Desulphurization of Crude Oil Using Solid Support Ionic Liquid

By

Aisyah Hasmad

Dissertation submitted in partial fulfilment of
The requirement for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

MAY 2011

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

(Assoc Prof Dr. Mohamad Azmi B. Bustam)

UNIVERTISI TEKNOLOGI PETRONAS
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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.

(AISYAH BINTI HASMAD)

ABSTRACT

Nowadays, the rapid development in each country in the world shows high demand for petroleum based product as an energy especially for fuel, thus specifications of fuels (particularly gasoline and diesel) became and are getting more and more stringent and Sulfur specifications getting lower and down to 50ppm. Conventional method for sulphur removal in refining process is the catalytic hydrodesulfurization (HDS technology) operating at high temperature and pressure. HDS is a very costly process that required high hydrogen consumption under severe condition and it is inefficient to reduce aromatic sulphur compounds.

Hence, green solvent known as ionic liquid was introduced as alternative to remove sulphur from hydrocarbon mixtures. Ionic liquids nominated as ideal candidates for this issue since most of the species are low melting salts (<100 °C) with no measurable vapour pressure, and represent a relatively new class of solvents and extracting agents. Ionic liquids also have excellent extraction properties for organic S- and N-compounds and if chosen wisely, insoluble in oil.

By using technique of solid-liquid extraction, 1-Butyl-3-methylimidazolium tetrachloroferrate [BMIM]($FeCl_4$) solid support ionic liquid was synthesized and tested for its capability to extract organic sulphur species from real, refinery obtained hydrocarbon fuels, natural raw crude oil and model oil in mild temperature (25°C) and offshore operation condition (80°C). The hydrocarbons consisted of various types of sulphur species as well as pre-treated, partially desulphurized hydrocarbon mixtures. The sulphur extracted from hydrocarbons mixtures were then analysed for total sulphur analyser. Total sulphur was significantly lowered in all tested hydrocarbon mixtures. Way forward to further study on reuse and regeneration of the solid support ionic liquid candidate were suggested after all results and analysis take place.

ACKNOWLEDGEMENT

The author would like to take the opportunity to thank everyone involved in making this Final Year Project a successful educational session. Highest praise is to Allah the Almighty, for the blessing of knowledge, endurance and perseverance in completing this Final Year Project within the prescribed timeline. Deepest gratitude goes to AP. Dr. Chong Fai Kait, Final Year Project supervisor and co-supervisor AP. Dr. Mohamad Azmi bin Bustam for the continuous and relentless support and guidance throughout the project. The author would also like to thank the following individuals for their professionalism and contribution to the research:

- Ms. Siti Hawatulaila, Ms. Wan Suzaini and Ms. Aisyah Azizah and all fellow research officers, postgrade students and technician from UTP ionic liquid group.
- Mr. Fazli, Chemical Engineering laboratory Technicians

Also, the author would like to express heartfelt appreciation to beloved parents, family and friends for continuous moral support and advices throughout the project completion, and to anyone who has directly or indirectly contributed towards the success of the project.

Thank you.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

In recent years, large amounts of fuel oils have been demanded in industries and daily life with the rapid development of society. Sulphur present in transportation fuels lead to SO_x emission to air and inhibits the performance of pollution control equipment on vehicles and environments. To minimize the negative health and environmental effects from automobile exhaust, increasing regulatory pressures are imposed on oil refineries to reduce the sulphurs levels of the fuels, with the ultimate goal of zero emissions (Babich & Mouljin, 2003).

Thus, many alternative technologies to absorb sulphur from its origin (crude oil, gasoline and diesel) have been developed extensively. The one that show promising result which are ionic liquid with properties of non-volatile, non-flammable, and recyclable and have high affinity to sulphur-containing compounds and high thermal stability been developed and study widely.

In the future, the S-content in crude oil, gasoline and diesel oil after desulfurization will be probably have reached an average value of about 10 ppm in many countries. This means that the degree of S-conversion needed to meet this limit is 99.9%, if a typical S-content of crude oil of 1 wt% is taken as basis (Eber, Wasserscheid, & Jess, Deep desulfurization of Oil Refinary Systems by Extraction with Ionic Liquids, 2004, 6).

1.2 Problem Statement

Sulphur is one of the fuel-fraction components of which levels have to be reduced because of new environmental and engineering standards. Because of new and stringent regulations, desulfurizing of fuels has become increasingly important to petroleum industry. In refineries, hydrdotreating is a commonly used method to reduced sulphur in fuels. Unfortunately, the associated costs (e.g., equipment and hydrogen) are high.

Newly developed methods (Greenwood, Kidd, Gislason, & Slater, 2002) can also achieve desulfurization of gasoline but are less effective for diesel fuels. Certain sulphur compounds in diesel are less prone to react and remain in the fuel. An associated problem is the cross-contamination of fuels during pipeline transportation. Low sulphur that exit a pipeline at terminals may contain unacceptable high sulphur levels. Thus, an effective and easily applicable method needs to be found that can lower or remove sulphur containing compound while not effecting the fuel properties themselves. Current continuing studies shows extracting these sulphur compound from fuels with ionic liquid could offer such a solution.

Ionic liquid are mixtures of salts with low melting points. Because of their salt-like characteristics, they are non-volatile and non-flammable and exhibit a high ionic conductivity. The liquid phase is found over a wide temperature range up to 300°C. Ionic liquid are generally highly solvating and non coordinating (Viser, Holbrey, & Rogers, 2002). Both cations and anions of the salt determine physical properties (e.g., melting points, viscosity, density, solubility, etc.). For cations organic salt forming compounds (e.g, pyridine, imidazole, etc.) are often chosen (Zhang, Zhang, & Zhang, 2004). The anion moiety often consist of inorganic anion-forming components ($AlCl_3$, BF_3, etc.). Recently, ionic liquid were found to be effective in the desulfurization of model diesel fuels (dibenzothiophene(DBT) in dodecane) under mild conditions (Lu, Cheng, Gao, Gao, & He, 2007).

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1.3 Objectives

The main objectives of this study are:

i. To develop cost effective solid support ionic liquid compound that can be used to desulfurized crude oil and other hydrocarbon mixtures under mild condition.
ii. To synthesize 1-butyl-3-methylimidazolium Tetrachloroferrate [BMIM $(FeCl)_4$] solid support ionic liquid (SSIL).
iii. To evaluate desulfurization performance of synthesized SSIL on various types of hydrocarbons.

1.4 Scope of Study

This study is conducted to develop a new approach for preparing an ionic liquid compound that can be used to desulfurize hydrocarbon mixtures. The timeframe for this study is 1 year and will be done in two phase:

In the first phase, the project will be more on studying and researching for information on the journal and experiment report available in the net and library.

As for the second phase, by using all information and data gained from the first phase, a proper experiment will be done to achieve the objectives stated earlier. The project will be in the form of laboratory experiments. It composes of two stages which are experimenting and data analyzing stage. The effectiveness extraction of S-content from hydrocarbon compounds by appropriate ionic liquid are the main elements to be investigated.

CHAPTER 2

LITERATURE REVIEW & THEORY

2.1 Hydrodesulfurization

Hydrodesulphurization (HDS) is widely used in oil refining. It is carried out at high temperature with high-pressurized hydrogen along with catalyst. Hydrodesulphurization efficiency is limited to increasingly severe operating conditions at escalated cost. Not only does the energy consumption become intensive, but also more severe conditions require result in an increase energy consumption, which causes undesired side reactions. When gasoline is desulphurized at higher pressure, many olefins are saturated, resulting in lowered octane numbers. Higher temperature processing also leads to increase coke formation and subsequent catalyst deactivation (Babich & Mouljin, 2003).

