REMOVAL OF BENZOTHIOPHENE FROM DODECANE CRUDE OIL MODEL USING BUTYLMETHYLIMIDAZOLIUM DIBUTYLPHOSPHATE IONIC LIQUID

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By

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Dissertation submitted in partial fulfillment of
the requirement for the
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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.

ANIS NURDHIANI BINTI ROSDI

ABSTRACT

Ionic liquids are well-known as green solvent. Besides that, it is also have many special criterion that inspired researcher to do deep research on the ability of ionic liquids in extracting sulfur compounds from crude oil. Instead, problems occur at plant due to the lack performance of current technology in extracting aromatic sulfur compounds which is hydrodesulfurization (HDS) make all the effort become more concentrated. Hence, the aim of this project is to find the best method of extraction by using ionic liquids. After going through related literatures, methods and procedures of experiment were proposed. To make the study more interesting, this research started with synthesis of ionic liquid which is [BMIM][DBP]. It is followed by the characterization of ionic liquids in order to confirm that ionic liquid has been synthesized successfully. An alternative to crude oil, dodecane is used as model oil. After synthesis, extraction and oxidation of Benzothiophene (BT) were conducted. The result shows that, [BMIM][DBP] can extract BT from dodecane model oil from 6% up to 54%. As a conclusion, the ionic liquid showed the successful in extracting sulfur compounds from crude oil model.

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CHAPTER 1

INTRODUCTION

The world is looking for alternatives of sulfur-compounds removal in crude oil. Instead of using current Hydrodesulfurization (HDS) process there are several methods that have been introduced. These methods are based on adsorption, extraction and oxidation. However among them, extraction is most popular method. Extractive desulfurization (EDS) is a well established technology. It can be carried out in ambient temperature and pressure without present of hydrogen.

1.1 BACKGROUND OF STUDY

There are many molecular substances in crude oil such as asphaltenes, resins, aromatic hydrocarbons and also alkenes. Asphaltenes consist primarily of carbon, hydrogen, nitrogen, oxygen, and sulfur, as well as trace amounts of vanadium and nickel.

Compare to all of the substances, sulfur compounds are most concern in refinery. The composition of the sulfur in crude oil varies accordingly to the source of the crude. Some crude have composition of sulfur between 0.5 – 6%. From the other source, the sulfur composition is about 0.06 – 8%. Regardless the variations of the composition of crude oils from time to time and the places where the crude oils are taken the generalization of the crude oil composition have been made (John J. McKetta, 1992).

Ionic liquids are finding as new green chemical in academic as well as in chemical industries. Green solvent helped a lot in reducing the use of hazardous and polluting organic solvents. Although the term ionic liquid is already use a long time ago, but the significant of ionic liquids in synthesis and catalysis as solvent recently becomes famous (S. Keskin et al, 2007).

Due to the property that ionic liquids can dissolve many different organic, inorganic and organometallic materials, ionic liquids have been chosen as one of solvent to extract sulfur from crude oil. However, there are different properties of ionic liquids that accordingly depend on anion and cation of each ionic liquid.

1.2 PROBLEM STATEMENT

Hydrodesulfurization (HDS) is a well known method in industry to remove sulfur from natural gas and also from refined petroleum such as kerosene, jet fuel, gasoline or petrol, diesel fuel and fuel oils. The main purpose of doing HDS is to remove sulfur compounds in crude oils. However only some sulfur is reduced to naphtenes and only some aromatics sulfur are saturated. Besides, HDS method required high temperature and high pressure of hydrogen gas. In addition, HDS technology also confronted will the great challenge since the available catalyst is less effective for the hydrogenation of benzothiophene (BT), dibenzothiophene (DBT) and their alkyl derivatives. In addition, this process it's intensive and hydrogen demand.

Therefore, some technologies have been introduced such as adsorption, extraction and oxidation. Among these alternatives, extraction desulfurization (EDS) more attractive as of EDS is a well-establish process that can be carried out at or around ambient temperature and pressure without need for hydrogen and catalysts. More importantly, some BT and DBT series S-components can be extracted quite efficiently. Thus, the EDS process can at least be a complementary technology for the HDS process.

One of the new technologies is using ionic liquid as extractant. There are many advantages in using this method. Besides the process conditions are using ambient pressure and temperature, there is no hydrogen needed. Examples of two types of ionic liquids that can be used like [BMIM][$OcSO_4$] and [EMIM][$EtSO_4$] are halogen free and available from relatively cheap starting materials. Hence, extraction of sulfur using ionic liquids could be an alternative process to replace the common HDS.

If sulfur is not removed, some problems may occur in refinery processing plant. That is because Hydrogen Sulfide will lead to the corrosion and leaking of the pipeline and other equipments. Besides, sulfur compounds produced sulfur dioxide (SO_2) from the burning of fuel by automotive vehicle as well as from gas or oil burning from power plant. Thus, it will give effect to the environment if there are still exist in diesel or gasoline. Even in the extremely low in concentrations, sulfur compounds will also give poisons to the noble metal catalysts in the catalytic reforming units that are subsequently used to upgrade the octane rating of the naphtha streams. Hence, the sulfur compounds have to be removed. Types of ionic liquids much be chosen to increase the efficiency of the sulfur removal and also to avoid any side effect. Selection of the ionic liquids is considering the physical, chemical properties and efficiency of those ionic liquids in removing sulfur compounds.

1.3 OBJECTIVES OF STUDY

The main objective for this project is to determine the effectiveness of butylmetylimidazolium dibutylphosphate [BMIM][DBP] ionic liquid for extraction and oxidative extraction of benzothiophene from different concentration of sulfur in dodecane model oil.

1.4 SCOPE OF STUDY

This project is in the form of laboratory experiment. This project consists of four phases:

1. Preparation and characterization of [BMIM][DBP] ionic liquid.
2. Preparation of model oil.
3. Extraction process.
4. Oxidation and extraction process.

The ionic liquid used in this project is butylmethylimidazolium dibutylphosphate [BMIM][DBP]. The ionic liquid is prepared using synthesis method which needs the reaction of methylimidazolium and tributylphosphate. The model oils are prepared using dodecane and different amount of sulfur which is benzothiophene (BT). These model oils are 2wt% of BT in dodecane, 4wt% of BT in dodecane and 6wt% of BT in dodecane. After oxidation and extraction process the investigation on the efficiency of [BMIM][DBP] in extract BT in dodecane has been done by using XRF and CHNS.

