Performance Evaluation of Recyclability of Recovered 1-Butyl-3 Methylimidazolium-Based Ionic Liquids

by

Md. Tanzeev– Ul- Haque
(15005)

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

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Universiti Teknologi PETRONAS
32610 Bandar Seri Iskandar
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

AP Dr. Mohamed Azmi B Bustam @ Khalil

UNIVERSITI TEKNOLOGI PETRONAS

32610 BANDAR SERI ISKANDAR, PERAK

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(MD. TANZEEV- UL- HAQUE)

ABSTRACT

Ionic liquids are found to be a great solution to remove sulfur from diesel fuels efficiently but they are usually expensive. Thus, for a cost effective sulfur removal process, the recovery and recycling of ionic liquids are necessary after desulfurization. However, little research on the recovery of ionic liquids has been conducted so far. Extensive research on the recyclability performance of the ionic liquids has been missed out as well. This study emphasized on the recovery of three BMIM based ionic liquids which are 1-Butyl-3-Methylimidozolium Thiocyanate - BMIM [SCN], 1-Butyl-3-Methylimidozolium Methylsulfate- BMIM [CH_3SO_4] and 1-Butyl-3-Methylimidozolium Dicyanamide- BMIM [N (CN) $_2$] after extraction of DBT from dodecane and on the performance evaluation of recyclability of those recovered ionic liquids. The model oil was observed each time before and after extraction. It was found that, it is possible to recover and reuse the ionic liquids after extraction up to 4 cycles, and 1-Butyl-3-Methylimidozolium Thiocyanate showed the highest extraction capability after recycling of 59.87% at the 4th cycle, whereas, 1-Butyl-3-Methylimidozolium Methylsulfate showed the least extraction capabilities of 18.64% at the 4th cycle. It was also possible to get performance efficiency up to 113.2% for BMIM-SCN after recovery and reuse at the 4th cycle. It is possible to achieve huge saving on cost and energy, if this ionic liquid behaviour can be used in process design, instead of using new ionic liquids for each extraction.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Diesel is widely used fuel in transportation vehicles which can be both highway vehicles like cars, buses, trucks etc and non-highway systems like marine vessels or farm equipments because of its 25-40% more high efficiency than gasoline. Nevertheless, diesel engines suffer from associated particulates or soot, NOx and SOx emissions which are harmful to human health. Sulfur, a part of crude oil from which diesel fuel is derived, is the key reason for soot in diesel. Soot causes the black exhaust fumes and pollutes the air which is a serious environment threat. (Zhang et al., 2009; Shah et al., 2004; Phirun et al., 2005; Sydbom et al., 2001)

Therefore, the environmental regulations are being strict and forcing the oil refineries to reduce sulfur level for fuels in recent years. According to US Environment Protection Agency (2012), the S-limit in diesel fuel in USA was reduced to 15 ppm by 2012 and in European Union 10 ppm by 2010. Malaysia is in the process to reduce its S-limit in diesel fuel from 50 ppm to 10-15 ppm by 2015.

Conventional method that has been used for sulfur removal is called hydro-desulfurization (HDS) or hydro-treating unit which has limitations to remove sulfur efficiently from aromatic sulfur compounds such as thiophenes, benzothiophenes, dibenzothiophenesetc as these shows great resistance to HDS process. The process requires increased energy with drastic higher pressure and increase of hydrogen rate which leads to an expensive process for the high operating cost and capital cost. In addition, the side reactions also result in decrease of octane number of the fuels. (Swapnil et al., 2014)

Desulfurization of fuels by extraction with ionic liquids is found as a better solution for sulfur removal where ionic liquids showed good selectivity for the extraction of sulfur compounds from model diesel oil that contained DBT derivatives. (Bosmann et al., 2001) Further study shows that, 1-Butyl-3-Methylimidozolium (BMIM) based ionic liquids exhibit the highest extraction capabilities among other ionic liquids which were screened for its dibenzothiophene extraction ability. (Wilfred et al., 2012)

1.2 PROBLEM STATEMENT

In the recovery of ionic liquids after desulfurization process, not much of research work has been done yet on BMIM [SCN], BMIM [N (CN) $_2$] and BMIM [CH_3SO_4] ionic liquids.

While ionic liquids are found to be a great solution for the sulfur removal, it is also required to consider the cost of ionic liquids. Ionic liquids are usually expensive. Thus, for a cost effective sulfur removal process, the recovery and recycling of ionic liquids are necessary as well after desulfurization. However, extensive research has not been done yet as well to study recyclability performance of the ionic liquids.

This study will emphasize on the recovery of three BMIM based ionic liquids which are 1-Butyl-3-Methylimidozolium Thiocyanate - BMIM [SCN], 1-Butyl-3-MethylimidozoliumMethylsulfate- BMIM [CH_3SO_4] and 1-Butyl-3-Methylimidozolium Dicyanamide- BMIM [N (CN) $_2$] after extraction of DBT from dodecane and the performance evaluation of recyclability of those recovered ionic liquids.

1.3 OBJECTIVES

The main objectives of the study are:

- To recover 1-Butyl-3-Methylimidazolium based ionic liquids that have been used in desulfurization process.
- To study the performance or recyclability of the recovered BMIM based ionic liquids.

1.4 SCOPE OF STUDY

The main scopes of study for this project are:

1. Use of BMIM based ionic liquids which are BMIM [SCN], BMIM [N (CN) $_2$] and BMIM [CH_3SO_4] for desulfurization process to extract dibenzothiophene from dodecene.
2. Recovery and reuse of BMIM [SCN], BMIM [N (CN) $_2$] and BMIM [CH_3SO_4] for desulfurization.

CHAPTER 2

LITERATURE REVIEW

2.1 IONIC LIQUIDS (ILs)

Any type of liquid can be used as solvent; however, very few are in general use. As the concern over greener technologies with more strict regulations has been widely accepted, the search for a reliable solvent has become a high priority. Recently, ionic liquids (ILs) have gained much attention for their potential use in more diversified range of applications. ILs can be used in the separation of various substances like metallic ions, organic molecules, fuel desulfurization and gas separation. (Wasserscheid et al., 2000; Zhao et al., 2005)

Ionic liquids can replace volatile organic media in various ranges of chemical processes. They have been applied in organometallic catalysis, organocatalysis and biocatalysis, where they provide unique reaction media offering better selectivity, faster rates and greater catalytic activity or enzyme stability in comparison to conventional solvents. (Buszewski et al., 2008; Dupont et al., 2002; Liu et al., 2010; Mathews et al., 200; Minami, 2009; Welton, 1999).

There are few unique physical properties of the ILs that make them interesting as potential solvents for synthesis of inorganic nanomaterial. They are good solvents for a wide range of both inorganic and organic materials, and unusual combinations of reagents can be brought in the same phase. They have high thermal conductivity and are highly polar yet non-coordinating solvents. They are immiscible with a number of organic solvents and provide a non-aqueous, polar alternative for ionic liquid-based aqueous two phase systems. They have solved the problem of solvent loss and the concern of toxicity in solvent extraction. (Dharaskar et al., 2013) They are non-volatile which makes them not to evaporate in high vacuum system and have negligible vapour pressure. Their hydrophobic or hydrophilic nature can be adjusted by modifications in both anion and cation. (Brenneke et al., 2001; Wang et al., 2005; McFarlene et al., 2005)

There are two basic approaches to prepare ionic liquids: metathesis of a halide salt with, for example, a silver, group 1 metal or ammonium salt of the anion and acid-base neutralization reactions.

2.2 DESULFURIZATION PROCESS

2.2.1 Introduction

Desulfurization is the catalytic chemical process of removing sulfur from natural gas or refined petroleum products to reduce the SO_2 emissions which is also known as hydrodesulfurization or HDS. HDS process is widely used for sulfur removal from gasoline and diesel of high sulfur content. (Song et al., 2003)

In the process, using NiMo-CoMo/Al_2O_3 catalysts the organic compounds in the liquid fuels are broken down to H_2S, which is followed by the removal of H_2S. In hydrotreating reactions, sulfided Ni-Mo catalysts are used widely. (Zdrazil, 1988) Some other studies also found that, monometallic cobalt catalysts are active for HDS reactions. (Hayashi et al., 1997)

Diesel fuels contain a very complex mixture of various sulfur compounds with different reactivities. In order to accomplish ultra deep desulfurization diesel fuels, it is important to have wide knowledge on the types of sulfur compounds present in diesel fuels, their reactivity and reaction pathways, kinetics and mechanism and the factors influencing the reactivity of sulfur compounds in diesel fuels. These are discussed below in this section.

2.2.2 Sulfur Compounds in Diesel Fuels

Currently to analyse different types of sulfur compounds in diesel fuels, flame photometric detector (FPD) and sulfur chemiluminescence detector (SCD) which are combination of high resolution gas chromatography and sulfur selective detectors are used widely. Pulse flame photometric detector (PFPD), atomic emission detector (AED), FT-ICR-MS etc. also being used to detect sulfur compounds.

The diesel fuels contain a large number of sulfur compounds which belongs to two group which are benzothiophenes (BTs) and dibenzothiophene (DBT). The distribution of the BTs and DBTs are done with respect to their boiling points. Boiling points of BTs are usually <300 ◦C and for DBTs above 300◦C. These both groups are present usually in different gas oils but distributed bit differently in cracked and straight-run fuels. It mainly depends on the origin of the petroleum. (Kabe et al., 1992; Quimby et al., 2005; Garcia et al., 2002)

2.2.2 Mechanism

HDS is basically a hydrogenolysis reaction. Hydrogenation is a chemical reaction where the net result is the addition of hydrogen (H). The main HDS catalysts are based on molybdenum disulfide (MoS_2) and other metals which are small in number. The nature of the sites of catalytic activity remains an active area of investigation, but it is generally assumed basalplanes of the MoS_2 structure are not relevant to catalysis, rather the edges or rims of these sheets. At the edges of the MoS_2 crystallites, the molybdenum centre can stabilize a coordinatively unsaturated site (CUS), also known as an anion vacancy. Substrates, such as thiophene, bind to this site and undergo a series a reactions that result in both C-S scission and C=C hydrogenation. Thus, the hydrogen serves multiple roles—generation of anion vacancy by removal of sulfide, hydrogenation, and hydrogenolysis.

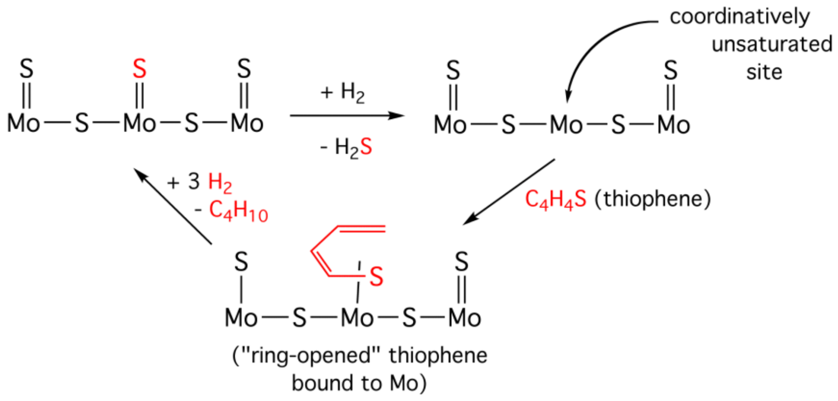

Figure 1: Simplified HDS cycle of thiophene

2.2.3 The Challenges

Although hydrodesulfurization processes are very effective for the removal of sulfur compounds, further improvement of the efficiency of HDS process requires severe operational conditions at escalated cost. In addition, energy and hydrogen consumption increases drastically and undesired side reactions induced. These side reactions decrease the octane number of the gasoline. Therefore, alternative methods are needed to remove sulfur more efficiently.