The reactivity of organosulphur compound over HDS catalyst depends on the molecular structures of S-containing compounds (Ma, Sakanishi, & Mochida, 1994). The aliphatic organosulphur compounds are very reactive in conventional hydrotreating process, and they can be completely removed from the fuels without much difficulty. The aromatic sulphur compounds including thiophenes, benzothiophenes, and their alkylated derivatives, however, are generally more difficult to convert over HDS catalyst. Therefore the aromatic sulphur compounds present the most difficult challenges to HDS process (Eber, Wasserscheid, & Jess, Deep desulfurization of oil refinary streams by extraction with ionic liquids, 2003).

2.2 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.

2.2.1 Petroleum hydrocarbon structures

Petroleum consists of three major classes of hydrocarbon groups:

2.2.1.1 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).

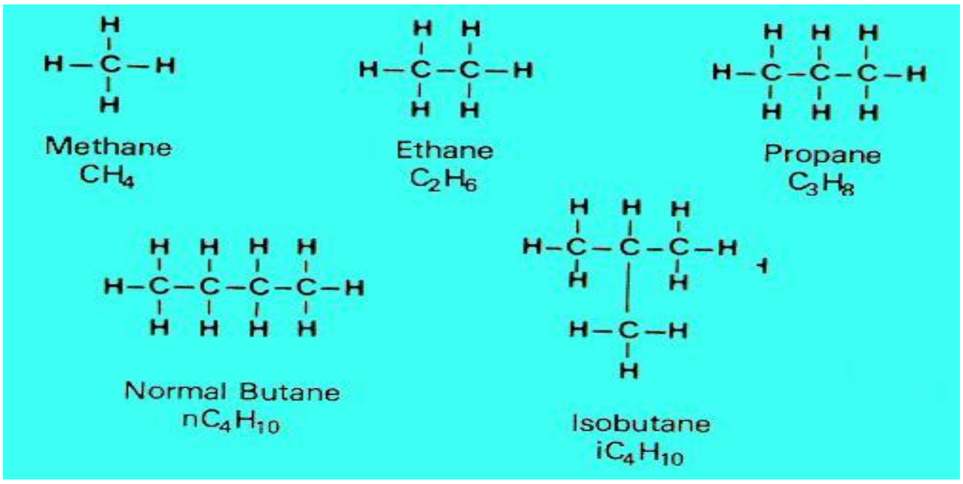
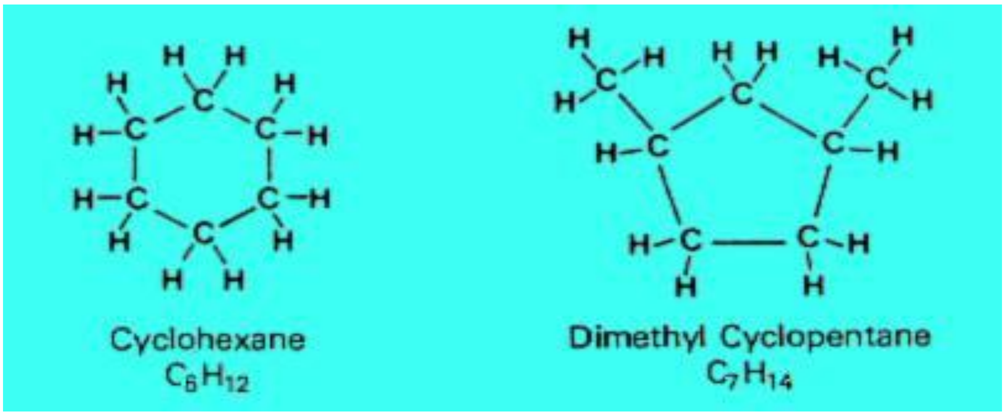


Figure 1 : Example of Paraffin Group

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.

2.2.1.2 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.



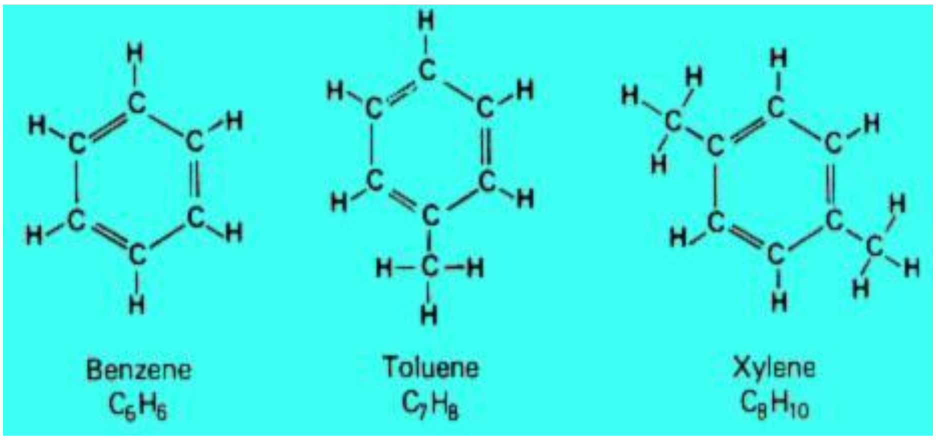
Cyclohexane C_6H_{12}

Dimethyl Cyclopentane C_7H_{14}

Figure 2 : Example of Napthenes Group

2.2.1.3 Aromatics

Aromatic hydrocarbons has the general formula of **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.



Benzene C_6H_6

Toluene C_7H_8

Xylene C_8H_{10}

Figure 3 : Example of Aromatic Groups

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 Ionic Liquid

Ionic liquids is a new class solvent in this chemistry world, the development of functionalized (or task-specific) ionic liquids received much attention due to the potential to impart the liquid with specific chemical and/or physical properties. These solvents are often fluid at room temperature, and consist entirely of ionic species. The ionic liquids also don't have measurable vapour pressure, and hence can emit no volatile organic compounds (VOCs) (Martyn & Kenneth, 2000). As they made up of at least two components which can be varied (the anion and cation), the solvents can be designed with a particular use in mind, or to possess a particular set of properties. In general, ionic liquids consist of a salt where one or both the ions are large, and the cation has a low degree of symmetry. These factors tend to reduce the lattice energy of the crystalline form of salt, and hence lower the melting point (Seddon, 1998).

Ionic liquids come in two main categories, namely simple salts (single anion and cation) and binary ionic liquids (salts with an equilibrium is involved). For example, $[EtNH_3][NO_3]$ is a simple salt, figure 2.1 shows simple room temperature ionic liquids.

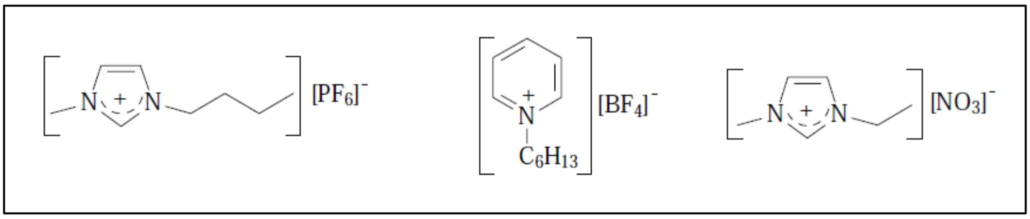


Figure 4 : Examples of simple room temperature ionic liquids

Whereas mixtures of aluminium (III) chloride and 1,3-dialkylimidazolium chlorides (a binary ionic liquid system) contain several different ionic species, and their melting point and properties depend upon the mole fractions of the aluminium (III) chloride and 1,3-dialkylimidazolium chlorides present (Hussey, Scheffler, Wilkes, & Fannin, 1986).

