DESULFURIZATION OF CRUDE OIL USING IMIDAZOLIUM-BASED-PHOSPHATE IONIC LIQUIDS

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MASTER OF SCIENCE
CHEMICAL ENGINEERING

UNIVERSITI TEKNOLOGI PETRONAS

DECEMBER 2011

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A Thesis
Submitted to the Postgraduate Studies Programme
as a Requirement for the Degree of

MASTER OF SCIENCE
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UNIVERSITI TEKNOLOGI PETRONAS
BANDAR SERI ISKANDAR,
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ACKNOWLEDGEMENTS

This dissertation was made possible by the help and support of many people. First of all, I would like to express my sincere gratitude and appreciation to my supervisor, Dr. Chong Fai Kait, for providing me with this unique research opportunity, and for her guidance and support all the way in my three years period of study and preparation of this thesis. Throughout my study and research project, she has constantly given me insightful advice. I have not only learnt from her but have also been inspired by her dedicated attitude to science. It has been a marvellous learning experience.

I would also like to thanks Dr. Zakaria Man as my co-supervisor, as he also help me along this long journey. Thank you for your wisdom and knowledge you shared with me.

My gratitude also goes out to Ionic Liquid station for all the financial help and equipment that helped a lot in my research

I would like to acknowledge all the staff members in the ionic liquid station and in the chemical Engineering Department for their contributions to an active academic atmosphere.

Lastly, and most importantly, I feel very grateful to my husband, children and parents for their unending support and love for the pursuit of my MSc. Thank you always for being there to support me

ABSTRACT

DESULPHURIZATION OF CRUDE OIL USING IMIDAZOLIUM-BASED-PHOSPHATE IONIC LIQUIDS

ABSTRACT

By

Hayyiratul Fatimah Mohd Zaid

Because of the dramatic environmental impact of sulphur oxides contained in engines emissions, sulphur content specification in fuels are becoming more and more stringent worldwide. In the petroleum refining industry, hydrodesulphurization (HDS) is the conventional process to reduce the sulphur levels of the fuels. However, HDS is cost consuming, besides requiring high temperature and high hydrogen pressure in order to eliminate the aliphatic and alicyclic sulphur compounds. Refractory sulphur compounds such as dibenzothiophene, methyl dibenzothiophene and 4,6-methyl dibenzothiophene are less reactive to this process. Due to this reason, alternative sulphur removal techniques are being explored. In the past years, due to its unique properties both as extractant and also as catalyst, ionic liquids have gained increasing interest. In this project, eight imidazolium-based-phosphate ionic liquids were successfully synthesized, namely, 1-methyl-3-methylimidazolium dimethylphosphate (MMIM[DMP]), 1-methyl-3-ethylimidazolium diethylphosphate (EMIM[DEP]), 1-methyl-3-butyllimidazolium dibuylphosphate (BMIM[DBP]), 1-ethyl-3-methylimidazolium dimethylphosphate (EMIM[DMP]), 1-ethyl-3-ethylimidazolium diethylphosphate (EEIM[DEP]), 1-butyl-3-methylimidazolium dimethylphosphate (BMIM[DMP]), 1-butyl-3-ethylimidazolium diethylphosphate (BEIM[DEP]), 1-butyl-3-butylimidazolium dibutylphosphate (BBIM[DBP]). These ionic liquids were characterized using Differential Scanning Calorimeter (DSC), CHNS Analyzer, Density and Viscosity meter and Coulometric Karl-Fisher. The ionic liquids were then screened for sulphur removal from dodecane model oil. The sulphur containing compound used in preparing the model oil, were dibenzothiophene (DBT), benzothiophene (BT), and 3-methylthiophene (3-MT). Ionic liquid 1-butyl-3-butyl imidazolium dibutylphosphate (BBIM[DBP]), 1-butyl-3-ethyl imidazolium diethylphosphate (BEIM[DEP]), and 1-ethyl-3-ethyl imidazolium diethylphosphate (EEIM[DEP]) showed the best sulphur removal with a percentage of 74%, 75% and 81% respectively, and were used for further study. A combination of catalytic oxidation and simple liquid-liquid extraction was employed for desulphurization (ECODS) utilizing molybdic catalyst, hydrogen peroxide (H_2O_2) and imidazolium-based-phosphate ionic liquids, namely, 1-butyl-3-butyl imidazolium dibutylphosphate (BBIM[DBP]), 1-butyl-3-ethyl imidazolium diethylphosphate (BEIM[DEP]), and 1-ethyl-3-ethyl imidazolium diethylphosphate (EEIM[DEP]). The precatalyst of molybdic compounds was oxidized with H_2O_2 to form peroxomolybdic compounds, which is soluble in ionic liquid and dissolved in oil. The sulphur containing compounds in the model oil were extracted into ionic liquid phase and oxidized to their corresponding sulfones by peroxomolybdic compounds. Further studies were conducted for research parameters such as the temperature, amount of H_2O_2, amount of catalyst, type of sulphur species and initial concentration of sulphur on the sulphur removal from the model oil. From the experiments, the optimum conditions for ECODS process were 70^oC, ratio of H_2O_2 to sulphur compound used was 4 ($[n(H_2O_2)/n(S)]=4$), and ratio of sulphur compounds to catalyst was 20 ($[n(S)/n(Cat)]=20$), giving 85.2% sulphur removal for ionic liquid BBIM[DBP]. Other desulphurization methods; extraction (EDS) and oxidation (ODS) were also compared. It was found that imidazolium base phosphate ionic liquids with longer alkyl chain displayed better sulphur removal efficiency. BBIM[DBP] was found to display the best performance in sulphur removal showing a removal of 85.2 % for ECODS process, 68.4% for EDS process and 65.8% for ODS process.

ABSTRAK

Disebabkan kesan dramatik oksida sulphur yang terkandung dalam gas pelepasan engine keatas alam sekitar, spesifikasi kandungan sulphur dalam bahan api menjadi lebih ketat di seluruh dunia. Dalam industri penapisan petroleum, hydrodesulphurization (HDS) adalah proses yang konvensional untuk mengurangkan tahap sulphur dalam bahan api. Walau bagaimanapun, proses HDS memakan kos yang tinggi, di samping memerlukan suhu tinggi dan tekanan hidrogen yang tinggi untuk menghapuskan alifatik dan sebatian sulphur alisiklik. Refraktori sebatian sulphur seperti dibenzothiofene, metil dibenzothiofene dan 4,6-metil dibenzothiofene kurang reaktif kepada proses ini. Oleh kerana ini, teknik penyingkiran sulphur yang lain sedang dikaji. Semenjak kebelakangan ini, disebabkan oleh sifat-sifat uniknya sebagai pengekstark dan juga sebagai pemangkin, cecair ionik telah mendapat faedah yang semakin meningkat. Dalam projek ini, lapan imidazolium berasaskan fosfat cecair ionik telah berjaya disintesis, iaitu, 1-metil-3-metilimidazolium dimetilfosfat (MMIM[DMP]), 1-metil-3-etilimidazolium dietilfosfat (EMIM[DEP]), 1-metil-3-butillimidazolium dibutilfosfat (BMIM [DBP]), 1-etil-3-metillimidazolium dimetilfosfat (EMIM[DMP]), 1-etil-3-etilimidazolium dietilfosfat (EEIM[DEP]), 1-butil-3-metilimidazolium dimetilfosfat (BMIM[DMP]), 1-butil-3-etilimidazolium dietilfosfat (BEIM[DEP]), 1-butil-3-butilimidazolium dibutilfosfat (BBIM[DBP]). Cecair ionik telah dicirikan menggunakan Kalorimeter Pengimbasan Pembezaan (DSC), CHNS Analyzer, Ketumpatan dan meter Kelikatan dan Coulometric Karl-Fisher. Cecair ionik kemudian disaring untuk pembuangan sulphur daripada minyak model dodekane. Kompaun sulphur yang digunakan dalam menyediakan minyak model adalah dibenzothiofene (DBT), benzothiofene (BT), dan 3-methylthiofene (3-MT). Cecair ionik 1-butil-3-butil imidazolium dibutilfosfat (BBIM[DBP]), 1-butil-3-etil imidazolium dietilfosfat (BEIM[DEP]), dan 1-etil-3-etil dietilfosfat (EEIM[DEP]) menunjukkan penyingkiran sulphur dengan peratusan 74%, 75% dan 81% masing-

masing, dan telah digunakan untuk kajian selanjutnya. Gabungan pengoksidaan sebagai pemangkin dan pengekstrakan cecair-cecair desulphurization (ECODS) menggunakan pemangkin molybdic, H_2O_2 dan imidazolium berasaskan fosfat cecair ionik, iaitu, 1-butil-3-butil imidazolium dibutilfosfat (BBIM[DBP]), 1-butil-3-etil imidazolium dietilfosfat (BEIM[DEP]), 1-etil-3-etilimidazolium dietilfosfat (EEIM[DEP]). Pre-pemangkin sebatian molybdik teroksida dengan H_2O_2 untuk membentuk sebatian peroxomolibdik, yang larut dalam cecair ionik dan larut dalam minyak. Sebatian yang mengandungi sulphur dalam minyak model yang telah diekstrak ke dalam fasa cecair ionik dan teroksida kepada sulfones oleh sebatian peroxomolybdic. penyelidikan selanjutnya telah dijalankan untuk menyiasat parameter seperti suhu, jumlah H_2O_2 yang digunakan, jumlah pemangkin yang digunakan, jenis spesies sulphur dan kepekatan sulphur awal terhadap penyingkiran sulphur daripada minyak model. Daripada eksperimen, keadaan optimum untuk proses ECODS adalah pada suhu 70^{o}C, nisbah hidrogen peroksida kepada kompaun sulphur yang digunakan adalah 4 ([n(H2O2)/n(S)] = 4), dan nisbah kompaun sulphur kepada pemangkin yang digunakan adalah 20 ([n(S)/n(Cat)] = 20), memberi 85.2% penyingkiran sulphur untuk cecair ionik BBIM[DBP]. Kaedah desulphurization lain; pengekstrakan (EDS) dan pengoksidaan (ODS) juga dibandingkan. Ia didapati bahawa imidazolium fosfat asas cecair ionik dengan rantai alkil ysng lebih panjang mempamirkan penyingkiran sulphur kecekapan yang lebih baik. BBIM[DBP] telah didapati mempamerkan prestasi terbaik dalam penyingkiran sulphur dengan menunjukkan penyingkiran 85.2% untuk proses ECODS, 68.4% untuk proses EDS dan 65.8% untuk proses ODS.

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LIST OF SYMBOLS

^{o}C - Celcius
K_N - Sulpur Partition Coefficient
K - Kelvin
Pa - Pascal
g - Gram
n - Mole
wt - Weight
eV - Electron Volt

LIST OF ABBREVATIONS

AlCL$_3$-TMAC - trimethylamine hydrochloride
API - American Petroleum Institute
BBIM[DBP] - 1-butyl-3-butyl-imidazolium dibutylphosphate
BEIM[DEP] - 1-butyl-3-ethyl-imidazolium diethylphosphate
BMIM[BF$_4$] - 1-butyl-3-methylimidazolium tetrafluoroborate
BMIM[DBP] - 1-methyl-3-butyl-imidazolium dibutylphosphate
BMIM[DMP] - 1-butyl-3-methyl-imidazolium dimethylphosphate
BMIM[OcSO$_4$] - 1-butyl-3-methylimidazolium Octylsulphate
BMIM[PF$_6$] - 1-butyl-3-methylimidazolium hexafluorophosphate
BT - Benzothiophene
CHNS - Carbon, Hydrogen, Nitrogen and Sulphur Analyzer
^{13}C-NMR - Carbon Nuclear Magnetic resonance
CoMo/Al$_2$O$_3$ - Alumina-supported cobalt-molybdenum catalyst
DBT - Dibenzothiophene
4,6-DMDBT - 4,6-dimethyldibenzothiophene
DSC - Differential Scanning Calorimeter
ECODS - Extraction and catalytic oxidative desulphurization
EDS - Extractive Desulphurization
EEIM[DEP] - 1-ethyl-3-ethyl-imidazolium diethylphosphate
EMIM[DEP] - 1-methyl-3-ethyl-imidazolium diethylphosphate
EMIM[DMP] - 1-ethyl-3-methyl-imidazolium dimethylphosphate
EPA - Environmental Protection Agency
EtNH$_3$[NO$_3$] - Ethanolammonium Nitrate
GC-MSD - Gas Chromatography Mass Spectroscopy Detector
HDS - Hydrodesulphurization
Hnmp[H$_2$PO$_4$] - N-methyl-pyrrolidonium Phosphate
^{1}H-NMR - Proton Nuclear Magnetic resonance
H$_2$O$_2$ - Hydrogen Peroxide
H$_2$S - Hydrogen Sulfide

ILs - Ionic Liquids

$Na_2MoO_4.2H_2O$ - Sodium Molybdate Dehydrate

$NiMo/Al_2O_3$ - Alumina-supported nickel-molybdenum catalyst

No_x - Nitrogen Oxides

MMIM[DMP] - 1-methyl-3-methyl-imidazolium dimethylphosphate

4-MDBT - 4-Methyldibenzothiophene

3-MT - 3-Methylthiophene

ODS - Oxidative Desulphurization

ppm - Part per million

RTIL - Room Temperature Ionic Liquids

S - Sulphur

SO_2 - Sulphur Dioxide

VOCs - Volatile Organic Compounds

CHAPTER I

INTRODUCTION

1.1 Background of Research

1.1.1 Petroleum

Petroleum or crude oil is the largest and most widely used energy resources in the world. The history of crude oil can be traced back to more than two thousand years, but the real production started on the 27th August 1859, when a 22 meter deep well was explored in Oil Creek, Pennsylvania. This was the first industrial crude oil well, and later there was a rapid development of the crude oil production and treatment. Figure 1.1 shows the world total primary energy supply [1].

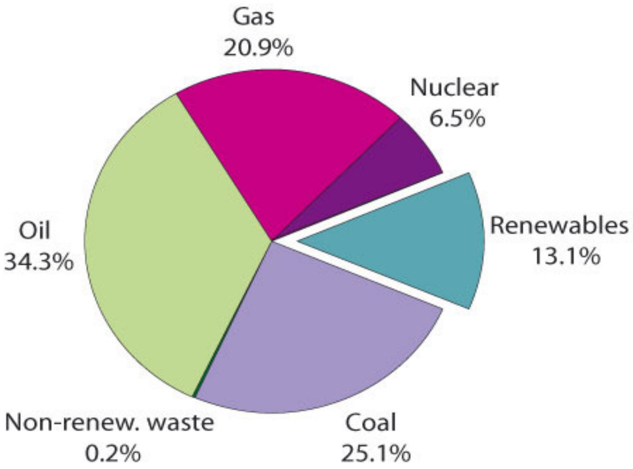


Figure 1.1 The world total primary energy supply.

Archaeologists have shown that crude oil had already been extracted and used in medicine, civil or construction works and even as source of military power in ancient times. It would be hard to imagine what our life today would be without crude oil. It brings power to all our machines and our houses, it is a lubricant for various products of machines and most of our modern devices rely on various products derived from crude oil to work. A major portion of the crude oil is used as transportation fuels such as gasoline, diesel and jet fuel. Figure 1.2 shows the global sectoral consumption of petroleum [1].

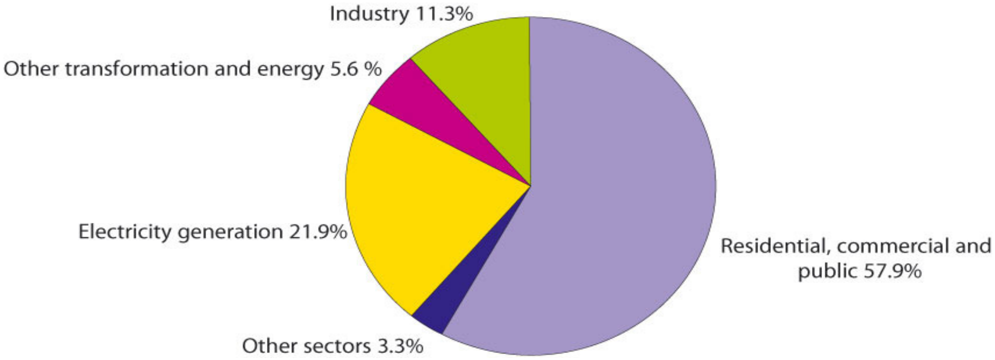


Figure 1.2 Global sectoral consumption of petroleum.

