DESULFURIZATION OF MODEL OIL USING IMIDAZOLIUM-BASED IONIC LIQUID

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**ABSTRACT**

Now a day, because of the dramatic environmental impact of sulfur oxides contained in engines emissions, sulfur content specification in fuels are becoming more and more stringent worldwide. In the petroleum refining industry, hydrodesulfurization (HDS) is the conventional process to reduce the sulfur levels of the fuels. However, HDS is cost consuming, besides requiring high temperature and high hydrogen pressure in order to eliminate the aliphatic and alicyclic sulfur compounds. Refractory sulfur compounds such as dibenzothiophene (DBT), methyl dibenzothiophene and 4, 6-methyl dibenzothiophene are less reactive to this process. Due to this reason, alternative sulfur removal techniques are being explored. In the past years, due to its unique properties both as extractant and also as catalyst, ionic liquids have gained increasing interest. 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF₄], has been study in this work. These ionic liquids were characterized using Fourier Transform Infrared spectroscopy (FTIR). The ionic liquids were then screened for sulfur removal from model oil (dodecane). The sulfur containing compound used in preparing the model oil, were DBT with different concentration, 250ppm, 500ppm, 750ppm, 1000ppm, and 2000ppm. In 2000ppm of DBT, contain of 348.04ppm of sulphur. The mixture was heated in the water bath at 30 ºC with a 185 rpm stirring for 30 minutes. The mass ratio of ILs to model oil was 1:1, 1:2, and 1:5. To analyze the model oil that contain of ILs by using High-Performance Liquid Chromatography (HPLC). From this experiment, it show that the higher efficiency of removal sulphur by using 1:1 volume ratio at 750ppm of DBT which is 56% removal.
ABSTRAK

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<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ppm</td>
<td>part per million</td>
</tr>
<tr>
<td>g/mol</td>
<td>gram per mol</td>
</tr>
<tr>
<td>g/cm³</td>
<td>gram per centimeter cubic</td>
</tr>
<tr>
<td>ρ</td>
<td>Density</td>
</tr>
<tr>
<td>mL</td>
<td>MiliLitre</td>
</tr>
</tbody>
</table>
### LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO</td>
<td>Sulfur Oxide</td>
</tr>
<tr>
<td>HDS</td>
<td>Hydrodesulfurization</td>
</tr>
<tr>
<td>ILs</td>
<td>Ionic Liquids</td>
</tr>
<tr>
<td>EMIM BF$_4$</td>
<td>1-ethyl-3-methylimidazolium tetrafluoroborate</td>
</tr>
<tr>
<td>DBT</td>
<td>Dibenzothiophene</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>FKKSA</td>
<td>Fakulti Kejuruteraan Kimia dan Sumber Asli</td>
</tr>
<tr>
<td>FPD</td>
<td>Flame Photometric Detector</td>
</tr>
<tr>
<td>BT</td>
<td>Benzothiophene</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas Chromatography Mass Spectroscopy</td>
</tr>
</tbody>
</table>
1 INTRODUCTION

1.1 Motivation and statement of problem

In the recent year, deep desulfurization (removal of sulfur at very low level < 200 ppm) of liquid fuel has been getting more attention due to the stringent regulation. Sulfur removal from fuel has increasing technical challenge as oil refineries face strong environmental pressures and strict regulatory requirement (Parkinson, 2001). Sulfur content in fuels leads to sulfur oxide (SOₓ) emission into the environment and inhibits the performance of pollution control element of vehicles. Therefore, to minimize the negative health and environment effects from automobile exhaust, many countries recently have mandated a reduction in the sulfur present in the motor fuel. In 2016, the maximum sulfur content is limited to 10 – 50 ppm, compared to earlier permitted value of 500 ppm in most countries (Dharaskar et al., 2013). The European Union has stringent fuel quality rules that require maximum diesel sulfur content of 50 ppm in 2005 (350 ppm in 2000), and maximum petrol (gasoline) sulfur content of 50 ppm in 2005 (150 ppm in 2005) (Kwak et al., 2000). Because of these phenomena, the deep desulfurization of fuel has attracted attention of the research community worldwide (Huang et al., 2004).