2.3 Imidazolium Based Ionic Lliquid

Salts of imidazole where the imidazole ring is in the cation are known as imidazolium salts (for example, imidazolium chloride). These salts are formed from the protonation or substitution at nitrogen of imidazole. These salts have been used as ionic liquids and precursors to stable carbons. Salts where a deprotonated imidazole is an anion are also possible; these salts are known as imidazolide salts (for example, sodium imidazolide).

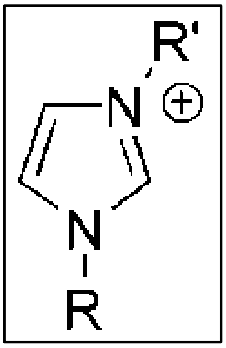


Figure 5 : Imidazolium structure

Interestingly, most of the published data relates to ionic liquids with imidazolium cations. 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.

The sulphur compounds studied by the literature are aromatic sulphur compounds, such as benzothiophene and DBT dissolved in dodecane as a model oil system. All those studies focused only on *N*-methylimidazolebased ILs. 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.

From studies of ionic liquids in refinery desulphurization, efficient sulphur removal could be achieved for imidazolium based ionic liquids with [BF_4], [PF_6], and alkylsulfate anions. In the first application (Eber, Wasserscheid, & Jess, Deep desulfurization of oil refinary streams by extraction with ionic liquids, 2003) used Lewis-acidic [RMIM]Cl/$AlCl_3$ (R=ethyl, butyl) compounds for extractive desulphurization, which could lower the sulphur content from 500 ppm to less than 10 ppm as shown in Figure (for R=butyl).

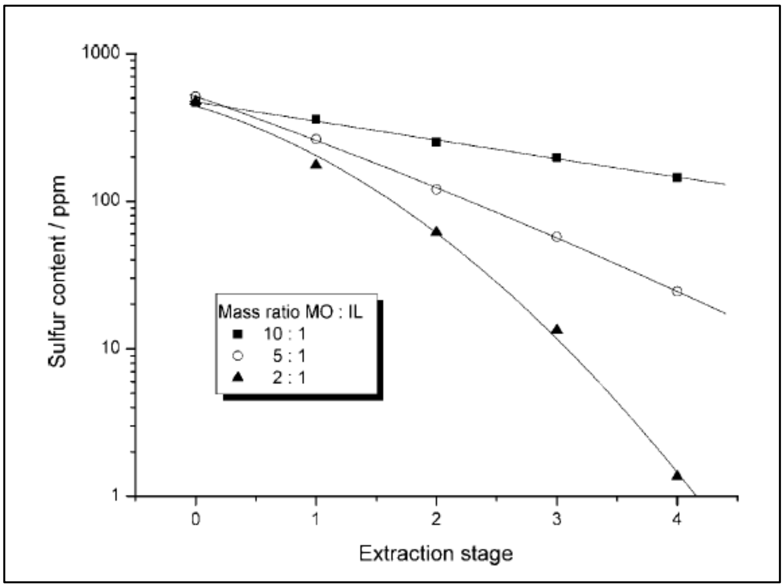


Figure 6 : Multistage extraction of a model oil (500 ppm dibenzothiophene in dodecane) using Lewis-acidic ionic liquid [BMIM]Cl/AlCl3 (0.35/0.65), as a function of different mass ratios between model oil and ionic liquid.

The extraction performance depended significantly on the mass ratio between the model oil (500 ppm DBT in dodecane) and the ionic liquid. With increasing ionic liquid mass ratio very low sulphur levels could be obtained after three or four extraction stages. The effective diffusion was low, probably because of the high viscosity of the ionic liquid. Because the reaction between DBT and the Lewis-acidic ionic liquid was not a physisorption but a chemisorption process, an efficient regeneration of the system is problematic. Zhang et al. studied the neutral ionic liquids [RMIM][BF_4] (R=ethyl, butyl) for the extraction of thiophenes.

Their results indicated that such aromatic sulphur compounds can be extracted efficiently, because p-interaction between the imidazolium ring and the substrate was observed. The use of halogen-free ionic liquids in a multistage extraction was also reported by (Eber, Wasserscheid, & Jess, Deep desulfurization of oil refinary streams by extraction with ionic liquids, 2003). Within five stages the sulphur content was reduced from 500 ppm to less than 10 ppm.

Regeneration of the ionic liquid was feasible because only physisorption occurred. The commercially available ionic liquid AMMOENG 102 was identified as a cheap and attractive ionic liquid for efficient liquid–liquid biphasic multistage extraction. Complete regeneration of the ionic liquid is mandatory for an economically viable desulphurization process because ionic liquids are expensive in comparison to molecular solvents. Regeneration can be achieved either by distillation, leaving the purified ionic liquid as the bottom phase, or by reextraction with another solvent. The re-extracted solvent can then itself be regenerated by distillation.

In addition to desulphurization, the denitrogenation of refinery streams is also of interest, as N-compounds (above all basic N compounds like quinolines and acridines) strongly inhibit the HDS reaction (Girgis & Gates, 1991). Alternative concepts discussed in this literature are adsorption and selective extraction. Extractive desulphurization is another alternative concept that is carried out at or around ambient temperature and pressure and without the need for hydrogen. In general, an ideal extracting agent should have the following properties:

1. The partition coefficient for S-compounds (ratio of S-concentration in the extracting agent to the one in the oil), above all for dibenzothiophene- derivatives, should be high (but not too high if the extracting agent has to be regenerated by reextraction with suitable hydrocarbons)
2. The regeneration should be easy, *e.g.* by distillation, or at least the extraction should be reversible.
3. The agent should be absolutely insoluble in oil.
4. The (S-free) hydrocarbons of the oil matrix should not, or only to a small extent, be soluble in the extracting agent.

5. The agent should feature a high thermal and chemical stability, be non-toxic and environmentally benign.

The method from Eber et. al.,(2004) by identified most ideal candidates for the application which is ionic liquids, which are low melting salts (<100°C) with no measureable vapour and pressure. It is found that Early experiments on the selective extraction of S-compounds from model diesel oil (mixture of *n*-dodecane with DBT-derivatives) using chloroaluminate ionic liquids like [BMIM][$AlCl_4$] showed promising results with a high Nernst partition coefficient K_N as shown in table below which is defined in this work as the ratio of the concentration of sulphur in the IL ($mg_S\ kg_{IL}^{-1}$) to the S-concentration in the oil ($mg_S\ kg_{oil}^{-1}$).

Table 1 : Sulphur partition coefficients K_N for extraction with ionic liquids

Ionic Liquid	**K_N in mg(S) kg (IL) $^{-1}$/ mg(S) kg(oil)$^{-1a}$**
[BMIM]Cl/$AlCl_3$	4.0
[BMIM][BF_4]	0.7
[BMIM] [PF_6]	0.9
[BMIM] [$OsCO_4$]	1.9
[BMIM] [$EtSO_4$]	0.8
[BMIM] [Me_2PO_4]	0.7
Model oil: 500 ppm S as DBT in n-Dodecane; mass ration 1:1 mixing time 15 min, room Temperature	

Nevertheless, the use of chlorometallate ILs is not desired for technical large scale applications due to their very limited hydrolysis stability and in some cases toxicity. Further screening experiments with alkylimidazolium tetrafluoroborate ([BMIM][BF4]) and hexafluorophosphate ILs ([BMIM][PF6]) were found to also have fairly high partition coefficients for model S- compounds. Although ILs of this type are significantlynmore stable to hydrolysis, their use as a large scale extracting agent is not optimal because of the relatively high price of the starting material. Additionally the formation of hydrolysis products especially HF is observed at elevated temperatures and in the presence of water (Swatloski, Holbrey, & Rogers, 2003).

