Removal of Thiophene and Benzothiophene by using 1-methyl-3-methylimidazolium dimethyl phosphate, [MMIM][DMP] Ionic Liquid from Dodecane

by

Mohd Alamin B Ibrahim

Dissertation submitted in partial fulfilment of
the requirements for the
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(Chemical Engineering)

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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

(Dr Chong Fai Kait)

DR CHONG FAI KAIT
Senior Lecturer
Fundamental & Applied Sciences Department
Universiti Teknologi PETRONAS, PERAK

UNIVERSITI TEKNOLOGI PETRONAS

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ABSTRACT

1-methyl-3methylimidazolium dimethylphosphate ([MMIM][DMP]) ionic liquid (IL), were prepared and demonstrated to be effective for the removal of aromatic sulfur compounds (S-compound) thiophene and benzothiophene (BT) from crude oil model (Dodecane) in terms of sulfur partition coefficient (K_N) at 298.15 K. The result shows that the sulfur removal selectivity for [MMIM][DMP] is depend on the molecular structure of the aromatic S-compounds and follow the order BT > thiophene. Some analysis has been done on [MMIM][DMP] IL in order to obtain its characteristic such as identification of IL's molecular structure by using Nuclear Magnetic Resonance (NMR) spectroscopy, density, water content and identification of IL's functional group by using Fourier Transform Infrared (FTIR) Spectroscopy. The knowledge of characteristics of IL is important from an engineering point of view because it plays a major role in a lot of operation such as heating, stirring and mixing.

ACKNOWLEDGEMENTS

I would like to take this opportunity to acknowledge and thank everyone that has given me all the supports and guidance throughout the whole period of completing the final year project. Firstly, many thanks to the university and the Final Year Project coordinators that have coordinated and made the necessary arrangements, especially in terms of the logistics, for this study.

I must also acknowledge the endless help and support received from my supervisor, Dr Chong Fai Kait throughout the whole period of completing the final year project. Her guidance and advices are very much appreciated. Apart from that, many thanks to ionic liquid's Research Officers; Ms. Siti Hawatulalia, Ms. Mona and Mrs. Naimatul Hani for their endless support in helping and guiding me in completing experiments and also in term of the preparation of logistics for this study. Their continuous support throughout the whole period of experiments are very much appreciated.

I would also like to thank the lab technicians in UTP, especially for technician from Chemical Engineering Department for helping me throughout the completion of the experiments.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

An ionic liquid is a liquid that contains essentially only ions (Earle & Seddon, 2000). Ionic liquids have been studied for application related to green chemical processes such as liquid-liquid extraction, gas separation, electrochemistry and catalysis. Ionic liquids are typically nonvolatile, nonflammable and thermal stable. In general, ionic liquids have higher density then organic liquids and water. Therefore, many ionic liquids exist as separate phase when in contact with organic and aqueous phases. These features enable ionic liquids to be recycled for multiple extractions without additional environmental concern. Since the melting points are low, ionic liquids can act as solvents in which reactions can be performed, and because the liquid is made of ions rather than molecules, such reactions often give distinct selectivity and reactivity compared to conventional organic solvents. Room-temperature ionic liquids have been utilised as clean solvents and catalysts for green chemistry and as electrolytes for batteries, photochemistry and electrosynthesis. They have no significant vapour pressure and thus create no volatile organic components. They also allow easy separation of organic molecules by direct distillation without loss of the ionic liquid. Their liquid range extend to 300 °C allowing good reaction kinetic control, which, coupled with their good solvent properties, allows small reactor volumes to be utilised. Salts based upon poor nucleophilic anions such as $[BF_4]^-$, $[PF_6]^-$, $[CF_3CO_2]^-$, $[CF_3SO_3]^-$, etc, are water and air insensitive and possess remarkably high thermal stability. Many of these materials are based around the imidazolium cation. By changing the anion or the alkyl chain on the cation, a wide variation in properties such as hydrophobicity, viscosity, density and solvation can be obtained. For example, they will dissolve a wide range of organic molecules to an appreciable extent, the solubility being controlled by the nature of the counter anion. A process for the removal of organosulfur compounds from hydrocarbon materials is disclosed. The process includes contacting an ionic liquid with a hydrocarbon material to extract sulfur-containing compounds into the ionic liquid. The sulfur-containing compounds can be partially oxidized to sulfoxides and/or sulfones prior to or during the extraction step. An ionic liquid is a non-volatile organic liquid salt, which potentially can extract sulfur and also organic nitrogen compounds in fuels by its polarity.

1.2 Problem Statement

In recent years, much attention has been given to deep desulfurization of diesel oil and gasoline, since exhaust gases containing SO_x can cause air pollution and acid rain. Concentrations of SO_2 in the ambient air twice the current standards are associated with adverse health effects. A considerable body of evidence suggests that there may be discernible human health effects from exposure to concentrations approximating the current standards. There is therefore no basis for relaxation of the present standards for sulfur oxides at this time. Since the scientific basis for this judgment is incomplete, further scientific information will be required either to validate the present standards or to justify alteration of these standards. The current process of catalytic hydrodesulfurization (HDS) is limited for such ultra-low sulfur fuels, therefore the expenses are high in order to meet these future requirements. The main issue in diesel HDS is the low reactivity of highly aromatic sulfur species such as benzothiophene and dibenzothiophene. This is because the available catalyst for HDS process is less effective and HDS is intensive energy with high hydrogen demand. Removing sulfur from the Fluid Catalytic Cracking (FCC) feed in HDS approach tends to be expensive in terms of the capital cost of the equipment as well as operationally since hydrogen consumption is high and operation conditions (temperature and pressure) are severe. Even in extremely low concentrations, sulfur compounds will also poison the noble metal catalysts in catalytic reforming units that are subsequently used to upgrade the octane rating of the naphtha streams. Hence, the sulfur compounds need to be removed. In order to meet the strict regulations, it is necessary to combine different desulfurization technologies and to develop new approaches. These might include selective adsorption, bio-desulfurization, oxidation/extraction, ionic liquid (IL) extraction, etc. For the extraction of sulfur-containing compounds from diesel fuel and gasoline, one of the most promising alternatives under development is the IL extraction. The (reversible) extraction of organic S-compounds by ionic liquids (ILs) could be an alternative to maximize the removal of S-compunds from crude oil.

1.3 Objective

The main objective for this project is to determine the effectiveness of 1-methyl-3methylimidazolium dimethylphosphate, [MMIM][DMP] ionic liquid for extractive removal of thiophene and benzothiophene, BT from dodecane. The extraction effectiveness is measure by sulfur partition coefficient, K_N where it is equal to ratio of total sulfur content extracted by IL by total sulfur content left in dodecane.

1.4 Scope of Study

The scope of studies involved for this project would be on investigating the efficiency of desulfurization of selected ionic liquid by using X-ray fluorescence, XRF. The project covered on the types of the sulfur-containing compounds in the crude oil. The criteria for choosing the ionic liquids depend on the efficiency of ILs in extracting the sulfur compounds. The laboratory experiment will involve the extraction of the selected sulfur compounds from the crude oil model using ionic liquid.

The main points as the scope of study consist of the following:

1. **Composition of crude oil** – The composition of the crude oil must be known to represent the crude oil model as the real crude oil.
2. **Sulfur-containing compounds** – The types of the sulfur determined which ionic liquids will be used to extract each type of sulfur compounds.
3. **Ionic liquids** – The ability if the ionic liquids to extract the sulfur compounds from the crude oil are proportional with the characteristic ionic liquids. Slightly change in the ionic liquids will give different effect to the extraction of sulfur compounds.

CHAPTER 2

LITERATURE REVIEW

There were many literatures found about the desulfurization of fuel, diesel and crude oil by using ionic liquids. A few of examples found were using imidazolium and pyridinium based IL. These literature would be able to help in explaining the results that are obtained by using [MMIM][DMP] IL in removing sulfur from crude oil model (dodecane).

According to research by Yie Nie *et al.* (2008), N-butylimidazole-derived dialkylphosphate ionic liquids (ILs) were demonstrated to be effective for extractive removal of aromatic sulfur compounds (S-compounds) from fuel oils, and show strong preferential extraction for aromatic S-compound versus toluene. Sulfur partition coefficients (K_N) between IL and fuel oil at 298.15 K are determined experimentally over a wide range of sulfur content. The results show that the sulfur removal selectivity for a specific IL is dependent on the molecular structure of the S-compounds and follows the order dibenzothiophene > benzothiophene > thiophene > 3-methylthiophene, and the efficiency of the ILs for removal of aromatic S-compounds is dependent on the size and structure of both cations and anions of the ILs. For the dialkylphosphate ILs studied with the same anion, the longer the alkyl substitute to the imidazolium ring is the higher the K_N value for that IL, and a similar trend is found for the ILs with same cation.

