Oxidative Desulfurization of Dibenzothiophene from Model Oil Using Acidic Ionic Liquid as Extracting Agent

by

SARAH IZZATI AZMI

DISSERTATION
Submitted in partial fulfilment of
The requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

SEPTEMBER 2012

Universiti Teknologi PETRONAS
Bandar Sri Iskandar
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Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

_______________ _______________________
(Dr Putri Nazrol Faizura)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
September 2012

CERTIFICATION OF ORIGINALITY

This is to certify 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.

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SARAH IZZATI AZMI

ABSTRACT

Due to the stricter engineering regulations for the oil industry regarding the sulphur content, there have been increasing initiatives for removal of sulphur contents in fuel by various, greener method such as ionic liquids. The oxidative desulfurization of dibenazothiophene (DBT) from model oil was carried out using as the extractant and catalyst, and hydrogen peroxide (H_2O_2) in combination with acetic acid and sulphuric acid as the oxidant. The acidic ionic liquid used is 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]). The effect of the catalyst and oxidant without any ionic liquid was studied first with the optimal desulfurization was removal of 35% of sulphur at a ratio of H_2O_2 to sulphur at 5:1.The same ratio and method using the acidic ionic liquid removed only 11% of the sulphur content. Using the same H_2O_2 to sulphur ratio, the effect of the ionic liquid to model oil ratio was studied with an optimum at 1:3 ionic liquid to model oil ratio with removal of 35% sulphur content.

ACKNOWLEDGEMENT

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Thank you.

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List of Abbreviations

API - American Petroleum Institute
BMIM[Cl] - 1-butyl-3-butyl-imidazolium chloride
BMIM[PF6] - 1-butyl-3-methylimidazolium hexafluorophosphate
BT - Benzothiophene
CHNS - Carbon, Hydrogen, Nitrogen and Sulphur Analyzer
DBT - Dibenzothiophene
ECODS - Extraction and catalytic oxidative desulphurization
EDS - Extractive Desulphurization
H2O2 - Hydrogen Peroxide
HDS - Hydrodesulfurization
ILs - Ionic Liquids
ODS - Oxidative Desulphurization
ppm - Part per million
S - Sulphur
SOx - Sulphur Oxides
VOCs - Volatile Organic Compounds

CHAPTER 1: INTRODUCTION

1.1: Project Background

Demand for fuel has rapidly increased in the last century and with it, an increase in necessity of sulphur removal from crude oil. Sulphur present in transportation fuels lead to sulphur oxides emission to air and causes negative impacts to 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 (I.V. Babich*, 2003).

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. HDS is the commercial process for crude oil desulfurization.

Thus, many alternative technologies to absorb sulphur have been developed extensively. One green alternative that show promising result are ionic liquid with properties of non-volatile, non-flammable, and recyclable and have high affinity to sulphur-containing compounds. There has been a growing interest in the synthesis of ionic liquid as there is a widespread application and uses for this category of solvents. Ionic liquids also have excellent extraction properties for organic S- and N-compounds and if chosen wisely, insoluble in oil.

By using technique of liquid-liquid extraction, 1-Butyl-3-methylimidazolium chloride [BMIM]Cl) is used to remove sulphur from synthesized model oil. The sulphur extracted from hydrocarbons mixtures were then analysed for total sulphur analyser. The total sulphur was significantly lowered in all tested hydrocarbon mixtures. A way forward is to further study on effects of the acidity of the ionic liquid on sulphurized hydrocarbons.

1.2: Problem Statement

Sulphur is one of the components fuel of which levels have to be reduced because of new environmental and engineering standards. Desulfurization of fuels has become increasingly important to petroleum industry. Unfortunately, with the current commercial methods to treat fuel, the associated costs (e.g., equipment and hydrogen) are high. Thus, an effective and easily applicable method needs to be found that can lower or remove sulphur containing compound while not affecting the fuel properties themselves. Current continuing studies shows extracting these sulphur compound from fuels with acidic ionic liquid could offer such a solution.