Crude oil is a complex mixture of hydrocarbons and other carbon compounds. It consists of carbon (83-87%), hydrogen (14%) and also of oxygen, nitrogen and sulphur (0.1-2%) at the elemental level. In some cases the percentage of sulphur can be up to 3-6%. Overall, crude oil consists of hydrocarbons, asphaltenes and resins, sulphur and ash. Paraffinic, naphthenic and aromatic hydrocarbons are the three main groups in crude oil.

Sulphur compounds in crude oil can exist in many forms such as hydrogen sulfide (H_2S), or as compounds like mercaptans, thiophenols, cycloalkanethiols, thiophenes, benzothiophenes, alkylbenzothiophenes, etc., or as elemental sulphur. Figure 1.3 shows some of the sulphur compounds that can be found in crude oil

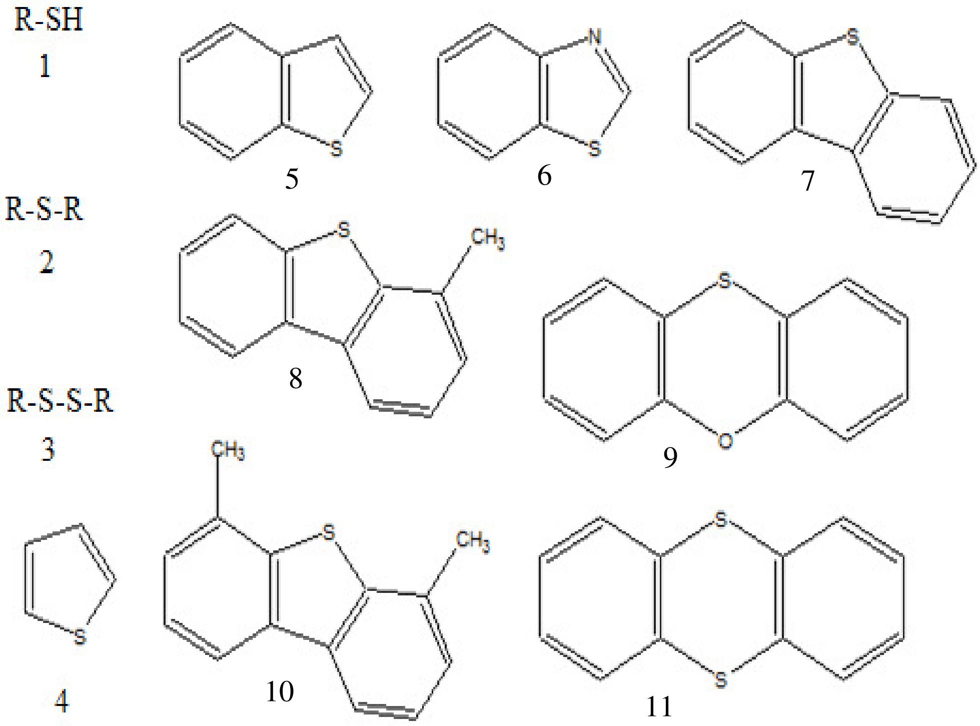


Figure 1.3 Structures of some sulphur containing compounds: mercaptanes (1), sulfides (2), disulfides (3), thiophene (4), benzothiophene (5), benzothiazole (6), benzothiophene (DBT) (7), 4-methyldibenzothiophne (4-DMDBT) (8), phenoxathin (9), 4,6-dimethyldibenzothiophne (4,6-DMDBT) (10) and thianthrene (11)

Different crude oils have different types and proportions of sulphur compounds. However the proportion, stability, and complexity of these compounds are greater in the heavier crude oil. The quality of fuels produced from crude oils decreases with the presence of sulphur compounds due to the emissions of hazardous air pollutants.

It is well known that sulphur compounds are undesirable in the refining process as they tend to deactivate some catalysts used in crude oil processing. Moreover, sulphur compounds can cause several other problems such as premature failure of combustion engines, poisoning of catalyst converters that are used in automotive engines and also corrosion problems. The primary contributor to corrosion in refinery processing units is hydrogen sulfide. Other corrosive sulphur materials are elemental sulphur and mercaptans. Corrosive action of sulphur compounds on iron and steel materials used in refinery process equipments, pipings and tanks produces pyrophoric iron sulfide that will ignite spontaneously in air. Sulphuric acid and sulphur dioxide are undesirable by-products, results from the combustion of crude oil that contains sulphur compounds. Sulphur compounds reduce activity of antidetonation additives and antioxidizing stability of gasoline, raise the propensity to form hard residues in cracking gasoline fractions, and results in environmental pollution [2].

1.1.2 Crude Oil Composition

Crude oil is a complex mixture of various organic compounds, consisting of different hydrocarbons and hetero-atomic compounds. Fractional composition is a very important crude oil property and is determined in the laboratory by slowly heating the oil and separating it into fractions having specified boiling ranges. Every fraction is determined by the temperature at which the boiling begins and ends.

The portion of hydrocarbons in crude oil varies from different oil fields and ranges from as much as 97% by weight in the lighter oils to as little as 50% in the heavier oils and bitumens. The hydrocarbons in crude oil are mostly alkanes, cycloalkanes and various aromatic hydrocarbons while the other organic compounds contain nitrogen, oxygen and sulphur, and trace amounts of metals such as iron, nickel, copper and vanadium. The exact composition varies widely from formation to formation but the proportion of elements varies over fairly narrow limits as tabulated in Table 1.1[3].

Table 1.1 Reagent percentage of element in crude oil.

Element	Percent Range(%)
Carbon	83-87
Hydrogen	10-14
Nitrogen	0.1-2
Oxygen	0.1-1.5
Sulphur	0.1-6
Metals	Less than 1000ppm

Malaysian crude oil contains little impurities, especially sulphur. Malaysian crude oil is the lightest and sweetest of the main types of crude oil. It has an API gravity of 45.5 ^{o}API and sulphur content of 0.1% (Malaysian Tapis Blend 44). Table 1.2 shows the chemical composition of oils from US, Canada and Russia [4].

Table 1.2 Chemical composition of oils from US, Canada and Russia. Ultimate analysis for crude oils [4].

Origin	Composition (wt.%)				
	Carbon	Hydrogen	Nitrogen	Oxygen	Sulphur
USA	86.6	11.8	-	-	-
	83.5	13.3	-	-	-
	85.5	14.2	-	-	-
	83.6	12.9	-	3.6	3.6
Canada	86.9	12.9	-	-	-
	83.4	10.4	0.5	1.2	4.5
	82.8	11.8	0.3	1.7	3.4
Russia	85.3	11.6	-	-	-
	86.1	12.8	-	0.9	0.2
	86.3	12.9	-	0.6	0.2

The crude oil appearance varies from one to another, depending on its composition. Crude oil usually has a black or dark brown colour, but sometimes it may be yellowish or greenish. Due to its high energy density, easy transportability and relative abundance, oil has become the world's most important energy source since the mid-1950s. Most of the crude oil (84% by volume of the hydrocarbons present) is converted into energy-rich fuels, including gasoline, diesel, jet, heating, and other fuel oils, and liquefied petroleum gas [5]. Crude oil is also the raw material for many chemical products, including pharmaceuticals, solvents, fertilizers, pesticides, and plastics; the 16% not used for energy production is converted into these materials.

1.1.3 Classification of crude oil

The petroleum industry generally classifies crude oil by the geographic location at which it is produced, its API gravity, and sulphur content. The geographic location is important because it affects transportation costs to the refinery.

Density is classified by the American Petroleum Institute ('API'). API gravity is defined based on density at a temperature of 15.6 ºC. The higher the API gravity, the lighter the crude. Light crude generally has an API gravity of 38 degrees or more, and heavy crude an API gravity of 22 degrees or less. Crude with an API gravity between 22 and 38 degrees is generally referred as medium crude.

Crude oil quality is measured in terms of density (light to heavy) and sulphur content (sweet to sour). Crude oil may be considered light if it has low density or heavy if it has high density; and it may be referred to as sweet if it contains relatively little sulphur (less than 0.5%) or sour if it contains substantial amounts of sulphur (greater than 0.5%). Light crude oil is more desirable than heavy oil since it produces a higher yield of gasoline, while sweet oil commands a higher price than sour oil because it has fewer environmental problems and requires less refining to meet sulphur standards imposed on fuels in consuming countries. Crude oils with low sulphur content are high quality oils, and are use for processing gasoline, kerosene and high quality diesel.

The impurities in sour crude oils need to be removed before these lower quality crude oils can be refined into gasoline, thereby increasing the cost of processing. This results in a higher-priced gasoline than that made from sweet crude. Thus sour crude is usually processed into heavy oil such as diesel and fuel oil rather than gasoline to reduce processing cost.

1.1.4 Sources of Sulphur in Crude oil

Sulphur has been known for many centuries. It occurs uncombined in nature, and when it is oxidized to sulphur dioxide it becomes a major pollutant.

Sulphur containing compounds in crude oil are generally divided into two major groups: inorganic sulphur and organic sulphur. After carbon and hydrogen, sulphur is considered as the most abundant element in crude oil. Crude oil with higher density contain more sulphur compounds. Distillation fractions with higher boiling point contains higher concentration of sulphur compounds. The average amount of total sulphur in crude oil may vary from 0.1 % to 6 %.

Organic and inorganic sulphur compounds naturally occur in crude oil. Inorganic sulphur compounds include elemental sulphur, H_2S and pyrite. These compounds may be in dissolved or suspended form in crude oil. Organic sulphur compounds in crude oil are generally aromatic or saturated forms of thiols, sulfides and heterocyles. Among these, aromatic compounds such as dibenzothiophene (DBT) or its derivatives are of significant importance because they have higher boiling points (more than 200^oC) and are difficult to remove from crude oil.

When crude oil is processed by distillation, it is separated into fractions that are defined by either their boiling point range or carbon chain length. The atmospheric residual fraction is the residue left after the distillation at 350^oC and at 1 atmosphere. Crude oil is distilled under vacuum at higher temperature, forming heavy gas oils and vacuum residual. The sulphur content increases with the increase in molecular weight of these fractions. In low boiling fractions, organic sulfides or disulfides, mercaptans and thiophenes are the main sulphur compounds and in the higher boiling fractions, sulphur is found mainly as thiophene derivatives such as benzothiophene and dibenzothiophenes [1].

1.1.5 Environmental Sulphur Level

In recent years, the concentration of sulphur dioxide and sulphate had been determined across the United Kingdom. It had been shown that SO_2 emissions have decreased from 240 000 metric tonnes (measured as S) in 1987 to 140 000 metric tone's in 1992-1994. Sulphur as sulphate has decreased from 230 000 metric tone's to 200 000 metric tone's in the same period. Today, the average concentration of SO_2 in the atmosphere is 33 ppm, most of which comes from anthropogenic sources. This figure is considerably smaller than it was in the past. This reduction in emissions is partly accounted for by the enforcement of the Clean Air Act of 1956 and 1968 [1].

Combustion of sulphur compounds in fossil fuels emits sulphur dioxides, which can cause adverse effects on health, environment and economy. SO_2 can be the cause of sulphate aerosol formation. The aerosol particles have an average diameter of 2.5 μm that can be transported into the lungs and cause irritation to the lungs and respiratory illness such as lung cancer. SO_2 can react with moisture in the air and cause acid rain or low pH fogs. The acid formed in this way can accelerate the erosion of historical buildings. It can be transferred to soil, damage the foliage, depress the pH of the lakes with low buffer capacity and endanger the marine life [7], [8], [9]. Therefore, the Directive of the European Parliament and the Environmental Protection Agency (EPA) Clean Air Act (Tier 2) required that the sulphur content to be further reduced to less than 10 ppm in transportation fuels [6].

As SO_2 is transported by air streams, it can be produced in one location and show its adverse impact in another remote place thousands of kilo meters away. Therefore, to control SO_2 emissions, international cooperation is required. Since 1979, Canada, the United States and the European nations in particular have signed several agreements to reduce and monitor SO_2 emissions. Most of these agreements targeting the quality of transport fuel because it was one of the important sources of SO_2 emission. In 1993, the Clean Air Act prescribed the sales and supply of diesel oil with sulphur concentration more than 500 ppm. In 1998, the European Union set the target for sulphur content in diesel fuel at the levels of 350 and 50 ppm for the year 2000 and 2005, respectively and under 10 ppm of sulphur free gasoline in 2011. Similar initiatives were taken in Canada and the United States to reduce the sulphur in diesel fuel and gasoline. New sulphur regulations took effect in Canada and the United States from June 1, 2006 to reduce the sulphur content in on-road diesel fuel and gasoline from 500 ppm and 350 ppm, respectively. The maximum allowable sulphur content in diesel is targeted at 10 ppm by 2011 in the US. The sulphur content in gasoline will probably reach an average value of about 10 ppm in many countries by 2011 [10], [11], [12], [13]. Existing EPA rules (AEO2008) requires that 80 percent of highway diesel supplies contain no more than 15 ppm sulphur for the period 2006-2010. After 2011 all highway diesel is required to contain less than 10 ppm sulphur [14], [15].

Sulphur removal is also important for the new generation of engines, which are equipped with nitrogen oxides (NO_x) storage catalysts. Sulphate produced by sulphur in the fuel has poisoning effect on the catalyst. Since sulphate is highly thermostable, it can saturate the reduction sites on the catalyst, causing the space availability for the reduction of NO_x decreases and the catalyst loses it efficiency. To overcome this problem, treatment procedures must be devised or improved to reach a sulphur level less than 10 ppm [16].

1.1.6 Methods for sulphur removal

In general, two different methods are used to lower sulphur oxide emissions: pre-combustions and post-combustions treatment methods. The pre-combustion treatment method has more advantages compared to the post-combustion method. For instance, in the case of flue gas treatment, the post-combustions method can be applicable. However, this method deals with hot corrosive effluents and it is expensive. Quality monitoring of the treated flue gas at every treatment location is practically not possible.

Furthermore, this method is limited and cannot be extended to all applications. On the other hand, pre-combustions treatment of fossil fuel reduces the sulphur oxide emissions regardless of the type of combustion process.

There are many pre-combustion treatment methods in the removal of sulphur from crude oil. The choice of a particular process depends on the specification required for the removal of sulphur, the quality of crude oil processed, and the composition of the crude oil being treated. There are two general classification in the removal of sulphur in crude oil: conventional hydrodesulphurization (HDS) and non-conventional desulphurization (non-hydrogen consuming desulphurization). The non-conventional desulphurization studies can be categorized into five methods: oxidative desulphurization (ODS), extractive desulphurization (EDS), extraction and catalytic oxidative desulphurization (ECOD), biodesulphurization, and sulphur adsorption.

Catalytic hydrodesulphurization (HDS) is the conventional sulphur compound removal method. This method requires high temperature, more active catalysts, longer residence time and high hydrogen gas pressure (needed for kinetic and catalyst stability purposes) in order to produce fuels that have a lower level of sulphur compounds [9], [17]. HDS eliminates the aliphatic (non aromatic compounds) sulphur compounds [16],[18], but more active catalysts are needed in order to achieve the very low sulphur content because the available catalyst is less effective for the hydrogenation of benzothiophene (BT), dibenzothiophene (DBT) and their alkyl derivatives [9], [19]-[21]. Therefore, employing HDS for removal of the recalcitrant organic sulphurs is extremely costly as it occurs under more extreme operating conditions such as elevated temperature (300 to 400 °C) and elevated pressures ranging from 30 to 130 atmospheres. In order to overcome such a formidable challenge, the renovation of the current sulphur removal plants and the erection of new desulphurization facilities are inevitable. The prohibitive desulphurization cost for refractory compounds has obliged researchers to find more efficient and economic alternatives. [6], [22], [23].