To avoid these stability and corrosion problems the present work concentrated on completely halogen-free ILs for the extraction of S- and N-compounds. Very promising ILs are 1-*n*-butyl-3-methylimidazolium octylsulfate, [BMIM][OcSO4], 1-ethyl-3-methyl-imidazolium ethylsulfate, [EMIM][EtSO4] and 1,3-dimethylimidazolium dimethylphosphate, [MMIM][Me2PO4]. This paper shown ionic liquids have an excellent extraction properties for organic S- and N-compounds and if carefully chosen, also will act as excellent extraction in insoluble oil.

Field of the synthesis of new ionic liquids and their application for the desulphurization of hydrocarbon fractions by means a liquid-liquid extraction (ionic liquid-hydrocarbon fraction) method. This removal of sulphur compounds is carried out due to the higher affinity among sulphur-containing compounds and the ionic liquid media with respect to the very low polarity of the hydrocarbon media. By means a vigorous stirring between the low immiscible phases following by phase separation step, the sulphur content in the hydrocarbon phase is considerably reduced.

The ionic liquids employed by Liknahova et. al.,(2009) present general formula C^+ and A^- where C^+ is an organic cation and A^- is the anion. The cation, C^+ can be for example an alkylpyridium, alkylimidazolium, dialkylimidazolium and 1,2,3-trialkylimidazolium while anion A^- is $FeCl_4$. Cation Imidazole and pyridine derivatives were derived in this literature.

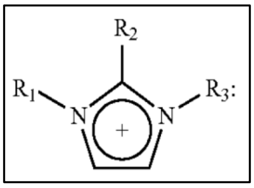


Figure 7 :
Imidazolium Ring

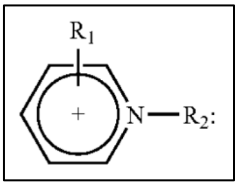


Figure 8 :
Pyridine Ring

Process for the synthesis of ionic liquids which can be used for the efficient removal of sulphur compounds from hydrocarbon mixtures. The ionic liquids related are insoluble in hydrocarbons but are able to dissolve aliphatic and aromatic sulphur compounds. Thus, the ionic liquids can be used for removal of sulphur compounds by a liquid-liquid extraction process at room temperature and pressure. The literature is also directed to a process for extracting sulphur from a hydrocarbon liquid by contacting the hydrocarbon with the ionic liquid.

More preferably, the synthesis of ionic liquids with general formula C^+A^-, where C^+ is an organic cation preferably but not exclusively alkyl pyridinium, dialkylimidazolium, and trialkylimidazolium, the anion A^- is preferably halogen ferrate (III), particularly $Cl*FeCl_3^-$ and $Br*FeCl_3$. The method is also directed to the process for the extraction of sulphur-containing compounds, such as sulphur compound that are present in gasoline and Diesel as contaminant obtained in petroleum refining processes by contacting with the ionic liquids. Result for several ionic liquid experiment shown in table below.

Table 2 : Hydrocarbon removal by extraction with ionic liquids

Ionic Liquid	**Final sulphur content in hydrocarbon (ppm)**	**% of total removed sulphur in hydrocarbon**
[BMIM][$FeCl_4$]	>10	99
[BDMIM][$FeCl_4$]	>10	99
[BDIM][$FeCl_4$]	14	97
[OP][$FeCl_4$]	152	70
[HEMIM][$FeCl_4$]	352	35

From table the ionic liquids with the tetrachloroferrate anion can almost quantitatively remove the sulphur content of the sample original model, especially the ionic liquids with imidazolium cation. Thus, the ionic liquids can be used for the deep desulphurization of hydrocarbon mixtures, such as, gasoline, diesel engine fuel, kerosene, jet fuel and light cyclical oil.

It can be concluded the use of ionic liquids containing halogens of Fe (III) as an anion for these purposes, where these compounds presented very high efficiency for extracting sulphur-containing compounds from gasoline, turbosin, diesel and other petroleum fractions. Another important and novel aspect of the invention is the use of microwave irradiation for synthesizing the ionic liquids suitable for use as extracting agents (symmetric and non-symmetric compounds) with a corresponding shorter time and higher yields in the synthesis of these ionic liquids compared to the conventional methods of synthesis.

Liknahova et. al.,(2009) method also directed to a process for extracting sulphur and sulphur compounds from a sulphur-containing hydrocarbon liquid by contacting the hydrocarbon liquid with an ionic liquid of the invention for sufficient time to extract the sulphur and sulphur-containing compounds, and thereafter recovering the hydrocarbon liquid.

2.4 Liquid-Liquid Extraction

Liquid-liquid extraction involves using a liquid solvent to remove a liquid component from a liquid mixture. The component dissolve preferably in the solvent. Applications of this process include removal of vitamins from aqueous solutions and aromatic compounds from crude oil fractions.

The transition component A is combined with the career liquid C as the initial mixture (feed). If the initial mixture and the solvent B are mixed together, the transition component A is transferred into the solvent B. The requirement for this is that the solubility of the transition component A in the solvent B is higher than in the carrier liquid C. in turn, the carrier liquid C should be almost insoluble in the solvent B.

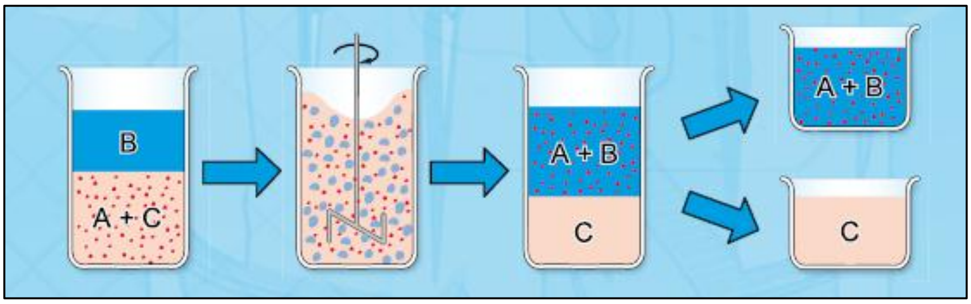


Figure 9 : Liquid-liquid extraction

The example in figure assumes an ideal situation in which the transition component A is completely taken up by the solvent. In reality, residual transition component always remains in the carrier liquid. In addition, complete insolubility of the carrier liquid in the solvent assumed. In practice, parts of one substance will always be found in the other.

