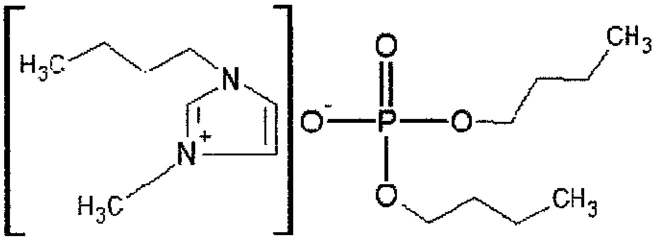


Figure 3.1: The Structure of [BMIM][DBP]

3.2 Characterization

The following methods were employed for the characterization of [BMIM][DBP]

i. HNMR

Nuclear magnetic resonance (NMR) spectroscopy is a technique which exploits the magnetic properties of certain nuclei. Many types of information can be obtained from an NMR spectrum. The most important applications for the organic chemist are proton NMR and carbon-13 NMR spectroscopy. The function of NMR is to identify functional groups and type of chemical entities in molecules. Proton NMR is the application of nuclear magnetic resonance in NMR spectroscopy with respect to hydrogen nuclei within the molecules of a substance, in order to determine the structure of its molecules. Proton NMR spectra are characterized by chemical shifts in the range +12 to -4 ppm and by spin-spin coupling between protons (Silverstein, Bassler, & Morrill, 1991).

ii. Density Meter (Density)

[BMIM][DBP] is inserted in the density meter and then the equipment will show the density at different temperatures (25°C, 35°C and 45°C). The density is measured based on the function of the oscillation of U-tube inside the density meter and it is more accurate than other density measurement equipment (Fitzgerald, 2000).

iii. Coulometer (Water Content)

Karl Fischer titration is a widely used analytical method for quantifying water content in a variety of products. The fundamental principle behind it is based on the Bunsen Reaction between iodine and sulfur dioxide in an aqueous medium. The alcohol reacts with sulfur dioxide (SO_2) and base to form an intermediate alkylsulfite salt, which is then oxidized by iodine to an alkylsulfate salt. This oxidation reaction consumes water. The reactive alcohol is typically methanol or 2-(2-Ethoxyethoxy)ethanol, also known as diethylene glycol monoethyl ether (DEGEE), or another suitable alcohol. Water and iodine are consumed in a 1:1 ratio in the reaction. Once all of the water present is consumed, the presence of excess iodine is detected voltametrically by the titrator's indicator electrode. That signals the end-point of the titration. The amount of water present in the sample is calculated based on the concentration of iodine in the Karl Fisher titrating reagent (i.e., titer) and the amount of Karl Fisher Reagent consumed in the titration (Aquastar, 2002).

iv. 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. FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum. Samples for FTIR can be prepared in a number of ways. For liquid samples, the easiest is to place one drop of sample between two plates of sodium chloride (salt). Salt is transparent to infrared light. The drop forms a thin film between the plates (Service, 2008).

v. Ion Chromatography

Ion chromatography is a process that allows the separation of ions and polar molecules based on the charge properties of the molecules. It is used for water chemistry analysis. Ion chromatographs are able to measure concentrations of major anions, such as fluoride, chloride, nitrate, nitrite, and sulfate, as well as major cations such as lithium, sodium, ammonium, potassium, calcium, and magnesium in the parts-per-billion (ppb) range. Concentrations of organic acids can also be measured through ion chromatography. Sample solutions pass through a pressurized chromatographic column where ions are absorbed by column constituents. As an ion extraction liquid, known as eluent, runs through the column, the absorbed ions begin separating from the column. The retention time of different species determines the ionic concentrations in the sample (Bruckner, 2008).

3.3 Liquid-liquid Extraction

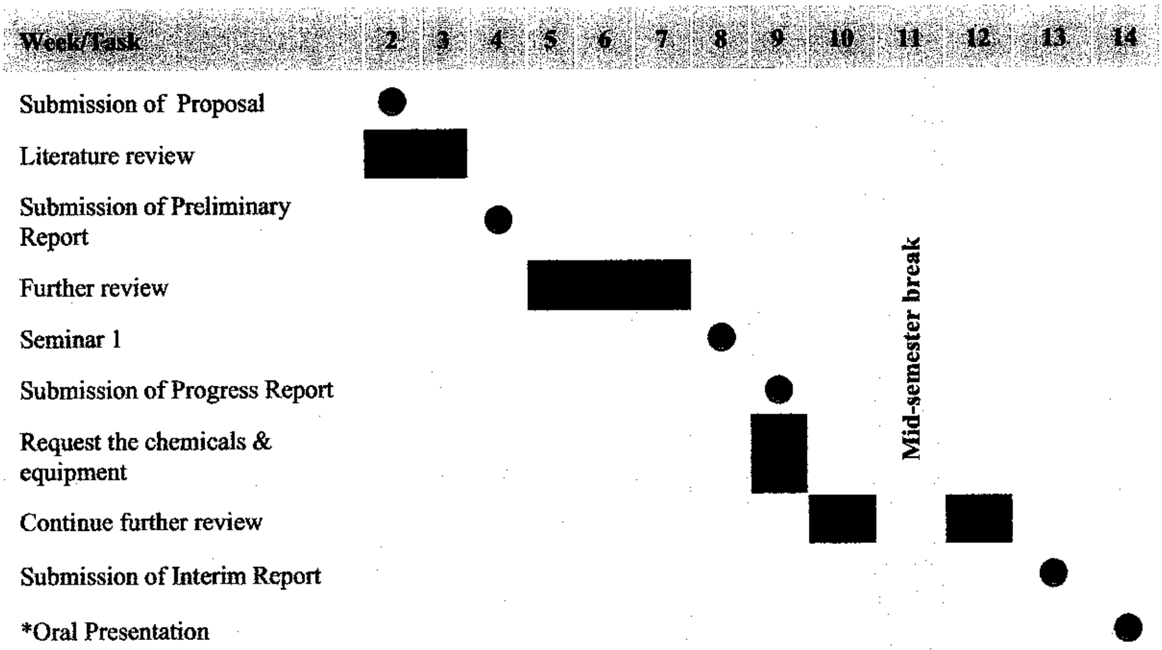
Model oil (dodecane) with known S-content in mg(S) kg(IL)$^{-1}$ was prepared by dissolving a definite amount of thiophene and benzothiophene in known quantities of dodecane. Known quantities of [BMIM][DBP] was used to extract the sulfur species from the crude oil model. Sulfur partition coefficient (K_N), which defined as ratio of S-concentration in dodecane, is an important parameter for EDS process, higher K_N indicates better desulfurization performance of IL. The samples with extracted sulfur content were analyzed with the CHNS elemental analyzer. For the beginning, 100ml crude model is prepared with 2% sulfur content in it. The detail calculations of the thiophene amount used in the model are shown in Appendix C. The crude model prepared is mixed with the [BMIM][DBP] in the ratio of 1:1 (2ml dodecane with thiophene : 2ml [BMIM][DBP]). The mixture was then mixed in the vortex mixer for about 1 minute. The samples were then centrifuged for about 5 minutes forming two phases of liquids. The layers were separated and transferred into vials and followed by analysis using CHNS elemental analyzer. The ionic liquid also tested on the crude oil to analyze the extraction performance. The procedure for the extraction is same with the crude model is same except the crude is preheated to 80°C before mixed using the vortex mixer for 10 minutes. Then, the mixture is then preheated again at 80°C and lastly centrifuged it for 15 minutes. The sample was transferred into the vials and the analyzed by the CHNS elemental analyzer.