In petroleum and hydrocarbon industry, hydro-cracking processes or hydro-treating processes are often used to obtain low sulfur fuels. Also catalytic processes for desulfurization through hydro processing are used. While the performance of conventional hydro-processing catalysts have been highly effective for the reducing the sulfur levels, further removal of residual sulfur from the processed fuels is seen to largely increase the cost of hydro-processing. Hence these are highly energy intensive and consumes large amount of hydrogen (Knudsen et al., 1999). Other than that, there are many other processes for deep desulfurization of liquid fuel like extraction, selective adsorption, absorption, azeotropic distillation, hydrodesulfurization (HDS), catalytic hydrodesulfurization and so on. The deep desulfurization of sulfur compound from diesel fuel using ionic liquids (ILs) is more attractive due to their removal efficiency and other noble properties (Salem et al., 1997; Takahashi et al., 2002).
ILs termed as green solvents that can be used for desulfurization of liquid fuel due to their unique physical and chemical properties. The potential of ILs for new chemical technologies is beginning to be recognized as they have different application in many areas like as solvent for synthesis, catalysis or extraction, as an enzyme-‘friendly’ co-solvent, in batteries, as lubricant additives, in polymerization, in synthesis of nanoparticles, in analytical chemistry, and etc. It option to industrialists looking to minimize the environmental impact and the processing cost.

ILs are liquids that are comprised entirely by ion. One of the most important advantages of ILs can be tuned or controlled by tailoring their cationic and anionic structures to optimize their physicochemical properties (Zhang et al., 2008; Wilkes et al., 1986). ILs does not remain in the organic phase in extraction solvent, which can be greatly convenient for separation (Jiguang et al., 2008). In this research, the desulfurization efficiency of 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM] [BF₄] has been tested in model oil based on volume ratio effect.

1.2 Objectives
The main objective of this research is to investigate the efficiency of desulfurization on model oil using imidazolium-based ionic liquids.

1.3 Scope of this research
The following are the scope of this research:

i) Study the characterization of 1-ethyl-3-methylimidazolium tetrafluoroborate by their molecular structure and functional group using Fourier Transform Infrared Spectroscopy (FTIR)

ii) Sulfur removal compound, DBT from model oil by extraction with IL: model oil volume ratio of 1:1, 1:2, and 1:5.

iii) The efficiency of imidazolium-based ionic liquid by calculated the percentage of sulfur removal using High Performance Liquid Chromatography (HPLC).
1.4 Significance and Rationale

There are several significant of this research about using ILs as a solvent to extract the sulfur content. Effective is the main significant of this study. ILs can remove sulfur and has high ability to extract aromatic compound. It also easy to conduct and less time for sulfur removal process. Secondly, the lower operating cost. ILs can be prepared without required any modern technology and it can done using common chemical solution. The energy cost for sulfur removal is less compare conventional HDS since it does not required high condition of temperature and pressure. ILs also environmental friendly. It can be re-use again by purified the ILs by rotary evaporation.

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a description of the fuel and sulfur composition. Also a brief description of the sulfur. The previous work for desulfurization by using hydrodesulfurization process was stated in this chapter. The description of review about ionic liquid, their properties, uses and applications.

Chapter 3 gives a review of materials and methods use for this experiment. Chemical and equipment that use are supplied from FKKSA chemical lab store. General flow of methodology for this research are characterization of ILs by using FTIR, preparation of model oil by mixed the dibenzothiophene (DBT) and dodecane, extractive desulfurization of model oil, preparation of mobile phase and lastly are analytical procedures by using HPLC.

Chapter 4 is review about desulfurization of model oil. This chapter focus on the results of this research. Consist of results of FTIR spectroscopy and HPLC spectroscopy. Also about the influence of ionic liquid to model oil volume ratio on DBT extraction, influence of ionic liquid to model oil volume ratio on the percentage of DBT content remover and the comparison on percentage.

Chapter 5 give a review about conclusion of the experiment base on the result get in the chapter four. Consist of conclusion and future work recommendation step to make the experiment more successful and accurate.
2 LITERATURE REVIEW

2.1 Fuels and Sulfur Composition

The compositions of transportation fuels vary widely depending on the crude oils used, the refining process, the product demand, and the product specifications. The approximate compositions of gasoline, diesel, and jet fuel are given in Table 1. Branched and n-alkanes are the main ingredients of these fuels, typically 70–80%. The major alkane is n-hexane and the main branched alkanes are C5 and C6 compounds. The aromatics are mainly benzene, toluene, xylenes, and alkyl benzenes, totalling about 20–30%.