Some research on the desulphurization technology have been carried out extensively in the last decade, including extraction, oxidation, and adsorption. Most of these technologies were focused on the desulphurization of fuels. However, removal of sulphur species in some chemicals is also important for the chemical industry. The elimination of thiophene and alkylthiophenes as impurities is a serious practical problem which is often encountered in the refinery industry. It is important to remove these cyclic sulphur compounds due to the corrosive products formed upon their degradation and the severe poisoning effect in many catalytic reactions. The difficulty involved in separation of thiophenes from aromatic hydrocarbons is due to their similar physicochemical property, such as the boiling point (BP) [24].

One of the viable potentials, as an alternative method, is the extraction of organic sulphur compounds by imidazolium-based ionic liquids. Ionic liquids (ILs) are chemically regarded as salt-like materials which exist in liquid state under $100^{o}C$. The compounds have practically no vapor pressure below their decomposition temperature. The cation portion in ILs is typically an organic molecule. ILs can be designed with numerous structures and depending on the design they may demonstrate different chemical or physical features [25].

Among typical imidazolium-based ILs, 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM[BF_4]) and 1-butyl-3-methylimidazolium hexafluoro phosphate (BMIM[PF_6]) are more widely studied in extractive procedures and desulphurization, due to the high symmetry and coordination ability of its anion.

1.1.7 Ionic Liquid

One major principle of green chemistry is that the volatile organic solvents used for reactions or separations should be avoided or made safer. Modern organic chemistry seeks efficient and cheap synthetic procedures as well as environmentally benign experimental conditions. Because of this, there have been of great interest in the properties of room temperature ILs. ILs are considered as a substitute for those volatile organic solvents, because ILs have low vapor pressure and thus being environmental friendly [25].

Ionic liquids (ILs) have been accepted as a new green chemical revolution which excites both the academia and the chemical industries. This new chemical group can reduce the use of hazardous and polluting organic solvents due to their unique characteristics as well as taking part in various new synthesis. The terms room temperature ionic liquid (RTIL), non-aqueous IL, molten salt, liquid organic salt and fused salt have all been used to describe these salts in the liquid phase. ILs are known as salts that are liquid at room temperature in contrast to high-temperature molten salts. They have a unique array of physico-chemical properties which make them suitable in numerous applications in which conventional organic solvents are not sufficiently effective or not applicable. In 1980, there were only a few patent for ILs, but increase to 800 patents in 2004. This is a clear indication of the high affinity of the academia and industry to the ILs.

ILs have been known for a long time, but their extensive use as solvents in chemical processes for synthesis and catalysis has recently become significant. Welton reported that ILs are not new, and some of the ILs such as Ethanolammonium nitrate $[EtNH_3][NO_3]$ was first described in 1914 [26]. The earliest IL in the literature was created intentionally in 1970s for nuclear warheads batteries. During 1940s, aluminum chloride-based molten salts were utilized for electroplating at temperatures of hundreds of degrees Celsius. In the early 1970s, Wilkes tried to develop better batteries for nuclear warheads and space probes which required molten salts to operate. These molten salts were hot enough to damage the nearby materials. Therefore, chemists searched for salts which remain liquid at lower temperatures and eventually they identified one which is liquid at room temperature. Wilkes and his colleagues continued to improve their ILs for use as battery electrolytes and then a small community of researchers began to make ILs and test their properties. In the late 1990s, ILs became one of the most promising chemicals as solvents. This new class of solvent emerged at the same time due to the increasing awareness of the public opinion on the crucial need to develop new, cleaner chemical processes [27].

The first ILs, such as organo-aluminate ILs, have limited range of applications because they were unstable to air and water. Furthermore, these ILs were not inert towards various organic compounds. After the first reports on the synthesis and applications of air stable ILs such as 1-butyl-3-methlyimidazolium tetrafluoroborate ([BMIM][BF_4]) and 1-butyl-3-methlyimidazolium hexafluorophosphate ([BMIM][PF_6]), the number of air and water stable ILs has started to increase rapidly. Recently, researchers have discovered that ILs are more than just green solvents and they have found several applications such as replacing them for volatile organic solvents, new materials, production of effective conductor, enzyme-catalyzed reactions, hosting a variety of catalysts, gas purification, homogenous and heterogeneous catalysis, biological reactions media and metal ions removal [28]-[30].

Researchers explained that ILs remain liquid at room temperature due to the reason that their ions do not pack well. Combination of bulky and asymmetrical cations and evenly shaped anions form a regular structure namely a liquid phase. The low melting points of ILs are a result of the chemical composition. The combination of larger asymmetric organic cation and smaller inorganic counterparts lower the lattice energy and hence the melting point of the resulting ionic medium. In some cases, even the anions are relatively large and play a role in lowering the melting point [31]-[33].

As solvents, ILs posses several advantages over conventional organic solvents, which make them environmentally compatible [23]. Among these advantage are:-

- ILs have the ability to dissolve many different organic, inorganic and organo metallic materials.
- ILs are highly polar.
- ILs consists of loosely coordinating bulky ions.
- ILs does not evaporate since they have very low vapor pressures.
- ILs are thermally stable, approximately up to 300^{o}C.
- Most of ILs have a liquid window of up to 200^{o}C which enables wide kinetic control.

- ILs have high thermal conductivity and a large electrochemical window.
- ILs are immiscible with many organic solvents.
- ILs are nonaqueous polar alternatives for phase transfer processes.
- The solvent properties of ILs can be tuned for a specific application by varying the anion cation combinations.

ILs does not produce vapors in contrast to traditional organic solvents such as benzene, acetone, and toluene. ILs are introduced as green solvents because unlike the volatile organic compounds (VOCs) they replace, many of these compounds have negligible vapor pressure, they are not explosive and it may be feasible to recycle and repeatedly reuse them [34]. For example, chemical reactions producing materials ranging from polyester to pharmaceuticals generally employ organic solvents. A common place example of one is paint thinner. Common organic solvents that are used in paint thinner are ethylbenzene, xylene and butan-1-ol. But their fumes are often dangerous if inhaled and can contribute to the formation of smog. Because of this, it is more convenient to work with ILs since the non-evaporating properties of ILs eliminate the hazardous exposure and air pollution problems[23],[34].

ILs are also known as 'designer solvents' since their properties can be tuned according to any specific particular need. The researchers can design a specific IL by choosing negatively charged small anions and positively charged large cations, and these specific ILs may be utilized to dissolve a certain chemical or to extract a certain material from a solution. The fine-tuning of the structure provides tailor-designed properties, such as solubility, viscosity and course price, to satisfy the specific application requirements. The physical and chemical properties of ILs are varied by changing the alkyl chain length on the cation and the anion. For example, Huddleston et al.[35] concluded that density of ILs increases with a decrease in the alkyl chain length on the cation and an increase in the molecular weight of the anion [35].

ILs usually consist of nitrogen containing organic cation combined with inorganic or organic anions. Common cations used in ILs include bulky dialky imidazolium, alkyl pyridinium, tetraalkyl ammonium, and tetraalky lphosphonium.

Common anion include chloride (Cl^-), bromide (Br^-), hexafluorophosphate (PF_6), tetrafluoroborate (BF_4), nitrate (NO^{3-}), halide and acetate (CH_3COO^-) [26], [36]-[39].

ILs dissolve many organic compounds but what is even more important, IL can dissolve many inorganic and metaloorganic compounds [40]. On the other hand, some organic compounds may be immiscible with particular ILs depending on its structure. This offers a possibility for conducting reactions between organic and inorganic compounds, both in homogeneous and heterogeneous conditions. ILs are highly polar due to their ionic nature, but non-coordinating therefore they may influence a course of ionic reactions. As electrolytes they may also serve as solvents for electrochemical processes. Specific solvent properties of ILs may be advantageous in certain applications, for example, there are already a few reports in the literature that some enzymes dissolved in ILs are more stable than when dissolved in organic solvents. ILs may have a liquid range of nearly 300°C exceeding the liquid range of typical solvents. Synthetic chemists are mainly interested in the application of ILs as solvents for conducting chemical reactions. This is especially attractive for organic chemist dealing with low molecular weight volatile compounds. ILs may dissolve variety of inorganic and metaloorganic catalyst. Therefore, very convenient reaction system may be devised: catalyst may be dissolved in IL, substrates introduced into resulting solution and after a time required for a reaction to proceed, products can be simply isolated by evaporation, leaving the catalyst in the ILs that may be used for the subsequent reaction cycle [27]. ILs also display excellent dissolution properties for many organic and inorganic substrates allowing smaller plant sizes and increased space-time-yields. Additionally, ILs have high thermal stabilities and can remain liquid in a wide range of temperature, allowing higher reaction temperatures. They also permit a range of separation techniques such as distillation or sublimation which are sometimes not possible using traditional organic solvents [41]-[43]. For all these reasons and among many other applications, these compounds have proved their efficiency as solvents in extractions of a variety of substances, including metallic ions, organic and bio-molecules, organosulphur from fuels, and gases [8], [44]-[46].

Electrochemical applications benefit from their good electrical conductivities in wide electrochemical windows. Other beneficial properties include enhanced enzyme stability, improved chemo-selectivity and easier catalyst recovery and recycling [47].

ILs are widely recognized as very suitable materials for separation processes such as extraction, gas cleaning and extractive distillations. This is due to their amazing combination of properties such as no measureable vapor pressure, no flammability and tenability of their solution properties which differentiates them from molecular solvents [22], [48], [49].

To summarize ILs have the following advantageous properties;

- No measureable vapor pressure
- Non-flammable below their decomposition temperature
- Tunable properties
- Excellent salvation properties for variety of organic and inorganic compounds
- High electric conductivities
- High thermal stabilities

With these properties, ILs have been investigated as medium to replace current organic solvents used for many chemical reactions, such as alkylation of naphthalene [50], alkylation of benzene [51], organocatalysis [52], extraction in the removal of sulphur compunds [10], and many more. ILs are currently the object of a very significant research effort in an enormous variety of areas in chemistry, biochemistry, physics, engineering and many more, and because of this ILs is applied in multiple fields [35].

1.1.8 Application of Ionic Liquids

The potential applications of ILs are among the reasons why ILs are being explored. ILs have the properties to be used in many areas. Among these applications are:

- In biotechnology, ILs are used in enzyme catalysis, biomass processing, protein synthesis and purification.
- In the engineering area, ILs can be used in extraction, extractive distillation and membrane technology
- ILs are also used for photovoltaics, batteries, and fuels cells in the energy department.
- For chemistry, ILs play a role in organic synthesis, inorganic synthesis, polymerization and catalysis
- Other applications of ILs can be seen in actuators, sensors, gas storage and analytics.

In general, an ideal extractant should have the following properties.

- The partition coefficient for the sulphur compounds above all for dibenzothiophene should be high,
- The regeneration of the extractant must be easy.
- The agent must not be soluble in oil for easy separation.
- The oil should not be soluble in the extractant.
- The extracting agent should have a high thermal and chemical stability, be non-toxic and environmentally benign [53]-[56].

For extracting sulphur compounds, some molecular solvents such as polyalkylene glycol, polyalkylene glycol ether, pyrrolidones, and pyrimidinones have been patented. However, sometimes their solubility in fuel and vice versa is noticeable, which can lead to cross contamination [22]. ILs have the ability of extracting aromatic sulphur compounds at ambient condition without the use of hydrogen consumption. In addition, ILs are immiscible with fuel, and can be regenerated by solvent washing and distillation [18].

1.2 Problem Statement

The classical desulphurization process involves catalytic hydrogenation of sulphur compounds (hydrodesulphurization, HDS) into hydrogen sulfide. Typical reaction conditions are 350^{o}C and 30-100 bar hydrogen pressure. HDS eliminates the aliphatic sulphur compounds, but more active catalysts are needed in order to achieve the very low sulphur content because the available catalyst is less effective for the hydrogenation of benzothiophene (BT), dibenzothiophene (DBT) and their alkyl derivative. This shows that HDS is not efficient when it comes to treating benzothiophenes (BTs), dibenzothiophenes (DBTs) and their derivatives.

If sulphur is not removed from the crude oil, some problems may occur in the refinery processing plant, such as corrosion and leaking of the pipeline due to the presents of hydrogen sulphide. Sulphur compounds also produces sulphur dioxide (SO_2) from the burning of fuel by automotive vehicles, as well as oil burning from power plants. Thus, effecting the environment. Because of this, alternative methods for removing sulphur from crude oil is being explored.

Extractive catalytic oxidative desulphurization (ECODS) is an alternative methods for removing sulphur from crude oil as the process can be carried out at mild conditions without the need of hydrogen consumption. More importantly, benzothiophenes (BTs), dibenzothiophenes (DBTs) and their derivatives can be extracted quite efficiently. Thus, the ECODS process can at least be a complementary technology for the HDS process.

ILs have gained increasing interest over the past years due to its unique properties both as extractant and also as catalyst. ILs are halogen free and are available from relatively cheap starting materials. Hence, extraction of sulphur using ILs could be an alternative extractant to replace the common organic solvents used.

1.3 Objective

The scope of this work is to

1- Identify the potential ILs for sulphur removal.
2- Synthesize the ILs selected.
3- Testing the synthesized ILs for removal of sulphur from model oil at room temperature.
4- Testing the ILs selected to find the optimum parameters for ECODS method.
5- Testing the efficiency of different methods, namely ECODS, EDS and ODS. and the sulphur removal efficiency is determined.

1.4 Thesis Outline

This thesis consists of several chapters, which comprises:

- Chapter 1 - Introduction
- Chapter 2 - Literature Review
- Chapter 3- Research Methodology
- Chapter 4 – Discussion
- Chapter 5 – Conclusion

CHAPTER 2

LITERATURE REVIEW

Removing organic sulphur from crude oil has become an increasingly challenging task for refineries. This is due to the stringent environmental regulation which are placing considerable pressure on refinery operators to reduce sulphur content in crude oil to 10 ppm by the year 2010 [54]. Sulphur compounds are present in crude oil in a wide range of both aliphatic and aromatic forms and mainly concentrated in the heavy part of crude oil. Currently, sulphur compounds are removed by conventional hydrodesulphurization (HDS) catalytic processes. However, the catalysts are not active in removing refractory sulphur compounds like thiophene and multi ring aromatic sulphur compounds, such as dibenzothiophene (DBT) and it derivatives especially 4,6-dimethyldibenzothiophne (4,6-DMDBT) [55]. In order to meet the future fuel specifications, such sulphur compounds must be removed or reduced to target limits within a regulatory period. Much effort has been devoted to developing techniques that can reduce or remove such refractory sulphur compounds by oxidation, extraction, oxidation-extraction, catalytic oxidation-extraction and biodesulphurization

2.1 Classification of desulphurization technologies

Desulphurization processes can be classified into two groups, the conventional desulfurization and the non-conventional desulfurization. In the conventional processes, hydrogen is used to decompose organosulphur compounds and eliminate sulphur from refinery streams while non-conventional processes do not require hydrogen [6].

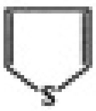
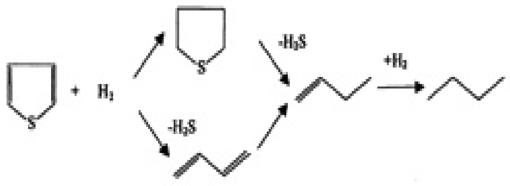
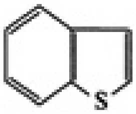
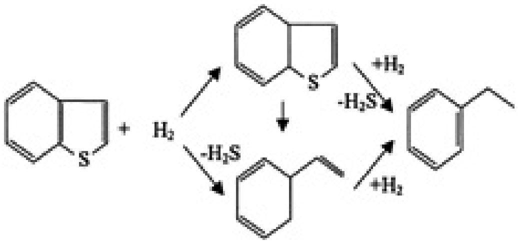
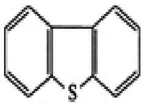
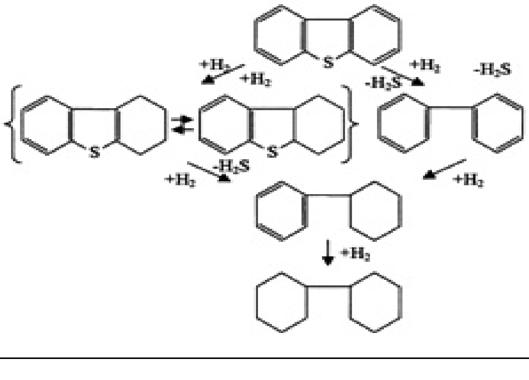
2.1.1 Conventional desulfurization technology

Generally, removal of organic sulphur from fossil fuel is difficult, because sulphur can only be detached from the organic molecule when certain chemical bonds are cleaved. Breakage of such bonds requires high temperature and pressure. One of the current technologies to reduce sulphur in the middle distillate/diesel fuel is known as hydrodesulphurization (HDS). Conventional hydrodesulphurization process conducted over sulfided $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts [56], at temperature around 200-425^oC and at hydrogen pressure of 3-10 MPa are widely used to reduce sulphur compounds to H_2S [12], [22], [40], [56], [57]. Their performance in terms of desulphurization level, activity and selectivity depends on the properties of the specific catalyst used, the reaction conditions, nature and concentration of sulphur compounds present in the feed stream, and reactor and process design [6], [12].