CHAPTER 2

LITERATURE REVIEW

Review for the study has taken abundantly from journals and internet. Basically, the spot to be highlighted for the study consists of general knowledge of ionic liquids, types and characteristics of ionic liquids, types of sulfur compounds involved in extraction and review of crude oil model.

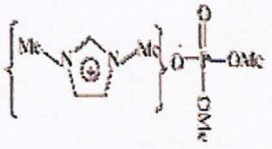
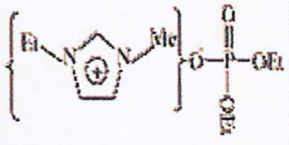
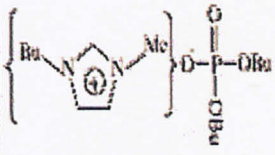
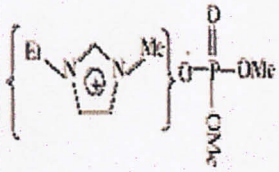
2.1 IONIC LIQUIDS

The term Ionic Liquids is commonly used for salts that have melting point below 100°C. In general, at room temperature, ionic liquid is in fluid form. These salts are also called room-temperature Ionic Liquids (RTILs). It consists of ionic species which combination of at least two components. These components are anion and cation.

Ionic liquids have been accepted as green solvent and designer solvent (Seda Keskin et al, 2007). Ionic liquids are known as green solvent because many of these compounds have negligible vapour pressure. Instead the vapour pressure of ionic liquids is not measurable. Hence, it can be release no volatile organic compounds. Besides, it is not explosive and can be repeatedly used and recycled.

The label of design solvent is given because ionic liquids properties can be change based on the size of its cation and anion. Its component can be adjusted accordingly due to the requirements of a particular process. According to Martyn J. Earle et al. (2000) slight change in ILs component will change the melting point, viscosity, density and its hydrophobicity. The miscibility of these ILs in water depends on the change of the structure. For example, 1-alkyl-3-methylimidazolium tetrafluoroborate salts are miscible in water at 25°C, where the alkyl chain length is less than six atoms but at or above six carbon atoms, they form a separate phase when added to water. However, this type of ionic liquids cannot be applied in this research, since most of the reported ILs say that the imidazolium cation with fluorous anions such as tetrafluoroborate and hexafluorophosphate will harm the environment (Dishun Zhao et al, 2008).

Table 2.1: Types of imidazolium based phosphoric ionic liquids.

Types	Short Name	Structure
N-Methyl imidazolium dimethylphosphate	[MMIM][DMP]	
N-Methyl imidazolium diethylphosphate	[EMIM][DEP]	
N-Methyl imidazolium dibutylphosphate	[BMIM][DBP]	
N-Methylimidazolium N-ethyl N-methylphosphate	[EMIM][DMP]	

Types of ionic liquids to be carried out in the experiment are Imidazolium-Based Phosphoric ionic liquids. There are many types of imidazolium based phosphoric ionic liquids. **Table 2.1** shows several types of imidazolium based phosphoric ionic liquid.

Out of these four types, the first three have been taken and comparison has been made. Refer to Yi nie et al. (2006) the desulfurization ability followed the order of [BMIM][DBP] > [EMIM][DEP] > [MMIM][DMP]. It is confirm by another journal because according to Xiaochan et al. (2007) the extraction ability of imidazolium is dominated by the structure of cation. It is prove by comparing all of these three, [BMIM][DBP] is having biggest size of cation. Instead of having high desulfurization ability, [BMIM][DBP] also perform good stability, fluidity, nontoxicity and nonsentivity to moisture and air. Hence, [BMIM][DBP] is selected for this project.

2.1.1 Sulfur partition coefficient

Sulfur partition coefficient (K_N) is used to determine the extraction ability of ionic liquids. It is defined as the ratio of S-concentration in ionic liquids to S-concentration in model oil (Xiaochua Jiang et al. 2008). The higher K_N value is indicating the higher performance of ionic liquids in extracting sulfur compounds.

2.1.2 Influence of water in ionic liquids on sulfur partition coefficient

In present of water, the performance of ionic liquids will be lowered. It is specify by the value of K_N. According to Xiaochua Jiang et al. 2008 even 1% of water content in ionic liquids can give rise to about 17 to 20% in lowering the extraction coefficient ability of ionic liquids. Therefore, this matter is taken seriously during synthesis of ionic liquids.

After the synthesis, ionic liquids have undergone drying process to make sure there is no or less water content in ionic liquids. Then, the characterization has been made to measure the amount of water left in ionic liquids.

2.1.3 Mutual solubility of ionic liquids in model oil.

Mutual solubility of ionic liquids in model oil also play important role to determine the successful of extraction process. Unnoticeable solubility of imidazolium based ionic liquids in model oil will lead to NO_X pollution because ionic liquids will contaminate in model oil (Xiaochua Jiang et al. 2008). The suggestion method to avoid this situation happened is by using gravimetric method. This method approaches the weighing process of ionic liquids after and before model oil removed from ionic liquids using vaporization at high temperature and reduced pressure.

2.1.4 Regeneration of ionic liquids.

Ionic liquids can be regenerated. There are several approaches to regenerate the used ionic liquids. The proposed approaches to separate S-compounds from the ionic liquids are heating the ionic liquids at high temperatures to remove the volatile S-compounds, back extraction with low boiling hydrocarbons like pentane and hexane, reextraction with supercritical Carbon dioxide (CO_2) and also precipitating the S-components using water dilution process. However, each of the method has its own advantages and disadvantages. First method is only sufficient for the low boiling point of S-compounds like thiophene. It is also less efficient for the long chain alkyl substituted benzothiophene (BT) and dibenzothiophenes (DBT) because their boiling temperature may disrupt the stable range of ionic liquids. Second method commonly suffers from

lack of effective solvent. The third method is not applicable since it requires high energy expenses (Xiaochuan Jiang et al, 2008).

