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)

JANUARY 2015

Universiti Teknologi PETRONAS 32610 Bandar Seri Iskandar Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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

by

Md. Tanzeev- Ul- Haque

(15005)

A project dissertation submitted to the

Chemical Engineering Programme

Universiti Teknologi PETRONAS

in partial fulfilment of the requirement for the

BACHELOR OF ENGINEERING (HONS)

(CHEMICAL ENGINEERING)

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 [CH₃SO₄] 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.

ACKNOWLEDGEMENT

First and foremost, I would like to express my sincere appreciation and praise to The Almighty, for His guidance and blessing throughout my study.

I would like to express my deepest gratitude to the Chemical Engineering Department of Universiti Teknologi PETRONAS (UTP) for providing me the chance to undertake this significant final year project. My gratitude also goes to my supervisor AP Dr. Mohamed Azmi B Bustam @ Khalil for his guidance and support, as well as assisting the project throughout the time which made it possible to carry out this project. I would like to thank all the staffs and research officers in Petronas Ionic Liquid Centre from Universiti Teknologi PETRONAS who had given me guidance throughout the period of the project. Besides that, I would also like to take this opportunity to express my deepest thanks to our coordinator Dr Asna binti Mohd Zain for her guidance throughout the time. In addition, to family members and fellow friends who gave moral support to motivates to complete this project.

Last, but certainly not least, I would like to apologize if any party was inadvertently excluded from being mentioned above and would like to thank all parties that were involved in making this project a success.

TABLE OF CONTENTS

CERTIFICATION	OF APPI	ROVAL	ii
CERTIFICATION	OF ORIO	GINALITY	iii
ABSTRACT			iv
ACKNOWLEDG	EMENT		v
LIST OF FIGURE	S		vii
LIST OF TABLES			viii
CHAPTER 1	INTRO	DUCTION	1
	1.1	Background of Study	1
	1.2	Problem Statement	2
	1.3	Objectives	2
	1.4	Scope of Study	2
CHAPTER 2	LITER	RATURE REVIEW	3
01111112112	2.1	Ionic Liquids	3
	2.2	Desulfurization Process	4
	2.3	Desulfurization of Fuels by Extraction with	6
		Ionic Liquids	-
	2.4	Reduction of Waste: Regeneration,	9
		Recovery, Reuse & Recycle	
CHAPTER 3	METH		11
	3.1	Project Activities	11
	3.2	Fauinment	11
	3.3	Experiment Details	12
CHAPTER 4	RESU	LT AND DISCUSSION	14
CHAPTER 4	CONC	CLUSION	23
REFERENCES			
APPENDICES			

LIST OF FIGURES

Figure 1	Simplified HDS cycle of thiophene
Figure 2	Desulfurization efficiency of various ionic liquids
Figure 3	Concept of deep desulfurization of refinery streams by
	extraction with ionic liquids.
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)
Figure 5	Reduction of wastes containing ionic liquids in industrial
	applications, and potential sources of ILs released to the
	environment
Figure 6	Schematic diagram of research project activities
Figure 7	DBT removal performance analysis of BMIM-SCN
Figure 8	Efficiency of recycled BMIM-SCN
Figure 9	DBT removal performance analysis of BMIM-DCM
Figure 10	Efficiency of recycled BMIM-DCM
Figure 11	DBT removal performance analysis of BMIM-MSF
Figure 12	Efficiency of recycled BMIM-DCM
Figure 13	DBT removal performance comparison of BMIM-based ionic
	liquids
Figure 14	Efficiency comparison of recycled BMIM-based ionic liquids

LIST OF TABLES

Table 1	List of Equipment	11
Table 2	Collected samples	15

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 hydrodesulfurization (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 [CH₃SO₄] 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 [CH₃SO₄] 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:

- Use of BMIM based ionic liquids which are BMIM [SCN], BMIM [N (CN)
 and BMIM [CH₃SO₄] for desulfurization process to extract dibenzothiophene from dodecene.
- 2. Recovery and reuse of BMIM [SCN], BMIM [N (CN) ₂] and BMIM [CH₃SO₄] 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 acidbase 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 SO₂ 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/Al₂O₃ 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 ndodecane was reduced to less than 10 ppm by a five-stage extraction using the ionic liquid [BMIM][OcSO₄] 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][OcSO₄], 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.

Desulfurization using BMIM based ILs BMIM based ILs used for desulfurization Performance evaluation of recovered ILs

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 [CH₃SO₄] 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 [CH₃SO₄].

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 $_3$ SO $_4$] 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 °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 $60 \, \circ C$.

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 $^{\circ}$ 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:

S-compound + O --> SO + Other Products
SO +
$$O_3$$
 --> SO₂ + O_2 + h (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 [CH₃SO₄]
- 2. Recovery of BMIM [SCN], BMIM [N (CN)₂] and BMIM [CH₃SO₄]

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.

Sample	Cycle	Desulfurization					Recov	ery			
Code	No.	Mas	lass (g) Extract		Extraction Time		s (g)	Washi	ng time	Dryii	ng time
		IL	MO	Start	Finish	IL	H20	Start	Finish	Start	Finish
SCN	1	40.37	40.24	30 mi	nutes	39.14	40.40	30 m	30 minutes		õhrs
SCN	2	29.69	30.46	30 mi	nutes	28.55	28.30	30 m	inutes	26	õhrs
SCN	3	25.11	25.12	30 mi	nutes	23.35	23.58	30 m	inutes	26	hrs
SCN	4	14.55	14.28	30 mi	nutes	12.49	12.48	30 m	inutes	26	õhrs
DCM	1	40.20	40.80	30 mi	nutes	38.40	38.50	30 minutes		26	õhrs
DCM	2	33.36	33.12	30 mi	nutes	31.02	31.40	30 minutes		26	õhrs
DCM	3	26.60	26.80	30 mi	nutes	24.28	24.78	30 m	inutes	26	õhrs
DCM	4	16.80	16.90	30 mi	nutes	14.47	14.74	30 m	inutes	26	õhrs
MSF	1	40.30	40.40	30 mi	nutes	37.10	37.10	30 m	inutes	26	õhrs
MSF	2	20.87	20.81	30 mi	nutes	17.87	18.02	30 m	inutes	26	õhrs
MSF	3	14.37	12.15	30 mi	nutes	10.15	10.25	30 m	inutes	26	õhrs
MSF	4	3.98	4.00	30 mi	nutes	2.00	2.10	30 m	inutes	26	hrs

Table 2: Collected samples

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.





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%.





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 3^{rd} recycling, it showed 45.84% removal efficiency where after the 1^{st} 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 – CH₃SO₄)

The third ionic liquid which was used in the analysis was BMIM- CH₃SO₄. 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.