The reactivity of the sulphur compounds depend on their structure and local sulphur atom environment. The low boiling point crude oil fraction contains mainly of aliphatic sulphur compounds such as, mercaptans, sulfides, and disulfides. There are very reactive in the conventional hydrodesulphurization process and can be completely removed with ease [6], [56]. For higher boiling point crude oil fraction, the sulphur compounds are thiophenes, benzothiophenes and their alkylated derivatives. These sulphur compounds are more difficult to remove compared to mercaptans and sulfides because these compounds are sterically hindered [13], [55], [56].

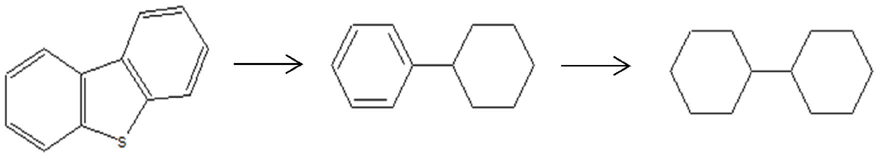
In Table 2.1 some of the organosulphur compounds of interest, namely, mercaptans, sulfides, disulfides, thiophenes and benzothiophenes (BT), and their alkylated derivatives are mentioned with the proposed mechanism of sulphur removal [6], [58], [59]

Table 2.1 Typical Organosulphur Compounds and Their Hydrotreating Pathway [56]

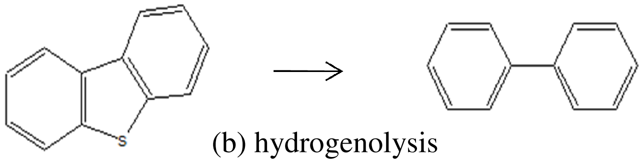
Type of organic sulphur compound	Chemical structure	Mechanism of hydrotreating reaction
Mercaptanes	R-S-H	$R\text{-}S\text{-}H + H_2 \rightarrow R\text{-}H + H_2S$
Sulfides	$R^1\text{-}S\text{-}R^2$	$R^1\text{-}S\text{-}R^2 + H_2 \rightarrow R^1\text{-}H + R^2\text{-}H + H_2S$
Disulfides	$R^1\text{-}S\text{-}S\text{-}R^2$	$R^1\text{-}S\text{-}S\text{-}R^2 + H_2 \rightarrow R^1\text{-}H + R^2\text{-}H + H_2S$
Thiophene	 	
Benzothiophene	 	
Dibenzonthiophene	 	

The reactivity of sulphur compounds in HDS follows this order (from most to least reactive): thiophene> alkylated thiophene>BT>alkylated BT>DBT and alkylated DBT without substituents at the 4 and 6 positions>alkylated DBT with one substituent at either the 4 or 6 position>alkylated DBT with alkyl substituents at the 4 and 6 positions. Deep desulphurization of the fuels implies that more and more of the least reactive sulphur compounds must be converted [6], [56].

HDS of sulphur compounds proceeds via two reaction pathways. In the first pathway, the sulphur atoms are directly removed from the molecules (hydrogenolysis pathway) without affecting the aromatic rings. This method is also known as direct desulphurization. The second pathway hydrogenates the aromatic rings to 4H- or 6H-DBT intermediates and then the sulphur compounds are subsequently removed (hydrogenation pathway). With these the rate of removal for hindered sulphur compounds is greatly increased through the hydrogenation pathway. Without one or both of the rings, the molecule is much more reactive and the sulphur atom can approach the catalyst surface much more easily. Both pathways can be seen in Figure 2.1. [6], [56].



(a) hydrogenation



(b) hydrogenolysis

Figure 2.1 (a) Hyrodesulphurization (hydrogenation) and (b) direct desulphurization (hydrogenolysis) pathways

Hydrodesulphurization is highly efficient at removing thiols, sulfides and disulfides, but it is less effective for aromatic compounds, due to the lack of high performance catalyst for the specific task [9], [11]. Therefore, some alternative technologies have been explored for example, the approaches based on adsorption, extraction, oxidation and biodesulphurization [2], [7], [12], [60]. In order to meet future fuel regulations on sulphur content, these sulphur compounds must be removed or reduced. In general, diesel fuel and gasoline contain 20 to 30% aromatic but less than 1% sulphur, so the removal of sulphur without removing the aromatics is difficult, particularly in HDS. Removal of the aromatics will cause the value of fuel to drop [55].

Moreover, HDS also has these following disadvantage, the process requires high temperature, elevated pressure, longer residence time and more noble metal catalyst, producing negative effects, such as reduced catalyst life, higher hydrogen consumption and higher yield loss, increasing the operating costs [10], [22], [49], [56], [61], [62]. There is also the problem of undesirable side reactions such as increased coke formation and the saturation of olefins which can result in decrease in octane number of gasoline [15], [18], [63], [64]. This process has some inherent problems in the treatment of dibenzothiophene (DBT) and its derivatives, such as the methylated derivatives (for example 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT)) that are difficult to break down due to their steric-hindrance [21], [22], [49], [54], [59], [61]. HDS also suffers cost efficiency to meet the more stringent sulphur level in fuels all over the world [24], [40], [65].

The search for alternative methods of deep desulphurization currently involves diverse techniques including oxidative desulphurization in liquid–liquid systems, complexation in liquid–liquid systems or on an adsorbent, biodesulphurization by action of bacteria, and extraction with ILs. The latter method makes use of the solubility differential between polarizable aromatic compounds and nonpolar aliphatic hydrocarbons in most imidazolium-containing ILs, and a variety of ILs have been tested for the purpose.[12], [19].

2.1.2 Non-conventional desulphurization technologies

Non-conventional desulphurization processes are processes that do not use hydrogen for the removal of sulphur compounds. The non-conventional desulphurization studies can be categorized into five techniques: biodesulphurization [88], adsorption, oxidative desulphurization (ODS) [66-85], extractive desulphurization (EDS) [80-87],extraction and catalytic oxidative desulphurization (ECOD) [88-90].

2.1.2.1 Biodesulphurization

Another possible desulphurization approach at mild conditions through is biodesulphurization (BDS). Biodesulphurization (DBS) process have been proposed as an alternative technology for removing the recalcitrant organic compounds found after the conventional hydrodesulphurization (HDS) treatment, mainly dibenzothiophene (DBT). This method uses desulphurization competent microorganisms to specifically cleave carbon-sulphur bond from the organic sulphur molecules. The desulphurized moiety returns to the hydrocarbon phase and the fuel value is retained. In literature, the most promising DBT desulphurization pathway described up to now is aerobic-based developed by natural strain *Rhodococcus erythropolos IGST8.* This bacteria selectively takes up the sulphur from the DBT molecule by four consecutive enzymatic steps, leaving intact the carbon skeleton as shown in the Figure 2.2 below [2].

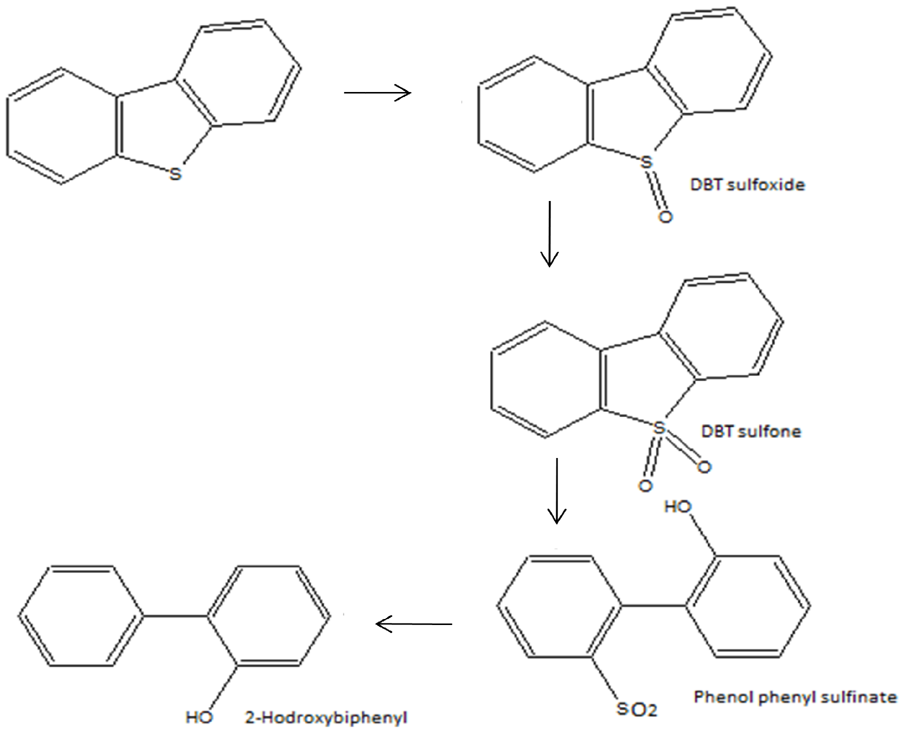


Figure 2.2 Conversion of DBT to sulfoxides, sulfones and finally to hydroxylbiphenyl [2]

However, this biological treatment is currently not commercially viable because of important process limitations, such as mass transfer problems, as the reaction is carried out in a complex medium with two immiscible liquid phases, and cellular deactivation [86], [87]. Other drawback of this procedure is that it is slow and the microorganisms can be suppressed by toxic compounds in the fuel. Therefore, high fuel to aqueous phase ratio cannot be used in biodesulphurization. In order to contact more fuel amounts with the microorganisms in the aqueous phase, the bioreactor sizes will considerably increased. Moreover, in regular biodesulphurization, the separation of the hydrocarbon and the aqueous phases at the end of the process is difficult due to the formation of microemulsion [86], [87], [91], [92]. Other than that, many ancillary processes novel to petroleum refining would be needed, including a biocatalyst fermentator to regenerate the bacteria. The process is also sensitive to environmental conditions such as sterilization, temperature, and residence time of the biocatalyst.

Finally, the process requires the existing hydro treater to continue in operation to provide a lower sulphur feedstock to the unit and is more costly than conventional hydro treating

Nowadays, a commercial technology is not possible unless BDS rate substantially increases. This can be achieved by reducing limiting process factors such as low enzymes activity, low mass transfer rates and cellular deactivation [86], [87].

2.1.2.2 Adsorption

Desulphurization by adsorption is based on the ability of a solid sorbent to selectively adsorb sulphur compounds from the refinery stream. Based on the mechanism of the sulphur compound interaction with the sorbent, adsorption can be divided into two groups, adsorptive desulphurization and reactive adsorption desulphurization.

Adsorptive desulphurization is based on the physical adsorption of sulphur compounds on the solid surface of the sorbent. Be washing the used sorbent with solvents (mixture of toluene and methanol), regeneration can be done and this results in a high sulphur compound concentration flow [93]. In reactive adsorption desulphurization, chemical interaction between the sulphur compounds and the sorbent is applied. Sulphur is fixed on the sorbent, usually as sulfide, and the S-free hydrocarbon is released into the purified fuel stream [93]. Regeneration of the spent sorbent results in sulphur elimination as H_2S, S, or SO_x, depending on the process applied. Efficiency of the desulphurization is mainly determined by the sorbent properties: its adsorption capacity, selectivity for the organosulphur compounds, durability and regenerability [6].

The major distinction of this process from conventional hydrotreating is that the sulphur adsorbs onto the catalyst after the feedstock-hydrogen mixture interacts with the catalyst. Thus the catalyst needs to be regenerated constantly.

2.1.2.3 Oxidative Desulphurization (ODS)

In the petroleum industry, solvent extraction techniques have been used to remove sulphur and nitrogen compounds from light oil without any pretreatment of the petroleum feedstock. The solvent can be recovered and reused through distillation process. In general, employing only solvent extraction of petroleum products to remove sulphur creates an associated loss of useful hydrocarbons, in addition to a poor sulphur removal. This is probably due to the small difference in the polarity between sulphur compounds and other aromatic hydrogen. Therefore, the selective oxidation approach of increasing the polarity of sulphur compounds, then removing them by selective extraction, has received much great attention recently with some success. Therefore, ODS has great potential to be a complementary process to traditional HDS for achieving deep desulphurization [2].

In particular, the oxidative desulphurization appears very promising and is currently receiving growing attention due to its advantages. Some advantages of this process include low cost, lower reactor temperature and pressure (ambient pressure), short residence time, no emissions and no use of expensive hydrogen [49], [54], [62]. For gas oil, ODS process is very efficient when it comes to removing benzothiophene, dibenzothiophene and their corresponding alkyl derivatives which are difficult to remove by HDS [60], [65].

ODS can be carried out under very mild conditions compared to the more severe conditions used in the conventional catalytic hydrodesulphurization (HDS) [9]. ODS is based on the well known propensity of organic sulphur compounds to be oxidized. It consists of an oxidation reaction followed by the extraction of the oxidized products. The physicochemical properties of sulfones are significantly different from those of hydrocarbon in the fuel oil and they can be easily removed by distillation, solvent extraction adsorption or decomposition. Many types of oxidant have been studied and hydrogen peroxide is considered the most promising oxidation agent in terms of selectivity, product quality, safety, environmental impact and process economics. One of the main advantage of the ODS is that the most refractory sulphur compound showed higher reactivity than that of the HDS in which expensive hydrogen is used. The reactivities of the compounds seem to correlate well with their electronic density. [94], [95].

ODS is basically a two-stage process: oxidation followed by liquid extraction. In the first stage, the sulphur compounds are oxidized using appropriate oxidants such as: peroxy organic acids, catalyzed hydroperoxides, inorganic peroxy acid or peroxy salts, hydrogen peroxide [90], [96-98], nitric acid [79], nitrogen oxides [79], organic hydroperoxides (tert-butyl hydropeorxide) [99], [100-102], ozone [103], air [104] and fenton's reagent [54], [59], [62]. Among these oxidants, hydrogen peroxide has been widely used because it is cheap, nonpolluting, is not strongly corrosive and commercially available. In ODS process, hydrogen peroxide is the most common oxidant and is used in the presence of a catalyst such as acetic acid [105], formic acid [90], [96] and polymolybdates [106]. The mechanism of this process is as below.

The sulphur compounds are converted to their corresponding sulfoxides and sulfones by oxygen donation to thiol and thiophene groups. These are preferentially extracted from the fuel due to their increased relative polarity. The known ability of several solvents to extract sulphur compounds selectively from petroleum fractions can be dramatically improved by oxidizing sulphur from the divalent state (sulfide) to the hexavalent state (sulfone). The oxidation process itself leads to the removal of a substantial portion of the existing sulphur and makes the remaining sulphur compounds amenable to efficient removal even by solvents such as methanol which are not effective in selective extraction of the unoxidized sulphur compounds. With this combination process the ability to remove sulphur compounds can be increased up to 99% [21], [54], [55].

Zhao Dishum et al. [9], in his review on desulphurization based on oxidation has indicated that there are two main catalysts used for selective desulphurization. They are polyoxometalates and organic acids. Polyoxometalates have long been studied for oxidation reactions, particularly, the polyoxometalates with hydrogen peroxides system for organic substrate oxidation.