1.3: Objective and Scope of Study

The main objectives for this project are:

1. Preparation of model oil.
2. Oxidative desulfurization process.
3. Data analysis of removal of sulphur.

This project is in the form of laboratory experiment. This project consists of three phases and the objectives are identified to cover the whole experimental work involved in the study including the analysis of the results which includes evaluating the performance of and acidic ionic liquid on the removal of dibenzothiophene from model oil. The ionic liquid used in this project is acquired and not synthesized. The model oils are prepared using dodecane and spiked with sulphur from dibenzothiophene. The efficiency of the removal of sulphur is obtained using gas chromatography.

Scope of Study

The scope of study is limited to only one acidic ionic liquid: [Bmim][Cl] and desulphurization is limited to room temperature.

CHAPTER 2: LITERATURE REVIEW

Sulphur compounds are found naturally in crude oil and it has been a continuous challenge to extract these sulphur compounds from the crude oil. Sulphur compounds reduce the quality of fuels. Fuel when used releases SOx to the air and the emission of these oxides is one of the major source of air pollution and can also cause serious respiratory diseases such as lung cancer. Stricter regulations are now being made compulsory in several nations. It is imposed on oil refineries to reduce sulfur contents to the range of 10-20ppm (Asghar Molaei Dehkordi, March 2009).

Current commercial method of desulfurization is by using the hydrodesulfurization (HDS) process. Deep desulfurization of refinery streams becomes possible when the severity of the HDS process conditions is increased` cost. Unfortunately, more severe conditions result not only in a higher level of desulfurization but also in undesired side reactions. When gasoline is desulphurized at higher pressure, many olefins are saturated. Higher temperature processing leads to increased coke formation and subsequent catalyst deactivation. It is also important to note that in practice the severity of the operating conditions is limited by the HDS unit design (I.V. Babich*, 2003).

Oxidative Desulfurization (ODS) is one of the alternative processes and is favorable as it can be conducted at mild conditions. It is considered favorable as aromatic sulfur compounds are easily converted by oxidation as compared to HDS. ODS is a two stage process where the sulfur compounds is first oxidized in the presence of an acid catalyst (turned into sulfoxides) and these in turn, having high polarity can be removed by solvent extraction. The solvent of interest are ionic liquids.

2.1 Ionic Liquids

The development of research activities related to green chemistry has been done in order to replace abundantly used solvents by suitable alternate solvent systems for better environmental condition. Gas and liquid separations using ionic liquids are among the first and most intensive investigated areas of research in the history of ionic liquids. Different groups with different focus of interest describe ionic liquid in various ways. The characteristics of ILs are as described below:

2.1.1 Melting Points

IL are a new class of purely ionic, salt-like materials that are liquid at unusually low temperatures. It is defined as an ionic compound which is liquid below 100℃ . More commonly, IL has melting points below 0℃. These materials are liquid over a wide temperature range ($300 - 400℃$) from the melting point to the decomposition temperature of the IL.

Different groups with different focus of interest describe ionic liquid in various ways. For this study we shall define ionic liquids as unique class of salts, consisting of anions and cations which are liquid at room temperature. ILs generally exhibit good solvent properties and can often facilitate chemical reactions without being transformed in the process (Rakita, 2003).

A major principle of green chemistry is that volatile organic solvents used for reactions or separations should be avoided or made safer. Modern organic chemistry demands efficiently cheap synthetic procedures along with having environmentally safe experimental conditions. Because of this, there have been great interest in the properties of room temperature ILs. ILs are considered as a good substitute, because ILs have low vapor pressure and are non flammable below their decomposition temperature, making their usage safer than volatile organic solvents,(A. Alberto, 2008). ILs also has tunable properties meaning the cations and anions can be configured to address specific needs and has excellent salvation properties for variety of organic and inorganic compounds. One exceptional properties of the ionic liquid is that it can be repeatedly used and recycled.