This means that the actual separation process results in two phases after settling:

i. Extract phase (mainly A and B, with residue of C)
ii. Raffinate phase (mainly C, with residue of A and B)

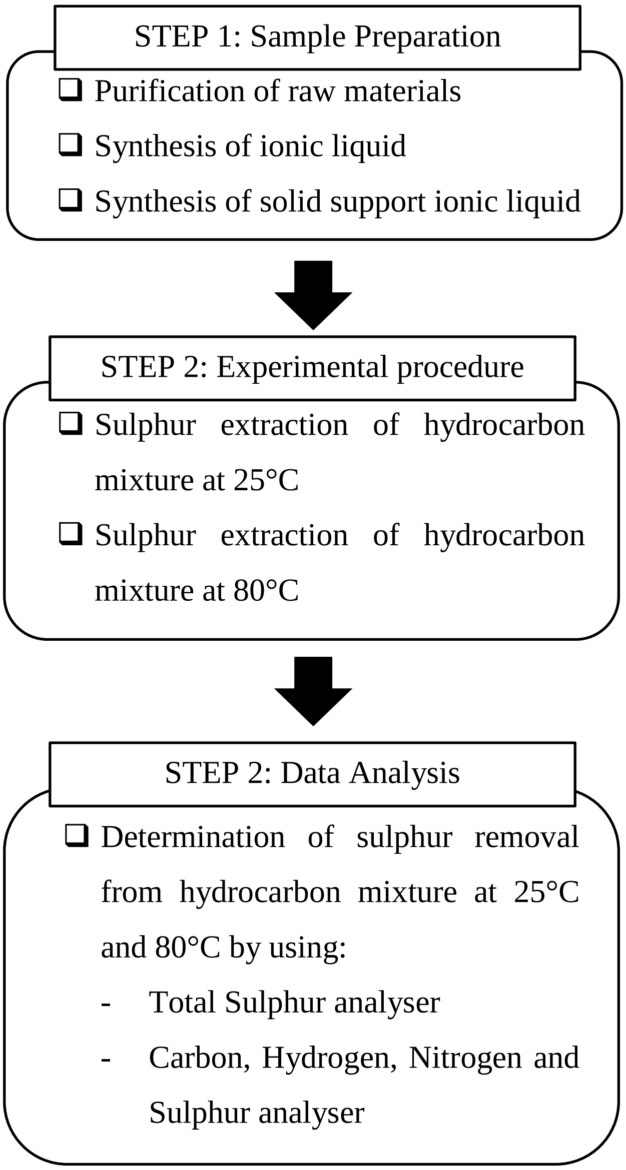
To obtain the purest possible transition component, the extraction is normally followed by a separating stage that takes the form of rectification, in which the solvent is separated from the transition component. The solvent can be recirculated and is then available for extraction again.

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

An experimental of the materials, experimental methodology and approach used for data analysis are presented in this chapter. Below are simplified overall methodology that has been completed to conduct this project.



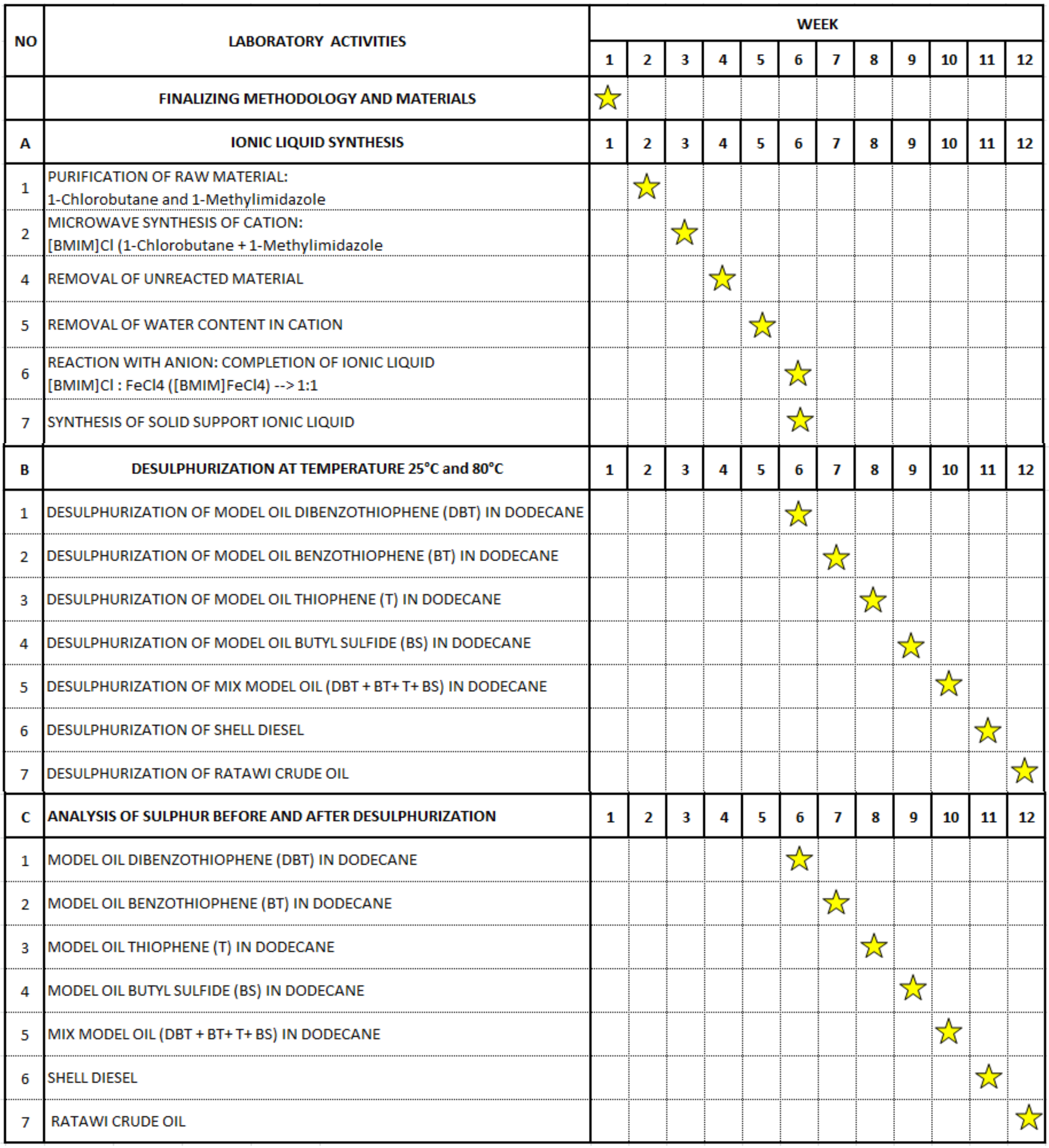
3.2 Key Milestone

Table 3 : Key milestone for project activities

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Project Work Continues	🟩	🟩	🟩	🟩	🟩	🟩	🟩	Mid-Semester Break								
2	Submission of Progress Report									●							
3	Project Work Continues									🟩	🟩	🟩	🟩	🟩			
4	Pre-EDX												●				
5	Submision of Draft Report													●			
6	Submission of Dissertation (soft bound)														●		
7	Submission of Technical Paper														●		
8	Oral Presentation															●	
9	Submission of Project Dissertation (Hard Bound)																●

3.3 Gantt Chart

Table 4 : Gantt chart for laboratory activities



NO	LABORATORY ACTIVITIES	WEEK											
		1	2	3	4	5	6	7	8	9	10	11	12
	FINALIZING METHODOLOGY AND MATERIALS	☆											
A	**IONIC LIQUID SYNTHESIS**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
1	PURIFICATION OF RAW MATERIAL: 1-Chlorobutane and 1-Methylimidazole		☆										
2	MICROWAVE SYNTHESIS OF CATION: [BMIM]Cl (1-Chlorobutane + 1-Methylimidazole			☆									
4	REMOVAL OF UNREACTED MATERIAL				☆								
5	REMOVAL OF WATER CONTENT IN CATION					☆							
6	REACTION WITH ANION: COMPLETION OF IONIC LIQUID [BMIM]Cl : FeCl4 ([BMIM]FeCl4) --> 1:1						☆						
7	SYNTHESIS OF SOLID SUPPORT IONIC LIQUID						☆						
B	**DESULPHURIZATION AT TEMPERATURE 25°C and 80°C**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
1	DESULPHURIZATION OF MODEL OIL DIBENZOTHIOPHENE (DBT) IN DODECANE						☆						
2	DESULPHURIZATION OF MODEL OIL BENZOTHIOPHENE (BT) IN DODECANE							☆					
3	DESULPHURIZATION OF MODEL OIL THIOPHENE (T) IN DODECANE								☆				
4	DESULPHURIZATION OF MODEL OIL BUTYL SULFIDE (BS) IN DODECANE									☆			
5	DESULPHURIZATION OF MIX MODEL OIL (DBT + BT+ T+ BS) IN DODECANE										☆		
6	DESULPHURIZATION OF SHELL DIESEL											☆	
7	DESULPHURIZATION OF RATAWI CRUDE OIL												☆
C	**ANALYSIS OF SULPHUR BEFORE AND AFTER DESULPHURIZATION**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
1	MODEL OIL DIBENZOTHIOPHENE (DBT) IN DODECANE						☆						
2	MODEL OIL BENZOTHIOPHENE (BT) IN DODECANE							☆					
3	MODEL OIL THIOPHENE (T) IN DODECANE								☆				
4	MODEL OIL BUTYL SULFIDE (BS) IN DODECANE									☆			
5	MIX MODEL OIL (DBT + BT+ T+ BS) IN DODECANE										☆		
6	SHELL DIESEL											☆	
7	RATAWI CRUDE OIL												☆