REFERENCES

Bosmann, L. Datsevich, A. Jess, A. Lauter, C. Schmitz, P. Wasserscheid, Deep desulfurization of diesel fuel by extraction with ionic liquids, Chem. Commun. (2001) 2494–2495.

Sydbom, A. Blomberg, S. Parnia, N. Stenfors, T. Sandstrom, S.-E. Dahlen, Health effects of diesel exhaust emissions, Eur. Respir. J. 17 (2001) 733.

B. Zielinska, J. Sagebiel, J.D. McDonald, W.K. Lawson, Emission rates and comparative chemical composition from selected in use diesel and gasolinefueled vehicles, J. Air Waste Manage. Assoc. 54 (2004) 1138.

B.D. Quimby, V. Giarrocco, K.A. McCleary, Fast analysis of oxygen and sulfur compounds in gasoline by GC–AED, J. High Resol. Chromatogr. 15 (2005) 705–709.

C. Lopez Garcia, M. Becchi, M.F. Grenier-Loustalot, O. Paisse, R. Szymanski, Analysis of aromatic sulfur compounds in gas oils using GC with sulfur chemiluminescence detection and high-resolution MS, Anal. Chem. 74 (2002) 3857

Dharaskar S., Wasewar K., Varma M., Shende D., and Yoo C., Environmentally Benign Process for Removal of Sulfur from Liquid Fuel using Imidazolium based Ionic Liquids, Res. J. Chem. Environ. **18** (**2**), 94-99 (**2014**)

Dharaskar S., Wasewar K., Varma M., Shende D. and Yoo C., Deep removal of sulfur from model liquid fuels using 1-Butyl-3-Methylimidazolium Chloride, Procedia Eng., **51**, 416-422, (**2013**)

Dharaskar S. et al, Ionic Liquids: The Novel Solvent for Removal of Dibenzothiophene from Liquid Fuel, Procedia Eng., **51**, 314-317 (**2013**)

Efforts to Limit Diesel Fuel Sulfur Levels. (2012). Retrieved from http://www.epa.gov/blackcarbon/2012report/Appendix4.pdf

G.F. Zhang, F.L. Yu, R. Wang, Research advances in oxidative desulfurization technologies for the production of low sulfur fuel oils, Petroleum & Coal 51 (2009) 196–207.

H. Zhao, S.Q. Xia, P.S. Ma, Use of ionic liquids as green solvents for extractions, J. Chem. Technol. Biotechnol. 80 (2005) 1089–1096.

H. Rang, J. Kann, V. Oja, Advances in desulfurization research of liquid fuel, Oil Shale 23 (2006) 164–176.

J. Eber, P. Wasserscheid, A. Jess, Deep desulfurization of oil refinery streams by extraction with ionic liquids, Ind. Eng. Chem. 43 (2004) 614-622

J.F. Brennecke, E.J. Maginn, Ionic liquids: innovative fluids for chemical processing, AIChE J. 47 (2001) 2384–2389.

J.J. Wang, Y.C. Pei, Y. Zhao, Z.G. Hu, Recovery of amino acids by imidazo1ium based ionic liquids from aqueous media, Green Chem. 7 (2005) 196–202.

J. McFarlane, W.R. Ridenour, H. Luo, R.D. Hunt, D.W. DePaoli, R.X. Ren, Room temperature ionic liquids for separating organics from produced water, Sep.

J. Zhang, K. He, Y. Ge, X. Shi, Influence of fuel sulfur on the characterization of PM10 from a diesel engine, Fuel 88 (2009) 504.

L. Alonso, A. Arce, M. Francisco, A. Soto, Thiophene separation from aliphatic hydrocarbons using the 1-ethyl-3-methylimidazolium ethylsulfate ionic liquid, Fluid Phase Equilibria 270 (2008) 97–102.

M.M. Mariq, R.E. Chase, N. Xu, P.M. Laing, The effects of the catalytic converter and fuel sulfur level on motor vehicle particulate matter emissions: light duty diesel vehicles, Environ. Sci. Technol. 36 (2002) 283.

P. Wasserscheid, W. Keim, Ionic liquids—new solutions for transition metal catalysis, Angew. Chem., Int. Ed. 39 (2000) 3772–3789.

S.D. Shah, D.R. Cocker, W.J. Miller, J.M. Norbeck, Emission rates of particulate matter and elemental and organic carbon from in-use diesel engines, Environ. Sci. Technol. 38 (2004) 2544.

S. Phirun, M. Lu, K. Tim, F. Liang, K.S. Jai, The effect of diesel fuel sulfur content on particulate matter emission for a non-road diesel generator, J. Air Waste Manage. Assoc. 55 (2005) 993.

Stanislaus, A., Marafi, A., & Rana, M. (n.d.). Recent advances in the science and technology of ultra low sulfur diesel (ULSD) production. *Catalysis Today*, *153* (2010), 1-68.

Sci. Techno. 40 (2005) 1245-1265.

T. Kabe, H. Tajima, Deep desulfurization of methyl-substituted benziothiophenes and dibenzothiophenes in light gas oil, J. Jpn. Petrol. Inst. 36 (1992) 467–471.

U.S. Energy Information Administration, The Transition to Ultra- Low-Sulfur Diesel Fuel: Effects on Prices and Supply, SR/OIAF/ 2001-01, 13–22 (**2001**)

Wilfred C.D, Kiat C.F, Man Z., Bustam M.A, Mutalib M. and Phak C.Z., Extraction of dibenzothiophene from dodecane using ionic liquids, Fuel Processing Technol., **93(1)**, 85-89 (**2012**)

Y.X. Wang, X.Y. Li, Extractive removal of thiophenesulfide from diesel using ionic liquids, The Proceedings of the 3rd International Conference on FunctionalMolecules, Dalian, 2005, pp. 273–277.