i. CHNS Elemental Analyzer

CHNS elemental analyzers provide a means for the rapid determination of carbon, hydrogen, nitrogen and sulfur in organic matrices and other types of materials (Thompson, 2008). They are capable of handling a wide variety of sample types, including solids, liquids, volatile and viscous samples, in the fields of pharmaceuticals, polymers, chemicals, environment, food and energy. It is used to determine the total sulfur compound in the samples.

The pictures of equipments for characterization and analysis are shown in Appendix E.

The suggested milestone for the study is shown in Figure 3.2 and Figure 3.3:



Week/Task	2	3	4	5	6	7	8	9	10	11	12	13	14
Submission of Proposal	●												
Literature review	■	■											
Submission of Preliminary Report			●							Mid-semester break			
Further review				■	■	■							
Seminar 1							●						
Submission of Progress Report								●					
Request the chemicals & equipment								■					
Continue further review									■		■		
Submission of Interim Report												●	
*Oral Presentation													●

Key:

● Suggested milestone

■ Process

**Note: The lab work will continue during the semester break (1st December 2008 onwards)*

Figure 3.2: The Milestone for FYP (First Semester)

Week/Task	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Project work continue	■	■	■											
Submission of Progress Report 1				●										
Project work continue				■	■	■	■							
Submission of Progress Report 2								Mid-semester break	●					
Seminar										■	■			
Project work continue									■	■	■			
Poster exhibition											●			
Submission of Project Dissertation (soft bound)												●		
Oral Presentation													●	
Submission of Project Dissertation (hard bound)														●

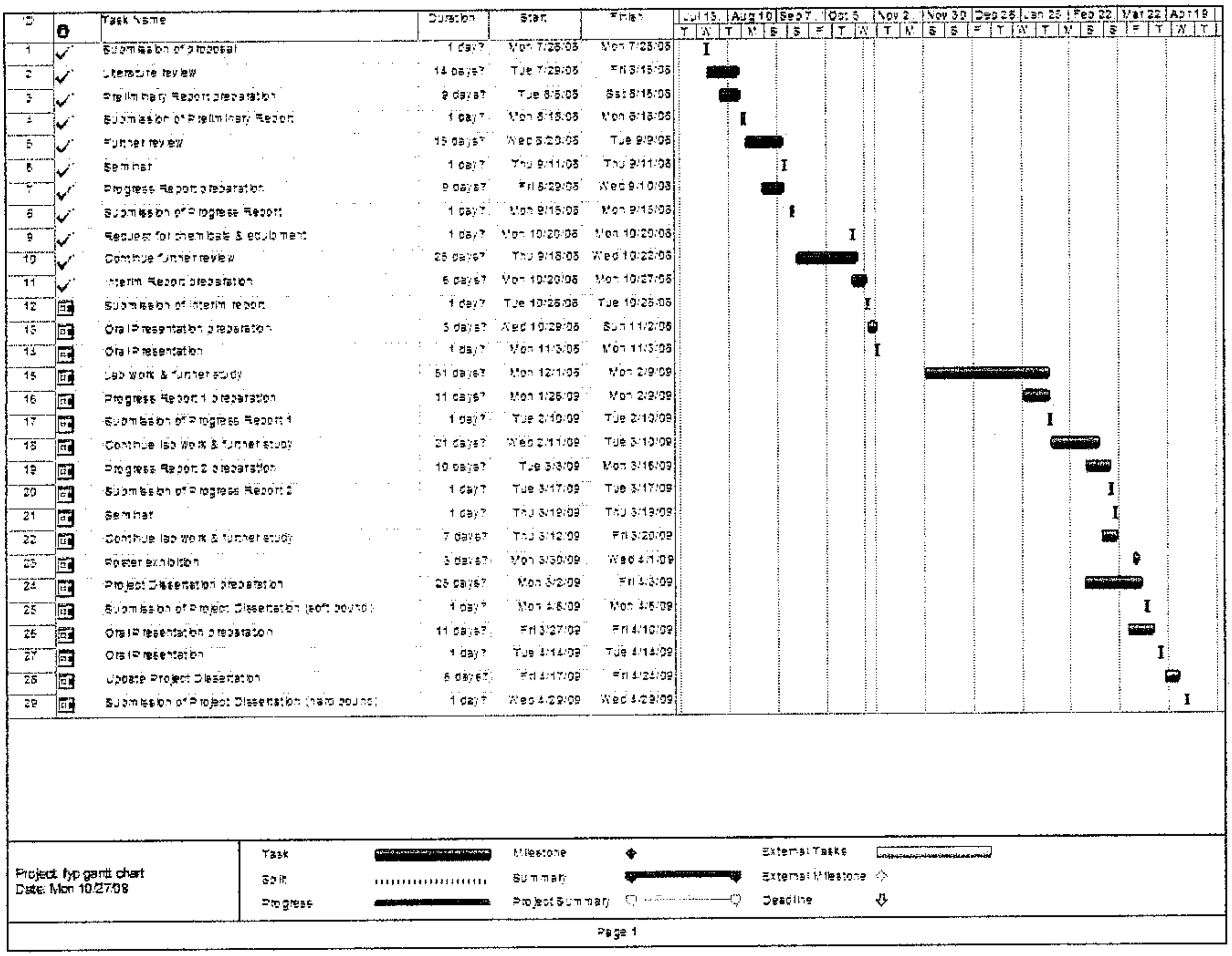
Key:

● Suggested milestone

■ Process

Figure 3.3: The Milestone for FYP (Second Semester)

The Gantt Chart for the project is shown in Figure 3.4:



ID	ⓘ	Task Name	Duration	Start	Finish
1	✓	Submission of proposal	1 day?	Mon 7/28/08	Mon 7/28/08
2	✓	Literature review	14 days?	Tue 7/29/08	Fri 8/15/08
3	✓	Preliminary Report preparation	9 days?	Tue 8/5/08	Sat 8/16/08
4	✓	Submission of Preliminary Report	1 day?	Mon 8/18/08	Mon 8/18/08
5	✓	Further review	15 days?	Wed 8/20/08	Tue 9/9/08
6	✓	Seminar	1 day?	Thu 9/11/08	Thu 9/11/08
7	✓	Progress Report preparation	9 days?	Fri 8/29/08	Wed 9/10/08
8	✓	Submission of Progress Report	1 day?	Mon 9/15/08	Mon 9/15/08
9	✓	Request for chemicals & equipment	1 day?	Mon 10/20/08	Mon 10/20/08
10	✓	Continue further review	25 days?	Thu 9/18/08	Wed 10/22/08
11	✓	Interim Report preparation	6 days?	Mon 10/20/08	Mon 10/27/08
12	▦	Submission of interim report	1 day?	Tue 10/28/08	Tue 10/28/08
13	▦	Oral Presentation preparation	3 days?	Wed 10/29/08	Sun 11/2/08
14	▦	Oral Presentation	1 day?	Mon 11/3/08	Mon 11/3/08
15	▦	Lab work & further study	51 days?	Mon 12/1/08	Mon 2/9/09
16	▦	Progress Report 1 preparation	11 days?	Mon 1/26/09	Mon 2/9/09
17	▦	Submission of Progress Report 1	1 day?	Tue 2/10/09	Tue 2/10/09
18	▦	Continue lab work & further study	21 days?	Wed 2/11/09	Tue 3/10/09
19	▦	Progress Report 2 preparation	10 days?	Tue 3/3/09	Mon 3/16/09
20	▦	Submission of Progress Report 2	1 day?	Tue 3/17/09	Tue 3/17/09
21	▦	Seminar	1 day?	Thu 3/19/09	Thu 3/19/09
22	▦	Continue lab work & further study	7 days?	Thu 3/12/09	Fri 3/20/09
23	▦	Poster exhibition	3 days?	Mon 3/30/09	Wed 4/1/09
24	▦	Project Dissertation preparation	25 days?	Mon 3/2/09	Fri 4/3/09
25	▦	Submission of Project Dissertation (soft bound)	1 day?	Mon 4/6/09	Mon 4/6/09
26	▦	Oral Presentation preparation	11 days?	Fri 3/27/09	Fri 4/10/09
27	▦	Oral Presentation	1 day?	Tue 4/14/09	Tue 4/14/09
28	▦	Update Project Dissertation	6 days?	Fri 4/17/09	Fri 4/24/09
29	▦	Submission of Project Dissertation (hard bound)	1 day?	Wed 4/29/09	Wed 4/29/09

Project: fyp gantt chart
Date: Mon 10/27/08

Page 1

Figure 3.4: Gantt Chart for FYP

For the lab work, this project is utilizing the following chemicals and equipments:

Equipments:

No.	Description	Purpose
1.	Separating funnel (100ml)	**Synthesize the ionic liquids**
2.	Syringes (10ml)	
3.	Measuring cylinder (100ml)	
4.	Retort stand	
5.	Clamp for retort stand	
6.	Beaker	
7.	Pipette (10ml)	
8.	Distillation apparatus (with tube)	
9.	Reflux apparatus (round bottom flask & reflux condenser)	
10.	Stirrer	
11.	Water bath	
12.	Rotavap	
13.	Rotavap flask with clamp	
14.	Vacuum oven	
15.	Storage bottle	**Store the ionic liquids**
16.	Test tube	**Analyze the ionic liquids**
17.	Liquid cup and mylar for XRF	
18.	Karl Fisher	
19.	XRF	
20.	FTIR	
21.	GC	
22.	NMR	

Chemicals:

No.	Description	Purpose
1.	Diethyl ether	**Synthesize the ionic liquids**
2.	1-Methylimidazole	
3.	Tributyl phosphate	
5.	Nitrogen gas	
4.	Dodecane (crude model)	**Determine the sulfur extraction ability in the crude model**
5.	Thiophene	
6.	Dibenzothiophene	

Table 3.1: List of Chemicals and Equipments Used for FYP

CHAPTER 4

RESULTS AND DISCUSSION

During the distillation of 1-methylimidazole, vacuum pump is used in order to lower the boiling point of 1-methylimidazole and hence make the process faster. The 1-methylimidazole was also mixed with potassium hydroxide to absorb the water and impurities in the 1-methylimidazole solution. The residue changed into yellowish colour when the mixture is heated up and slowly changes to white colour when become cool (Figure 4.1).

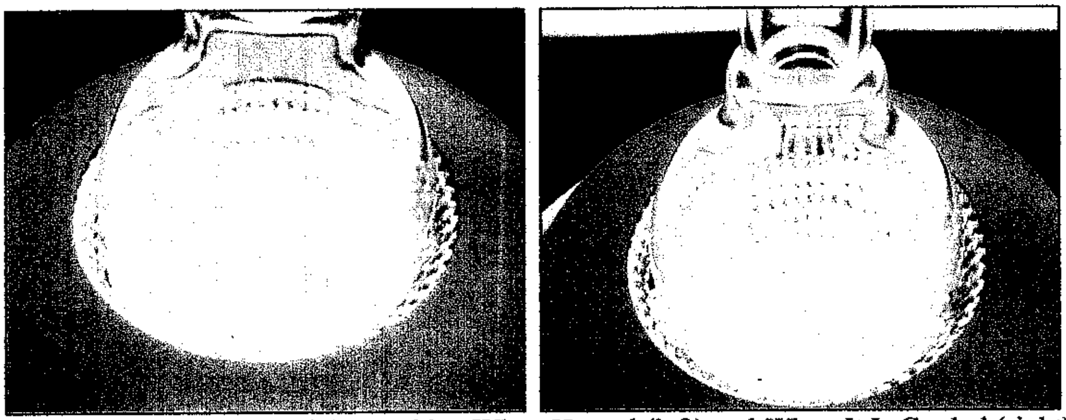


Figure 4.1: The Colour of the Residue When Heated (left) and When It Is Cooled (right)

