# Desulfurization of Oil Obtained from the Pyrolysis of Waste Tyres Using Ionic Liquids

by

Vickneshwaran Gonasergar

17002

Dissertation submitted in partial fulfilment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

MAY 2015

Universiti Teknologi PETRONAS

32610 Bandar Sri Iskandar

Perak Darul Ridzuan

## CERTIFICATION OF APPROVAL

# Desulfurization of Oil Obtained from the Pyrolysis of Waste Tyres Using Ionic Liquids

By

Vickneshwaran Gonasergar
17002

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

______________________
(Dr. Muhammad Moniruzzaman)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
May 2015

# 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.

VICKNESHWARAN GONASERGAR

# ABSTRACT

The aim of this study is to investigate the possible use of ionic liquids to remove the sulfur from the oil produced through the pyrolysis of waste tyres. This study also focuses on the selection of the type of ionic liquid used to obtain the best sulfur removal, particularly, dibenzothiophene. Liquid-liquid extraction was the preferred method in this study followed by an analysis using the analytical instrument Total Sulfur Analyzer. The ionic liquids that are considered to be the best is 1-butyl-1-methylpyrrolidinium dicyanamide [bmPYR][DCA]. The two parameters that were tested in this project are stirring period of mixture of pyrolytic oil and the ionic liquid and the temperature of the water bath at which the mixture was stirred in. The highest percentage of removal of sulfur was around 75% when the mixture of oil and ionic liquid was stirred at 40°C for 6 hours. From this project, it has been found that for efficient removal of sulfur, the stirring period has to be long enough for the ionic liquid to react completely with the pyrolytic oil and also the temperature at which the mixture was stirred should also be low.

# ACKNOWLEDGEMENT

First and foremost, I would like to express my deepest gratitude to Chemical Engineering Department of Universiti Teknologi PETRONAS (UTP) for providing me a platform to undertake this remarkable Final Year Project (FYP) course as a medium to enhance my skills and knowledge regarding my undergraduate studies in Chemical Engineering.

Furthermore, a very special note of thanks to my kind supervisor, Dr Muhammad Moniruzzaman who is always willing to spend his time in assisting me and provided good support since the start of the project until it reaches completion. Through the weekly discussions with my supervisor, I have received numerous share of insight on the different aspects to be assessed for this project to become feasible. His excellent support, patience and effective guidance have brought a great impact to my project. Nevertheless, I would also like to thank the FYP committees for arranging various seminars as support and knowledge transfer for the project. The seminars were indeed very helpful and provided useful tips to be implemented.

Besides that, I would also like to take this opportunity to express my deepest thanks to all relatives and third party members whom had also contributed either directly or indirectly towards the completion of this final year project. Last but not least, my heartfelt gratitude goes to my family and friends for providing me continuous support throughout the easy and challenging times. Thank you

# TABLE OF CONTENTS

## List of Figures

## List of Tables

# CHAPTER 1

# INTRODUCTION

## 1.1 Background of study

The remarkable increase in the number of vehicles worldwide and the lack of both technical and economical mechanisms make waste tires a serious pollution problem in terms of waste disposal (Juan Daniel Martı´nez et al, 2013). Multiple researches in the past have shown that rubber from tires have a calorific value higher than coal and also a considerable amount of carbon black. It is for these reasons that it makes sense to convert these rubbers into oil through pyrolysis. My area of focus in this research would however be on the removal of sufur (desulfurization) from the liquid end product of the pyrolysis of tyres.

The importance of desulfurization has been discussed in many journals. Presence of sulfur in the conventional crude oil during refining process tends to poison the catalysts used in the refining process. Sulfur compounds are also responsible for causing several corrosion problems in pipeline, pumping and refining equipment as well as the premature failure of combustion engines and poisoning the catalytic converters used in automobile engines (Mohammad Nahid Siddiqui et al 2013).

Sulfur in the conventional oil has to be removed also to prevent the emission of SOx, which is often linked to acid rain phenomena and plays a crucial role in pollution problems of large conglomerates (Urszula Domanska, 2014). Hydrodesulfurization has long been used as the preferred and standard way of removing sulfur from the convention oil. However, with rising stringent rules on sulfur emission, other methods need to be explored as well.

## 1.2 Problem Statement

The current existing method to remove sulfur from oil is the hydrodesulfurization (HDS) method. While this method has long been the standard way of desulfurization, with current stringent sulfur emission standards, finding for new methods of desulfurization is of paramount importance. While countries like the United States of America, Canada, Japan and the European Union have adopted Ultra Low Sulfur Diesel (ULSD), it still not very common in most Asian countries (Report to Congress on Black Carbon, 2012). For example, Mexico adopted ULSD (<15 ppm) in 2009 while Chile and Brazil have dictated ULSD in urban areas between 2009 and 2013. Malaysia required 50 ppm diesel in 2010 and is now requiring 10 ppm diesel in 2015. The same goes to Korea. In the South Asia, China is limiting diesel sulfur to ppm in Beijing (2008), Hong Kong and Macau.

To suit these standards, certain modifications need to be performed on the existing hydrodesulfurization technology. The current HDS technology does not work effectively in the ultra-deep desulfurization range down to sulfur content 100 ppm or less. The HDS technology uses a hydrogen pressure of 30-100 bar at a temperature of 350°C. To achieve low sulfur targets, very high temperature and pressure is needed besides requiring for a large reactor volume and more active catalyst (Marek Krolikowski, et al 2014). These modifications consume a huge amount of costs and energy making it uneconomical to pursue such modifications.

Presently, there are many methods of removing sulfur from oil namely UOP Merox extraction, oxidation, adsorption and using ionic liquids. The extraction process has a sulfur-reducing capacity of about 30% and is therefore unable to produce low sulfur end products. Oxidation converts low-level sulfur compounds such as thiophene, benzothiphene, dibenzothiophene and their methyl and higher alkyl derivatives into sulfones and sulfoxides. These compunds are then extracted by using polar solvents, adsorption or cooling. However, a problem with obtaining low-level oil still persists. Like extraction processes, adsorption alone does not have the capacity to reach the deep desulfurization levels for liquid fuels. Ionic liquids are used as selective agents of sulfur compounds because of their novelty and theoretical interest.

Usage of ionic liquids is proposed for deep desulfurization through liquid-liquid extraction (LLE) because of mild operating conditions and its simplicity (Urszula Domanska, 2014). These new ionic liquids, which are organic solvents, are generally not volatile non-flammable and revealed large intermolecular interaction mainly via hydrogen bonding. Ionic liquids are already known as very good entrainers in many processes.

## 1.3 Objectives

The objectives of this project are as follow:

I. To remove low-level sulfur compunds such as thiophene, benzothiophene, methyldibenzothiophene and others using ionic liquids.
II. To select the ionic liquid that has the best sulfur-removal affinity from the oil produced from the pyrolysis of the waste tyres.
III. To know the chemical composition of oil produced from the pyrolysis of waste tyres.
IV. To know the suitable parameters at which the desulfurization process is optimized eg. Rate of stirring, temperature at which the the oil and ionic liquid mixture is stirred at.

## 1.4 Scope of Study

As discussed in the previous sections, there are many ways to remove sulfur from oil such as extraction, adsorption, oxidation and using ionic liquids. This research in particular will focus on the selection of the ionic liquid that has the best affinity for removing sulfur from the oil and its respective parameters at which the desulfurization process is most optimum. Once liquid-liquid extraction has been performed, the resulting sample will then be tested using Total Sulfur Analyzer (TSA) available at Block 4 to calculate the percentage removal of sulfur compounds from the oil.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Pyrolysis of Waste Tyres

With drastic socio-economic growth, the direct increase in vehicles usage and thus increase in scrap tires is inevitable. The complicated structure of scrap tires doesn't allow its disposal without thermal degradation (Shahzad, A. 2013). Due to sulfur presence and hazardous effects of sulfur compounds, the direct use of scrap tires as an alternative fuel is perilous for the environment. The flue gas produced as a result of tire burning is a serious threat to the environment. With the passage of time alternative techniques were developed for disposal of scrap tires. Pyrolysis is one such approach towards scrap tire disposal and utilization of high percentage of carbon for energy. In pyrolysis of scrap tires, tires are thermally degraded in the absence of oxygen and converted into vapours. The vapours are then condensed into liquid while the non-condensable vapours are emitted as gases into the environment and the solid residue is left behind in the reactor (Proceedings of the World Congress on Engineering, 2014)

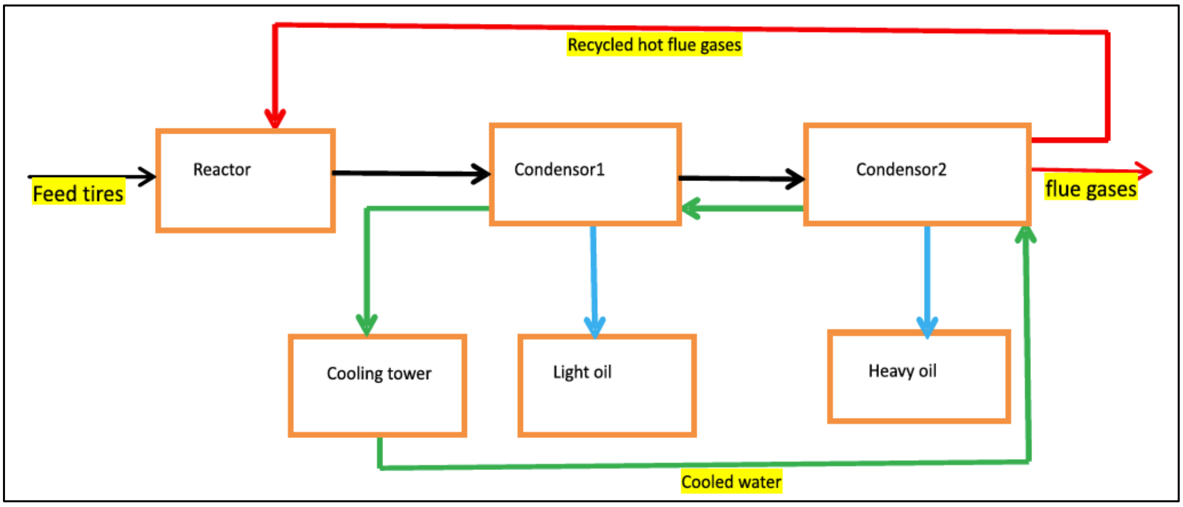
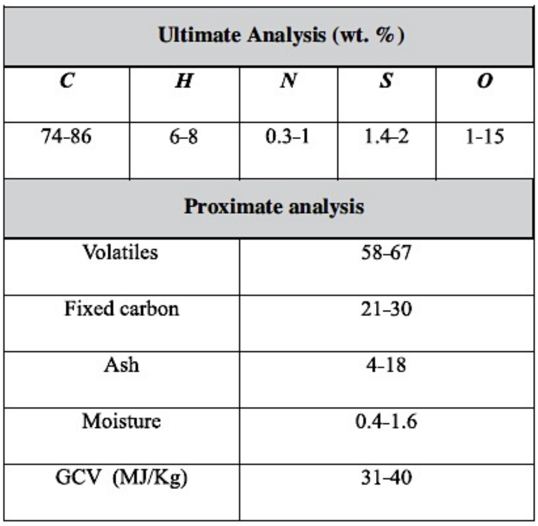