Xiaochuan Jiang *et al.* (2007), were demonstrated N-ethyl-imidazolium-based alkylphosphate ionic liquid (IL); 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]) to be effective for the removal of aromatic sulfur compounds (S-compound) 3-methylthiophene (3-MT), benzothiophene (BT) and dibenzothiophene (DBT) from fuel oils in terms of sulfur partition coefficients (K_N) at 298.15 K. It was shown that 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 with their K_N-value being 1.72, 1.61 and 1.17, respectively for DBT. For a specified IL the sulfur selectivity followed the order DBT > BT > 3-MT with their KN-value being 1.61, 1.39 and 0.78, respectively for [EEIM][DEP]. The alkylphosphate ILs are insoluble in fuel while the fuel solubility in ILs varies from 20.6 mg(fuel)/g(IL) for [EMIM][DMP] to 266.9 mg(fuel)/g(IL) for [BEIM][DBP]. The results suggest that [EEIM][DEP] might be used as a promising solvent for the extractive desulfurization of fuel, considering its higher sulfur extractive ability, lower solubility for fuel and thus negligible influence on the constituent of fuel, and the ease of regeneration for the spent IL via water dilution process.

Cláudia C. Cassol *et al.* (2007) were investigated that the liquid-liquid equilibrium for the ternary system formed by *n*-octane and aromatic (alkylbenzenes) and heteroaromatic compounds (nitrogen and sulfur containing heterocyles) and 1-alkyl-3-methylimidazolium ionic liquids (ILs) associated with various anions. The selectivity on the extraction of a specific aromatic compound is influenced by anion volume, hydrogen bond strength between the anion and the imidazolium cation and the length of the 1-methyl-3-alkylimidazolium alkyl side chain. The interaction of alkylbenzenes and sulfur heterocyles with the IL is preferentially through CH-p hydrogen bonds and the quantity of these aromatics in the IL phase decreases with the increase of the steric hindrance imposed by the substituents on the aromatic nucleus. In the case of nitrogen heterocycles the interaction occurs preferentially through N(heteroaromatic)-H(imidazolium) hydrogen bonds and the extraction process is largely controlled by the nitrogen heterocycle pKa. Competitive extraction experiments suggest that benzene, pyridine and dibenzothiophene do not compete for the same hydrogen bond sites of the IL.

In other experiment, Wang Jian-long *et al.* (2007) were prepared and tested six *N*-alkyl-pyridinium-based ionic liquids which are *N*-butyl-pyridinium nitrate ([BPy]NO3), *N*-ethyl-pyridinium nitrate ([EPy]NO3), *N*-butyl-pyridinium tetrafluoroborate ([BPy]BF4), *N*-ethyl-pyridinium tetrafluoroborate ([EPy]BF4), *N*-ethyl-pyridinium acetate ([EPy]Ac), and *N*-butyl-pyridinium acetate ([BPy]Ac), in the extraction desulfurization of gasoline. It is found that $[BPy]BF_4$ has the best effect on the selective removal of sulfur-containing compounds from gasoline at room temperature among these ionic liquids. The extraction rate of $[BPy]BF_4$ is

45.5%. The desulfurization effect of [EPy]BF is the lowest. The used ionic liquids can be regenerated by rotary evaporation or re-extraction using tetrachloro-methane.

Roland Schmidt (2008) was synthesized and examined 1-Butyl-3-methylinidazolium tetrachloroaluminate for its capability to extract organic sulfur species from real, refinery obtained hydrocarbon fuels. The fuels consisted of sulfur rich gasoline and diesel as well as pre-treated, partially desulfurized gasoline and diesel. The IL extracted fuels were then analyzed for total sulfur, nitrogen and chlorine. Total sulfur was significantly lowered in all tested fuels. Nitrogen level were also significantly reduced mainly due to a pretreatment with molecular sieve. Only traces of chloride originating from the IL could be detected in three of the four samples after all extraction stages. Sulfur-speciation analyses revealed that some sulfur compounds in the feed were converted to a new compounds.

All literature review above were summarized in *Table 2.1.*

Table 2.1: Summary of literature review

<table>
<tr><th>IL(s)</th><th>Journals</th><th>Articles/Authors</th><th>Preparation IL</th><th>Characterization</th><th>Performance</th><th>Remarks</th></tr>
<tr><td>[BMIM][DMP]</td><td>Fuel Processing Technology</td><td>N,N-diakylimidazolium diakylphosphate ionic liquids: Their extractive performance for thiophene series compounds from fuel oils versus the length of alkyl group/Yi Nie, Chunxi Li*, Hong Meng, Zihao Wang</td><td>[BMIM][DMP] 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%.</td><td>Sulfur partition coefficient on mass basis (K_N) <i>[ratio of sulfur concentration (S-concentration) in IL to the S-concentration in fuel oil]</i> of IL increase due to increasing size of alkyl group in the imidazolium ring.</td><td>[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.</td><td>[BMIM][DMP] shows remarkable selectivity for the extraction of aromatic compounds 3-MT and DBT</td></tr>
<tr><td>N-butyl-pyridinium tetrafluoroborate, [BPy][BF_4]</td><td>Journal of Fuel Chemistry and Technology</td><td>Desulfurization of gasoline by extraction with N-alkyl-pyridinium-based ionic liquids/ WANG Jian-long, ZHAO Di-shun, ZHOU Er-peng, DONG Zhi</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</td><td>The lone pair electrons of pyridine and the electron-donating ability of alkyl substitutions make the <i>N</i>-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><td rowspan="3">IL</td><td colspan="3">Sulfur removal η / %</td></tr>
<tr><td colspan="3">mass ratio of IL to the model oil</td></tr>
<tr><td>1:1</td><td>1:2</td><td>1:3</td></tr>
<tr><td>[BPy][BF_4]</td><td>45.5</td><td>28.6</td><td>16.9</td></tr>
</table></td><td>ILs cannot be applied in this research because although it is air stable, it rapidly absorbs water from the atmosphere, and is hydrolytically unstable, generating five</td></tr>
</table>

			removed by vacuum evaporation.			moles of HF for every mole of ionic liquid.
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])	Fuel 87 (2008) 79–84	Imidazolium-based alkylphosphate ionic liquids – A potential solvent for extractive desulfurization of fuel/Xiaochuan Jiang, Yi Nie, Chunxi Li, Zihao Wang	ILs [EMIM][DMP], [EEIM][DEP] and [BEIM][DBP] 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

[BMIM][AlCl$_4$]	Energy & Fuels 2008, 22, 1774-1778	[BMIM][AlCl$_4$] Ionic Liquid for Deep Desulfurization of Real Fuels / Roland Schmidt	200ml of N-methylimidazolium is added to 500ml of n-butyl chloride in a 1L three-neck flask under nitrogen. After second phase form, the mixture was reflux for 30 min. Then, the mixture is continuously reflux for 7 hr to complete the reaction. Excess n-butyl chloride is distilled off in vacuum at elevated temperature. The remaining phase is crystallized after 3 days at 20°C and will form 125g of n-butyl-N-methylimidazolium chloride. 175g of dry AlCl$_3$ is add in small portions and the flask is cooled to 0°C during the addition due to the exothermic reaction while forming the ionic liquid. N-Butyl-N-methylimidazolium tetrachloroaluminate is obtain as a dark green liquid. The IL is filtered through a glass-frit filled with glass wool to remove traces of solids. No further purification is attempt. The IL is transfer into a glovebox for storage.	The sulfur content in sulfur-rich gasoline and diesel show significantly lower than original value. Nitrogen content also reduce due to pretreatment.	About >90% sulfur and nitrogen being removed after repeating 4 times extraction stages.	-Some chloride was detected in three out of four fuel tested after fourth stages extraction. -IL sensitive toward water and possible difficulties in regeneration.

AlCl$_3$-TMAC	Ind. Eng. Chem. Res. 2004, 43, 614-622	Extractive Desulfurization and Denitrogenation of Fuels using Ionic Liquids. / Shuguang Zhang, Qinglin Zhang, Z. Conrad Zhang.	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.	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	Application of AlCl3-based ILs is limited to certain aromatic compounds only such as DBT because their contact with thiol-containing compounds resulted in the formation of dark precipitates.

CHAPTER 3

METHODOLOGY

3.1 Preparation of 1-methyl-3-methylimidazolium dimethyl phosphate, [MMIM][DMP] ionic liquid

The procedure for preparation of [MMIM][DMP] ionic liquid started with the distillation of 1-methylimidazole. Distillation apparatus is set up as shown in *Figure A1* in *Appendix A.1.* 100ml of 1-methylimidazole was poured into a three-necked round bottom flask at room temperature. Potassium hydroxide (KOH) was added to 1-methylimidazole to avoid the production of moisture in the flask. The solvent was heated in vacuum pressure condition until it reached its boiling point (≈ 140°C) and the product produced in the round flask is the pure 1-methylimidazole.

The [MMIM][DMP] ionic liquid was prepared by mixing purified 1-methylimidazole (0.5 mol) and trimethyl phosphate (0.5 mol) in a three-necked round bottom flask fitted with a reflux condenser and a drying tube. The set up of the reflux apparatus is shown in *Figure A2* in *Appendix A.1.* The temperature was maintained between the range 55 – 65°C in nitrogen and the reaction was carried out for 3 days. Table 3.1 show the corresponding volume that was added between 1-methylimidazole and trimethyl phosphate.

Table 3.1 : Calculation for equimolar volume for 1-methylimidazole and trimethyl phosphate.