Organic acids include formic acid, acetic acid and so on. Mohammad Farhat Ali et al. [55] reported on the desulphurization process based on oxidation with hydrogen peroxide and acetic acid using sulphuric acid as catalyst. This report showed that with an increase in acetic acid and sulphuric acid ratio from 1:0 to 2:1, the oxidation product also increased resulting in the removal of sulphur compounds up to 90%. The oxidative desulphurization of DBT in n-octane as model oil with Bronsted acidic ionic liquid, N-methyl-pyrrolidonium phosphate ([Hnmp]H_2PO_4) as catalytic solvent and H_2O_2 as oxidant. In this investigation, it was reported that the sulphur removal of DBT could reach 99.8% under optimal conditions with molar ratio of H_2O_2 to sulphur 16:1, reaction temperature of 60^oC, reaction time of 5 h and volume ratio of model oil to IL of 1:1 [10]. Yong Chuan Dai et al. [54], researched on ODS using ultrasound and Fenton's reagent. The use of ultrasound was to accelerate the reaction, and by that increase the rate of sulphur removal. Fenton's reagent improves the hydro treater fuel by increasing the concentration of available hydroxyl ions. Through their work, the sulphur content in the fuel was reduced from 568.75 ppm to 9.50 ppm (98%).

The application of ODS on real refinery feedstock (non-hydrotreated kerosene with total sulphur mass content of 0.16%) with a mixture of hydrogen peroxide and acetic acid was conducted by Asghar Molaei Dehkordi et al. [60]. The influence of various operating parameters including reaction temperature, acid to sulphur molar ratio and oxidant to sulphur molar ratio on the sulphur removal of kerosene were studied. The results revealed that an increase in the reaction temperature and molar ratio of catalysts to sulphur enhanced the sulphur removal percentage to 83.3%.

Although these ODS processes are effective, the use of large amount of flammable and volatile organic compounds raises further environmental and safety concerns [49], [59].

2.1.2.4 Extractive Desulphurization (EDS)

Extractive desulphurization (EDS) is a well-established process that can be carried out at or around ambient temperature and pressure. EDS process also operates without the need of hydrogen and catalyst as in HDS. More importantly, some BT and DBT sulphur compounds can be extracted quite efficiently [22]. The process does not change the chemical structure of the fuel oil components. The organosulphur components can be recovered at high concentration following the extraction process if the solvents chosen for such a process can be regenerated. Therefore, the extractive solvents should be sufficiently selective for absorption of sulphur compounds at high capacity without affecting the olefin contents in fuels [107]. As the equipment used is rather conventional without special requirements, the process can be easily integrated into the refinery [6]. Therefore, the EDS process can at least be a complementary technology to the HDS process [13], [22], [56], [61], [107].

The key to an EDS process is to find a good extractant featuring the following attributes, for example, good extractive ability for the sulphur compounds, ease of regeneration for the used extractant, contamination-free to the fuels, non-toxicity and environmentally benignity, and high stability for repetitive uses [7], [17]. Extractive desulphurization is based on the fact that organosulphur compounds are more soluble compared to hydrocarbons in an appropriate solvent. When the fuel and the extracting solvent are mixed together, the sulphur compounds are transferred from the fuel into the solvent due to their higher solubility in the solvent. The hydrocarbon is then separated from the solvent. The solvent is then distilled to remove the sulphur compounds that were extracted and with that the solvent is recycled. To make the process efficient, the solvent must be carefully selected to satisfy a number of requirements. The organosulphur compounds must be highly soluble in the solvent. The solvent must have a boiling temperature different than that of the sulphur containing compounds, and it must be inexpensive to ensure economic feasibility of the process [13], [22].

Regarding the EDS process some molecular solvents like polyalkylene glycol, imidazolidinone, pyrimidinone, and dimethyl sulfoxide, have been patented. However, their abilities for EDS are not sufficient and solubility in the fuel is noticeable, which may cause cross contamination. Compared to molecular solvents, some ILs show high extractability for sulphur compounds, which indicates that ILs might be a novel and competitive extractive solvent [61].

2.1.2.5 Extractive and catalytic oxidative desulphurization (ECODS)

In recent years, desulphurization of fuels by extraction using ILs have been reported. However the percentage of sulphur removal by extraction alone is rather low and in the range of 10-30% by only oil and ILs biphasic extraction [9]. Shuguang Zhang et al. [107], reported that the removal of sulphur compounds by extraction with the use of $AlCL_3$-TMAC IL was only 15-20%.This is due to the similarity between the sulphur compounds and the remaining fuels. The sulphur removal percentage can be increased by combining oxidative desulphurization and extractive desulphurization together with the use of ILs as the extracted reagent. Bosmann [90] described that $[Bmim]PF_6$, $[Bmim]BF_4$, and $[Bmim]OcSO_4$ were utilized as extractant in the extraction process. However the sulphur removal were only 12%, 16%, and 30%, respectively. A combination of chemical oxidation and extraction can change this situation and increase the sulphur removal percentage [59].

Wen-Hen Lo et al. [49], reported that the percentage of sulphur removal via oxidation or extraction alone was low, in the range of 10-30%, but when combining the two processes together the sulphur removal can reach up to 99%. They also reported that the percentage of sulphur removal was higher for ILs when compared to the percentage of sulphur removal when using volatile organic compounds such as dimethyl sulfoxide. The uses of volatile organic compounds raises environmental and safety concern as these solvents are flammable and fire hazardous. On the other hand, ILs are considered as “Green solvents”, because ILs have high melting points making them non-volatile.

Selective catalytic oxidation of sulphur species (to the corresponding sulfoxide and sulfone) combined with extraction is one of the most promising desulphurization approaches. Recently, Lu et al. have reported a catalyst $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$, assembled in an emulsion in diesel, could selectively oxidize BT, DBT, and their derivatives into their corresponding sulfones under mild conditions. The emulsion reaction systems as the reaction medium can overcome reagent incompatibility problems because of the high concentrations of both hydrophilic and hydrophobic compounds that can dissolved simultaneously and also provide a high interfacial area per unit volume, therefore the reaction rates in the emulsion system can be greatly increased [108].

Polymolydbates are efficient catalyst and are usually adopted in organic reaction. For example, alumina-supported polymolybdates have been for denitrogenation [84]. Peroxomolydbates have been employed in catalytic oxidation of tertiary amines, alkenes, and alcohols [110]. Peroxophosphomolydbate will be used in this research.

2.2 Recent development of ionic liquids as solvent for desulfurization process

Using of large amount of flammable and volatile organic compounds raises environmental and safety concerns. Therefore, ILs have become an alternative solution to this problem, by replacing these volatile organic solution.

It was stated by Liang Lu et al. [21], that the sulphur removal of DBT containing model oil can reach 60-93% under different reaction temperature for ODS in which IL $[HMIm]BF_4$ was used as a catalyst and solvent. The IL used was also recycled 6 times without a significant decrease in activity. This reaction was more superior to a simple extraction with IL alone. It was stated by Liang Lu et al that the sulphur removal of DBT containing model oil can reach 60-93% under different reaction temperature for ODS in which IL $[HMIm]BF_4$ was used as a catalyst and solvent. The IL used was also recycled 6 times without a significant decrease in activity. This reaction was more superior to a simple extraction with IL alone.

Yi Nie et al. [20], did a research on the N-butylimidazole-derived dialkylphosphate ILs on the extractive removal of aromatic sulphur compounds from fuel oils. The sulphur partition coefficient (K_N) between the IL and fuel at 298.15 K are determined experimentally over a wide range of sulphur content. The results obtained showed that the sulphur removal selectivity for a specific IL depends on the molecular structure of the sulphur compounds and follows the order of DBT>BT>3-MT. the efficiency of the ILs for the removal of aromatic sulphur compounds depends on the size and structure of both the cation and anion of the IL. It was reported that for the dialkylphosphate ILs studied with the same anion, the longer the alkyl substitute to the imidazolium ring, the higher the K_N value.

The extractive desulphurization process using ILs can be a complementary technology for the HDS process, with some studies reported. These studies indicate that the ILs have high extraction ratios and greater selectivity compared to molecular solvents because of the unique solvent characteristics of ILs [40].

It was reported by Yi Nie et al. [22], that imidazolium based phosphate ionic liquids showed a high sulphur removal for fuel. The ILs reported were [MMIM][DMP], [EMIM][DEP] and [BMIM][DMP]. In this experiment IL [BMIM][DMP] showed the best sulphur removal with a K_N value of 1.59 compared to [MMIM][DMP] and [EMIM][DMP] with a K_N values of 0.46 and 1.27, respectively. It was shown that the desulphurization ability of these ILs followed the order of [BMIM][DBP] > [EMIM][DEP] > [MMIM][DMP] and the sulphur removal selectivity for the sulphur compounds followed the order of DBT > BT > 3-MT. Considering the relatively high sulphur removal ability, immiscibility with fuel, low oil solubility, and hence small influence on the fuel composition as well as ease of being reclaimed by dilution with water, the imidazolium based phosphate ILs may be used as a promising solvent and worth recommendation for practical uses.

Xiaochuan Jiang et al. [7], studied the removal of sulphur compounds from gasoline using imidazolium base phosphate ILs. The three ILs used were n-methy-n-ethylimidazolium dimethylphosphate (EMIM[DMP]), n-ethyl-n-ethylimidazolium diethylphospahte (EEIM[DEP]) and n-butyl-n-ethylimidazolium dibutylphosphate (BEIM[DBP]). It was shown that these three ILs showed good desulphurization ability for the removal of 3-MT, BT and DBT out of fuel oils. The ability of these three IL followed the order of BEIM[DBP] > EEIM[DEP] > EMIM[DMP] with K_N value of 1.72, 1.61, and 1.17, respectively, and the sulphur removal selectivity for the sulphur compounds followed the order of DBT > BT > 3-MT. The results suggested that IL EEIM[DEP] might be a promising solvent for extractive desulphurization of fuel, considering its higher sulphur extractive ability, lower solubility for fuel and thus negligible influence on the constituent of fuels, and the ease of regeneration for the IL by dilution process [7].

Lo et al. [109], combined the ODS and EDS with ionic liquid $[BMIM]BF_4$ (1-butyl-3-methylimidazolium tetrafluoroborate) and $[BMIM]PF_6$ (1-butyl-3-methylimidazolium hexafluorophosphate) and hydrogen peroxide catalyzed with acetic acid as the oxidizing agent to remove DBT from the model oil. The results indicated that the sulphur concentration in the oil phase can be reduced effectively at 60-90^{o}C. Lu [98] and Zhao [99] studied the desulphurization system of acidic IL ($[HMin]BF_4$ and $[Hnmp]BF_4$) and hydrogen peroxide. They reported that the sulphur removal using the combination of oxidation and extraction method could reach more than 90%.

For the extraction process, the key to success is to find an effective IL that is nontoxic, chemically stable to moisture and air, and not expensive for commercial application. Considering these requirements, the imidazolium based phosphate ILs are advantageous as they are easy to be manufactured in the commercial scale with very high yield. Feng et al. [112], has studied the extraction performance of imidazolium-based phosphate ILs MMIM[DMP], EMIM[DEP] and BMIM[DBP] for the removal of sulphur compounds from model oil with encouraging results [22], [25], [111].

Sulphur removal ability of phosphate ILs are satisfactory in comparison with other ILs reported in literature, in addition to high desulphurization ability, these ILs also feature good stability, fluidity, non-toxicity and non-sensitivity moisture and air, which make them superior to ILs such as $[BMIM]CI/AlCI_3$ and $[BMIM][CU_2CI_3]$ [Yi Nie et al, 2006]. Even though $A1C1_3$ based ILs are effective for the removal of sulphur containing compounds, they often from dark precipitates by contacting compounds that contain thiols and cause darkened colour in processed fuels. Thus the application of this type of ILs is limited to the absorption of certain aromatic compounds such as dibenzothiophene [13].

CHAPTER 3

RESEARCH METHODOLOGY

Several alkyl imidazole based ionic liquids (ILs) with alkyl phosphate as the anion, were synthesized. The application of these ILs on the desulphurization process for the removal of sulphur species from model oil and also crude oil was also considered.

The experimental section is divided into two parts, synthesis and characterization of the ILs and application of the synthesized ILs for desulphurization of model oil and crude oil. Parameters, such as, temperature, reaction time, amount of catalyst, amount of hydrogen peroxide and the use of these ILs for desulphurization processes were also tested.

3.1 Materials and Chemicals

Table 3.1 lists all the chemicals used in the synthesis of the ILs, and their physical properties. All chemicals were used without drying nor further purification.

Table 3.1 Chemicals used in the synthesis of ILs

Chemical name	Purity (%)	Molar Mass (g/mol)	Density (g/cm^3)	Boiling poinnt (^{o}C)	Brand
1-Methylimidazole	-	82.11	1.030	198	Merck
2-Ethylimidazole	99	96.13	-	268	Acros Organic
1-butylimidazole	98	124.19	0.950	114	Sigma-Aldrich
Trimethyl phosphate	-	140.08	1.210	197	Merck
Triethyl phosphate	>99	182.16	1.060	215	Merck
Tributyl phosphate	>99	266.32	0.970	289	Merck
Diethyl ether	$\geq$99.7	74.12	0.714	35	Merck

3.2 Synthesis of alkyl-imidazolium-based phosphate ionic liquids

In this work, a recent synthetic path via direct combination for preparing the ILs was employed without using the metathesis approach [59]. The design of functionalized ILs via direct combination may reveal higher conversion and the ILs synthesized do not require further extensive purification since no by-products were produced along with the ILs [20], [22], [61].

In order to study the effect of alkyl chain length in the ILs on sulphur removal efficiency from model oil and crude oil, ILs having imidazolium and phosphate portion with different chain length were synthesized.

Figure 3.1 represents the synthesis route of the imidazolium based phosphate ILs. A certain amount of alkyl imidazole as can be seen in Table3.2, was added to a 250 ml three necked round bottom flask immersed in a heating oil bath, which was equipped with a nitrogen inlet adapter, an internal thermometer adapter, an overhead mechanical stirrer, and a reflux condenser. This was followed by drop-wise addition of equal molar amount of trialkylphosphate using a syringe.

Calculation for the synthesis of all eight ILs are shown in Appendix A. All materials were loaded into a syringe and injected into the three-neck round bottom flask, except 2-ethylimidazole which was weighed, as it was in solid form [20].

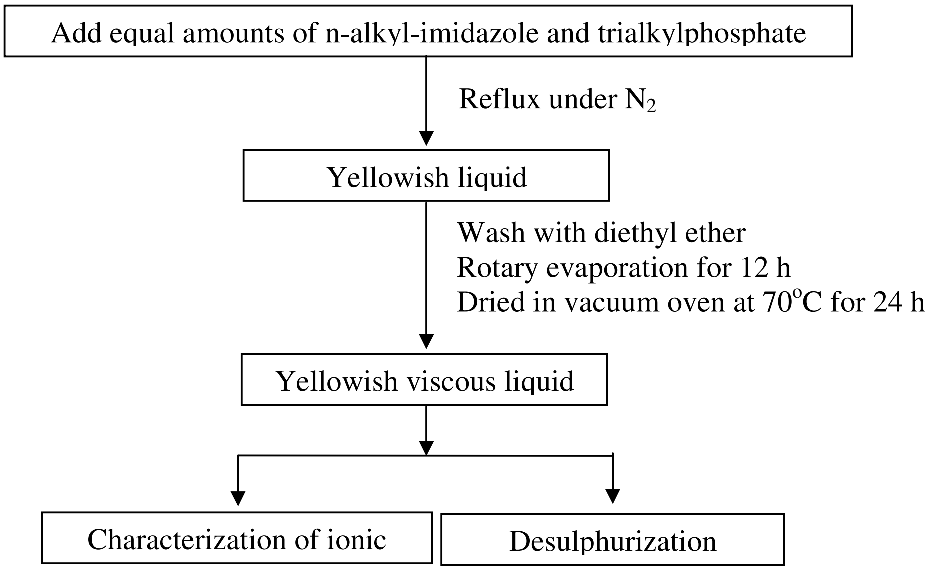


Figure 3.1 Flow diagram of the synthesis of ILs [20].