After the vacuum distillation has completed, 1-methylimidazole was then refluxed with tributyl phosphate in the nitrogen atmosphere for 3 days. Nitrogen gas is 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 is 90°C and 1 atm. This temperature was selected because 1-methylimidazole will decompose if the temperature is higher than 90°C. If it is decomposed, the ionic liquid will not form. After 3 days, the viscous liquid can be seen (Figure 4.2) and the mixture is washed with diethyl ether to remove the residual in the mixture. The washing process was repeated several times until there were no two layers formed in the mixture. Then, the mixture was rotaevaporated for 3 hours to remove any diethyl ether residual. Finally, the ionic liquid was dried using the vacuum line connected to liquid nitrogen.

Figure 4.2: The Change of the Liquid Before and After the Reflux Process

The properties of the ionic liquid such as the density and water content were analyzed using the density meter and coulometer. The result of the analyses is shown in Table 4.1 and Table 4.2:

Table 4.1: Density of [BMIM][DBP]

Temperature (°C)	**Density (g/cm^3)**	**SG**
25.001	1.039866	1.04295
34.995	1.032855	1.03906
44.999	1.025906	1.03605

**Equipment Model: Anton Paar, DMA 5000 Density Meter*

Table 4.2: Water Content of [BMIM][DBP]

Run No.	**H_2O Content (ppm)**
1	3088.529
2	4052.154
3	4064.154

**Equipment Model: Karl Fischer Coulometer DL 39 Mettler Toledo*

From the analyses, the density of [BMIM][DBP] is higher than water and the average water content is about 3735ppm, approximately 0.3%-0.4% (Aquastar, 2002). The ionic liquid produced should not have high water content since it will affect the extraction performance.

The synthesized ionic liquid is analyzed and verified using FTIR and NMR. The results of FTIR are shown in figure below:

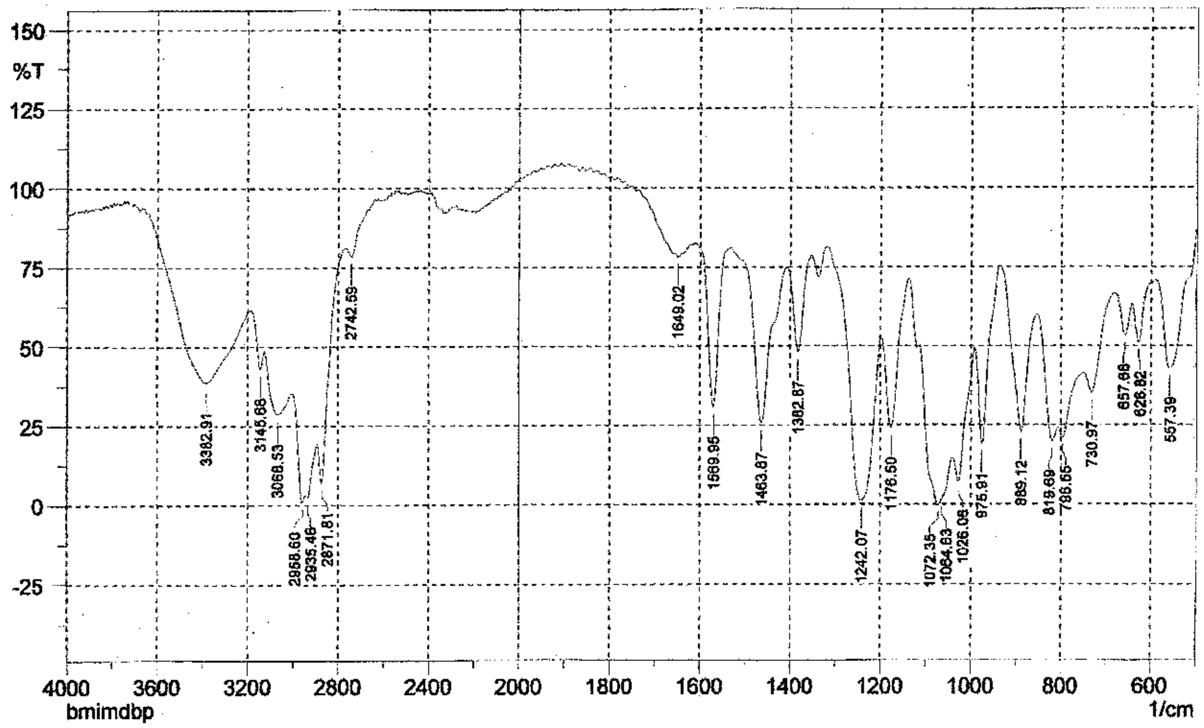


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Figure 4.3: Fourier Transform Infrared Spectroscopy Analysis of [BMIM][DBP]
**Equipment Model: Shimadzu FTIR 8400S*

Based on the analyses in Figure 4.3, the valley of the wavenumber indicates the types of the functional group in the ionic liquid. The types of functional group can be determined through the correlation table in Appendix F. From the analyses, the ionic liquids (based on Figure 3.1) contains O-H bond (wavenumber: 3600-3200cm^{-1}), alkyl group (wavenumber: 2900-2800cm^{-1}), amine with alkyl group (wavenumber: 1200-1025cm^{-1}) and phosphine oxide (wavenumber: 1210-1140cm^{-1}). Therefore, the analysis illustrate that the [BMIM][DBP] is verified.

For NMR analysis, the resulting data are as follows:
HNMR, δ_H (400 MHz, D_2O)

H	δ (Shift)
2	8.56
4,5	7.32
6,7	4.05
8	3.74
10	3.73

The result is compared with the NMR predictor. Basically, the result is similar with the predictor and is acceptable.