Solutions	**Mol**	**Molecular Weight (gmol)**	**Density (g/cm^3)**	**Volume (cm^3)**
MIM	0.5	82.11	1.03	39.86
M_3PO_4	0.5	140.08	1.21	57.88

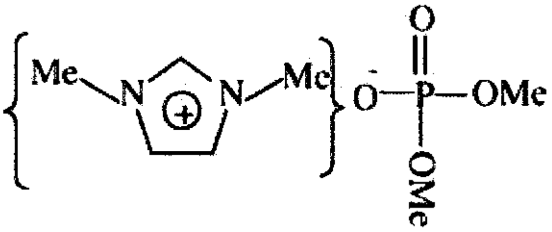


Figure 3.1: Structure of [MMIM][DMP]

After 3 days, the [MMIM][DMP] ionic liquid was washed with diethyl ether. Equi-volume of diethyl ether was added into [MMIM][DMP] ionic liquid producing two layers. The washing steps was repeated for another 3 times. The residual diethyl ether was removed using a rotary evaporator. The IL was rotavap at 50 °C for 3 hours. Finally the ionic liquid was further dried using a vacuum line as shown in *Figure A5* in *Appendix A.1.*

3.2 Characterization of ionic liquids

Several main equipment that were used in IL characterization study such as Nuclear Magnetic Resonance (NMR) spectroscopy, Karl Fischer Coulometer (Mettler Toledo DL39), Anton Paar, DMA 5000 density meter and Fourier Transform Infrared (FTIR) spectroscopy. They are used to determine the molecular structure, water content, density and functional group of the [MMIM][DMP] IL. Apart from main equipments, other experimental apparatus are also required for this study. The other apparatus are mainly the normal equipments needed for jar tests such as syringes, beaker, stirring rod, burette, pipette and others.

3.2.1 NMR analysis

Nuclear Magnetic Resonance Spectroscopy or NMR is an important tool of the chemist for the determination of molecular structure of unknown organic compounds. For organic structure determination, the two most important types of NMR spectra are the proton and carbon spectra. They give information about the number of hydrogens and carbons in a molecule and how those hydrogens and carbons are connected together as well as information about functional groups. NMR complements IR for determination of structures of organic compounds. IR spectra help identify functional groups in a molecular structure.

3.2.2 Water content analysis

The amount of moisture content in [MMIM][DMP] IL was determined by using Karl Fischer Titration's technique. The Karl Fischer Coulometer model DL39 as shown in *Figure A12* in *Appendix A.3* was used. This technique is based on a reagent which reacts with water and converts the water into a non conductive chemical. The advantages of the coulometric method was the capability to accurately measured small amount of moisture. The result of water content analysis was recorded in Table 4.2 in Chapter 4.

3.2.3 Density analysis

The density was measured as a function of temperature for [MMIM][DMP] ionic liquid. Density were obtained using a vibrating tube densimeter from Anton Paar model DMA 5000 as shown in *Figure A11* in *Appendix A.3*, at temperature up to 25°C and 65°C with an accuracy of 10^{-3} g cm^{-3} (Jacquemin et al, 2005). Before start the sample measurement, waste bottle was prepared at the oulet of the measuring cell. 2 ml of sample was injected into the filling nozzle by pushing the plunger of the syringe slowly and continuously until a drop emerges from the outlet nozzle into a waste bottle. The filling process was observed through the inspection window to make sure that there were no gas bubbles in the measuring cell. In order to prevent the sample leaking, the syringe was leaved in the filling position. The result of experiment can be print out or recorded after completing all the previous methods.

3.2.4 FTIR analysis

Fourier Transform Infrared Spectroscopy (FTIR) model 8400S as shown in *Figure A9* in *Appendix A.3,* is a powerful tool for identifying types of chemical bonds and functional groups in a molecule by producing an infrared absorption spectrum. A small drop of [MMIM][DMP] IL was placed on one of the potassium bromide (KBr) plates. The second KBr plate was placed on the top and a quarter turn was made to obtain a nice even thin film as shown in *Figure A10* in *Appendix A.3*. The plates was then placed into the sample holder before run the spectrum. If the sample is too concentrated, the plates need to separate back and wipe one side clean before putting them back together. After completed this procedure, the KBr plates must be thoroughly cleaned to prevent contamination of future samples. The windows was wiped with tissue and then washed several times with deionized water so that it can take off the samples left on KBr plates. The washing steps was then finalized using ethanol. The plates then was polished by using polishing kit in the lab so that the cleaned surfaces was clear and free from scratches.

3.3 Preparation of crude oil model

Three crude oil models, 100 ml each one with different concentration of sulphur were prepared by mixing corresponding volume of thiophene (sulphur species) solution with corresponding volume of dodecane (model oil). The calculation for preparation of crude oil model between dodecane and BT was different since BT was in solid phase in room temperature. The 100g sample of crude oil model was prepared by mixing corresponding weight of BT with dodecane. All the calculations for the preparation are shown in *Appendix B*. Below are the result from the calculations.

Table 3.2 : Percentage sulphur and corresponding volume and weight of mixtures

Sulfur Content (%)	**Thiophene (ml)**	**Dodecane (ml)**	**BT (g)**	**Dodecane (g)**
2	5.24	94.76	91.63	8.37
4	10.45	89.55	83.25	16.75
6	15.67	84.33	74.88	25.12

3.4 Desulfurization of crude oil model by ionic liquid.

Desulfurization of crude oil model was carried out by extracting the crude oil model with [MMIM][DMP] with a volume ratio 1:1. 2ml of crude oil model and 2ml of [MMIM][DMP] ionic liquid were added into a syringe at room temperature. The outlet of each syringe was sealed. The biphasic mixture was then stirred by using the vortex mixer for 1 minute as shown in *Figure A6* and *Figure A7* in *Appendix A2.* The sulphur content in both [MMIM][DMP] IL and dodecane was quantitative analyzed by using X-ray Fluorescence (XRF) spectrometer as shown in *Figure A13* in *Appendix A.4.*

3.5 Chemicals and Equipments used

Table 3.3: List of Chemicals Used

No.	Description	Purpose
1.	1-methylimidazole	Synthesis of [MMIM][DMP] ionic liquid
2.	Trimethylphosphate	
3.	Potassium Hydroxide (KOH)	
5.	Diethyl ether	To wash synthesised Ionic Liquid
6.	Thiophene	Sulphur compound model
7.	Benzothiophene	
7.	Dodecane	Crude Oil Model
8.	Nitrogen gas	To prevent accumulation moisture

Table 3.4: List of Equipments Used

No.	Description	Purpose
1.	XNMR	Analyze Ionic Liquids
2.	FTIR	
3.	XRF	
4.	Rotary Evaporator	Synthesis of Ionic Liquids
5.	Conical Flask	
6.	Stirrer	
7.	Measuring Cylinder (100ml)	
8.	Beaker	
9.	Pipette (10ml)	
10.	Distillation Apparatus (with tube)	
11.	Reflux Apparatus	
12.	Retort Stand (with clamp)	
13.	Separating Funnel	
14.	Syringes (10ml)	
15.	Water bath	

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Preparation of [MMIM][DMP] ionic liquid

First the distillation of 1-methylimidazole was done by using the distillation apparatus, vacuum pump which the function is to create the vacuum pressure in the column then lowering the boiling point of 1-methylimidazole. Some potassium hydroxide was added in order to absorb the moisture and other impurities. The residue left at the end of distillation process was potassium hydroxide with absorbed water molecules which changed to yellowish as the reaction approaching the end (*Figure 4.1*).

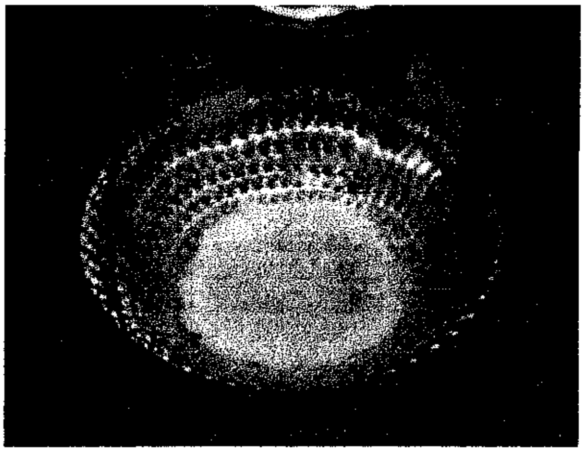


Figure 4.1: The colour of the residue change to yellowish as the reaction approaching to the end.

Nitrogen gas used during the reaction between 1-methylimidazole and trimethyl phosphate is to remove the moisture from contaminated the ionic liquid. The reaction temperature and pressure is set at 60°C and 1 atm. The ionic liquid produced will decomposed if the reaction temperature is set higher than 60°C. The reaction process that left for three days and the solution become more viscous and reddish in colour shown that the ionic liquid is completely formed.

Figure 4.2: The colour of the product changed to reddish colour.

4.2 Properties of [MMIM][DMP] IL

4.2.1 Water Content

The data in *Table 4.1* show the water content in three different samples of [MMIM][DMP] determined using Karl Fisher (KF) titrations Coulometer (Mettler Toledo DL39) as shown in *Figure A12* in *Appendix A.3*. Hygroscopic (tendency of material to absorb water from environment) character for [MMIM][DMP] ionic liquid was evaluated by KF coulometric titration. As shown in *Table 4.1*, [MMIM][DMP] appears to be hygroscopic in ambient atmosphere. The water content in ionic liquid shouldn't exceed 1 wt% in order to obtain the better extractive properties in desulfurization process. Drying by using the vacuum line was not as effective as by using vacuum oven.

