# DESULFURIZATION OF MODEL OIL USING IMIDAZOLIUM-BASED IONIC LIQUIDS

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## BACHELOR OF CHEMICAL ENGINEERING (GAS TECHNOLOGY) UNIVERSITI MALAYSIA PAHANG

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# DESULFURIZATION OF MODEL OIL USING IMIDAZOLIUM-BASED IONIC LIQUID

## WAN MOHD SYAZWAN BIN WAN ABDULLAH

Thesis submitted in partial fulfilment of the requirements For the award of the degree of Bachelor of Chemical Engineering (Gas Technology)

Faculty of Chemical & Natural Resources Engineering UNIVERSITI MALAYSIA PAHANG

JUNE 2013

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## SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering (Gas Technology).

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| Position                | : Senior Lecturer                 |
| Date                    | : 9 July 2013                     |

## STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature:Name: Wan Mohd Syazwan Bin Wan AbdullahID Number: KC09010Date: 9 July 2013

## Dedication

Dedicated, in thankful appreciation for support, encouragement and understanding to my beloved family, friends and my supervisor. May Allah S.W.T bless our life.

#### ACKNOWLEDGEMENT

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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. 1ethyl-3-methylimidazolium tetrafluoroborate  $[EMIM][BF_4]$ , 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 °C 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

Kandungan oksida sulfur yg terkandung di dalam enjin pelepasan kenderaan memberi kesan yang buruk terhadap alam sekitar. Kandungan spesifik sulfur di dalam petroleum semakin meningkat di seluruh dunia. Dalam industri penapisan petroleum, prosess yang biasa digunakan ialah hydrodesulfurization (HDS) untuk mengurangkan tahap kandungan sulfur daripada bahan api. Walau bagaimanapun, proses hydrodesulfurization (HDS) memerlukan kos yang tinggi, disamping suhu dan tekanan hidrogen yang tinggi untuk menyingkirkan alifatik dan sebatian alicyclic sulfur. Pengurangan kandungan sulfur seperti dibenzothiophene (DBT), metil dibenzothiophene dan 4,6-metil dibenzothiophene adalah kurang berkesan melalui proses ini. Oleh sebab itu, alternatif untuk mengurangkan kandungan sulfur perlu dikaji. Kebelakangan ini, disebabkan oleh sifat-sifat yang unik oleh cecair terion dalam mengurangkan kandungan sulfur baik sebagai pemangkin atau tidak telahpun diperkenalkan. Dalam kajian ini, 1-etil-3-metilimidazolium tetrafluoroborate [EMIM][BF<sub>4</sub>] telah digunakan sebagai cecair terion. Kriteria cecair terion ini di analisis menggunakan Fourier Transform Infrared Spectroscopy (FTIR). Kemudian, cecair terion digunakan dalam proses penyaringan untuk mengurangkan kandungan sulfur daripada model minyak (dodecane). DBT digunakan sebagai sebatian sulfur, dengan menggunakan kepekatan sebanyak 250ppm, 500ppm, 750ppm, 1000ppm dan 2000ppm. Pada kepekatan 2000ppm DBT, sulfur yang terkandung adalah 348ppm. Campuran DBT dan dodecane dipanaskan dalam water bath pada suhu 30 °C dengan digongcang pada 185rpm selama 30 minit. Nisbah cecair terion kepada model minyak adalah 1:1, 1:2 dan 1:5. HPLC digunakan dalam analisis ini. Daripada kajian ini, ia menunjukkan bahawa kebolehan untuk menyingkirkan sulfur dalam nisbah 1:1 pada kepekatan 750ppm DBT sebanyak 56% penyingkiran.

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## LIST OF SYMBOLS

ppmpart per million $g.mol^{-1}$ gram per mol $g.cm^{-3}$ gram per centimeter cubic $\rho$ DensitymLMiliLitre

## LIST OF ABBREVIATIONS

| SO                   | Sulfur Oxide                                  |
|----------------------|-----------------------------------------------|
| HDS                  | Hydrodesulfurization                          |
| ILs                  | Ionic Liquids                                 |
| EMIM BF <sub>4</sub> | 1-ethyl-3-methylimidazolium tetrafluoroborate |
| DBT                  | Dibenzothiophene                              |
| HPLC                 | High Performance Liquid Chromatography        |
| FTIR                 | Fourier Transform Infrared Spectroscopy       |
| FKKSA                | Fakulti Kejuruteraan Kimia dan Sumber Asli    |
| FPD                  | Flame Photometric Detector                    |
| BT                   | Benzothiophene                                |
| GC-MS                | Gas Chromatography Mass Spectroscopy          |

## **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 (SO<sub>x</sub>) 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 hydrotreating 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' cosolvent, 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] [BF<sub>4</sub>] 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:

- 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  $C_5$  and  $C_6$  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).

|                     | Gasoline <sup>a</sup> | Diesel <sup>b</sup> | Jet fuel <sup>c</sup> |
|---------------------|-----------------------|---------------------|-----------------------|
| Boiling range (° C) | 40 - 204              | 232 - 350           | 165 – 265             |
| Aromatic            | 30.5                  | 17                  | 18                    |
| Olefins             | 1.8                   | 5                   | 2                     |
| n-Alkanes           | 17.3                  |                     |                       |
| Branched alkanes    | 32                    |                     |                       |
| Cycloalkanes        | 5                     |                     |                       |
| Saturates           |                       | 78                  |                       |
| paraffins           |                       |                     | 60                    |
| Naphthenes          |                       |                     | 20                    |

Table 2-1: Typical composition of transportation fuels (vol %).

<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)

| Heteroatoms                     | Content (ppmw) |  |
|---------------------------------|----------------|--|
| Nitrogen                        | 16.0           |  |
| Oxygen                          | 14.0           |  |
| Mercaptan sulfur                | 24.2           |  |
| Sulfide sulfur                  | 7.3            |  |
| Thiophene sulfur                | 61.9           |  |
| C <sub>1</sub> thiophene sulfur | 115.0          |  |
| $C_2$ thiophene sulfur          | 130.6          |  |
| $C_3$ thiophene sulfur          | 90.9           |  |
| $C_4$ thiophene sulfur          | 88.0           |  |
| Benzothiophene and              | 238.1          |  |
| dibenzothiophene sulfur         |                |  |
| Total                           | 786.0          |  |

**Table 2-2:** Example of Heteroatom Contents in the FCC Gasoline.

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 tiophen 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.

| Physical Properties  | Description                     |  |
|----------------------|---------------------------------|--|
| Atomic Number        | 16                              |  |
| Atomic Mass          | $32.06 \text{ g.mol}^{-1}$      |  |
| Density              | 2.07 g.cm <sup>-3</sup> at 20°C |  |
| Melting Point        | 113°C                           |  |
| <b>Boiling Point</b> | 445°C                           |  |
| Specific Gravity     | 2.07 at 70°F                    |  |
| Solubility in Water  | Insoluble                       |  |