2.3 DESULFURIZATION OF FUELS BY EXTRACTION WITH IONIC LIQUIDS

2.3.1 Introduction

Ionic liquids (ILs) are ionic, salt-like materials that are liquid below 100 ◦C or even at room temperature. They are non-volatile and have very negligible vapour pressure. Due to these unique physical properties, liquid–liquid extractions by ionic liquids are growing rapidly. Their hydrophobic nature can be modulated by modifications in both cation and anion. (Brenneke, 2001) They are also used in the separation processes of various substances for example metallic ions, organic molecules, fuel desulfurization and gas separation (Zhao et al., 2005).

Wilfred et al. (2011) investigated the effect of ionic liquid loading, extraction temperature and time while removing dibenzothiophenefrom dodecane. There were eighteen (18) ionic liquids which were screened for its dibenzothiopheneextraction capability. Among those 18 ionic liquids, Imidazolium based ionic liquids with thiocyanate, dicyanamide and octylsulfate anions exhibited the highest extraction capabilities with 66.1%, 66.1%, and 63.6% of extraction efficiency respectively.

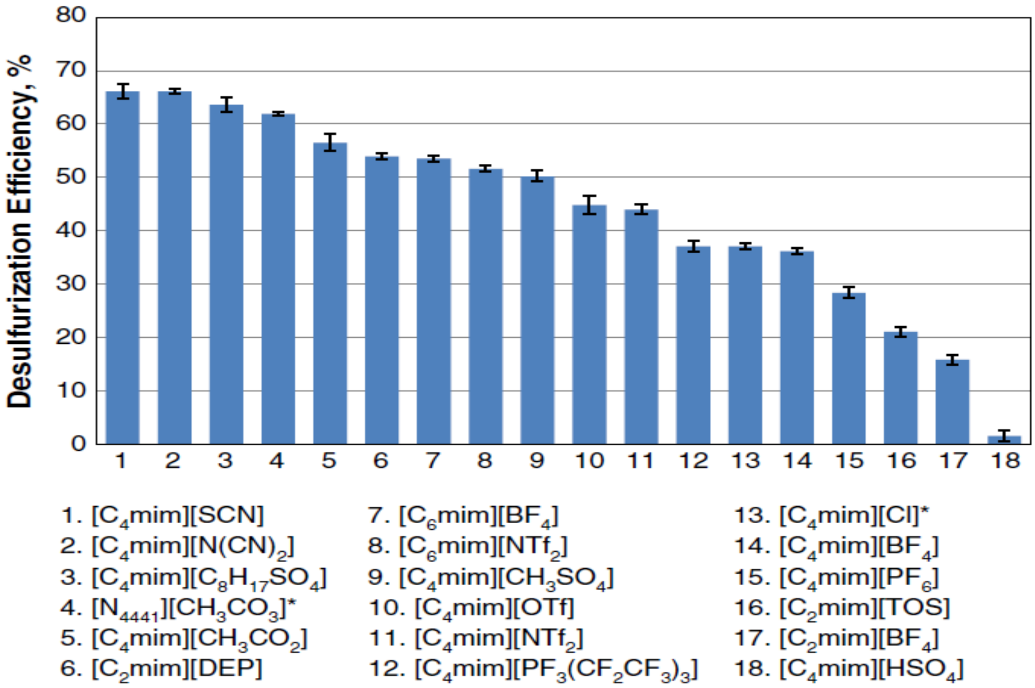

Figure 2: Desulfurization efficiency of various ionic liquids (Wilfred et al., 2011)

2.3.2 Process Concept and Mechanism

The main driving force for the extraction is the formation of liquid-clathrates and π–π interaction in between aromatic structures of the DBTs and the imidazolium ring system. The process concept illustrated in Figure 3 is still in the laboratory experimentation stage. The experiment was carried out with specific amount of ionic liquids with the high sulfur contaminated diesel mixed and stirred properly. After that the separation takes place and the low sulfur diesel is collected. The contaminated ionic liquid is further was regenerated and recycled to use for more extraction. (Eber et al., 2004)

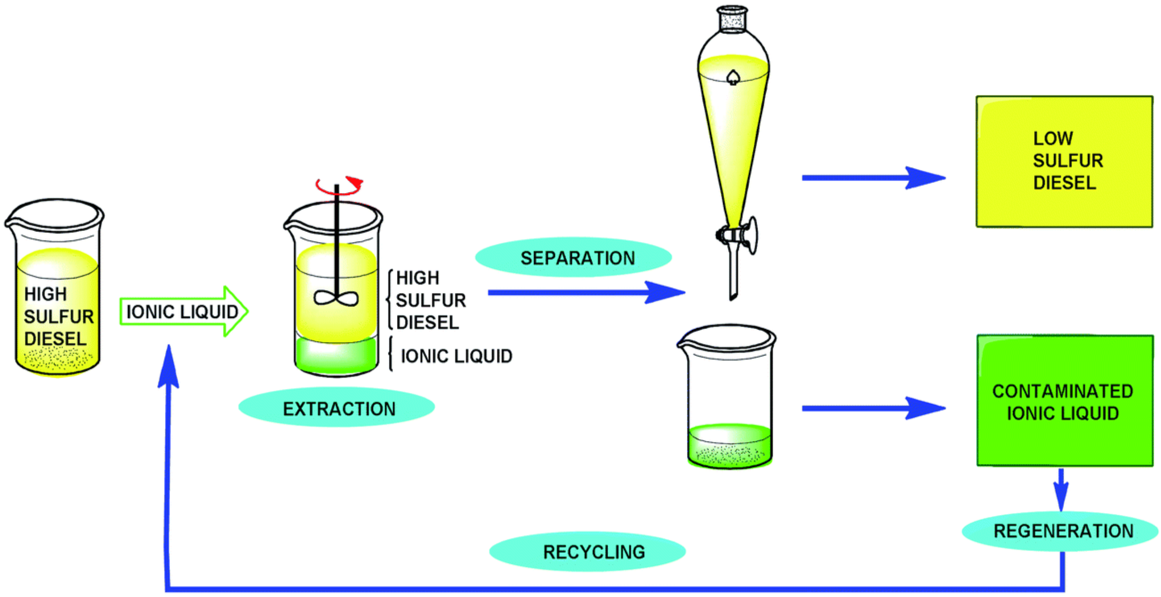

Figure 3: Concept of deep desulfurization of refinery streams by extraction with ionic liquids. (Eber et al., 2004)

The sulfur content of a model oil that contained 500 ppm sulfur as DBT in n-dodecane was reduced to less than 10 ppm by a five-stage extraction using the ionic liquid [BMIM][OcSO$_4$] at room temperature. (Eber et al., 2004)

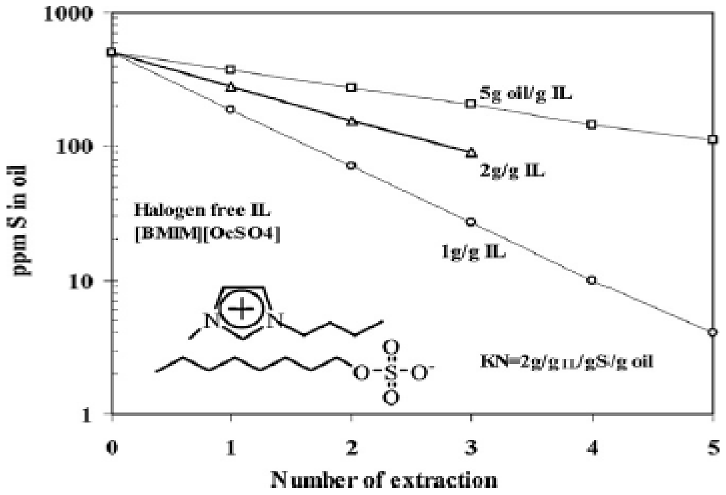

Figure 4: Influence of the oil to IL ratio for cross current extraction of a model oil (500 ppm S as DBT in n-dodecane; IL; [BMIM][OcSO$_4$], room temperature) (Eber et al., 2004)

2.3.3 The Challenges

There are several issues, such as regeneration of sulfur-loaded ionic liquids, minimization of cross solubility of valuable hydrocarbon liquids in the ionic liquids, reducing the number of stages for efficient separation, cost-effectiveness of the process, etc. have to be resolved before any attempt to commercialize the process is made. (Eber et al., 2004)

2.4 REDUCTION OF WASTES – REGENERATION, RECOVERY, REUSE & RECYCLE

Ionic liquids can be used for developing new processes which are technologically, environmentally and economically beneficial. This will include the possibilities of reusing and relatively easily recovering ILs, which is a way to effectively reduce the amount of waste generated during the productions. It is, however, important to remember that ionic liquids are still quite expensive media, and their recycling after regeneration or recovery makes such a technological method economically more justified. Among those available technologies, conventional processes such as distillation, membrane separation and extraction can be applied (Fernandez et al., 2010).

Distillation in mild conditions may be the first choice for the separation of volatile products owing to the negligible vapour pressure of ILs. For separating non-volatile products, extraction and membrane processes such as nano filtration and evaporation is used. The operations to recover ILs from aqueous solutions are classified as phase addition, force field and barrier. Since the recovery of ILs on a large industrial scale will consume a great amount of energy, or if they are to be recovered from very dilute solutions where either investment or operational costs can be so high that they make the recovery operation not feasible, effective treatment is needed prior to the final application. Most ILs are not readily biodegradable, so advanced oxidation processes (AOPs) are frequently suggested as effective processes (Siedlecka et al., 2010; Stolte et al., 2010).

According to the waste hierarchy developed by the European Union Directive 2008/98/EC, the effort priorities for dealing with spent material are expressed as

"Reduce, Reuse, and Recycle". This means that only minimum amounts of substances should be used in a process. If possible, the substance should then be reused and reincorporated into the system and eventually recovered from the waste stream. Different operations are required in order to comply with the regulations.

Regeneration is often necessary if a substance cannot be reused directly. For the recycling of waste, recovery operations are applicable. Removal operations are then the final step to prevent a negative impact on the environment or human health when the final step waste is disposed of.