FIGURE 2.1. Process flow diagram of tyre pyrolysis

## 2.2 Composition of Oil Produced from Pyrolysis of Waste Tyres

The pyrolytic oils consist of paraffins, olefins and aromatic compounds. Composition of pyrolytic oil varies with different tire compositions and operating conditions of pyrolysis. Density, viscosity and flash point of pyrolytic oils are mostly similar to those of diesel and gasoline while the high percentage of sulfur in pyrolytic oils needs to be separated. The waste tyre pyrolytic liquid is an oily organic compound, dark brown in colour and with a strong acrid smell (Mohammad Nahid Siddiqui et al 2013).

TABLE 2.1: Composition of tyres



| **Ultimate Analysis (wt. %)** | | | | |
|---|---|---|---|---|
| ***C*** | ***H*** | ***N*** | ***S*** | ***O*** |
| 74-86 | 6–8 | 0.3–1 | 1.4–2 | 1-15 |

| **Proximate analysis** | |
|---|---|
| Volatiles | 58–67 |
| Fixed carbon | 21–30 |
| Ash | 4-18 |
| Moisture | 0.4–1.6 |
| GCV (MJ/Kg) | 31–40 |

The calorific value of the oil (44MJ/kg) is also higher than that of bituminous coal, 28 MJ/kg and wood charcoal, 30 MJ/kg which suggests that the oil can be used as liquid fuels for industrial furnaces, power plants and boilers. The oil has a relatively low ash content and residual carbon. The oil have high carbon content leading to the production of high value carbon materials for various applications (Shahzad, A. 2013).

The olefinic composition of the waste tyre pyrolytic oil is similar to that of condensates from petroleum residues cracking and thermal steam cracking of gasoline. Hence, pyrolytic oil may be blended witht these condensates and subjected to the same thermal treatment (Ahmad, M.A. 2013).

## 2.3 What is an Ionic Liquid?

An ionic liquid is a salt in which the ions are poorly coordinated, which results in these solvents being liquid below 100°C, or even at room temperature (room temperature ionic liquids, RTIL's). At least one ion has a delocalized charge and one component is organic, which prevents the formation of a stable crystal lattice. The methylimidazolium and pyridinium ions have proven to be good starting points for the development of ionic liquids (Gmehling, O., 2013).

Properties, such as melting point, viscosity, and solubility of starting materials and other solvents, are determined by the substituents on the organic component and by the counterion. Many ionic liquids have even been developed for specific synthetic problems. For this reason, ionic liquids have been termed "designer solvents" (BASF, retrieved: 2015). The absence of volatility is one of the most important benefits of ionic liquids, offering a much lower toxicity as compared to low-boiling-point solvents.

One of the first RTILs was a mixture of [emim]Cl with $AlCl_3$ forming a series of equilibria between [emim][$AlCl_4$], [emim][$Al_2Cl_7$], and [emim][$Al_3Cl_{10}$]. This RTIL is not water stable. The discovery of water-insoluble RTILs such as [bmim][$PF_6$] allowed the development of new work-up methods, including the separation of water-soluble byproducts by simple extraction. Some transition metal catalysts that are soluble in ionic liquids may be recycled together with the ionic liquid, after extraction with water and the non-polar organic solvent used for product separation. The catalyst and ionic liquid may be recycled several times (Gmehling, O., 2013).

## 2.4 Methods to Remove Sulfur

There are many ionic liquids that can be used in the removal of sulfur from the oil. However, the two important parameters that need to be taken into consideration in the proper selection of the ionic liquid would be solute distribution ratios, β and selectivity, S. Klaudia Walczak, 2014, conducted a research on the selectivity of 1-alkylpyrrolidinium-based ionic liquids ith different anions in ternary liquid-liquid extraction (ionic liquid + thiophene + heptane) at a T = 298.15K. The highest selectivity ($S_{max}$ = 133.4) with high solute distribution ratio (β = 3.47) was found to be for 1-butyl-1-methylpyrrolidinium tricyanomethanide [BMPYR][TCM]. The experiment was conducted with two other ionic liquids namely 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate [BMPYR][$CF_3SO_3$] and I-hexyl-3-methylimidazolium tetracyanoborate [HMIM][TCB].

This experiment also explains that the ionic liquid which is the entrainer should not be found in the raffinate (heptane layer) after the liquid-liquid extraction experiment.

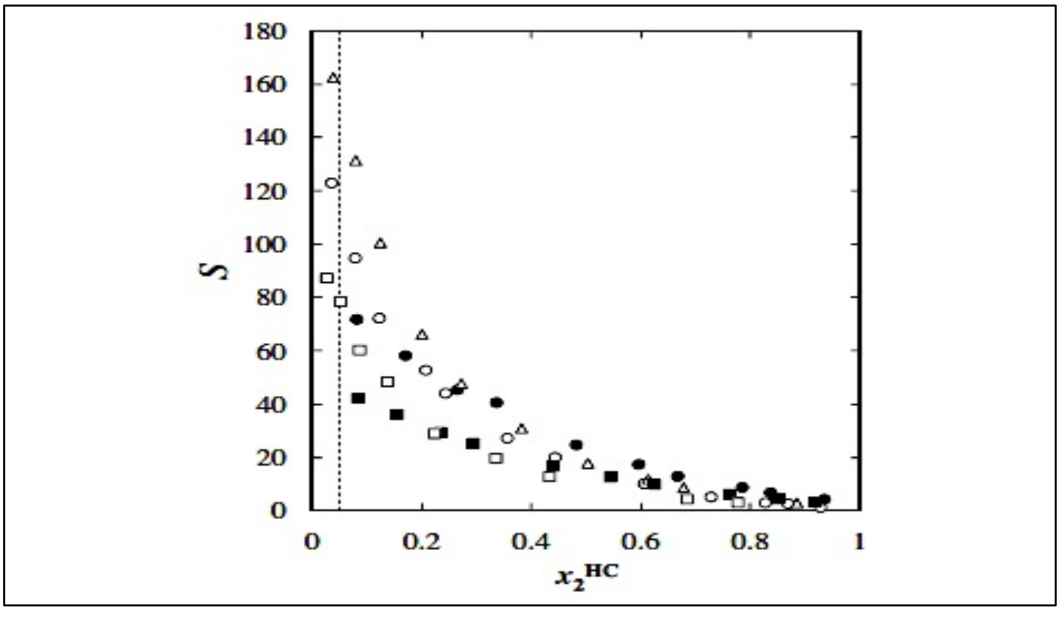


FIGURE 2.2: Plot of the selectivity as a function of the mole fraction of solute in the hydrocarbon rich phase for the ternary system. ●- system with CF3SO3 + thiophene + heptane, ○- system with CF3SO3 + benzothiophene + heptane, ▲- TCM + benzothiophene + heptane, ■-TCB + thiophene + heptane, □- TCB + benzothiophene + heptane at T=308.15K

In another project conducted by Borja Rodriguez et al, 2013, desulfurization was performed through liquid-liquid extraction using only 1-ethyl-3-methylimidazoliumm ionic liquids. This research paper claims that although in earlier researches polysubstituted pyridinium-based ionic liquids are usually proposed for desulfurization of fuel oils, this particular ionic liquid shows better selectivities and is a good alternative for this application. Another major revelation in this research is that despite the influence of the anion on the solubilities and selectivities of the desulfurization process is important, the influence of the cation is bigger. This research also took selectivity as their basis of choosing the right ionic liquid instead of solubility. According to the results of this research, pyridium ionic liquid showed higher solubilities and lower selectivities than imidazoliums. They assume that recovery of ionic liquids can be carried out therefore selectivity is is considered as the criteria to select the best ionic liquid.