Table 2-3: Properties table of Sulfur

#### 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.

| Table 1—A summary of some physico-chemical properties of ionic liquids at 25°C |                               |                   |                                        |
|--------------------------------------------------------------------------------|-------------------------------|-------------------|----------------------------------------|
| Ionic liquid                                                                   | Density $(g \text{ cm}^{-3})$ | Viscosity<br>(cP) | Conductivity<br>(mS cm <sup>-1</sup> ) |
| [BMIM][BF <sub>4</sub> ]                                                       | 1.12                          | 1.7               | 233                                    |
| [BMIM][PF <sub>6</sub> ]                                                       | 1.368                         | 450               | n.a.                                   |
| [BMIM][Tf <sub>2</sub> N]                                                      | 1.436                         | 52                | n.a.                                   |
| [BMIM] I                                                                       | 1.44                          | 1110              | n.a.                                   |
| [BMIM][TfO]                                                                    | 1.29                          | 90                | 3.7                                    |
| [BMIM][CF <sub>3</sub> CO <sub>2</sub> H]                                      | 1.21                          | 73                | 3.2                                    |
| $[OMIM][PF_6]$                                                                 | 1.237                         | 682               | n.a.                                   |
| [EMIM][Tf <sub>2</sub> N]                                                      | 1.519                         | 28                | n.a.                                   |
| [EMIM][NMs <sub>2</sub> ]                                                      | 1.343                         | 787               | 1.7                                    |
| [EM2IM][Tf <sub>2</sub> N]                                                     | 1.51                          | 88                | 3.2                                    |
| $[OMIM][PF_6]$                                                                 | 1.237                         | 682               | n.a.                                   |
| [OMIM][Tf <sub>2</sub> N]                                                      | 1.320                         |                   | n.a.                                   |
| [OMIM]Cl                                                                       | 1.00                          | 337               | n.a.                                   |
| n.a. not available                                                             |                               |                   |                                        |

Table 2-4: Summary of some physico-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/AlCl<sub>3</sub>, for example, shows interesting trend in their melting point. The experimental phase diagram for [EMIM] Cl/AlCl<sub>3</sub> system is shown in figure 2-2. One can see that the melting point of [EMIM] Cl/AlCl<sub>3</sub> 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.



Figure 2-2: Experimental phase diagram for [EMIM] Cl/AlCl<sub>3</sub> system.

## 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 1.36g cm<sup>-3</sup> at ambient temperature (Pringle et al, 2003).

#### 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  $[BF_4]^-$ . The sum of cationic and anionic diffusion coefficients for each IL follows the order:  $[EMIM][Tf_2N] > [EMIM] [BF_4] > [BP] [Tf_2N] > [BP] [BF_4]$ . 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<sub>2</sub>N], for instance is 28 cP, while that of [BMPYRR][NMs<sub>2</sub>] 1680 cP at 298 K. [BMPYRR] stands for 1-butyl-1-methylpyrrolidinium, whereas [NMs2] for bis-(methanesulfonyl)amide species. It is important to note here that viscosities of ILs show non-Arrhenius behaviour. Efforts have, however, been made tofit 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<sub>4</sub>] 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.



Figure 2-3: Pressure dependence on viscosity,  $\eta$ , for [BMIM] BF<sub>4</sub> at 25°C



**Figure 2-4**: The changes in viscosity, η, of [OMIM] I upon addition of dichloromethane at 25°C.

#### 2.4.1.6 Enthalpy of ILs

The measurement of enthalpies of ILs is still at the state of infancy. The solution enthalpies have been measured for some ILs based on imidazolium cation in different solvents at 25°C by using isothermal titration calorimeter. In figure 2.6, the mole fraction,  $x_i$  dependence on the excess partial molar enthalpies,  $H_i^E$  for the IL is shown (Marczak et al, 2003). One finds a strong exponential dependence of  $H_i^E$  in very dilute solutions for 1-hexanol, ethylene glycol, while for t-butanol, methanol, toluene and chloroform, the dependence is linear. No modelling work of enthalpies in ILs has so far been initiated.



Figure 2-5: Typical structures combine organic cations with inorganic or organic anions

## 2.4.2 Use and Applications

Ultimately, the possible combinations of organic cations and anions places chemists in the position to design and fine-tune physical and chemical properties by introducing or combining structural motifs and, thereby, making tailor-made materials and solutions possible. The following chart summarizes important properties of ILs and their potential and current applications:



Figure 2-6: Important properties of ILs and their potential and current applications

### 2.4.2.1 Pharmaceuticals

Recognising that approximately 50% of commercial pharmaceuticals are organic salts, ILs forms of a number of pharmaceuticals have been investigated. Combining a pharmaceutically active cation with a pharmaceutically active anion leads to a Dual Active ILs in which the actions of two drugs are combined (Rogers et al, 2010).

## 2.4.2.2 Cellulose Processing

At a volume of some 700 billion tons, cellulose is the earth's most widespread natural organic chemical and, thus, highly important as a renewable resource. But even out of nature's annual 40 billion tons output, only approx. 5% is used as feedstock for further processing. More intensive exploitation of cellulose, as a renewable feedstock, is aided by the development of suitable solvents for mechanical and chemical processing. ILs has been shown to be highly effective at solvating cellulose to technically useful concentrations (Roger et al, 2002). This may allow for development of new processes and intensification of existing ones substituting existing cellulose solvents for ILs. The use of molten salts in cellulose processing originally dates back to a patent application from 1930 where mixtures of molten 1-alkylpyridinium chlorides were used to dissolve cellulose, followed by subsequent chemical and mechanical processing. Further advances have generally led to lowering of melting points and viscosities to a point where there are now room temperature ILs available that dissolve cellulose (Fukuya et al, 2009).

Making viscose-based fibres from dissolving pulp currently involves the use, and subsequent disposal, of great volumes of various chemical auxiliaries, esp. carbon disulfide (CS<sub>2</sub>). Major volumes of wastewater need to be disposed of. Following in the footsteps of the lyocell process, which uses hydrated N-Methylmorpholine N-oxide, as a novel non-aqueous solvent for the dissolution of the pulp, it has been suggested that ILs can greatly simplify these processes, serving as solvents that are potentially recyclable. The "Institut für Textilchemie und Chemiefasern" (ITCF) in Denkendorf and BASF are jointly investigating the properties of fibers spun from solutions of cellulose dissolved in ILs in a pilot plant. The dissolution of cellulose–based materials like tissue paper waste, generated in chemical industries and at research laboratories, in room temperature ILs 1-butyl-3-methylimidazolium chloride, [BMIM] [Cl] and the recovery of valuable compounds by electro deposition from this cellulose matrix was studied (Nagarajana et al, 2007)

### 2.4.2.3 Gas Handling

ILs have several properties that make them useful in gas storage and handling applications, including low vapor pressure, stability at high temperatures, and solvation for a wide variety of compounds and gases. They also have weakly coordinating anions and cations which are able to stabilize polar transition states. Many ionic liquids can be reused with minimal loss of activity. The company Air Products uses ILs instead of pressurized cylinders as a transport medium for reactive gases such as trifluoroborane, phosphine and arsine. The gases are dissolved in the liquids at or below atmospheric pressure and are easily withdrawn from the containers by applying a vacuum.

Gas manufacturer Linde exploits the low solubility of hydrogen in ILs to compress the gas up to 450 bar in filling stations by using an ILs piston compressor, which has only 8 moving parts (down from about 500 in a conventional piston pump). ILs [BMIM][Cl] has been used for separating hydrogen from ammonia borane (Karkamkar et al, 2007). ILs and amines can be used to capture carbon dioxide CO2 and purify natural gas.