The last one is the best method, which is the regeneration of the ionic liquids using water. The solubility of the sulfur compounds such as BT and DBT in an ionic liquid aqueous solution can be determined by stepwise diluting the S-concentrated ionic liquid with water. According to Xiaochuan Jiang et al., the two phases are formed in successive water dilution process.

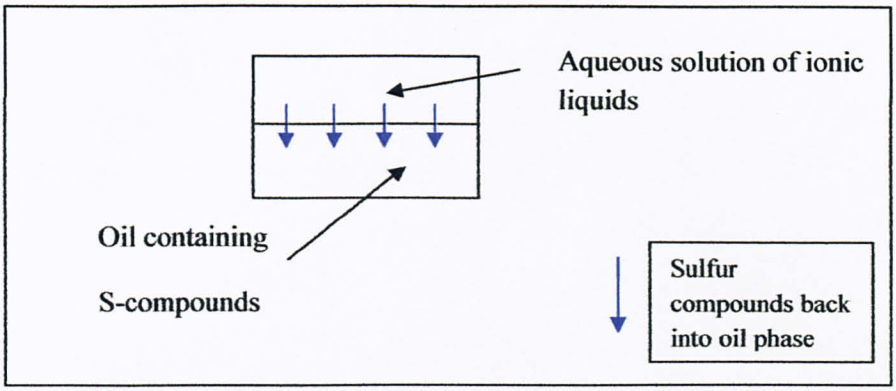


Figure 2.1: Successive water dilution processes

The figure above shows how the layers are formed after the successive water dilution processes. The S-compounds in the ionic liquids will be repelled back into oil phase. This is due to the strong hydrophilicity of ionic liquids and the strong hydrophobic of S-compounds.

However the water residue in the ionic liquids phase must be removed in order to avoid less effect of the ionic liquids to remove the S-compounds for the next process. In the end of the process the sulfur compounds will be precipitated and crystallized, after removed by centrifugation process.

2.1.3 Characterization of ionic liquids

Characterization of the synthesis ionic liquids have been made to determine the functional group of ionic liquids, density, water content, ion chromatography and determine whether that ionic liquids is organic or inorganic. The testing and equipment used is summaries in the table below:

Table 2.2: Characterization of ionic liquids

Testing	Equipment
To determine the functional group of ionic liquids.	Nuclear magnetic resonance (NMR)
To measure the density of ionic liquids.	Density meter
To measure the water content in ionic liquids.	Coulometer (Karl Fischer)
To determine whether the ionic liquids is organic or inorganic.	FTIR

2.2 CRUDE OIL

Crude oil is made up from hydrocarbon containing carbon and hydrogen. The simplest component in crude oil is methane which has only one carbon and four hydrogen atoms. The chains of hydrocarbon may vary till sixty carbons. The hydrocarbon that made up with below than four carbon atoms are in gaseous phase, while the hydrocarbon which has five up to 19 are normally liquids. Then, the carbon atoms above 20 are in solid form.

Table 2.3: Composition of the hydrocarbon in crude oil

Hydrocarbon	Average	Range
Paraffins	30%	15 to 60%
Naphthenes	49%	30 to 60%
Aromatics	15%	3 to 30%
Asphaltics	6%	remainder

These are four types of hydrocarbon compounds found in crude oil, which are paraffins, aromatics, naphthenes and asphaltics. Paraffins has found in crude oil are in straight chain of carbon atoms or branches of that chain, called isomer. Examples of paraffins are methane, butane and propane. Aromatics are made up by at least one single ring of benzene. Naphthenes appear in form of cyclic hydrocarbon. Besides these three structures, there are also other types of hydrocarbon known as alkenes, dienes and alkynes. Asphaltics has the lowest composition in the crude oil.

Table 2.4: Composition of the chemical elements in crude oil

Element	Percent Range
Carbon	83 to 87%
Hydrogen	10 to 14%
Nitrogen	0.1 to 2%
Oxygen	0.1 to 1.5%
Sulfur	0.5 to 6%
Metals	Less than 1000ppm

Besides, having various types of hydrocarbon, crude oil also contain others other types of chemical elements. **Table 2.4** shows the summaries of these chemical elements shown in the.

2.2.1 Crude oil model

Crude oil model is a significance of real crude oil. As the composition of real crude oil is very complex and having different amounts and various types of chemical elements, the crude oil model is introduced. However, the composition of the real crude oil is used as guideline in modelling crude oil. From **Table 2.4** above, it is shown the highest percentage of chemical element is carbon followed by hydrogen. Hence, crude oil model must have high composition of hydrogen and carbon.

As stated previously, this project conducted to determine the amount of sulfur extracted in the crude oil. So that, some amount of model oil must also be added with sulfur compounds. Theoretically, model oil that having high percentage of hydrocarbons are difficult to vaporize. This characteristic is very helpful in doing experiment. For example, dodecane is widely use as model oil. From journal, dodecane has those two criteria which having high composition of carbon atoms and it is difficult to vaporize. Other than that, n-Heptane and n-Hexadecane also can be used as model oil.

2.3 SULFUR COMPOUNDS

Sulfur compounds are non-hydrocarbon. There are three different types of sulfur compounds in crude oil, which are hydrogen sulphide (H_2S), elemental sulfur and aromatic sulfur compunds. Based on the journal produced by Xiaochan Jian et al. (2008) and Wang Jian-long et al. (2007), the most difficult sulfur compound to eliminate by using HDS method are aromatic sulfur compounds such as thiophenes and

dibenzothiophenes. This problem is due to the low efficiency of catalyst to eliminate sulfur compounds. It is because these sulfur compounds cannot achieve high surface contact due to structure of aromatic sulfur compounds that are sterically hindered. Elemental sulfur compounds which are aliphatic and alicyclic are easier to eliminate.

Failure to eliminate sulphur in crude oils will result in undesirable compounds such as sulphuric acid and sulfur dioxide when crude oil is combusted in the air.