The sulfur compounds in transportation fuels can be analyzed with x-ray fluorescence spectroscopy or by gas chromatography equipped with a capillary column plus a flame photometric detector (FPD). (McGaughey 1980). The remaining sulfur compounds after HDS are mainly thiophene (T), BT, DBT and their alkylated derivatives. The alkylated derivatives with alkyl groups at the 4- and 6-positions are most difficult to remove and are referred to as refractory sulfur species. The GC-FPD chromatograms of a sample each of commercial gasoline, diesel, and jet fuel, are shown in Fig. 2.

The FPD only detects sulfur compounds. The dominant sulfur compounds in the gasoline were (in decreasing order): 3-MT, BT, T, 2-MT, and 2,4-DMT. Those in the diesel were: 4-MDBT, 4,6-DMDBT, 2,4,6-TMDBT, 3,6-DMDBT, DBT, 2,3,7-TMBT, 2,3,5 TMBT, 2,3-DMBT, and others. The sulfur compounds in the jet fuel were: 2,3,7-TMBT, 2,3-DMBT, and the minor species 2,3,5-TMBT and 2,3,6-TMBT. An example for the sulfur composition of gasoline is given in Table 2. More details on the sulfur composition of all commercial fuels can be found elsewhere. (Ma, Sun et al. 2002).
<table>
<thead>
<tr>
<th></th>
<th>Gasoline&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Diesel&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Jet fuel&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling range (°C)</td>
<td>40 – 204</td>
<td>232 – 350</td>
<td>165 – 265</td>
</tr>
<tr>
<td>Aromatic</td>
<td>30.5</td>
<td>17</td>
<td>18</td>
</tr>
<tr>
<td>Olefins</td>
<td>1.8</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>n-Alkanes</td>
<td>17.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Branched alkanes</td>
<td>32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cycloalkanes</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saturates&lt;br&gt;paraffins</td>
<td></td>
<td>78</td>
<td>60</td>
</tr>
<tr>
<td>Naphthenes</td>
<td></td>
<td></td>
<td>20</td>
</tr>
</tbody>
</table>

<sup>a</sup>Sciences International, Inc., “Toxicological Profile for Gasoline,” Report to Department of Health and Human Services, June, 1995.<sup>b</sup>Ma et al.<sup>c</sup>Ma et al.
Figure 2-1: GC-FPD chromatograms of a commercial gasoline (A) or jet fuel (B) or diesel (C). (Herna’ndez-Maldonado and Yang 2004)
Table 2-2: Example of Heteroatom Contents in the FCC Gasoline.

<table>
<thead>
<tr>
<th>Heteroatoms</th>
<th>Content (ppmw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>16.0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>14.0</td>
</tr>
<tr>
<td>Mercaptan sulfur</td>
<td>24.2</td>
</tr>
<tr>
<td>Sulfide sulfur</td>
<td>7.3</td>
</tr>
<tr>
<td>Thiophene sulfur</td>
<td>61.9</td>
</tr>
<tr>
<td>( \text{C}_1 ) thiophene sulfur</td>
<td>115.0</td>
</tr>
<tr>
<td>( \text{C}_2 ) thiophene sulfur</td>
<td>130.6</td>
</tr>
<tr>
<td>( \text{C}_3 ) thiophene sulfur</td>
<td>90.9</td>
</tr>
<tr>
<td>( \text{C}_4 ) thiophene sulfur</td>
<td>88.0</td>
</tr>
<tr>
<td>Benzo thiophene and</td>
<td>238.1</td>
</tr>
<tr>
<td>dibenzo thiophene sulfur</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>786.0</strong></td>
</tr>
</tbody>
</table>

Source from: (Irvine 1998)

### 2.2 Sulfur

Sulfur has been known since ancient times. The name may have been derived from the Arabic ‘sufra’ meaning yellow, or the Sanskrit ‘shulbari’ meaning enemy (ari) of copper (shulba) (Weichert et al., 2004). The Sanskrit possibility is appealing, because it carries a message about people’s knowledge of chemistry from long ago: sulfur actually does react easily with many metals, including copper. Sulfur is present in petroleum in a form of different compounds of which about 70% are made up by thiophen and its derivates. The range of the sulfur is between 0.1 to 10% depending on a place of origin. (Miloslaw et. al, 2005). As the temperature of boiling point of individual fractions increase, the sulfur content in diesel fuel fraction increase.
### Table 2-3: Properties table of Sulfur