#### 2.4.2.4 Solar Thermal Energy

ILs have potential as a heat transfer and storage medium in solar thermal energy systems. Concentrating solar thermal facilities such as parabolic troughs and solar power towers focus the sun's energy onto a receiver which can generate temperatures of around 600°C (1,112°F). This heat can then generate electricity in a steam or other cycle. For buffering during cloudy periods or to enable generation overnight, energy can be stored by heating an intermediate fluid. Although nitrate salts have been the medium of choice since the early 1980s, they freeze at 220°C (428°F) and thus require heating to prevent solidification. Ionic liquids such as 1-alkyl-3-methylimidazolium tetrafluoroborate,  $C_4$ mim [BF<sub>4</sub>] have more favourable liquid-phase temperature ranges (-75 to 459°C) and could therefore be excellent liquid thermal storage media and heat transfer fluids (Roger et al, 2001).

#### 2.4.2.5 Batteries

Researchers have identified ILs that can replace water as the electrolyte in metal-air batteries. ILs have great appeal because they evaporate at much lower rates than water, increasing battery life by drying slower. Further, ILs have an electrochemical window of up to six volts (Armand et al, 2009) (versus 1.23 for
water) supporting more energy-dense metals. Energy densities from 900-1600 watthours per kilogram appear possible.

A Metal-air battery draws oxygen through a porous ambient "air" electrode (cathode) and produces water, hydrogen peroxide, or hydroxide anions depending on the nature oxygen reduction catalyst and electrolyte. These compounds store the electrons released by the oxidation of the anode.

# 2.5 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy has been a workhorse technique for materials analysis in the laboratory for over seventy years. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis.

Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was needed. A solution was developed which employed a very simple optical device called an interferometer. The interferometer produces a unique type of signal which has all of the infrared frequencies "encoded" into it. The signal can be measured very quickly, usually on the order of one second or so. Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes.

# 2.5.1 The Sample Analysis Process



Figure 2-7: Work flow FTIR analysis



Figure 2-8: Schematic diagram for FTIR analysis

Because there needs to be a relative scale for the absorption intensity, a background spectrum must also be measured. This is normally a measurement with no sample in the beam. This can be compared to the measurement with the sample in the beam to determine the "percent transmittance." This technique results in a spectrum which has all of the instrumental characteristics removed. Thus, all spectral features which are present are strictly due to the sample. A single background measurement can be used for many sample measurements because this spectrum is characteristic of the instrument itself.

## 2.5.2 Advantages of FTIR

Some of the major advantages of FT-IR over the dispersive technique include:

• **Speed**: Because all of the frequencies are measured simultaneously, most measurements by FT-IR are made in a matter of seconds rather than several minutes. This is sometimes referred to as the Felgett Advantage.

• **Sensitivity**: Sensitivity is dramatically improved with FT-IR for many reasons. The detectors employed are much more sensitive, the optical throughput is much higher (referred to as the Jacquinot Advantage) which results in much lower noise levels, and the fast scans enable the co-addition of several scans in order to reduce the random measurement noise to any desired level (referred to as signal averaging).

• Mechanical Simplicity: The moving mirror in the interferometer is the only continuously moving part in the instrument. Thus, there is very little possibility of mechanical breakdown.

• **Internally Calibrated**: These instruments employ a HeNe laser as an internal wavelength calibration standard (referred to as the Connes Advantage). These instruments are self-calibrating and never need to be calibrated by the user.

These advantages, along with several others, make measurements made by FT-IR extremely accurate and reproducible. Thus, it a very reliable technique for positive identification of virtually any sample. The sensitivity benefits enable identification of even the smallest of contaminants. This makes FT-IR an invaluable tool for quality control or quality assurance applications whether it be batch-to-batch comparisons to quality standards or analysis of an unknown contaminant. In addition, the sensitivity and accuracy of FT-IR detectors, along with a wide variety of software algorithms, have dramatically increased the practical use of infrared for quantitative analysis. Quantitative methods can be easily developed and calibrated and can be incorporated into simple procedures for routine analysis.

Thus, the Fourier Transform Infrared (FT-IR) technique has brought significant practical advantages to infrared spectroscopy. It has made possible the development of many new sampling techniques which were designed to tackle challenging problems which were impossible by older technology. It has made the use of infrared analysis virtually limitless.

# 2.6 High Performance Liquid Chromatography (HPLC)

High Performance Liquid Chromatography (formerly referred to as high-pressure liquid chromatography), HPLC, is a chromatographic technique used to separate the components in a mixture, to identify each component, and to quantify each component. HPLC is considered an instrumental technique of analytical chemistry (as opposed to a gravitimetric technique). In general, the method involves a liquid sample being passed over a solid adsorbent material packed into a column using a flow of liquid solvent. Each analyte in the sample interacts slightly differently with the adsorbent material, thus retarding the flow of the analytes. If the interaction is weak, the analytes flow off the column in a short amount of time, and if the interaction is strong, then the elution time is long. HPLC has been used in medical (e.g. detecting vitamin D levels in blood serum), legal (e.g. detecting performance enhancement drugs in urine), research (e.g. separating the components of a complex biological sample, or of similar synthetic chemicals from each other), and manufacturing (e.g. during the production process of pharmaceutical and biological products).

#### 2.6.1 HPLC Work Analysis

In HPLC, a sample is injected into a mobile liquid phase and it passes along a stationary phase. Although manual injection of samples is still possible, most HPLCs are fully automated and controlled by a PC, allowing up to 200 or more samples to be injected. The stationary phase comprises a column which is usually stainless steel and packed with silica particles bonded with alkyl chains. The length of the chain depends on the type of molecule being analysed. For example, for large protein molecules a C4 column could be used but for smaller molecules C8 or even C18 may be more appropriate.



Figure 2.9: HPLC column

After the sample passes over the column, it is detected by ultraviolet absorption. The sample and the mobile phase are collected as waste and the absorption spectrum is outputted as a chromatogram. This process is fully automated and controlled by a PC. The time taken for a sample to pass through the system is recorded as its retention time and is one of the characteristics used to identify a compound. From the chromatogram, the area under a peak is used for calculating the concentration of a sample.



Figure 2.10: HPLC chromatogram

The concentration of compounds can be calculated by first running a series of standards at known concentrations. A curve is then plotted of the concentration of the standards (x-axis) versus their peak area (y-axis). From the chromatogram peak areas, it is possible to calculate the concentration of the compounds in sample.



Figure 2.11: Standard curve used to calculate concentrations

# **3 MATERIALS AND METHODS**

# 3.1 Overview

This chapter gives a review of the procedures for this research. This includes the characterization of ILs by using FTIR, preparation of mobile phase, preparation of model oil, extractive desulfurization of model oil, and lastly the analytical procedure using HPLC.

## 3.2 Chemicals

The chemicals used in this experiment are 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF<sub>4</sub>] as the ILs, dibenzothiophene (DBT) and dodecane (90% purity) as model oil that will tested with ionic liquid to remove sulfur and methanol (99% purity) are of the HPLC grade as a standard for tested the reaction by using High Performance Liquid Chromatograpy (HPLC).

# 3.3 Equipments

# 3.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy is an important technique in organic chemistry. It is an easy way to identify the presence of certain functional groups in a molecule. Also, one can use the unique collection of absorption bands to confirm the identity of a pure compound or to detect the presence of specific impurities.



Figure 3-1: Perkin Elmer Spectrum 100 FTIR Spectrometer

# 3.3.2 High Performance Liquid Chromatography (HPLC)

This equipment is a measurement technique to separate a mixture of compounds in analytical chemistry and biochemistry with the purpose of identifying or purifying the individual component mixture.



