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PROGRESS REPORT

DESULPHURIZATION OF DBT IN CYCLOHEXANE MODEL OIL USING IONIC LIQUID

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Dissertation submitted in partial fulfilment of

the requirements for the

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CERTIFICATE OF APPROVAL

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MAY 2011

CERTIFICATE OF ORIGINALITY

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

(SYARIFAH SITI MARIAM BINTI SYED IBRAHIM AL-YAHYA)

ABSTRACT

Crude oil is conventionally processed by distillation followed by various cracking, solvent refining and hydro conversion processes to produce a desired slate of petroleum end products. However, increasingly tighter regulations on contaminant in fuels, particularly sulphur and aromatics content around 30ppm, have forced many refiners to hydro refine most and often all, of the fuel products.

In response to the more stringent requirements for cleaner fuels, refiners have added Hydrodesulphurization (HDS) process unit to produce low sulphur, low aromatics diesel. Unfortunately, the aromatic sulphur compounds present the most difficult challenges to the HDS processes in both cost and technology wise. The discovery of ionic liquid extraction power has attracted many attentions to do further researches as environmentally solvent to encounter HDS problem.

The purpose of this research is to extend the study on desulphurization trending produced by 1-Butyl-3-Methyl-Imidazolium Tiocyanate-[BMIM][SCN] ionic liquid on dibenzothiophene (DBT) in cyclohexane model oil. This experiment is carried out by manipulating various parameters tested on mixture of model oil and ionic liquid. From the result omitted, the most optimum parameters in desulphurization process using [BMIM][SCN] can be determined. This experiment is segregated into 3 different parameters which are mixing time, effect of temperature and the mixing ratio.

The samples are then analysed using Gas Chromatography (GC) and High Performance Liquid Chromatography (HPLC) to measure their desulphurization efficiency. All the experiment is repeated using imidazolium and pyridinium based ionic liquid which paired up with different anions to observe their ionic liquid extraction capability. Hypothetically, further studies will be done on the most promising ionic liquid with high extraction ratio to improve chemical and mechanical properties of crude oil products for large scale production and to replace the current desulphurization technology.

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CHAPTER 1
INTRODUCTION

1.1 Background of Study

The process of hydrodesulphurization (HDS) has been developed to meet the following objectives:

a. To reduce or to remove organic sulphur from crude oil-derived fuels.
b. To satisfy the product quality and stringent environmental requirement in producing ultra-low sulphur specification.

Hydroprocessing catalysts such as Co–Mo–(Ni–Mo–)-sulphide alumina catalysts have been highly effective for the reduction of sulphur levels. This unit functions to convert organic sulphur to hydrogen sulphide gas by reacting crude oil fractions with hydrogen at high pressures and temperatures.

The reactivity of organosulphur compounds over HDS catalysts depends on the molecular structures of sulphur containing compounds. The aliphatic organosulphur compounds like thiols (R–SH), thioethers (R–S–R) and disulphides (R–S–S–R) are very reactive in conventional hydroprocessing and they can be completely removed from the fuels without much difficulty.

The aromatic sulphur compounds including thiophenes, benzothiophenes, and their alkylated derivatives are generally more difficult to convert over hydroprocessing catalysts. Furthermore, environmental regulation on sulphur released has become more and more stringent and can be as low as 15ppm. Therefore, the aromatic sulphur compounds present the most difficult challenges to the HDS processes in both cost and technology wise.

In these past decades, so much attention has been paid on ionic liquid as one of green solution towards this problem. Ionic liquids (ILs) are organic salts with melting points around or below ambient temperature.

The possible choices of cation and anion that will result in the formation of ILs are numerous. They are also getting much attention because of their unique chemical and physical properties such as negligible vapour pressure, low toxicity, high chemical and thermal stabilities, and ability to dissolve a wide range of organic and inorganic compounds.

1.2 Problem Statement

The interest in ILs is due to many possible combinations of cations and anions, allowing the fine-tuning of their density, viscosity, melting point, hydrophobicity and most importantly their solvent power In order to find the best possible choice of available of ionic liquid, there are a few factors that need to be considered such as distribution coefficient, activity coefficient, partition ratio and selectivity.

However, the studies carried out so far with various IL's have not led to any concrete conclusion or trend and in most cases a single component of diesel has been taken. Data available are limited to certain types of cation or anion. Moreover most of the experimental data are available for the imidazolium based ionic liquids are using dodacane model oil which represent the paraffinic behaviour of crude oil. There is still no enough data which shows the extractive ability of IL's based on the cations: pyridine, pyrrolidinium and its derivatives and use cyclohexane as their model oil.

1.3 Objectives & Scope of Study

The objectives of this Final Year Project are as follow:

- To determine the best mixing temperature for the ternary system.
- To determine the best mixing time for extractive process.
- To determine the best mixing ratio between ionic liquid towards the system.

For this project, the scope of this work is to study the extraction of S-compound – dibenzothiophene (DBT) from model fuel oils using ILs. With the basis on previous essays of solubilities, Imidazolium and Pyridinium-based ionic liquid was selected as a suitable solvent to carry out this extraction. To confirm the suitability of this ionic liquid for desulfurization, a series of experiments will be conducted based on above mentioned parameters and will be analysed. All the results obtained will be compared based their extractive power.

Another modification will be done while conducting this project. The model oil that will be use is cyclohexane instead dodecane. The reason of doing so is most experimental data that have been published in testing the extraction feasibility of ionic liquids only use straight chain hydrocarbon such as dodecane as model oil. By using cyclohexane as the model oil, this project can observe the extraction process in different perspective because cyclohexane represents the naphtanic behaviour of crude oil.

The end result is expected to reveal the optimum parameters that can contribute to betterment of current technology used in the industries

CHAPTER 2
LITERATURE REVIEW & THEORY

General Overview

2.1 Crude Oil.

Petroleum is a complex mixture of organic liquids called crude oil and natural gas, which occurs naturally in the sea ground layers from the remains of marine plant and animal life. From the accumulation of organics, these remains were deposited along with rock-forming sediments under the sea where they were decomposed anaerobically and then converted over millions of years into petroleum by the combined action of heat and pressure. Crude oil varies from oilfield to oilfield in colour, composition or viscosity from a pale yellow low viscosity liquid to heavy black 'treacle' consistencies.