APPENDICES

1. GC Analysis Report of Model Oil Sample

						=	
Acq. Operator	: Aisyah			Seq. Line	: 8		
Acq. Instrument	: Instrume	ent 1		Location	: Vial 87		
Injection Date	: 4/10/200	15 8:10:22 B	PM	Inj	: 1		
-				Ini Volume	: 1 ul		
Acg. Method	: C:\CHEM		NZEEV\DEF (C 2015-04-1	10 18-49-50	NO 5100 1	00415.M
Last changed	t changed : 4/10/2015 6:48:57 PM by bisyab						
Analysis Method	 C • \ CHEM: 	32\1\METHODS\MO_S100_100415_CALL.M					
Last changed	· 4/10/20	15 9:18:48 8	PM by Aisvah))			
AIB2 D 4th Si	anal (TANZEEV)	DEE_GC 2015-04-	10 18-49-50/087E0	- 801 D)			
15 uV					E		
					E C		
					+		
25000 -							
]							
20000 -							
1							
-							
15000 -							
10000							
1							
5000 -							
5000 - 2 2 5	986	55 ST	582 574 749 913 913	110	8 B	325	8 879 344 245
5000	9949	1.229	1.582 1.674 1.749 1.913 2.075	2.410	2.739	3.625	3.968 4.143 4.200 4.457
5000	884:0	1:845	1.582 1.674 1.749 7.913 2.075	2.410	2.739	3.625	3.968 4.103 4.402 4.457
5000 - 50000 - 50000 - 5000 - 5000 - 5000 - 5000 - 5000 - 5000 - 5000 - 5	88 97 0.5	576 576 1 1.5	1.582 1.674 1.749 0.1.913	01472 2.5	6	3.5 3.5	+ 3.968 3.968 = 4.086 = 4.086 = 4.005 = 4.402 = 4.457
	884/ <u>9</u>	1 1.5	1.582 1.749 1.749 7.1.913	014 Z.5	5-739 2.739 3.084	959°C	+
5000	8 19 0.5		1.582 1.674 1.749 0.1913 1.913 2.075	0147 2.5	6	378 878 875 	
	0.5 Exte	200 20 20 20 20 20 20 20 20 20 20 20 20	2002 1291 1291 1291 1291 1291 1291 1291	2.5	2.739 6.1	\$28 828 828 82 82 82 82 82 82 82 82 82 82	+
	0.5 Exte	27 57 58 58 50 50 50 50 50 50 50 50 50 50 50 50 50	17.82 17.84 17.84 17.84 17.84 19.12 19.13	2.5	2.739	3.5 3.5	+
	麗 0.5 	27 27 28 28 28 28 28 28 28 28 28 28 28 28 28	2022 2027	2.5	m2.739	3.5 3.5	+
5000- 5000- 5000- 5000- 5000- 5000- 5000- 5000- 5000- 5000- 5000- 5000- 5000- 5000- 5000- 5000- 5000- 5000- 5000- 50	20.5 	ernal Standa	8451 1913 1913 1913 1913 1913 1913 1913 19	0; ¥7, C	0.084	9298 	+
Sorted By Calib. Data Modi	2.5 Exte fied :	Signal 4/10/201	289:10 149:10 ard Report 15 9:17:53 1	94 77 2.5 2.5	-2.739 	9299 	+
Sorted By Calib. Data Modi Multiplier:	20.5 	Signal 4/10/201	285. 1.5 9:17:53 I 1.0000	9 99 7 2.5	-5.739 	9299 <u>2</u> 	+
Sorted By Calib. Data Modi Multiplier: Dilution:	82 67 Exte fied :	Signal 4/10/201 :	2851 10000 1.0000 1.0000	2.5 2.5	-2.739 084	579 E 	+
Sorted By Calib. Data Modi Multiplier: Dilution: Use Multiplier &	0.5 Ext: fied : Dilution	signal 4/10/201 : Factor with	2851 15 9:17:53 F 1.0000 1.0000 1.STDs	2.5 2.5	α -2.739 -2	SC9 E 	+
Sorted By Calib. Data Modi Multiplier: Dilution: Use Multiplier &	Extended and the second	Signal 4/10/201 : Factor with	289:10 15 9:17:53 F 1.0000 1.0000 1.0500	2.5 2.5	-2.739 	scere 3.5 =	+
Sorted By Calib. Data Modi Multiplier: Dilution: Use Multiplier & Signal 1: AIB2 D	Extended of the second	Signal 4/10/201 : Factor with	289:10 15 9:17:53 1 1.0000 1.0000 1.STDs	2.5 M	-2.739 	3.5 3.5 =	+
Sorted By Calib. Data Modi Multiplier: Dilution: Use Multiplier & Signal 1: AIB2 D	Extended of the second	Signal 4/10/201 : Factor with	289:10 15 9:17:53 F 1.0000 1.0000 1.STDs	2.5 2.5	-2.739 2.739	3.5 	+
Sorted By Calib. Data Modi Multiplier: Dilution: Use Multiplier & Signal 1: AIB2 D RetTime Type	Dilution 4th Sign	Signal 4/10/201 : Factor with nal Amt/Area	Amount	2.5 2.5 2.5 2.7 2.7 2.7 2.7 2.7 2.7 2.7 2.7 2.7 2.7	2.739 	3.5 3.5	+
Sorted By Calib. Data Modi Multiplier: Dilution: Use Multiplier & Signal 1: AIB2 D RetTime Type [min]	Dilution Area 15 uV*al	Signal 4/10/201 : Factor with hal Amt/Area	Amount [%]	2.5 2.5 M Grp Name	m2.739	3.5 3.5	
Sorted By Calib. Data Modi Multiplier: Dilution: Use Multiplier & Signal 1: AIB2 D RetTime Type [min] [Extr fied : Dilution , 4th Sign Area 15 µV*s]	Signal 4/10/201 : Factor with hal Amt/Area	Amount [%]	2.5 2.5 PM	0000	3.5 3.5	+
Sorted By Calib. Data Modi Multiplier: Dilution: Use Multiplier & Signal 1: AIB2 D RetTime Type [min] [25 05 Exta fied : Dilution 4th Sign Area 15 µV*s] .75164e4	Signal 4/10/201 : Factor with hal Amt/Area	Amount [%]	9 8 7 2.5 2.5 2.5 2.5 2.5 2.5 2.5 2.5 2.5 2.5	-2.739 		+
Sorted By Calib. Data Modi Multiplier: Dilution: Use Multiplier & Signal 1: AIB2 D RetTime Type [min] [25 05 Exta fied : Dilution 4th Sign Area 15 µV*s] .75164e4	Signal 4/10/201 : Factor with hal Amt/Area 2.14752e-3	Amount [%] 80.56737	Grp Name 	2.739 		
Sorted By Calib. Data Modi Multiplier: Dilution: Use Multiplier & Signal 1: AIB2 D RetTime Type [min] [25 05 Exta fied : Dilution 4th Sign Area 15 µV*s] .75164e4	Signal 4/10/201 : Factor with hal Amt/Area 2.14752e-3	Amount [%] 80.56737 80.56737	Grp Name 	φ2.739 -2.739 -2.739		
Sorted By Calib. Data Modi Multiplier: Dilution: Use Multiplier & Signal 1: AIB2 D RetTime Type [min] [25 05 Exta fied : Dilution , 4th Sign Area 15 µV*s] .75164e4	Signal 4/10/201 : Factor with hal Amt/Area 2.14752e-3	Amount [%] 80.56737 80.56737	9 8 2.5 2.5 2.5 2.5 2.5 2.5 2.5 2.5 2.5 2.5	-2.739 		+
Sorted By Calib. Data Modi Multiplier: Dilution: Use Multiplier & Signal 1: AIB2 D RetTime Type [min] [25 05 Ext fied : Dilution , 4th Sign Area 15 µV*s] .75164e4	Signal 4/10/201 : Factor with hal Amt/Area [] 2.14752e-3	Amount [%]	Grp Name 	-2739 		+
Sorted By Calib. Data Modi Multiplier: Dilution: Use Multiplier & Signal 1: AIB2 D RetTime Type [min] [25 05 Ext fied : Dilution , 4th Sign Area 15 μV*s] .75164e4	Signal 4/10/201 : Factor with hal Amt/Area [] 2.14752e-3	Amount [%] 80.56737 80.56737	Grp Name 			
Sorted By Calib. Data Modi Multiplier: Dilution: Use Multiplier & Signal 1: AIB2 D RetTime Type [min] [25 05 Ext: fied : Dilution , 4th Sign Area 15 µV*s] .75164e4	Signal 4/10/201 : Factor with hal Amt/Area 2.14752e-3	Amount [%] 80.56737 80.56737 80.56737	Grp Name 	2.739 	-	