The mixture was stirred under N_2 gas at a certain temperature and time, depending on the type of IL synthesized. The temperature and time needed for each IL are tabulated in Table 3.2. The end product, a yellowish brown liquid was cooled to room temperature before washing with diethyl ether. This was followed by rotary evaporation under reduced pressure for 12 h, in order to remove any volatile residues (un-reacted reactants and diethyl ether). After the evaporation process has completed, the IL was dried in a vacuum oven at 70°C for 24 h. The IL was then analyzed to confirm the general structure and purity by ^{1}H-NMR and ^{13}C-NMR [22]. The structure of all eight ILs are shown in Appendix B.

Table 3.2 Reactant used to synthesize IL.

Amount of starting material		Conditions	IL synthesized
Alky imidazole	Trialkyl phosphate		
1-methylimidazole 39.86 cm^3 (0.5 mol)	Trimethylphosphate 57.79 cm^3 (0.5 mol)	100°C 72 h	1-methyl-3-methyl-imidazolium dimethylphosphate (MMIM[DMP])
1-methylimidazole 31.89 cm^3 (0.4 mol)	Triethylphosphate 68.19 cm^3 (0.4 mol)	100°C 48 h	1-methyl-3-ethyl-imidazolium diethylphosphate (EMIM[DEP])
1-methylimidazole 39.22 cm^3 (0.3 mol)	Tributylphosphate 81.78 cm^3 (0.3 mol)	110°C 72 h	1-methyl-3-butyl-imidazolium dibutylphosphate (BMIM[DBP])
2-ethylimidazole 38.45 g (0.4 mol)	Trimethylphosphate 46.23 cm^3 (0.4 mol)	90°C 72 h	1-ethyl-3-methyl-imidazolium dimethylphosphate (EMIM[DMP])
2-ethylimidazole 28.84 g (0.3 mol)	Triethylphosphate 51.17 cm^3 (0.3 mol)	80°C 96 h	1-ethyl-3-ethyl-imidazolium diethylphosphate (EEIM[DEP])
1-butylimidazole 58.83 cm^3 (0.45 mol)	Trimethylphosphate 52.01 cm^3 (0.45 mol)	65°C 72 h	1-butyl-3-methyl-imidazolium dimethylphosphate (BMIM[DMP])
1-butylimidazole 45.75 cm^3 (0.35mol)	Triethylphosphate 59.70 cm^3 (0.35 mol)	95°C 72 h	1-butyl-3-ethyl-imidazolium diethylphosphate (BEIM[DEP])
1-butylimidazole 52.30 cm^3 (0.4 mol)	Tributylphosphate 59.70 cm^3 (0.4 mol)	85°C 6 days	1-butyl-3-butyl-imidazolium dibutylphosphate (BBIM[DBP])

3.3 Characterization of the ionic liquids

Characterization of the ILs was carried out to determine the physical and chemical properties of the ILs prepared. The characterization was conducted using nuclear magnetic resonance (NMR), differential scanning calorimeter (DSC), Carbon, hydrogen, nitrogen and sulphur element analyzer (CHNS), viscosity and density meter and Karl Fisher Coulometric

3.3.1 ^{1}H NMR and ^{13}C NMR

For ^{1}H, 20 mg IL is dissolved in about 600 µL to 1000 µL of deuterated solvent ($CDCl_3$). For ^{13}C NMR five times the concentration was needed, because ^{13}C is five thousand times less sensitive than ^{1}H. After the IL has been dissolved it can was transferred directly to a NMR tube by passing the solution through the cotton filter or a kimwipe in the end of a pipette. Finally, the sample volume can be adjusted by adding the remaining solvent to the NMR tube so that a final sample volume is about 700 µL or a sample height of about 4.5 cm is reached. This is followed by vigorous shaking of the sample to effectively mix its content.

^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Spectrospin Avance DPX-400 spectrometer. The ^{1}H NMR spectra were recorded with a 200 and a 400 MHz and ^{13}C NMR spectrum were recorded with a 50 and a 100 MHz using $CDCl_3$ and D_2O. ^{1}H NMR chemical shifts are expressed in parts per million (δ) relative to the $CDCl_3$ ($\delta = 7.26$) and ^{13}C NMR chemical shifts are expressed in parts per million (δ) relative to the $CDCl_3$ resonance ($\delta = 77.0$) and D_2O as the internal standards.

3.3.2 Differential Scanning Calorimeter (DSC)

Differential scanning calorimeter (DSC), is used to the determination of melting point of ILs [120].

Measurements of phase-transition temperatures was done with a Mettler-Toledo differential scanning calorimeter (DSC), model DSC822. The instrument was calibrated for temperature and heat flow with zinc and indium reference samples provided by Mettler-Toledo. An empty aluminium pan was used as the reference. The samples inside the differential scanning calorimeter furnace were exposed to flowing N_2 atmosphere. Samples were dried in situ on the differential scanning calorimeter by holding the samples at 200°C for 1-3 h. This is important because the presence of volatiles, especially water, can affect the melting temperatures [113]-[115], [118]. Measurements for melting temperatures were determined by heating the samples from -120°C to 200°C, at a rate of 10°C/min. The melting temperatures were determined as the onset of the transition [118].

3.3.3 CHNS Analyzer

The presence of carbon (%C), hydrogen (%H), nitrogen (%N) and sulphur (%S) content in the ILs were determined by using the Leco-CHNS-932 analyzer, according to the approved standard method ASTM D-5291. The ILs were weighed (less than 2 mg) in a silver capsule containing a sorbid pad. The capsule was folded and then analyzed. The equipment settings are as follow; Oxygen dose: 20cc, oxidation furnace temperature: 1000°C, reduction furnace temperature 650°C, and helium gas was used as the carrier gas for the instrument. This method is also used to determine the % of sulphur in model oil and crude oil before and after the desulphurization process.

3.3.4 Density and Viscosity meter

Other important properties of the ILs such as the density and the viscosity were determined by using the SVM 3000 Anton Paar viscometer. The density of ILs was measured with an Anton Paar, Oscillating U-tube density meter, from of 20 to 80°C with an uncertainty of $\pm$ 0.01°C. The apparatus was calibrated by measuring the density of Millipore quality water at regular intervals according to the supplier instructions. The calibrated apparatus was also verified using few pure organic liquids of known densities. The overall precision in experimental density measurements for all samples was found to be better than $\pm 2 \times 10^{-5}$ g.cm^{-3}.

3.3.5 Coulometric Karl-Fisher

The water contents of ILs were investigated using a coulometric Karl Fischer titrator, DL 39 (Mettler Toledo), using Hydranal coulomat AG reagent (Riedel-de Haen). 5 mL of IL samples are transferred into a syringe. The determination is started at the KF coulometer (or KF titrator). The samples are injected into the titration cell through the septum stopper and readings were taken. Each measurement was made in triplicate and the values are reported as an average with an accuracy of 5% [116]

3.4 Desulphurization Process

Three different desulphurization methods were employed for model oil and the results are compared. The desulphurization methods were oxidative desulphurization (ODS), extractive desulphurization (EDS) and extractive catalytic oxidative desulphurization (ECODS).

3.4.1 Materials and Chemicals

The chemicals used in this part were sulphur species (BT, DBT, 3-MT), dodecane, sodium molybdate dihydrate ($Na_2MoO_4.2H_2O$) as catalyst and hydrogen peroxide (H_2O_2). Table 3.3 lists all the chemicals used with their physical properties.

Table 3.3 Reactant used with their physical properties.

Chemical name	Purity (%)	Molar mass (g/mol)	Density (g/cm^3)	b.p. (^{o}C)	Brand
3-Methylthiophene (3-MT)	99.0+	98.160	-	115-117	Acros Organic
Thianaphthene/ Benzothiophene (BT)	97.0	134.20	1.140	221-222	Acros Organic
Thiophene / Dibenzothiophene (DBT)	99.5	184.26	1.051	84	Acros Organic
Hydrogen Peroxide (H_2O_2)	30.0 %wt	34.000	1.110	107	Merck
Sodium molybdate dehydrate (extra pure)	99.9	241.95	2.710	Not applicable	Merck

3.4.2 Preparation of Model Oil

The model oil used in this study was n-dodecane spiked with dibenzothiophene (DBT), benzothiophen (BT) or 3-Methylthiophene (3-MT) as the sulphur containing compounds.

In order to prepare the model oil with a concentration of 1000 ppm of sulphur using DBT, 1.4470 g of DBT was weighed and then dissolved in n-dodecane and diluted to 250 ml in a volumetric flask. Model oil containing BT and 3-MT with the same concentration as DBT (1000 ppm) were also prepared. For the model oil with 1000 ppm of sulphur in the form of BT, 0.10809 g of BT was dissolved in n-dodecane and diluted to 25 ml in a volumetric flask. 1000 ppm of sulphur in the form of 3-MT was prepared by dissolving 0.07746 g of 3-MT in n-dodecane and diluted to 25 ml. Calculation for the preparation of model oil can be seen in Appendix C.

Model oils with different sulphur content (1%, 2% and 3%) were prepared using 1.0809 g, 2.1620 g and 3.2426 g of BT respectively. The model oils were then analyzed using the CHNS analyzer to confirm the sulphur content in model oil.

The accuracy of the CHNS instrument is ± 0.01% for the measurement of the CHN and S. It was calibrated with an acentanilide standard for carbon, hydrogen, and nitrogen and with a sulfamethazine standard for sulphur. The results from these experiments were normalized to 100% without considering the presence of oxygen. The standards were analyzed with 1 ± 0.1 mg of a weighed sample loaded in a silver capsules. The samples were analyzed with 1 ± 0.1 mg of sample. The average of five measurements of each sample was reported as the CHNS measurement of each sample [117].

3.4.3. Extractive catalytic oxidative desulphurization process (ECODS)

A combination of extractive and catalytic oxidative desulphurization (ECODS) using IL was used to remove sulphur compound DBT from model oil. ECODS method was selected because sulphur removal by either extractive desulphurization (EDS) or Oxidative desulphurization (ODS) are low. It has been reported that the combination of the two methods can increase the sulphur removal significantly [49], [59], [108]-[110].

3.4.3.1 Ionic Liquids Screening

In this part, the ILs synthesized in the first part were screened for the extractive and catalytic oxidative desulphurization process (ECODS) at room temperature using model oil containing DBT. The reaction was monitored for 8 h with sampling conducted every one hour interval to determine the equirilibium of the reaction and to determine the optimum reaction time. This was done in order to identify the best ILs among the eight that were synthesized. The desulphurization process was divided into two sections, namely, testing the parameters to obtain optimum conditions for the desulphurization process and testing the ability of the ILs selected for other desulphurization processes.

ECODS process was carried out in a 50 ml centrifugal tube. 0.00378 g of sodium molybdate dihydrate $[(n_{S_{DBT}}/n_{Cat})=20]$ was weighed and added to 2 ml of IL in the centrifuge tube. 0.12770 ml of 30% wt H_2O_2 $[(n_{H2O2}/n_{S_{DBT}})=4]$ was added to the mixture and stirred well. Calculations can be seen in Appendix D. 10 mL of model oil was then added and the mixture was left to stir at room temperature for 8 h. At every 1 hour interval, the mixture was centrifuged to separate the IL phase and oil phase. Samples were taken from the oil phase (upper phase) using a syringe and the sulphur contents were analyzed using the CHNS analyzer. The reaction time was determined during the selection of IL as mentioned above. A graph was plotted against time and the reaction time was determined from the graph. Figure 3.2 summarizes the ECODS process.

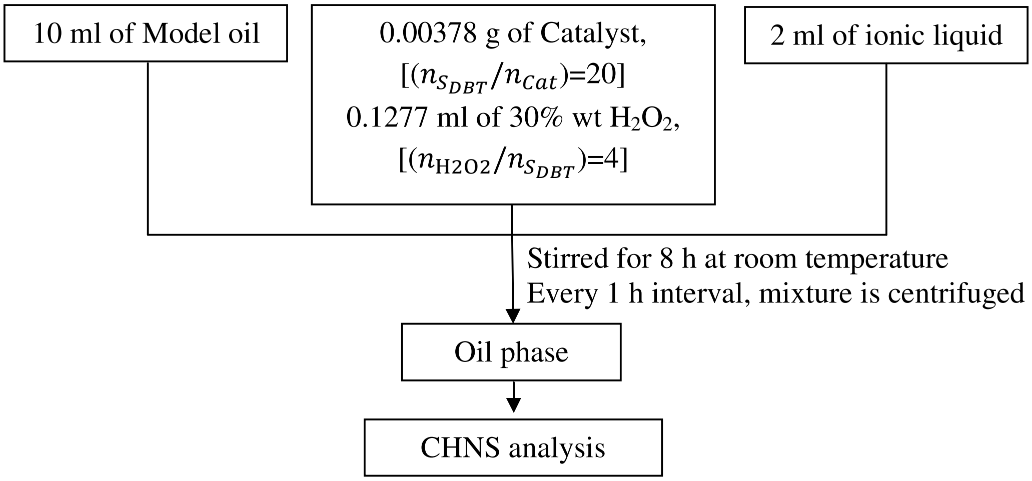


Figure 3.2 Flow diagram of the ECODS process.

Further studies were conducted to determine the effect of temperature, amount of H_2O_2, amount of catalysts, type of sulphur species, and different percentage of sulphur compounds in the model oil on the efficiency of ECODS, as can be seen in Figure 3.3.

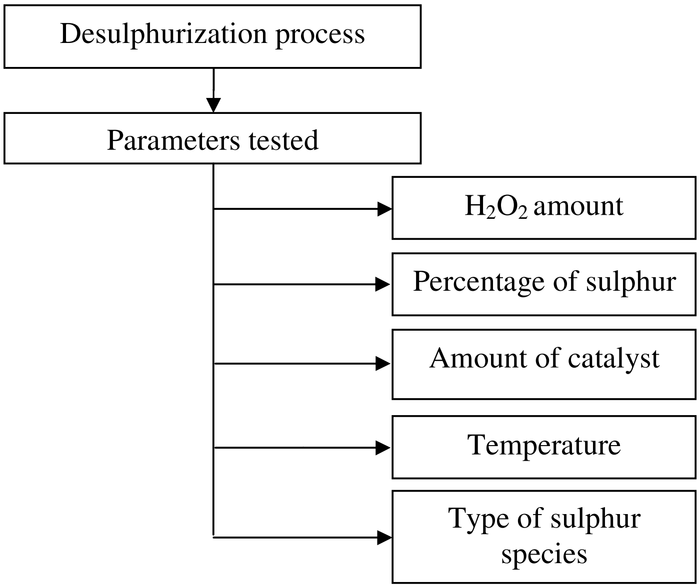


Figure 3.3 Flow diagram of the ECODS parameters.

3.4.3.2 Effect of temperature

To investigate the effect of temperature on the efficiency of the ECODS process, the reaction was conducted at various temperature, 40°C, 60°C, 70°C and 80°C, with the best IL BBIM[DBP], identified from the previous section. The ECODS process was carried out in 50 ml centrifuge tubes. 0.00378 g of sodium molybdate dihydrate [$(n_{S_{DBT}}/n_{Cat})$=20] was weighed and added to 2 ml of ionic liquid in the centrifuge tube. 0.12770 ml of 30% wt H_2O_2 [$(n_{\mathrm{H2O2}}/n_{S_{DBT}})$=4] was added to the mixture and stirred well. 10 ml of model oil was then added and the centrifuge tube was left to stir at different temperatures for 6 h. This was the time equilibrium taken from the ILs screening. Every 1 h interval the mixture was centrifuged to separate the IL and model oil phase. Samples were taken using a syringe from the model oil phase and analyzed using the CHNS analyzer.

3.4.3.3 Effect of the amount of H_2O_2

Different amounts of H_2O_2 were used to study the effect on the ECODS process. 30 wt % H_2O_2 with different amounts $[(n_{\mathrm{H2O2}}/n_{S_{DBT}})$=2, 4, 6] and 0.00378 g of catalyst $[(n_{S_{DBT}}/n_{Cat})$=20] was added to 2 ml of ILs BBIM[DBP], BEIM[DEP] and EEIM[DEP]. 10 ml of model oil that contained DBT as the sulphur compound with a percentage of 1000 ppm was added to the ILs mixture. The mixtures were stirred vigorously at temperature of 70°C (identified from section 3.4.3.2) for 4 hours. Temperature and time, were taken from the previous experimental, as the optimum condition. After 4 h the mixtures were centrifuged and the oil phase was withdrawn and analyzed with CHNS**.** Calculation for the effect of the amount of H_2O_2 are shown in Appendix E.