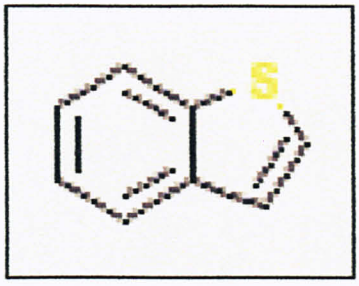


Figure 2.2: Structure of benzothiphene molecule

Three types of aromatic sulfur compounds have been compared. These are thiophene (T), benzothiophene (BT) and dibenzothiophene (DBT). From journal, Xiaochan Jian et al. (2008) the ability of aromatic sulfur compounds to be extracted by ionic liquids are followed as DBT > BT > T. From this finding, it is prove that ionic liquids have ability to extract the most complex sulfur compounds which is DBT. However, due insoluble of DBT in dodecane during DBT preparation, the types of aromatic sulfur compound is replaced with BT.

CHAPTER 3

METHODOLOGY

3.1 RESEARCH FLOW

The overall of the research methodology is based on the process flow below:

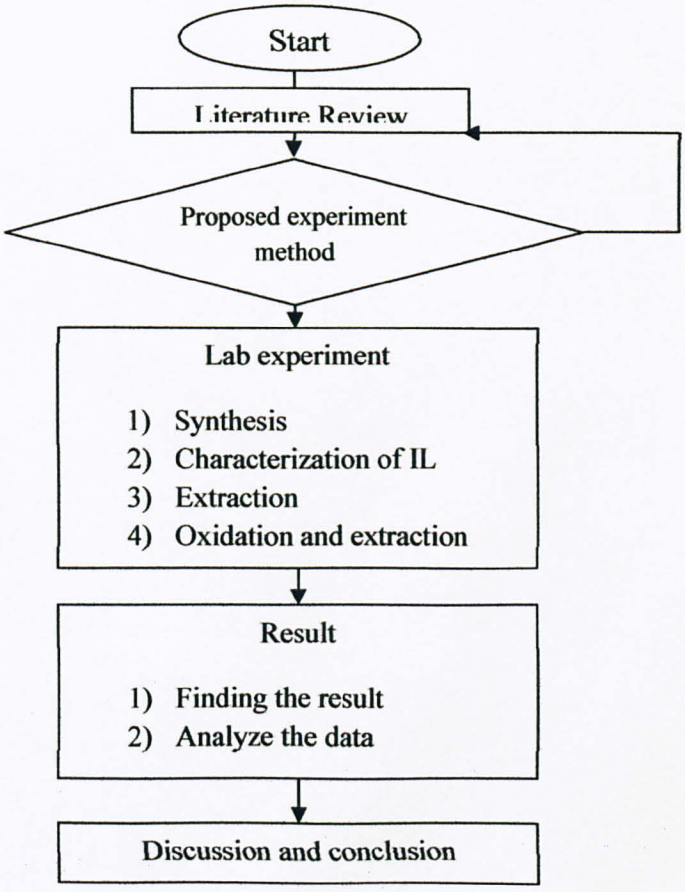


Figure 3.1: Research flow

3.2 PROJECT ACTIVITIES

Based on the guidance from literature review, the methods have been divided into four parts which are preparation of ionic liquids, preparation of model oils, extraction and oxidation process and characteristics of ionic liquids.

3.2.1 Preparation of butylmethylimidazolium dibutylphosphate [BMIM][DBP] ionic liquid

Figure 3.2: Rotary evaporation process to remove volatiles residue.

The procedure of preparation of [BMIM][DBP] ionic liquid started with the distillation of 100ml 1-metylimidazole. The purpose of purification is to purify the 1-metylimidazole. The process followed with the reflux.

The [BMIM][DBP] ionic liquid was prepared by mixing equimolar purified 1-methylimidazole (0.2 mol) and the tributylphosphate in a three neck flask fitted with a reflux condenser and drying tube. The temperature was maintained at the reaction temperature at 363K for 3 days days (yield of 98%) with nitrogen gas.

After three days, the [BMIM][DBP] ionic liquids was washed by diethyl ether. Equivolume of diethyl ether was added into [BMIM][DBP] ionic liquid producing two layers. The washing steps were repeated for another three times. The residual diethyl ether was removed using a rotary evaporator. The ionic liquid was rotavap under reduced pressure of about 1 kPa for 3 hours to remove all volatile residues. Finally, the ionic liquid is dried using the vacuum line with the liquid nitrogen.

3.2.2 Preparation of model oils

There were three types of model oils prepared. The amount of benzothiophene that added to the dodecane was first calculated. The samples of calculation have been put in Appendix B. Benzothiophene was weighted based on amount calculated. Then, bezothiophene was put in the 1 liter beaker and dodene was added till the amount of dodecane reach I liter. The steps repeated for 4% of benzothiophene in dodecane and 6% of benzothiophene in dodecane.

3.2.2 Oxidation process

10 ml model oil was mixed with 1 ml of hydrogen peroxide. Then the mixture was oxidized for 15 minute using vortex mixture. The pictures of the oxidization process have been included in Appendix C.

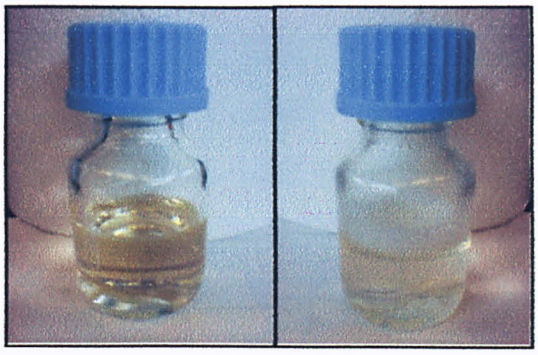


Figure 3.3: Comparison of model oil color before (left) and after (right) oxidation process.

3.2.3 Extraction process using model oil without oxidation.

Figure 3.4: Mixing process using vortex mixture.

Model oil and ionic liquids were added with 1:1 ratio with 2ml each. Then, the mixture was mixed using vortex mixture for 5 minute. The process followed with the separation of these two mixtures using centrifuge for 1 minute. After centrifuge, the mixture was separated. The above portion and the below portion were transferred to different vials for testing.

3.2.4 Extraction process using model oil with oxidation.

The steps in 3.2.3 were repeated by using the model oil that already oxidizes in oxidation process.

3.2.3 Characteristic of ionic liquids

Characterizations of ionic liquids have been done followed the procedure attached in Appendix E.