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\D	EF_GC 2015-04-10 18-49-50\MO_S100_100415.M
Last changed : 4/10/2015 6:48:57 PM by Ai	syah
Analysis Method : C:\CHEM32\1\METHODS\MO_S10	0_100415_CALI.M
Last changed : 4/10/2015 9:18:48 PM by Ai	syah
AIB2 D, 4th Signal (TANZEEV/DEF_GC 2015-04-10 18-49-50)	088F0901.D)
15 µV -	I
10000 -	μ μ
	\$
	¢
9000 -	
8000 -	
7000 -	
6000	
5000 -	
4000 -	
2000	
	2 P 27 28 28 28 29 29 2
-000 000 000 000 000 000 000 000 000 00	4 4 5 00 00 10 10 10 10 10 10 10 10 10 10 10
2000	pharman where a second stand and the second stand and a second second and a second second second second second
	2 25 2 25 4 min
0.0 1 1.0	
External Standard Repo	rt
Sorted By · Signal	
Calib Data Modified : 4/10/2015 9:17:	52 DM
Multiplier. 1 0000	55 EM
Dilution: 1 0000	
We Multiplier (Dilution Tester with ISTR-	
Use Multipiler & Dilution Factor with ISTDS	
Signal I: AIB2 D, 4th Signal	
RetTime Type Area Amt/Area Amoun	t Grp Name
[min] [15 µ∇*s] [%]	
3.154 BB S 1.14123e4 2.24694e-3 25.64	0.07 555
	287 DBT
	287 DBN
Totals : 25.64	287 082
Totals : 25.64	287 082
Totals : 25.64	287 082
Totals : 25.64	287

28

Acq. Operator : Aisyah	Seq. Line : 10	
Acq. Instrument : Instrument 1	Location : Vial 89	
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 Aisyal	h	
Analysis Method : C:\CHEM32\1\METHODS\MO_S100_1	UU415_CALI.M	
AIR2 D 4th Signal (TANZEEV/DEE GC 2015-04-10-19-40-50/09051	n 1001 D)	
AID2 D, 401 Signal (TANZEEVIDER_GC 2015-04-10 10-49-500089F1	H.	
10 µV	8 9	
	4	
12000 -	o	
10000 -		
8000 -		
4000 -		
000 7 7 8 8 7	N 40 40 00 00 4 7 4 4 7	
2008 000 000 000 000 000 000 000 000 000		
2000		
2000	to perform the second and the second second and the second s	
2000		
2000		
2000		
2000		
2000		
2000 0.5 1 1.5 2 External Standard Report Sorted By : Signal Calib. Data Modified : 4/10/2015 9:17:53 Multiplier: : 1.0000		
2000 0.5 1 1.5 2 External Standard Report Sorted By : Signal Calib. Data Modified : 4/10/2015 9:17:53 3 Multiplier: : 1.0000 Dilution: : 1.0000	PM	
Sorted By : Signal Calib. Data Modified : 4/10/2015 9:17:53 : Multiplier: : 1.0000 Dilution: : 1.0000 Use Multiplier & Dilution Factor with ISTDs	Image: Contract of the second seco	
Sorted By : Signal Calib. Data Modified : 4/10/2015 9:17:53 Multiplier: : 1.0000 Dilution: : 1.0000 Use Multiplier & Dilution Factor with ISTDs	PM	
Sorted By : Signal Calib. Data Modified : 4/10/2015 9:17:53 : Multiplier: : 1.0000 Dilution: : 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: AIB2 D, 4th Signal	PM	
Sorted By : Signal Calib. Data Modified : 4/10/2015 9:17:53 : Multiplier: : 1.0000 Dilution: : 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: AIB2 D, 4th Signal	Image: Contract of the second seco	
Sorted By : Signal Calib. Data Modified : 4/10/2015 9:17:53 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	
Sorted By : Signal Calib. Data Modified : 4/10/2015 9:17:53 : Multiplier: : 1.0000 Dilution: : 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: AIB2 D, 4th Signal RetTime Type Area Amt/Area Amount [min] [15 µV*s] [%]	Grp Name	
Sorted By : Signal Calib. Data Modified : 4/10/2015 9:17:53 : Multiplier: : 1.0000 Dilution: : 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: AIB2 D, 4th Signal RetTime Type Area Amt/Area Amount [min] [15 µV*s] [%]	Grp Name	
2000 0.5 1 1.5 2 External Standard Report External Standard Report Sorted By : Signal Calib. Data Modified : 4/10/2015 9:17:53 : Multiplier: : 1.0000 Dilution: : 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: AIB2 D, 4th Signal RetTime Type Area Amt/Area Amount [min] [15 μV*s] [%]	Grp Name II	
2000 0.5 1 1.5 2 External Standard Report External Standard Report Sorted By : Signal Calib. Data Modified : 4/10/2015 9:17:53 : Multiplier: : 1.0000 Dilution: : 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: AIB2 D, 4th Signal RetTime Type Area Amt/Area Amount [min] [15 μV*s]	Grp Name II	
2000 0.5 1 1.5 2 External Standard Report External Standard Report Sorted By : Signal Calib. Data Modified : 4/10/2015 9:17:53 : Multiplier: : 1.0000 Dilution: : 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: AIB2 D, 4th Signal RetTime Type Area Amt/Area Amount [min] [15 μV*s] [%] Joint Colspan="2">Sorted By : Signal Signal Calib. Data Modified : 4/10/2015 9:17:53 : Multiplier: : 1.0000 Dilution: : 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: AIB2 D, 4th Signal RetTime Type Area Amt/Area Amount [min] [15 μV*s]	Grp Name II	
2000 0.5 1 1.5 2 External Standard Report External Standard Report Sorted By : Signal Calib. Data Modified : 4/10/2015 9:17:53 : 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 	
2000 0.5 1 1.5 2 External Standard Report External Standard Report Sorted By : Signal Calib. Data Modified : 4/10/2015 9:17:53 : 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 I	
2000 0.5 1 1.5 2 External Standard Report External Standard Report Sorted By : Signal Calib. Data Modified : 4/10/2015 9:17:53 : Multiplier: : 1.0000 Dilution: : 1.0000 Use Multiplier & Dilution Factor with ISTDs Signal 1: AIB2 D, 4th Signal RetTime Type Area Amt/Area Amount [min] [15 μV*s] [*] Joint Colspan="2">Signal 1: AIB2 D, 4th Signal RetTime Type Area Amt/Area Amount [min] [15 μV*s] [*] Joint Colspan="2">Joint Colspan="2">Joint Colspan="2">Signal 1: AIB2 D, 4th Signal RetTime Type Area Amt/Area Amount [min] [15 μV*s] [*] Joint Colspan="2">Joint Colspan= 2 Joint Colspan= 2 Joint Colspan= 2 Joint Colspan= 2 Joint Colspan= 2 Signal Colspan= 2 RetTime Type Area Amt/Area Amount [*] <td colspa<="" td=""><td>Grp Name </td></td>	<td>Grp Name </td>	Grp Name