3.4.3.4 Effect of the amount of catalyst

Based on the results from section 3.4.3.3, the optimum ratio of H_2O_2:DBT was 4. Therefore, 0.1277 ml of 30 wt % H_2O_2 $[(n_{\mathrm{H2O2}}/n_{S_{DBT}})$=4] and different amount of catalyst ratio $[(n_{S_{DBT}}/n_{Cat})$=10, 20, 40, 60, 80, 100] was added to 2 ml of ILs BBIM[DBP], BEIM[DEP] and EEIM[DEP]. 10 ml of model oil that contained DBT as the sulphur compound with a percentage of 1000 ppm was added to the ILs mixture. The mixtures were stirred vigorously at a temperature of 70°C for 4 h. After 4 h the mixtures were centrifuged and the oil phase was withdrawn and analyzed with CHNS**.** Calculations can be seen in Appendix F.

3.4.3.5 Effect of types of sulphur species in model oil

0.1277 ml of 30 wt % H_2O_2 $[(n_{\mathrm{H2O2}}/n_s)$=4] and 0.00378 g of catalyst $[(n_s/n_{Cat})$=20] was added to 2 ml of ionic liquids BBIM[DBP], BEIM[DEP] and EEIM[DEP]. 10 ml of model oil that contained DBT, BT and 3-MT as the sulphur compounds with a percentage of 1000 ppm was added to the ILs mixture. The mixtures were stirred vigorously at room temperature for 4 h at 70°C. After the reaction completed the mixtures were centrifuged and the oil phase was withdrawn and analyzed with CHNS to determine sulphur percentage (S %)**.** Calculation can be seen in Appendix G.

3.4.3.6 Effect of different initial sulphur concentration

1.277 ml, 2.553 ml and 3.830 ml of 30 wt % H_2O_2 [($n_{H2O2}/n_{S_{BT}}$)=4] and 0.03780 g, 0.07560 g and 0.11340 g of catalyst [($n_{S_{BT}}/n_{Cat}$)=20] was added to 2 ml of ILs BBIM[DBP], BEIM[DEP] and EEIM[DEP]. 10 ml of model oil that contained BT with different percentage, that is 1 %, 2% and 3% was added to the ILs mixture. The mixtures were stirred vigorously at room temperature for 4 h at 70^{o}C. After the reaction has completed, the mixtures were centrifuge and the oil phase was withdrawn and analyzed with CHNS**.** Calculation can be seen in Appendix H.

3.4.3.7 Product identification

For product identification, GC-MS was used to determine the oxidation of sulphur species (DBT) in the ionic liquid phase.

A Hewlet Packard model 6890N Gas Chromatography/ Mass Spectroscopy Detector system (GC-MSD) was used for the identification of sulphur and corresponding sulfones formed during the ECODS. The GC-MSD was set up with column DB-1, 60 m, 0.25 mm ID, 0.25 mm film thickness. The GC temperature program used was T_i=80°C for 3 minutes. The temperature was then ramped @3°C/min to 320°C and held for 20 minutes. The carrier gas used was Helium at 1.3ml/min. Injection temp was set at 250°C. The MS parameters were as follows: total scan from 20 to 600 mass units at a scan rate of 2.56scan/sec, EIectrical energy 70eV, MS source temp 230°C.

3.4.4. Oxidative desulphurization process (ODS)

3.4.4.1 H_2O_2 as the oxidizing agent

In 50 ml centrifuge tubes 2 ml of IL BBIM[DBP], BEIM[DEP] and EEIM[DEP] were mixed with 0.1277 ml of H_2O_2 [($n_{H2O2}/n_{S_{DBT}}$)=4]. 10 ml of model oil containing 1000 ppm DBT was then added. The mixtures were left to react at of 70^{o}C for 4 h. The mixtures were then centrifuged and the oil phase was withdrawn for analysis.

3.4.4.2 Catalyst as the oxidizing agent

A second reaction was conducted by adding the catalyst. 0.00378 g of catalyst $[(n_{S_{DBT}}/n_{Cat})$=20] was added to 2 ml of IL BBIM[DBP], BEIM[DEP] and EEIM[DEP]. 10 ml of model oil containing 1000 ppm DBT was then added. The mixtures were then left to react at 70^0C for 4 h. After the reaction has completed, the mixture was centrifuged and the oil phase was withdrawn for analysis.

3.4.5. Extractive desulphurization process (EDS)

2 ml of IL BBIM[DBP], BEIM[DEP] and EEIM[DEP] and 10 ml of model oil were added into 50 ml centrifuge tubes. The mixtures were stirred for 4 h, at of 70^0C. After the reaction has completed the mixtures were centrifuged and the oil phase was withdrawn and analyzed by using the CHNS analyzer for S %.

3.4.6. Desulphurization process with crude oil

In order to investigate the ability of the selected ionic liquid BBIM[DBP] for sulphur removal in the ECODS process, the model oil was substituted with crude oil.

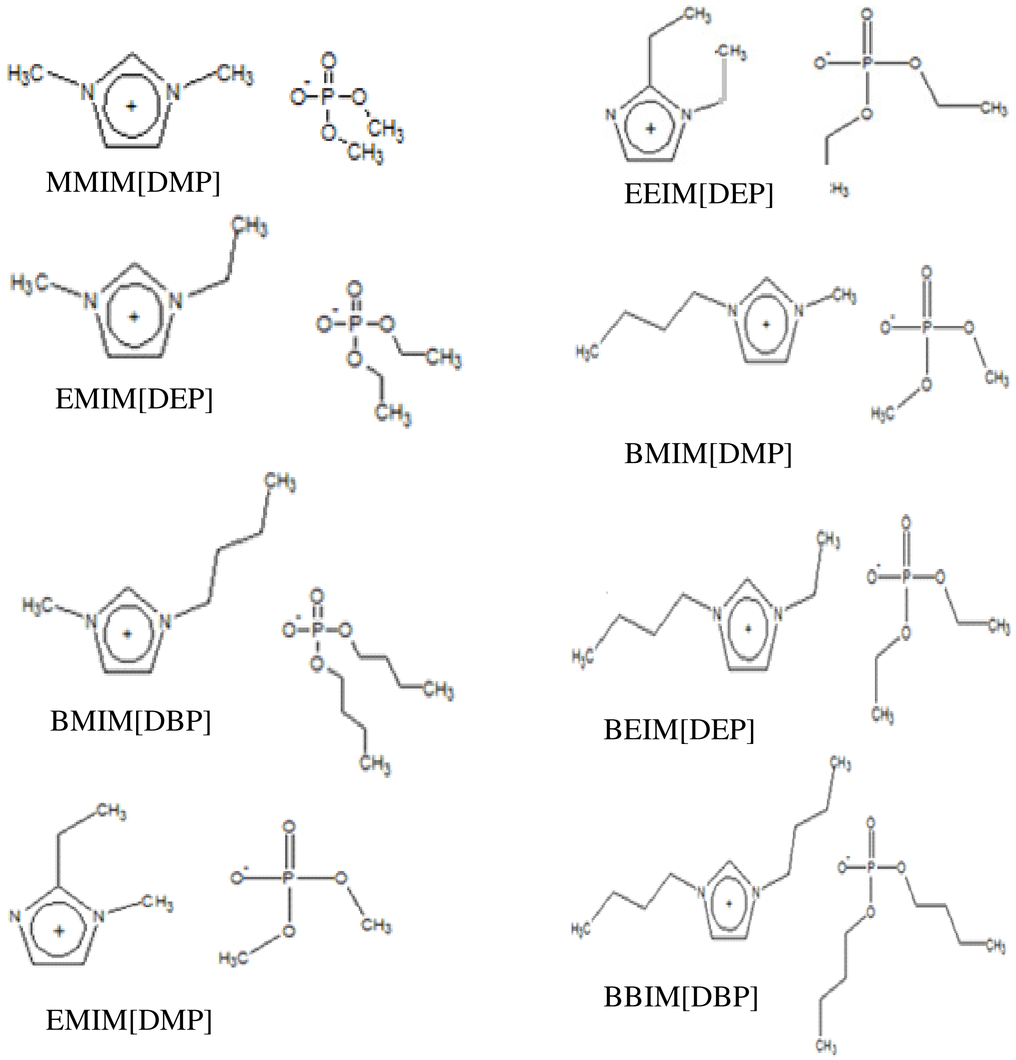
The ECODS process was carried out in a 50 ml centrifuge tube. The concentration of sulphur in the crude oil was 4.3%. 0.16256 g of sodium molybdate dihydrate $[(n_s/n_{Cat})$=20] was weighed and added to 2 ml of IL in the centrifuge tube. 5.4896 ml of H_2O_2 $[(n_{\mathrm{H2O2}}/n_s)$=4] was added to the mixture and stirred well. 10 ml of crude oil was then added and the centrifuge tube was left to stir at a temperature of 70°C for 4 h. The mixture was centrifuged to separate the IL and oil phase. Samples were taken using a syringe from the oil phase (upper phase) and analyzed by using the CHNS analyzer. Calculations can be seen in Appendix I

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Ionic liquid synthesis

Eight imidazolium based phosphate ionic liquids were synthesized namely, 1-methyl-3-methyl-imidazolium dimethylphosphate (MMIM[DMP]), 1-methyl-3-ethyl-imidazolium diethylphosphate (EMIM[DEP]), 1-methyl-3-butyl-imidazolium dibutylphosphate (BMIM[DBP]), 1-ethyl-3-methyl-imidazolium dimethylphosphate (EMIM[DMP]), 1-ethyl-3-ethyl-imidazolium diethylphosphate (EMIM[DEP]), 1-butyl-3-methyl-imidazolium dimethylphosphate (BMIM[DMP]), 1-butyl-3-ethyl-imidazolium diethylphosphate (BEIM[DEP]) and 1-butyl-3-butyl-imidazolium dibutylphosphate (BBIM[DBP]), their structures displayed in Figure 4.1. The synthesis procedures for alkyl imidazolium based phosphate ionic liquids were obtained elsewhere [20], [22], [61].



MMIM[DMP]

EEIM[DEP]

EMIM[DEP]

BMIM[DMP]

BMIM[DBP]

BEIM[DEP]

EMIM[DMP]

BBIM[DBP]

Figure 4.1 Structure of the ionic liquids synthesized.

4.2 Identification of ILs

All the ILs were characterized by using proton and carbon nuclear magnetic resonance analysis (^{1}H-NMR) and (^{13}C-NMR), to determine their structures and purity. The results are as shown in Table 4.1 below. The ^{1}HNMR and ^{13}C-NMR spectra are provided in Appendix J. All the eight ILs were successfully prepared.

Table 4.1 ^{1}HNMR and ^{13}C-NMR result of the synthesized ILs

Structure code	Molecular formula	^{13}C-NMR (100 MHz, D_2O, Me_4Si)δ	^{1}H-NMR (400 MHz, D_2O, Me_4Si)δ
MMIM [DMP]	$C_7H_{15}N_2O_4P$	35.32, 35.74 (N***C***H_3) 52.60, 52.67 (PO***C***H_3) 35.31, 35.66 (N***C***H_3) 123.09, 123.57 (N***C***H***C***HN) 136.28 (N***C***HN)	8.56 (s, 1H) 7.34 (s, 1H) 7.33 (s, 1H) 3.80 (s, 6H) 3.49,3.46 (d, 6H)
EMIM [DEP]	$C_{10}H_{21}N_2O_4P$	14.57 (NCH_2***C***H_3) 15.41 (POCH_2***C***H_3) 15.78 (POCH_2***C***H_3) 35.31, 35.66 (N***C***H_3) 44.70 (N***C***H_2CH_3) 62.14, 62.19 (PO***C***H_2CH_3) 122.03, 123.16 (N***C***H***C***HN) 135.29 (N***C***HN)	8.60 (s, 1H) 7.38 (s, 1H) 7.31 (s, 1H) 4.12 (t, 2H) 3.83,3.81(m, 4H) 3.79 (s, 3H) 1.37 (s, 3H) 1.16, 1.14 (s, 6H)

Structure code	Molecular formula	^{13}C-NMR (100 MHz, D_2O, Me_4Si)δ	^{1}H-NMR (400 MHz, D_2O, Me_4Si)δ
BMIM [DBP]	$C_{16}H_{33}N_2O_4P$	12.81 ($NCH_2CH_2CH_2\boldsymbol{C}H_3$) 13.17 ($POCH_2CH_2CH_2\boldsymbol{C}H_3$) 18.34 ($NCH_2CH_2\boldsymbol{C}H_2CH_3$) 18.70 ($POCH_2CH_2\boldsymbol{C}H_2CH_3$) 31.22 ($NCH_2\boldsymbol{C}H_2CH_2CH_3$) 31.91, 31.99($POCH_2\boldsymbol{C}H_2CH_2CH_3$) 35.33 ($N\boldsymbol{C}H_3$) 49.24 ($N\boldsymbol{C}H_2CH_2CH_2CH_3$) 65.90, 65.96 ($PO\boldsymbol{C}H_2CH_2CH_2CH_3$) 122.40, 123.23 ($N\boldsymbol{C}HCHN$) 135.57 ($N\boldsymbol{C}HN$)	8.62 (s, 1H) 7.39 (s, 1H) 7.34 (s, 1H) 4.10 (t, 2H) 3.80,3.76(m, 7H) 1.75 (m, 2H) 1.53,1.49(m, 4H) 1.29 (m,4H) 1.21 (m, 2H) 0.83 (m, 9H)
EMIM [DMP]	$C_8H_{17}N_2O_4P$	16.43, 16.21($POCH_2\boldsymbol{C}H_3$) 34.44 ($N\boldsymbol{C}H_3$) 42.31 ($N\boldsymbol{C}H_2CH_3$) 53.64($NCH_2\boldsymbol{C}H_3$) 118.28, 121.62 ($N\boldsymbol{C}HCHN$) 148.86 ($N\boldsymbol{C}HN$)	8.76 (s, 1H) 7.16, 7.15 (s, 2H) 3.64 (s, 3H) 3.47 (s, 3H) 3.44 (s, 3H) 2.86 (q, 2H) 1.23 (t, 3H)
EEIM [DEP]	$C_{11}H_{23}N_2O_4P$	10.16 ($NCH_2\boldsymbol{C}H_3$) 14.72, 15.69 ($POCH_2\boldsymbol{C}H_3$) 16.16 ($NCH_2\boldsymbol{C}H_3$) 18.41 ($N\boldsymbol{C}H_2CH_3$) 42.94 ($N\boldsymbol{C}H_2CH_3$) 62.53, 62.91($PO\boldsymbol{C}H_2CH_3$) 118.02, 120.36 ($N\boldsymbol{C}HCHN$) 148.86 ($N\boldsymbol{C}HN$)	8.78(s, 1H) 7.26(s, 1H) 7.16(s, 1H) 4.04(t, 2H) 3.80(m, 4H) 2.83(t, 2H) 1.31, 1.21(t, 6H) 1.13, 1.11(t, 6H)
BMIM [DMP]	$C_{10}H_{21}N_2O_4P$	12.71 ($N\boldsymbol{C}H_2CH_2CH_2CH_3$) 18.67 ($NCH_2\boldsymbol{C}H_2CH_2CH_3$) 31.20 ($NCH_2CH_2\boldsymbol{C}H_2CH_3$) 35.33 ($NCH_2CH_2CH_2\boldsymbol{C}H_3$) 49.20 ($N\boldsymbol{C}H_3$) 52.62, 52.69 ($PO\boldsymbol{C}H_3$) 122.36, 123.18 ($N\boldsymbol{C}HCHN$) 135.58 ($N\boldsymbol{C}HN$)	8.60(s, 1H) 7.37,7.32(m, 2H) 4.08(t, 2H) 3.78(s, 3H) 3.48,3.45(d, 6H) 1.74(m, 2H) 1.21(q, 2H) 0.81(t, 3H)

