

**Desulfurization of Dibenzothiophene, DBT from Model Oil and Real Diesel by
Extraction with [BMIM]CoCl₃ Ionic Liquids**

by

Mohamad Yamin Mohamad Yacob

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

MAY 2012

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,



(AP Dr. Mohamad Ibrahim Abdul Mutallib)

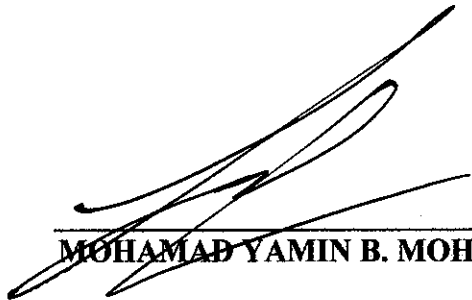
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May 2012

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.



MOHAMAD YAMIN B. MOHAMAD YACOB

ABSTRACT

The ionic liquids 1-Butyl-3-methylimidazolium-Cobalt Chloride ([BMIM]CoCl₃) was utilized as the solvent for the extractive desulfurization of model oil (Dodecane) and diesel fuel at different temperatures and ratios of [BMIM]CoCl₃ and Dodecane or Diesel. The extraction performance was tested first using dodecane spiked with known quantity of Dibenzothiophene (DBT) before moving to the commercial diesel from refinery. The amount of DBT extracted decreases with increasing temperature of the extraction. Nevertheless the extraction performance on the model oil seems to be almost complete with extremely little sulfur left over. [BMIM]CoCl₃ was found to work best at ambient temperature of T=25°C as the DBT extraction for every single ILs:Oil ratio tested resulted in complete is extraction.. A test with non-sulfur component spikd in the dodecane shows that the ionic liquid did not extract it. The [BMIM]CoCl₃ shows great potential to be an excellent sulfur extractant agent especially DBT compounds in both model oil and real diesel.

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Abbreviations and Nomenclatures

ILs	Ionic Liquids
DDC	Dodecane
DBT	Dibenzothiophene
HDS	Hydrodesulfurization

CHAPTER 1

INTRODUCTION

1.1. Project Background

Sulfur compounds or its derivatives which present in the fuels it the cause of environmental pollution which will produce SO_x from the exhaust. In order to cope this problems, many countries are planning to reduce the sulfur level in fuels to 10 ppm or below in the next few years. It is also a promising alternative method to the conventional method of removing sulfur compounds from fuels using catalytic hydrodesulfurization (HDS) for industrial purpose. The major drawbacks of HDS are operating at high temperature ($>300\text{ }^\circ\text{C}$), high pressure ($> 4\text{ Mpa}$), contribute to high energy consumption and having difficulty to remove aromatic sulfur compounds such as Dibenzothiophene (DBT).

So far, Ionic Liquids (ILs) are getting much attention in research world especially in extractive desulfurization process. ILs are organic salts with unique chemical and physical properties such as negligible vapour pressure, low toxicity, high chemical and thermal stability and ability to dissolve in a wide range of organic and inorganic compounds. Previous studies work by Gao [1] has reported and confirmed that ILs have high extraction ratios and greater selectivity compared to molecular solvents because of its unique characteristics. Many researchers have been experimenting on different species of ILs with different conditions such temperatures, molar ratios, reaction times and the recycling extractive effectiveness.

The sulfur compounds of DBT is studied as it is the most difficult sulfur derivatives to be extracted from the fuels, so the experiments will be run using Dodecane which will be injected with certain amount of DBT and the results will be the extractive capabilities of $[\text{BMIM}]\text{CoCl}_3$ IL.

1.2. Problems Statements

Sulfur compounds present in the fuels lead to the emission of SO_x and further pollute the environment. To reduce the sulfur emission to the atmosphere, fuels used by vehicles has to be very low in sulfur. Strict environmental regulations have put this into much attention to invent new methods to achieve deep desulfurization (< 10ppm) which conventional methods cannot achieve. .

Current technology which is HDS has many drawbacks as mentioned above in the Introduction section. High energy consumption put HDS in a very bad positioned especially in industrial applications. Furthermore, HDS is not very capable of removing aromatic sulfur compounds such as DBTs and benzothiophenes from the fuels. In order to remove DBT in HDS, the required conditions, that is, temperatures about 373 °C and pressures in the range of 50 to 100 bar. These operating conditions resulting in large hydrogen consumption and further increase the energy consumption.

1.3. Objective & Scope of Study

The scope of this project will be focusing on the extractive performance or capability of $[\text{BMIM}]\text{CoCl}_3$ IL to extract DBT from Dodecane in specified conditions. Below are the objectives of this study:

- i. To understand the behaviours of ILs, generally and $[\text{BMIM}]\text{CoCl}_3$, specifically.
- ii. To determine the DBT extractive capability of $[\text{BMIM}]\text{CoCl}_3$.
- iii. To compare the DBT extractive capability of $[\text{BMIM}]\text{CoCl}_3$ with other studied ILs

CHAPTER 2

LITERATURE REVIEW

2.1. Ionic Liquids Properties

As mentioned earlier, 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, but focusing on extractive desulfurization, attention is centred in finding ILs which is nontoxic, thermally stable, nonsensitive to moisture and air, has a low cost for commercial applications and has high extractive performance. General ILs properties are presented as below:

Table 1: Ionic Liquids Properties

A salt	Cation and anion quite large
Freezing Point	< 100 °C
Liquidus range	> 200 °C
Thermal stability	Usually High
Viscosity	< 100 cP
Dielectric constant	Implied < 30
Polarity	Moderate
Specific conductivity	< 10mScm ⁻¹ , "Good"
Molar conductivity	< 10 Scm ² mol ⁻¹
Vapor pressure	Negligible

The solubility of different species in imidazol ILs depends mainly on polarity and hydrogen bonding ability. According to Johnson [2], saturated aliphatic compounds are generally only sparingly soluble in ILs; whereas olefins show greater solubility and aldehydes can be completely miscible. On the other hand, light hydrocarbons such as gasoline and diesels are nearly immiscible in ILs. This has been exploited in liquid extraction of fuels to remove unwanted compounds such as sulfur as the separation of both liquids can be separate physically and the cost for ILs regeneration is very low.

2.2. Conventional Fuel Hydrodesulfurization, HDS Process

In the petroleum industry, low-sulfur fuels such as gasoline and diesel are mostly obtained from hydrocracking or hydrotreating processes. Although hydrotreating such as hydrodesulfurization has been very effective for the reduction of sulfur levels to below than 500ppm, but the process required severe operational conditions and cost.

2.2.1. HDS Process Description

The image below is a schematic depiction of the equipment and the process flow streams in a typical refinery HDS unit.