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	I Inj	: 1	
-	Inj Volume	: 1 ul	
Acq. Method : C:\CHEM32\1\DATA\TAN	ZEEV\DEF GC 2015-04-1	0 18-49-50∖MO S100 100415.	М
Last changed : 4/10/2015 6:48:57 PM	l by Aisyah		
Analysis Method : C:\CHEM32\1\METHODS\	MO_S100_100415_CALI.M		
Last changed : 4/10/2015 9:18:48 PM	by Aisyah		
AIB2 D, 4th Signal (TANZEEV/DEF_GC 2015-04-10	18-49-50\090F1101.D)		
15 µV		BT	
14000 -		f.	
		4	
		f	
12000 -			
10000 -			
8000 -			
6000 -			
4000 -		0	
	4		
4212 86 4517 4272 86 4517	735 267 267 267 267 267 267	922 922 922 922	495
2000	TT ATA A A		
4			
0.5 1 1.5	2 2.5	3 3.5 4	min
Eutomal Standar	d Demonst		
External Standar	a Report		
Santad Bu			
Calib Data Modified : 4/10/2015	0.17.52 DM		
Multiplier. 4/10/2013	0000		
Dilution:	0000		
Use Multiplier & Dilution Faster with	ISTD:		
use Multiplier & Dilution Factor with	15105		
Signal 1: MTR2 D Ath Signal			
Signal 1: AIB2 D, 4th Signal			
Signal 1: AIB2 D, 4th Signal	Amount Cun Nama		
Signal 1: AIB2 D, 4th Signal RetTime Type Area Amt/Area	Amount Grp Name		
Signal 1: AIB2 D, 4th Signal RetTime Type Area Amt/Area [min] [15 µV*s]	Amount Grp Name [%]		
Signal 1: AIB2 D, 4th Signal RetTime Type Area Amt/Area [min] [15 µV*s] 	Amount Grp Name [%] 		
Signal 1: AIB2 D, 4th Signal RetTime Type Area Amt/Area [min] [15 µV*s] 	Amount Grp Name [%] 37.96709 DBT		
Signal 1: AIB2 D, 4th Signal RetTime Type Area Amt/Area [min] [15 µV*s] 	Amount Grp Name [%] 37.96709 DBT		
Signal 1: AIB2 D, 4th Signal RetTime Type Area Amt/Area [min] [15 µV*s] 	Amount Grp Name [%] 37.96709 DBT 37.96709		
Signal 1: AIB2 D, 4th Signal RetTime Type Area Amt/Area [min] [15 µV*s] 	Amount Grp Name [%] 37.96709 DBT 37.96709		

5. GC Analysis Report of MO_SCN_f_4 Sample

Acq. Operator : Aisyah		Seq. Line	: 12			
Acq. Instrument : Instrume	ent 1	Location	n : Vial 91			
Injection Date : 4/10/201	15 8:53:31 PM	Inj	j: 1			
		Inj Volume	e:1µl			
Acq. Method : C:\CHEM	32\1\DATA\TANZEE	V\DEF_GC 2015-04-	-10 18-49-50\1	MO_S100_1004	15.M	
Last changed : 4/10/201	15 6:48:57 PM by	Aisyah				
Analysis Method : C:\CHEM	32\1\METHODS\MO_	S100_100415_CALI.	M			
Last changed : 4/10/201	עמ PM 15 9:18:48 PM עמ	Aisyah				
AIB2 D, 4th Signal (TANZEEV)	DEF_GC 2015-04-10 18-48	9-50/091F1201.D)	F			
- 44			8			
12000 -			4			
1			5			
]						
10000 -						
6000 -						
]						
4000						
	ତ୍ତନ ଡିଅଟନ୍ତି	10 20 1	80	2007	5 8 99	
0.54 130	1.45 1.65 1.65 1.65 1.65 1.65 1.65 1.65 1.6	2.42	2.79	3.92	4 203	
2000					fingring arms	~~~~
0.5	1 1.5	2 2.5	3	3.5	4	min
			-			
Exte	ernal Standard Re	eport				
Sorted By :	Signal					
Calib. Data Modified :	4/10/2015 9:	17:53 PM				
Multiplier:	: 1.00	00				
Dilution:	: 1.000	00				
Use Multiplier & Dilution	Factor with 151	Ds				
Signal 1: AIB2 D, 4th Sign	nal					
RetTime Type Area	Amt/Area Am	ount Grp Name	2			
[min] [15 µV*s]	[*	8]				
3.154 BB S 1.45894e4	2.21583e-3 32	.32755 DBT				
lotals :	32	.32755				