3.2.4 Process of determines sulfur in model oil and ionic liquids.

To determine the amount of sulfur extract by the ionic liquids and the amount of sulfur left in model oil, the sample were send to XRF and NMR. Two equipments used in order to compare the result.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 RESULT

The table below shows that the comparison of the results using XRF and CHNS and comparison between different method which is extraction and oxidative extraction.

Table 4.1: Result from the experiment.

Method of testing	XRF		CHNS
	Sulfur content (%)		
Method of experiment	Oxidative extraction	Extraction	
Result			
% of sulfur in IL from model oil 1	20.6	54.0	33.0
% of sulfur in IL from model oil 2	19.7	19.0	13.0
% of sulfur in IL from model oil 3	19.1	8.0	3.0

Note:

IL = Ionic Liquid: [BMIM][DBP]

Model oil:

Dodecane + Benzothiophene (BT)

1: 2% of BT in dodecane

2: 4% of BT in dodecane

3: 6% of BT in dodecane

The graph plotted based on the percentage of sulfur in ionic liquid versus total amount of sulfur in model oils.

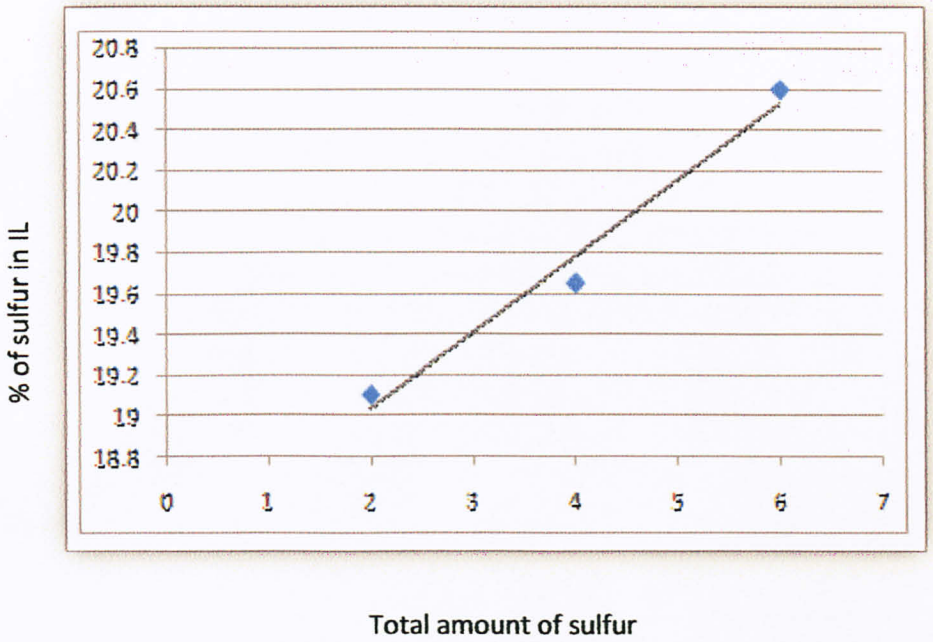


Figure 4.1: Graph oxidation and extraction result tested with XRF.

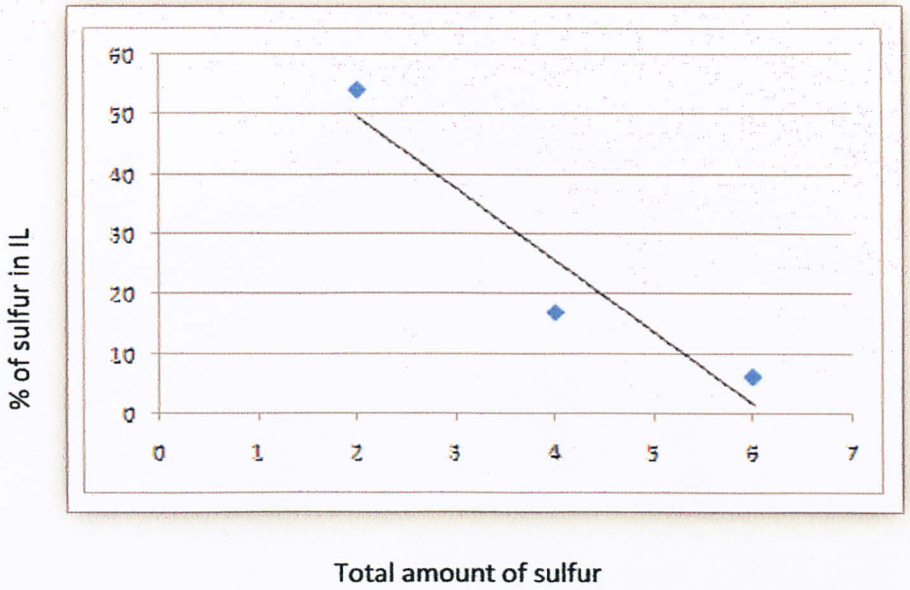


Figure 4.2: Graph of extraction result tested with XRF.

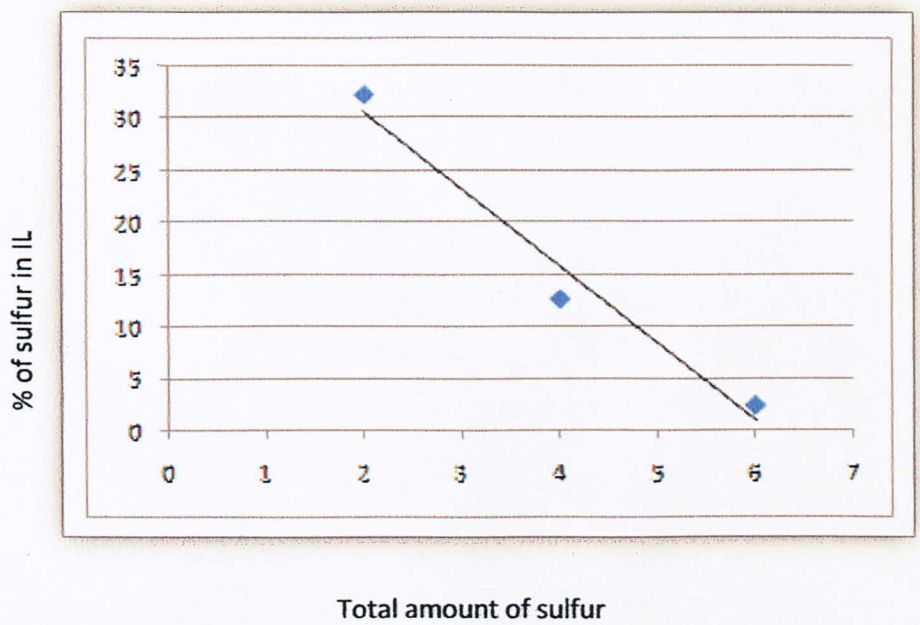


Figure 4.3: Graph of extraction result tested with CHNS.