This procedure also valid for ILs, not just for legislative reasons, but also because of their relatively high production costs. However, the continual reuse of ILs will lead to a concentration of contaminants. Regeneration can then enhance the reusability of the IL and prolong its lifetime by separating it from the suspected contaminant. This was the first operation to be used and developed. (Fernandez et al., 2010)

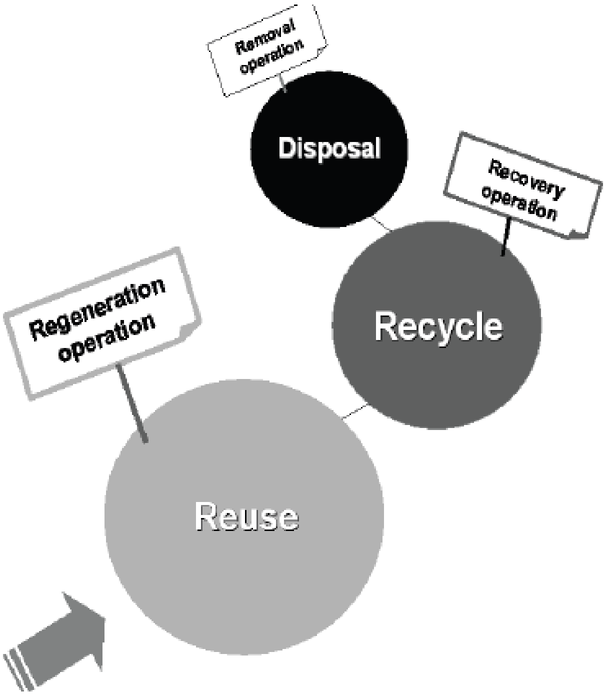

Figure 5: Scheme of the effort priorities for dealing with spent ionic liquids (Fernandez et al., 2010)

CHAPTER 3

METHODOLOGY

3.1 PROJECT ACTIVITIES

The methodology for conducting project will be through experimental methods. As this project is mainly in the field of Research and Development (R&D), the results obtained from this study can be used to compare with other literature available with similar scope of study. Figure 5 shows the general experimental procedure that will be implemented in this research project.

Figure 6: Schematic diagram of research project activities

3.2 EQUIPMENTS

To conduct experiments for this study several equipment will be needed to synthesize and recover 1-Butyl-3-Methylimidozolium based ionic liquids. The equipment that are going to be used to conduct experiments for this study are listed in Table 1.

Table 1: List of equipment

Equipment
Hot Stirrer Plate, Fume Hood
Rotavapory (Silicon oil & water bath), Vacuum Oven
Gas Chromatography – Sulfur Chemiluminescence Detector

3.3 EXPERIMENT DETAILS

3.3.1 Materials

All the materials like n-Dodecane, dibenzothiophene, BMIM [SCN], BMIM [N (CN) $_2$], BMIM [CH_3SO_4] were purchased from Sigma Aldrich. All the ILs were dried in vacuum oven at 60◦C prior to being used again.

3.3.2 Preparation of DBT in dodecane

Dodecane containing around 5wt.% dibenzothiophene (DBT) was prepared by dissolving solid dibenzothiophene in n-dodecane which is referred as model oil in the study. 5 wt.% of DBT in n-dodecane is equivalent to 8701 ppm of sulfur in n-dodecane.

3.3.3 Desulfurization of model oil using BMIM based ionic liquids:

The chemicals that used in the experiment are n-dodecane, dibenzothiophene, BMIM [SCN], BMIM [N (CN) $_2$], BMIM [CH_3SO_4].

The experiment was held at 30◦C temperature and atmospheric pressure. The experiment was carried out with specific amount of IL with the mass ratio between model oil and IL as 1:1 in a hot stirrer plate for 30 minutes at the stir rate of 400 rpm. (Wilfred et al., 2012)

First, the model oil was prepared by mixing n-dodecane and 5 wt.% of dibenzothiphene. BMIM [SCN], BMIM [N (CN) $_2$] and BMIM [CH_3SO_4] were used accordingly to extract dibenzothiophene from the model oil. Then, using the ratio of ionic liquids and model oil as 1:1, both were mixed in a hot plate stirrer for 30 minutes with the rate of 400 rpm at 30 ^{o}C temperature. After the mixing, two layers were observed in the solution, because of low density model oil float in ionic liquids.

Separating funnel was used to separate the layers. The total sulphur content in the model oil is measured before and after the desulfurization process.

3.3.4 Recovery of BMIM based ionic liquids:

After the desulfurization process, firstly, the ionic liquids were mixed with water with mass ratio of IL and water as 1:1. Then it was sent to a hot plate stirrer for further mixing. The mixing was carried at 25◦ C temperature vigorously stirring for 30 minutes at the rate of 500 rpm. While IL was mixed with water, white precipitate was formed in the solution which is dibenzothiophene (DBT). Using filtration method, the precipitate was removed from the solution.

Then the ionic liquid was sent to rotavapory for 2 hours to remove the water solvent from the solution. Once the water content is removed, the ionic liquid is sent to dry further using distillation method under vacuum for 24 hours. The vacuum oven temperature was around 60 ◦C.

3.3.4 Determination of Desulfurization efficiency:

The collected model oil samples before and after extraction was sent for gas chromatography analysis. The equipment used for the analysis was Gas Chromatography with Sulfur Chemiluminescene Detector which is manufactured by Agilent Technologies.

The determination of parameters for GC with sulfur chemiluminescence detector (GC-SCD) was accordingly where the injection temperature was 280 ◦C with the split ratio of 100:1. The carrier gas used was helium. The flowing rate was 3.5 ml/min. The oven temperature was 140 ◦C – 250 ◦C with ramping value of 20 ◦C/ min. The column was 30 mm × 0.32 mm, 1 mm film thickness.

The Agilent Sulfur Chemiluminescence Detector (SCD) utilizes the combustion of sulfur compounds to form sulfur monoxide (SO) and chemiluminescence reaction of SO with ozone (O3). The unique combustion process achieves high temperatures (>1,800 °C) which are unattainable by standard pyrolysis methods. The technology allows the SCD to make ultra-sensitive measurements of any sulfur-containing compound that can be analyzed by gas chromatography (GC) or supercritical fluid chromatography (SFC).

The reaction mechanism is:

$$\text{S-compound} + \text{O} \text{ --> } \text{SO} + \text{Other Products}$$

$$\text{SO} + \text{O}_3 \text{ --> } \text{SO}_2 + \text{O}_2 + h \text{ (300-400 nm)}$$

The light (h) passes through an optical filter and is detected by a photomultiplier tube. The light emitted is directly proportional to the amount of sulfur in the sample.

CHAPTER 4

RESULT AND DISCUSSION

This chapter discusses the results obtained from the gas chromatography with sulfur chemiluminescence detector of the model oil before and after extraction to see the percentage of DBT removal from the model oil. The recyclability performance of the ionic liquids after recovery is also discussed here. The detailed analysis of gas chromatography can be found in the Appendix I.

The main experiments involved in the study were:

1. Desulfurization of model oil using BMIM [SCN], BMIM [N $(CN)_2$] and BMIM [CH_3SO_4]
2. Recovery of BMIM [SCN], BMIM [N $(CN)_2$] and BMIM [CH_3SO_4]

The following table shows the overall experiment of the study where it is seen the total number of recycle for each ionic liquid is up to 4th cycle.

Table 2: Collected samples

Sample Code	**Cycle No.**	**Desulfurization**				**Recovery**					
		Mass (g)		**Extraction Time**		**Mass (g)**		**Washing time**		**Drying time**	
		IL	**MO**	**Start**	**Finish**	**IL**	**H20**	**Start**	**Finish**	**Start**	**Finish**
SCN	1	40.37	40.24	30 minutes		39.14	40.40	30 minutes		26hrs	
SCN	2	29.69	30.46	30 minutes		28.55	28.30	30 minutes		26hrs	
SCN	3	25.11	25.12	30 minutes		23.35	23.58	30 minutes		26 hrs	
SCN	4	14.55	14.28	30 minutes		12.49	12.48	30 minutes		26hrs	
DCM	1	40.20	40.80	30 minutes		38.40	38.50	30 minutes		26hrs	
DCM	2	33.36	33.12	30 minutes		31.02	31.40	30 minutes		26hrs	
DCM	3	26.60	26.80	30 minutes		24.28	24.78	30 minutes		26hrs	
DCM	4	16.80	16.90	30 minutes		14.47	14.74	30 minutes		26hrs	
MSF	1	40.30	40.40	30 minutes		37.10	37.10	30 minutes		26hrs	
MSF	2	20.87	20.81	30 minutes		17.87	18.02	30 minutes		26hrs	
MSF	3	14.37	12.15	30 minutes		10.15	10.25	30 minutes		26hrs	
MSF	4	3.98	4.00	30 minutes		2.00	2.10	30 minutes		26 hrs	

Here, the model oil samples for cycle 1 were labelled as MO_SCN_i_1 for the initial oil before desulfurization with SCN and final sample after desulfurization was labelled as MO_SCN_f_1. Ionic liquid samples were labelled as Pure_SCN_1 for the initial sample, Spent_SCN_1 for the sample after desulfurization and Recovered_SCN_1 for the recovered ionic liquid after drying.

DBT removal performance or efficiency here in this study is defined by the following equation:

$$DBT\ removal\ performance = \frac{[DBT]initial - [DBT]final}{[DBT]initial} \times 100\%$$

1. DBT Removal Performance of Recovered 1-Butyl-3-Methylimidazolium Thiocyanate [BMIM – SCN]

BMIM - SCN ionic liquid was used for extraction of organic sulfur compound DBT from dodecane. Based on the column below of gas chromatography analysis, it has been observed that the 1st cycle of extraction managed to remove 68.18 % of DBT from the model oil where the amount of DBT was 5 wt.%. After recovery of the same ionic liquid that has been used for desulfurization, at the 2nd cycle BMIM-SCN showed 56.11% of DBT removal performance. At the 3rd and 4th cycle accordingly it showed 52.87% and 59.87% of DBT removal performance.

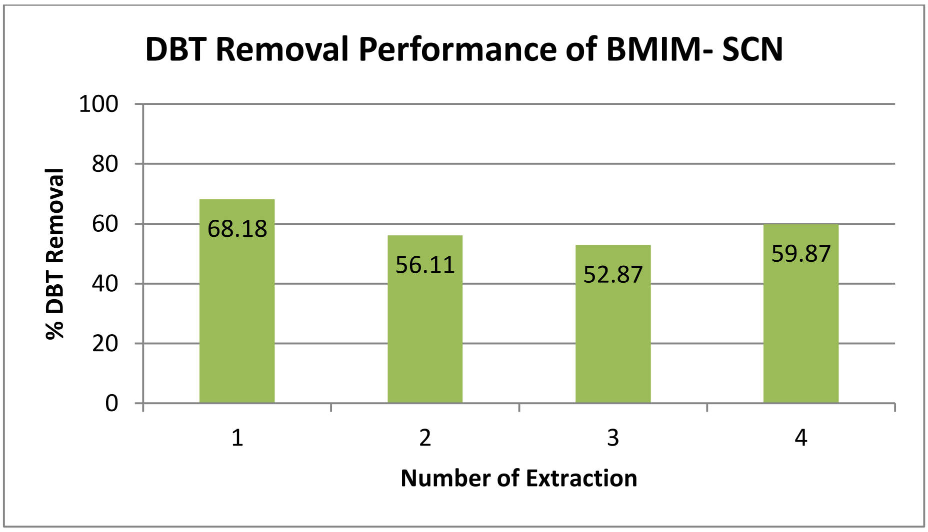

Figure 7: DBT removal performance analysis of BMIM-SCN

Based on the figure 8, where the removal efficiency of IL was observed after each recycling, it is seen that the efficiency increased up to 113.2% after 3rd recycle.