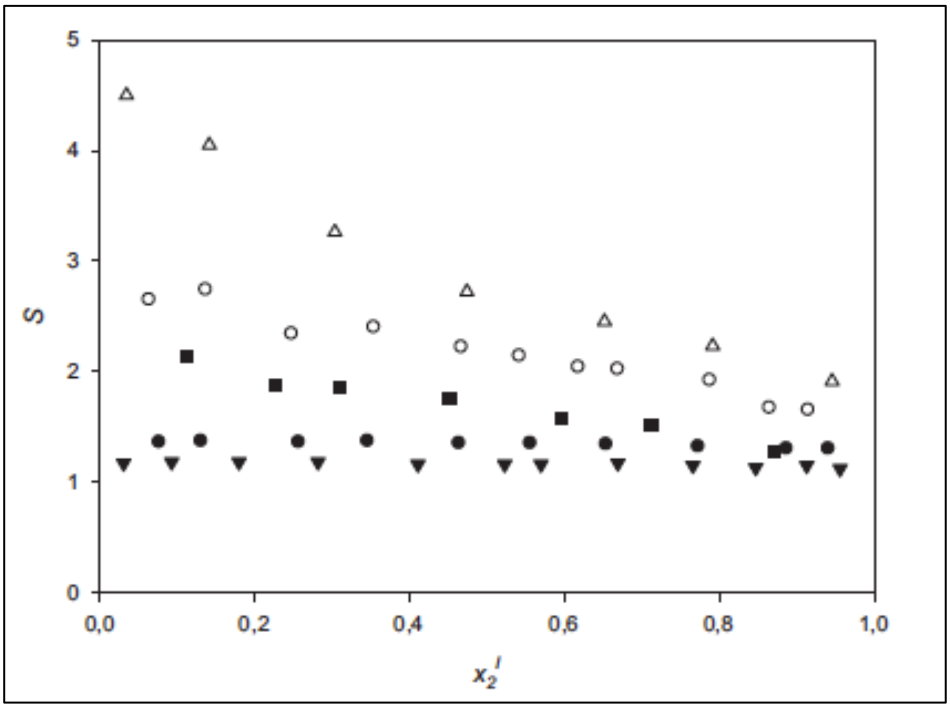
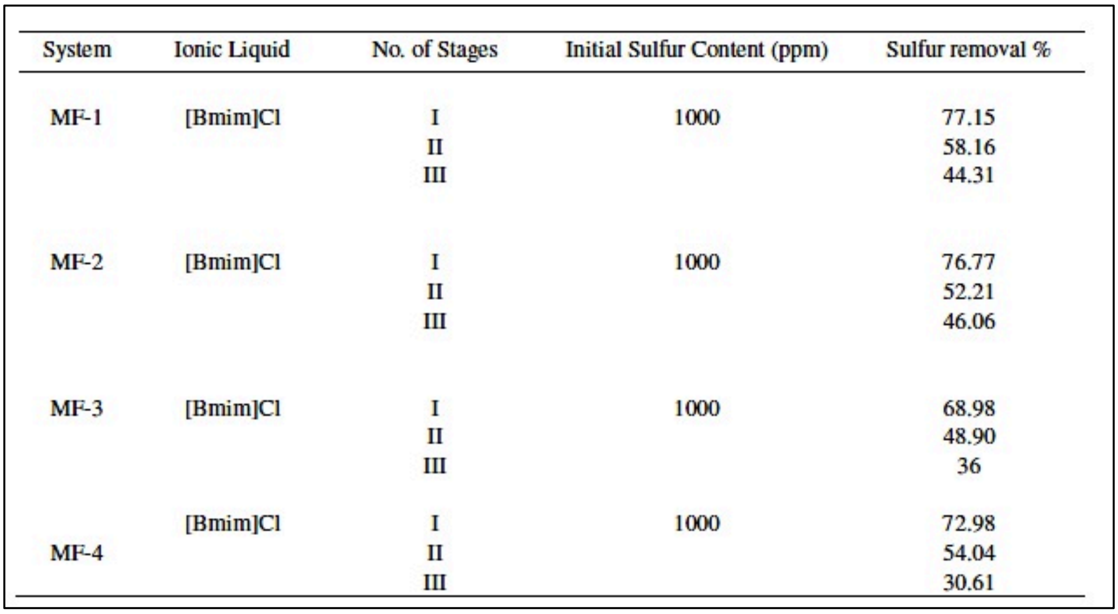


FIGURE 2.3: Selectivity values for the ternary system: ● – NTf2 + thiophene + toluene, ○-EtSO4 + thiophene + toluene, ▼ – NTf2 + thiophene + toluene, Δ- OAc + thiophene + toluene, ■- DEP + thiophene + toluene

According to Dharaskar, S. et al (2012), deep removal of sulfur from model liquid fuels was performed using the ionic liquid 1-butyl-3-methylimidazolium chloride. This particular IL is proposed to be a novel extractive solvent because it has the ability to remove sulfur compunds that are not able to be removed using the common desulfurization technique. This team has found that [Bmim][Cl] was the most effective in the removal of dibenzothiophene containing model liquid fuels and it can reach to 77.15% for a single stage extraction at 30℃ in 90 minutes.

The table below shows the desulfurization efficiency of [bmim][Cl] in model fuels which was reused for three times without regeneration. The used ionic liquid was able to extract dibenzothiophene from model fuels even without regeneration, however, at a lower efficiency.

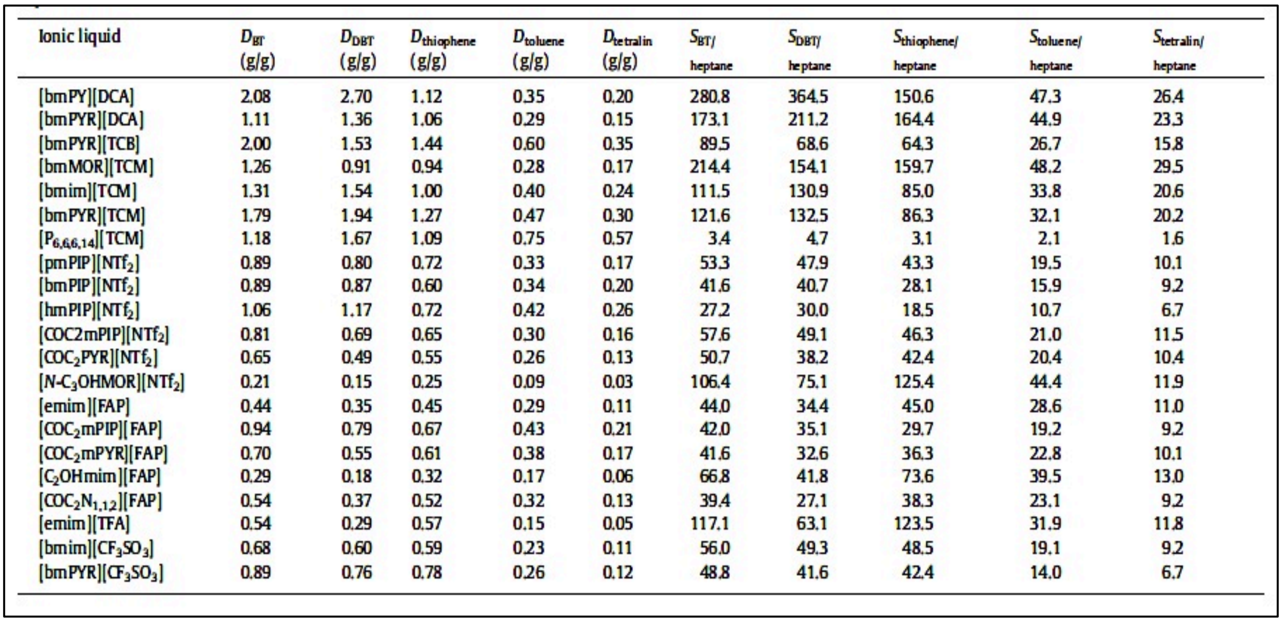
TABLE 2.2: Desulfurization efficiency of [Bmim][Cl]



| System | Ionic Liquid | No. of Stages | Initial Sulfur Content (ppm) | Sulfur removal % |
|---|---|---|---|---|
| MF-1 | [Bmim]Cl | I | 1000 | 77.15 |
| | | II | | 58.16 |
| | | III | | 44.31 |
| MF-2 | [Bmim]Cl | I | 1000 | 76.77 |
| | | II | | 52.21 |
| | | III | | 46.06 |
| MF-3 | [Bmim]Cl | I | 1000 | 68.98 |
| | | II | | 48.90 |
| | | III | | 36 |
| | [Bmim]Cl | I | 1000 | 72.98 |
| MF-4 | | II | | 54.04 |
| | | III | | 30.61 |

Ursula Domanska & Michal Wlatzo, 2014, came up with a research paper that compared the effect of cations and anions of 21 different ionic liquids. This gives a comparison on the activity of different types of ionic liquids. Like the previous researches, liquid-liquid extraction is used. The basis of choosing the best solvent are solute distribution coefficient and solubility. According to this report, 1-butyl-4-methylpyridinium dicyanamide [BMPY][DCA], 1-butyl-1-methylpyrrolidiniumndicyanamide [BMPYR][DCA] and N-butyl-N-methylmorpholinium tricyanomethanide [BMMOR][TCM] showed high selectivities and (>200) and high distribution coefficients (>1.2) for sulfur extraction.