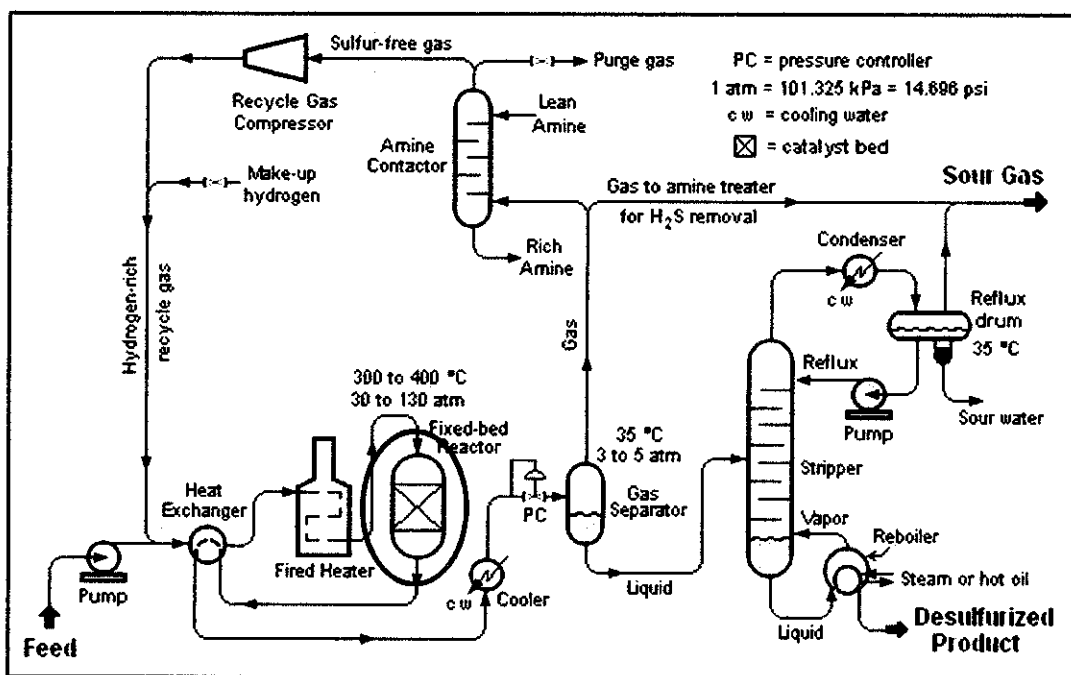


Figure 1: Schematic diagram of a typical Hydrodesulfurization (HDS) unit in a petroleum refinery

The HDS process takes place in a fixed bed reactor at elevated temperatures ranging from 300 to 400 °C and elevated pressures around 30 to 130 atm in the presence of a catalyst consisting of an alumina base impregnated with cobalt and molybdenum (CoMo Catalyst). Sometimes, a combination of nickel and molybdenum is used together with CoMo catalyst to treat hardcore feedstock such as those containing a high level of chemically bound nitrogen.

The refinery HDS feedstocks (naphtha, kerosene, diesel oil, and heavier oils) contain a wide range of organic sulfur compounds, including thiols, thiophenes, organic sulfides and disulfides, and many others. These organic sulfur compounds are products of the degradation of sulfur containing biological components, present during the natural formation of the fossil fuel, petroleum crude oil.

The most common substrates presences in crude oil feedstock is aromatic sulfur-containing heterocycles called thiophenes. There are various kinds of thiophenes ranging from thiophenes itself to more condensed species or derivatives called benzothiophenes and dibenzothiophenes. The species of thiophenes to benzothiophenes is fairly easy to be removed but dibenzothiophenes are the most challenging compounds to be removed by HDS process.

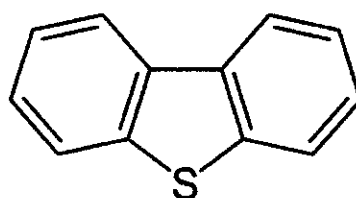


Figure 2: Dibenzothiophene Molecular Structure

That is why this project is focusing on DBT extraction as assuming if the DBT extraction is a success, this ILs is a success to remove any other sulfur compounds.

2.3. Other studied Desulfurization Methods

2.3.1. Oxidative Desulfurization

The most recent studies done by Dan Liu and colleagues [3] are on the deep removal of sulfur from real diesel by catalytic oxidation with halogen-free ionic liquid. Most recently, it has been reported that the efficiency of the extraction will greatly increase if the S-species are previously oxidised to the corresponding sulfoxides or sulfones because the distribution coefficient of these species is much higher than that of non-oxidised derivatives. In this research, their team used a halogen-free ILs which is 1-ethyl-3-methylimidazolium diethyl phosphate, [EMIM][DEP] to extract the sulfur from model oil, Dodecane and real diesel.

In this process known as oxidative desulfurization, the aromatic sulfur compounds are oxidised to the sulfones compounds, which exhibit larger polarity thus easy to be removed using polar solvent. The reason of not using halogen contained ILs such as BF_4^- and PF_6^- , it will produce white fumes of HF or hydrate precipitates and will cause further environmental problems. From the studied done, it is proven that oxidative type of desulfurization will increase the sulfur extraction but it requires to have another unit to extract the oxidized sulfur from the model oil or real diesel. That is the major drawback of this type of desulfurization but it is still a good choice compared to the conventional HDS.

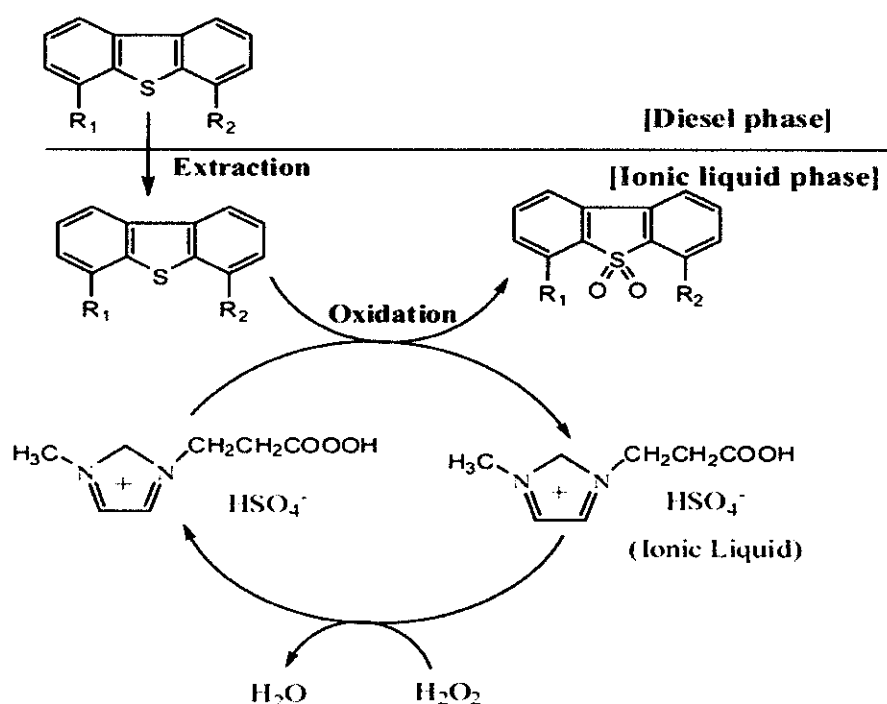


Figure 3: Oxidation Mechanism

2.3.2. Adsorption Desulfurization

Adsorption desulfurization is method where certain adsorbent is used to remove sulfur from diesel as well as Dodecane to determine the extraction performance. Adsorption properties of adsorbent such as Ag-MAS, Ag-MCM-41 and Ag-y, were tested for adsorption capacity and selectivity towards DBT extraction [4]. The result of adsorbent performance is shown below:

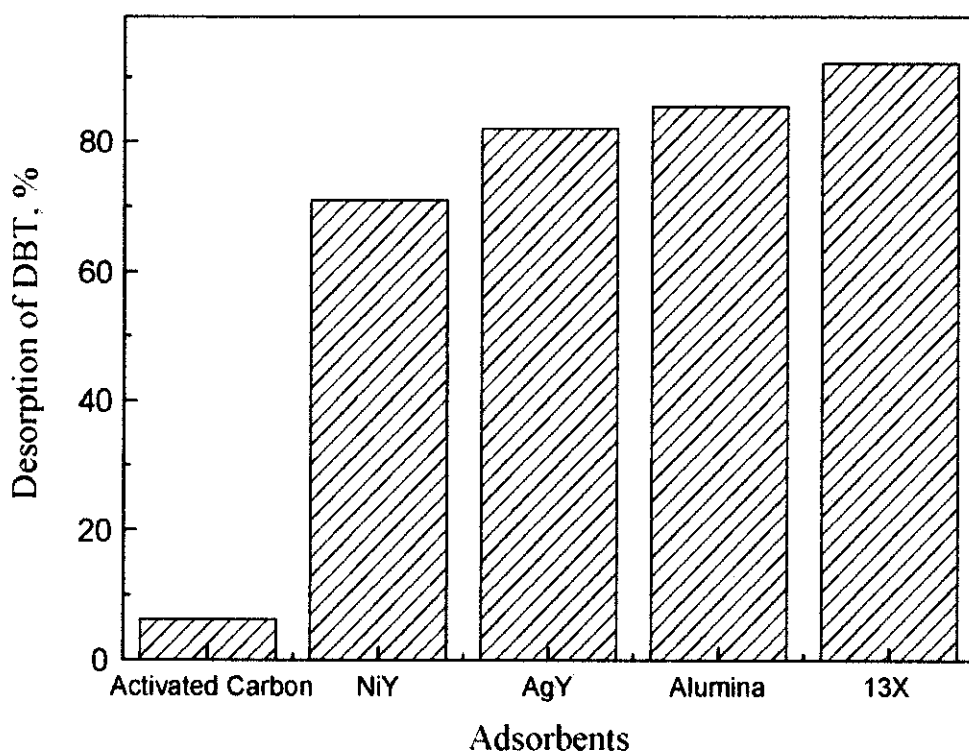


Figure 4: Desorption of DBT on different Adsorbents

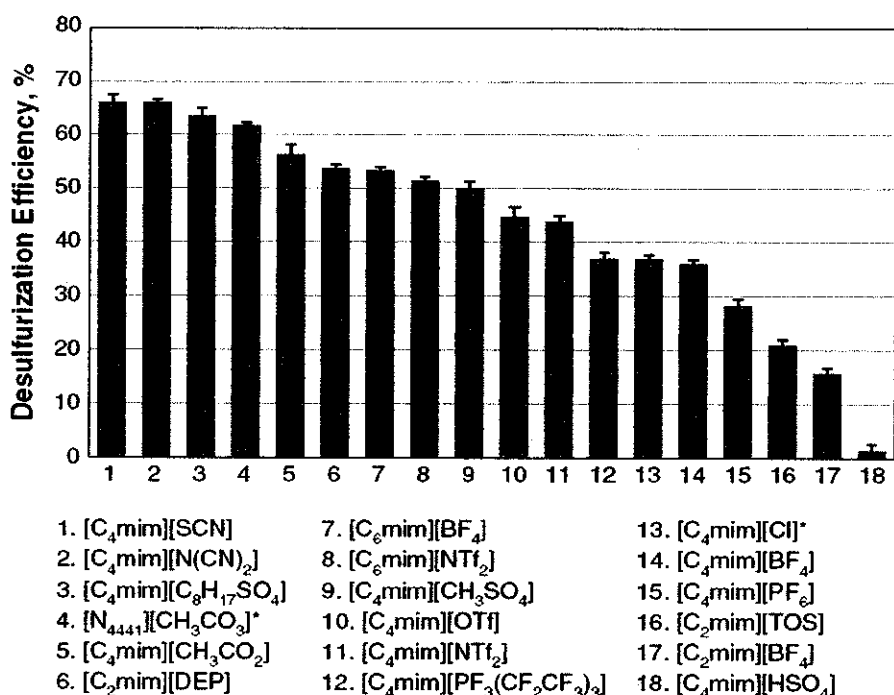
Wangliang Li [4] reported that adsorption desulfurization has some problems that need to be solved regarding the selectivity of the adsorbent used. When the selectivity increases, the spent adsorbents become difficult to be regenerated and the cost would be high.

2.3.3. Solvent Extraction

Various solvent has been tested and patented for removing sulfur compounds. Some of the examples are aqueous acetone, ethanol, mesityl oxide and formic acid. Based on experiments and testing done by H. Rang [4], they concluded that it is impossible to achieve deep desulfurization with only solvent extraction process. But, if this method is combined with hydrotreating or oxidation method, it can be very effective.

2.4. Ionic liquids Special Characteristics

Various species or derivations of ILs have been studied in the past few decades especially in desulfurization process for fuels. As example of work that has been established is a total of eighteen (18) different ILs were used to extract DBT from Dodecane respectively, and their extraction performances was correlated with their specific volume [6] .The ILs tested and their performances are as below:



Mixing temp = 30°C, Mixing time = 30mins, IL:Oil weight ratio = 1:1 (5g each), stirring speed = 400rpm, mixing vessel = 50ml screw-cap glass bottle. * Mixing temp = 80°C for non room temperature IL

Figure 5: ILs Desulfurization Efficiency

First three ILs is imidazolium based and from the graph above, it is obvious, the performance of of imidazolium based ILs is superior compared to the other ILs. This experiment was run at 30 °C, 30 minutes of mixing time, weight ratio IL:Oil is 1:1 and stirring speed is 400 rpm. This research also published something really interesting to look forward. It is the relation between specific volumes of ILs and the extraction capability. It is proven that the higher specific, the better the extraction of DBT from the model oil. The reason behind this; ILs with higher specific volume had more free space between ions to accommodate DBT molecules, so these ILs is capable of extracting more DBT molecules compared to ILs with low specific volume.

$$\text{Desulfurization efficiency} = \frac{[DBT]_{\text{initial}} - [DBT]_{\text{final}}}{[DBT]_{\text{initial}}} \times 100\%$$

Imidazolium based ILs exhibited much higher extraction performances compared to Tributylmethylammonium methylcarbonate [6].