While the extraction using ILs are combined with oxidative desulfurization process with the addition of the oxidant H2O2, the efficiency of the sulphur removal increases, the ionic liquid dosage decreases, and the desulfurization cost is reduced, (ZHANG Cun1, September 2011). ILs has been used for oxidative desulfurization in numerous researches. This is due to their ability to extract aromatic sulfur compounds as well as being immiscible with fuel oil, (Chi Yansheng, 2011).

Acidity of these ionic liquids is based on the Lewis Acid definition where a Lewis acid is an electron pair acceptor and a Lewis base is an electron pair donor. These ionic solvents have adjustable Lewis acidity. The acidity of the ionic liquids depends on the group of anions and not on their alkyl cations. Optimization of ODS process using acidic ionic liquids have a few predecessor research, (Di-shun ZHAO, April 2009).

Types of ionic liquids to be carried out in the experiment are Imidazolium-Based Phosphoric ionic liquids. There are many types of imidazolium based phosphoric ionic liquids.

2.2 Model Oil

As stated previously, this project is conducted to see the amount of sulphur that can be extracted from crude oil. Because of this, model oil is used with additional sulphur compounds and will be analyzed as a mixture instead. Theoretically, model oil that has high percentage of hydrocarbons is difficult to vaporize. This characteristic of n-dodecane is very helpful in doing experiment. For example, dodecane is widely used as model oil. From journals, (Luisa Alonso, 2008), dodecane has those two criteria which have high composition of carbon atoms and it is difficult to vaporize.

2.3 Sulphur Compounds

Sulphur compounds are non-hydrocarbon even though they occur naturally in hydrocarbon mixtures such as crude oil. There are three different types of sulphur compounds found in crude oil, which are hydrogen sulphide (H_2S), elemental sulphurs and aromatic sulphur compounds. Based on the journal article in Fuel, (Xiaouchan Jiang, 2008) the most difficult sulphur compound to eliminate by using HDS method are aromatic sulphur compounds such as thiophenes and dibenzothiophenes. This problem is due to the low efficiency of catalyst to eliminate sulfur compounds.

The structures of these aromatic sulphur compounds make high surface contact highly difficult as the structures are sterically hindered. Elemental sulphur compounds which are aliphatic and alicyclic are easier to eliminate. Negative by products from failure to eliminate sulphur in crude oils include compounds such as sulphuric acid and sulphur dioxides when crude oil is combusted in the air. Three types of aromatic sulfur compounds have been compared for use in the experiment. These are thiophene (T), benzothiophene (BT) and dibenzothiophene (DBT). From the previous journal, the ability of aromatic sulphur compounds to be extracted by ionic liquids are the highest using dibenzothiphene. Ionic liquids have the ability to extract the most complex sulphur compounds which is DBT.

The sulphur compounds studied by the literature and precedent research are aromatic sulphur compounds, such as dibenzothiophene dissolved in dodecane as a model oil system. Previous studies focused only on *imidazolium*-based ILs. For the IL extractive desulfurization process, although the ionic liquid chosen are imidazolium based the attention is focused on finding an acidic 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.

2.4 Liquid-Liquid Extraction

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

As can be explained by the diagram in Figure 2.1, 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. This applied to the experiment in the future where the model oil which is spiked with sulphur is mixed with the acidic liquid.