TABLE 2.3: Experimental results for fuel models at T = 298.15K

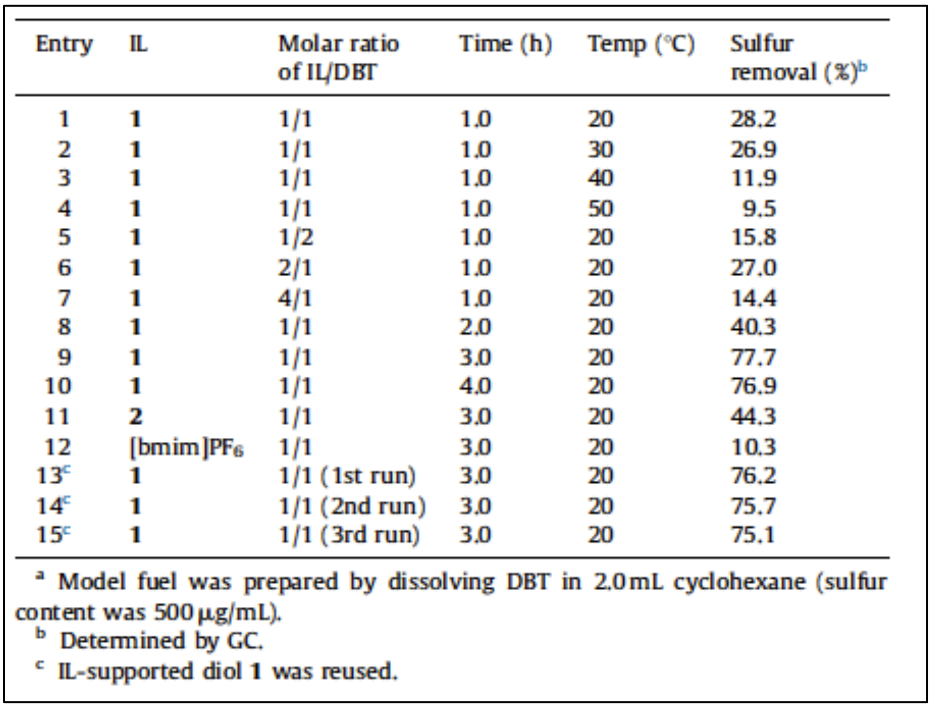


| Ionic liquid | $D_{BT}$ (g/g) | $D_{DBT}$ (g/g) | $D_{thiophene}$ (g/g) | $D_{toluene}$ (g/g) | $D_{tetralin}$ (g/g) | $S_{BT/heptane}$ | $S_{DBT/heptane}$ | $S_{thiophene/heptane}$ | $S_{toluene/heptane}$ | $S_{tetralin/heptane}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| [bmPY][DCA] | 2.08 | 2.70 | 1.12 | 0.35 | 0.20 | 280.8 | 364.5 | 150.6 | 47.3 | 26.4 |
| [bmPYR][DCA] | 1.11 | 1.36 | 1.06 | 0.29 | 0.15 | 173.1 | 211.2 | 164.4 | 44.9 | 23.3 |
| [bmPYR][TCB] | 2.00 | 1.53 | 1.44 | 0.60 | 0.35 | 89.5 | 68.6 | 64.3 | 26.7 | 15.8 |
| [bmMOR][TCM] | 1.26 | 0.91 | 0.94 | 0.28 | 0.17 | 214.4 | 154.1 | 159.7 | 48.2 | 29.5 |
| [bmim][TCM] | 1.31 | 1.54 | 1.00 | 0.40 | 0.24 | 111.5 | 130.9 | 85.0 | 33.8 | 20.6 |
| [bmPYR][TCM] | 1.79 | 1.94 | 1.27 | 0.47 | 0.30 | 121.6 | 132.5 | 86.3 | 32.1 | 20.2 |
| [$P_{6,6,6,14}$][TCM] | 1.18 | 1.67 | 1.09 | 0.75 | 0.57 | 3.4 | 4.7 | 3.1 | 2.1 | 1.6 |
| [pmPIP][$NTf_2$] | 0.89 | 0.80 | 0.72 | 0.33 | 0.17 | 53.3 | 47.9 | 43.3 | 19.5 | 10.1 |
| [bmPIP][$NTf_2$] | 0.89 | 0.87 | 0.60 | 0.34 | 0.20 | 41.6 | 40.7 | 28.1 | 15.9 | 9.2 |
| [hmPIP][$NTf_2$] | 1.06 | 1.17 | 0.72 | 0.42 | 0.26 | 27.2 | 30.0 | 18.5 | 10.7 | 6.7 |
| [COC2mPIP][$NTf_2$] | 0.81 | 0.69 | 0.65 | 0.30 | 0.16 | 57.6 | 49.1 | 46.3 | 21.0 | 11.5 |
| [$COC_2PYR$][$NTf_2$] | 0.65 | 0.49 | 0.55 | 0.26 | 0.13 | 50.7 | 38.2 | 42.4 | 20.4 | 10.4 |
| [N-$C_3$OHMOR][$NTf_2$] | 0.21 | 0.15 | 0.25 | 0.09 | 0.03 | 106.4 | 75.1 | 125.4 | 44.4 | 11.9 |
| [emim][FAP] | 0.44 | 0.35 | 0.45 | 0.29 | 0.11 | 44.0 | 34.4 | 45.0 | 28.6 | 11.0 |
| [$COC_2$mPIP][FAP] | 0.94 | 0.79 | 0.67 | 0.43 | 0.21 | 42.0 | 35.1 | 29.7 | 19.2 | 9.2 |
| [$COC_2$mPYR][FAP] | 0.70 | 0.55 | 0.61 | 0.38 | 0.17 | 41.6 | 32.6 | 36.3 | 22.8 | 10.1 |
| [$C_2$OHmim][FAP] | 0.29 | 0.18 | 0.32 | 0.17 | 0.06 | 66.8 | 41.8 | 73.6 | 39.5 | 13.0 |
| [$COC_2N_{1,1,2}$][FAP] | 0.54 | 0.37 | 0.52 | 0.32 | 0.13 | 39.4 | 27.1 | 38.3 | 23.1 | 9.2 |
| [emim][TFA] | 0.54 | 0.29 | 0.57 | 0.15 | 0.05 | 117.1 | 63.1 | 123.5 | 31.9 | 11.8 |
| [bmim][$CF_3SO_3$] | 0.68 | 0.60 | 0.59 | 0.23 | 0.11 | 56.0 | 49.3 | 48.5 | 19.1 | 9.2 |
| [bmPYR][$CF_3SO_3$] | 0.89 | 0.76 | 0.78 | 0.26 | 0.12 | 48.8 | 41.6 | 42.4 | 14.0 | 6.7 |

The sulfur in liquid oil produced from the pyrolysis of waste tyres is mainly in the form of thiophenes, benzothiazoles, benzothiophenes, dibenzothiophenes, and their alkylated derivatives while minor groups were also found such as naphthothiophenes, benzonaphthothiophenes, and their alkylated derivatives (Ritthichai Yuwapornpanit & Sirirat Jitkarnka, 2014). This gives an idea on which particular low-level sulfur compounds to be removed. The present research would be performed by removing thiophene and benzothiphene.

A study done by Yue-Qin Cai et al (2014) used 1,2-dimethylimidazolium ionic liquids to remove the sulfur. The reason for choosing this ionic liquid is because the imidazolium cations could not interact easily with the π-systems in the 1,3-dialkylimdazolium form due to the H(2) acidic proton was strongly linked to the anion by hydrogen bonding and aromatic molecules could not cleave this hydrogen bond.

TABLE 2.4: Sulfur removal from model fuel by 1,2-dimethylimidazolium ionic liquid



| Entry | IL | Molar ratio of IL/DBT | Time (h) | Temp (°C) | Sulfur removal (%)[b] |
|---|---|---|---|---|---|
| 1 | **1** | 1/1 | 1.0 | 20 | 28.2 |
| 2 | **1** | 1/1 | 1.0 | 30 | 26.9 |
| 3 | **1** | 1/1 | 1.0 | 40 | 11.9 |
| 4 | **1** | 1/1 | 1.0 | 50 | 9.5 |
| 5 | **1** | 1/2 | 1.0 | 20 | 15.8 |
| 6 | **1** | 2/1 | 1.0 | 20 | 27.0 |
| 7 | **1** | 4/1 | 1.0 | 20 | 14.4 |
| 8 | **1** | 1/1 | 2.0 | 20 | 40.3 |
| 9 | **1** | 1/1 | 3.0 | 20 | 77.7 |
| 10 | **1** | 1/1 | 4.0 | 20 | 76.9 |
| 11 | **2** | 1/1 | 3.0 | 20 | 44.3 |
| 12 | [bmim]$PF_6$ | 1/1 | 3.0 | 20 | 10.3 |
| 13[c] | **1** | 1/1 (1st run) | 3.0 | 20 | 76.2 |
| 14[c] | **1** | 1/1 (2nd run) | 3.0 | 20 | 75.7 |
| 15[c] | **1** | 1/1 (3rd run) | 3.0 | 20 | 75.1 |

[a] Model fuel was prepared by dissolving DBT in 2.0 mL cyclohexane (sulfur content was 500 µg/mL).

[b] Determined by GC.

[c] IL-supported diol **1** was reused.

# CHAPTER 3

# METHODOLOGY

## 3.1 Sample Preparation

### 3.1.1 Materials

The oil from the pyrolysis of waste tyres will be given to me by a student undergoing her Final Year Project 2. From the research papers that I have stated in the previous sections, I have stated that I will be using 1-butyl-4-methylpyridinium dicyanamide [bmPY][DCA] and 1-butyl-1-methylpyrrolidinium dicyanamide [bmPYR][DCA] by purchasing them through the help of the lab technicians. However, upon heeding the advice given to me by the research officer, Siti Hawa, I have decided to synthesize my own ionic liquid. From the raw materials that are present in the laboratory at Block 4, I have also chosen to synthesize only 1 of the ionic liquid namely 1-butyl-1methylpyrrolidinium dicyanamide because of economical reasons.

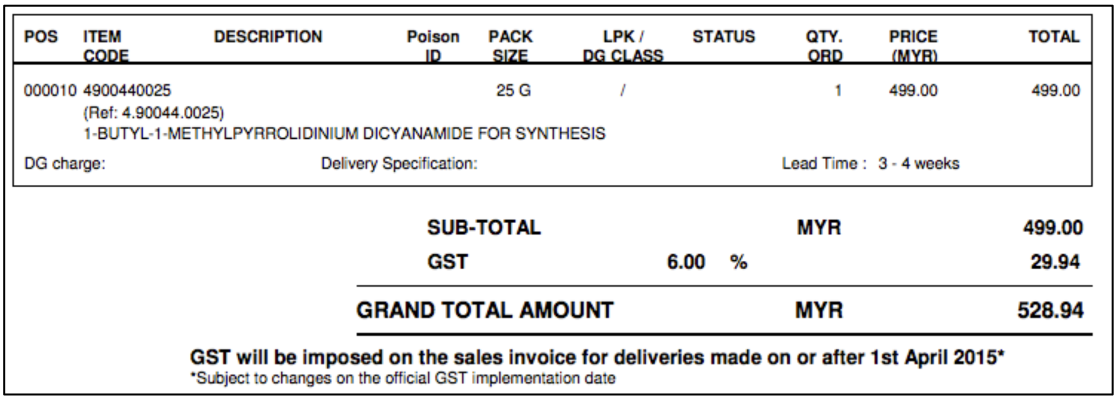
**1) Obtaining the Pyrolytic Oil from Waste Tyres**

The oil that was given to me was obtained from Professor Yoshimitsu Eumera from Block 5. Upon receiving the sample oil, the research officer had informed that the quantity of the oil sample is too small and that it would be difficult to do the testing with the ionic liquid later on. A good 3 weeks were spent on securing a high quality pyrolytic oil for this project. Most of the companies supplying pyrolytic oil are located in the east coast of the Peninsular Malaysia and was proven difficult to go there due to its distance. After about the first 2 weeks of intense researching, a company named Eco-Materials was found to be specializing in this industry and is located in Gopeng, which is about 20 km from Universiti Teknologi Petronas. The company agreed to give me a sample of 250 ml of pyrolytic oil for free of charge. The conditions at which the pyrolytic oil are obtained were not revealed by the person in charge due to company formalities.

FIGURE 3.1: (Left) The sample oil given by the senior student which was not sufficient in order to proceed with my project and (right) the oil sample given by the Eco-Materials factory.