Another good property of ILs that has been researched is on the recyclability before it has to be regenerated to be used in extraction again. Dan Liu reported ILs (Halogen Free Ionic Liquids) can be used up to 5 times before regenerated, on the other hand, Dishun Zhao [7] showed in their result that ILs used (Bronsted Acid Ionic Liquids) can be used 7 times before its sulfur removal capability drop below 99%. It is very stunning result to look upon and the same procedures will be tested on the proposed ionic liquid, [BMIM]CoCl₃.

Cycle	Sulfur removal (%)	Cycle	Sulfur removal (%)
1	100	7	99.6
2	99.8	8	98.1
3	99.3	9	95.2
4	98.9	10	97.3
5	99.7	11	95.0
6	99.5	12	93.4

^a Conditions: $T = 60\text{ }^{\circ}\text{C}$; O/S = 3; DBT ($1550\text{ }\mu\text{g mL}^{-1}$); $V_{\text{model oil}}/V_{\text{IL}} = 1 : 1$.

Figure 6: Result of Recycle [Hnmp]BF₄ in desulfurization of model oil

Nan Hee Ko [8] and teams found out that Lewis acidic ILs prepared from 3-butyl-1-methylimidazolium chloride ([BMIM]Cl) and FeCl₃ are highly effective for the extraction of sulfur compounds present in hydrocarbon at an ambient temperature. Ambient temperature for high extraction capability is mostly preferred as it will reduce the cost for desulfurization.

molar ratio (FeCl ₃ /[BMIm]Cl)	degree of desulfurization (%)
[BMIm]Cl ^b	17.2
0.5	34.1
0.7	38.9
1	42.2
1.5	77.4
2	100
2.5	100
3	100
5	100
FeCl ₃ ^c	33.9

Figure 7: Degree of Desulfurization

From the results above, FeCl₃ alone exhibited lower extraction capability than the Fe-ILs, that shows the importance role of [BMIM]Cl [7]. This suggest why [BMIM]CoCl₃ is suggested to be tested as combination of ionic liquid [BMIM]Cl and ionic solid[CoCl₂] might give a better result than FeCl₃-[BMIM]Cl in desulfurization ability.

Another critical criterion of good extractive behaviour is that, ILs must have relatively high sulfur partition coefficient, K_N [9]. K_N can be mathematically defined as:

$$K_N = \frac{\text{Sulfur Mass Fraction Before Treatment}}{\text{Sulfur Mass Fraction After Treatment}}$$

K_N value is experimentally determined and the more higher the value is, the more effective of the ILs to extract sulfur in this case DBT from oil.

2.5. Advantages

In the point view of sulfur extraction from fuels, ILs is the most preferred technology to replace conventional HDS as it is cheap, green technology, low maintenance, regeneration is cheap and low power consumption. What make ILs become the main attention in research world is because of its environmentally friendly characteristic which is very essential to help reduce the overly polluted world problems currently we are facing.

Zhao reported that, certain ILs can be recycled up to 7 times before the desulfurization effectiveness decrease below 99% [10]. It is a very remarkable characteristic that can reduce the operating cost to a very minimum compared to the HDS.

2.6. Other Applications of ILs

2.6.1. Electrochemistry

Electrical energy storage technologies have increasingly become important with great growth of portable electronic gadgets such as smart phone, laptop and tablet. Electrical Double Layer Capacitors or EDLC is a new technology that is for electrical storage has shown promising result to be developed and perhaps replace current technology for better performance. EDLC research has focused on improving energy density without compromising power density or cycle life. Aqueous electrolytes typically enable a voltage window of ± 1 V, while organic electrolytes allow ± 3.5 V [11]. Using organic electrolytes and especially ILs are preferred for high energy density applications [12], since the energy density is proportional to square of voltage window. Other desired characteristics of EDLC electrolytes are high conductivity, wide operating temperature range, large voltage window, and good stability during charge–discharge cycles and low viscosity.

2.6.2. Catalysis

ILs is known for decades for the ability to dissolve transition metal complexes and support organic chemistry. Previous researcher like Chauvin [13] proved nickel complexes can dissolve in acidic chloroaluminate ILs catalyze the dimerization of alkenes; on the other hand, Osteryoung [14] used Ziegler-Natta catalyst in the similar solvent in polymerization of ethylene. Zaworotko in different case study, produce water-stable ionic liquids that contain tetrafluoroborate, hexafluorophosphate, nitrate, sulphate and acetate anions that actually helped Chauvin and Dupont to demonstrate the potential of ILs for hydrogenation catalysis in term of reaction rates and selectivities. There are

countless times of testing of catalyzed reaction in ILs with different degree of success. The important thing to be remembered is, well-established homogeneous catalyst has to be modified prior using it in ILs to make sure it works better without it.

2.6.3. Separation

ILs have been applied in different areas of separation, such as ionic liquid supported membranes, as mobile phase additives and surface-bonded stationary phases in chromatography separations and as the extraction solvent in sample preparations, because they can be composed from various cations and anions that change the properties and phase behavior of liquids. Although the applications of ILs in separations are still in their early stages, the academic interest in ILs is increasing.

Their application in separation technology has attracted great attention. Alkylimidazolium-based ILs have been used as a stable stationary phase for gas chromatography [15]. These ILs exhibit an unusual selectivity with a “dual nature”, where they separate polar compounds as if they were polar stationary phases and non-polar compounds, which suggests that ILs might be useful multi-modal media in chromatographic separations. ILs can be used as mobile phase additives in reversed-phase chromatography when they are mixed with other low viscosity solvents [16, 17]. ILs have been used as electrolyte additives, running buffer modifiers and supported coatings on the capillary walls in capillary electrophoresis (CE) [18, 19].

CHAPTER 3

METHODOLOGY

Before this project can commence, the basic principles and concepts governing the process must first be understood. Properties of ILs, synthesizing ILs and handling also will be studied before experimenting in the laboratory. Therefore, methodical research and literature review will be conducted using resources from the library, online journal database and the internet.

This research project aims are to determine the extractive capability of [BMIM][CoCl₃] to extract DBT from model oil, Dodecane and also determine the best conditions for [BMIM][CoCl₃] to work at its best. For this purpose, series of experiments will be run to get the best or optimum working conditions for [BMIM][CoCl₃] in sulfur extraction performance.. The experiment will have three (3) main components:

1. Synthesizing or preparing the [BMIM]CoCl₃.
2. Preparations for DBT in Dodecane.
3. Extraction experimenting of [BMIM]CoCl₃ with Dodecane (dissolved with DBT).

3.1. Procedures for [BMIM]CoCl₃ Preparation

- i. [BMIM]Cl is mixed with CoCl₂ (hexahydrate) at equal molarity, this is done by weighing CoCl₂ for 10 g (0.042 mol) and 7.35 g (0.042 mol) [BMIM]Cl.
- ii. Mix both chemicals in a reaction bottle. Seal it and stir it for the next 24 hours (500 rpm) at ambient temperature.
- iii. After 24 hours, the ILs produced is tested using Nuclear Magnetic Resonance, NMR to determine the structure of new [BMIM]CoCl₃.