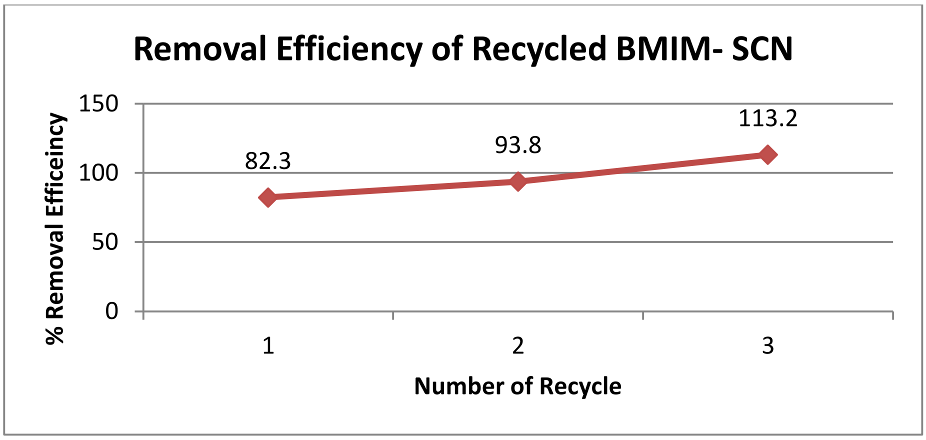

Figure 8: Efficiency of recycled BMIM-SCN

2. DBT Removal Performance of Recovered 1-Butyl-3-Methylimidazolium Dicyanamide [BMIM – N $(CN)_2$]

BMIM – DCM was used accordingly to extract DBT content from the model oil where 5 wt.% of DBT was present. Based on the figure 9 below, the first cycle of extraction showed 58.74% of DBT removal from the model oil. Then the second cycle had 61.69% of DBT removal. The third and fourth cycle accordingly showed DBT removal of 47.01% and 21.55%.

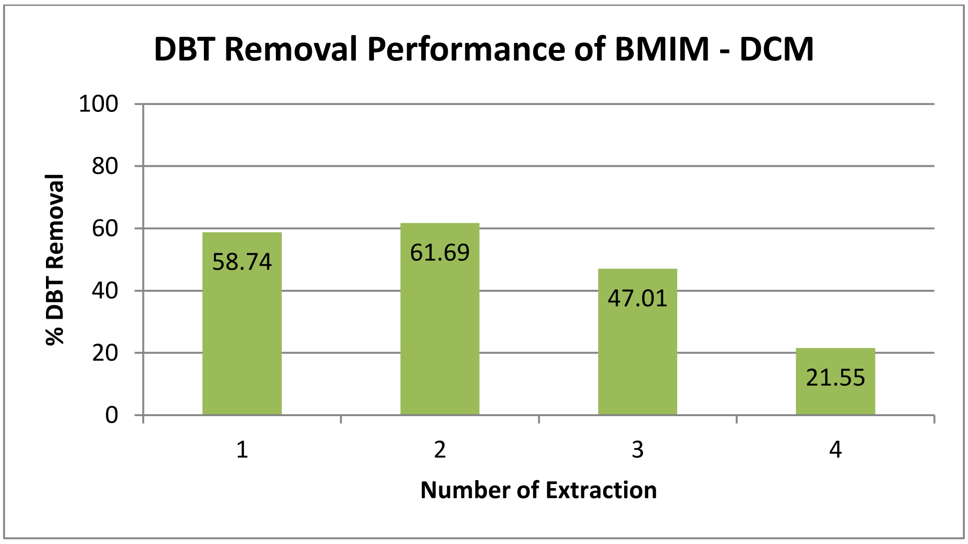

Figure 9: DBT removal performance analysis of BMIM – DCM

Studying the efficiency of recycled BMIM-DCM, based on the figure 10, it is seen that the efficiency tend to reduce over the increase of number of cycle. After the 3rd recycling, it showed 45.84% removal efficiency where after the 1st recycle it showed 105.02% of removal efficiency.

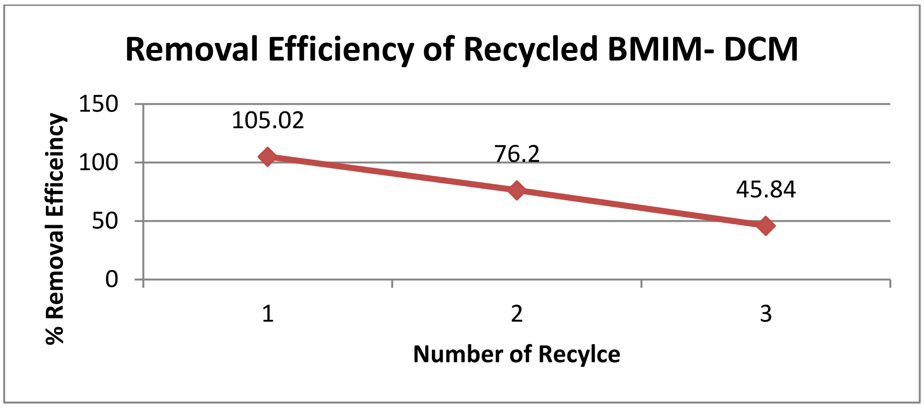

Figure 10: Efficiency of recycled BMIM-DCM

3. DBT Removal Performance of Recovered 1-Butyl-3-Methylimidazolium Methylsulfate [BMIM – CH_3SO_4)

The third ionic liquid which was used in the analysis was BMIM- CH_3SO_4. The ionic liquid was used to remove DBT from the same model oil as used before where 5 wt% of DBT was present.

Based on the figure 11 below, BMIM- Methylsulfate showed less DBT removal performance compared to BMIM-SCN and BMIM-DCM. The first cycle of extraction removed 46.28% of DBT where the second cycle removed 41.83% after recovery. The third and the fourth cycle of extraction showed 41.09% and 18.64% of DBT removal performance.

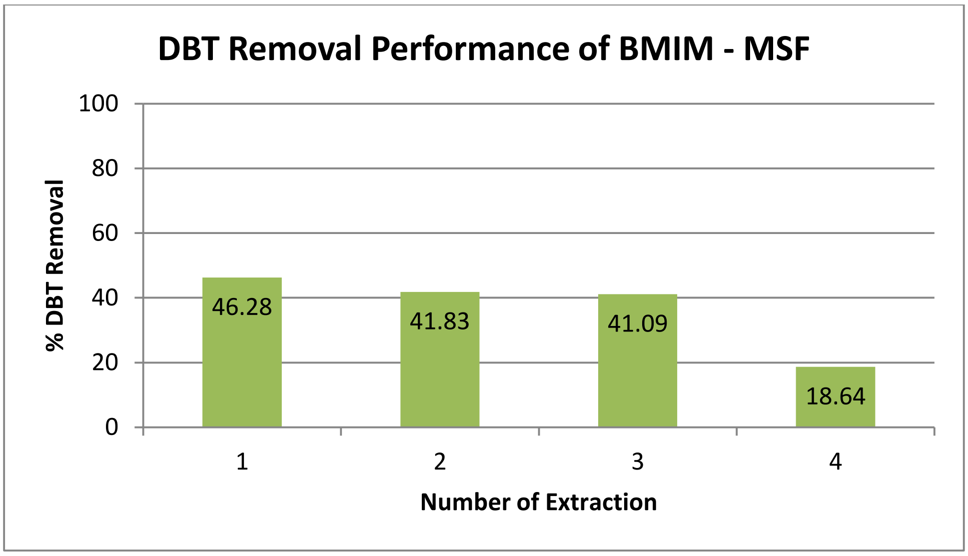

Figure 11: DBT removal performance analysis of BMIM-MSF.

Based on the figure 12, it is seen that BMIM-MSF showed 90.38% of removal efficiency after the first cycle, then at the second cycle the efficiency increased to 98.23% and at the third recycle it showed only 45.36% of efficiency.

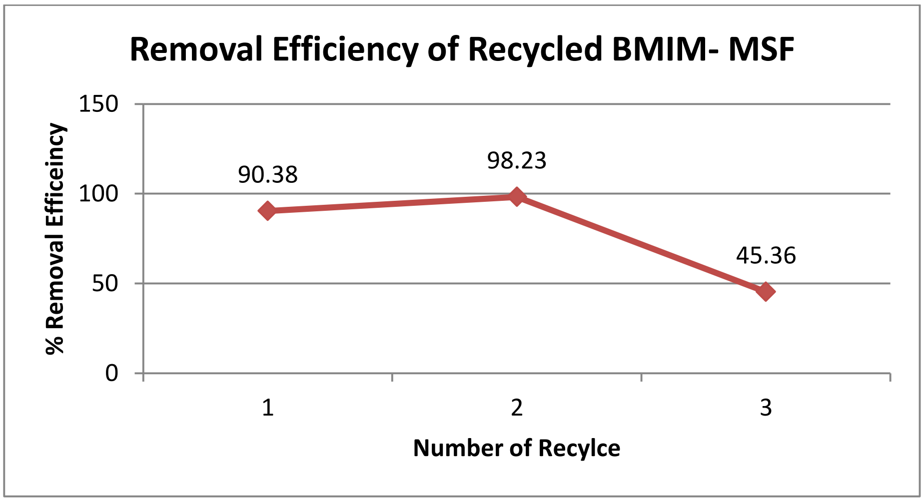

Figure 12: Efficiency of recycled BMIM-MSF

4. DBT Removal Performance Evaluation of Recyclability of Ionic Liquids

The trend for the desulfurization performance was further analysed in the figure 13 below. According to the figure, overall it is seen that the BMIM-SCN showed comparatively slightly better DBT removal performance than BMIM-DCM, whereas, BMIM-MSF showed least performance than the other two ionic liquids.

The desulfurization performance tends to reduce with the increasing number of recovery cycle. It is due to the sulfur contamination which was unable to remove and the amount of water content was increased which eventually reduces the performance of desulfurization.