Table 4.1: Water content in [MMIM][DMP]

	Weight (g)	**Water Content (ppm)**	**Water Content (wt%)**
Sample #1	0.4978	17149.16	1.714916
Sample #2	0.6505	12973.21	1.297321
Sample #3	0.4064	20784.36	2.078436
Total		**50870.73**	**5.087073**
Average		**16956.91**	**1.695691**

4.2.2 Density

Figure 4.3 below shows the density of [MMIM][DMP] were obtain as a function of temperature from 25°C to 65°C.

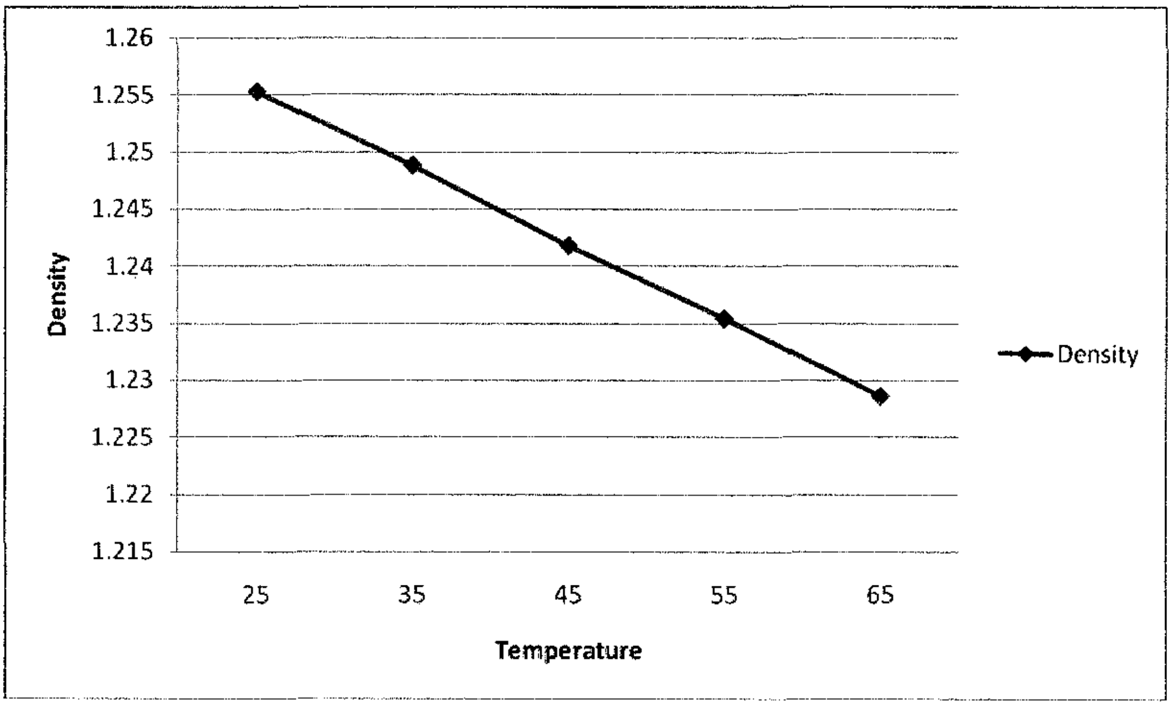


Figure 4.3: Density of [MMIM][DMP] vs temperature

The results show that the density of [MMIM][DMP] decrease as the temperature was increased by 10°C from 25°C until 65°C. This temperature range study shows that density of [MMIM][DMP] decrease linearly with increasing temperature. J. Jacquemin et al. (2005) says that the density of [MMIM][DMP] ionic liquid cannot be measure at higher temperatures in order to avoid changes in the composition of the sample due to the vaporization of water. Below 70°C, the vapour pressure of the water is sufficiently low (less than 0.031 MPa) to consider this change in composition as negligible.

4.2.3 FTIR Analysis

The result of FTIR analysis shown in the *Figure 4.4* below

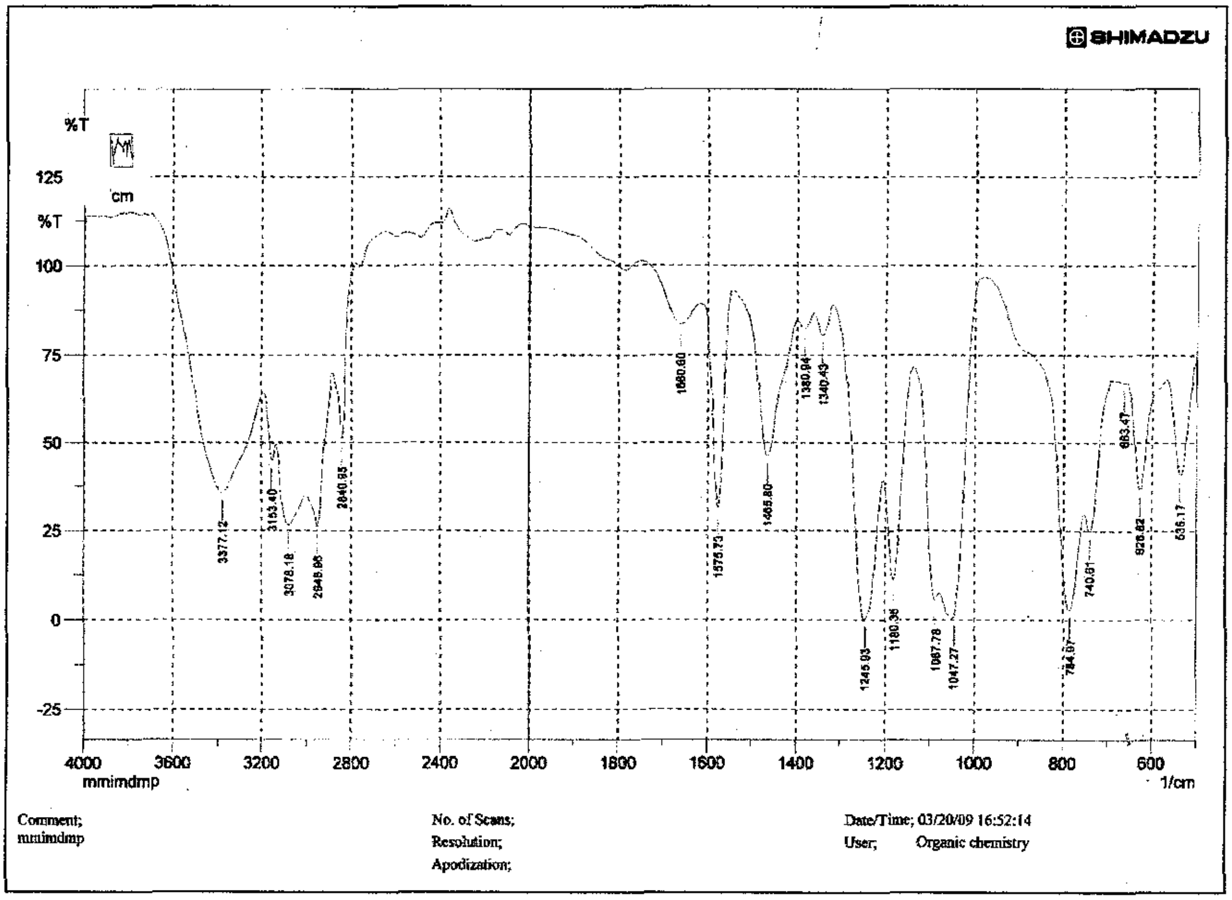


Figure 4.4: FTIR Analysis of [MMIM][DMP]

The types of functional group of a sample can be identified by referring to the valley of the wavenumber occurred. The FTIR correlation table attached in *Appendix C* was used to determine the types of functional group based on wavenumber. By referring to the structure of [MMIM][DMP] IL in *Figure 3.1* in Chapter 3 and *Figure 4.4* above, the IL contains the functional group of alcohols (O-H bond with wavenumber range between 3650–3300cm^{-1}), alkanes (wavenumber range between 2950–2800cm^{-1}), amines with C-N stretch (wavenumber range between 1200–1025cm^{-1}) and phosphine oxides (wavenumber range between 1210–1140cm^{-1}). Therefore, the analysis illustrate that the [MMIM][DMP] is verified.

4.2.4 NMR Analysis

The result of NMR analysis shown in *Figure 4.5* below.