**2) Deciding Between Purchasing or Synthesizing the Ionic Liquid**

It was initially planned that I will be purchasing the ionic liquid from Merc Malaysia which has sent me the quotation for the required ionic liquid. However, after much discussion with the research officer, it was then decided to synthesize the ionic liquid in the laboratory. This decision was reached due to the fact that the delivery time of the ionic liquid would be very long which could take up to 6 months and also due to the avalability of the raw materials needed to synthesize the ionic liquid in the lab.



| POS | ITEM CODE | DESCRIPTION | Poison ID | PACK SIZE | LPK / DG CLASS | STATUS | QTY. ORD | PRICE (MYR) | TOTAL |
|---|---|---|---|---|---|---|---|---|---|
| 000010 | 4900440025<br>(Ref: 4.90044.0025)<br>1-BUTYL-1-METHYLPYRROLIDINIUM DICYANAMIDE FOR SYNTHESIS | | | 25 G | / | | 1 | 499.00 | 499.00 |

DG charge: Delivery Specification: Lead Time : 3 - 4 weeks

| | | | |
|---|---|---|---|
| SUB-TOTAL | | MYR | 499.00 |
| GST | 6.00 % | | 29.94 |
| GRAND TOTAL AMOUNT | | MYR | 528.94 |

**GST will be imposed on the sales invoice for deliveries made on or after 1st April 2015***

*Subject to changes on the official GST implementation date

FIGURE 3.2: The quotation slip from Merc Malaysia.

### 3.1.2 Experimental procedures

### a) Synthesis of 1-butyl-1-methylpyrrolidinium dicyanamide

1. Methyl pyrrolidine and 1-bromobutane were heated under reflux in acetonitrile at 60°C for 72 hours.

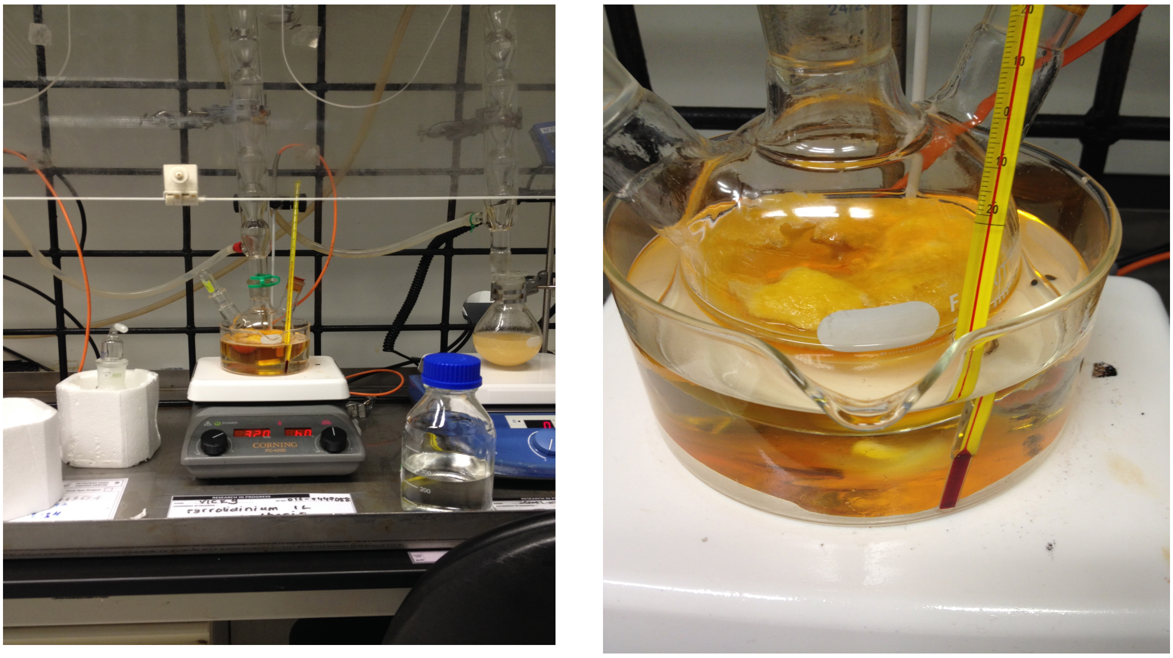


FIGURE 3.3: Methyl pyrrolidine and 1-bromobutane heated under reflux.

2. The solvent was removed and the resulting liquid was dissolved in dichloromethane

to crystalise from toluene at -50°C within 12 hours. The slighly yellow product was wished with toluene.

3. The product is then dried in vacuum at 60°C until the product turns white.
4. The product, 1-butyl-1methylpyrrolidinium bromide, and sodium dicyanamide were stirred for 12 hours in dichloromethane.
5. After filtration, the product was washed with 10 ml of water three times and the solvent was evaporated.

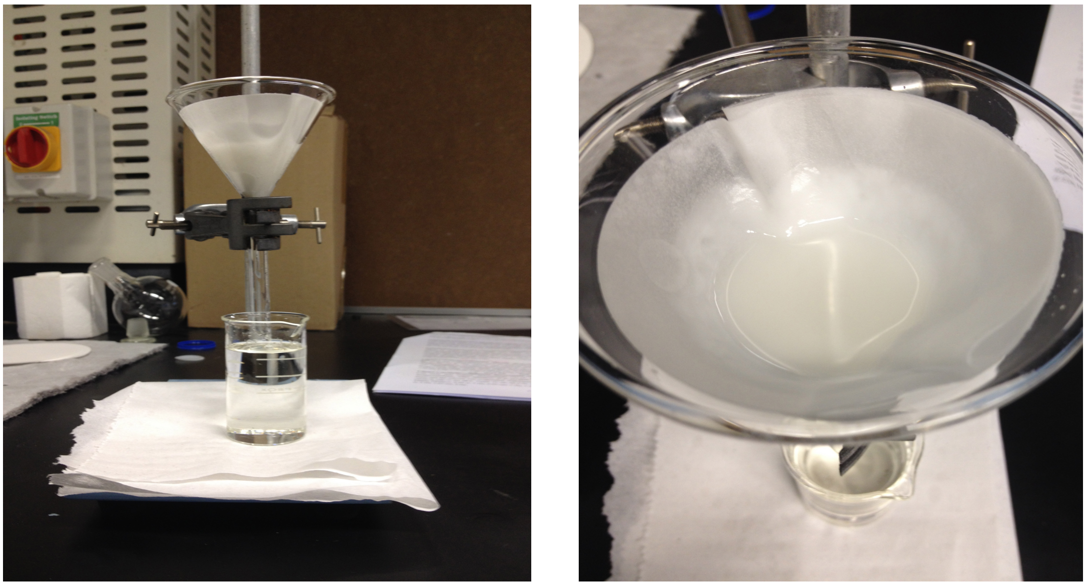


FIGURE 3.4: The residual viscous liquid left after filtration

6. Subsequently, the residual viscous liquid was dried in vacuum at 100°C for 48 hours.

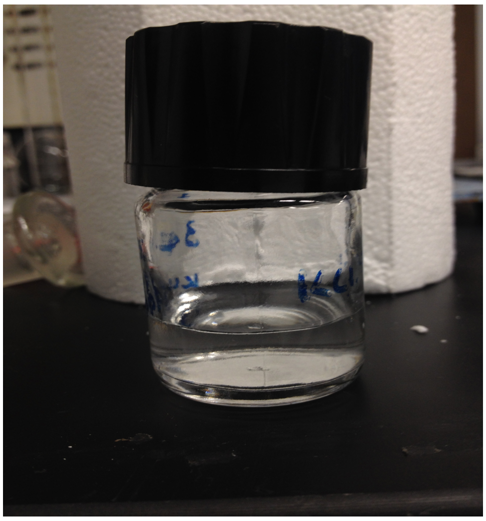


FIGURE 3.5: The product before drying.

### 3.2 Sample Characterization

The Nuclear Magnetic Resonance spectroscopy was used to determine the purity of the ionic liquid synthesized. Nuclear Magnetic Resonance (NMR) spectroscopy is an analytical chemistry technique used in quality control and reserach for determining the content and purity of a sample as well as its molecular structure. For example, NMR can quantitatively analyze mixtures containing known compounds. For unknown compounds, NMR can either be used to match against spectral libraries or to infer the basic structure directly. Once the basic structure is known, NMR can be used to determine molecular conformation in solution as well as studying physical properties at the molecular level such as conformational exchange, phase changes, solubility, and diffusion.

#### 3.2.1 How NMR works?

The principle behind NMR is that many nuclei have spin and all nuclei are electrically charged. If an external magnetic field is applied, an energy transfer is possible between the base energy to a higher energy level (generally a single energy gap). The energy transfer takes place at a wavelength that corresponds to radio frequencies and when the spin returns to its base level, energy is emitted at the same frequency. The signal that matches this transfer is measured in many ways and processed in order to yield an NMR spectrum for the nucleus concerned.

When the excited nuclei in the beta orientation start to relax back down to the alpha orientation, a fluctuating magnetic field is created. This fluctuating field generates a current in a receiver coil that is around the sample. The current is electronically converted into a peak. It is the relaxation that actually gives the peak not the excitation.

A peak will be observed for every magnetically distinct nucleus in a molecule. This happens because nuclei that are not in identical structural situations do not experience the external magnetic field to the same extent. The nuclei are shielded or deshielded due to small local fields generated by circulating sigma, pi and lone pair electrons.

The general rule of thumb in analyzing the NMR spectroscopy is that, The number of peaks is directly related to symmetry. If a compound has three significantly different types of hydrogens, it should have three different NMR absorptions. The relative areas (or integrals) of the various absorptions in an NMR spectrum equals the relative number of hydrogens absorbing. If we know the molecular formula of a compound, we can use this ratio to figure out the actual number of each type of hydrogen. From the numbers of each type, we can infer the carbon structure.