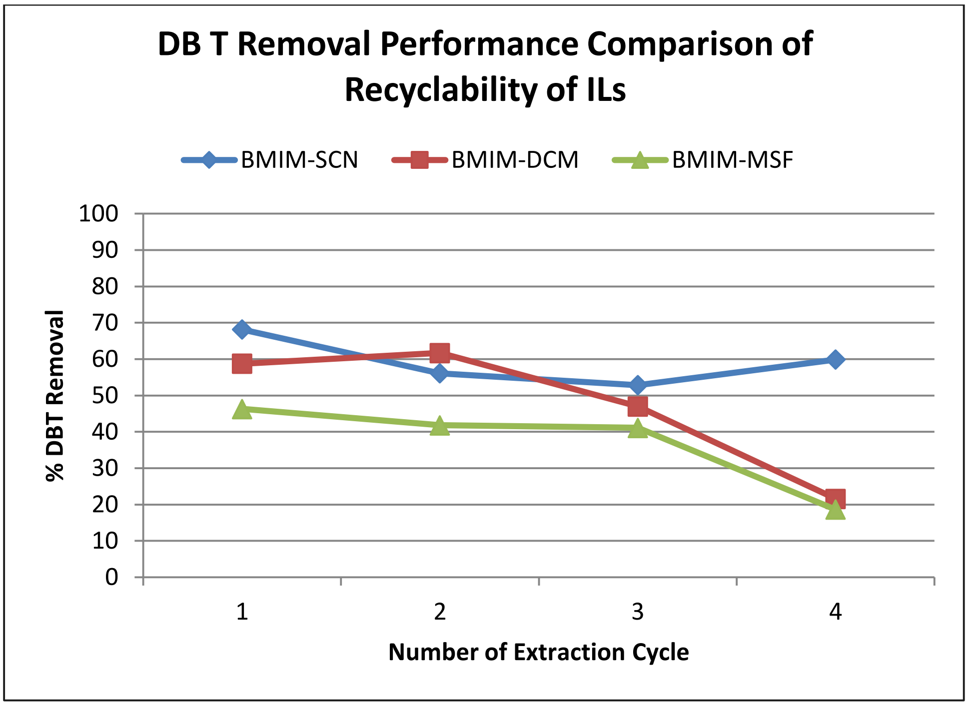

Figure 13: DBT removal performance comparison of recyclability of ionic liquids.

Based on the figure 14 below, BMIM-SCN showed increasing efficiency up to 113.2% with the increase of number of recycle, whereas, BMIM-MSF showed gradually decreasing efficiency. BMIM-DCM showed increasing efficiency after 2nd cycle however, it decreased to 45.36% efficiency after its 3rd recycle.

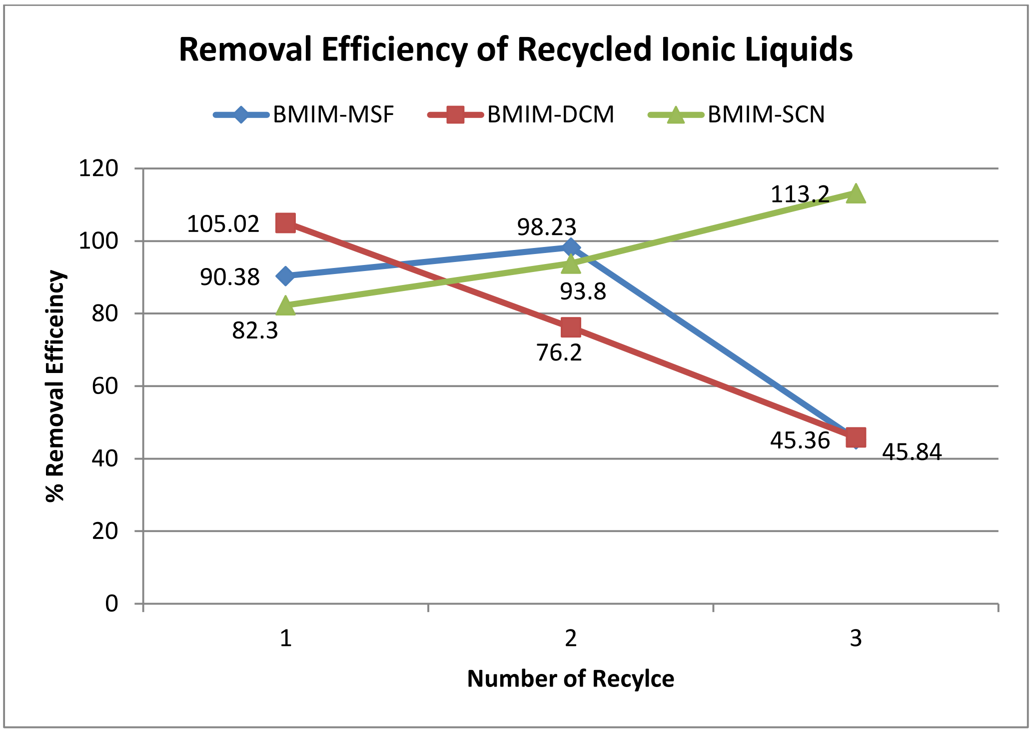

Figure 14: Efficiency comparison of recycled ionic liquids.

CHAPTER 5

CONCLUSION & RECOMMENDATION

From the study, it can be concluded that it was possible to recover the ionic liquids which were used for desulfurization process. The recovered ionic liquids showed great DBT removal performance up to 4 cycles. It is seen that the BMIM-SCN showed comparatively better DBT removal performance and efficiency than BMIM-DCM, whereas, BMIM-MSF showed least performance than the other two ionic liquids. Observing the recyclability efficiency, it is seen that up to 113% of efficiency was possible at the 4th cycle. Even though the performance decreased with the increasing number of cycles, it was possible to get at least 20% of DBT removal performance at the 4th cycle.

It was found that the ionic liquids can be recovered and reused in extraction with considerable desulfurization efficiency. Huge savings on cost is possible if we make use of this recyclability behaviour of ionic liquids in process design, instead of using new ionic liquids for each extraction.

Therefore, it can be said that the scope of the studies were done properly and the objectives of the study were fulfilled accordingly. However, it is recommended to conduct the high performance liquid chromatography in future to detect the ionic liquids in the organic layer.

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APPENDICES

1. GC Analysis Report of Model Oil Sample

```
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Acq. Operator   : Aisyah                          Seq. Line :   8
Acq. Instrument : Instrument 1                     Location : Vial 87
Injection Date  : 4/10/2015 8:10:22 PM                  Inj :   1
                                                 Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\DATA\TANZEEV\DEF_GC 2015-04-10 18-49-50\MO_S100_100415.M
Last changed    : 4/10/2015 6:48:57 PM by Aisyah
Analysis Method : C:\CHEM32\1\METHODS\MO_S100_100415_CALI.M
Last changed    : 4/10/2015 9:18:48 PM by Aisyah
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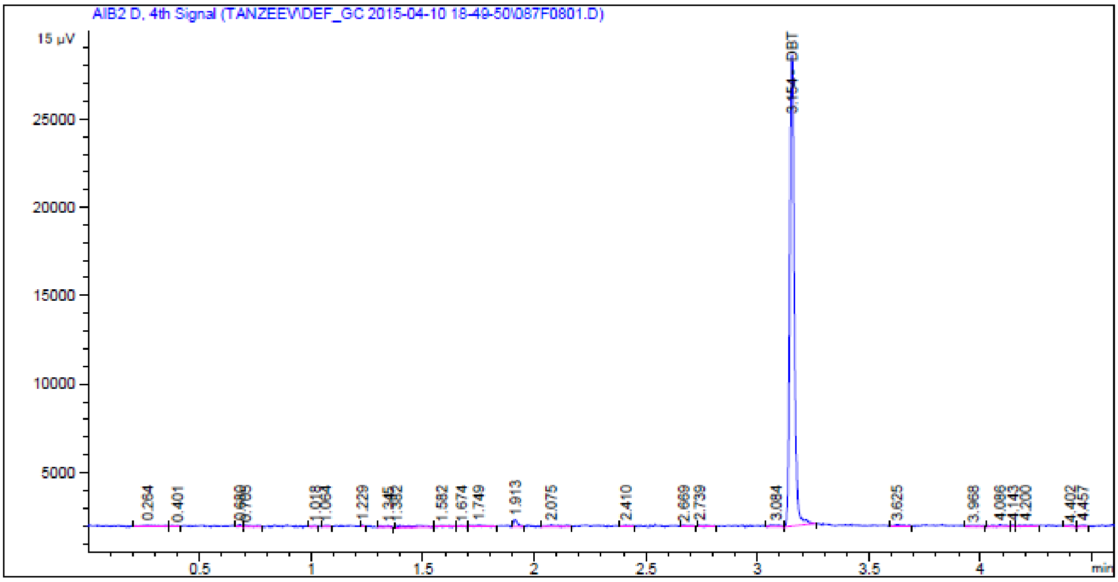

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Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: AIB2 D, 4th Signal

RetTime  Type     Area     Amt/Area     Amount    Grp   Name
 [min]          [15 µV*s]               [%]
-------|------|----------|----------|----------|--|------------------
  3.154 VB S   3.75164e4  2.14752e-3   80.56737    DBT

Totals :                               80.56737


=====================================================================
                          *** End of Report ***
```

2. GC Analysis Report of MO_SCN_f_1

```
======================================================================
Acq. Operator   : Aisyah                          Seq. Line :    9
Acq. Instrument : Instrument 1                     Location : Vial 88
Injection Date  : 4/10/2015 8:21:09 PM                  Inj :    1
                                                 Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\DATA\TANZEEV\DEF_GC 2015-04-10 18-49-50\MO_S100_100415.M
Last changed    : 4/10/2015 6:48:57 PM by Aisyah
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Last changed    : 4/10/2015 9:18:48 PM by Aisyah
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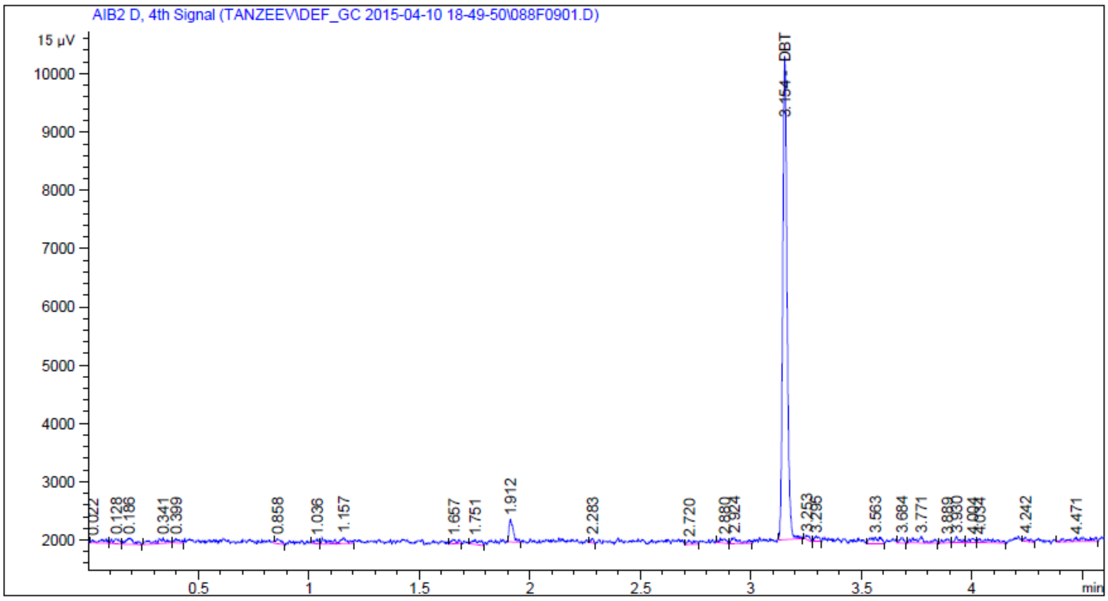

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======================================================================
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======================================================================

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Multiplier:                  :       1.0000
Dilution:                    :       1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: AIB2 D, 4th Signal

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]         [15 µV*s]                  [%]
-------|------|----------|----------|----------|--|------------------
  3.154 BB S   1.14123e4  2.24694e-3   25.64287     DBT

Totals :                               25.64287


======================================================================
                          *** End of Report ***
```