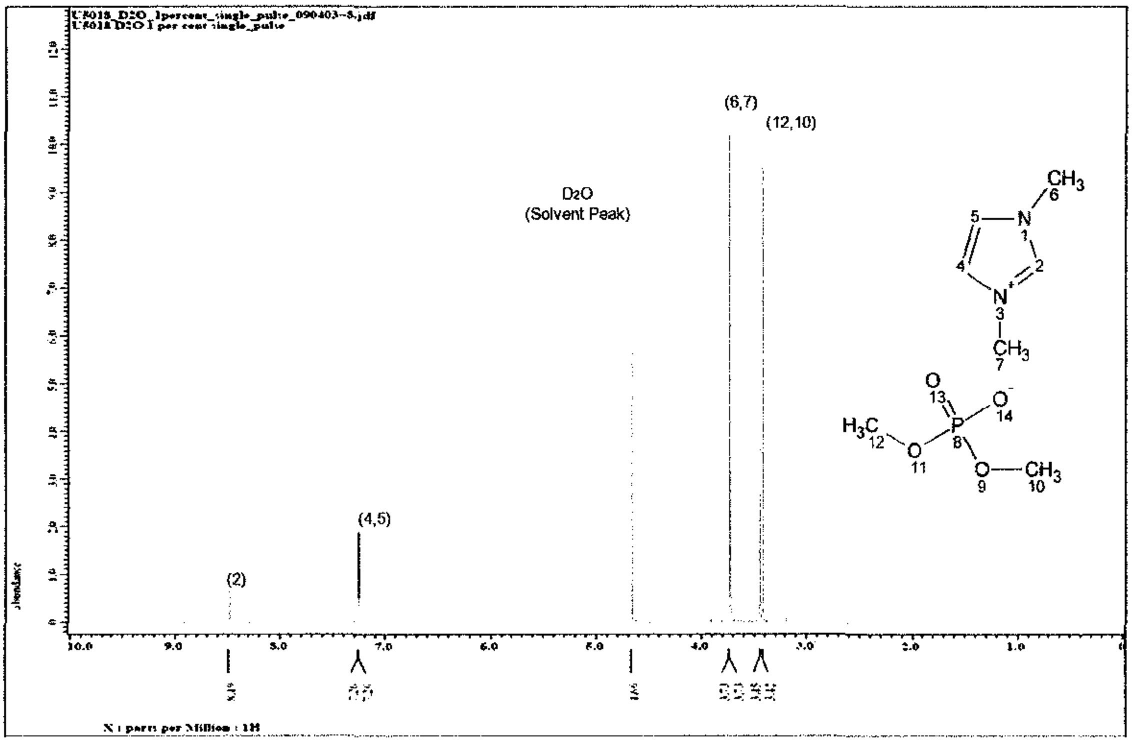


Figure 4.5: NMR Analysis of [MMIM][DMP]

The general structure of [MMIM][DMP] IL as shown in *Figure 3.1* have been identified by NMR. The resulting data are as follows.

Table 4.2: Result for NMR analysis

H	δ (Shift)
2	8.49
4,5	7.26
6,7	3.73
12	3.45
10	3.42

4.3 Extraction of sulfur by [MMIM][DMP]

The results from the extraction performance of [MMIM][DMP] towards thiophene and BT in dodecane shown in *Table 4.3.*

Table 4.3: Percentage of Thiophene and BT removal by [MMIM][DMP]

Thiophene Content, % (ppm)			**% removal**	**BT Content, % (ppm)**			**% removal**
Dodecane + Thiophene		**[MMIM] [DMP]**		**Dodecane + DBT**		**[MMIM] [DMP]**	
Before	**After, S_{MO}**	**S_{IL}**		**Before**	**After, S_{MO}**	**S_{IL}**	
0.237 (2370)	0.097 (970)	0.144	**59.07**	1.883 (18830)	0.978 (9780)	0.219	**48.06**
3.829 (38290)	1.749 (17490)	0.210	**54.32**	3.415 (34150)	1.881 (18810)	0.174	**44.92**
4.148 (41480)	1806 (18060)	0.141	**56.46**	4.661 (46610)	2.822 (28220)	0.204	**39.46**

Based on *Table 4.3*, the [MMIM][DMP] shows that the percentage removal of BT from dodecane was slightly lower compared to thiophene. This is different from what have been pointed out by Yie Nie et al. (2008) where the removal efficiency always follow the order BT > Thiophene. From the experiment, the thiophene content in dodecane after the mixing process shows a lower value compared to the calculated one because of the thiophene is volatile therefore affecting the original thiophene content prepared in dodecane. The percentage of sulfur removal also can be optimized by repeating the extraction process several times.

From the result obtained, the K_N value can be calculated by using the equation

$$K_N = \frac{S_{IL}\,(ppm)}{S_{MO}\,(ppm)}$$

Where:

S_{IL} = Sulfur content in [MMIM][DMP] in ppm after the extraction process

S_{MO} = Sulfur content in dodecane in ppm after the extraction process

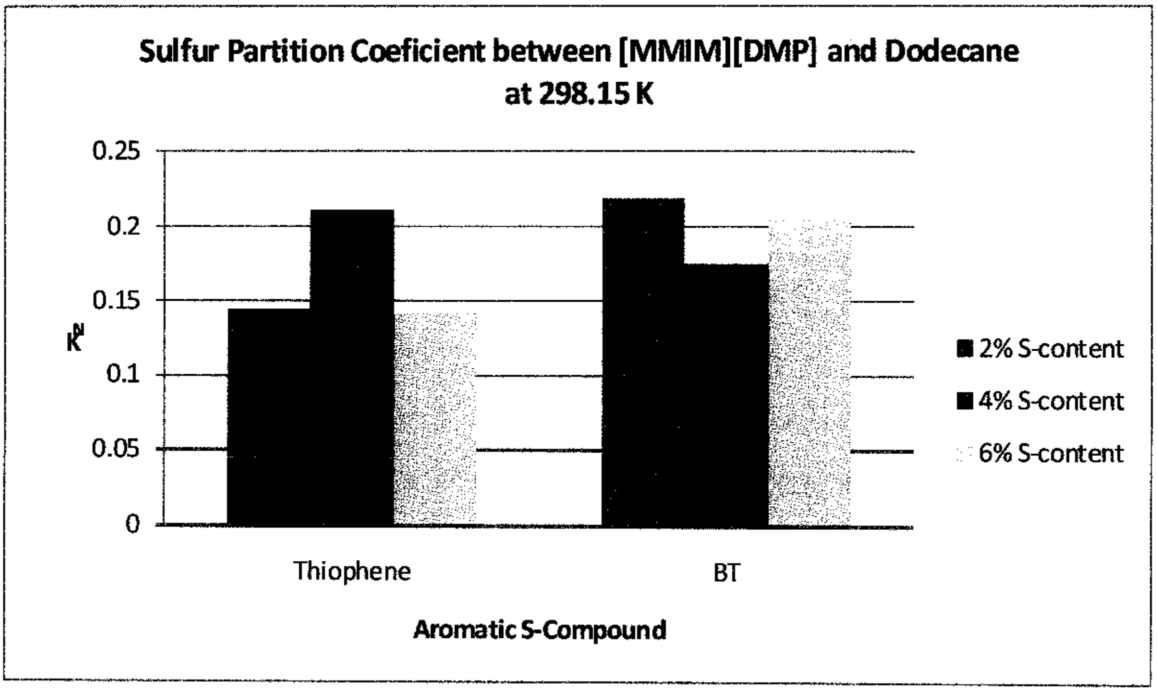


Figure 4.6: K_N values for different sulphur concentration in model oil

As shown in *Figure 4.6*, the sulphur partition coefficient, K_N for [MMIM][DMP] ionic liquid follows the order BT > Thiophene except for 4% S-content which is opposite to hydrodesulfurization, HDS process (C.S. Song, 2003, p.211-263). The extraction of BT and thiophene by [MMIM][DMP] is likely relevant 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). This property shows how thiophene and BT can be extracted efficiently by the [MMIM][DMP] ionic liquid although they are difficult to be removed by HDS process. Therefore, the extractive desulfurization, EDS process by using [MMIM][DMP] can be a complementary process to HDS process.

CHAPTER 5

CONCLUSION

Ionic liquid [MMIM][DMP] was successfully prepared by using one-pot method by adding the equimolar of 1-methylimidazole and trimethyl phosphate. This method can reduce the synthesis cost and also produced high yield and ease of purification. [MMIM][DMP] shows remarkable selectivity for the extraction of aromatic S-compound thiophene and BT from dodecane. The result shows the percentage of aromatic S-compound removal can be as high as 59.07% for thiophene and 48.06% for BT. The K_N values for this experiment are 0.210 for thiophene and 0.219 for BT respectively. Considering the relatively high sulfur removal ability, lower oil solubility, cheaper cost and one-pot synthesis, [MMIM][DMP] seems promising for commercial application in the future.

REFERENCES

[1] Yi Nie, Chunxi Li, Hong Meng, Zihao Wang. 2008, "N,N-dialkylimidazolium dialkylphosphate ionic liquids: Their extractive performance for thiophene series compounds from fuel oils versus the length of alkyl group", *Fuel Processing Technology.*

[2] J.M. Campos-Martin, M.C. Capel-Sanchez, J.L.G. Fierro. 2004, *Green Chemistry* **6**: 557–562.

[3] A. Bösmann, L. Datsevich, A. Jess, A. Lauter, C. Schmitz, P. Wasserscheid. 2001, *Chemical Communication* **23**: 2494–2495.

[4] J. Eßer, P. Wasserscheid, A. Jess, 2004, *Green Chemistry* **7**: 316–322.

[5] Martyn J. Earle and Kenneth R. Seddon, 2000, *Pure Appl. Chem,* **72**: 1391-1398.