Crude oil and natural gas are extracted from the ground, on land or under the oceans, by sinking an oil well and are then transported by pipeline and/or ship to refineries where their components are processed into refined products. As crude oil comes from the well, it contains a mixture of hydrocarbon compounds and relatively small quantities of other materials such as oxygen, nitrogen, sulphur, salt and water in varying portion. In the refinery, most of these non - hydrocarbon substances are removed and the oil is broken down into its various components, and blended into useful products.

An oil refinery is an organised and coordinated arrangement of manufacturing processes. Fractional distillation and other technologies are designed to produce physical and chemical changes in crude oil to convert it into everyday products like petrol, diesel, lubricating oil, fuel oil, kerosene and bitumen. Petroleum products and chemicals are used in large quantities in the manufacture of detergents, artificial fibres, plastics, insecticides, fertilizers, pharmaceuticals, toiletries, and synthetic rubber. In simpler words, petroleum is ultimately a very useful natural resource.

2.2 Petroleum Hydrocarbon Structures

Petroleum consists of three major classes of hydrocarbon groups:

(a) Paraffins:

These group consist of straight or branched carbon rings saturated with hydrogen atoms with general formula $\mathbf{C_nH_{2n+2}}$ (n is a whole number, usually from 1 to 20), the simplest of which is methane (CH_4) the main ingredient of natural gas. Others in this group include ethane (C_2H_6), and propane (C_3H_8).

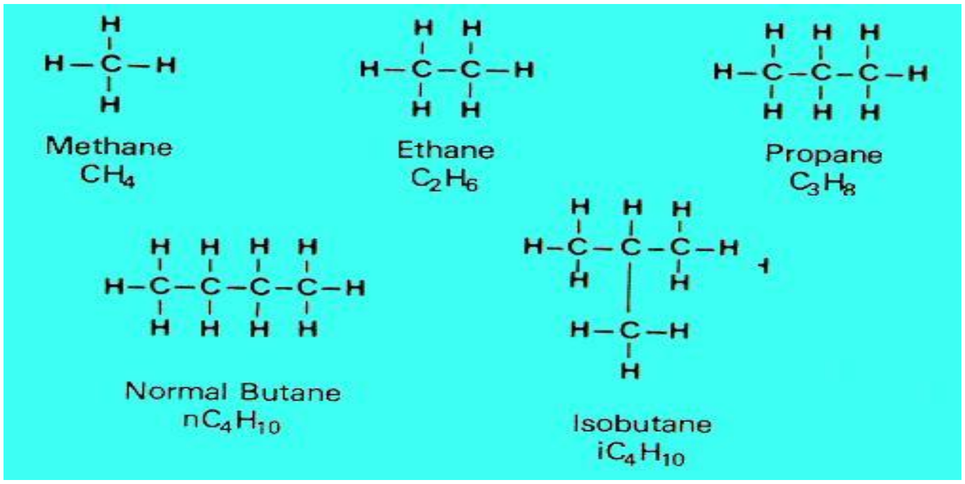

Figure 2.1: Example of Paraffin Group

With very few carbon atoms (C_1 to C_4) are light in density and are gases under normal atmospheric pressure but it also can be liquids depending upon the molecule. Chemically paraffins are very stable compounds.

(b) Naphthenes or Cycloalkanes:

Naphthenes has general formula of $\mathbf{C_nH_{2n}}$ (n is a whole number usually from 1 to 20) and consist of carbon rings, sometimes with side chains, saturated with hydrogen atoms. Naphthenes are chemically stable; they occur naturally in crude oil and have properties similar to paraffins.

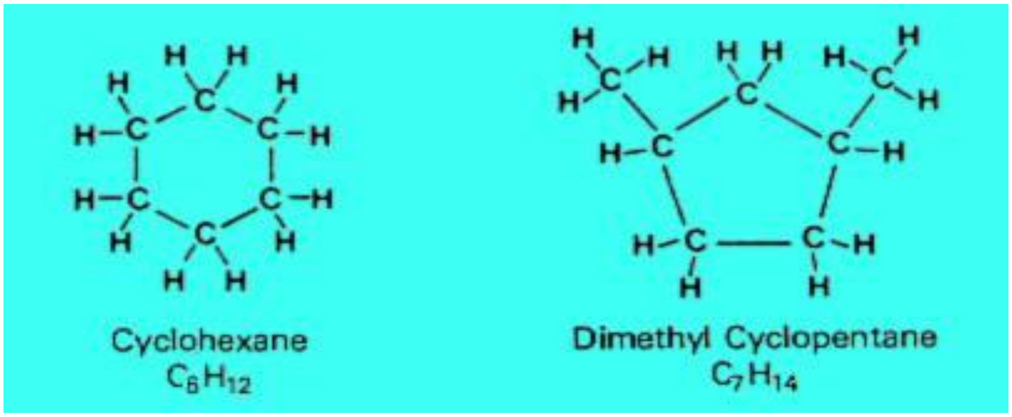

Figure 2.2: Example of Napthenes Group

(c) Aromatics:

Aromatic hydrocarbons has the general formula of $\mathbf{C_6H_5}$ **-** Y (Y is a longer, straight molecule that connects to the benzene ring). They are compounds that contain a ring of six carbon atoms with alternating double and single bonds and six attached hydrogen atoms. This type of structure is known as a benzene ring. They occur naturally in crude oil, and can also be created by the refining process.