3. GC Analysis Report of MO_SCN_f_2

```
=====================================================================
Acq. Operator   : Aisyah                          Seq. Line :  10
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Injection Date  : 4/10/2015 8:31:59 PM                  Inj :   1
                                                Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\DATA\TANZEEV\DEF_GC 2015-04-10 18-49-50\MO_S100_100415.M
Last changed    : 4/10/2015 6:48:57 PM by Aisyah
Analysis Method : C:\CHEM32\1\METHODS\MO_S100_100415_CALI.M
Last changed    : 4/10/2015 9:18:48 PM by Aisyah
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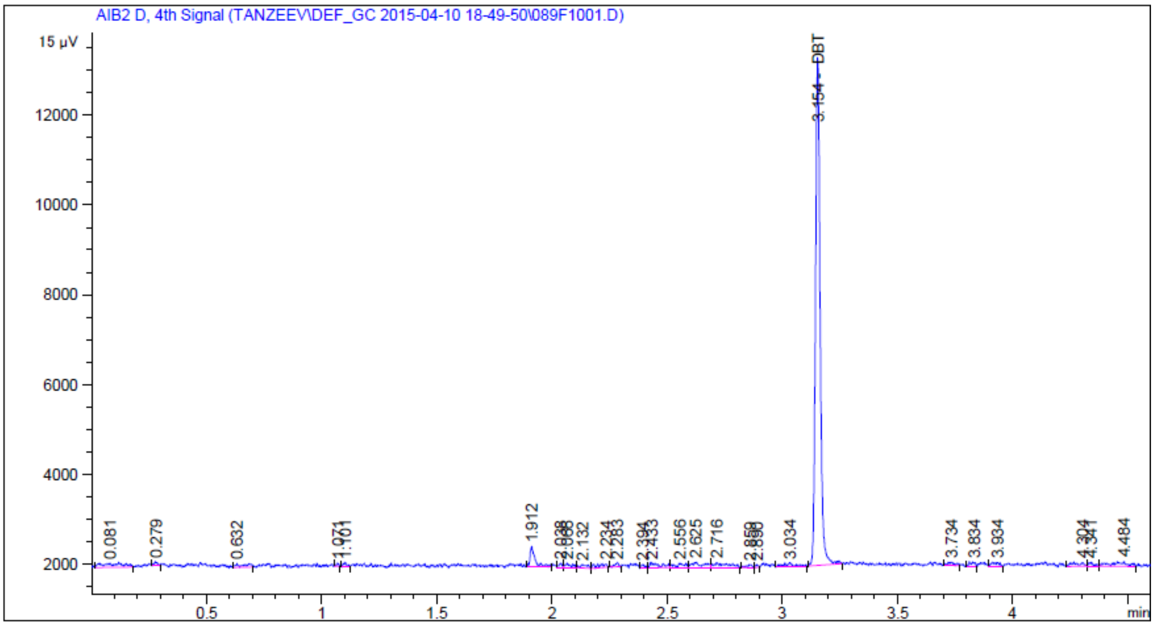

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Multiplier:                    :      1.0000
Dilution:                      :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: AIB2 D, 4th Signal

RetTime  Type     Area     Amt/Area     Amount    Grp   Name
 [min]          [15 µV*s]                [%]
-------|------|----------|----------|----------|--|------------------
  3.154 VB S   1.60311e4  2.20578e-3   35.36111     DBT

Totals :                               35.36111


=====================================================================
                          *** End of Report ***
```

4. GC Analysis Report of MO_SCN_f_3 Sample

```
=====================================================================
Acq. Operator   : Aisyah                          Seq. Line :  11
Acq. Instrument : Instrument 1                     Location : Vial 90
Injection Date  : 4/10/2015 8:42:47 PM                  Inj :   1
                                                Inj Volume : 1 µl
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Last changed    : 4/10/2015 6:48:57 PM by Aisyah
Analysis Method : C:\CHEM32\1\METHODS\MO_S100_100415_CALI.M
Last changed    : 4/10/2015 9:18:48 PM by Aisyah
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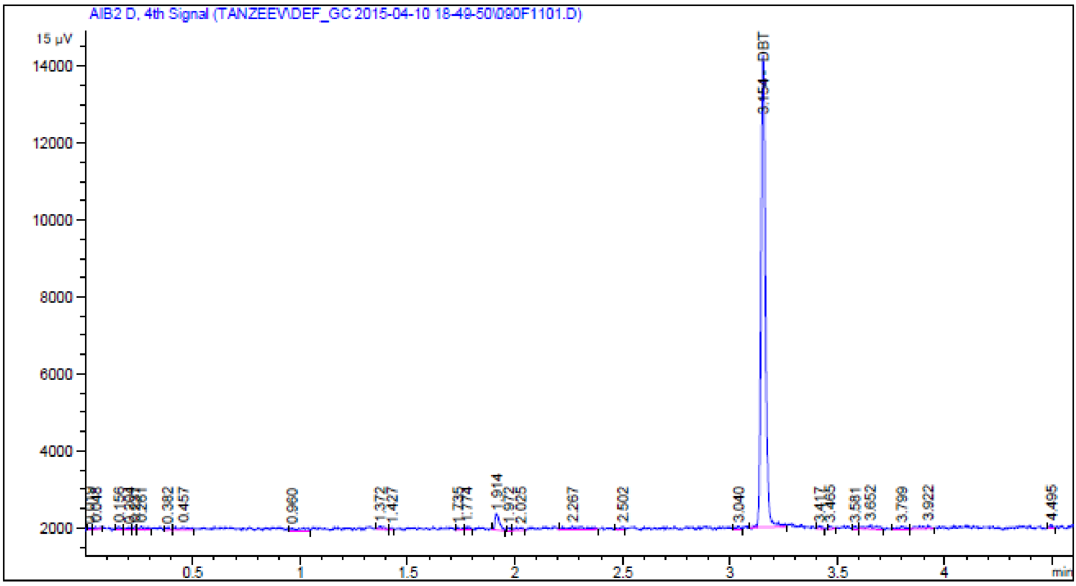

```
=====================================================================
                     External Standard Report
=====================================================================

Sorted By              :      Signal
Calib. Data Modified   :      4/10/2015 9:17:53 PM
Multiplier:                   :       1.0000
Dilution:                     :       1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: AIB2 D, 4th Signal

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]         [15 µV*s]                  [%]
-------|------|----------|----------|----------|--|------------------
  3.154 BB S   1.72697e4  2.19848e-3   37.96709     DBT

Totals :                               37.96709


=====================================================================
                         *** End of Report ***
```

5. GC Analysis Report of MO_SCN_f_4 Sample

```
=====================================================================
Acq. Operator   : Aisyah                         Seq. Line :  12
Acq. Instrument : Instrument 1                    Location : Vial 91
Injection Date  : 4/10/2015 8:53:31 PM                 Inj :   1
                                                Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\DATA\TANZEEV\DEF_GC 2015-04-10 18-49-50\MO_S100_100415.M
Last changed    : 4/10/2015 6:48:57 PM by Aisyah
Analysis Method : C:\CHEM32\1\METHODS\MO_S100_100415_CALI.M
Last changed    : 4/10/2015 9:18:48 PM by Aisyah
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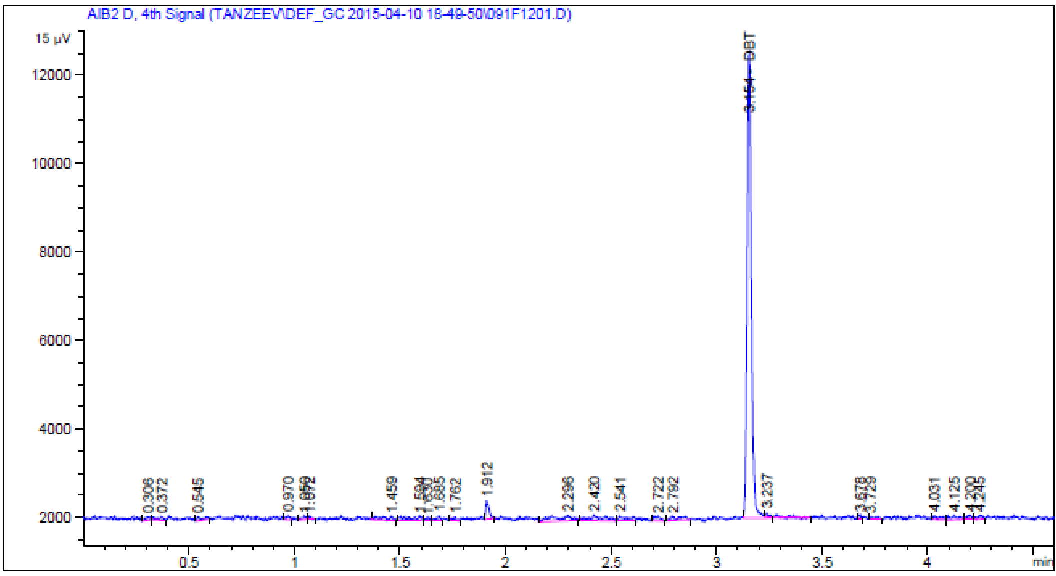

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=====================================================================
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=====================================================================

Sorted By             :      Signal
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Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: AIB2 D, 4th Signal

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]          [15 µV*s]                 [%]
-------|------|----------|----------|----------|--|------------------
  3.154 BB S   1.45894e4  2.21583e-3   32.32755    DBT

Totals :                               32.32755


=====================================================================
                          *** End of Report ***
```

6. GC Analysis Report of MO_DCM_f_1

```
=====================================================================
Acq. Operator   : Aisyah                          Seq. Line :  16
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Injection Date  : 4/10/2015 9:36:42 PM                  Inj :   1
                                                 Inj Volume : 1 µl
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Last changed    : 4/10/2015 9:18:48 PM by Aisyah
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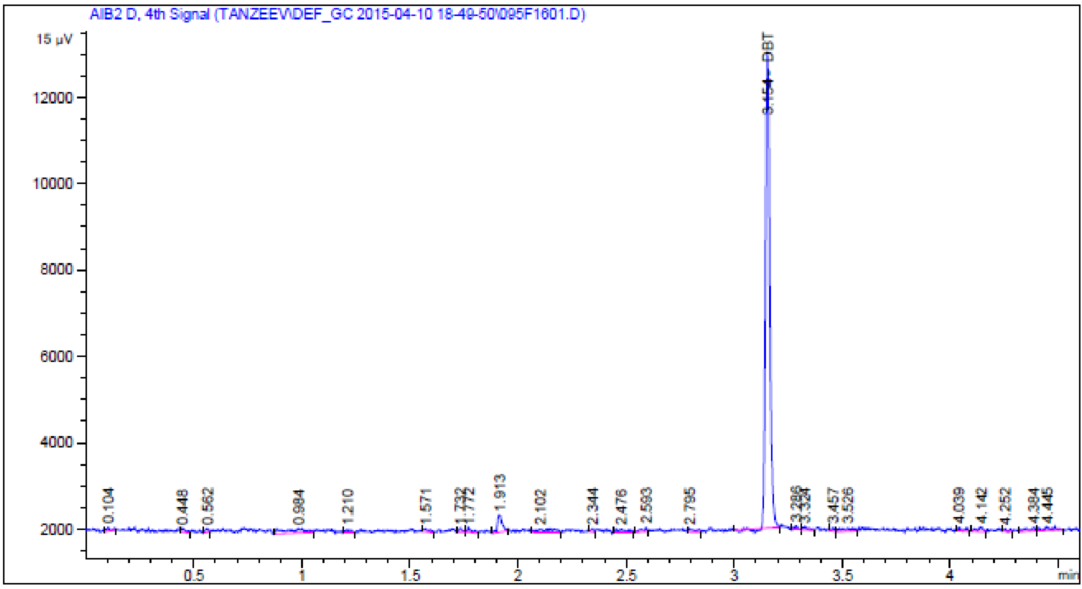