[6] Sarah Houlton, 2004, "Ionic liquids for greener processes", *Manufacturing Chemist.*

[7] S. Zhang, Q. Zhang, Z.C. Zhang, 2004, *Indusrtrial & Engineering Chemistry Research* **43**: 614–622.

[8] A. Jess, J. Eßer, "Deep Desulfurization of Oil Refinery Streams by Extraction with Ionic Liquids", University Bayreuth, Bayreuth, Germany

[9] Xiaochuan Jiang, Yi Nie, Chunxi Li, Zihao Wang. 2008. "Imidazolium-based alkylphosphate ionic liquids – A potential solvent for extractive desulfurization of fuel", *Fuel* **87**: 79–84

[10] Silverstein, R. M., Bassler, G. C., & Morrill, T. C. 1991, *Spectrometric Identification of Organic Compounds.* Wiley.

[11] Service, W. C., *Fourier Transform Infrared Spectroscopy*, 2008, Retrieved from http://www.wcaslab.com/TECH/tech2.htm

[12] J. Jacquemin, P. Husson, A. A. H. Padua & V. Majer, 2005, "Density and viscosity of several pure and water-saturated ionic liquids", *Green Chemistry* **8**: 172-180.

[13] Thompson, M., CHNS Elemental Analyzers, (2008, April), *AMC Technical Briefs* . RSC.

[14] Roland Schmidt, 2008, "[BMIM]$AlCl_4$ Ionic Liquid for Deep Desulfurization of Real Fuels", *Energy & Fuels* **22**: 1774-1778

[15] Jurgen Gmehling, "Ionic Liquids in Separation Processes"

[16] Sophie Legeai, Sebastien Diliberto, Nicolas Stein, Clotilde Boulanger, Julien Estager, Nicolas Papaiconomou, Micheline Draye, 2008, "Room-temperature ionic liquid for lanthanum electrodeposition", *Electrochemistry Communications* **10**: 1661–1664

[17] University of Colorado, Boulder, Chemistry and Biochemistry Department, 2003. <http://orgchem.colorado.edu/hndbksupport/nmrtheory/NMRtutorial.html>

[18] Table of IR Absorption Page. 3 May 2009 <http://www.chemistry.ccsu.edu/glagovich/teaching/316/ir/table.html>