In the extraction process, 100ml crude oil model was prepared by adding thiophene (sulfur compound) into dodecane. The sulfur content in the model is about 2% and the ionic liquid used is [BMIM][DBP]. The model and IL is mixed by 1:1 ratio. The mixture is mixed using the vortex mixer in order to have the higher mass transfer area which can increase the extraction of the sulfur content. The mixture was then centrifuged to separate the mixture into two phases: ionic liquid with sulfur extracted and the crude oil model. The mixture was then transferred into vials for analyses using the CHNS elemental analyzer. From the result obtained, the sample with mixing time 5 minutes extract more content of sulfur compared to the others.

For the next experiment, the crude model is tested with the [BMIM][DBP] with different sulfur content (benzothiophene). The same procedure as the first experiment is applied and the mixture is analyzed using the CHNS elemental analyzer. The analyses of CHNS elemental analyzer for the crude oil model with different concentration of thiophene and benzothiophene after extraction is shown in the Table 4.3:

Table 4.3: Sulfur Content of Crude Oil Model and [BMIM][DBP]

Model oil (dodecane + thiophene)		**Extraction Performance (%)**
Before extraction (%)	**After extraction (%)**	
0.038	0.018	52.63
0.042	0.025	40.48
0.046	0.015	67.39

Model oil (dodecane + benzothiophene)		**Extraction Performance (%)**
Before extraction (%)	**After extraction (%)**	
1.907	0.947	50.34
3.848	0.716	81.39
5.868	0.498	91.51

**Equipment Model: CHNS 932 Leco*

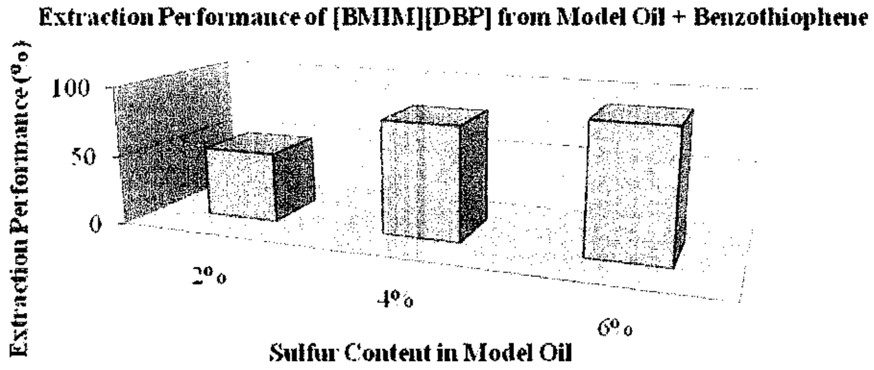


Figure 4.4: Extraction Performance of [BMIM][DBP] from Crude Oil Model with Benzothiophene

The ionic liquid also tested on the crude to analyze the extraction performance. The result of CHNS for the crude with the ionic liquid is shown in the Table 4.4:

Table 4.4: Sulfur Content of Crude Oil and [BMIM][DBP]

Crude Oil		**Extraction Performance (%)**
Before extraction (%)	**After extraction (%)**	
3.579	3.423	4.36
3.481	3.387	2.70

**Equipment Model: CHNS 932 Leco*

Based on the result in Table 4.3 and Figure 4.4, the extraction performance for the IL is good since it is only single pass extraction. The performance could be improved if the extraction process is done through multiple extractions. The sulfur content using thiophene is quite low because thiophene is highly volatile therefore affecting the sulfur content during the preparation of the model oil.

The result of the extraction from the crude model with benzothiophene is increasing (from 50% to 92%) since ionic liquid has its own K_N value which is constant. In order to achieve equilibrium, if the sulfur concentration is increasing and the other condition is constant, the extraction performance is increasing according to Le Châtelier's Principle (If a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to counteract the change) (Clark, 2002). This is same with the extraction of thiophene by [BMIM][DBP].

From Table 4.4, it is shown that the extraction performance from the crude oil is low since there are many complex structure of organosulfur compound compared to the crude model. Besides, the extraction performance also decreases because of the sterical hindrance of the organosulfur compounds and makes the extraction less effective. Based on the literature, the sulfur content will be reduced because the mechanism for the extraction of aromatic S-compounds with imidazolium-based IL is related to the formation of liquid clathrate due to the π–π interaction between unsaturated bonds of aromatic S-compound and the imidazole ring of ILs (Holbrey et al., 2003).

CHAPTER 5

CONCLUSION AND RECOMMENDATION

Based on the result obtained, the extraction of benzothiophene from the crude oil model using [BMIM][DBP] is ranging from 50% to 92%. The extraction performance of [BMIM][DBP] for thiophene is between 40% to 67%. This shows that the extraction performance of [BMIM][DBP] is remarkable. The extraction performance can be improved if the multiple pass extraction is done.

The extraction performance of sulfur compounds from the crude oil using [BMIM][DBP] is low since there are many complex sulfur compound structure making the extraction less reactive. Therefore, further study is needed to find suitable ionic liquid so that the EDS can be developed in the future.

Based on the recent studies by the researchers on the EDS, S-component can be extracted by the ionic liquids. Therefore, the EDS process can at least be used as a complementary technology for the traditional HDS process.

As a conclusion, the EDS has high potential to extract sulfur compound which is cannot done by the HDS due to the steric hindrance of the sulfur compound molecules. Besides, EDS is also economical compared to HDS because it is done in ambient condition and without utilizing the hydrogen gas. Besides, usage of ionic liquids, known as 'green chemicals', also have reduced the environmental impact and the pollution because the ionic liquid used in EDS can be recycled.