3.4 Experimental

Taken together, the results of these past researches indicate that certain species of ionic liquids gives promising result to desulphurize sulphur from model oil (Kuhlmann et. al, 2009, Eber et. al.,2004, Liknahova et. al.,2009). It can be assumed from technical paper that temperature, species of ionic liquids, molar ratio and time taken will give significant effect to the desulphurization of crude oil even if the properties and chemical in crude oils differ from model oil. Therefore, the various process variable will help to determine the efficient result of desulphurization.

Hence, this project is basically the continuation and improvement of the studies done by the said researchers (Kuhlmann et. al, 2009, Eber et. al.,2004, Liknahova et. al.,2009). In the research Liknahova et. al.,(2009), most efficient and promising anions is $FeCl^-$ species. Properties of chemical, reaction and physical of $FeCl^-$ are evaluated thus the ionic liquid anion $FeCl^-$ based studied in this project.

Experiment will be conducted in three stages which are:

a) Purification of raw materials
b) Synthesis of ionic liquids and solid support ionic liquid
c) Sulphur extraction using solid support ionic liquid

3.4.1 Purification of raw materials

Raw materials of the ionic liquid needs to be purified to obtain pure ionic liquid with less impurities. There are two raw materials to synthesis ionic liquid [BMIM]$FeCl_4$ which are 1-Chlorobutane and 1-methyimidazole. In this project, only 1-Chlorobutane been purified by author since 1-methylimidazole have been purified by researcher in the laboratory.

3.4.1.1 Purification of 1-Chlorobutane:

Chemicals needed:

2. 1-Chlorobutane
3. Concentrated hydrochloric acid (H_2SO_4)
4. Distilled water
5. Aqueous sodium bicarbonate ($NaHCO_{3(aq)}$)
6. Calcium Chloride ($CaCl_2$)

Reaction & Chemicals:

1-Chlorobutane + H_2SO_4 + Distilled Water + $NaHCO_{3(aq)}$ + more water + $CaCl_2$

Procedure:

1. Shake repeatedly 1-Chlorobutane and concentrated H_2SO_4 in funnel separator.
2. Two layers will be identified in the funnel.
3. 1-Chlorobutane will be at the upper layer. While H_2SO_4 will be the lower layer. *H_2SO_4 will absorb any impurities in 1-chlorobutane. (very cloudy color of H_2SO_4 shows present of many impurities)*
4. Decant off the lower layer. Add more H_2SO_4.
5. Repeat shake and add H_2SO_4 (approximate 3 times) until no further colour develop in the acid.

Figure 10 : Two layers of impurities and 1-chlorobutane

6. Decant off clear color of H_2SO_4. Wash remain 1-Chlorobutane with Aqueous $NaHCO_3$ and more water.
7. Decant off $NaHCO_3$.
8. Add $CaCl_2$ into the funnel separator to absorb remain water presence with 1-Chlorobutane.
9. To separate $CaCl_2$ from washed 1-chlorobutane, use funnel and filter paper.
10. Distilled separated 1-Chlorobutane.
11. Add boiling chips to enhance boiling rate of 1-chlorobutane and anti-bumping granule to prevent overshoot of 1-chlorobutane during distillation.

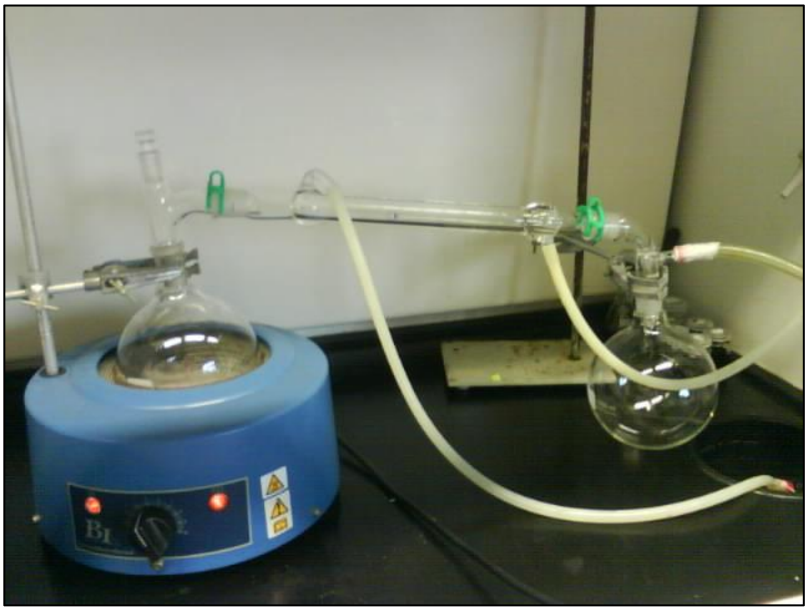


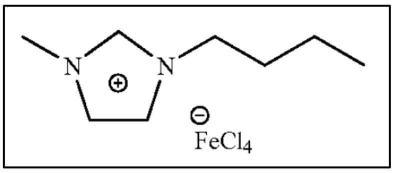
Figure 11 : Distillation of washed 1-chlorobutame

12. Finally purified 1-chlorobutane obtained

Figure 12 : Purified 1-Chlorobutane

3.4.2 Synthesis of ionic liquid

[BMIM]$FeCl_4$ (1-butyl-3-methylimidazolium Tetrachloroferrate)



Materials:

1. 10.0 mL of 1-methylimidazole
2. 17.2 mL of 1-chlorobutane
3. 3x20 ml ethyl acetate
4. 1.22 g or 7.5 mmol iron chloride (iii) anhydrous

Equipment:

1. 4 units of Quartz Vessel
2. Microwave
3. Magnetic stirrer

The experiment was performed utilizing the Anton Paar Synthos 3000, employing a fully equipped Rotor 8XQ80 with immersing T-Probe. Each quartz vessel equipped with a stir bar, was charge with 10.0 mL of purified 1-methylimidazole and 17.2 mL purified 1-chlorobutane. with maximum of 1000 W the nest mixtures were heated in a 5 min ramp up to 170°C and kept the target temperature for additional 7 minutes.

After cooling the resulting highly viscous ionic liquid can be poured out of the vessel, likely even crystallization will occur (mp~60°C)

Figure 13 : Anton paar microwave

3.4.2.2 Synthesis of anion [BMIM]Cl

1. 10.0 mL of purified 1-methylimidazole was mixed with 17.2 mL purified 1-chlorobutane in quartz vessel.
2. Two phase mixture was formed after 10 hours of stirring and heating in microwave. The top layer that consist of unreacted material was decanted off.
3. Residue of unreacted was washed and absorbed with 3x20 ml ethyl acetate.