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Number</td>
<td>16</td>
</tr>
<tr>
<td>Atomic Mass</td>
<td>32.06 g.mol⁻¹</td>
</tr>
<tr>
<td>Density</td>
<td>2.07 g.cm⁻³ at 20°C</td>
</tr>
<tr>
<td>Melting Point</td>
<td>113°C</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>445°C</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>2.07 at 70°F</td>
</tr>
<tr>
<td>Solubility in Water</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>

2.3 **Hydrodesulfurization**

Hydrodesulfurization (HDS) is a conventional method that is widely used for the removal of sulfur compounds in the petroleum refining industry (Prashant, 2010). This method can eliminate the aliphatic and non-aliphatic sulfur compounds effectively. However, some thiophene-based organic sulfur compounds, such as benzothiophene, dibenzothiophene (DBT), and their derivatives, are difficult to remove by HDS because of their high steric hindrance (Bosmann, 2001).

To achieve the target of deep desulfurization, the reactor pressure and treatment time of the classic HDS process have to be elevated. At the same time, the HDS needs to consume a large amount of hydrogen and energy. Thus, the free hydrodesulfurization process has become a hot issue, such as biodesulfurization, adsorption, and extraction (Jochen, 2004). The principle of extraction desulfurization is that organic sulphides and hydrocarbons have different solubilities in the solvent.

One of its most important advantages is that it can be carried out in normal temperature and pressure. However, the common extractants used for the desulfurization process are traditional organic solvents, which pollute the environment seriously because of their strong volatile characteristic and high toxicity. Therefore, the finding of greener, more safe and efficient novel extractants can be of great significance to improve the extraction desulfurization process.
2.4 Ionic Liquids (ILs)

ILs offer new opportunities for the development of extraction solvents. The term ILs implies a material that is fluid at (or close to) ambient temperature, is colourless, has a low viscosity and is easily handled (Sheldon, 2001). The ILs known today are based on different large, organic cations combined with a great variety of organic and inorganic anions. Compared to molecular solvents, ILs have the advantage of being liquid over a wide range of temperatures and of having a non-volatile nature (Zhao et al, 2008). The latter property has been the reason to call ILs ‘green solvents’ and to start their development as alternative, environmental-friendly solvents.

The properties of an ILs are determined by the combination of cation and anion. Due to the large number of possible ion combinations, which gives the opportunity to tailor a specific solvent for a particular separation, ILs are also called designer solvents. Since, in recent years ILs gained more and more interest for different fields of application, (Maase, 2008) suggests the classification in process chemicals, performance chemicals and engineering fluids.

2.4.1 Properties of ILs

Physical and chemical properties of ILs can be altered by impurities such as water, organic solvents and chloride ions. In table 2.3 are listed important properties for some ILs. The compilation is provided for prospective research workers to obtain an idea about the characteristic of ILs. Below are summarized some pertinent physical and chemical properties of ILs.
**2.4.1.1 Melting Points**

This is the most significant characteristic property of ILs that can be correlated with the structure and composition of ILs. Selection of both the cation and anion determine with the melting point of an ILs. An ILs with a cation with low symmetry possesses low melting point than the one with high symmetry. Weak intermolecular interactions and a good distribution of charge in the cation favor low melting point of ILs. Chloroaluminate ILs comprising of [EMIM] Cl/AlCl3, for example, shows interesting trend in their melting point. The experimental phase diagram for [EMIM] Cl/AlCl3 system is shown in figure 2-2. One can see that the melting point of [EMIM] Cl/AlCl3 is very sensitive to the composition of IL (Fenin et al, 1984). It seems that it is possible to combine two species to form a suitable IL that will have low melting point. This is an important characteristic of ILs, which can be helpful in designing ILs suitable for a given application.
2.4.1.2 Density

In general ILs is denser than water. The magnitude of density, \( \rho \), in the case of ILs depends upon the constituent cation and anion. For instance, the \( \rho \) value of ILs varies with the length on N-alkyl chain on the imidazolium cation. As a thumb rule, the density of comparable ILs decreases with the increase in the bulkiness of organic cation. Further, the density of ILs also depends upon the choice of the anion. Normally, \( \rho \) of an ILs varies in the range of 1.05 to 1.36 g cm\(^{-3}\) at ambient temperature (Pringle et al, 2003).