APPENDIX A

Calculations of the Solvent Volume

Solvent	No. of mol	Molecular Weight (g/mol)	Density (g/cm^3)	Volume (ml)	Boiling Point (°C)
1-methylimidazole	0.2	82.11	1.03	15.94	198
Tributyl phosphate	0.2	266	0.97	54.85	289

$$n=\frac{m}{MW};\ m=MW\times n$$

for the imidazole,

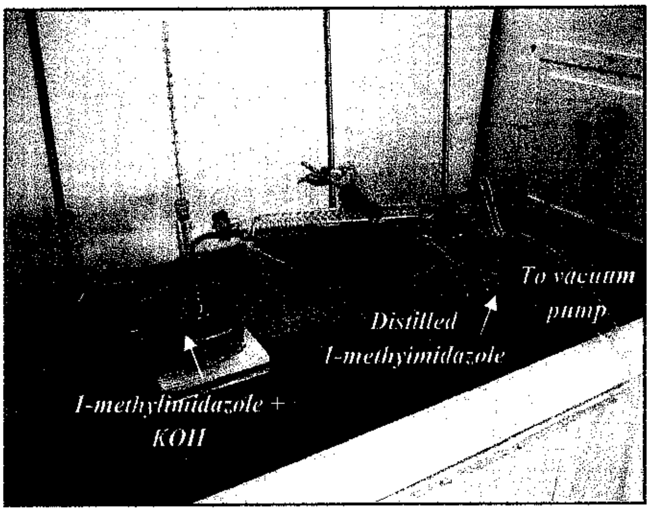
$$n=0.2\text{mol},\ m=82.11\times0.2$$
$$=16.42\text{g}$$
$$\rho=\frac{m}{V};V=\frac{m}{\rho}$$
$$\therefore V=\frac{16.42\text{g}}{1.03\text{g/cm}^3}=15.94\text{ml}$$

for the tributyl phosphate,

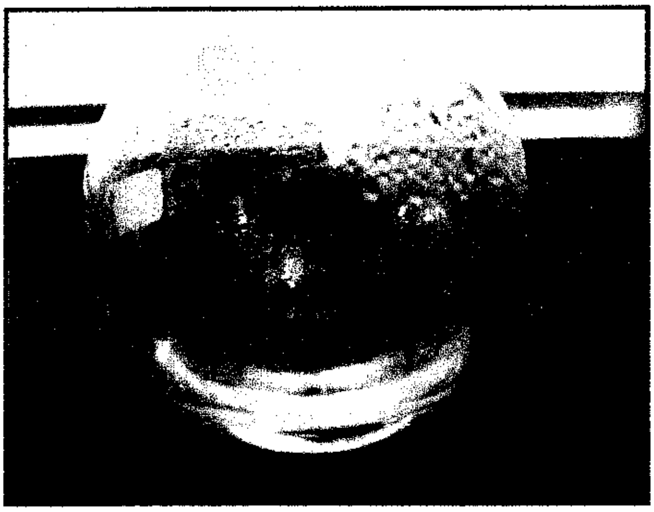
$$n=0.2\text{mol},\ m=266\times0.2$$
$$=53.2\text{g}$$
$$\rho=\frac{m}{V};V=\frac{m}{\rho}$$
$$\therefore V=\frac{53.2\text{g}}{0.97\text{g/cm}^3}=54.85\text{ml}$$