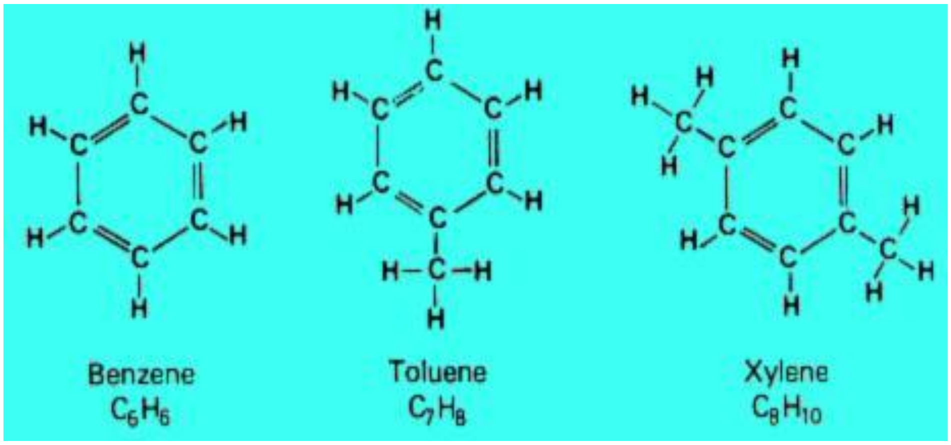

Figure 2.3: Example of Aromatics Group

The more carbon atoms a hydrocarbon molecule has, the "heavier" it is (the higher is its molecular weight) and the higher is it's the boiling point.

Small quantities of a crude oil may be composed of compounds containing oxygen, nitrogen, sulphur and metals. Sulphur content ranges from traces to more than 5 per cent. If a crude oil contains appreciable quantities of sulphur it is called as sour crude; if it contains little or no sulphur it is called as sweet crude

Heavy crude is:

- Harder to handle (it is too thick to pump easily through pipelines unless diluted with light crude)
- More expensive to refine to produce the most valuable petroleum products such as petrol, diesel and aviation fuel.

Sweet crude is preferable to sour because it is also (like light crude) more suited to the production of the most valuable refined products.

2.3 Crude Oil Refining- Hydrotreating and sulphur Plants

Sulphur denoted by "S" letter is naturally occurring element which present in petroleum oils and natural gas but sulphur compound formed due to chemical refinement of oil such as sulphuric acid treatment during distillation process.

The presence of sulphur either in crude oil or refined petroleum products is considered as contaminant as it can damage the equipment, poisoning catalysts and quality of the products.

Hydrotreating is one way of removing many of the contaminants from many of the intermediate or final products. In the hydrotreating process, the entering feedstock is mixed with hydrogen and heated to **300 - 380°C**. The oil combined with the hydrogen then enters a reactor loaded with a catalyst which promotes several reactions:

- hydrogen combines with sulphur to form hydrogen sulphide (H_2S)
- nitrogen compounds are converted to ammonia
- any metals contained in the oil are deposited on the catalyst

- Some of the olefins, aromatics or naphthenes become saturated with hydrogen to become paraffins and some cracking takes place, causing the creation of some methane, ethane, propane and butanes.

Even though crude oil undergoes series of sulphur treatment, it still has some pro and cons. The sulphur level is successfully decreased to desired level but also formed several other derived sulphur compounds which more difficult to be removed.

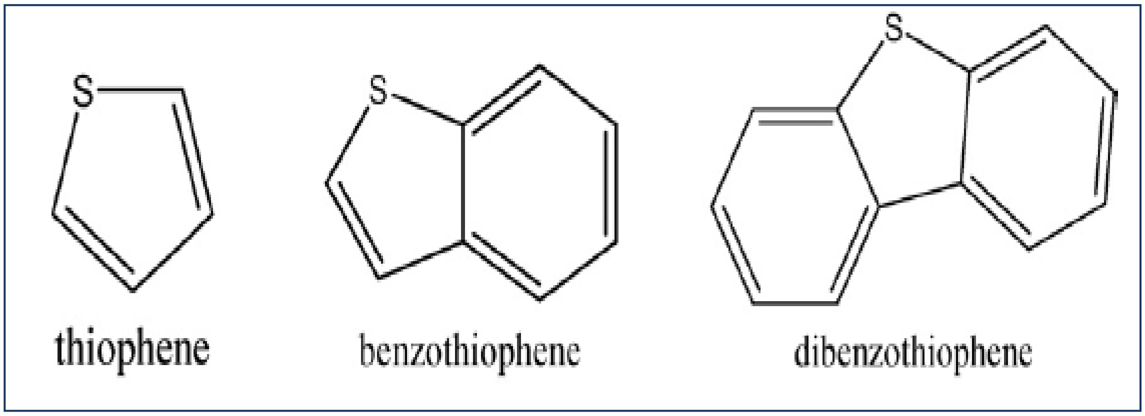

Figure 2.4: Different Structural Diagram of Sulphur Derivatives

2.4 Environmental Regulations

Uncontrolled sulphur emission will lead to huge detrimental effects whether it comes from refineries or vehicle emission. . Even worse, the limit of sulphur release has become more and more stringent as it can leads to severe environmenta i.e : acid rain ,crop damage and low visibility. Meanwhile from health wise it can cause respiratory problem ans skin irritation.

Currently, the new standard regulations to S-limit as been proposed by Directive of European Parliament is 10ppm and Environmental Protection Agency (EPA) of USA has stated allowable suphur release for refineries must not exceeded average of 15 parts per million (ppm) . Eventhough it is not imposibble, the process will still caused a great technical challenge to oil refineries as it consume high operating cost and cutting edge technology.

2.5 Hydrodesulphurization (HDS)

Refineries industry utilizes hydrodesulphurization (HDS), a conventional catalytic process to remove sulphur compounds. While the performance of conventional hydroprocessing catalysts have been highly effective for the reduction of sulphur levels, further removal of residual sulphur from the processed fuels is seen to largely increase the cost of hydroprocessing. The main drawbacks of HDS include high temperature (>300 ^{o}C), high pressure (4MPa), and it cannot remove aromatic sulphur compounds such as dibenzothiophene (DBT) and its derivatives.