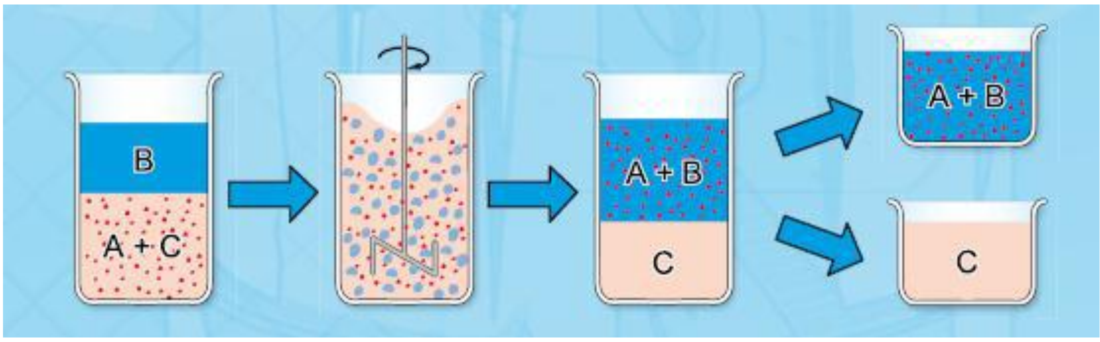

Figure 2.1: Liquid-liquid extraction

However, the figure above only happens theoretically and in reality, some of the liquid will still be in a mixture. 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 before the compound is analyzed. The ionic liquid solvent can be regenerated and is then available for extraction again.

CHAPTER 3: METHODOLOGY

This study aims to achieve maximum desulfurization of the model oil in optimum condition by using acidic ionic liquid. Below are among the experimental procedure carried out to achieve the objectives of this study.

3.1: Preparation of Model Oil

As the experiment requires using model oil, n-dodecane and dibenzothiophene is mixed to create the model oil that will be used for desulphurization. The amount of DBT is set at 2% to follow 1000ppm sulphur content and is first calculated. The calculation for this can be referred to in the appendix.

Procedure:

1. Weigh 1.477g of DBT accordingly.
2. Prepared measured DBT is added into a beaker and diluted continuously with 250ml dodecane.
3. Solution of dodecane fill dissolves the rest of the volumetric flask and is shaken until all of the visible DBT has been dissolved.

3.2: The Effect of H_2O_2:S Ratio

Several ratios of hydrogen peroxide to sulphur are studied in this paper.

Parameter of the first condition extraction process are as follow:

1. Type of extraction :Liquid-Liquid extraction
2. Temperature : 25°C (Room temperature)
3. Extraction time : 10 mins, 20 mins, 30 mins, continued by hourly extraction
4. Stir rate : 400 rpm

Extraction was done by mixing in the appropriate amount of model oil, acetic acid, hydrogen peroxide and the IL. Each of the components is measured separately before being mixed in the tube. While having different ratios of oxidizing agent, the amount of model oil for each system is kept at 25ml. Any lesser amount could result in the system being out of equilibrium after samplings.

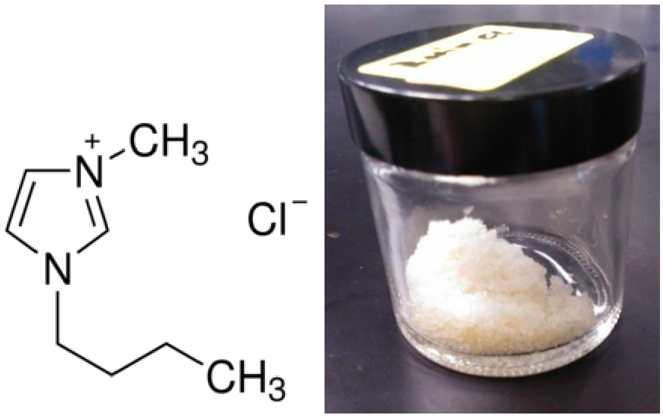

Figure 3.1: [Bmim][Cl]

[Bmim][Cl] is a solid at room temperature and first have to be liquefied. The salt is melted by placing in an oven at 70 degrees celcius and ensured that it only liquefies and not vaporizes. Extraction occurs at room temperature condition which are mild condition (24 - 26°C) while continuously stirred at 400rpm using magnetic stirrer.

Each sample was repeated three times.