Figure 3-2: Agilent 1100 Series HPLC

# 3.4 General Flow of Methodology



Figure 3-3: General Flow for Methodology

## 3.4.1 Characterization of Ionic Liquid

In this research, 1-ethyl-3-methylimidaolium tetrafluoroborate [EMIM] [BF4] are used as ILs. It was analyze by using FTIR to determine the functional group of ionic liquid. FTIR analysis is a technique that provides the information about chemical bonding or molecular structure of the ILs use for sulfur extraction in this research.

## 3.4.2 Preparation of Model Oil

140mg of DBT was dissolved in 70mL dodecane to form 2000ppm DBT content in the model oil. From 2000ppm DBT, it was diluted to 1000ppm, 750ppm, 500ppm and 250ppm of DBT. The sample was used to be analyzed for standard calibration curve in this research.

| Concentration (ppm) | Area (mAU*s) |
|---------------------|--------------|
| 250                 | 106.51221    |
| 500                 | 166.12195    |
| 750                 | 263.54721    |
| 1000                | 366.32355    |
| 2000                | 720.53772    |

Table 3-1: Concentration and Area for Standard Calibration Curve



Figure 3-4: Area versus DBT Concentration

## 3.4.3 Extractive Desulfurization model Oil.

All the extractive desulfurization experiment was conducted by using model oil with 2000ppm, 1000ppm, 750ppm, 500ppm, and 250ppm of DBT. ILs and model oil were mixed at 1:1 volume ratio which is 0.5mL 0f ILs and 0.5mL model oil in the

universal bottle, 10mL. The mixture in the bottle was heated in water bath at 30 °C with 185rpm stirring for 30 minutes. The mixture then allowed settling for 12 hours to obtain the splitting and settling. Two phases were formed after settling whereby oil is found in the upper phase.

After that, sample from upper phase was withdrawn from the mixture by using needle syringe 6mL. Before the sample is transferred to the vial bottle, the needle was change by nylon filter so that, the sample was filter before filled into the vial bottle. The same procedure was repeated for different volume ratio (1:2 and 1:5).

#### **3.4.4 Preparation of Mobile Phase**

The choice of mobile phase is based on the desired retention behaviour and the physicochemical properties of the analyte. So in this analysis, the methanol and ultrapure water used as a mobile phase with the volume ratio is 90:10. 900mL of methanol and 100mL of ultrapure water was mixed in the one litre scotch bottle. The mobile phase then was filtered with membrane-type filter with a porosity of 0.45µm to remove particle by pumping it using a vacuum pump. After that, the mobile phase was degassed under sonification to avoid the creation of gas bubbles in the detector cell.

#### **3.4.5** Analytical Procedures Test

In order to measure DBT concentration in IL phase and dodecane phase, Agilent 1100 Series High Performance Liquid Chromatography equipped with diode array detector (DAD). Mobile phase that already prepared was used for Zorbax SB-C18 (4.6mm X 150mm, 5 $\mu$ m) with a flow rate of 1mL/min. The sample was injected into the HPLC directly at 1 $\mu$ L without dilution. The ultra violet (UV) wavelength used was 310 nm with retention time 10 minutes for each sample.

# 4 Result and Discussion

## 4.1 Overview

In this research, [EMIM][BF<sub>4</sub>] was used as ILs, and the model oil which is the mixture of dodecane and DBT. This chapter is discussed based on the result gathered from FTIR spectroscopy analysis and HPLC analysis. From the FTIR graph, it showed the present peak of functional group of the [EMIM][BF<sub>4</sub>]. From HPLC analysis result, it determined the DBT removal from the model oil based on 1:1, 1:2 and 1:5 whereas referred to [EMIM][BF<sub>4</sub>] : model oil volume ratio.

# 4.2 Characterization of Imidazolium-based ILs by Using FTIR

In this research, FTIR analysis was used to determine the functional group of ILs, [EMIM][BF<sub>4</sub>] in order to characterize it. FTIR analysis is a success analysis technique that provides information about the chemical bonding or molecular structure of an ILs use for sulfur extraction in this research. Figure 4.1 shows the molecular structure for [EMIM][BF<sub>4</sub>].



Figure 4-1: Molecular Structure for [EMIM][BF<sub>4</sub>]



Figure 4-2: FTIR absorbance peak for [EMIM][BF<sub>4</sub>]

| Peak No. | Wavenumber (cm <sup>-1</sup> ) | Molecular Motion     | Funtional Group |
|----------|--------------------------------|----------------------|-----------------|
| 1<br>2   | 3165.23<br>3123.52             | =CH stretch          | Alkenes         |
| 3        | 1463.98                        | CH <sub>2</sub> bend | Alkanes         |
| 4<br>5   | 1286.08<br>1170.87             | C–C stretch          | Ketones         |
| 6        | 846.63                         | C–H bend (para)      | Aromatics       |
| 7        | 754.52                         | C–H bend (ortho)     |                 |

Table 4-1: Functional Group Based on the Wavenumber for [EMIM][BF<sub>4</sub>]

From Figure 4-1, it showed the cation at the left (1-ethyl-3-methylimidazolium), and anion at the right (tetrafluoroborate). From Figure 4-2, =CH stretch refer to alkenes group at 3165.23 and 3123.52 cm<sup>-1</sup> wavelength with indicate in Figure 4-1 label as 1. CH<sub>2</sub> bend refer to alkanes group at 1463.98 cm<sup>-1</sup> wavelength label as 2 at Figure 4-1. For the ketones group which is C–C stretch at wavelength 1286.08 and 1170.87 cm<sup>-1</sup> indicate in Figure 4-1 label as 2 to 3 bonding. The aromatic group, C–H bend (para and ortho positioning) at wavelength 846.63 and 754.52 cm<sup>-1</sup> label as 3.

# 4.3 Influence of Volume Ratio on DBT Extraction

The extraction of sulfur compounds (DBT) in dodecane by [EMIM][BF<sub>4</sub>] ILs under various volume ratio of ILs to model oil was investigated. The result shown in figure below, shows influence of ILs to model oil volume ratio on DBT content for 250ppm, 500ppm, 750ppm, 1000ppm, and 2000ppm DBT. It also shows at once that when the volume ratio of ILs to model oil has strong influence on the sulfur content for extraction process using ILs.



Figure 4-3: Influence of ILs to model oil ratio on DBT content for 250ppm DBT

Based on figure 4-2, the DBT content in the model oil reduces as the volume ratio goes from 1:1. As in early experiment, the DBT content is 250ppm. When the model oil is extracted with ILs to model oil volume ratio of 1:1, 1:2, and 1:5, the DBT content was reduced to 172ppm, 205ppm and 220ppm, respectively. From the past research on extraction of DBT (Chong et al., 2012) compound by using ILs 1-butyl-3-methylimidazolium thiocyanate [C<sub>4</sub>mim][SCN], the graph have been produced are

directly proportional to volume ratio. So for this research, the results shown were satisfied with previous findings.



Figure 4-4: Influence of ILs to model oil ratio on DBT content for 500ppm DBT

Based on figure 4-3, the DBT content in the model oil reduces as the volume ratio goes to 1:1. As in early experiment, the DBT content is 500ppm. When the model oil is extract with ILs to model oil volume ratio of 1:1, 1:2, and 1:5, the DBT content were reduced to 327ppm, 364ppm and 449ppm respectively. From the past research on extraction of DBT compound by using ILs, the graph produced directly proportional. So that the results shown was satisfy for this research.