Figure 14 : Two layers of anion and unreacted materials

4. After wash [BMIM]Cl_3 with ethyl acetate. Remove the remain ethyl acetate from [BMIM]Cl_3.
5. Ethyl Acetate that could not be removed physically can remove by using Rotary Evaporator.
6. Set Temperature to 80°C and time for approximate 10 hours.

Figure 15 : Removal of ethyl acetate and unreacted material by rotary evaporator

7. A highly viscous colourless liquid of 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) was obtained.
8. Liquid [BMIM]Cl then converted to solid form to prevent water from moisture easily penetrate through the anion. Solidification is to prevent impurities formation of the chemical with water presence.
9. To enhance solidification process. Seeding process is recommended.

Seeding: Add small portion of commercial [BMIM]Cl3 into formed $[BMIM]Cl_3$ *and put it in ice bath for approximate 1-2 hour.*

Figure 16 : Commercial $[BMIM]Cl_3$

Figure 17 : $[BMIM]Cl_3$ in ice bath after seeding

Figure 18 : Solidified [BMIM]Cl

3.4.2.2 Synthesis of ionic liquid

1. In glass reactor that is equipped with magnetic stirring mechanism 73.74 1-butyl-3-methylimidazolium chloride was introduced and 73.74 g iron chloride (iii) anhydrous was added.
2. Mixture was stirred for 24 hours at room temperature under an inert atmosphere.
3. A dark liquid of [BMIM]($FeCl_4$) was obtained.

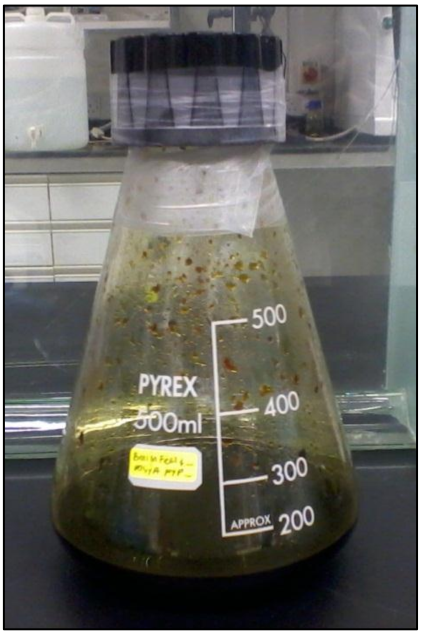


Figure 19 : Dark liquid of [BMIM]$FeCl_4$

3.4.2.3 Solid support ionic liquid

The pore size for 5A Molecular Sieve is used. It can adsorb all kinds of molecular smaller that this size. It is mainly used in separation of the normal an isomerism-alkyl, pressure swing adsorption for gases: Co-adsorption for moisture and carbon dioxide, based on the industrial application specialties.

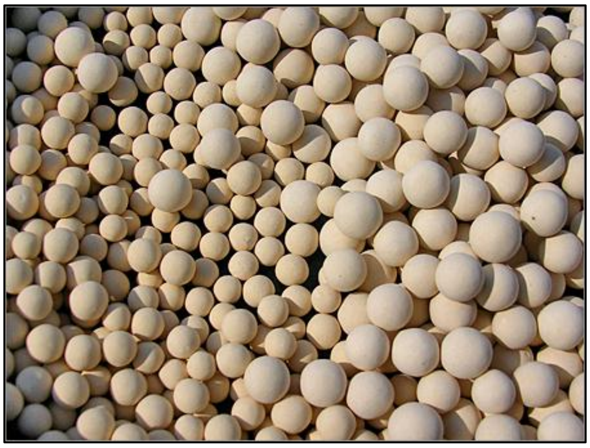


Figure 20 : Molecular sieve beads

Solid Support Ionic Liquid were suggested as sulfur extraction material since naked eye can’t differentiate separation between ionic liquid and crude oil because of dark colour of both materials.

Figure 21 : Ionic liquid and Ratawi crude oil could not be differentiated

To create an optimum, evenly and nicely distributed ionic liquid content in molecular sieve, 20 wt% of ionic liquid in molecular sieve was prepared.

Procedure:

1. 50 g of molecular sieve place into oven for drying.
2. 10g or ionic liquid mixed together with 40 g molecular sieve and methanol used as solvent to enhance mixing and distribution between molecular sieve and ionic liquid.
3. Methanol solvent removed from solid support by rotary evaporator process.
4. Dry solid support ionic liquid obtained.

Figure 22 : Solid support ionic liquid

3.4.3 Sulphur extraction using solid support ionic liquid

Extraction were done by contacting 1g of solid support ionic liquid with 5g of hydrocarbon mixtures. The ratio is equivalent to 1g of ionic liquid with 25g of hydrocarbon mixtures.

Extraction occurs at two temperature condition which are mild condition (25°C) and offshore based temperature (80°C) for 1 hour. Since 1 hour is optimum time for refinery to stabilize crude oil from offshore and cracking process.

There are five types of hydrocarbon used to test the performance of solid support ionic liquid

i. Dibenzenethiophene (DBT) in dodecane.
ii. Benzenethiophene (BT) in dedecane.
iii. Thiophene (T) in dodecande.
iv. Butyl Sulfide (BS) in dodecane.
v. Shell Diesel
vi. Ratawi crude oil

Each sample was triplicate for each condition extraction process to get average value of extraction and obtain accuracy of the process.

Figure 23 : Extraction process of hydrocarbon mixtures

3.4.3.1 Analysis of sulphur content before and after extraction

Since there are so many sulphur species presence in Ratawi crude oil, final sulphur content were determined by total sulphur analyser (TSA). Total sulphur analyser is a complete analytical system allowing the direct measurement of total sulphur in a wide variety of sample matrices and concentrations. It consist of a dual zone, high temperature furnace and a sulphur coulometer.

Figure 24 : Total sulphur analyzer

CHAPTER 4

RESULTS AND DISCUSSION

Parameter of the first condition extraction process are as follow:

1. Type of extraction : Solid-Liquid extraction
2. Temperature : 25°C (Room temperature)
3. Extraction time : 1 hour/extraction
4. Stirr rate : 800 rpm (Ratawi crude oil highly viscous)

Table 5 : Sulphur removal at room temperature

Sample	Before	After	% S Removal
DBT in Dodecane	0.9405	0.7556	20 %
BT in Dodecane	2.6234	2.0449	22 %
T in Dodecane	1.8815	1.7638	6 %
BS in Dodecane	2.0683	1.8500	11 %
Shell Diesel	0.1282	0.1095	15 %
Mix Model Oil in Dodecane	6.2305	6.1464	1 %
Ratawi Crude	4.2592	4.1461	3 %

Parameter of the first condition extraction process are as follow:

1. Type of extraction : Solid-Liquid extraction
2. Temperature : 80°C (Operation temperature)
3. Extraction time : 1 hour/extraction
4. Stirr rate : 800 rpm (Ratawi crude oil highly viscous)

Table 6 : Sulphur removal at operating condition

Sample	**Before**	**After**	**% S Removal**
DBT in Dodecane	0.8075	0.7154	11 %
BT in Dodecane	2.8520	2.0697	27 %
T in Dodecane	1.9753	1.9214	3 %
BS in Dodecane	2.2858	2.1068	8 %
Shell Diesel	0.1239	0.1122	9 %
Mix Model Oil in Dodecane	6.9060	6.5288	5 %
Ratawi Crude	4.0080	3.4094	15 %

Summarize of extraction:

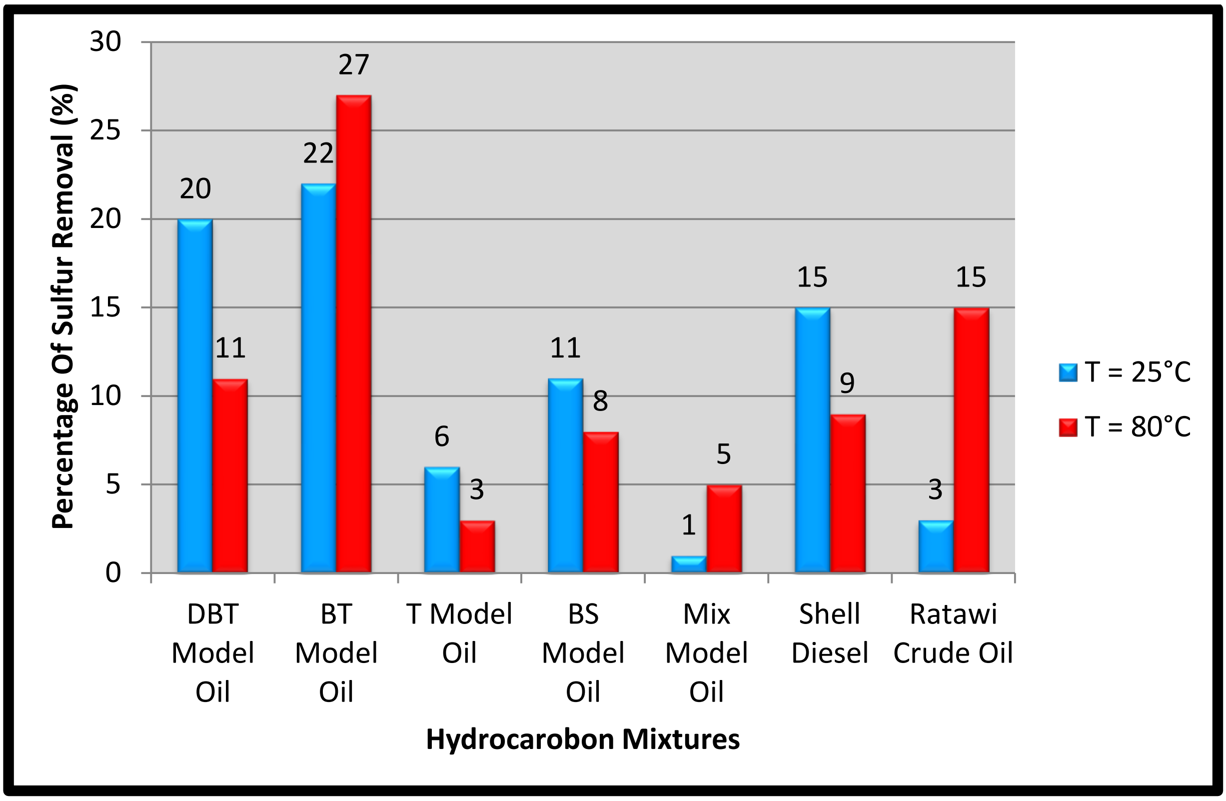


Figure 25 : Summarize of sulphur in hydrocarbon extraction

From the results obtain, it is concluded that solid support extraction performance of 1:5 solid support ionic liquid to hydrocarbon mixtures take place differently with different types of sulphur species in model oil and temperature.

It is observed that extraction of Ratawi crude oil most effective at temperature of 80°C which is 15% compared to at room temperature, 3%. However, the performance was different with shell diesel where its performance most effective on mild condition of 25°C which is 15% compared to operation temperature, 3%.

Hence, this method can be apply to Ratawi crude oil before the oil enter processing stage. A five stages packed bed reactor can be installed before furnace with expected of sulphur removal 75%. On Shell diesel, this method can be apply after cracking process before the diesel send to storage tank with expected sulphur removal of 75%.

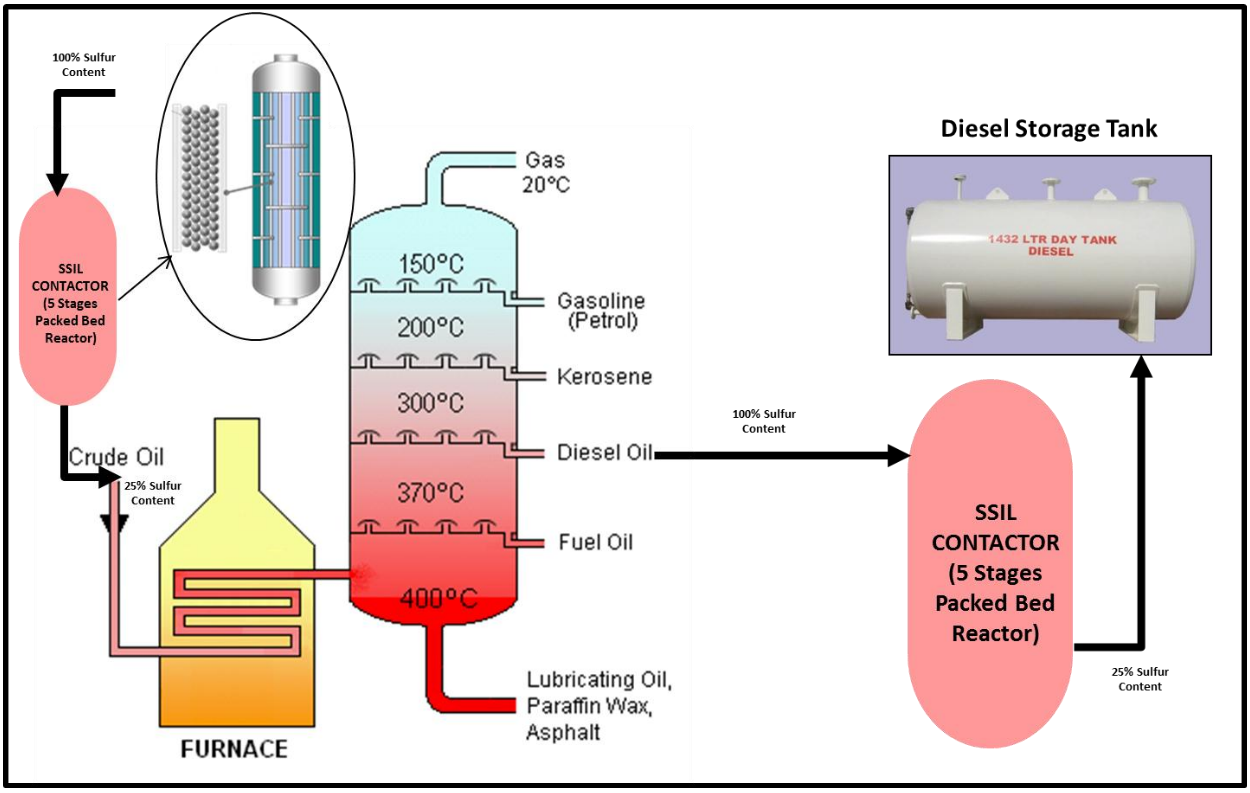


Figure 26 : Suggestion application of solid support ionic liquid

CHAPTER 5

CONCLUSION AND RECOMMENDATION

In conclusion, result and analysis of the experiment is coherent with the information obtained from the literature reviews previously done. The results prove that solid support ionic liquid can minimize usage of ionic liquid in the extraction process but still able to perform well for extracting sulphur content from natural sources.

Since the ionic liquid candidate itself can be reuse and regenerated, further research can be conducted on recycle and regeneration of solid support ionic liquid. Therefore the success of the experiment will change the industry application of desulphurization in term of safety and cost effective.

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