APPENDICES

APPENDIX A

A.1 Preparation of Ionic Liquid

1. Distillation of 1-methylimidazole

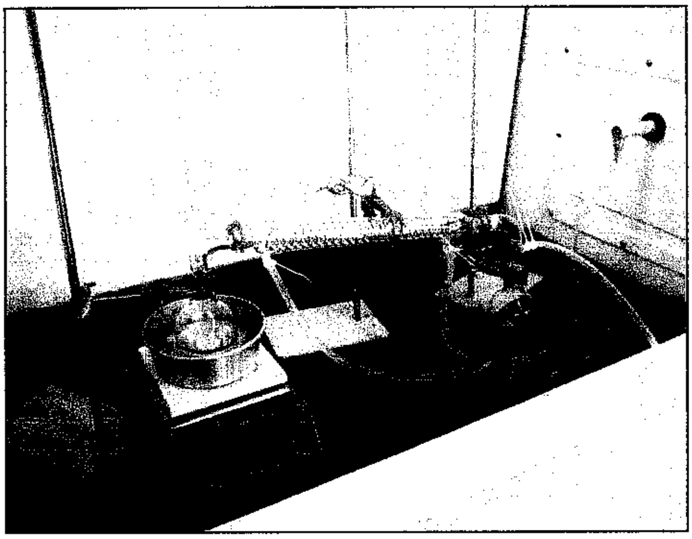


Figure A1: Set up of distillation apparatus

2. Preparation of MMIM DMP ionic liquid (Reflux)

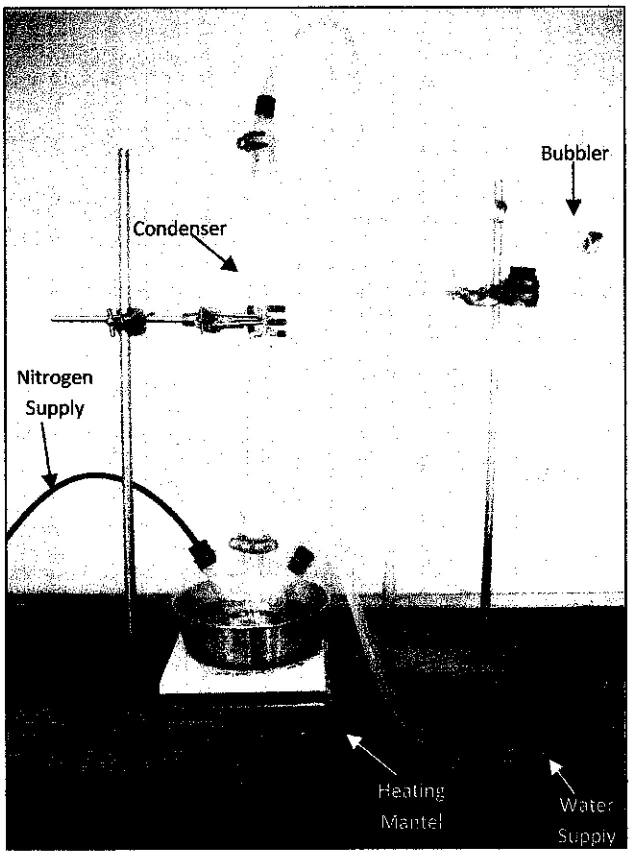


Figure A2: Reflux Set

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

Figure A3: Two layer of diethyl ether and IL

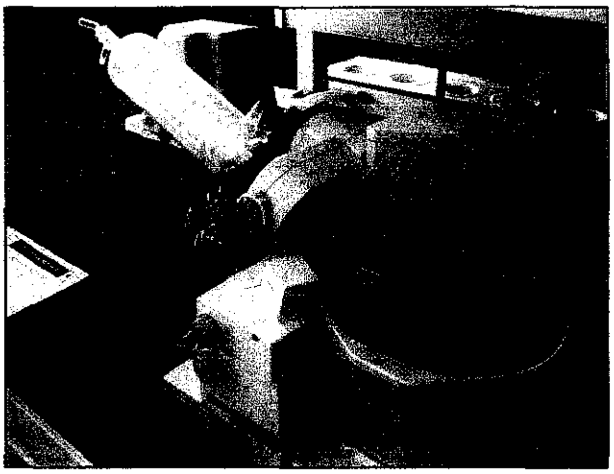


Figure A4: Rotary evaporator set

4. Drying of ionic liquid

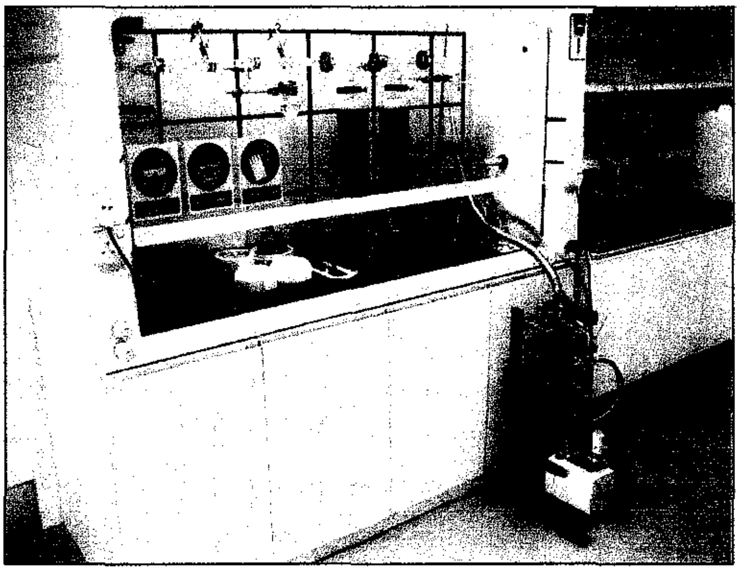


Figure A5: Vacuum Line

A.2 Desulfurization Process

1. Mixing ionic liquid and crude oil model

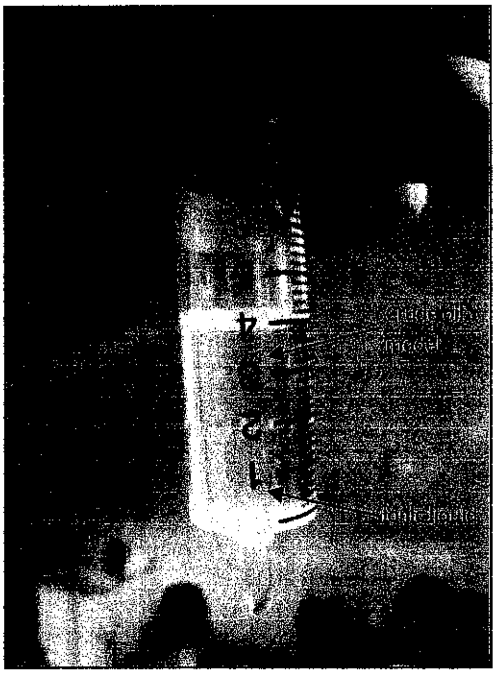


Figure A6: Mixed IL and crude oil model with 1:1 ratio

2. Vortex Mixer

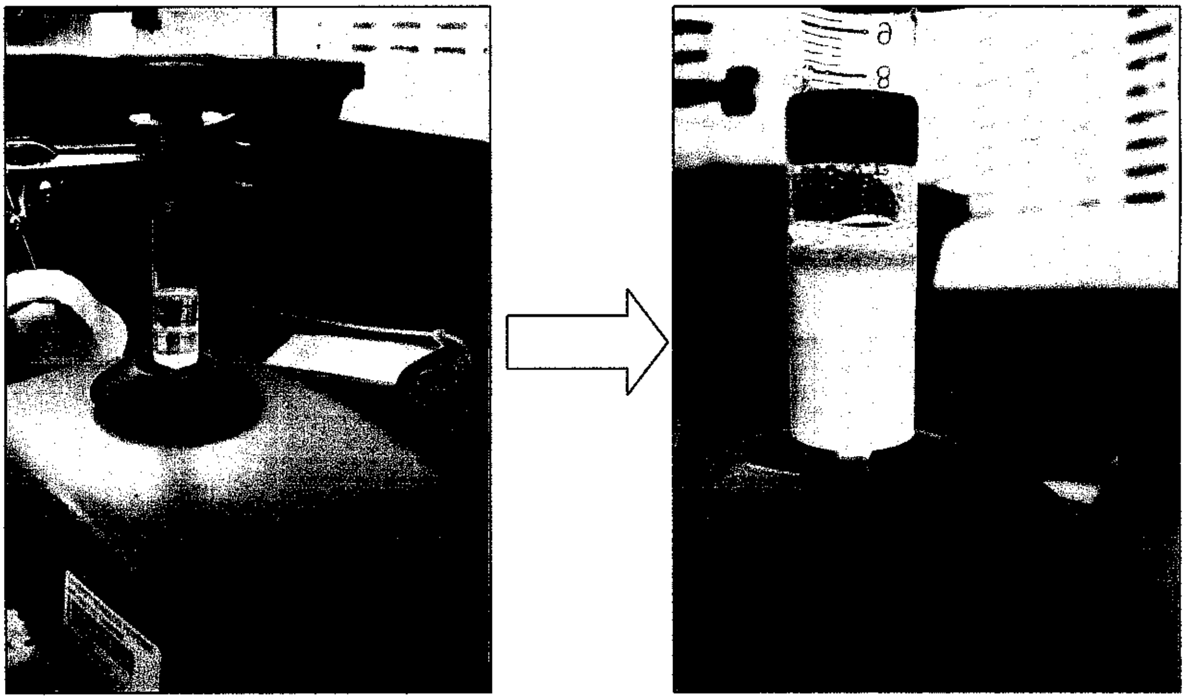


Figure A7: Mixing the mixture for 1 minute

3. Centrifuge separation

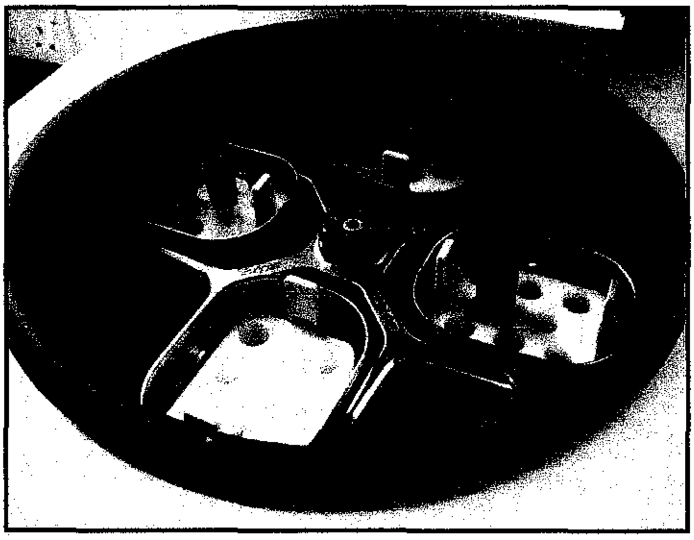


Figure A8: Centrifuge used to settle down the mixture

A.3 Characterization of [MMIM][DMP]