Figure 4-5: Influence of ILs to model oil ratio on DBT content for 750ppm DBT

Based on figure 4-4, the DBT content in the model oil reduces as the volume ratio goes to 1:1. As in early experiment, the DBT content is 750ppm. When the model oil is extract with ILs to model oil volume ratio of 1:1, 1:2, and 1:5, the DBT content were reduced to 546ppm, 573ppm and 686ppm respectively. From the past research on extraction of DBT (Chong et al., 2012) compound by using ILs 1-butyl-3-methylimidazolium thiocyanate [C<sub>4</sub>mim][SCN], the graph have been produced are directly proportional to volume ratio. So for this research, the results shown were satisfied with previous findings.



Figure 4-6: Influence of ILs to model oil ratio on DBT content for 1000ppm DBT

Based on figure 4-5, the DBT content in the model oil reduces as the volume ratio goes to 1:1. As in early experiment, the DBT content is 1000ppm. When the model oil is extract with ILs to model oil volume ratio of 1:1, 1:2, and 1:5, the DBT content were reduced to 907ppm, 959ppm and 980ppm respectively. From the past research on extraction of DBT compound by using ILs, the graph produced directly proportional. So that the results shown was satisfy for this research.



Figure 4-7: Influence of ILs to model oil ratio on DBT content for 2000ppm DBT

Based on figure 4-6, the DBT content in the model oil reduces as the volume ratio goes to 1:1. As in early experiment, the DBT content is 2000ppm. When the model oil is extract with ILs to model oil volume ratio of 1:1, 1:2, and 1:5, the DBT content were reduced to 1532ppm, 1723ppm and 1911ppm respectively. From the past research on extraction of DBT (Chong et al., 2012) compound by using ILs 1-butyl-3-methylimidazolium thiocyanate [C<sub>4</sub>mim][SCN], the graph have been produced are directly proportional to volume ratio. So for this research, the results shown were satisfied with previous findings.

# 4.4 Influence of IL to Model Oil Volume Ratio on the Percentage of DBT Content Remover

Based on the above figure, the percentage of DBT removal can be obtained and illustrated in figure below. Figure 4-7 shows influence of ILs to model oil volume ratio based on percentage of DBT removal for 250ppm. Figure 4-8 shows influence of ILs to model oil volume ratio based on percentage of DBT removal for 500ppm. Figure 4-9 shows influence of ILs to model oil volume ratio based on percentage of DBT removal for 750ppm. Figure 4-10 shows influence of ILs to model oil volume ratio based on percentage of DBT removal for 1000ppm. Figure 4-11 shows influence of ILs to model oil volume ratio based on percentage of DBT removal for 2000ppm.



Figure 4-8: Influence of ILs to model oil volume ratio based on percentage of DBT removal for 250ppm

From the calculation, the percentage of DBT removal shows the performance of  $[EMIM][BF_4]$  is not good for commercial desulfurization process stage yet resulting from the low percentage of DBT removal. The percentage removal DBT at 1:1 is 31%, 1:2 is 18% and for 1:5 is 12%. It shows the relation between volume ratios of ILs to

model oil toward the percentage of DBT removal is proportionally reducing as the number of model oil volume ratio is increasing. The efficiency of ILs to model oil ratio for 250ppm was concluded as in table 4-1.

| ILs to Model Oil Volume Ratio | DBT Removal (%) |
|-------------------------------|-----------------|
| 1:1                           | 31              |
| 1:2                           | 18              |
| 1:5                           | 12              |

**Table 4-2**: Efficiency of ILs to model oil volume ratio on DBT content removal at250ppm



Figure 4-9: Influence of ILs to model oil volume ratio based on percentage of DBT removal for 500ppm

Based on figure 4-8, the relation between ILs to model oil volume ratio also is directly proportional. It shows that, the highest percentage of DBT removal at 1:1 which is only 35% removal. Having said that, it indicate that this [EMIM][BF<sub>4</sub>] is not compatible yet for industry uses. The efficiency of ILs to model oil ratio for 500ppm was concluded as in table 4-2.

| ILs to Model Oil Volume Ratio | DBT Removal (%) |
|-------------------------------|-----------------|
| 1:1                           | 34              |
| 1:2                           | 27              |
| 1:5                           | 10              |

**Table 4-3:** Efficiency of ILs to model oil volume ratio on DBT content removal at500ppm



Figure 4-10: Influence of ILs to model oil volume ratio based on percentage of DBT removal for 750ppm

Based on figure 4-8, the relationship between ILs to model oil volume ratio is also directly proportional. It shows that, the highest percentage DBT removal at 1:1 which is only 56%, more than half of the sulfur content was removed. It also not good for commercial desulfurization process because of the ratio is 1:1 that same volume of the IL and model oil. The investment was very high as many as volumes IL were used. It was deemed uneconomic for practical application in the industry. Similar experimental results were published by other researchers, where increasing the IL: model oil volume ratio would result in the increase of desulfurization efficiency (Chu. X.M et al, 2008). The efficiency of ILs to model oil ratio for 750ppm was concluded as in table 4-3.

 ILs to Model Oil Volume Ratio
 DBT Removal (%)

 1:1
 56

 1:2
 51

 1:5
 40

 Table 4-4: Efficiency of ILs to model oil volume ratio on DBT content removal at

 750ppm



Figure 4-11: Influence of ILs to model oil volume ratio based on percentage of DBT removal for 1000ppm

Based on figure 4-10, the relation between ILs to model oil volume ratio also is directly proportional. It shows that, the highest percentage DBT removal at 1:1 which is 9.28% compared to 1:2 and 1:5 which is 4.08% and 2.04%. So, it is very not compatible for industry of desulfurization process. The efficiency of ILs to model oil ratio for 1000ppm was concluded as in table 4-4.

| ILs to Model Oil Volume Ratio | DBT Removal (%) |
|-------------------------------|-----------------|
| 1:1                           | 9               |
| 1:2                           | 4               |
| 1:5                           | 2               |

 Table 4-5: Efficiency of ILs to model oil volume ratio on DBT content removal at 1000ppm



Figure 4-12: Influence of ILs to model oil volume ratio based on percentage of DBT removal for 2000ppm

Based on figure 4-10, the relation between ILs to model oil volume ratio also is directly proportional. It show that, the highest percentage DBT removal at 1:1 which is only 23% removal compared to 1:2 and 1:5 which is 14% and 4% removal. So, it is very not compatible for industry of desulfurization process. The efficiency of ILs to model oil ratio for 2000ppm was concluded as in Table 4-5.

| ILs to Model Oil Volume Ratio | DBT Removal (%) |
|-------------------------------|-----------------|
| 1:1                           | 23              |
| 1:2                           | 14              |
| 1:5                           | 4               |

**Table 4-6:** Efficiency of ILs to Model Oil Volume Ratio on DBT Content Removal at2000ppm of DBT

4.5 Comparison on Percentage of DBT Removal Based on 250ppm, 500ppm, 750ppm, 1000ppm, and 2000ppm of DBT Content.



Figure 4-13: Influence of sulfur concentration on percentage of DBT removal

From Figure 4-12, it shows that 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF<sub>4</sub>] has high efficiency to remove sulfur content for 750ppm with 1:1 ILs: model oil volume ratio which is 56% DBT removal others than 250ppm, 500ppm, 1000ppm and 2000ppm of DBT. The lowest DBT removal for 1000ppm at 1:5 ILs: model oil volume ratio which is only 4% removal.