To achieve the almost no sulphur specification, the refineries must able to operate at lower temperature and higher hydrogen pressure but both have their disadvantages. At lower pressure, the reaction goes slower. In other words, more refining capacity must be added and more crude oil must be used to produce normally yield diesel. Vice versa, at higher pressure, the HDS wall thickness need to be doubled or tripled to endure such operating pressure hence increase plant’s operating cost. Higher temperature processing also leads to increased coke formation and subsequent catalyst deactivation.

Therefore, the search for alternative method has put a lot of interest in ionic liquid as the green solution to this problem. The extractive desulfurization process using ionic liquids can be a complementary technology for the HDS process, and some studied work has been reported. These studies indicated that the ILs have high extraction ratios and greater selectivity compared to molecular solvents because of the unique solvent characteristics of ILs.

Literature Review on Ionic Liquid

2.6 Ionic Liquid

What is Ionic Liquid?

Generally ionic liquid define as a salt in which ions are poorly coordinated, which results in these solvent being in liquid form below 100^{o}C or even at these room temperature. At least one ion has been delocalised charge and one component is organic.

Green solvents like ionic liquids provide an important alternative in removing such compounds by liquid–liquid extraction. ILs are attractive solvents for desulphurisation and are competitive with respect to molecular solvents.

ILs are environmentally benign and designable, non-volatile, non-flammable, highly solvating and non-coordinating media having a high-thermal stability over a wide liquid range, have higher sulphur extracting ability and are virtually immiscible with diesel, preventing cross contamination, and recovery and regeneration involves simple heating to recover the sulphur compounds.

The interest in ILs is due to many possible combinations of cations and anions, allowing the fine-tuning of their density, viscosity, melting point, hydrophobicity and most importantly their solvent power.

Types of Ionic Liquid

(a) Imidazolium

Imidazole is an organic compound with the formula $C_3H_4N_2$. This aromatic heterocyclic is a diazole and is classified as an alkaloid. Imidazole refers to the parent compound, whereas imidazoles are a class of heterocycles with similar ring structure, but varying substituents. This ring system is present in important biological building blocks, such as histidine, and the related hormone histamine. Imidazole can serve as a base and as a weak acid.

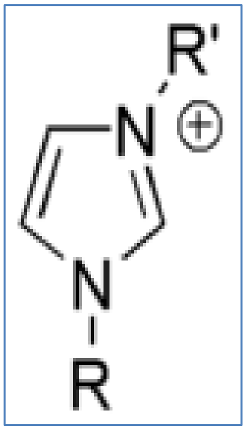

Figure 2.5: Imidazole Structural Diagram

(b) Pyridinium

Pyridinium refers to the cationic form of pyridine. This is either due to protonation of the ring nitrogen or because the addition of a substituent to the nitrogen ring (alkylation). The lone pair of the electrons on the nitrogen atom of pyridine is not delocalized

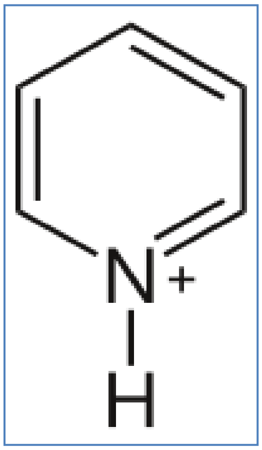

Figure 2.6 :Pyridinium Structural Diagram

Why interested in Imidazolium and Pyridinium-Based Ionic Liquid?

Interestingly, most of the published data relates to ionic liquids with imidazolium cations.1-Alkylpyridinium salts, for example, are described in the patent literature only as organic salt additives in liquid–liquid separations. With the variety of ionic liquids available, especially considering those with different types of cations, we reasoned that a more general study to examine the influence of different cationic and anionic species on the partitioning might lead to better ionic liquid extracting systems. It is also to evaluate their extraction capability in different model oil (cyclohexane)

Extraction of dibenzothiophene from dodecane using ionic liquids as the extracting phase has been investigated for a range of ionic liquids with varying cation classes (imidazolium, pyridinium, and pyrrolidinium) and a range of anion types using liquid–liquid partition studies and QSPR (quantitative structure–activity relationship) analysis. The partition ratio of dibenzothiophene to the ionic liquids showed a clear variation with cation class (dimethylpyridinium > methylpyridinium > pyridinium ≈ imidazolium ≈ pyrrolidinium), with much less significant variation with anion type.

From this comparison, the selection of using pyrindinium-based ionic liquid in this project is the make further discoveries and studies in pyrindinium-based ionic liquid. As found in a number of journals which makes studies on extractive feasibility of imidazolium-based ionic liquid, pyrindinium is another type of cationic ionic liquid which has comparable extractive feasibility to imidazolium-based ionic liquid.

Here, we describe an investigation of the role of different cationic and anionic components of an ionic liquid extracting phase on the efficiency of partitioning of DBT from cyclohexane as a model for extractive desulphurisation of oils.

The sulphur compounds studied by most of the literature are aromatic sulphur compounds, such as thiophene, benzothiophene (BT) and dibenzothiophen (DBT) dissolved in dodecane as a model oil system. All For the IL extractive desulfurization process, the attention is focused on finding an effective IL which is nontoxic, is thermally stable, is non-sensitive to moisture and air, has a low cost for commercial application, and has high extractive performance.

CHAPTER 3:
METHODOLOGY

The experiment was done to prepare samples of extracted dibenzothiophene (DBT) samplings under different parameters. Following the sampling process, analyses are done to investigate the properties of the product samples after extraction process by using Gas Chromatography. Below are the work flows for each experiment conducted in this project.