4.2 DISCUSSION

From the results above it is shown that the percentage of sulfur extraction between extraction and oxidative extraction method is different with the extraction only. This is because by using oxidative extraction the probability of the high concentration of sulfur to extract is higher. Instead, by using the method that involved extraction only, the extraction of the less concentration of sulfur in dodecane is higher.

The result of same method which is extraction process shown there is no huge different either the testing is doing by the XRF or CHNS. Hence, the result can be obtaining as a good result. However if the comparison is make, the value of sulfur extracted referred to CHNS testing is slight lower than XRF testing. This is due to the human error during the preparation of sample for CHNS the testing.

4.3 CHARACTERIZATION OF IONIC LIQUIDS

The properties of the ionic liquid such as density and water content are analyzed using the density meter and coulometer. The result of the analysis of the density and water content is shown in **Table 4.4** and **Table 4.5:**

Table 4.4: 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 4.5: Water Content in [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 result in **table 4.4** and **table 4.5**, it is shown that the density of ionic liquids used which is [BMIM][DBP] is slightly higher than normal water. Besides, the water content is averaging about 3735ppm which concludes as about 0.3%-0.4%. The ionic liquid produced should not have high water content since it will affect the extraction performance.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Based on the result obtained from previous part, it can be proved that [BMIM][DBP] ionic liquids have ability to extract sulfur. It is shown from the result tested by two types of equipments which are CHNS and XRF. It is also prove that [BMIM][DBP] ionic liquids have been successful synthesized in this project because the criterion of ionic liquid is clearly shown.

As stated, the objective of this project is to determine the effectiveness of [BMIM][DBP] in extracting sulfur. [BMIM][DBP] has shown the ability in extracting large amount of sulfur compounds in crude oil. The average of sulfur removal for this method is 20%. Hence, this ionic liquid can be applied in order to extract large amount of sulfur. Besides, the repeated cycle of extraction also can be applied.

Besides, by comparing the methods used it can be concluded that the extraction of aromatic sulfur compounds can be more effective by using the oxidation followed with extraction method. There are large amount of sulfur compounds in crude oil. Hence, the oxidation and extraction method is the best because it can extract large amount of sulfur. Instead of using extraction only, there is still can extracted sulfur compounds but in a lesser concentration.

The characterization result also shows that the density of ionic liquids is slightly higher than normal water. That proved because compared to water, ionic liquids are more viscous. Besides, the ionic liquids prepared also have low water concentration. The high water content in ionic will reduce the performance of ionic liquids in extracting the sulfur compounds. Hence, the ionic liquids that have been prepared can be assumed as good because can obtained the water content less than 1%.

5.2 RECOMMENDATIONS

This project is very interesting project in which is shown that the ability of ionic liquids in extracting sulfur from crude oil model. However, in order to reduce human error and to add some other findings in this project. Therefore, a few recommendations should be applied such as:

- The crude oil can be used for the application part in order to determine the successful of this project.
- The testing must be doing by the instrument that encounter less human error as the CHNS need the preparation of sample first before the testing. It is consume human error.
- Do the analysis with FTIR on the chemical bonding in model oil after the oxidation process to find out the reason of oxidation followed by extraction method can extract the high percentage of aromatic sulfur compounds.

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APPENDICES

Appendix A: Preparation of [BMIM][DBP] ionic liquid

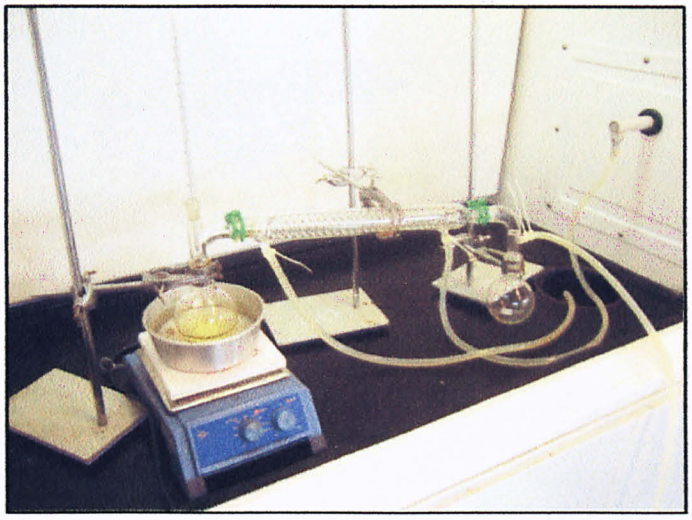

Figure A.1: Set up of distillation apparatus

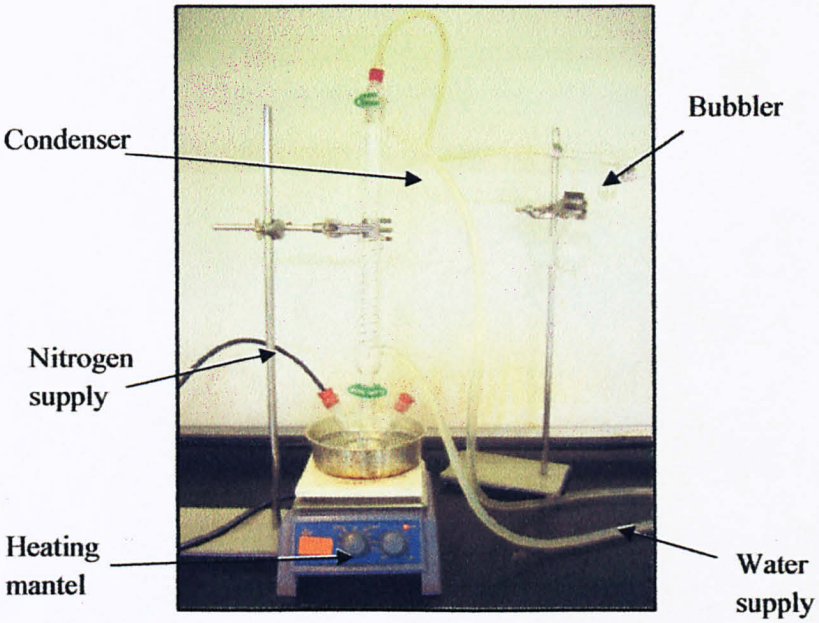

Figure A.2: Reflux set

Figure A.3: Rotary evaporation process to remove residual.