# **5 CONCLUSION**

# 5.1 Conclusion

As we all know, ILs has their own unique characteristic that has been seen as one of the potential method to remove sulfur compound in the model oil. Before the ionic liquids were used in this research, it must undergo a characterization process by FTIR. It because to know the chemical compound or the functional group that has in the ionic liquid. By this research, [EMIM][BF<sub>4</sub>] was used as a ionic liquid to removed sulfur content in the model oil. From the FTIR analysis, it show that the aimed product [EMIM][BF<sub>4</sub>].

From the result HPLC analysis, it showed that the desulfurization efficiency increased when its volume ratio was increased, however the increase of desulfurization of efficiency was slower at high ILs: model oil volume ratio. Therefore, it was obviously less efficient if we tried to increased desulfurization efficiency by increasing ILs: model oil volume ratio. The higher efficiency of removal sulfur by using 1:1 volume ratio at 750ppm of DBT which is 56% then 250ppm of DBT which is 31%, 500ppm of DBT which is 23%.

# 5.2 Future work

In this research, the some modification or recommendation will be suggested. Firstly, the right selection of ionic liquid that used for extraction. In the future, the ionic liquids can reusability without regeneration. The used ILs was able to extracts DBT from model oil even without regeneration, however, at lower efficiency. The desulfurization efficiency of reused ILs could also be calculated from its partition coefficient (Man Zakaria et al, 2012). The effectiveness of the ILs also can be improved by increase a little bit the extraction time and also the rpm stirring effect in order to ensure sulfur is highly extracted from the oil.

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# **APPENDICES**

Appendix A:

1. Calculation for Total Sulfur in DBT Content

$$ppm = \frac{mass of solute (g)}{mass of solute \& Solvent (g)}$$
$$= \frac{1mg}{L}$$

| Table A1: | List of mo | olecular | weight |
|-----------|------------|----------|--------|
|-----------|------------|----------|--------|

|                                          | Molecular Weight (g/mol)                 |                                                   |                              |
|------------------------------------------|------------------------------------------|---------------------------------------------------|------------------------------|
|                                          | DBT                                      | 184.26                                            |                              |
|                                          | Sulphur                                  | 32.065                                            |                              |
| $\frac{x \ ppm \ S}{2000 ppm \ DBT} =$   | 32.065 g/mol<br>184.26 g/mol             | $\frac{x \ ppm \ S}{500 ppm \ DBT} = \frac{1}{2}$ | 32.065 g/mol<br>184.26 g/mol |
| <i>x</i> =                               | : 348.02 ppm S                           | <i>x</i> =                                        | = 87. <i>ppm S</i>           |
| $\frac{x \ ppm \ S}{1000 \ ppm \ DBT} =$ | = $rac{32.065 \ g/mol}{184.26 \ g/mol}$ | $\frac{x \ ppm \ S}{250 ppm \ DBT} = \frac{2}{3}$ | 32.065 g/mol<br>184.26 g/mol |
| <i>x</i> =                               | = 174.02 <i>ppm S</i>                    | x = 4                                             | 3.51 ppm S                   |
| $\frac{x \ ppm \ S}{750 ppm \ DBT} =$    | 32.065 g/mol<br>184.26 g/mol             |                                                   |                              |

 $x = 130.52 \, ppm \, S$ 

| Table | A2: | Total | Sulfur | content |
|-------|-----|-------|--------|---------|
| Table | AZ. | TOtal | Sullui | coment  |

| DBT (ppm) | Total Sulfur (ppm) |
|-----------|--------------------|
| 2000      | 348.04             |
| 1000      | 174.02             |
| 750       | 130.52             |
| 500       | 87.01              |
| 250       | 43.51              |

# 2. Calculation on Dilution

Dilution formula,

$$M_1 V_1 = M_2 V_2$$

Where,

 $M_1$  = Initial Concentration  $M_2$  = Final Concentration  $V_1$  = Initial Volume  $V_2$  = Final Volume

a) For 2000ppm of DBT

$$2000ppm = \frac{x mg DBT}{0.07 L}$$
$$x = 140 mg DBT$$
$$x = 0.140 g DBT$$

b) Calculation to dilute 2000ppm to 1000ppm of DBT

$$M_1V_1 = M_2V_2$$

 $(2000 \, ppm)(0.015 \, L) = (1000 \, ppm)V_2$ 

 $V_2 = 0.03 L$  $V_2 = 30 mL$ 

c) Calculation to dilute 2000ppm to 750ppm of DBT

$$M_1 V_1 = M_2 V_2$$

$$(2000 ppm)(0.010 L) = (750 ppm)V_2$$

$$V_2 = 0.027 L$$

$$V_2 = 27 mL$$

d) Calculation to dilute 2000ppm to 500ppm of DBT

$$M_1V_1 = M_2V_2$$
(2000 ppm)(0.008 L) = (500 ppm)V\_2  

$$V_2 = 0.032 L$$

$$V_2 = 32 mL$$

e) <u>Calculation to dilute 2000ppm to 500ppm of DBT</u>

$$M_1V_1 = M_2V_2$$

 $(2000 \, ppm)(0.004 \, L) = (250 \, ppm)V_2$ 

 $V_2 = 0.032 L$ 

 $V_2 = 32 \, mL$ 

# Appendix B

a) Standard for 250 ppm of DBT



Figure B-1: Chromatogram of DBT in dodecane at 250ppm (STD)

| Table B-1: Area | percentage for 250ppm | DBT (STD) |  |
|-----------------|-----------------------|-----------|--|
|-----------------|-----------------------|-----------|--|

b) Standard for 500 ppm of DBT



Figure B-2: Chromatogram of DBT in dodecane at 500ppm (STD)

| Table B-2: Area percentage for | for 500ppm DBT | (STD) |
|--------------------------------|----------------|-------|
|--------------------------------|----------------|-------|

```
Area Percent Report
Signal
1.0000
Sorted By
           :
Sorted By :
Multiplier :
Dilution
           :
                1.0000
Use Multiplier & Dilution Factor with ISTDs
Signal 1: DAD1 B, Sig=310,16 Ref=360,100
Peak RetTime Type Width Area Height
# [min] [min] [mAU*s] [mAU]
                           Area
                            8
1
   5.492 BB 0.1344 166.12195 18.56949 100.0000
Totals :
               166.12195 18.56949
```
c) Standard for 750 ppm of DBT



Figure B-3: Chromatogram of DBT in dodecane at 750ppm (STD)

| Table B-3: A | Area percentage | for 750ppm | DBT | (STD) |
|--------------|-----------------|------------|-----|-------|
|--------------|-----------------|------------|-----|-------|

```
Area Percent Report
_____
      : Signal
: 1.0000
: 1.0000
Sorted By
Multiplier
Dilution
Use Multiplier & Dilution Factor with ISTDs
Signal 1: DAD1 B, Sig=310,16 Ref=360,100
Peak RetTime Type Width Area Height
# [min] [min] [mAU*s] [mAU]
                           Area
                            융
5.486 BB 0.1406 263.54721 27.80117 100.0000
 1
Totals :
               263.54721 27.80117
```