Figure 2-2: Experimental phase diagram for [EMIM] Cl/AlCl\(_3\) system.
2.4.1.3 Thermal Stability

Most of ILs are stable at and above 400°C. The thermal decomposition depends on the nature of anions rather than on that of cations. Further thermal decomposition also decreases with increase in hydrophilic of anions. Due to contrasting reports on thermal stability of various ILs, it is recommended that high decomposition temperature of ILs be calculated from fast Thermo Gravimetric Analysis (TGA) scans under a protective environment (Kosmulski et al, 2004).

2.4.1.4 Diffusion and conductivity

In order to effectively use ILs for different applications, it is necessary to study diffusion and conductivity behaviour of ILs. From the pulse-gradient spin-echo NMR data, it has been shown that both [BMIM] and [BPy] cations diffuse almost at the same rate as [BF₄]⁻. The sum of cationic and anionic diffusion coefficients for each IL follows the order: [EMIM][Tf₂N] > [EMIM] [BF₄] > [BP][Tf₂N] > [BP][BF₄]. One should note that the relationship between chemical structures and transport properties of ILs is not properly investigated so far. The Stokes-Einstein and Nernst-Einstein equations have been employed to analyse the ionic diffusivity of ILs (Noda et al, 2001). The analysis of the data showed that diffusion of an ion was strongly correlated with the counter ion used to constitute on ILs. The diffusion coefficients of ILs have been observed to be strongly influenced by ion-pairs and ion-aggregates present in ILs. The issue pertaining to the contrast between the information obtained from the analysis of conductivity and diffusion data merits investigation. The relationship between fluidity and conductance of ILs indicated that ILs could be characterized with ideal quasi lattice structure (Xu et al, 2003). It is now observed that the viscosity alone does not account for the conductivity of ILs. Other factors like ionic size and ion pairs also play significant role in governing the conductivity of ILs (Every et al, 2004).
2.4.1.5 Viscosities

Viscosity of ILs is of immense importance if ILs needs to use as solvent media during a chemical reaction or for any other applications. For example, if the viscosity of ILs is very high, it will be detrimental to the process of a reaction. Several ILs possess very high viscosities and therefore have been noted to be less suitable as solvent media. Further, high viscosities of ILs also reduce the diffusion rates of redox reactions. The viscosity of [EMIM][Tf$_2$N], for instance is 28 cP, while that of [BMPYRR][NMs$_2$] 1680 cP at 298 K. [BMPYRR] stands for 1-butyl-1-methylpyrrolidinium, whereas [NM$_2$s] for bis-(methanesulfonyl)amide species. It is important to note here that viscosities of ILs show non-Arrhenius behaviour. Efforts have, however, been made to fit viscosity data with the Vogel-Tammann-Fulcher (VFT) equation. Viscosity of a majority of ILs remains constant with increasing shear rate; hence these substances are termed as Newtonian fluids (Huddleston et al, 2001).

Viscosity data of ILs have also been investigated at high pressures. Figure 2.4 the pressure dependence of viscosity of [BMIM][BF$_4$] at 25°C is shown. As is clear from the illustration, the viscosity-pressure plot for the ILs shows normal variation. The high pressure viscosity data have been analysed in terms of Litovitz and VFT equations.

The viscosity of ILs changes drastically upon addition of a solvent. Several years ago, it was shown that viscosity of a high melting point tetra-n-butylammonium picrate (m.pt. ~89°C) reduced dramatically upon addition of anisole, nitrobenzene and n-butanol (Kumar, 1993). This phenomenon is also noted in ILs and their mixtures with solvent at or around room temperature. Accordingly, the viscosities of these ILs can be lowered by adding a solvent possessing low viscosity. This observation bears great significance in carrying out chemical reactions in those ILs the viscosities of which are very high. For instance, the viscosity of [OMIM] I can decrease exponentially upon addition of dichloromethane in the ILs-rich mixture as shown in figure 2.5. The authors are not aware of any possibility exists to employ the concept of hole formation to examine the composition dependence of viscosity of ILs. More data on a variety of ILs and their mixtures with solvents of different polarity are required to ascertain this behavior.