APPENDIX B

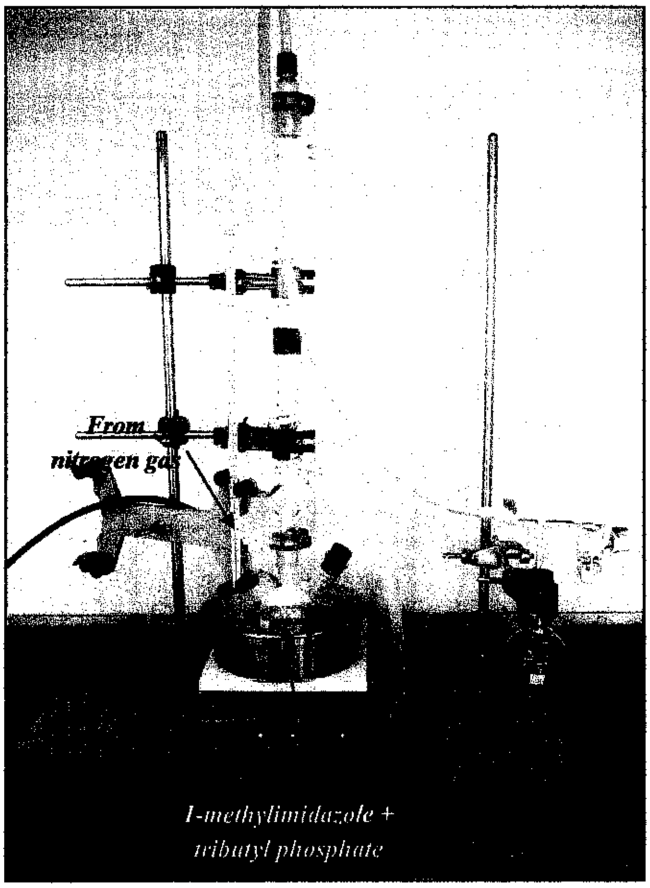
Ionic Liquid Synthesis Process



Equipment setup for the distillation process

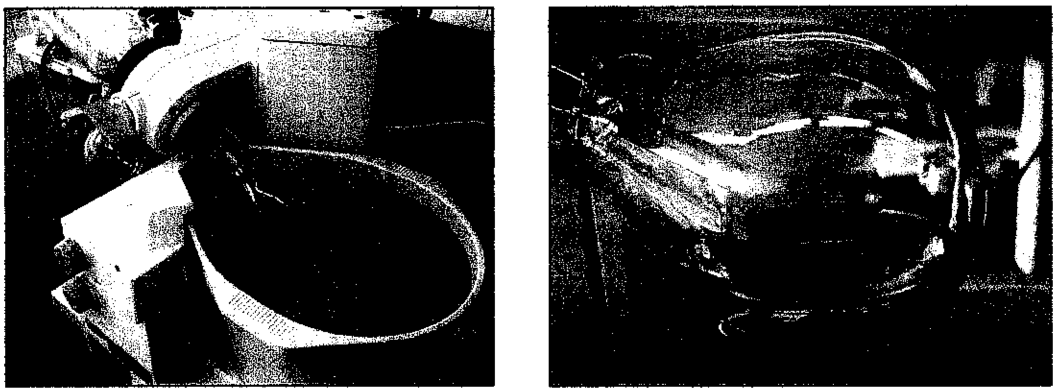


Purified 1-methylimidazole

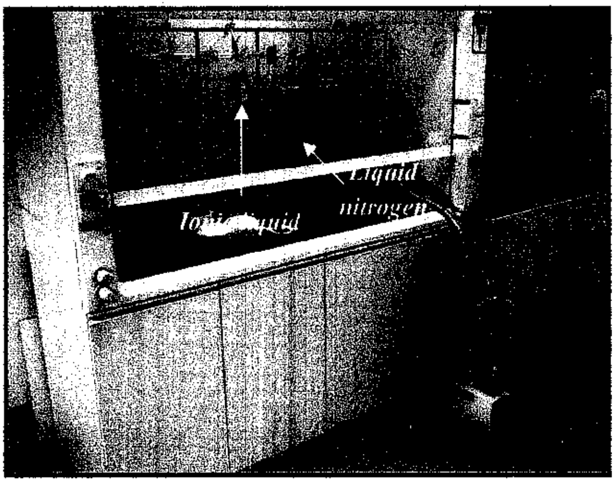


Equipment setup for the reflux process

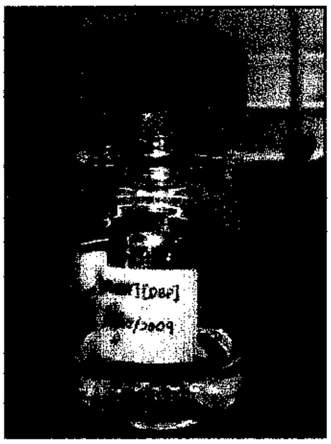
Two layers formed during the washing process



Rotary evaporator setup to remove the residual in mixture (left) and the ionic liquid after the process (right)



Ionic liquid drying equipment setup



The IL synthesized [BMIM][DBP]

APPENDIX C

Sulfur Compound in Crude Oil Model Calculations

for thiophene (99.5% purity),

Molecular formula = C_4H_4S

Molecular mass = 84.14 g/mol

Density = 1.05 g/cm^3

Molecular mass of sulfur = 32.06 g/mol

$$\% \text{ of sulfur in thiophene} = \frac{\text{Molecular mass of sulfur in thiophene}}{\text{Molecular mass of thiophene}} \times 100$$

$$= \frac{32.06 \text{ g/mol}}{84.14 \text{ g/mol}} \times 100$$

$$= 38.1\%$$

38.1% sulfur → 99.5% thiophene

$$\therefore\ 2\% \text{ sulfur} = \frac{2 \times 99.5}{38.1}$$

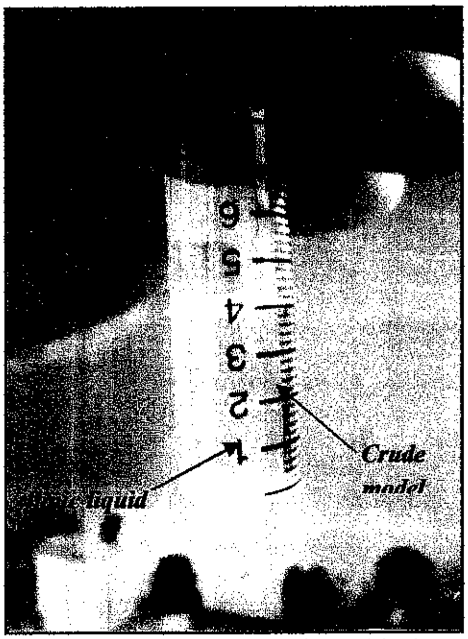
$$= 5.22\% \text{ thiophene}$$

$\therefore$ 100ml crude model requires 94.8ml dodecane and 5.2ml thiophene.

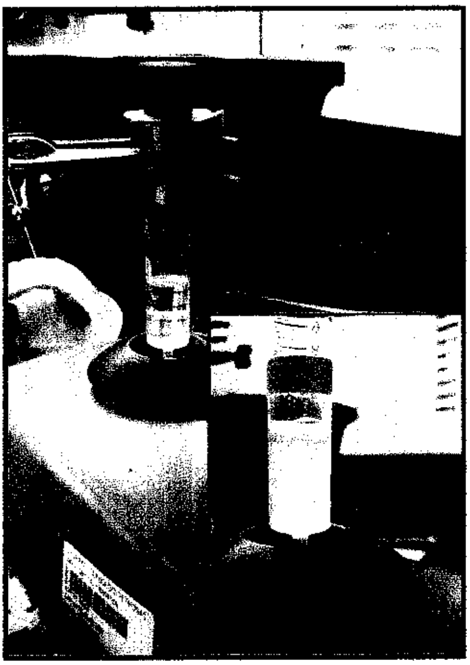
Same calculations applied for the different concentrations of thiophene and benzothiophene.