#### d) Standard for 1000 ppm of DBT



Figure B-4: Chromatogram of DBT in dodecane at 1000ppm (STD)

| Table B-4: Area | percentage for | 1000ppm DBT | (STD) |
|-----------------|----------------|-------------|-------|
|-----------------|----------------|-------------|-------|

```
Area Percent Report
  : Signal
: 1.0000
: 1.0000
Sorted By
Multiplier
Dilution
Use Multiplier & Dilution Factor with ISTDs
Signal 1: DAD1 B, Sig=310,16 Ref=360,100
Peak RetTime Type Width Area Height
# [min] [min] [mAU*s] [mAU]
                                Area
                                 8
1 5.484 BB 0.1435 366.32355 37.64295 100.0000
                  366.32355 37.64295
Totals :
```

e) Standard for 2000 ppm of DBT



Figure B-5: Chromatogram of DBT in dodecane at 2000ppm (STD)

| Table B-5: Area | percentage for | 2000ppm DBT | (STD) |
|-----------------|----------------|-------------|-------|
|-----------------|----------------|-------------|-------|

```
Area Percent Report
_____
           : Signal
Sorted By
      1.0000
1.0000
Multiplier
Dilution
Use Multiplier & Dilution Factor with ISTDs
Signal 1: DAD1 B, Sig=310,16 Ref=360,100
Peak RetTime Type Width Area Height
# [min] [min] [mAU*s] [mAU]
                          Area
                          8
1 5.478 BB 0.1410 720.53772 75.76391 100.0000
              720.53772 75.76391
Totals :
```

#### 1. ILs:Model Oil Volume Ratio (1:1)



Figure B-6: Chromatogram of DBT in dodecane at 250ppm (1:1)

```
        Table B-6: Area percentage for 250ppm DBT (1:1)
```

#### a) 500ppm



Figure B-7: Chromatogram of DBT in dodecane at 500ppm (1:1)

| Table B-7: Area | percentage | for 500ppm | DBT (1:1) |
|-----------------|------------|------------|-----------|
|-----------------|------------|------------|-----------|

```
_____
             Area Percent Report
 Sorted By
           :
               Signal
        : 1.0000
: 1.0000
Multiplier
Dilution
Use Multiplier & Dilution Factor with ISTDs
Signal 1: DAD1 B, Sig=310,16 Ref=360,100
Peak RetTime Type Width Area Height
# [min] [min] [mAU*s] [mAU]
                           Area
                            8
1 5.490 BB 0.1317 117.62732 13.23987 100.0000
Totals :
               117.62732 13.23987
```

#### b) 750ppm



Figure B-8: Chromatogram of DBT in dodecane at 750ppm (1:1)

 Table B-8: Area percentage for 750ppm DBT (1:1)

```
_____
             Area Percent Report
Sorted By : 519....
Multiplier : 1.0000
Silution : 1.0000
Use Multiplier & Dilution Factor with ISTDs
Signal 1: DAD1 B, Sig=310,16 Ref=360,100
                   Height
[mAU]
Peak RetTime Type Width
               Area
                           Area
          [min] [mAU*s]
# [min]
                           8
1 5.490 BB 0.1338 196.40648 22.08246 100.0000
Totals :
               196.40648 22.08246
```

#### c) 1000ppm



Figure B-9: Chromatogram of DBT in dodecane at 1000ppm (1:1)

| Table B-9: Area | percentage for | 1000ppm DBT | (1:1) |
|-----------------|----------------|-------------|-------|
|-----------------|----------------|-------------|-------|

```
_____
             Area Percent Report
Sorted By
           : Signal
           : 1.0000
: 1.0000
Multiplier
Dilution
Use Multiplier & Dilution Factor with ISTDs
Signal 1: DAD1 B, Sig=310,16 Ref=360,100
         Width Area Height
[min] [mAU*s] [mAU]
Peak RetTime Type Width
                          Area
# [min]
                           8
1
   5.455 BB 0.1420 326.59781 34.00753 100.0000
              326.59781 34.00753
Totals :
```

#### d) 2000ppm



Figure B-10: Chromatogram of DBT in dodecane at 2000ppm (1:1)

| Table B-10: | Area percentage | for 2000ppm | DBT (1:1) |
|-------------|-----------------|-------------|-----------|
|-------------|-----------------|-------------|-----------|

- 2. IL:Model Oil Volume Ratio (1:2)
- a) 250ppm



Figure B-11: Chromatogram of DBT in dodecane at 250ppm (1:2)

| Table B-11: | Area percentage | for 250ppm | DBT (1:2) |
|-------------|-----------------|------------|-----------|
|-------------|-----------------|------------|-----------|

```
Area Percent Report
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs
Signal 1: DAD1 B, Sig=310,16 Ref=360,100
Peak RetTime Type Width
               Area
                    Height
                           Area
          [min] [mAU*s]
                     [mAU]
                           8
# [min]
1 5.465 BB 0.1347 87.34256
                     9.73497 100.0000
               87.34256 9.73497
Totals :
```

#### b) 500ppm



Figure B-12: Chromatogram of DBT in dodecane at 500ppm (1:2)

Table B-12: Area percentage for 500ppm DBT (1:2)

```
Area Percent Report
: Signal
: 1.0000
Sorted By
Multiplier
Dilution
              1.0000
          :
Use Multiplier & Dilution Factor with ISTDs
Signal 1: DAD1 B, Sig=310,16 Ref=360,100
# [min] [min] [mAU*s] [mAU]
Peak RetTime Type Width
                        Area
                        8
1 5.490 BB 0.1336 131.19055 14.76951 100.0000
             131.19055 14.76951
Totals :
```

#### c) 750ppm



Figure B-13: Chromatogram of DBT in dodecane at 750ppm (1:2)

| Table B-13: | Area percentag | e for 750ppm | DBT (1:2) |
|-------------|----------------|--------------|-----------|
|-------------|----------------|--------------|-----------|

```
_____
            Area Percent Report
_____
                      _____
          : Signal
: 1.0000
Sorted By
Multiplier
Dilution
               1.0000
           :
Use Multiplier & Dilution Factor with ISTDs
Signal 1: DAD1 B, Sig=310,16 Ref=360,100
       [min] [mAU*s] [mAU]
Peak RetTime Type Width
# [min]
1 5.461 BB 0.1363 206.29950 22.65075 100.0000
              206.29950 22.65075
Totals :
```

## d) 1000ppm



Figure B-14: Chromatogram of DBT in dodecane at 1000ppm (1:2)

| Table B-14: Area | percentage for | 1000ppm DB' | T (1:2) |
|------------------|----------------|-------------|---------|
|------------------|----------------|-------------|---------|

| Area Percent Report          |                |                 |                 |           |  |
|------------------------------|----------------|-----------------|-----------------|-----------|--|
|                              |                |                 |                 |           |  |
| Sorted By                    | :              | Signal          |                 |           |  |
| Multiplier                   | :              | 1.0000          |                 |           |  |
| Dilution                     | :              | 1.0000          |                 |           |  |
| Use Multiplier &             | Dilution 1     | Factor with     | ISTDs           |           |  |
| Signal 1: DAD1 B,            | Sig=310,1      | l6 Ref=360,1    | L00             |           |  |
| Peak RetTime Type<br># [min] | Width<br>[min] | Area<br>[mAU*s] | Height<br>[mAU] | Area<br>% |  |
| 1 5.448 BB                   | 0.1382         | 345.30295       | 34.01085        | 100.0000  |  |
| Totals :                     |                | 345.30295       | 34.01085        |           |  |
|                              |                |                 |                 |           |  |