Acq. Operator : Aisyah	1	Sec	q. Line :	16			
Acq. Instrument : Instru	ment l	Lo	ocation :	Vial 95			
Injection Date : 4/10/2	015 9:36:42 PM	1	Inj :	1			
		Inj	Volume :	1 µl			
Acq. Method : C:\CHE	M32\1\DATA\TAN	NZEEV\DEF_GC 20	015-04-10	18-49-50	\MO_S100_1004	15.M	
Last changed : 4/10/2	015 6:48:57 PM	1 by Aisyah					
Analysis Method : C:\CH	M32\1\METHODS\	MO_S100_100418	CALI.M				
Last changed : 4/10/2	015 9:18:48 PM	1 by Alsyan					
AIB2 D, 4m Signal (TAM2E)	2VIDEF_GG 2010-04-10	18-49-50/085P1001.07		F			
				8			
1				4			
12000 -				2			
10000 -							
1							
8000 -							
]							
6000 -							
4000							
2 9 K	1 0 5	5 a13	<u>z 6 8 8</u>	2	85 15 8	ខ្លួម្ល	<u></u> π₩
	1.57	2.10	2.47		1999	4 4 00	84
2000		~~ 64 ~~~			and the second se		+
0.5	1 1.5	2	2.5	3	3.5	4	min
Ea	ternal Standar	nd Report					
	;===============						
Sonted Br	Signal						
Calib Data Modified :	4/10/2015	9.17.53 PM					
Multiplier:	• 1	.0000					
Dilution:	: 1	.0000					
Use Multiplier & Dilutio	on Factor with	ISTDs					
-							
Signal 1: AIB2 D, 4th Si	.gnal						
		_					
RetTime Type Area	Amt/Area	Amount Grp	Name				
[min] [15 µV*s]		[%]					
3.154 BB S 1.50226e4	2.21260e-3	33.23904 I)BT				
Totals :		33.23904					

*** End of Report ***

Acq. Operator : Aisyah	Seq. Line :	: 14
Acq. Instrument : Instrument 1	Location :	: Vial 93
Injection Date : 4/10/2015 9:15:07 PM	Inj :	: 1
	Inj Volume :	: 1 µl
Acq. Method : C:\CHEM32\1\DATA\TANZH	CEV\DEF GC 2015-04-10	0 18-49-50\MO_S100_100415.M
Last changed : 4/10/2015 6:48:57 PM h	oy Aisyah	
Analysis Method : C:\CHEM32\1\METHODS\MC	S100 100415 CALI.M	
Last changed : 4/10/2015 9:18:48 PM h	oy Aisyah	
AIB2 D, 4th Signal (TANZEEV/DEF_GC 2015-04-10 18	-49-50\093F1401.D)	
15 µV		BT
12000 -		ę
		\$
		ð
10000 -		
8000 -		
8000		
4000 -		
5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	38 000 11	1791 1322 1322 1326 1326 1326 1326 1326 132
2000	- And a state of the state of t	Equiting & Sugar Spran Epilopular
· · · · · · · · · · · · · · · · · · ·		
0.5 1 1.5	2 2.5	3 3.5 4 mi
Eutownal Standard	Deport	
External Standard	Report	
Control Day		
Sorted By : Signal	17.50 DM	
Calib. Data Modified : 4/10/2015	9:17:53 PM	
Multiplier: : 1.0	0000	
Dilution: : 1.0	0000	
Use Multiplier & Dilution Factor with IS	STDs	
Signal I: AIB2 D, 4th Signal		
RetTime Type Area Amt/Area A	Amount Grp Name	
[min] [15 µV*s]	[%]	
3.154 BB S 1.38963e4 2.22140e-3 3	30.86922 DBT	
Totals :	30.86922	

Acq. Operator :	Aisyah			Seq. Li	ne : 15				
Acq. Instrument :	Instrum	ent l		Locati	on : Vial	94			
Injection Date :	4/10/20	15 9:25:51	PM	I	nj: 1				
-				Ini Volu	me: lul				
Acg. Method :	C:\CHEM	32\1\DATA\T	ANZEEV\DEB	GC 2015-0	4-10 18-4	9-50\MO S	100 10041	5.M	
Last changed :	4/10/20	15 6:48:57	PM by Aisy	 vah		_	_		
Analysis Method :	C:\CHEM	32\1\METHOD	S\MO_5100	100415 CAL	т.м				
Last changed	4/10/20	15 9:18:48	PM by Aist	ah					
AIB2 D. 4th Sig	nal (TANZEEV	ADEE GC 2015-04	10 18-49-50/09	E1501 D)					
15 uV _	(t.			
						F			
						*			
14000 -						1			
-									
1									
12000 -									
1									
10000 -									
						0			
1									
8000 -									
1									
6000 -									
1									
						- 11			
4000 -									
<u> 2</u> 85 2	9 E	22	913	8 864	35 5	8	8 2 8 2 8	8	44
0 23	0.6	13	5.5	2 CN C	96 96 9 17 17 1		5 9 8 8 8 5 9 8 8 8	4 2	4.5
2000					Ledden and a second				
	5	1	5	25		3	5	4	min
		1 12		2.0		0.		-	
	Ext	ernal Stand	and Report						
				, 					
Control Dr.		Signal							
Sortea By Calib Data Madid		Signal	15 0.17.5						
Calib. Data Modii	ilea :	4/10/20	15 9:17:5:	PM					
Multiplier:		:	1.0000						
Dilution:			1.0000						
Use Multiplier &	Dilution	Factor wit	h ISTDs						
Signal 1: AIB2 D,	4th Sig	mal							
RetTime Type	Area	Amt/Area	Amount	Grp Na	me				
[min] []	L5 μV*s]		[%]						
3.155 BB S 1.	95166e4	2.18761e-3	42.6940	0 DBT					
Totals :			42.6946	0					

Acq. Operator	: Aisyah			Seq. Line	: 13				
Acq. Instrume	nt : Instru	ment 1		Location	: Vial	92			
Injection Date	e : 4/10/2	015 9:04:20 H	PM	Inj	: 1				
			1	Inj Volume	: 1 µl				
Acq. Method	: C:\CHE	M32\1\DATA\TA	NZEEV\DEF_GO	2015-04-1	0 18-49	-50\MO	_S100	100415.M	
Last changed	: 4/10/2	015 6:48:57 B	PM by Aisyah						
Analysis Meth	od : C:\CHE	M32\1\METHODS	S\MO_S100_100	0415_CALI.M					
Last changed	: 4/10/2	015 9:18:48 H	PM by Aisyah						
AIB2 D, 4	th Signal (TANZEE	VDEF_GC 2015-04-	10 18-49-50\092F130)1.D)					
15 µV						BT			
22000						ï			
						Ŧ			
20000 -						ſ			
1									
17500									
15000 -									
10000									
12000 -									
10000									
7500 -									
5000						11			
			10			11			
	492 492 837 761 761	262 262 262 262 262 262 262 262 262 262	568 630 1.91! 103	316 437 565	795 901 010	11	445	777 932 082	88 5
2500 -		- Friffit	Him the Pi	N N N	NN	1 Com	ei -	<u> </u>	44.4
1,					<u>-</u>				
	0.5	1 1.5	2	2.5	3		3.5	4	min
		townol Stonds	and Deposit						
	LX	ternal Standa	ard Report						
Souted Dr.		Signal							
Colib Data M	dified	A/10/201	5 0.17.52 DA	,					
Multiplier.	Juilleu .	4/10/201	1 0000	1					
Multipiler:			1.0000						
Use Multiplie	Dilutio	i Fastan with	1.0000						
Use Multiplie	r & Dilution	h Factor With	1 15105						
Signal 1: ATB	D Ath Siz	nn a l							
Signal I. Alb.	2 D, 400 DI	gilar							
RetTime Type	Area	Amt/Area	Amount (Sro Name					
[min]	[15 uV*el	Anto/Arca	[\$]	sip Mane					
	-l	-	[°]						
3.154 VB S	2.89905e4	2.16031e-3	62.62843	DBT					
	2								
Totals :			62.62843						
Totals :			62.62843						
Totals :			62.62843						