3.3 The Effect of Model Oil: Ionic Liquid ratio

Parameter of the first condition extraction process are as follow:

1. Type of extraction :Liquid-Liquid extraction
2. Temperature : 25°C (Room temperature)
3. Extraction time : 10 mins, 20 mins, 30 mins, continued by hourly extraction
4. Stir rate : 400 rpm

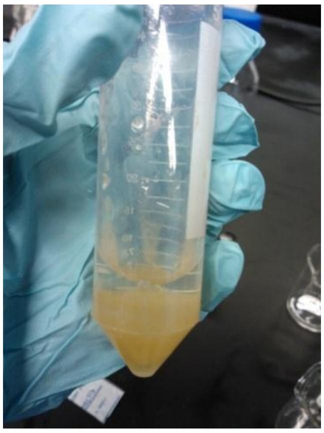

Figure 3.2: ODS process

The runs are repeated three times to get a more accurate and precise reading.

3.4: Data Analysis

Figure 2.3 Sample Extraction Process

For analysis, collections of the samples are taken from the system accordingly. Samples are taken in the time interval stated (varying between 10mins, 30 mins –at the beginning of the experiment, and hourly collection of samples.) To collect samples, the tubes are centrifuged to separate the oil and IL layer before taking 0.5ml of the top oil layer for analysis, as shown in Figure 3.3. As can be seen in Figure 2.2, the centrifuged sample has two distinct layers, the bottom being mostly the IL used. Only the model oil layer taken will be analyzed.

The method for data analysis is by using a Gas Chromatography as seen in figure 2.4. The column is readily available and is able to detect sulphur content. The retention time is at 20mins.

Figure 3.3: Gas Chromatography

CHAPTER 4: RESULTS AND DISCUSSION

Two parameters are studied closely in this paper. The first of which is the H_2O_2 ratio to the sulphur content and the second is the ratio of the IL to the model oil. To calculate the percentage of sulphur removal, the equation used is :

% Sulphur Removal = $\frac{s_i - s_f}{s_i}$ x 100%

Where s_i = initial concentration of sulphur

And s_f = final concentration of sulphur

4.1 The Effect of H_2O_2:S Ratio

The first parameter to be considered is the hydrogen to sulphur ratio. The experiment was repeated with another two parameters with one not using ionic liquid and another using the chosen ionic liquid, [Bmim][Cl].

Table 4.1: Sulphur removal at different H202 Ratio

	% of Sulphur Removal of different H_2O_2 Ratio				
Ratio	3:1	4:1	5:1	6:1	7:1
Without IL	26 %	24 %	35%	-	-
With [Bmim][Cl]	3.2 %	4 %	11%	9%	7%

To study the effect of H_2O_2:S Ratio, the IL ratio is kept at a constant 1:5 to model oil as advised. Focusing on the experiment that involves the IL, we can graph out the percentage of sulphur extracted after the experiment.