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=====================================================================
                     External Standard Report
=====================================================================

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Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: AIB2 D, 4th Signal

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]         [15 µV*s]                  [%]
-------|------|----------|----------|----------|--|------------------
  3.154 BB S  1.50226e4  2.21260e-3   33.23904    DBT

Totals :                              33.23904


=====================================================================
                         *** End of Report ***
```

7. GC Analysis Report of MO_DCM_f_2

```
=====================================================================
Acq. Operator   : Aisyah                        Seq. Line :  14
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Injection Date  : 4/10/2015 9:15:07 PM                Inj :   1
                                               Inj Volume : 1 µl
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Last changed    : 4/10/2015 6:48:57 PM by Aisyah
Analysis Method : C:\CHEM32\1\METHODS\MO_S100_100415_CALI.M
Last changed    : 4/10/2015 9:18:48 PM by Aisyah
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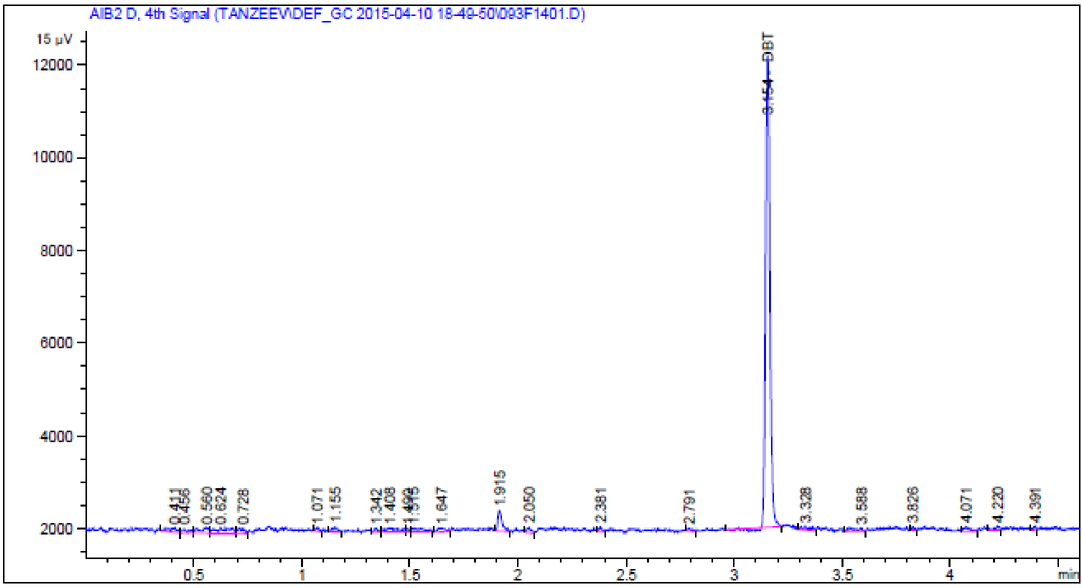

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=====================================================================
                     External Standard Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      4/10/2015 9:17:53 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: AIB2 D, 4th Signal

RetTime  Type    Area     Amt/Area     Amount    Grp   Name
 [min]         [15 µV*s]                [%]
-------|------|----------|----------|----------|--|------------------
  3.154 BB S  1.38963e4  2.22140e-3   30.86922     DBT

Totals :                              30.86922


=====================================================================
                          *** End of Report ***
```

8. GC Analysis Report of MO_DCM_f_3

```
=====================================================================
Acq. Operator   : Aisyah                          Seq. Line :  15
Acq. Instrument : Instrument 1                     Location : Vial 94
Injection Date  : 4/10/2015 9:25:51 PM                  Inj :   1
                                                Inj Volume : 1 µl
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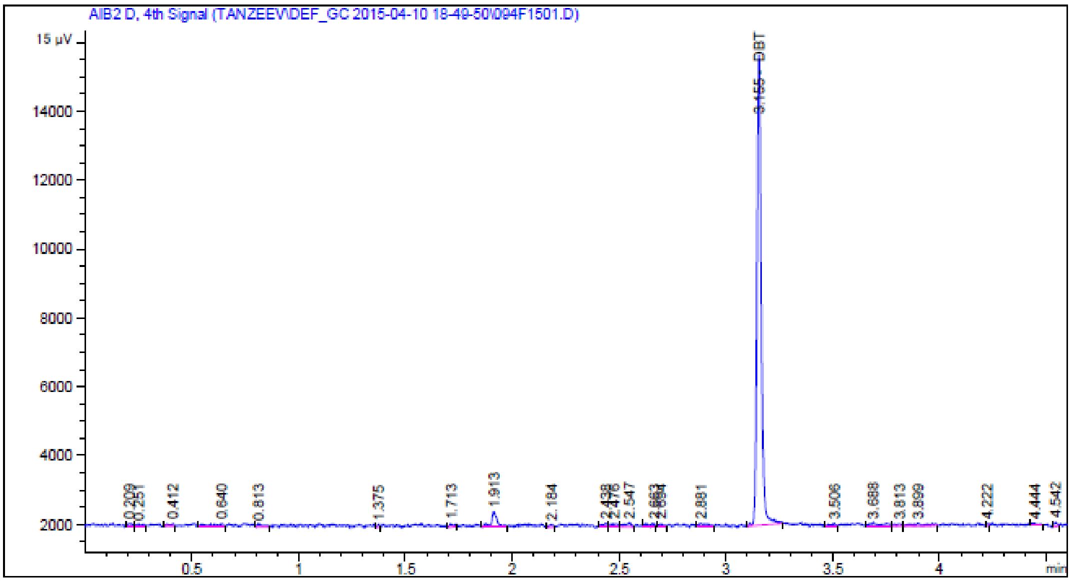

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                     External Standard Report
=====================================================================

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Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: AIB2 D, 4th Signal

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]         [15 µV*s]                  [%]
-------|------|----------|----------|----------|--|------------------
  3.155 BB S   1.95166e4  2.18761e-3   42.69460     DBT

Totals :                               42.69460


=====================================================================
                         *** End of Report ***
```

9. GC Analysis Report of MO_DCM_f_4

```
=====================================================================
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Injection Date  : 4/10/2015 9:04:20 PM                 Inj :   1
                                                Inj Volume : 1 µl
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Last changed    : 4/10/2015 6:48:57 PM by Aisyah
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Last changed    : 4/10/2015 9:18:48 PM by Aisyah
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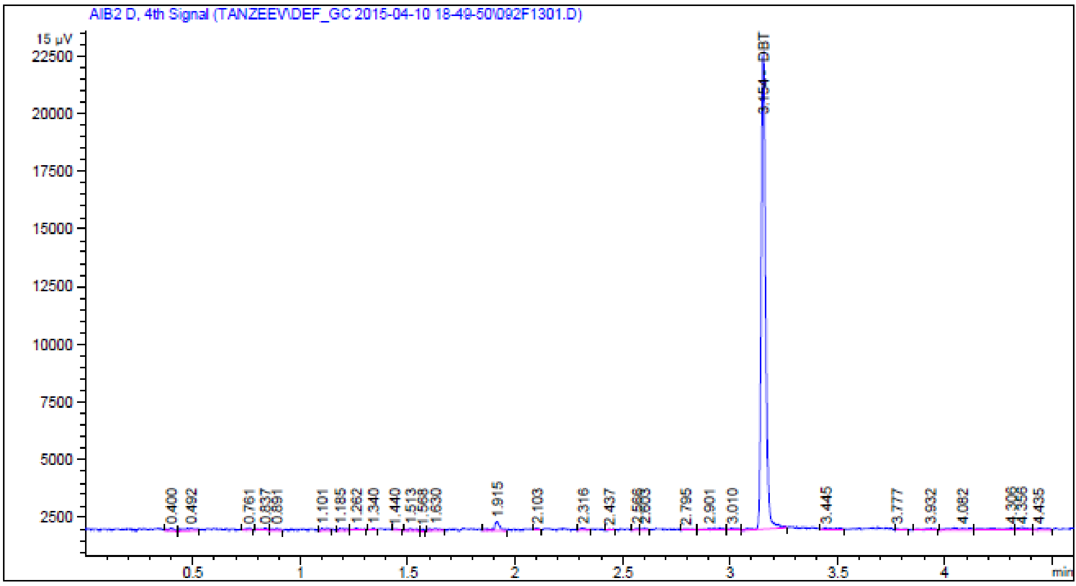

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=====================================================================
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=====================================================================

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Calib. Data Modified  :      4/10/2015 9:17:53 PM
Multiplier:                  :      1.0000
Dilution:                    :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: AIB2 D, 4th Signal

RetTime  Type     Area     Amt/Area      Amount   Grp   Name
 [min]          [15 µV*s]                  [%]
-------|------|----------|----------|----------|--|------------------
  3.154 VB S   2.89905e4  2.16031e-3   62.62843     DBT

Totals :                               62.62843


=====================================================================
                          *** End of Report ***
```

10. GC Analysis Report of MO_MSF_f_1

```
=====================================================================
Acq. Operator   : Aisyah                           Seq. Line :  20
Acq. Instrument : Instrument 1                      Location : Vial 99
Injection Date  : 4/10/2015 10:19:46 PM                  Inj :   1
                                                  Inj Volume : 1 µl
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Last changed    : 4/10/2015 6:48:57 PM by Aisyah
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Last changed    : 4/10/2015 9:18:48 PM by Aisyah
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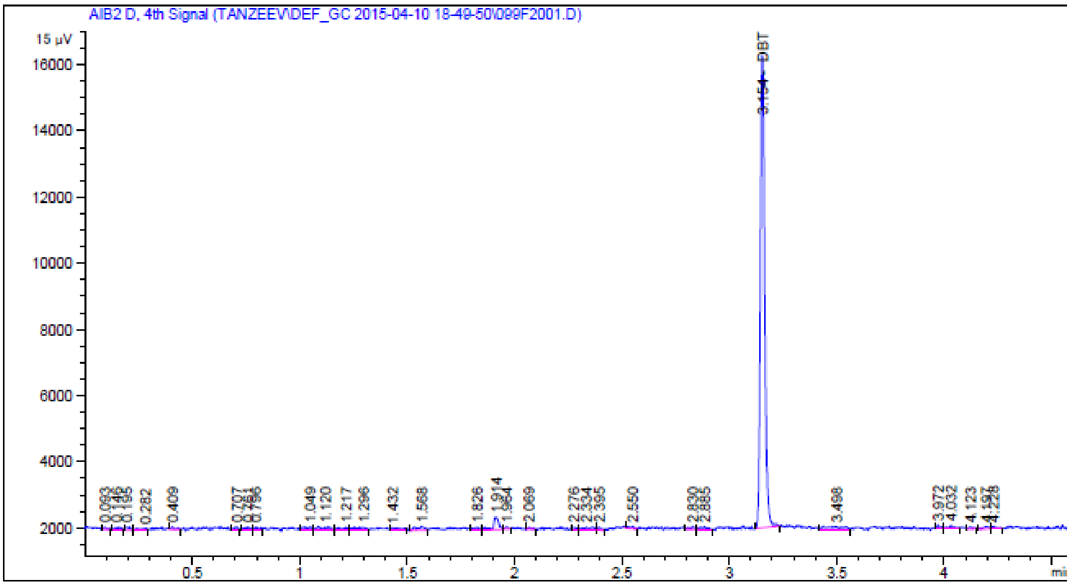