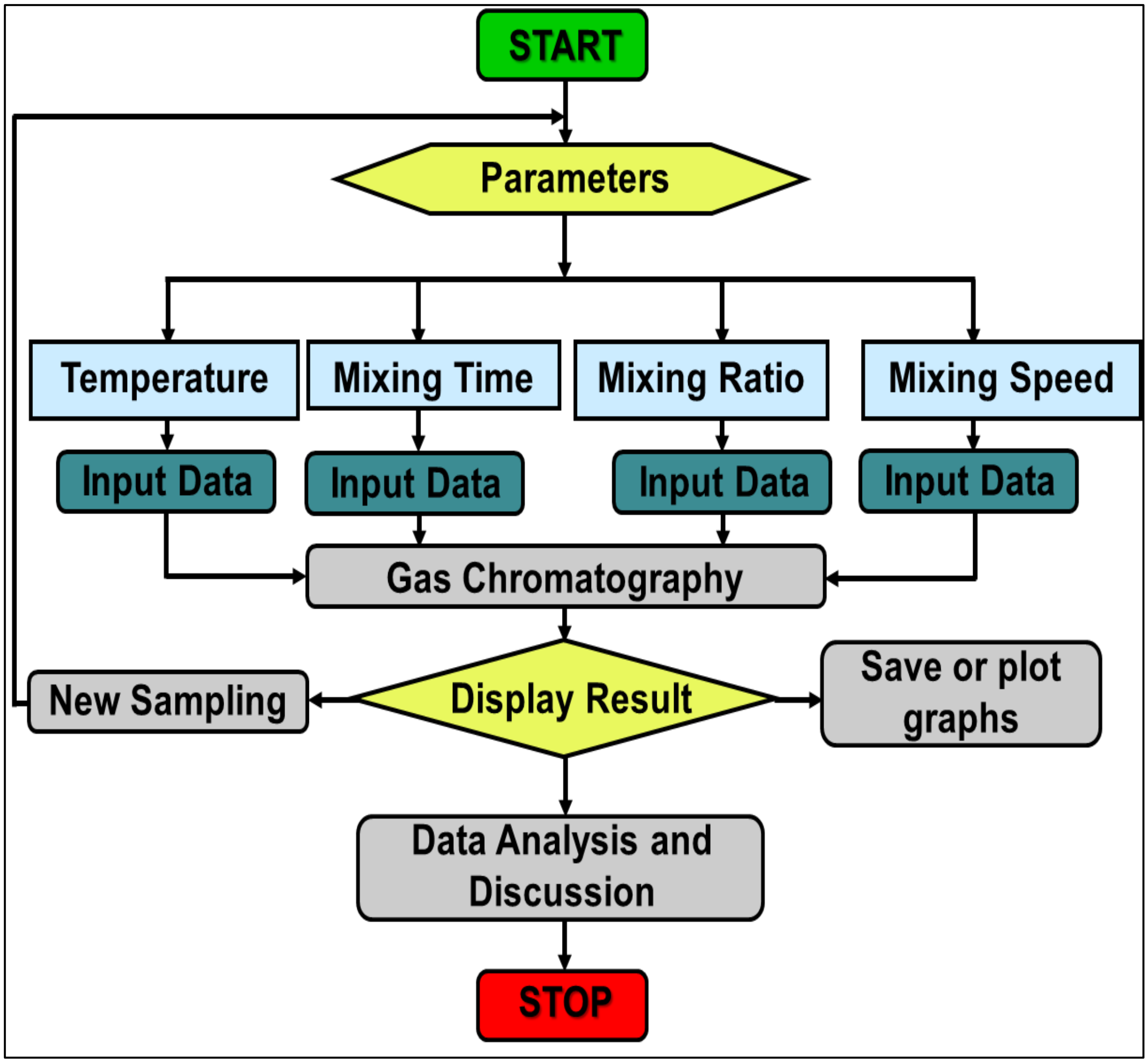

Figure 3.1: Experiment Work Flow

3.1 General Methodology

Good condition of ionic liquid is very essential before running these experiments. To ensure the usability of [BMIM][SCN], the ionic liquid was first characterized using FT Raman Analysis The importance of using Raman is to check any abnormalities within the peaks produced by [BMIM][SCN] and [BMIM][Ac] compared to the peaks stored in FT Raman library.

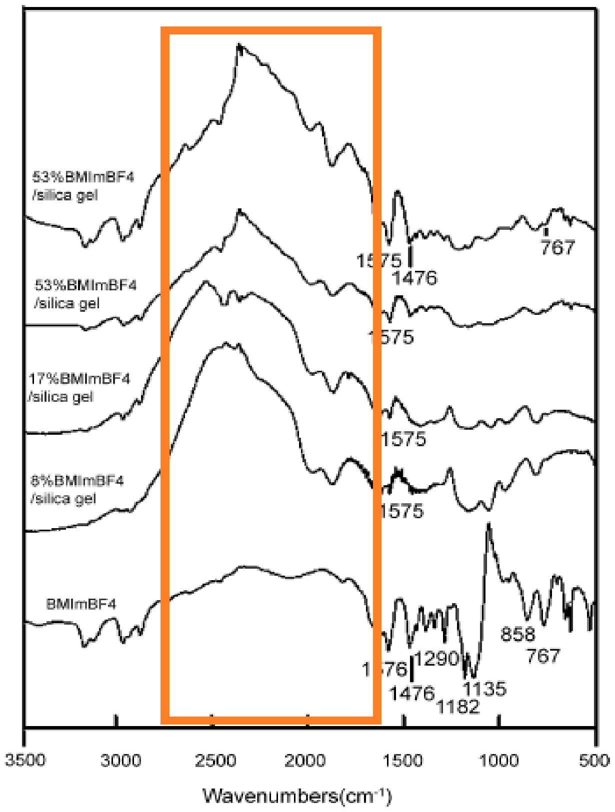

Fig. 3. DRIFTS spectra of ionic liquid $BMImBF_4$ before and after confinement.

Figure 3.2: Example of Analyzed IL using FT Raman Spectrometer

If the result omitted from FT Raman analysis is approximately similar to diagram above, the ionic liquid is feasible to be used. Next step is ionic liquids were dried for 24 hour in vacuum oven at 70^0C. This is to remove the moisture from the ionic liquid and reduced the variability in the end result.