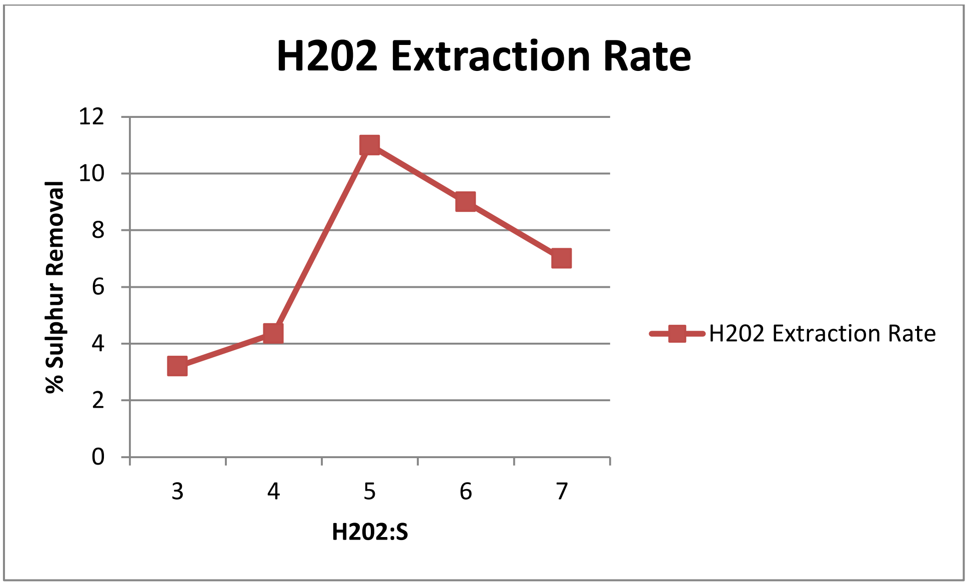

Figure 4.1: Graph of Ratio to Extraction

From this graph, we can clearly see the optimum parameters regarding the oxidizing agent ratio to sulphur. The graph can be interpreted that having too high of an oxidizing agent ratio diminishes the IL's capability of sulphur removal as Figure 4.1 shows a decreasing slope beginning at 5:1 ratio. It can then be concluded that the optimum for extraction is placed at 5:1 ratio.

4.2 The Effect of IL: Model Oil Ratio

Having seen that the optimum parameter in terms of oxidizing agent, we can further the study by ranging the IL: Model Oil Ratio. It is known that the mass ratio of the ionic liquid to model oil greatly changes the extraction rate.

Previous studies have done a 1:1 ratio of IL to model oil with great success. Due to this, a reduction in IL: Model Oil ratio is favoured as less ionic liquid used for a higher extraction would be beneficial in terms of cost. The main purpose of considering cost is for future projection of idealizing ODS as a method for sulphur removal on a larger scale.

Summary of Effect of IL ratio:

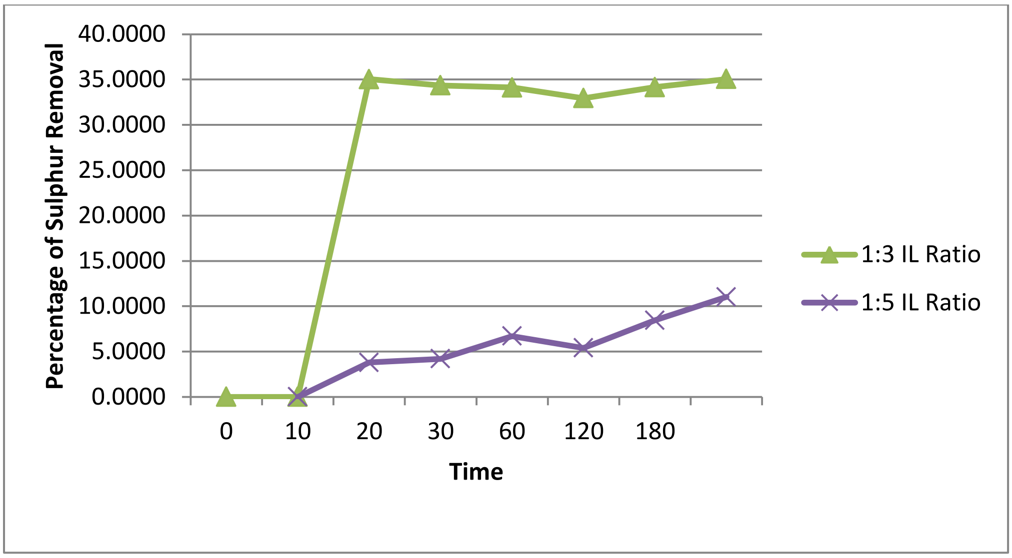

Figure 4.2: Sulphur removal by different IL Ratio

From the results it can be seen that decreasing the ratio of model oil from 1:5 ratio of IL to model oil to 1:3 increases the extraction rate from 11% to 35%. The increase can be seen as having more IL in contact and being able to extract the sulphur from the model oil.