### e) 2000ppm



Figure B-15: Chromatogram of DBT in dodecane at 2000ppm (1:2)

| Table B-15: Area | percentage for | or 2000ppm | DBT (1:2) |
|------------------|----------------|------------|-----------|
|------------------|----------------|------------|-----------|

| A                                        | rea Percent 1   | Report                 |  |  |
|------------------------------------------|-----------------|------------------------|--|--|
|                                          |                 |                        |  |  |
| Sorted By :                              | Signal          |                        |  |  |
| Multiplier :                             | 1.0000          |                        |  |  |
| Dilution :                               | 1.0000          |                        |  |  |
| Use Multiplier & Dilution                | Factor with     | ISTDs                  |  |  |
|                                          |                 |                        |  |  |
|                                          |                 |                        |  |  |
| Signal 1: DAD1 B, Sig=310,               | 16 Ref=360,1    | .00                    |  |  |
| Peak RetTime Type Width<br># [min] [min] | Area<br>[mAU*s] | Height Area<br>[mAU] % |  |  |
| 1 5.487 BB 0.1636                        | 620.40106       | 65.88258 100.0000      |  |  |
| Totals :                                 | 620.40106       | 65.88258               |  |  |
|                                          |                 |                        |  |  |
|                                          |                 |                        |  |  |

- 3. ILs:Model Oil Volume Ratio (1:5)
- a) 250ppm



Figure B-16: Chromatogram of DBT in dodecane at 2000ppm (1:5)

 Table B-16: Area percentage for 250ppm DBT (1:5)

```
Area Percent Report
Multiplier :
Dilution
            Signal
1.0000
1.0000
Use Multiplier & Dilution Factor with ISTDs
Signal 1: DAD1 B, Sig=310,16 Ref=360,100
Peak RetTime Type Width
                        Area
              Area
                  Height
         [min] [mAU*s]
                  [mAU]
# [min]
                        8
 1 5.458 BB 0.1347 93.73959
                  10.44979 100.0000
             93.73959 10.44979
Totals :
```

## b) 500ppm



Figure B-17: Chromatogram of DBT in dodecane at 500ppm (1:5)

| <b>Table B-17</b> : | Area percentag | e for 500ppm | DBT (1:5) |
|---------------------|----------------|--------------|-----------|
|                     | 1 0            | , II         |           |

| A                          | rea Percent  | Report   |          |
|----------------------------|--------------|----------|----------|
|                            |              |          |          |
|                            |              |          |          |
| Sorted By :                | Signal       |          |          |
| Multiplier :               | 1 0000       |          |          |
| Dilution .                 | 1.0000       |          |          |
| Dilucion :                 | _ 1.0000     |          |          |
| Use Multiplier & Dilution  | Factor with  | ISTDS    |          |
|                            |              |          |          |
|                            |              |          |          |
| Signal 1: DAD1 B, Sig=310, | 16 Ref=360,1 | 00       |          |
|                            |              |          |          |
| Peak RetTime Type Width    | Area         | Height   | Area     |
| # [min] [min]              | [mAII*e]     | [mAII]   | 2<br>2   |
| * [m±n] [m±n]              |              | [1010]   |          |
|                            | 1 (1 70(22)  | 1.00000  | 100 0000 |
| 1 5.490 BB 0.1417          | 101./8033    | 10.90290 | 100.0000 |
|                            |              |          |          |
| Totals :                   | 161.78633    | 16.90290 |          |
|                            |              |          |          |
|                            |              |          |          |
|                            |              |          |          |

## c) 750ppm



Figure B-18: Chromatogram of DBT in dodecane at 750ppm (1:5)

|--|

| A                                                                      | rea Percent D                               | Report          |           |  |
|------------------------------------------------------------------------|---------------------------------------------|-----------------|-----------|--|
|                                                                        |                                             |                 |           |  |
| Sorted By :<br>Multiplier :<br>Dilution :<br>Use Multiplier & Dilution | Signal<br>1.0000<br>1.0000<br>Factor with 3 | ISTDs           |           |  |
| Signal 1: DAD1 B, Sig=310,                                             | 16 Ref=360,10                               | 0 0             |           |  |
| Peak RetTime Type Width<br># [min] [min]                               | Area<br>[mAU*s]                             | Height<br>[mAU] | Area<br>% |  |
| 1 5.458 BB 0.1439                                                      | 247.06937                                   | 25.29766        | 100.0000  |  |
| Totals :                                                               | 247.06937                                   | 25.29766        |           |  |
|                                                                        |                                             |                 |           |  |

# d) 1000ppm



Figure B-19: Chromatogram of DBT in dodecane at 1000ppm (1:5)

| Table B-19: Area | percentage for | 1000ppm | DBT ( | (1:5) |
|------------------|----------------|---------|-------|-------|
|------------------|----------------|---------|-------|-------|

|                                                                        | Area Percent                              | Report          |           |  |  |
|------------------------------------------------------------------------|-------------------------------------------|-----------------|-----------|--|--|
|                                                                        |                                           |                 |           |  |  |
| Sorted By :<br>Multiplier :<br>Dilution :<br>Use Multiplier & Dilution | Signal<br>1.0000<br>1.0000<br>Factor with | ISTDs           |           |  |  |
| Signal 1: DAD1 B, Sig=310                                              | ,16 Ref=360,1                             | 0 0             |           |  |  |
| Peak RetTime Type Width<br># [min] [min]                               | Area<br>[mAU*s]                           | Height<br>[mAU] | Area<br>% |  |  |
| 1 5.455 BB 0.1401                                                      | 352.65292                                 | 37.37020        | 100.0000  |  |  |
| Totals :                                                               | 352.65292                                 | 37.37020        |           |  |  |
|                                                                        |                                           |                 |           |  |  |

### e) 2000ppm



Figure B-20: Chromatogram of DBT in dodecane at 2000ppm (1:5)

| Table B-20: | Area percentage | for 250ppm | DBT (1:5) |
|-------------|-----------------|------------|-----------|
|-------------|-----------------|------------|-----------|

| P                          | rea Percent 1                           | Report   |          |  |
|----------------------------|-----------------------------------------|----------|----------|--|
|                            | ======================================= |          |          |  |
|                            |                                         |          |          |  |
| Sorted By :                | Signal                                  |          |          |  |
| Multiplier :               | 1.0000                                  |          |          |  |
| Dilution :                 | 1.0000                                  |          |          |  |
| Use Multiplier & Dilution  | Factor with                             | ISTDs    |          |  |
| 1                          |                                         |          |          |  |
|                            |                                         |          |          |  |
| Signal 1: DAD1 B, Sig=310, | 16 Ref=360.1                            | 00       |          |  |
|                            |                                         |          |          |  |
| Peak RetTime Type Width    | Area                                    | Height   | Area     |  |
| # [min] <sup>1</sup> [min] | [mAU*s]                                 | [mAU]    | 90       |  |
|                            |                                         |          |          |  |
| 1 5.471 BB 0.1662          | 688.31110                               | 70.96472 | 100.0000 |  |
|                            |                                         |          |          |  |
| Totals :                   | 688.31110                               | 70.96472 |          |  |
|                            |                                         |          |          |  |
|                            |                                         |          |          |  |
|                            | ======================================= |          |          |  |