*** End of Report ***

10. GC Analysis Report of MO_MSF_f_1

Acq. Operator	: Aisyah	5	Seq. Line :	20			
Acq. Instrument	: Instrument 1		Location :	Vial 99			
Injection Date	: 4/10/2015 10:19:	46 PM	Inj :	1			
		Ir	nj Volume :	1 µl			
Acq. Method	: C:\CHEM32\1\DATA	\TANZEEV\DEF_GC	2015-04-10	18-49-50\M	0_S100_100	415.M	
Last changed	: 4/10/2015 6:48:5	7 PM by Aisyah					
Analysis Method	: C:\CHEM32\1\METH	ODS\MO_S100_1004	415_CALI.M				
Last changed	: 4/10/2015 9:18:4	8 PM by Aisyah					
AIB2 D, 4th	Signal (TANZEEV/DEF_GC 2015	-04-10 18-49-50\099F2001	.D)				
15 µV				BT			
16000 -				Ĩ			
				- 4			
14000				°			
12000 -							
10000							
8000							
-							
1							
6000 -							
1							
4000							
4000 -		4					
4000 - 8858 88	403 1120 2317 2396 2396 2317 2317 2317	432 568 562 669 669 669 669	3354 3354 3355 3355	S.S.	498	972 032 123 123	
4000	0.409 0.766 0.766 1.1.120 1.296	1.432 1.568 1.826 1.826 2.069	-2.276 -2.334 -2.395 -2.550	2830	3.498		
4000 -	0.409 0.409 0.409 1.1049 1.1049 1.217 1.286	1.432 	2 276 2 334 2 395 2 395 2 395 2 550	2833	3,498		
4000	0.5	889 15 1.5 20 1.5 20 1.5 20 1.5 20 20 20 20 20 20 20 20 20 20	965 23 965 27 925 27 925		884 67 	4.258	mi
4000	0.5	889 889 1.5 1.5 200 1	2.550 2.334 2.550 2.550		89 90 3.5	4 13,372 14,123	mi
4000	8000 2000 105 1 1 1 1 1 1 1 1 1 1 1 1 1	22 88 92 1 4 6 6 6 0 0 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	2.5 2.5		89¥6 	+	mi
	0.5 1 External Sta	25 88 82 88 80 1.5 2 ndard Report	25 25		884 87 3.5	+	mi
	0.5 1 External Sta	25 88 88 75 88 1.5 2 ndard Report	25	3	884 84 3.5	+	 mii
4000	0.5 1	25 8 8 7 8 8 7 7 8 8 7 7 7 7 7 7 7 7 7 7	25 25	3	884 6 3.5	+	mi
4000 2000 Sorted By	0.5 1 External Sta	1 2015 0.17.52 DM	2.5 2.5	3	89¥6 	+ + 4 002 - 4 123 - 4 123 - 4 123 - 4 123	mi
4000 2000 Sorted By Calib. Data Mod	0.5 1 External Sta : Signa lified : 4/10/	1.5 9:17:53 PM	2.5 2.5		89 9 1 3.5	+ + 4 002 - 4 123 - 4 123 - 4 123 - 4 123	mi
4000 2000 Sorted By Calib. Data Mod Multiplier:	0.5 External Sta ified : 4/10/ :	ndard Report	9682 2.5 2.5		88¥¢ 3.5	+ + 4 002 - 4 123 - 4 123 - 4 123	mii
4000 2000 Sorted By Calib. Data Mod Multiplier: Dilution:	0.5 External Sta ified : 4/10/ Dilution Free	1 2015 9:17:53 PM 1.0000 1.0000	968 595 2,5 2,5 2,5		88¥¢.	+ + 4002 - 4123 - 4123 - 4123	mi
4000 2000 Sorted By Calib. Data Mod Multiplier: Dilution: Use Multiplier	External Sta : Signa lified : 4/10/ : 6 Dilution Factor w	1.0000 1.0000 1.0000 1.0000 1.0000	9999 5999 2.5 2.5		88¥¢.	+ + 4 002 - 4 123 - 4 123 - 4 123	mi
4000 2000 2000 Sorted By Calib. Data Mod Multiplier: Dilution: Use Multiplier Signal 1: MP2	External Sta : Signa ified : 4/10/ : 6 Dilution Factor w	1.0000 1.0000 1.0000 1.0000 1.0000	969 957 2.5 2.5		884r 	+ + 4 002 - 4 123 - 4 123 - 4 123	
4000 2000 Sorted By Calib. Data Mod Multiplier: Dilution: Use Multiplier Signal 1: AIB2	External Sta External Sta ified : 4/10/ i c Dilution Factor w D, 4th Signal	1.0000 1.0000 1.0000 1.0000 1.0000 1.0000	9999 99522 1 2.5		8846 	+ + + 4 002 - 4 123 - 4 123 - 4 123	
4000 2000 2000 Sorted By Calib. Data Mod Multiplier: Dilution: Use Multiplier Signal 1: AIB2 RetTime Time	External Sta External Sta : Signa lified : 4/10/ : & Dilution Factor W D, 4th Signal	1.5 1.5 1.5 1.5 1.5 1.5 2 1.5 1.5 2 1.5 1.00000 1.00000 1.00000 1.00000 1.00000 1.00000 1.00000 1.00	2.5 1 2.5		8846 	+ + + 4 002 - 4 123 - 4 123 - 4 123 - 4 123	
4000 2000 2000 Sorted By Calib. Data Mod Multiplier: Dilution: Use Multiplier Signal 1: AIB2 RetTime Type	External Sta External Sta : Signa lified : 4/10/ : © Dilution Factor w D, 4th Signal Area Amt/Are	1.5 1.5 1.5 1.00000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000	2.5 		846 	+	
4000 2000 2000 Sorted By Calib. Data Mod Multiplier: Dilution: Use Multiplier Signal 1: AIB2 RetTime Type [min]	External Sta External Sta : Signa lified : 4/10/ : © Dilution Factor w D, 4th Signal Area Amt/Are [15 µV*s]	1.0000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000	2.5		846 	+ 1022 14,123 14,123 14,125	- T mi
4000 2000 2000 Sorted By Calib. Data Mod Multiplier: Dilution: Use Multiplier Signal 1: AIB2 RetTime Type [min] 	0.5 External Sta : Signa lified : 4/10/ : & Dilution Factor w D, 4th Signal Area Amt/Are [15 µV*s] 	15 1 10 10 10 10 10 10 10 10 10	rp Name		846 	+	mi
4000 2000 2000 Sorted By Calib. Data Mod Multiplier: Dilution: Use Multiplier Signal 1: AIB2 RetTime Type [min] 	0.5 External Sta : Signa ified : 4/10/ : & Dilution Factor w D, 4th Signal Area Amt/Are [15 µV*s] 	1 1 2015 9:17:53 PM 1.00000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000 1.0000	rp Name		846 	+	mi
4000 2000 2000 Sorted By Calib. Data Mod Multiplier: Dilution: Use Multiplier Signal 1: AIB2 RetTime Type [min] 	0.5 External Sta : Signa ified : 4/10/ : & Dilution Factor w D, 4th Signal Area Amt/Are [15 µV*s] 	1.0000 1.0000	25 25 25 25 25 25		SFC 	+ + 4002 - 4 4022 - 4 123 -	
4000 2000 2000 Sorted By Calib. Data Mod Multiplier: Dilution: Use Multiplier Signal 1: AIB2 RetTime Type [min] 	0.5 External Sta : Signa ified : 4/10/ : & Dilution Factor w D, 4th Signal Area Amt/Are [15 µV*s] 1.97977e4 2.18642e	A Amount Ga (%) A Amount Ga	2.5		SFC 3.5	+ + + 4002 - + 4002 - + 123 - + 123	