3.2 Gas Chromatography for Desulphurization Efficiency

Shimadzu GC-2010 Gas Chromatography (SGE BP1 capillary column, 30 m x 0.25 mm, 0.25 um film thickness) with flame ionization detector was used to determine the concentration of DBT remained in model oil layer before and after desulphurization. The carrier gas was nitrogen, with column flow rate of 1.39 ml.min$^{-1.}$. The injector temperature was held at 593.15 K, and the temperature of the detectors was fixed at 601.15 K. The injection volume was 1 ul with split ratio of 1:50. The oven temperature was from 323.15 K to 373.15 K with ramp of 5 K.min^{-1}, and then up to 593.15 K at 20 K.min $^{-1`}$

After each extraction process, sampling need to done on each sample before it can be used for Gas Chromatography Analysis. These samples will be diluted using cyclohexane for 10 times. This is a very important step as to not jeopardized GC column due to over-loaded samples.

1. Top Layer of each samples are separated using syringe and placed into 1.5ml vial. This will be done for 3 readings to get the average value.
2. These samples were diluted 10 times by using cyclohexane (0.1g sample: 0.9 g cyclohexane) and placed into another 1.5ml vial.
3. Vial caps were carefully folded using parafilm and labelled.
4. Prepared samples were placed into the slot inside the analyzer.
5. Each of the samples takes about 45 minutes to be analyzed.

3.2.1 Materials

- Cyclohexane with ≥ 99% purity from Merck
- Dibenzothiophene (DBT) 99% purity from Acros.
- 1-Butyl-3-Methyl-Imidazolium Tiocyanate-[BMIM][SCN]
- 1-butyl-3-methylimidazolium acetate -[BMIM][Ac]

*The Ionic Liquids used in this experiment were listed purchased from Sigma Aldrich and also obtained from PETRONAS Ionic Liquid Centre.

3.2.2 Solubility Test

Solubility test was done to determine the supersaturated point of DBT in cyclohexane. The whole process is done in fume hood due to cyclohexane high volatility. Since weight per cent ratio is used throughout this experiment, it is essential to use gram dimension instead of millilitre for cyclohexane.

Conversion of cyclohexane ml into gram:

$$5\,ml * \left(\frac{0.78g}{cm3}\right) * \left(\frac{1000cm3}{1Litre}\right) * \left(\frac{1Litre}{1000ml}\right) = 3.9\,g$$

3.2.3 Preparation of Model Oil

Model oil containing around 5% dibenzothiophene (DBT) was prepared by dissolving solid dibenzothiophene in cyclohexane.

Calculation of Weight Percentage

-Assume to prepare 5% of DBT in cyclohexane:

$$5\%\ solubility\ of\ DBT\ in\ \ C6H12 = \frac{x}{x+3.9}$$

$$0.05 = \frac{x}{x+3.9g}$$

$$0.05\ (x+3.9) = x$$

$$0.05x + 0.195 = x$$

$$x = 0.2053\ g\ of\ DBT\ need\ to\ be\ dissolved\ in\ cyclohexane$$

3.2 Determination of Suitable Mixing Temperature

The ionic liquid and model oil were mixed at 1:1 mass ratio (2 g each). The mixture was heated in oil bath at selected temperatures with 400 rpm stirring for 30 minute and to settle for 10 minute. Liquids from the model oil layer and ionic liquid layer were separated using syringe. The same procedure was repeated using 40 ^{0}C, 50 ^{0}C, 60 ^{0}C, 70 ^{0}C and 80^{0}C. Desulphurization of model oil using [BMIM][DCA] and [BMIM][Ac] was carried out using the same procedure.

This experiment is also repeated at 800 rpm with the same procedures because throughout the experiment, it can be observed that at 400 rpm, ionic liquid and model oil is not vigorously mixed.

Reading (wt%)	***30^{0}C***	***40^{0}C***	***50^{0}C***	***60^{0}C***	***70^{0}C***	***80^{0}C***	***400 rpm***
1							
2							
3							
Reading (wt%)	***30^{0}C***	***40^{0}C***	***50^{0}C***	***60^{0}C***	***70^{0}C***	***80^{0}C***	***800 rpm***
1							
2							
2							

Table 3.1: Tabulated Result of Suitable Mixing Temperature

Stirring Speed: 400 rpm/800 rpm

Mixing Time: 30 minute

Settling Time: 10 minute

3.3 Determination of Suitable Mixing Time

Desulphurization of Model Oil

[BMIM][SCN] was subjected to do the same DBT extraction methodology as described in section X at 30 ^{0}C, except the mixing time was varied (5,10,20,30 and 60 minutes). Desulphurization of model oil using [BMIM][Ac] was carried out using the same procedure to determine the suitable mixing time. An additional experiment was carried out with 60^{0}C with 5 minutes mixing time; Determination of desulphurization efficiency was carried out as a for-mentioned.

Mixing time(minute)							
Reading (wt%)	***5***	***10***	***20***	***30***	***40***	***60***	***30^{0}C***
1							
2							
3							
Mixing time(minute)							
Reading (wt%)	***5***	***10***	***20***	***30***	***40***	***60***	***70^{0}C***
1							
2							
3							

Table 3.2: Tabulated Result Suitable Mixing Time

Stirring Speed: 400 rpm

Settling Time: 10 minute

3.4 Determination of Suitable Mixing Ratio between Model Oil and IL

[BMIM][SCN] was subjected to do the same DBT extraction methodology as described earlier at 30^0C, except the mixing ratio between IL and model oil was varied (3:1, 2:1, 1:1, 1:5, 1:10). Desulphurization of model oil using [BMIM][Ac] was carried out using the same procedure. Determination of desulphurization was carried out as described below.