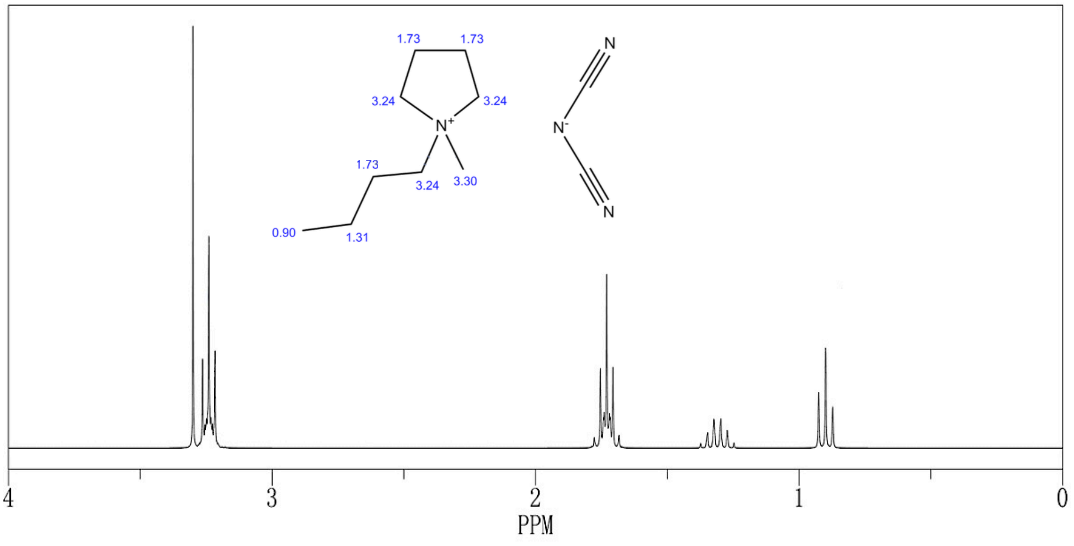


FIGURE 3.6: NMR spectroscopy of [BMPYR][DCA]. The value indicated on the structure of the IL directly corresponds to the peaks.

# CHAPTER 4

# KEY PROJECT MILESTONES

Throughout the course of the this project so far, many adjustments have been made to further improve the execution and the smoothness of this project. Though the major key project milestones have been indicated in the next few pages, there are also some important events that have taken place which are considered key milestones. The first challenge was to acquire a quality pyrolytic oil sample since the existing one was too little. Eco-Materials have been nothing but helpful in the entire process. Having acquired the sample of pyrolytic oil has immensely lighten my workload by not purchasing it from companies from the east coast of Peninsular Malaysia.

The second challenge was the sudden switch from purchasing the ionic liquids to synthesizing them in the lab. The process of synthesizing ionic liquids can be tedious and cumbersome. A few days were spent on searching for the procedure to synthesize the required ionic liquid. Familiarising oneself with the new analytical instruments in Block 4 also consumed some time. I would consider this to be the second key milestone.

# CHAPTER 4: GANTT CHART

| ACTIVITIES | WEEKS | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | FINAL YEAR PROJECT 1 | | | | | | | | | | | | | | FINAL YEAR PROJECT 2 | | | | | | | | | | | | | |
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| Introductory Lecture with The Coordinator | 🟦 | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Selection of Project Title | | 🟦 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| First Meeting with Supervisor | | 🟦 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Literature Review | | | 🟦 | 🟦 | 🟦 | 🟦 | 🟦 | | | | | | | | | | | | | | | | | | | | | |
| Selection of Model Compound | | | | 🟦 | 🟦 | | | | | | | | | | | | | | | | | | | | | | | |
| Selection of Methodology | | | | | | 🟦 | 🟦 | | | | | | | | | | | | | | | | | | | | | |
| Submission of Extended proposal | | | | | | | | Δ | | | | | | | | | | | | | | | | | | | | |
| Proposal Defense | | | | | | | | | | Δ | | | | | | | | | | | | | | | | | | |
| Experimental Work Commences | | | | | | | | | | Δ | 🟦 | 🟦 | 🟦 | 🟦 | 🟦 | 🟦 | 🟦 | 🟦 | | | | | | | | | | |
| Submission of Interim Draft Report | | | | | | | | | | | | 🟦 | | | | | | | | | | | | | | | | |
| Submission of Interim Report | | | | | | | | | | | | | Δ | | | | | | | | | | | | | | | |
| Sample Testing | | | | | | | | | | | | | | | | | 🟦 | 🟦 | 🟦 | 🟦 | 🟦 | | | | | | | |
| Submission of Progress Report | | | | | | | | | | | | | | | | | | | | | Δ | | | | | | | |
| Analysing the results | | | | | | | | | | | | | | | | | | | | | 🟦 | 🟦 | Δ | | | | | |
| Pre-SEDEX | | | | | | | | | | | | | | | | | | | | | | | | 🟦 | | | | |
| Submission of Draft Final Report | | | | | | | | | | | | | | | | | | | | | | | | | 🟦 | | | |
| Submission of Project Dissertation (Soft Bound) | | | | | | | | | | | | | | | | | | | | | | | | | | Δ | | |
| Submission of Technical Paper | | | | | | | | | | | | | | | | | | | | | | | | | | 🟦 | | |
| Viva | | | | | | | | | | | | | | | | | | | | | | | | | | | Δ | |
| Submission of Project Dissertation (Hard Bound) | | | | | | | | | | | | | | | | | | | | | | | | | | | | 🟦 |

**Δ - Denotes key milestones**

# CHAPTER 5

# RESULTS AND DISCUSSION

The percentage removal of sulfur is calculated using the formula below:

$$\frac{Amount\ of\ sulfur\ after\ mixed\ with\ IL}{Initial\ amount\ of\ sulfur\ in\ oil}\times 100\%$$

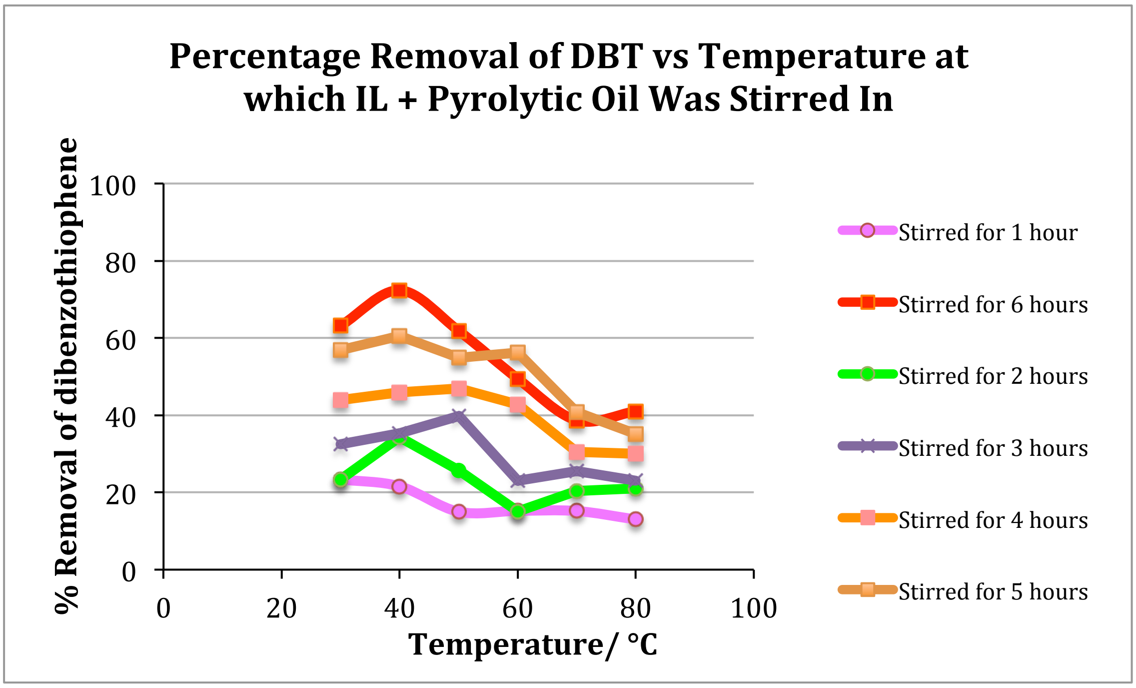


FIGURE 5.1: Percentage removal of dibenzothiophene with increasing temperature and stirring period.

From the graph, it can be observed that maximum removal of dibenzothiophene occurs at a temperature of 40°C and that of which has been stirred for 6 hours. The rate of desulfurization decreases with increasing temperature and decreasing stirring period.

High percentage removal of sulfur from oil is usually due to the strong interaction between the aromatic sulfur compounds and the ILs. The π-π bond in a sandwich like manner explains this interaction. However, the pyrrolidnium based ILs used in this experiment is without an aromatic cation. This might be explained by the possible hydrogen bonding of the hetero-atoms of sulfur compounds with the IL cation.

Molecules with highly polarizable π-electron density preferably insert into the molecular structure of the ionic liquids. From the graph, it can be observed that maximum removal of dibenzothiophene occurs at a temperature of 40°C and that of which has been stirred for 6 hours. The rate of desulfurization decreases with increasing temperature and decreasing stirring period.

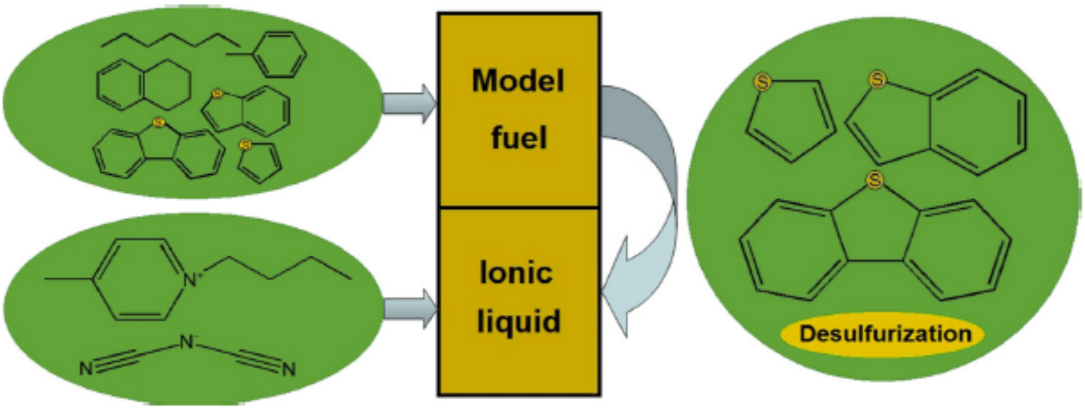


FIGURE 5.2: Removal of sulfur by ionic liquid

Rate of desulfurization gradually decreases with stirring period because the longer the IL is allowed to mix with the oil, the better the extraction rate. The general trend of the line is that it decreases with time because the amount of dibenzothiophene present in the oil reduces and therefore the rate of extraction also decreases.

Rate of desulfurization decreases with increasing temperature because this particular IL forms hydrogen bonding with the hetero-atoms of sulfur compounds. High temperatures break this bond and desulfurization does not take place.