APPENDIX D

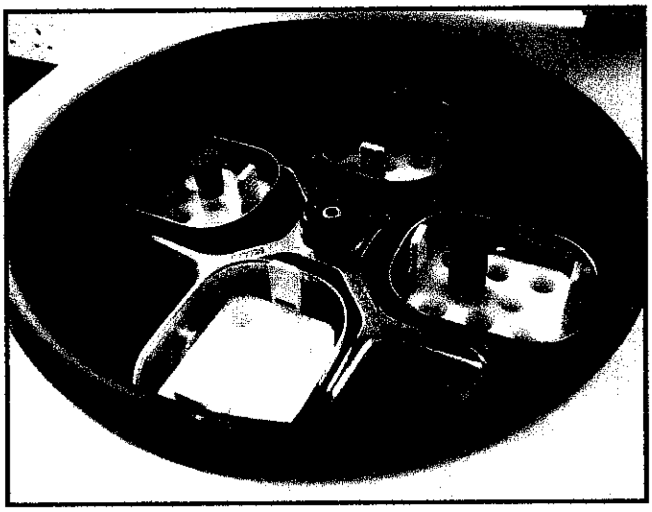
Desulfurization of Crude Model Process



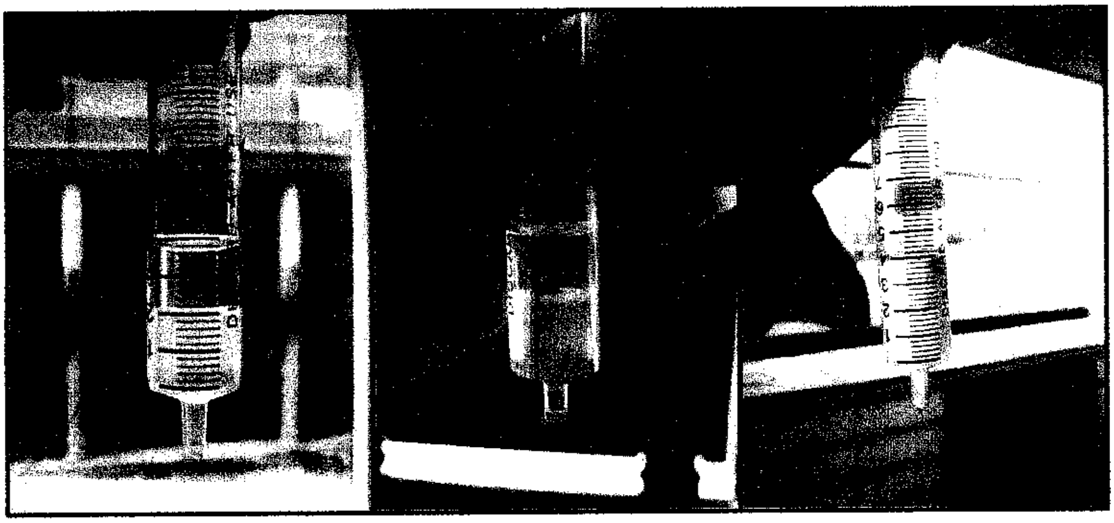
Ionic liquid and crude model used is 1:1 ratio



The mixture is mixed for 1 minute using the vortex mixer and the mixture after 1 minute (inset)



The centrifuge is used to settle down the mixture (1 minute)

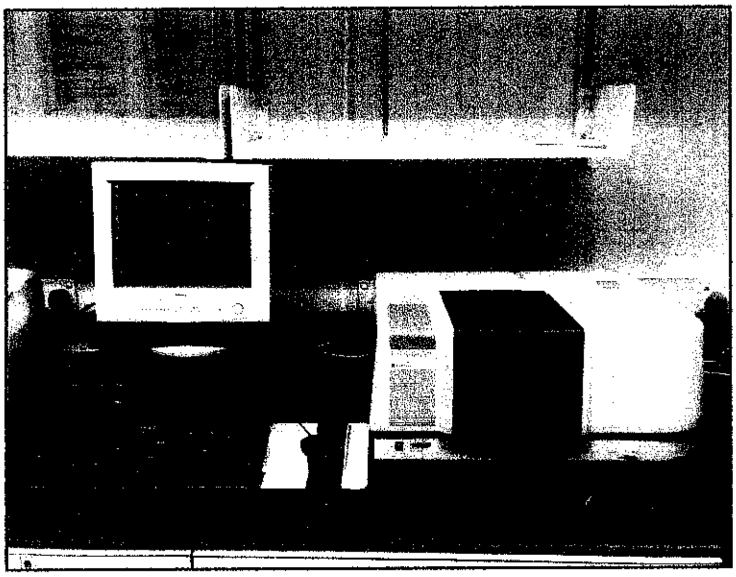


The result of the mixture after centrifuge

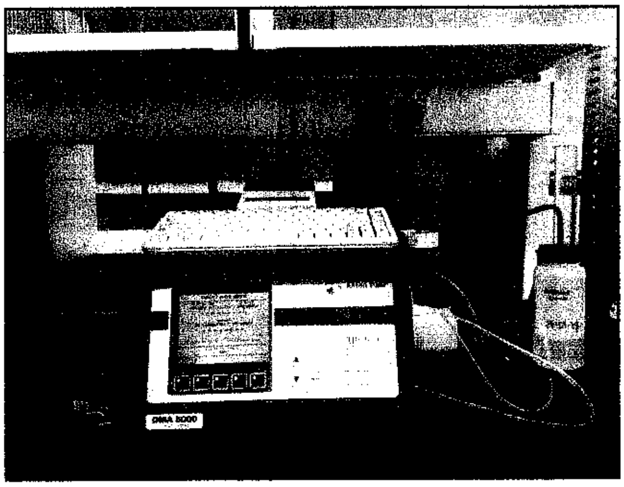
The experiment repeated with model oil with different sulfur species and concentrations

APPENDIX E

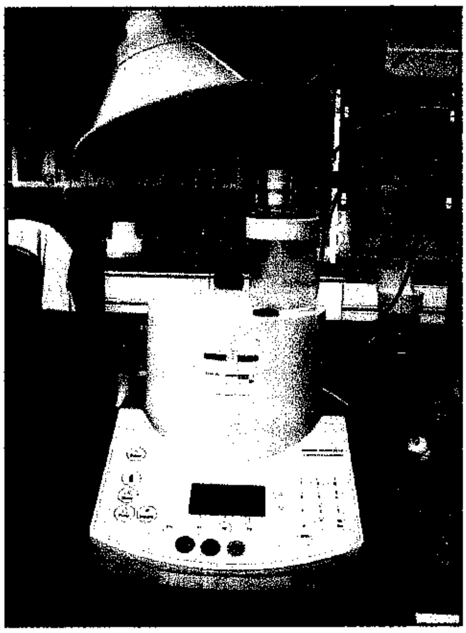
Equipment Used for Characterization and Analysis of the Extraction Performance



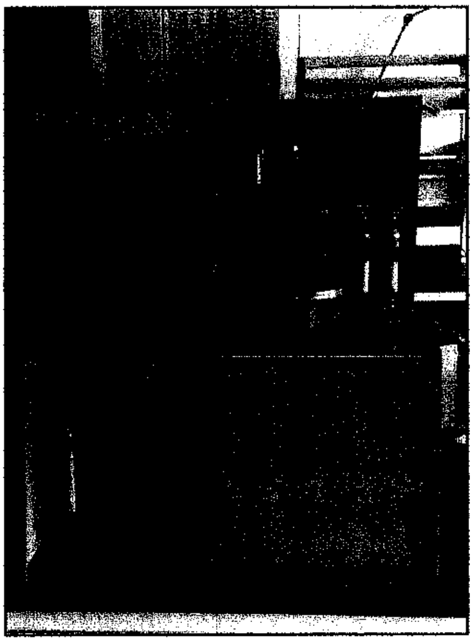
FTIR 8400S Shimadzu



Anton Paar, DMA 5000 Density Meter



Karl Fischer Coulometer DL 39 Mettler Toledo



CHNS 932 Leco

APPENDIX F

FTIR Correlation Table (Glagovich, 2009)

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
	C-H bend (trisubstituted)	~815
alkynes	acetylenic C-H stretch	~3300
	C,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_2C=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

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