Reading (wt%)	***3:1***	***2:1***	***1:1***	***1:5***	***1:10***
1					
2					
3					

Table 3.3: Tabulated Result Suitable Mixing Ratio between Model Oil and IL

Stirring Speed: 400 rpm

Mixing Time: 30 minute

Settling Time: 10 minute

3.5 Gantt Chart of Project

Final Year Project 1:

Title/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Literature Review														
i. Experimental work	🟨	🟨	🟨	🟨	🟨	🟨								
ii. Experimental work	🟨	🟨	🟨	🟨	🟨	🟨								
Progress Report (3rd Sept)					🟨	🟨								
Seminar (3rd Sept)					🟨	🟨								
Calculations						🟨	🟨	🟨	🟨	🟨	🟨			
Experimental work						🟨	🟨	🟨	🟨	🟨	🟨			
Experimental work							🟨	🟨	🟨	🟨	🟨			
Modifications								🟨	🟨	🟨	🟨	🟨	🟨	
Interim Report (1st Nov)														🟨
Oral Presentation (1st Nov)														🟨

Final Year Project 2:

Title/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Project Work Continues	🟨	🟨	🟨	🟨	🟨	🟨	🟨							
Progress Report								🟨						
Project Work Continues								🟨	🟨	🟨	🟨	🟨		
Submission of Draft Report											🟨			
Submission of Dissertation(soft bound)												🟨		
Submission of Technical Paper												🟨		
Oral Presentation													🟨	
Submission of Dissertation(hard bound)														🟨

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CHAPTER 4
Result and Discussion

4.1 Solubility Test Result:

Cyclohexane (C_6H1_2)	DBT (g)	Solubility (wt%)	Miscible (yes/no)	Physical appearance
3.9022	0.1022	2.5522	yes	clear
4.0440	0.0500	3.7176	yes	clear
4.0940	0.0542	4.9783	yes	clear
4.1482	0.0196	5.4225	no	cloudy
4.1678	0.0210	5.7744	no	cloudy

Table 4.1: Tabulated Result of Solubility Test

The mixture was then stirred-heated at 30^0C for 1 hour and left at ambient temperature. Higher stirring temperature cannot be used as the solvent (cyclohexane) has high volatility characteristics. From the tabulated result, at solubility 5.4225 wt%, cloudy appearance started to form. After 1 hour duration at ambient temperature, the mixture did not show any physical change which is clear.

Figure 4.1: Supersaturated Model Oil

This indicates the mixture already hit saturation point where the solvent cannot dissolved DBT even though with external energy (heating). It was finally decided 5 wt% model oil will be used though out this project. Due to cyclohexane high volatility, model oil need to be kept in fume hood.

4.2 Determination of Suitable Mixing Temperature Result:

Temperature	***30^{0}C***		***40^{0}C***		***50^{0}C***		***60^{0}C***		***70^{0}C***		***80^{0}C***	
	MO(g)	IL(g)	MO(g)	IL(g)	MO(g)	IL(g)	MO(g)	IL(g)	MO(g)	IL(g)	MO(g)	IL(g)
	2.0039	2.0129	2.0042	2.0236	2.0045	2.0044	2.0036	2.0044	2.0162	2.0360	2.0015	2.0070
Sampling Reading (diluted 10x)												
Sample	S30		S40		S50		S60		S70		S80	
1	3.23223		3.21105		2.96071		3.11562		2.86489		2.92823	
2	3.36640		3.36100		2.99854		3.32541		3.02923		2.97741	
3	3.43200		3.45858		3.05732		3.58962		3.12247		3.11092	
Average	3.34354		3.34354		3.00552		3.34354		3.00552		3.00552	

Table 4.2: Tabulated Value Suitable Mixing Temperature

4.2.1 Gas Chromatography Result:

Sample	Sulphur Content Before GC (wt%)	Sulphur Content After GC (wt%)	Sulphur Percentage removal (wt%)
D30	3.34354	2.45326 e-1	92.6627
D40	3.34354	3.18230 e-1	90.4822
D60	3.34354	2.85247 e-1	91.4687
D70[2]	3.00552	3.50251 e-1	94.7338
D80	3.00552	1.88874 e-1	93.7157

Table 4.3: Tabulated Gas Chromatography Result

Example Calculation for Sulphur Percentage Removal:

$Sulphur\ Percentage\ Removal\ (wt\%)$

$$= \frac{Sample\ wt\%\ before - Sample\ wt\%\ after}{Sample\ wt\%\ before}\ x\ 100\ \%$$

$$\text{D30} = \frac{3.34354\ wt\% - 2.45326e{-1}\ wt\%}{3.34354\ wt\%}\ x\ 100\ \%$$