3.2. Preparations for DBT in Dodecane.

- i. A stock solution of 5000 ppm is prepared by dissolving 5.7 g of DBT powder in 94.3 g of Dodecane.
- ii. Then 10 g of stock solution is weighed and put in 4 different sample bottles.
- iii. Each sample of concentration will be tested using HPLC to construct the standard curve for DBT concentration in Dodecane.

Concentration (ppm)	Dodecane Added (g)
1000	40
2000	30
3000	20
4000	10

Table 1: DBT Concentrations

3.3. Procedure for Desulfurization Performance Test

- i. [BMIM]CoCl₃ is mix with prepared Dodecane with 6 set of samples. 1 g of [BMIM]CoCl₃ is mix together with 1g, 2g, 3g, 4g, 5g and 10 g of Dodecane in the sample bottles.
- ii. Those samples will be stirred for 30 minutes at ambient temperature.
- iii. The mixture is left to settle for 10 minutes.
- iv. The Dodecane sample is taken and analysed using High Performance Liquid Chromatography, HPLC and compared with the standard curve to know the sulfur extraction percentage.
- v. Experiment is repeated with different temperature 40 °C and 50 °C.

The result collected from this experiment will be compared to each conditions and the best extraction performance will be pointed out and studied further. And also, the best conditions will be applied to real diesel to study on the sulfur extraction performance.



Preparation of
[BMIM]CoCl₃

Figure 8: [BMIM]CoCl₃ Preparation



Figure 9: Dodecane and [BMIM]CoCl₃

Extraction with
[BMIM]CoCl₃

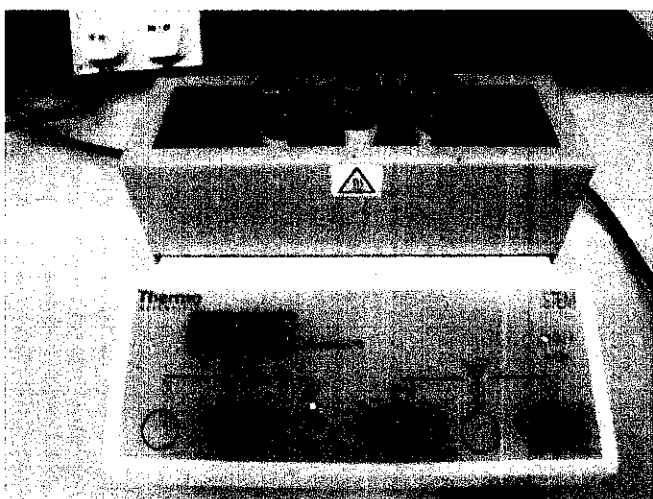


Figure 10: Extraction Procedure

Sample is heated and
stirred at different
temperature. (25°C, 40°C
and 50 °C)

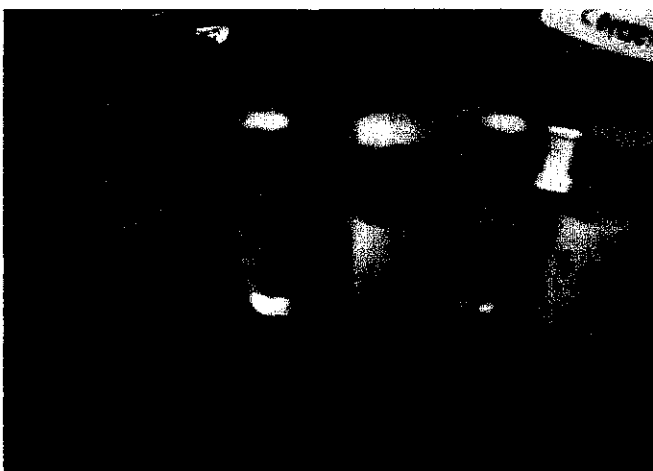


Figure 11: Analysing Sample

After experiment is
finished, Dodecane or
Diesel layer is collected in
sample bottle to be tested
using HPLC, TSA or
CHNS

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. Standard Solution and Curve for Dodecane

The standard solution is prepared by diluting certain amount of DBT in Dodecane and tested using High Performance Liquid Chromatography, HPLC.

Table 2: Standard Solution

Area	PPM
5769.3	500
14131.0	1000
25267.2	2000
37637.0	3000
48943.8	4000

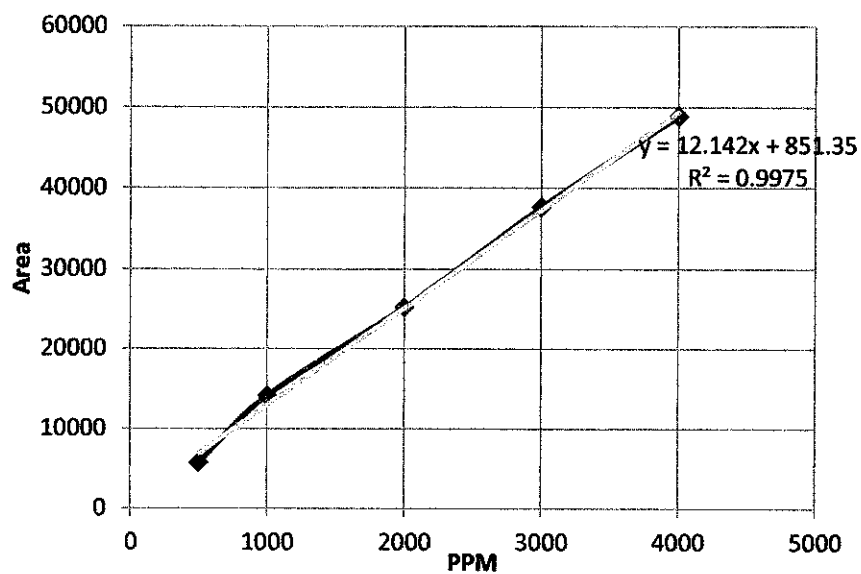


Figure 12: Standard Solution Graph

Average Peak Time for DBT in Dodecane is 3.124 – 3.129 minutes.

For the experiments, 5000 ppm of DBT in Dodecane is used as the pre-extracted model oil.