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=====================================================================
                     External Standard Report
=====================================================================

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Calib. Data Modified  :      4/10/2015 9:17:53 PM
Multiplier:                   :       1.0000
Dilution:                     :       1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: AIB2 D, 4th Signal

RetTime  Type     Area      Amt/Area     Amount    Grp   Name
 [min]          [15 µV*s]                 [%]
-------|------|----------|----------|----------|--|------------------
  3.154 BB S   1.97977e4  2.18642e-3   43.28616    DBT

Totals :                               43.28616


=====================================================================
                        *** End of Report ***
```

11. GC Analysis Report of MO_MSF_f_2

```
======================================================================
Acq. Operator   : Aisyah                          Seq. Line :  18
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Injection Date  : 4/10/2015 9:58:15 PM                  Inj :   1
                                                 Inj Volume : 1 µl
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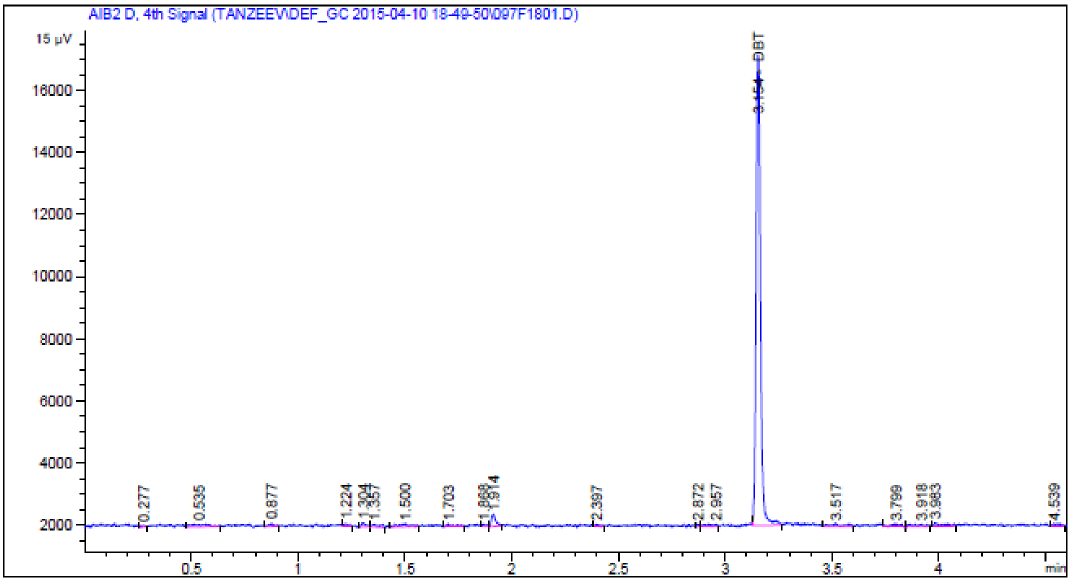
Last changed    : 4/10/2015 6:48:57 PM by Aisyah
Analysis Method : C:\CHEM32\1\METHODS\MO_S100_100415_CALI.M
Last changed    : 4/10/2015 9:18:48 PM by Aisyah
```



```
======================================================================
                      External Standard Report
======================================================================

Sorted By             :      Signal
Calib. Data Modified  :      4/10/2015 9:17:53 PM
Multiplier:                  :       1.0000
Dilution:                    :       1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: AIB2 D, 4th Signal

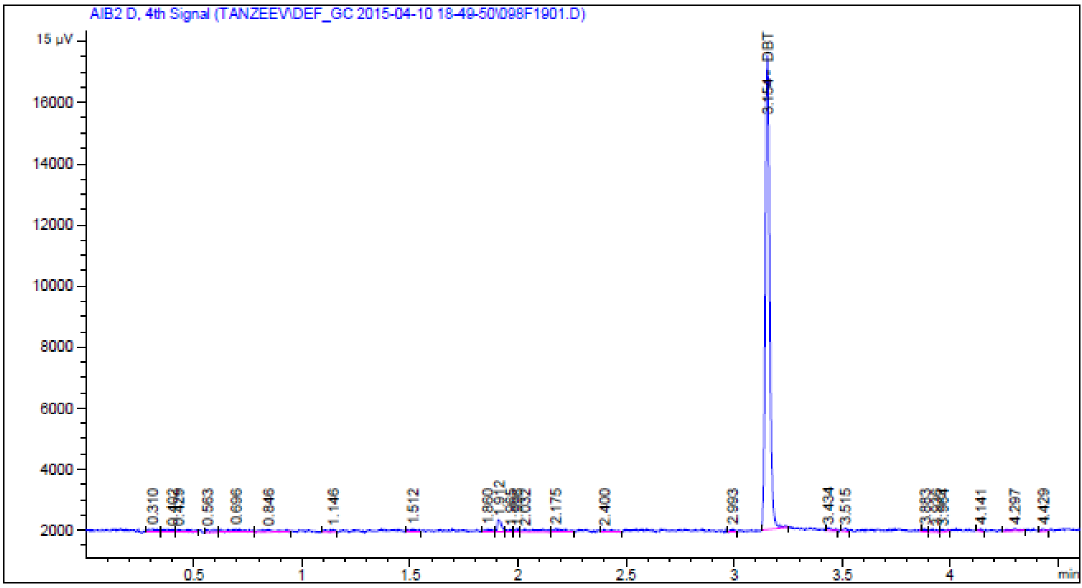
RetTime  Type     Area     Amt/Area     Amount    Grp   Name
 [min]         [15 µV*s]                 [%]
-------|------|----------|----------|----------|--|------------------
  3.154 BB S   2.15029e4  2.17989e-3   46.87409     DBT

Totals :                               46.87409


======================================================================
                          *** End of Report ***
```

12. GC Analysis Report of MO_MSF_f_3

```
=====================================================================
Acq. Operator   : Aisyah                           Seq. Line :  19
Acq. Instrument : Instrument 1                      Location : Vial 98
Injection Date  : 4/10/2015 10:09:02 PM                  Inj :   1
                                                  Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\DATA\TANZEEV\DEF_GC 2015-04-10 18-49-50\MO_S100_100415.M
Last changed    : 4/10/2015 6:48:57 PM by Aisyah
Analysis Method : C:\CHEM32\1\METHODS\MO_S100_100415_CALI.M
Last changed    : 4/10/2015 9:18:48 PM by Aisyah
```



```
=====================================================================
                      External Standard Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      4/10/2015 9:17:53 PM
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: AIB2 D, 4th Signal

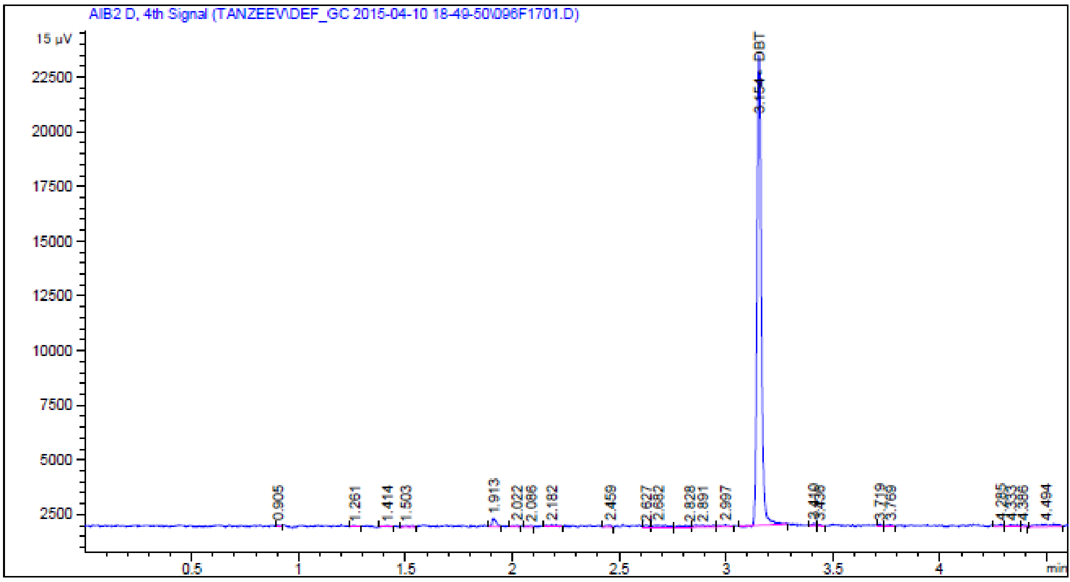
RetTime  Type     Area     Amt/Area      Amount    Grp   Name
 [min]          [15 µV*s]                  [%]
-------|------|----------|----------|----------|--|------------------
  3.154 BB S   2.17845e4  2.17891e-3   47.46642     DBT

Totals :                               47.46642


=====================================================================
                          *** End of Report ***
```

13. GC Analysis Report of MO_MSF_f_4

```
=====================================================================
Acq. Operator   : Aisyah                          Seq. Line :  17
Acq. Instrument : Instrument 1                     Location : Vial 96
Injection Date  : 4/10/2015 9:47:30 PM                  Inj :   1
                                                Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\DATA\TANZEEV\DEF_GC 2015-04-10 18-49-50\MO_S100_100415.M
Last changed    : 4/10/2015 6:48:57 PM by Aisyah
Analysis Method : C:\CHEM32\1\METHODS\MO_S100_100415_CALI.M
Last changed    : 4/10/2015 9:18:48 PM by Aisyah
```



```
=====================================================================
                     External Standard Report
=====================================================================

Sorted By             :      Signal
Calib. Data Modified  :      4/10/2015 9:17:53 PM
Multiplier:                 :      1.0000
Dilution:                   :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: AIB2 D, 4th Signal

RetTime  Type     Area     Amt/Area    Amount    Grp   Name
 [min]          [15 µV*s]              [%]
-------|------|----------|----------|----------|--|------------------
  3.154 BB S   3.03803e4  2.15773e-3   65.55254    DBT

Totals :                               65.55254


=====================================================================
                        *** End of Report ***
```