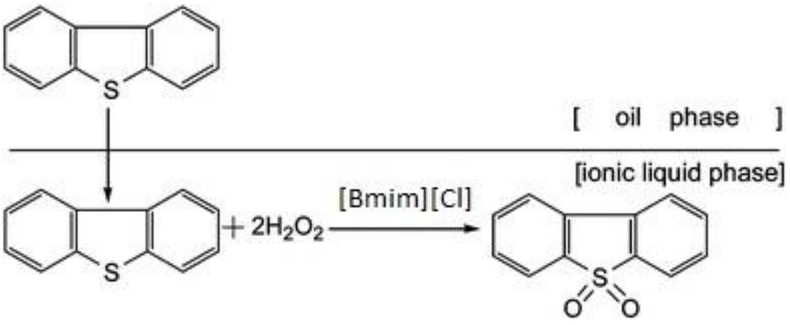

Figure 4.3: Oxidative Process

The process can be simply described as the figure above, where the ionic liquid phase acts as the medium (with the help of the oxidative agent) to extract the aromatic sulphur compound, oxidizing it and removing it from the oil phase. A higher ratio of IL would mean a better removal of DBT from the model oil.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Based on the results in the previous chapter it can be viewed that using the acidic IL [Bmim][Cl] using only a one time extraction is evaluated as less than a viable option as the extraction rate stops at 35% having the parameters of 5:1 hydrogen peroxide ratio. The sulphur removal using ODS without ionic liquid has a higher percentage, thus discrediting usage of [Bmim][Cl] as an effective extraction solvent. It is known that the extraction rate varies greatly with having a higher IL: Model Oil ratio and the system is found to be promising with a much higher extraction rate, however the cost associated with using ionic liquid undermines the usage of it in large scale.

In conclusion, the optimum parameter for [Bmim][Cl] for this system is at a ratio of 1:3 IL to model oil with the oxidizing agent, H_2O_2 to S of 5:1.

5.2 Recommendation

Although [Bmim][Cl] is deemed to be lacking in extraction, it was considered as the choice as it was in abundance and fit the criteria of being an acidic ionic liquid. Other preferred acidic ionic liquid for studies include BMIM[PF6], a bronsted-lewis acid.

Another issue mentioned here is the fact that the temperature for all the experiments are kept at room temperature. While it is known that the temperature is kept at room temperature to address that HDS uses a higher temperature and pressure parameter, it is not practical for a high extraction. It is ideal that the temperature is increased in future experiments as the oxidizing agent from literature, has been viewed to oxidize more at room temperature, hence increasing the oxidation of sulphur compounds and increasing removal rates of sulphur.

As this study and the system of using hydrogen peroxide with acetic acid catalyst can be further analyzed, below are the recommendations that are suggested for further investigations:

- Use other types of ILs in the ODS process to see the efficiency, which includes different length of cation chains IL.
- Apply different ratio of catalyst to optimize the ODS process.
- Continue the ODS process by extraction stages.

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APPENDIXES

Appendix A - Calculations

MW of Chemicals Used

Hydrogen Peroxide	H_2O_2	34.0147
Acetic Acid	CH_3C00H	60.05
Sulphur	S	32.06
[Bmim][Cl]	$C_8H_{15}ClN_2$	174.67
[Bmim][PF$_6$]	$C_8H_{15}F_6N_2P$	284.18g/mol

Calculation for preparation of Model Oil

For varying number of moles,

1) Find the % sulphur in the DBT concentration.
   Equation is as such:

$$\frac{MW\ Sulphur}{MW\ DBT}$$

2) 3 diff concentrations are used in the experiment, which are 2%, 4% and 6% weight.
   To calculate the 2% of DBT in dodecane, the equation used is

$$\frac{2\%\ \times\ \%\,concentration\ DBT}{\%\,S\ in\ DBT}$$

Calculation for Ratio of Oxidizing Agent

n_{sDBT} : n_{H202} at 4:1 ratio:

n_{H202} = 4 x 4.53 mmol

= 18.12mmol

Mass H_2O_2 = 18.12 x 34.01

= 616.2612mg

Vol of H_2O_2 $= \frac{616.2612\ x\ 10^{-3}\ g}{1.11gml^{-1}}$

= 0.5519ml

At 6% H_2O_2 Concentration: $\frac{0.5519}{9.253\ ml}$ = 9.253ml

Calculation for Ratio of Catalyst

n_{sDBT} : n_{cat} at 2:1 ratio:

n_{CAT} = 2 x 4.53 mmol

= 9.0625mmol

Mass H_2O_2 = 9.0625mmol x 60.05g/mol

= 544.203125mg

Vol of H_2O_2 = $\frac{544.203125\ x\ 10^{-3}\ g}{0.99 g ml^{-1}}$

= 0.5497ml

At 6% H_2O_2 Concentration: $\frac{0.5519}{9.253\ ml}$ = 9.253ml

Appendix B – Equipment and Analysis

Column for Gas Chromatography

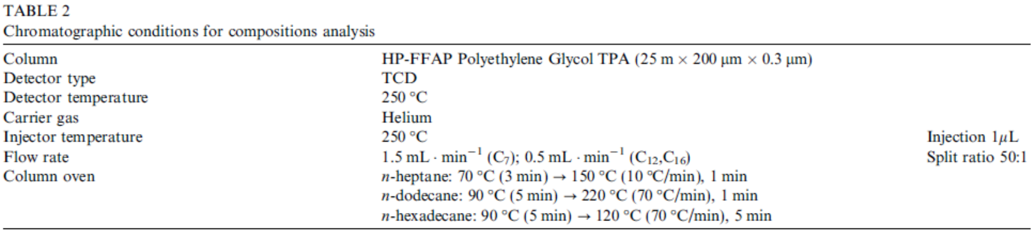
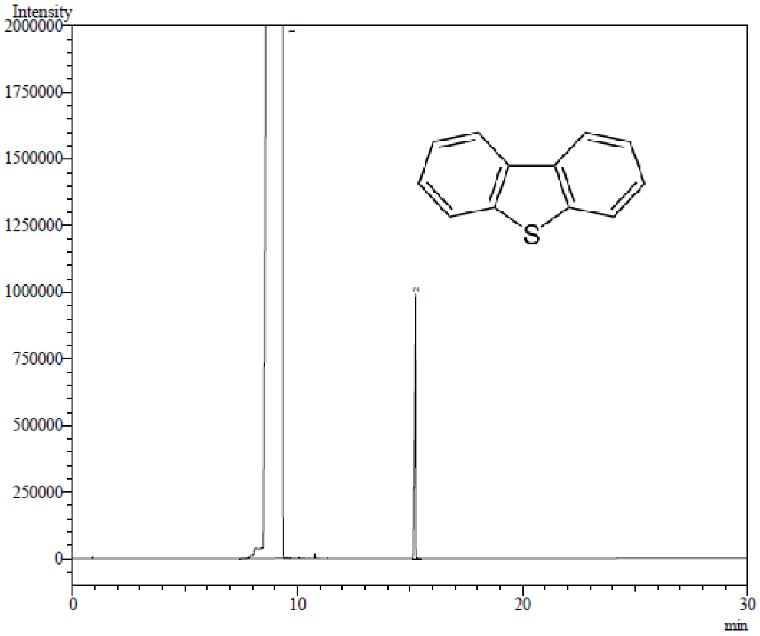


TABLE 2
Chromatographic conditions for compositions analysis

Column	HP-FFAP Polyethylene Glycol TPA (25 m × 200 μm × 0.3 μm)	
Detector type	TCD	
Detector temperature	250 °C	
Carrier gas	Helium	
Injector temperature	250 °C	Injection 1μL
Flow rate	1.5 mL · min^{-1} (C_7); 0.5 mL · min^{-1} (C_{12},C_{16})	Split ratio 50:1
Column oven	*n*-heptane: 70 °C (3 min) → 150 °C (10 °C/min), 1 min *n*-dodecane: 90 °C (5 min) → 220 °C (70 °C/min), 1 min *n*-hexadecane: 90 °C (5 min) → 120 °C (70 °C/min), 5 min	

Sample of Gas Chromatography Reading of Model Oil with 0.1% DBT



Peak#	Ret.Time	Area	Height	Conc.	Units	Name
1	9.607	38493982.11	21991763.76	0.0000		
2	15.497	3841111.73	989525.94	0.0000		
Total		42335093.84		0.0000		