# CHAPTER 6

# CONCLUSION AND RECOMMENDATION

Pyrolysis of waste tyres is one of the many ways in which waste tyres can safely be disposed and the ability to derive oil from it only adds to its benefits. From the literature about the desulfurization of oil produced from the pyrolysis of waste tyres, it is found that different ionic liquids have different affinities for sulfur removal. This research would use the ionic liquids 1-butyl-1-methylpyrrolidinium dicyanamide [bmPYR][DCA] to remove the low-level sulfur compunds such as thiophene, benzothiophene and others.

Besides that, the two important parameters that were tested are effect of temperature and stirring period on the percentage removal of sulfur. Based on the literature, the effect of these two parameters on the percentage removal of sulfur is discussed in the previous section. Using the ionic liquid [BMPYR][DCA], highest removal of sulfur obtaained at 40°C and that of stirred for 6 hours.

The only recommendation that I would suggest is that, the technicians at Block 4 are encouraged to test the usability of analytical instruments so that the students can be prepared beforehand. Informing the students that a particular instrument cannot be used due to faultiness at the last minute should be prevented

# REFERENCES

[1] A. Bosmann, L. D. (2005). Deep desulfurization of diesel fuel by extraction with ionic liquids. *47*(2), 449-451.

[2] Borja Rodriguez-Cabo, A. A. (7 May, 2013). Desulfurization of fuels by liquid-liquid extraction with 1-ethyl-3-methylimidazolium ionic liquids. *356*, 126-135.

[3] Chu Xuemei, H. Y. (30 January, 2008). Desulfurization of diesel fuel by extraction with [bf4] anion based ionic liquids. *16*(6), 881-884.

[4] H. Rang, J. K. (2006). Advances in desulfurization research of liquid fuel. *23*(2).

[5] Michal Wlazlo, U. D. (20 March, 2014). Effect of the cation and anion of the ionic liquid on desulfurization of model fuels. *134*.

[6] Mohammad Nahid Siddiqui, K. R. (2013). Desulfurization of model fuels oil using novel ionic liquids. *58*(1), 1022-1023.

[7] Nasrallah M. Deraz, S. A.-E. (2 November, 2013). Environmental evaluation for desulfurization of gas oil with [BMIM][FeCl4] based on catalytic ionic liquids at room temperature. *7*, 387-393.

[8] Natalya V. Likhanova, D. G.-L.-A.-P. (10 December, 2009). Ionic liquids screening for desulfurization of natural gasoline by liquid-liquid extraction. 777-787.

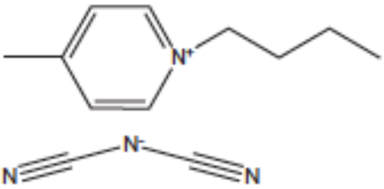
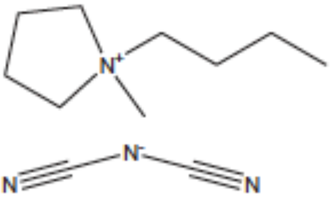
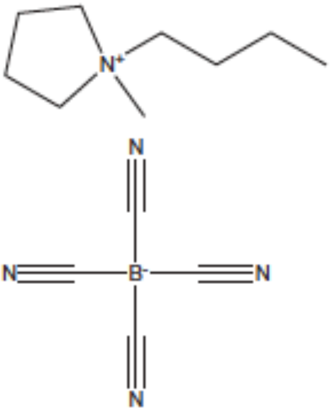
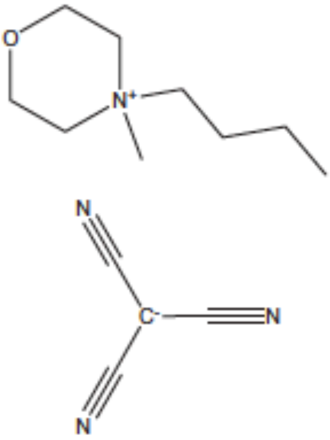
[9] Swapnil A. Dharaskar, K. L. (2013). Deep removal of sulfur from model liquid fuels using 1-butyl-3-methylimidazolium chloride. *51*, 416-422.

[10] Urszula Domanska, K. W. (2014). Extraction Desulfurization Process of Fuels with Ionic Liquids. *Science Direct*, 40-45.

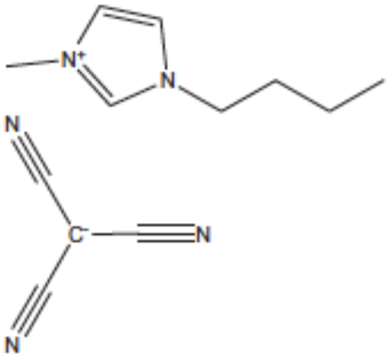
[11] Yue-Qin Cai, G.-H. S.-N. (29 July, 2014). Desulfurization Using the 1,2-dimethylimidazolium Ionic Liquid as an Adsorbent. *Science Direct*.

# APPENDIX

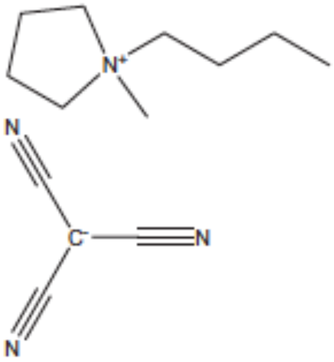
## The list of ionic liquids that have been tested before with crude oil

| Structure | Name, abbreviation |
|---|---|
|  | 1-Butyl-4-methylpyridinium dicyanamide, [bmPY][DCA] |
|  | 1-Butyl-1-methylpyrrolidinium dicyanamide, [bmPYR][[DCA] |
|  | 1-Butyl-1-methyl-pyrrolidinium tetracyanoborate, [bmPYR][TCB] |
|  | *N*-Butyl-*N*-methylmorpholinium tricyanomethanide, [bmMOR][TCM] |

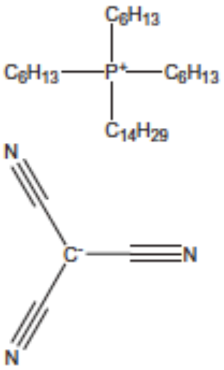
1-Butyl-3-methylimidazolium tricyanomethanide, [bmim][TCM]



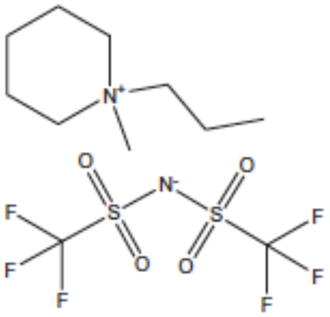
1-Butyl-1-methylpyrrolidinium tricyanomethanide, [bmPYR][TCM]



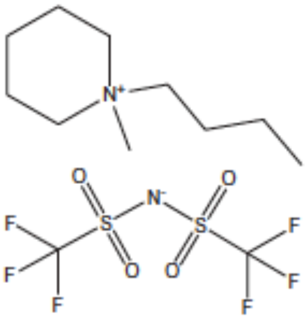
Trihexyl-tetra-decyl-phosphonium tricyanomethanide, [$P_{6,6,6,14}$][TCM]

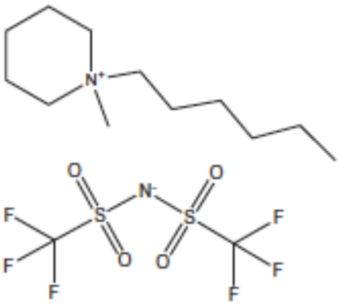


1-Propyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)-imide, [pmPIP][$NTf_2$]

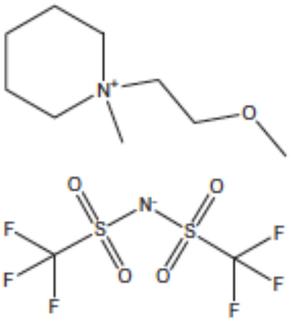


1-Butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)-imide, [bmPIP][$NTf_2$]

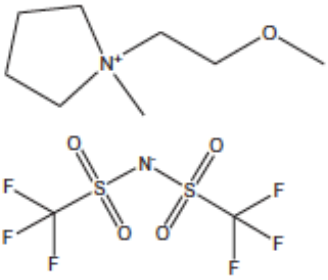




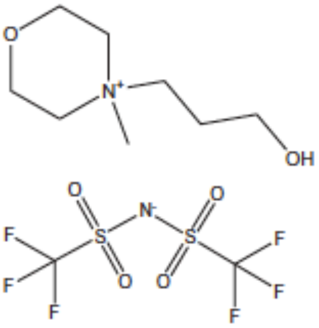
1-Hexyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)-imide, [hmPIP][NTf$_2$]



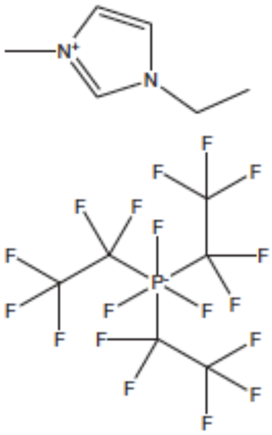
1-(2-Methoxyethyl)-1-methylpiperidinium bis(trifluoromethylsulfonyl)-imide, [COC$_2$mPIP][NTf$_2$]



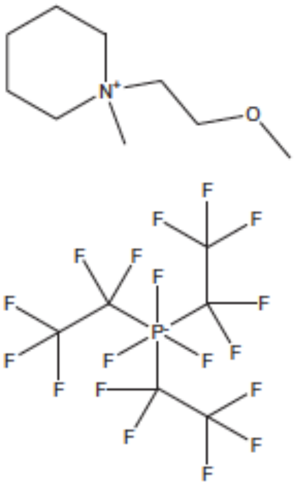
1-(2-Methoxyethyl)-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)-imide, [COC$_2$mPYR][NTf$_2$]



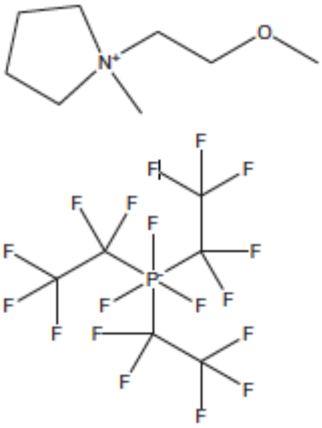
4-(3-Hydroxypropyl)-4-methylmorpholinium bis(trifluoromethylsulfonyl)-imide, [*N*-C$_3$OHmMOR][NTf$_2$]