1. FTIR

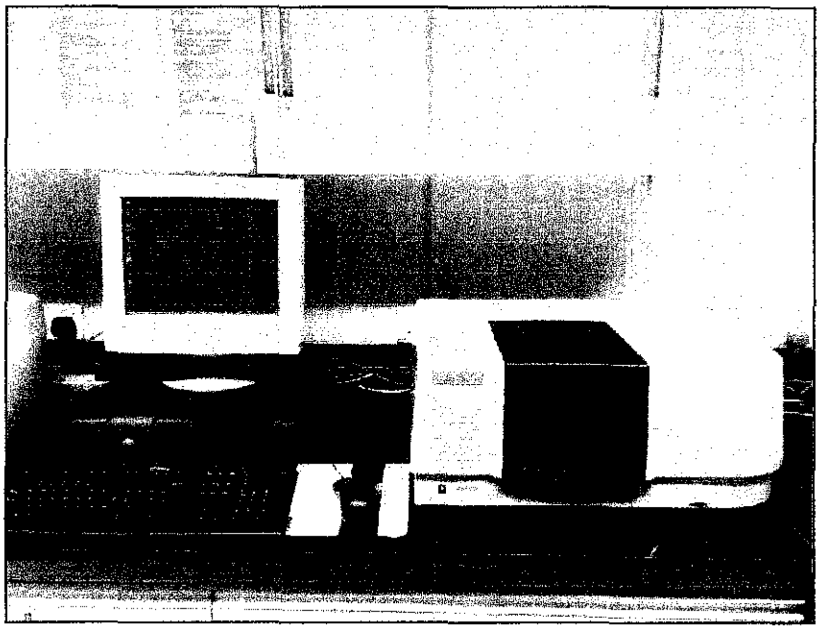


Figure A9: FTIR 8400S Shimadzu

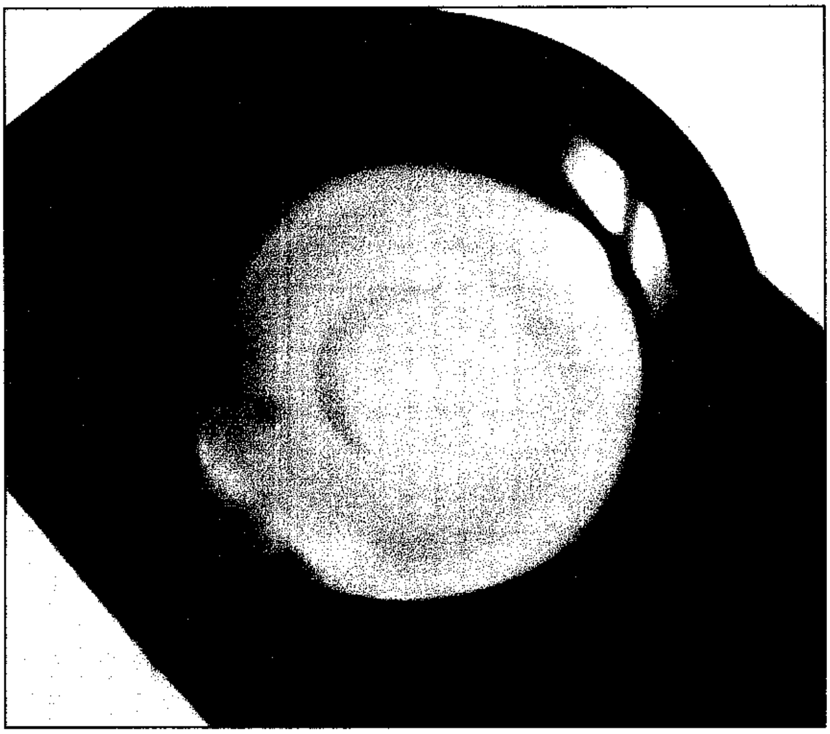


Figure A10: Sample preparation for FTIR analysis

2. Density Meter

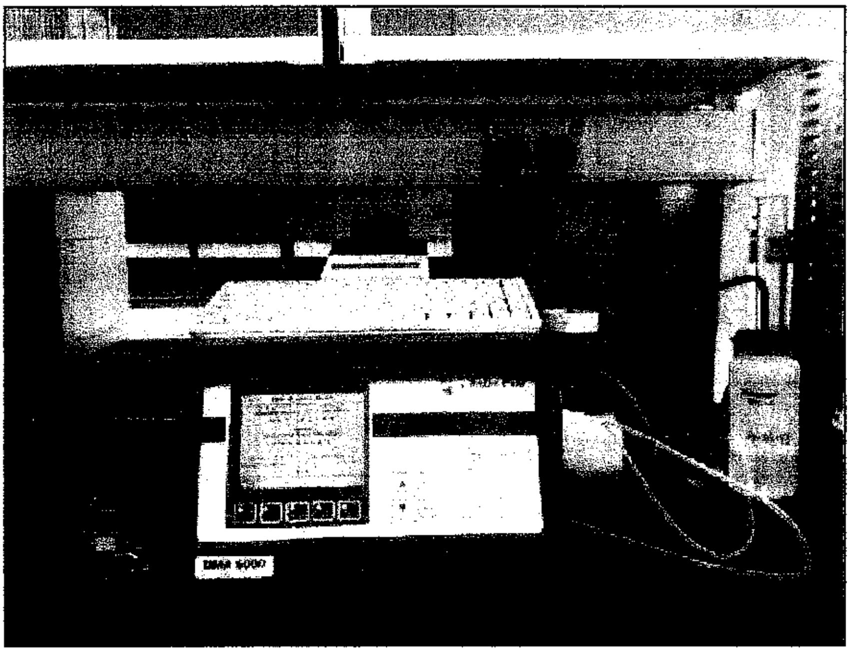


Figure A11: Anton Paar, DMA 5000 Density Meter

3. Water content determination

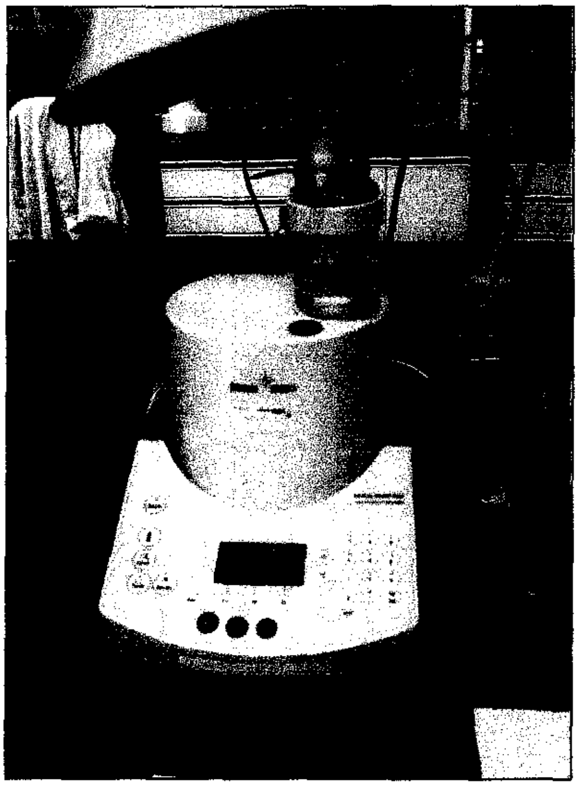


Figure A12: Karl Fisher Coulometer (Mettler Toledo DL39)

A.4 Extraction Performance Analysis

1. XRF

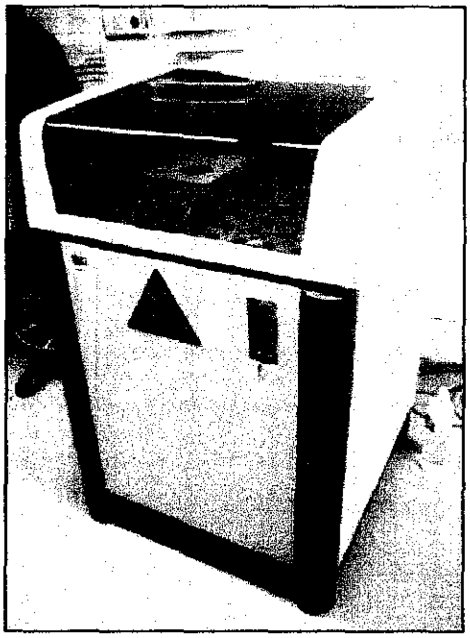


Figure A13: XRF Spectrometer

APPENDIX B

B.1 Calculation for corresponding volume mixed between 1-methylimidazole and trimethylphosphate

$$Mass = Mole \times Molecular\ Weight \qquad Density = \frac{Mass}{Volume}$$

$$m = n \times MW \qquad \rho = \frac{m}{V}$$

For 1-methylimidazole:

$$m = 0.5\ mol \times 82.11 \frac{g}{mol}$$

$$= 41.05\ g$$

$$V = \frac{41.05\ g}{1.03 g/cm^3}$$

$$= 39.85\ cm^3$$

For Trimethyl phosphate

$$m = 0.5\ mol \times 140.08 \frac{g}{mol}$$

$$= 70.04\ g$$

$$V = \frac{70.04\ g}{1.21\ g/cm^3}$$

$$= 57.88\ cm^3$$

B.2 Calculation for preparation of crude oil model

$For\ Thiophene\ (99.5\%\ purity)$

$Molecular\ formula = C_4H_4S$

$Molecular\ mass = 84.14\ g/mol$

$Molecular\ mass\ of\ sulfur = 32.06\ g/mol$

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

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

$$= 38.1\%$$

$38.1\%\ sulfur \rightarrow 99.5\%\ thiophene$

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

$= 5.22\%\ BT$

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

$For\ Benzothiophene, BT\ (97\%\ purity)$

$Molecular\ formula = C_8H_6S$

$Molecular\ mass = 134.2\ g/mol$

$Molecular\ mass\ of\ sulfur = 32.06\ g/mol$

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

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

$$= 23.17\%$$

$23.17\%\ sulfur \rightarrow 97\%\ BT$

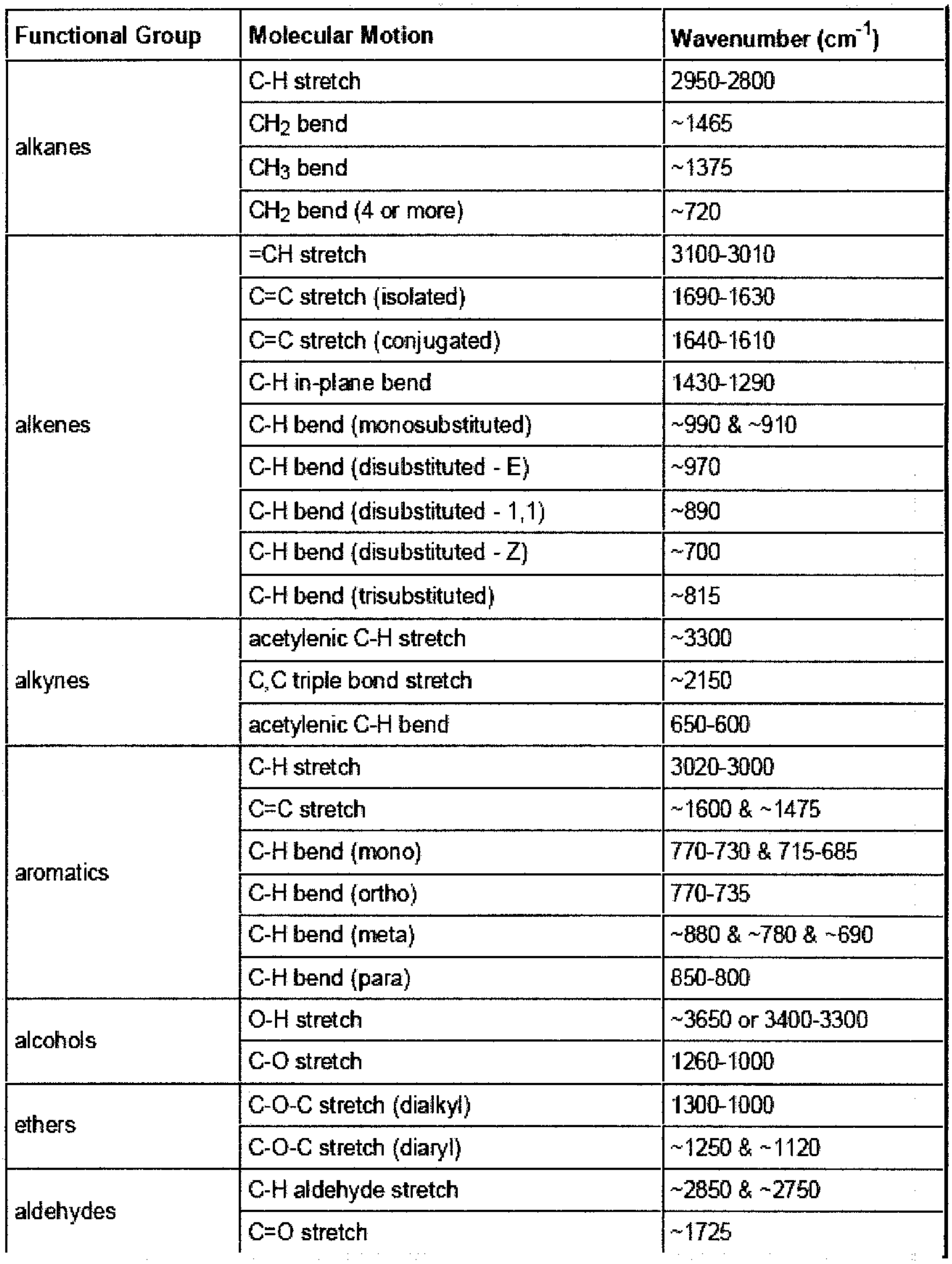
$\therefore 2\%\ sulfur = \frac{2\times 97}{23.17}$

$= 8.37\%\ BT$

$\therefore 100g\ crude\ oil\ model\ requires\ 91.63g\ dodecane\ and\ 8.37g\ BT$

APPENDIX C

FTIR Correlation Table



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^o)	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 & ~11750
	S-O stretch	1000-750
phosphines	P-H stretch	2320-2270
	PH bend	1090-810
phosphine oxides	P=O	1210-1140