			===	
Acq. Operator : Aisyah	Seq	Line : 18		
Acq. Instrument : Instrument 1	Loc	ation : Vial	97	
Injection Date : 4/10/2015 9:58	:15 PM	Inj: 1		
	Inj V	/olume : l μl		
Acq. Method : C:\CHEM32\1\DA	TA\TANZEEV\DEF_GC 201	5-04-10 18-49	-50\MO_S100_100415.	М
Last changed : 4/10/2015 6:48	:57 PM by Aisyah			
Analysis Method : C:\CHEM32\1\ME	THODS\MO_S100_100415	CALI.M		
Last changed : 4/10/2015 9:18	:48 PM by Aisyah			
AIB2 D, 4th Signal (TANZEEV/DEF_GC 2	015-04-10 18-49-50/097F1801.D)			
15 µV			981	
			I	
16000			*	
			Y	
14000 -				
12000				
10000 -				
8000				
6000 -				
4000				
4000	T		N N N	
122 187	20 20 20 20 20 20 20 20 20 20 20 20 20 2	87 87	51. 1796 1918	53
2000	ᡏ᠊ᢇ᠋᠋ᠴ᠆ᠮᠰ᠇᠁	44		
	15 2	25 3	35 4	min
0.0	1.0 2	2.0 0	3.0 4	
			===	
External S	tandard Report			
			===	
Sorted By : Sig	nal			
Calib. Data Modified : 4/1	0/2015 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/A	rea Amount Grp	Name		
[min] [15 µV*s]	[%]			
3.154 BB S 2.15029e4 2.1798	9e-3 46.87409 DH	BT		
Totals :	46.87409			

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 A	isyah
Analysis Method : C:\CHEM32\1\METHODS\MO S1	00 100415 CALI.M
Last changed : 4/10/2015 9:18:48 PM by A	isvah
AIB2 D, 4th Signal (TANZEEV/DEF GC 2015-04-10 18-49-50	
15 µV –	
	Ψ
	1
16000 -	5
14000	
12000 -	
10000	
8000 -	
6000 -	
4000 -	
238 2 8 9 2 2	2000 £ 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2
	ਿਆਨ ਨੇ ਨੇ ਕਿਹਾ ਹੈ ਕਿਹਾ ਹੈ ਕਿਹਾ ਕਿਹਾ ਕਿਹਾ ਕਿ ਕਿ ਕਿ ਕਿ
2000	╡╪╪╪╔╍╾╞╍┰╍┉╘╍┍╍┅╌╌┙╍╌┉┥┥╌┙╴╴╧╄┈┈╼╄┧╄┈╸╌┉╸┥╡┾┼╸┙┝╌╘╌┍╘┌╌┈
	2 25 2 25 4 min
0.0 1 1.5	2 2.0 5 5.0 4
Futernal Standard Den	~~* +
External Standard Rep	
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 Amou	nt Grp Name
[min] [15 uV*s] [%]	
3.154 BB S 2.17845e4 2.17891e-3 47.4	6642 DBT
Totals: 47.4	6642

Acq. Ope	erator	: Ais	yah				Seq.	Line	: 17					
Acq. Ins	strument	t : Ins	- strume	ent 1			Loc	ation	: Vial	96				
Injectio	on Date	: 4/1	0/20	15 9:41	7:30 P	М		Inj	: 1					
							Inj V	olume	: 1 µl					
Acq. Met	thod	: C:\	CHEM	32\1\D	ATA\TA	NZEEV\DEF	GC 201	5-04-1	0 18-4	9-50	\MO_S10	0_100	415.M	
Last cha	anged	: 4/1	0/20	15 6:40	3:57 P	M by Aisya	h							
Analysis	s Method	: C:\	CHEM	32\1\M	ETHODS	\MO_S100_1	00415	CALI.M						
Last cha	anged	: 4/1	0/20	15 9:10	8:48 P	M by Aisya	h							
	AIB2 D, 4th	Signal (TA	NZEEV	DEF_GC:	2015-04-1	0 18-49-50/096F	1701.D)							
15 µV										BT				
22500										1				
22000										4				
20000										9				
20000 -														
17500 -														
15000 -														
12500														
10000 -														
7500 -														
										- 11				
5000										11				
1 1				_	-	e					a n	(Dep		100000 #
2500			6	ġ	4 4 8	1.91	19 19 19	662 682 882	830	11	R	15		義務 4
2000				ī				T de	90 0		T ifi	1		1444 4
-		0.5		1				25			2.5			
		0.5			1.0	2		2.0	3		3.0		4	
			Exte	ernal (Standa	rd Report								
Sorted H	Bv			Sic	nal									
Calib. I	- Data Moo	dified	:	4/	10/201	5 9:17:53	PM							
Multipli	ier:			:		1.0000								
Dilution	1:					1.0000								
Use Mult	tiplier	& Dilu	tion	Factor	r with	ISTDs								
	-													
Signal 1	1: AIB2	D, 4th	n Sign	nal										
RetTime	Type	Are	a	Amt/A	Area	Amount	Grp	Name						
[min]		[15 µ\	/*s]			[%]								
3.154	BB S	3.0380)3e4	2.157	73e-3	65.55254	DE	βT						
Totals :	:					65.55254								