Figure A.4: Vacuum line used for drying process.

Appendix B: Model Oil Preparation

B.1 Calculation

Before doing the preparation of model oil, a few calculations have been done to get the amount of benzothiophene (BT) that will be used. The calculations are as followed:

Table B.1: Data of benzothiophene.

Chemicals	Benzothiophene
Molecular formula	C_8H_6S
Molecular weight	134.2 g mol^{-1}
Concentration	97%

Calculate sulfur in BT,

$$\% \text{ of S in BT} = \frac{32.06}{134.2}$$

$$= 23.17\%$$

There is contained 23.17% of sulfur in 97% of BT concentration.

For 2% of benzothiophene,

$$\frac{2 \times 97}{23.17} = 8.37\text{g of BT}$$

Figure B.1: 2% BT in dodecane

For 4% of benzothiophene,

$\frac{4 \times 97}{23.17}$ = 16.75g of BT

Figure B.2: 4% of BT in dodecane

For 6% of benzothiophene,

$\frac{6 \times 97}{23.17}$ = 25.12g of BT

Figure B.3: 6% of BT in dodecane

Appendix C: Oxidation process.

This example takes from model oil containing 6% benzothiophene in dodecane.

Figure C.1: Mixture of 10ml of model oil and 1ml of Hydrogen Peroxide before oxidation.

Figure C.2: Oxidation process.

Figure C.1: Mixture of 10ml of model oil and 1ml of Hydrogen Peroxide after oxidation

Appendix D: Extraction process.

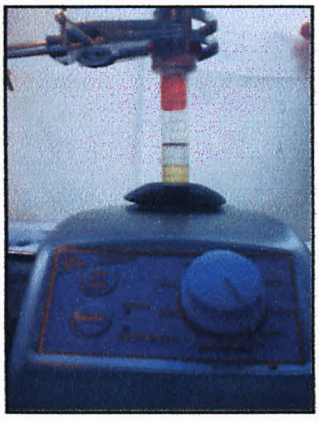

Figure D.1: Mixing of [BMIM][DBP] ionic liquid with model oil using vortex mixer.

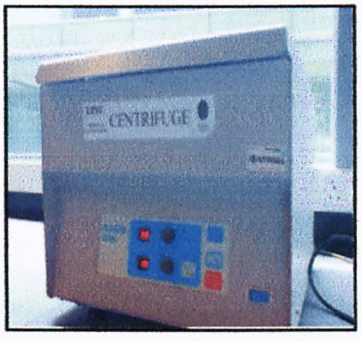

Figure D.2: Separation of [BMIM][DBP] ionic liquid and model oil using centrifuge.

Appendix E: Characterization of ionic liquids procedure

E.1 Standard operating procedure (SOP) of Karl Fisher.

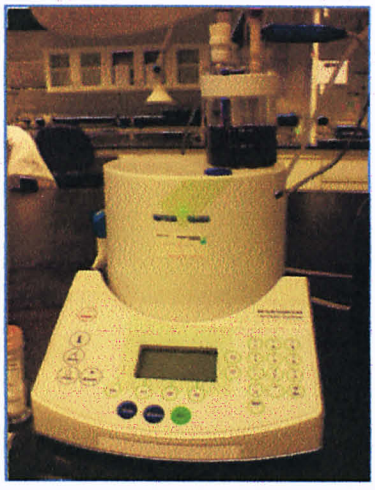

Figure B.1: Karl Fischer Coulometer DL 39 Mettler Toledo

To switch on Karl-fisher

1. Switch on the switch that is located left hand side at the reactor instrument.

2. Press RUN.

3. Choose method 1 (H2O standard).

4. Press OK.

5. Pretitration takes place.

6. After pre-titration completed, it will go to standby mode. (Check drift must be ,ess than 20)

7. Press sample.

8. Analysis of sample will come out (max weight 5g).

9. Please add sample.

10. Inject sample into the titration cell.

11. Press OK.

12. Press sample. Enter weight value.

To switch off Karl-fisher

1. Clean the working area after use.
2. Switch off the main switch that is located left hand at the reactor instrument.

C.2 Standard operating procedure (SOP) of Ion Chromatography.

Switch on Ion Chromatography

1. Switch on the computer and 761 Compact IC.
2. Double click the "761 Compact IC" software icon.
3. Click "log in" icon.
4. Click on icon 761 Compact IC with the computer icon will appear.

Run sample

1. Click the "FILL" button at 761 Compact IC icon.
2. Put the syringe filter at the sample input opening. Put the syringe on the top of filter.
3. Push the syringe to fill the sample loop with the sample solution.
4. Press the "CONTROL" icon follow by "START DETERMINATION".
5. Wait until the analysis complete.
6. Repeat steps 1 to 5 for next sample.

Stop operation

1. If the IC running without sample injection in 1 hour, change system to "MSM".
2. After finish analysis of samples, follow the below sequence:

CONTROL → SHUTDOWN HARDWARE → CLOSE

Appendix F: Comparison of NMR result and trend generated from software.