D30 = 92.6627 wt %

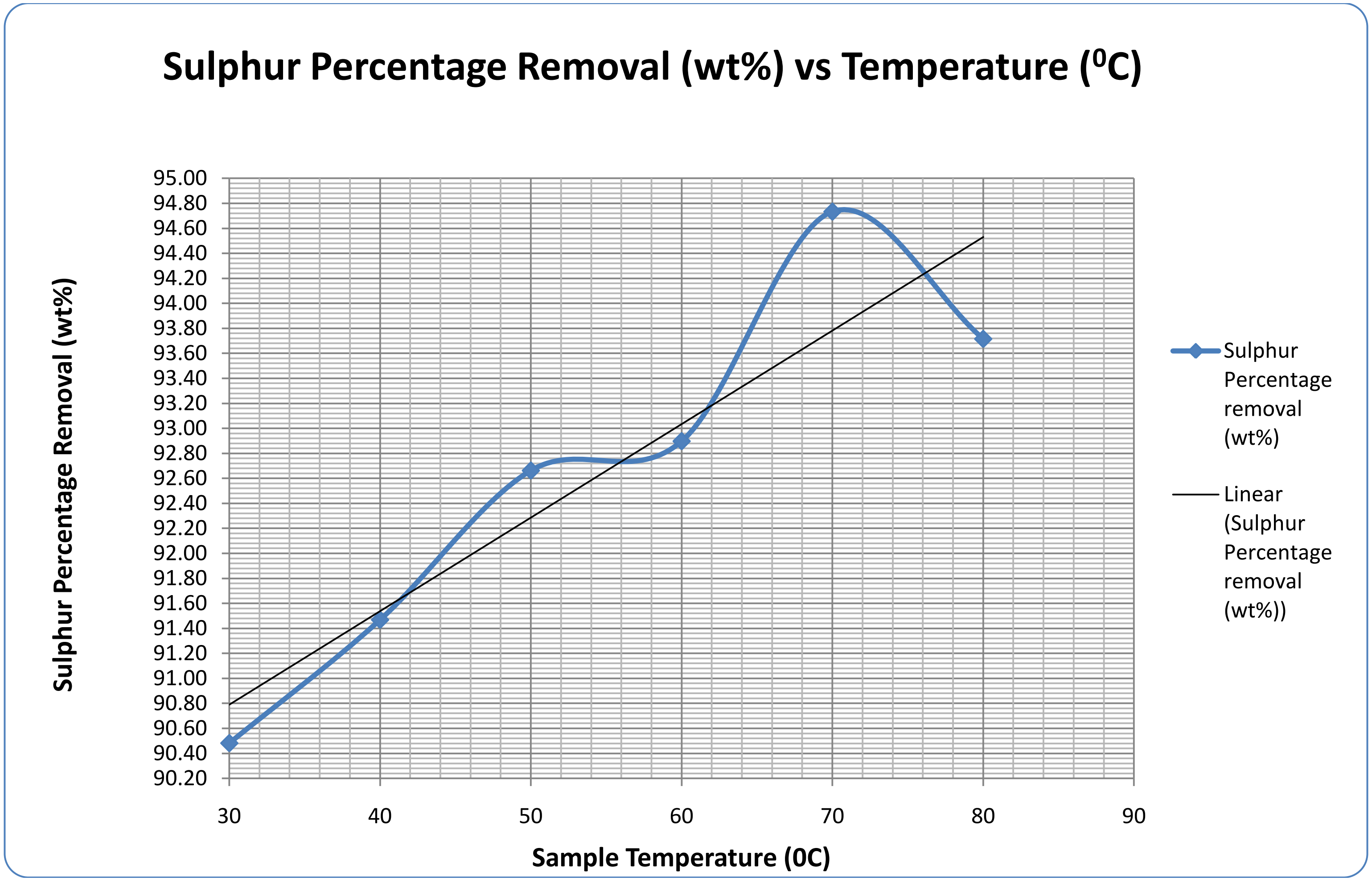

Figure 4.2: Plotted Graph of Sulphur Percentage Removal (wt%)

Discussion:

From the graph above, it can be concluded that the most effective sulphur removal occurred at 70^0C with 94.7228 %. Gradual increment of extraction can be observed from overall linear sulphur removal but as can be seen in the graph, there is significant percentage drop occurred at 80^0C. Decrement as much as 1.0181 % from extraction percentage at 70^0C.

This is slightly different to most result obtained or published in most journals. It is obtained that the most optimum temperature for extraction process to occur is at 80 ^{0}C but this is reported on dodecane as the model oil. (D.Liu et.al, 2009). Meanwhile for cyclohexane, the experiment runs at 70 ^{0}C

The most realistic reason which caused this difference is maybe due to some errors while conducting the experiment such as when separating the top layer after extraction process, the syringe used is constantly have blockage due to white precipitate /clump. This is because cyclohexane evaporated at considerably at a very short time even though throughout the experiment, it was being done in fume hood. It is recommended to use syringe with needle because the separation can happen more efficiently and it can lower the possibilities of used ionic liquid being sucked up into syringe. Whenever this happened, the small existence of ionic liquid within sample vial may cause overloading during GC analysis and jeopardize the column.

4.3 Determination of Suitable Mixing Time Result:

Temperature	***10 min***		***20 min***		***30 min***		***40 min***		***50 min***		***60 min***	
70^{0}C	MO(g)	IL(g)	MO(g)	IL(g)	MO(g)	IL(g)	MO(g)	IL(g)	MO(g)	IL(g)	MO(g)	IL(g)
	1.0154	1.0061	1.0290	1.0026	1.0011	1.0018	1.0088	1.0111	1.0004	1.0229	1.0356	1.0114
Sampling Readings (diluted 10x)												
Sample	S30		S40		S50		S60		S70		S80	
1												
2												
3												
Average												

Table 4.4: Tabulated Value of Suitable Mixing Time

Discussion:

Due to limited amount of 1-Butyl-3-Methyl-Imidazolium Tiocyanate-([BMIM][SCN]), the ration has been scaled down to model oil : ionic liquid = 1g : 1g. The result analysis for this section is still on hold due to gas chromatography breakdown. The breakdown was caused by overloading on the column.

Action Plan/ Expected Result:

Instead of diluting the sample 10 times with cyclohexane wash, we can increase the dilution into 100 times. While waiting the GC to be repaired, another alternative qualitative analysis which can be used to tackle this matter are High Performance Liquid Chromatography (HPLC), Total Sulphur Analysis (TSA) or Carbon Hydrogen Nitrogen Sulphur Analyser (CHNS)

4.4 Regeneration of Sulfur-Loaded ILs

For the technical application of the IL-extraction the regeneration and subsequent recycling of the IL is of vital importance. The most promising re-extraction mediums are low-boiling hydrocarbons like pentane or hexane. In order to examine the regenerability of the ionic liquid, the ionic liquid was extracted by n-hexane (2 ml 3) and vacuumized for 4 h at 393 K for another cycle. Analysis of the ionic liquid by 1H NMR spectroscopy (Mercury-Plus 300BB instruments, Varian, Australia) indicated that its purity was retained.

Chapter 5
Conclusion

As a conclusion, the result of the experiment and analysis so far is coherent with the information obtained from the literature reviews previously done. Sulphur Extraction percentage and graphs obtained does not deviate too far from other published literature value yield showed similar pattern as reported by previous researches done. The chemical reactions and behaviour deduced from the proximate and ultimate analyses are also in agreement with discussions in journals reviewed prior to the experiment.

From the result we obtained, it is ideal to run the extraction process at $70^{o}C$ for cyclohexane model oil. Due to a few unexpected hick-up in running this experiment has prolong the lab work period such as unavailability of sufficient ionic liquid and equipment breakdown.

It is recommended to continue this project especially on the study of model oil: ionic liquid ratio and regeneration of the used ionic liquid as it can be great reference in finding the best ionic liquid that can be implied in standard industrial scale.

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