4.1.1. Result After Extraction Using Dodecane(T = 25 °C)

Temperature: 25°C

Stirrer: 500 RPM

Time: 30 minutes

Run 1

Table 3: Extraction at T = 25 °C Run 1

Ratio	Area	Peak Time
1:1	57469.8	3.235
1:2	60419.2	3.235
1:3	60164.2	3.241
1:4	60293.5	3.232
1:5	59535	3.238
1:10	59377.1	3.242

Temperature: 25°C

Stirrer: 500 RPM

Time: 30 minutes

Run 2

Table 4: Extraction at T = 25 °C Run 2

Ratio	Area	Peak Time
1:1	65436	3.136
1:2	71778	3.237
1:3	68924.2	3.263
1:4	83414.7	3.255
1:5	79403.8	3.258
1:10	18822.1	3.231
	59811.5	3.286

Cross result between Dodecane sample and above results does not meet any cross point so, the concentration of DBT in Dodecane after extraction cannot be determined at this point of experiment. Based on early assumption, the DBT can be said totally extracted from Dodecane which means 100% extraction by [BMIM]CoCl₃. But looking at the time of the peak, it shows it is not DBT compounds. That's mean, most probably; DBT is

replaced with unknown compounds after extraction and it seems that DBT is completely extracted into [BMIM]CoCl₃ ionic liquid phase. Further test will be conducted using NMR and GC to confirm the compounds present in the sample after extraction procedures.

Result After Extraction Using Dodecane (T = 40 °C)

Temperature: 40°C

Stirrer: 500 RPM

Time: 30 minutes

Run 1

Table 5: Extraction at T = 40 °C Run 1

Ratio	Area	Time
1:1	68648.7	3.254
1:2	21183.2	3.253
1:3	12640.1	3.304
	41647.6	3.346
	78203.9	3.275
1:4	31010.6	3.279
	47029	3.36
1:5	31589.9	3.285
	44694.4	3.35
1:10	19292.8	3.245
	60533.1	3.305

Run 2

Table 6: Extraction at T = 40 °C Run 2

Ratio	Area	Time
1:1	55429.6	3.268
1:2	57164.8	3.261
1:3	55900.4	3.263
1:4	57705.6	3.281
1:5	40.1	1.192
	26527.4	3.353
	34755.4	3.435
1:10	60607.5	3.311

4.1.2. Result After Extraction Using Dodecane (T = 50 °C)

Temperature: 50°C

Stirrer: 500 RPM

Time: 30 minutes

Run 1

Table 7: Extraction at T = 50 °C Run 1

Ratio	Area	Time
1:1	60231.9	3.249
1:2	78296	3.253
1:3	73426.1	3.259
1:4	6720.5	3.262
1:5	34855.7	3.268
	51423.4	3.358
1:10	35732.9	3.289
	41967.6	3.382

Run 2

Table 8: Extraction at T = 50 °C Run 2

Ratio	Area	Time
1:1	62925.9	3.227
1:2	78844.6	3.225
1:3	33485.4	3.228
	49357.8	3.392
1:4	71222.4	3.225
1:5	36388.4	3.342
	47569.4	3.342
1:10	32115.1	3.22
	10076.7	3.327
	35396.4	3.372

Table 9: Overall Data for Different Temperatures and Ratios

T=25 °C			T = 40 °C			T = 50 °C		
Ratio	Area	Average	Ratio	Area	Average	Ratio	Area	Average
1:1	57469.8	61452.9	1:1	68648.7	62039.15	1:1	60231.9	61578.9
	65436			55429.6			62925.9	
1:2	60419.2	60419.2	1:2	21183.2	39174	1:2	78296	78570.3
	60419.2			57164.8			78844.6	
1:3	60164.2	64544.2	1:3	41647.6	48774	1:3	73426.1	61391.95
	68924.2			55900.4			49357.8	
1:4	60293.5	71854.1	1:4	47029	52367.3	1:4	6720.5	38971.45
	83414.7			57705.6			71222.4	
1:5	59535	69469.4	1:5	31589.9	46098.7	1:5	34855.7	35622.05
	79403.8			60607.5			36388.4	
1:10	59377.1	59594.3	1:10	60533.1	60570.3	1:10	35732.9	35564.65
	59811.5			60607.5			35396.4	

The area here is not representing DBT concentration but unknown compound which replaced DBT after extraction. The higher the value of area projects the higher the concentration of this unknown compound and the higher DBT extraction. Even though the data collected is not that accurate but figure below can be constructed to give an overall picture how [BMIM]CoCl₃ behave at different temperatures and ratios.

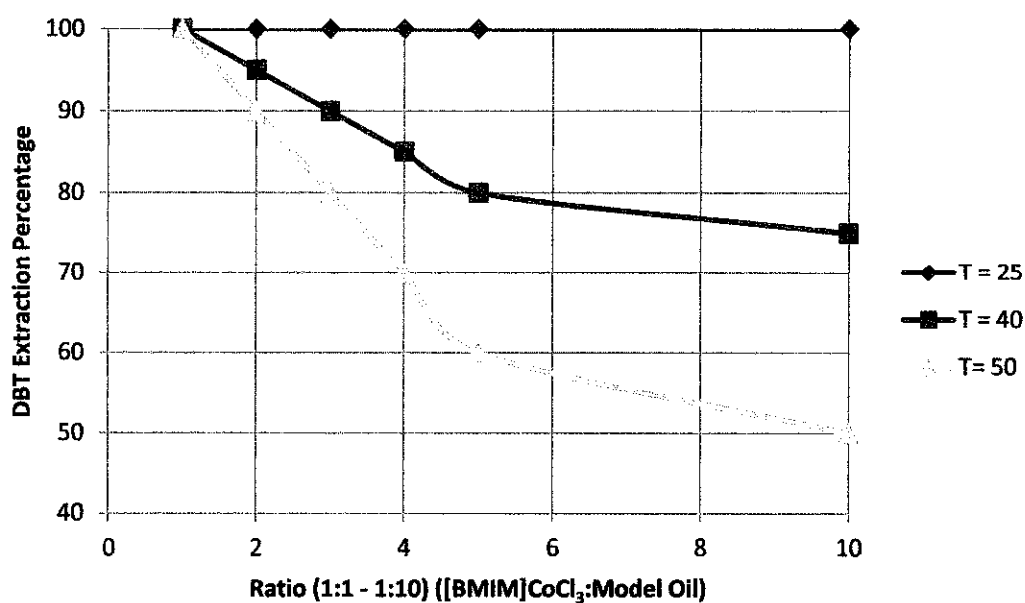


Figure 13: DBT Extraction at Different Temperatures and Ratios

4.2. Result After Extraction Using Real Diesel

4.2.1. After HDS Diesel Sample Tested Using CHNS

Each sample is tested 2 times using CHNS

T = 25°C

Table 10: After HDS Diesel – CHNS Result for T =25 °C

Ratio	Sample Weight(mg)		Sulfur Percentage (%)		Sulfur Weight (mg)		Removal Percentage (%)	
	Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2
1:1	1.467	1.531	0.001	0.019	1.5E-05	0.000291	98.0067935	60.47690217
1:2	2.134	1.475	0.018	0.002	0.00038	2.95E-05	47.8097826	95.99184783
1:3	1.557	2.215	0.018	0.011	0.00028	0.000244	61.9211957	66.89538043
1:4	1.777	1.699	-0.002	-0.007	0.00000	0.00000	100.0000	100
1:5	1.921	1.577	0.002	0.028	3.8E-05	0.000442	94.7798913	40.00543478
1:10	1.537	1.882	0.012	0.012	0.00018	0.000226	74.9402174	69.31521739