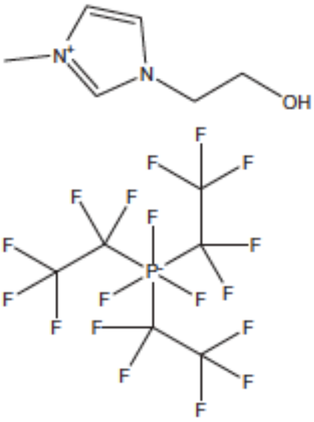
1-Ethyl-3-methylimidazolium trifluorotris(perfluoroethyl)-phosphate, [emim][FAP]



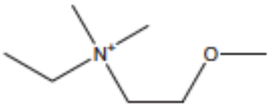
1-(2-Methoxyethyl)-1-methylpiperidinium trifluorotris(perfluoroethyl)-phosphate, [COC$_2$mPIP][FAP]



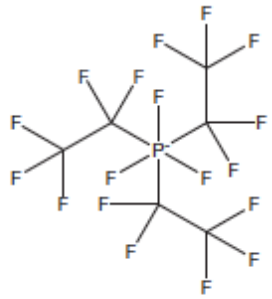
1-(2-Methoxyethyl)-1-methylpyrrolidinium trifluorotris(perfluoroethyl)-phosphate, [COC2mPYR][FAP]



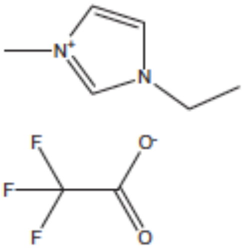
1-(2-Hydroxyethyl)-3-methylimidazolium trifluorotris(perfluoroethyl)-phosphate, [C$_2$OHmim][FAP]



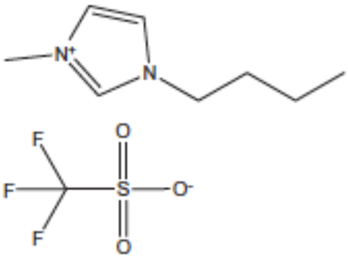
Ethyldimethyl-(2-methoxyethyl)ammonium trifluorotris(perfluoroethyl)-phosphate, [COC$_2$N$_{1,1,2}$][FAP]



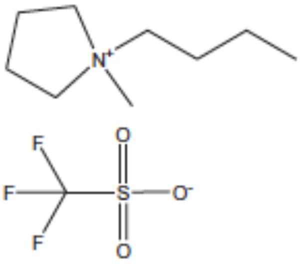
1-Ethyl-3-methylimidazolium trifluoroacetate, [emim][TFA]

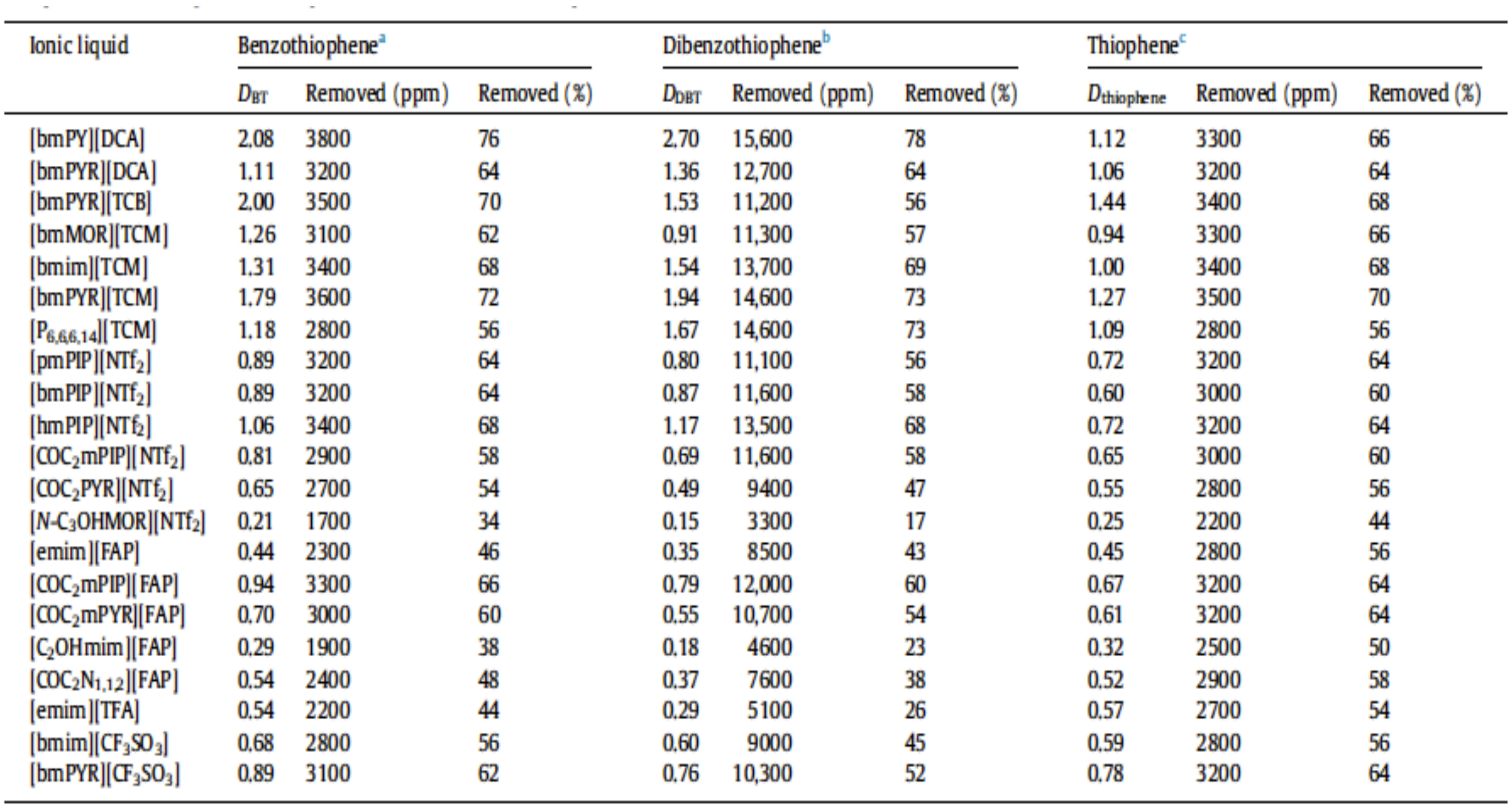


1-Butyl-3-methylimidazolium trifluoromethanesulfonate, [bmim][CF$_3$SO$_3$]



1-Butyl-1-methyl-pyrrolidinium trifluoromethanesulfonate, [1,3bmPYR][CF$_3$SO$_3$]





| Ionic liquid | Benzothiophene[a] | | | Dibenzothiophene[b] | | | Thiophene[c] | | |
|---|---|---|---|---|---|---|---|---|---|
| | $D_{BT}$ | Removed (ppm) | Removed (%) | $D_{DBT}$ | Removed (ppm) | Removed (%) | $D_{thiophene}$ | Removed (ppm) | Removed (%) |
| [bmPY][DCA] | 2.08 | 3800 | 76 | 2.70 | 15,600 | 78 | 1.12 | 3300 | 66 |
| [bmPYR][DCA] | 1.11 | 3200 | 64 | 1.36 | 12,700 | 64 | 1.06 | 3200 | 64 |
| [bmPYR][TCB] | 2.00 | 3500 | 70 | 1.53 | 11,200 | 56 | 1.44 | 3400 | 68 |
| [bmMOR][TCM] | 1.26 | 3100 | 62 | 0.91 | 11,300 | 57 | 0.94 | 3300 | 66 |
| [bmim][TCM] | 1.31 | 3400 | 68 | 1.54 | 13,700 | 69 | 1.00 | 3400 | 68 |
| [bmPYR][TCM] | 1.79 | 3600 | 72 | 1.94 | 14,600 | 73 | 1.27 | 3500 | 70 |
| [$P_{6,6,6,14}$][TCM] | 1.18 | 2800 | 56 | 1.67 | 14,600 | 73 | 1.09 | 2800 | 56 |
| [pmPIP][$NTf_2$] | 0.89 | 3200 | 64 | 0.80 | 11,100 | 56 | 0.72 | 3200 | 64 |
| [bmPIP][$NTf_2$] | 0.89 | 3200 | 64 | 0.87 | 11,600 | 58 | 0.60 | 3000 | 60 |
| [hmPIP][$NTf_2$] | 1.06 | 3400 | 68 | 1.17 | 13,500 | 68 | 0.72 | 3200 | 64 |
| [$COC_2$mPIP][$NTf_2$] | 0.81 | 2900 | 58 | 0.69 | 11,600 | 58 | 0.65 | 3000 | 60 |
| [$COC_2$PYR][$NTf_2$] | 0.65 | 2700 | 54 | 0.49 | 9400 | 47 | 0.55 | 2800 | 56 |
| [*N*-$C_3$OHMOR][$NTf_2$] | 0.21 | 1700 | 34 | 0.15 | 3300 | 17 | 0.25 | 2200 | 44 |
| [emim][FAP] | 0.44 | 2300 | 46 | 0.35 | 8500 | 43 | 0.45 | 2800 | 56 |
| [$COC_2$mPIP][FAP] | 0.94 | 3300 | 66 | 0.79 | 12,000 | 60 | 0.67 | 3200 | 64 |
| [$COC_2$mPYR][FAP] | 0.70 | 3000 | 60 | 0.55 | 10,700 | 54 | 0.61 | 3200 | 64 |
| [$C_2$OHmim][FAP] | 0.29 | 1900 | 38 | 0.18 | 4600 | 23 | 0.32 | 2500 | 50 |
| [$COC_2N_{1,1,2}$][FAP] | 0.54 | 2400 | 48 | 0.37 | 7600 | 38 | 0.52 | 2900 | 58 |
| [emim][TFA] | 0.54 | 2200 | 44 | 0.29 | 5100 | 26 | 0.57 | 2700 | 54 |
| [bmim][$CF_3SO_3$] | 0.68 | 2800 | 56 | 0.60 | 9000 | 45 | 0.59 | 2800 | 56 |
| [bmPYR][$CF_3SO_3$] | 0.89 | 3100 | 62 | 0.76 | 10,300 | 52 | 0.78 | 3200 | 64 |

**Efficiency of different ionic liquids in removing sulfur**