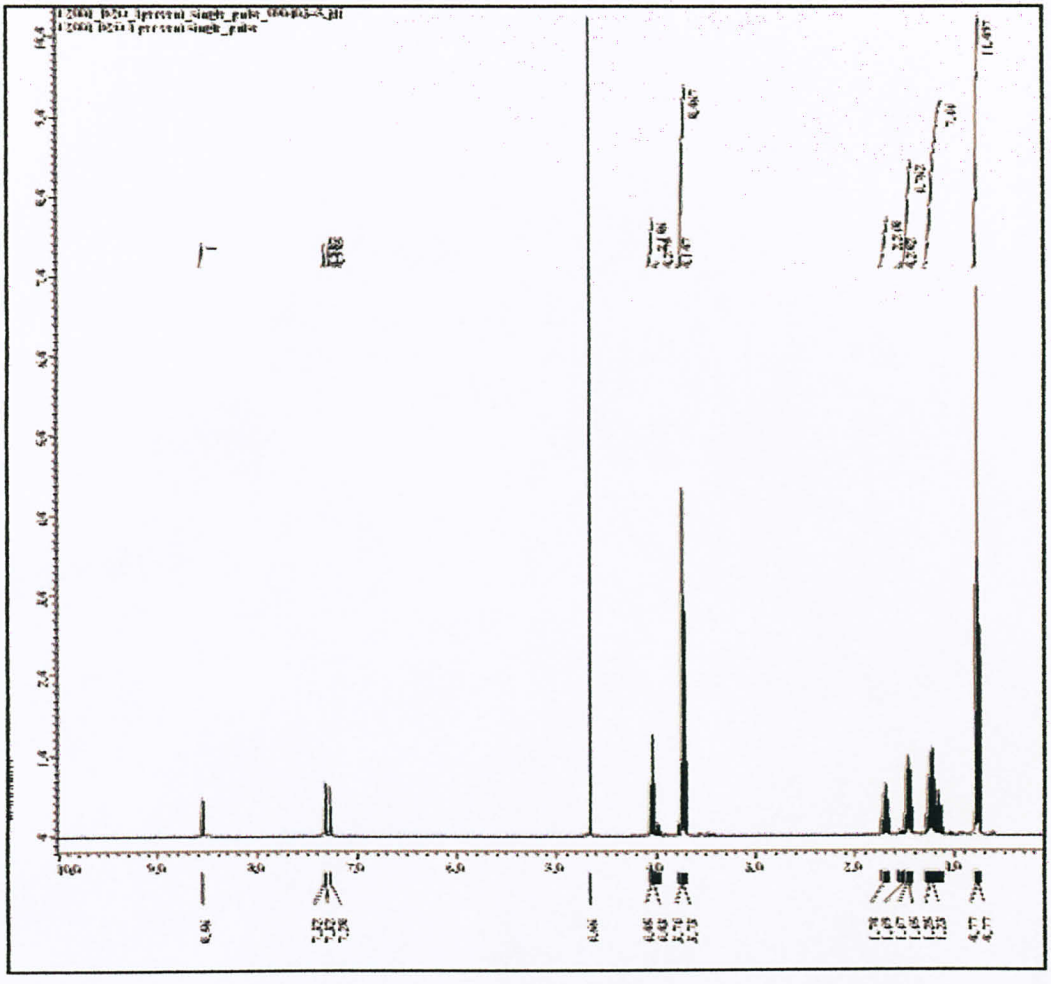

Figure F.1: Result from NMR testing

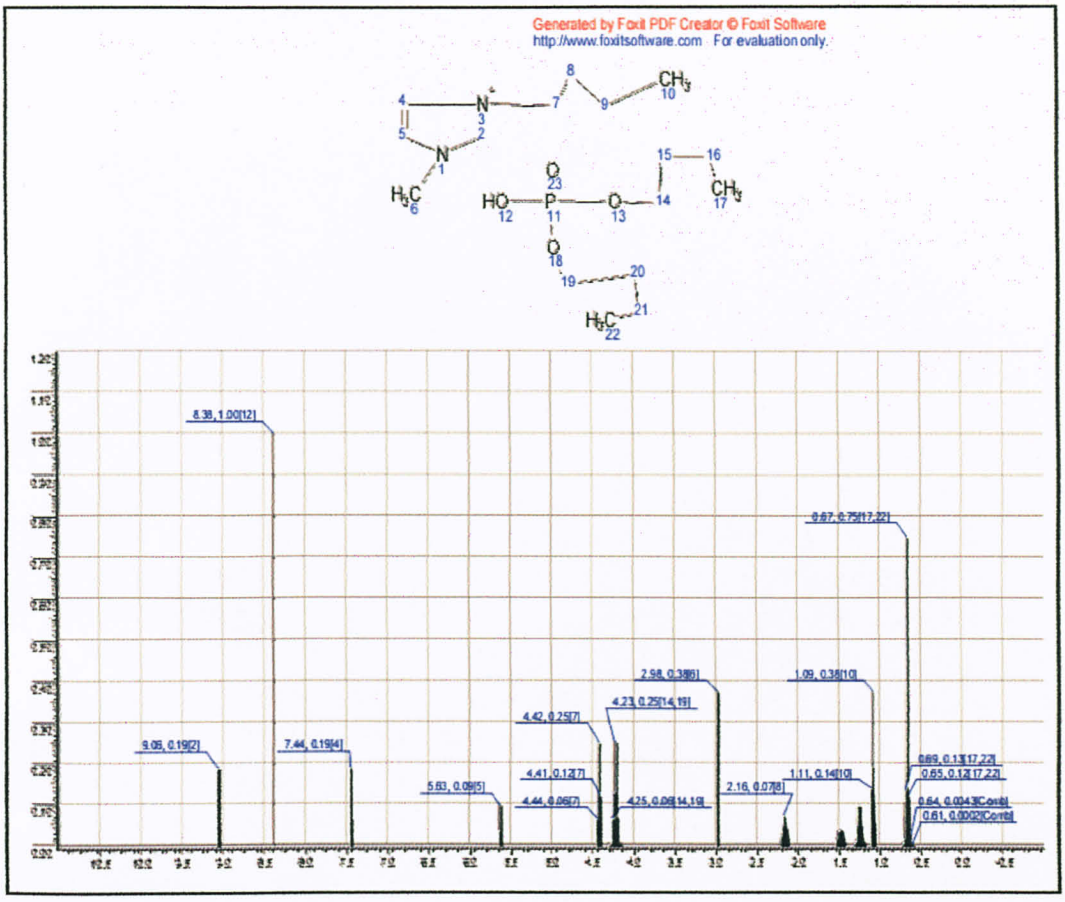

Figure F.2: Result generated from software