T = 40 °C

Table 11: After HDS Diesel – CHNS Result for T =40 °C

Ratio	Sample Weight(mg)		Sulfur Percentage (%)		Sulfur Weight (mg)		Removal Percentage (%)	
	Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2
1:1	2.288	1.974	0.028	0.006	0.00064	0.000118	12.9565217	83.9076087
1:2	1.875	1.508	0.026	0.051	0.00049	0.000769	33.763587	
1:3	1.577	1.697	0.038	0.008	0.0006	0.000136	18.5788043	81.55434783
1:4	1.865	2.081	0.008	0.021	0.00015	0.000437	79.7282609	40.6236413
1:5	1.825	1.628	-0.003	0.006	0.0000	9.77E-05	100.00000	86.72826087
1:10	1.73	2.136	0.006	0.011	0.0001	0.000235	85.8967391	68.07608696

T = 50 °C

Table 12: After HDS Diesel – CHNS Result for T =50 °C

Ratio	Sample Weight(mg)		Sulfur Percentage (%)		Sulfur Weight (mg)		Removal Percentage (%)	
	Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2
1:1	1.497	1.543	0.003	0.007	4.5E-05	0.000108	93.8980978	85.32472826
1:2	1.733	1.744	0.007	0.003	0.00012	5.23E-05	83.517663	92.89130435
1:3	2.165	1.771	0.009	0.008	0.00019	0.000142	73.5258152	80.75
1:4	1.57	1.739	0.013	0.013	0.0002	0.000226	72.2690217	69.28396739
1:5	1.697	1.601	-0.014	0.026	0.0000	0.000416	100.0000	43.44293478
1:10	2.241	1.625	0.028	0.011	0.00063	0.000179	14.7445652	75.71331522

Untreated Sample of After HDS Diesel

Table 13: Untreated Sample of After HDS Sample

Sample Weight			Sulfur Percentage (%)			Sulfur Weight in Sample(mg)			
Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3	Average
1.523	1.991	1.484	0.059	0.033	0.044	0.00089	0.000657	0.000653	0.000736

The diesel sample used is from Penapisan Melaka taken after the HDS unit which average sulfur content is 0.000653 mg to 0.000890 mg.


 Out of Range Data

Table 14: Overall Data of Real Diesel Treatment

T=25 °C			T = 40 °C			T = 50 °C		
Ratio	Removal Percentage (%)	Average	Ratio	Removal Percentage (%)	Average	Ratio	Removal Percentage (%)	Average
1:01	98.0068	79.2418	1:01	12.9565	48.4321	1:01	93.8981	89.6114
	60.4769			83.9076			85.3247	
1:02	47.8098	71.9008	1:02	33.7636	33.7636	1:02	83.5177	88.2045
	95.9918			33.7636			92.8913	
1:03	61.9212	64.4083	1:03	18.5788	50.0666	1:03	73.5258	77.1379
	66.8954			81.5543			80.75	
1:04	100	100	1:04	79.7283	60.176	1:04	72.269	70.7765
	100			40.6236			69.284	
1:05	94.7799	67.3927	1:05	100	93.3641	1:05	100	71.7215
	40.0054			86.7283			43.4429	
1:10	74.9402	72.1277	1:10	85.8967	76.9864	1:10	14.7446	45.2289
	69.3152			68.0761			75.7133	
Average for all Ratios		75.8452	Average for all Ratios		60.4648	Average for all Ratios		73.7801

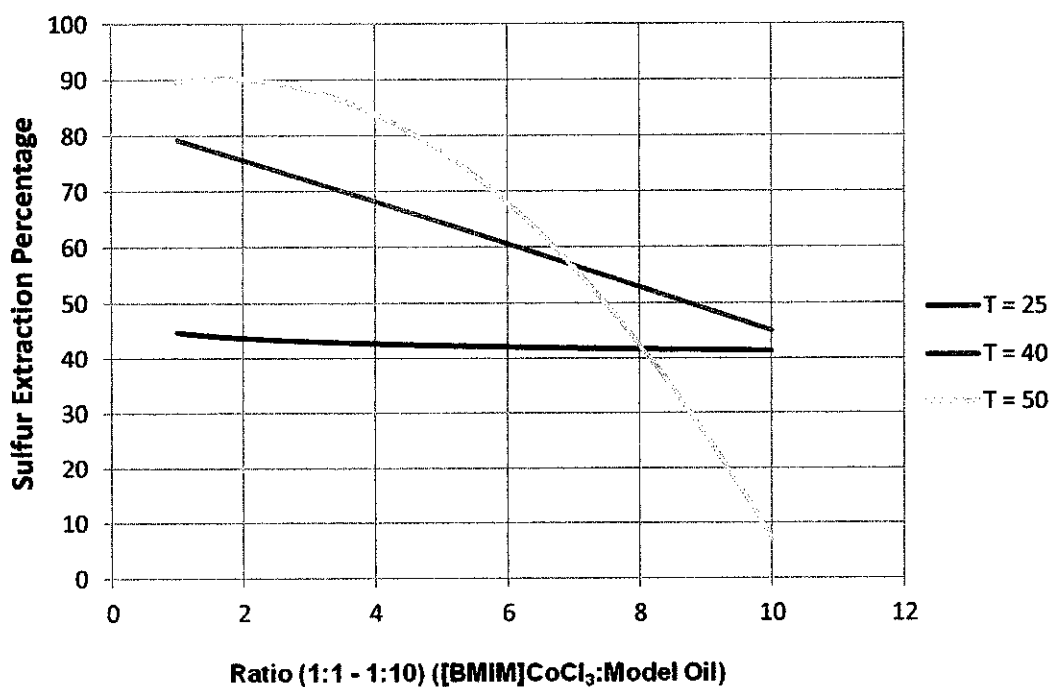


Figure 14: Sulfur Extraction at Different Temperatures and Ratios

4.3. Discussion

4.3.1. Dodecane Desulfurization

The result of extraction performance by [BMIM]CoCl₃ are as shown in Figure 13. [BMIM]CoCl₃ shows spectacular ability for sulfur removal in model oil. After extraction with [BMIM]CoCl₃ ionic liquid at T = 25°C, 100% of the sulfur compounds in model oil have been removed for all ratio up to 1:10, whereas for T = 40 °C, the sulfur removal is dropping from 100% to 75% for ratio from 1:1 up to 1:10. For T = 50 °C, the extraction is 100% for 1:1 ratio and drop from 90% to 50% for ratio of 1:2 to 1:10. From all this data collected, it can be concluded that, [BMIM]CoCl₃ worked best at ambient temperature, T = 25°C, which the sulfur removal is 100% for ratio of up to 1:10. This is quite a stunning and spectacular result as it is very rare for an ionic liquid to achieve 100% sulfur removal at ambient temperature. To explain the ability of sulfur removal of [BMIM]CoCl₃ is mainly because of interaction of the aromatic ring of [BMIM]CoCl₃ and DBT or known as $\pi - \pi$ interaction. The second reason is because of the electrostatic attraction between IL (negatives charges) and aromatic sulfur species (positive charges). The major interaction seems to be the $\pi - \pi$ interaction in this case. Both interactions will be weakened with temperature increasing as the molecules of IL and aromatic sulfur move faster and this cause shorter period of interaction between them. This seems to be the best explanation of the data shown in Figure 13.

The treated Dodecane is tested to determine the unknown compound present besides DBT after the treatment. The test was conducted using NMR, Raman and HPLC but unfortunately the compound could not be identified due to equipments' limitation. However, from these testing, it can be confirmed that the unknown compound does not belong to sulfur species. It means here, the original sulfur present in the DBT has been completely extracted during the extraction process into the ionic liquid phase and was replaced with some unknown compounds. Further testings with other analyser equipment such as GC and TSA are conducted to confirm the unknown compounds present. The data and result collected from this series of experiments is very useful to

show that new [BMIM]CoCl₃ ionic liquid is very excellent in sulfur extraction for Dodecane compared to other ILs tested until today.

From the series of experiments, it can be concluded that [BMIM]CoCl₃ works best at ambient temperature, the ratio can be up to 1:10 where the extraction is still 100%.

4.3.2. Real Diesel Desulfurization

The results collected from CHNS can be referred as above. The samples are run twice and general interpretation can be done using this data. The error can be caused by many factors especially the equipments itself and during sample preparation. From general interpretation it can be concluded that, the result pattern is almost the same as for the Dodecane. The sulfur extraction is in the range of 40% to 90%. This confirms that, after extraction using [BMIM]CoCl₃, the sulfur compound present in the diesel is extracted into [BMIM]CoCl₃ phase up to 90%. But still, the unknown product from the extraction is still unidentified. In addition, in term of sulfur extraction performance, [BMIM]CoCl₃ is showing the highest value at T = 25 °C averagely for all ratios.

The data collected reliability and accuracy is fairly low as mainly caused by analysers' limitation. Diesel sample is known to be really hard to be analysed and cause a lot of disturbances and errors to the results. To get more reliable and accurate result, a lot of repetitions need to be done in the future. For Industry Application, the result collected has to be ran with Pilot Plant to get accurate stirring time and ratio of [BMIM]CoCl₃ and Diesel for optimum plant operation cost (Scaling Up Procedure).

General view of how [BMIM]CoCl₃ behave towards diesel can be known and concluded that [BMIM]CoCl₃ is an excellent sulfur extraction agent in real diesel application.

From both result collected from the experiments, [BMIM]CoCl₃ shows a great potential to be sulfur extracting agent for both Dodecane and real diesel. [BMIM]CoCl₃ work best at ambient temperature and the optimum ratio of [BMIM]CoCl₃ to Dodecane or Diesel for application is 1:5.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

In conclusions, this research study on extraction of sulfur using [BMIM]CoCl₃ is a great discovery especially in Ionic Liquids field. [BMIM]CoCl₃ has proven that, it has a very good extractive performance compared to other Ionic Liquids preferably at ambient temperature. The study has also conducted investigation as below;

1. *Effect of Temperature*

From the series of experiment using three(3) set of Temperature which are 25°C, 40°C and 50°C, both testing on Dodecane and Real Diesel showed best performance at ambient temperature, 25°C.

2. *Effect of Stirring Time*

Stirring time has no effect on the sulfur extraction performance for this experiment. So thorough out the testing, stirring time of 30 minutes is used.

3. *Ratio of [BMIM]CoCl₃ to Dodecane*

The best sulfur extraction performance would be the 1:1 ratio. Optimum ratio for real application is 1:5.

4. *Effect on Usage upon Dodecane and Diesel*

[BMIM]CoCl₃ sulfur extraction performance in Dodecane can be said as very excellent, almost 100 percent, on the other hand, in Diesel this ionic liquid performance drop a bit at 80 – 90 percent. Considering the results collected, even not that reliable, [BMIM]CoCl₃ is showing outstanding performance.

5.2. Recommendations

1. Sample after treatment with [BMIM]CoCl₃ need to be tested with other equipments to determine the unknown compound species and compositions.
2. Real diesel sample analysing need to be repeated to achieve reliable and accurate results preferably with better analyser equipments.

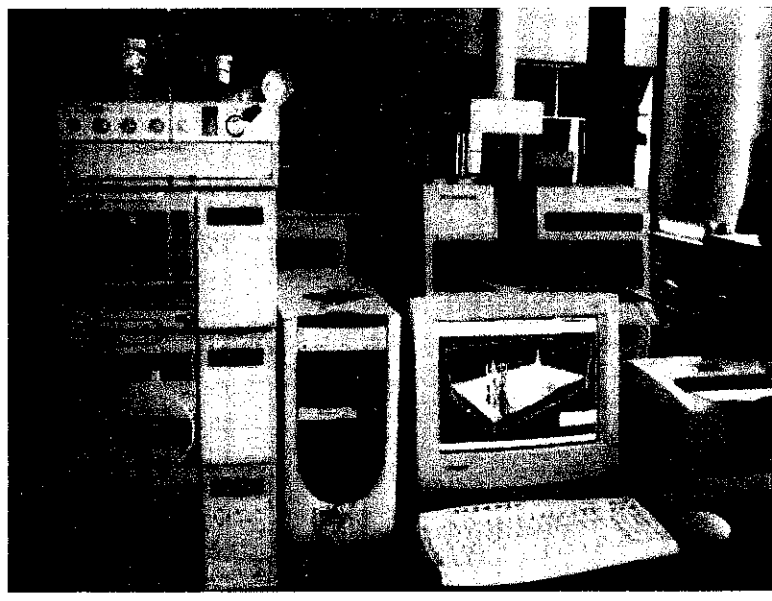
3. For Dodecane sample, the results need to be established more widely on every possibility to get better picture how [BMIM]CoCl₃ effect the desulfurization process.

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APPENDIX



HPLC METHOD PROCEDURE (Model Oil Sample)

- Column: Zorbax SB-C18 (4.6 x 100 mm x 5 μ) - 25°C
- Mobile Phase: MeOH:H₂O (9:1)
- Flow: 1ml/min
- Detector: DAD
- Run Time: 20 min
- Injection Volume: 10 μ L



CHNS Analyzer (Real Diesel Sample)

Detection Range: 0 to 100% for all elements with the capacity of measuring at least 40 mg absolute carbon for high carbon containing in homogeneous samples and should be compulsorily able to perform analysis of marine sediments.

- C: 0-40mg (or 100%)
- N: 0-15 mg (or 100%)
- H: 0-3 mg (or 100%)
- S: 0-6 mg (or 100%)
- O: 0-6 mg (or 100%)

Operating modes for measurement: CHNS, CHN, CNS, CN, N, S Trace S (detection limit of 2 ppm for sulfur with IR), O, CI, as add on modules.

Sample weight Range: 1.4 mg to 2.0 mg