Structure code	Molecular formula	^{13}C-NMR (100 MHz, D_2O, Me_4Si)δ	^1H-NMR (400 MHz, D_2O, Me_4Si)δ
BEIM [DEP]	$C_{13}H_{27}N_2O_4P$	12.40 ($NCH_2CH_2CH_2\boldsymbol{C}H_3$) 15.76,15.35,14.25 ($NCH_2\boldsymbol{C}H_3$,$POCH_2\boldsymbol{C}H_3$) 18.70 ($NCH_2\boldsymbol{C}H_2CH_2CH_3$) 31.19 ($NCH_2CH_2\boldsymbol{C}H_2CH_3$) 44.72 ($N\boldsymbol{C}H_2CH_2CH_2CH_3$) 49.23 ($NCH_2CH_3$) 62.12, 62.17 ($PO\boldsymbol{C}H_2CH_3$) 122.09, 122.01 ($N\boldsymbol{C}H\boldsymbol{C}HN$) 134.51 ($N\boldsymbol{C}HN$)	8.66 (s, 1H) 7.39,7.37 (d, 2H) 4.10,4.0 (m, 4H) 3.81,3.79(m, 4H) 1.74 (t, 2H) 1.39 (t, 3H) 1.21 (m, 2H) 1.16,1.14(m, 6H) 0.81 (t, 3H)
BBIM [DBP]	$C_{19}H_{39}N_2O_4P$	12.06,12.41 ($NCH_2CH_2CH_2\boldsymbol{C}H_3$) 12.81,13.20 ($POCH_2CH_2CH_2\boldsymbol{C}H_3$) 17.79,18.36 ($NCH_2CH_2\boldsymbol{C}H_2CH_3$) 18.74,19.15 ($POCH_2CH_2\boldsymbol{C}H_2CH_3$) 31.14,31.23 ($NCH_2\boldsymbol{C}H_2CH_2CH_3$) 31.78,31.91 ($POCH_2\boldsymbol{C}H_2CH_2CH_3$) 48.90,49.58 ($N\boldsymbol{C}H_2CH_2CH_2CH_3$) 65.24, 65.84 ($PO\boldsymbol{C}H_2CH_2CH_2H_3$) 122.12, 122.52 ($N\boldsymbol{C}H\boldsymbol{C}HN$) 134.87 ($N\boldsymbol{C}HN$)	8.63 (s, 1H) 7.34 (s, 2H) 4.06,4.04 (d, 4H) 3.72,3.70 (d, 4H) 1.69 (m, 4H) 1.45 (m, 4H) 1.23 (m, 4H) 1.16 (m, 4H) 0.78,0.76,0.75,0.74 (t, 12H)

4.3 Melting point

The melting points of imidazolium-based-phosphate ILs were determined using DSC, and their values are tabulated in Table 4.2. A representative DSC thermogram is shown in Figure 4.2 for IL BBIM[DBP]. All the other thermograms are displayed in Appendix K.

Table 4.2 Melting points of imidazolium-based phosphate ILs

Structure code	m.p. (°C)
MMIM[DMP]	149.10
EMIM[DEP]	147.20
BMIM[DBP]	146.50
EMIM[DMP]	122.28
EEIM[DEP]	145.82
BMIM[DMP]	119.65
BEIM[DEP]	109.30
BBIM[DBP]	151.11

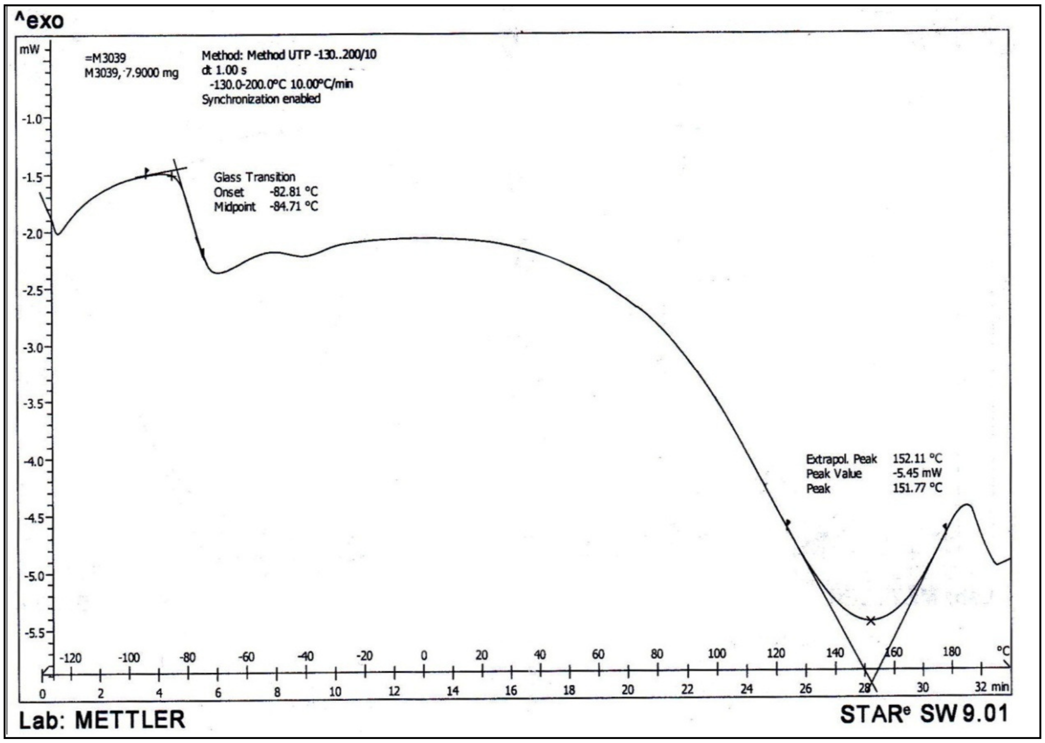


Figure 4.2 DSC thermogram for 1-butyl-3-butylimidazolium dibutylphosphate (BBIM[DBP])

Based on the data, it is found that for ILs with the same anion, [DMP], but different cation i.e. MMIM[DMP], EMIM[DMP] and BMIM[DMP]. The different length of the substituted alkyl group, i.e, methyl, ethyl and butyl, affects the melting points. Increase in the length of the alkyl chain (MMIM[DMP], EMIM[DMP] and BMIM[DMP]), results in the decrease of the melting point from 149.10, 122.28, to 119.65°C for the respective IL. Similar observation was reported for the EMIM[DEP], EEIM[DEP], and BEIM[DEP], where increasing the alkyl chain length, decreases the melting point according to methyl>ethyl>butyl, with the measured melting point of 147.20, 145.82 and 109.30°C, respectively [119], [120]. However, when comparing ionic liquid BMIM[DBP] and BBIM[DBP], there is an increase in the melting point from 146.50 to 151.11°C, instead of a decrease. This may be due to the larger cation , having more asymmetrical, which increases the melting point [119].

When comparing ILs with the same cation but different anion, it was observed that the melting point increased when the length of the alkyl chain in the anion increased. When comparing ionic liquid EMIM[DMP] with EMIM[DEP] and BMIM[DMP] with BMIM[DBP], it can be seen that by increasing the alkyl chains in the anion from methyl to ethyl, the melting point increases. For ionic liquid with cation EMIM, but different anion DMP and DEP, the melting point was 122.28°C and 147.2°C, respectively. The melting point for BMIM[DMP] and BMIM[DBP] was 119.65°C and 146.50°C respectively. ILs melting point increased as the length of the anion side chain is increased, because increasing the alkyl chain gives stronger inter-molecular van der Waals forces, which gives rise to greater melting points of chains. This trend can also be explained in terms of cation-anion interactions in ionic liquids, such as van der Waals forces, hydrogen bonding and electrostatic forces [120-121].

4.4 CHNS analysis

CHNS analyzer was used to determine the element content as can be seen in Appendix L, of the synthesized ILs. The values are in agreement with their respective theoretical values. Table 4.3 shows the results of CHNS analysis of the eight IL.

Table 4.3 CHNS results for the eight imidazolium based phosphate ILs.

IL		C (%)	H (%)	N (%)	S (%)
MMIM[DMP]	Experimental	37.78 ± 0.02	6.81 ± 0.01	12.37 ± 0.04	0.00 ± 0.00
	theoretical	37.84	6.76	12.61	0.00
EMIM[DEP]	Experimental	45.50 ± 0.04	7.98 ± 0.05	10.77 ± 0.01	0.00 ± 0.00
	theoretical	45.45	7.95	10.61	0.00
BMIM[DBP]	Experimental	55.23 ± 0.02	9.58 ± 0.02	8.03 ± 0.03	0.00 ± 0.00
	theoretical	55.17	9.48	8.05	
EMIM[DMP]	Experimental	40.62 ± 0.05	7.23 ± 0.02	11.90 ± 0.01	0.00 ± 0.00
	theoretical	40.68	7.20	11.86	0.00
EEIM[DEP]	Experimental	47.52 ± 0.03	8.21 ± 0.05	10.08 ± 0.04	0.00 ± 0.00
	theoretical	47.48	8.27	10.07	0.00
BMIM[DMP]	Experimental	45.62 ± 0.03	7.97 ± 0.01	10.70 ± 0.05	0.00 ± 0.00
	theoretical	45.45	7.96	10.61	0.00
BEIM[DEP]	Experimental	51.10 ± 0.01	8.85 ± 0.05	9.24 ± 0.06	0.00 ± 0.00
	theoretical	50.98	8.82	9.15	0.00
BBIM[DBP]	Experimental	73.50± 0.04	12.82± 0.05	9.12± 0.05	0.00 ± 0.00
	theoretical	73.79	12.62	9.06	0.00

4.5 Viscosity analysis

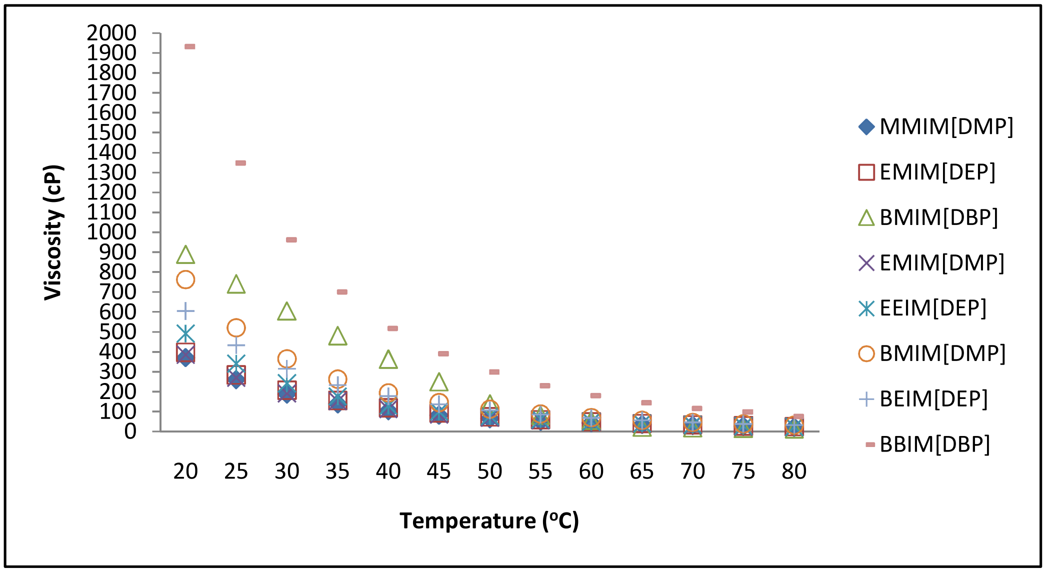


Figure 4.3 Viscosity of ILs synthesized versus temperature.

The viscosities for the ILs were analyzed as a function of temperature. Their measurements were obtained using an SVM 3000 Anton Paar. The analyses were performed in triplicate, within a temperature range of 20 to 80°C. The absolute viscosity of ILs is usually reported in centipoises (cP) [122]. Figure 4.3 shows the viscosity of all 8 imidazolium-based-phosphate ILs.

As can be seen in the Figure 4.3, the influence of temperature on viscosity is significant. In fact, increasing the temperature leads to a reduced probability of the colliding molecules capturing one another. This strong decrease with increasing temperature makes the application of ILs in catalysis easier. However, no considerable decrease was observed over 60°C, as reported by Wasserscheid and Welton [122].

In order to discuss the effect of changing the side chain and the temperature on the ILs viscosities, the analysis were divided into the length of cations and anions. From engineering point of view, the viscosity of ILs is of prime importance as it is playing a major role in stirring and mixing. In addition, it affects one of the transport properties such as diffusion [123-124].

At 20°C, the imidazolium based phosphate ILs showed a range of viscosity between 189.87 – 1930.5 cP, as shown in Table 4.4. Most of the obtained values are in the range of reported viscosity by other researches being varied between 66 – 1110 cP [122-123], except for BBIM[DBP] that showed a viscosity of 1930.5 cP.

Table 4.4 Viscosity data for imidazolium based phosphate ILs (at 20°C)

Structure code	Viscocity (cP)
MMIM[DMP]	371.33
EMIM[DEP]	397.30
BMIM[DBP]	889.87
EMIM[DMP]	385.50
EEIM[DEP]	491.91
BMIM[DMP]	762.47
BEIM[DEP]	604.69
BBIM[DBP]	1930.5

IL is governed by the van der Waals and hydrogen bonding. The structure of the anion affects the viscosity; a decrease in the size of the anion, due to substitution of alkyl chain, decreases the van der Waals, and so decreases the viscosity of the IL. This can be seen for ionic liquid EMIM[DMP] and EMIM[DEP], which have the same cation (EMIM) but different alkyl length in the anion. EMIM[DMP] and EMIM[DEP] has a viscosity of 385.50 cP and 397.30 cP, with a methyl and ethyl anion group respectively, as can seen in Figure 4.4. When comparing ionic liquid BMIM[DMP] and BMIM[DBP], the viscosity also shows the same trend (Figure 4.5). With the same cation (BMIM) but different length in the anion, i.e, methyl and ethyl respectively, the viscosity increase from 762.47 cP to 889.87 cP. This shows that the length in the anion plays a role in the viscosity of ILs, the longer the length, the higher the viscosity, similar to these reported by Wasserscheid and Welton [122], and Vaderrama and Zarricueta [125].

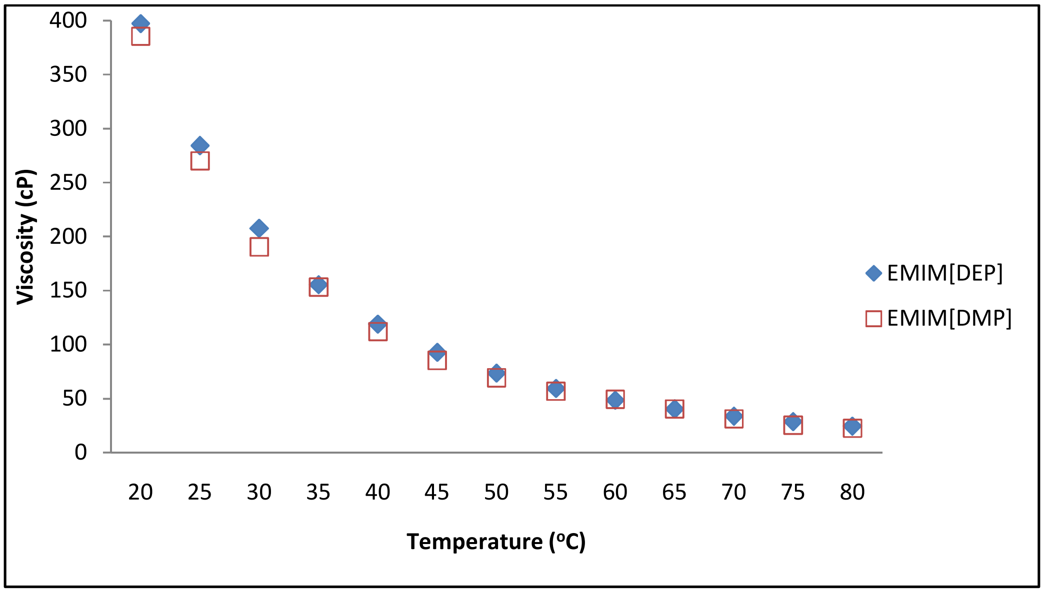


Figure 4.4 Viscosity of EMIM[DEP] and EMIM[DMP] versus temperature.

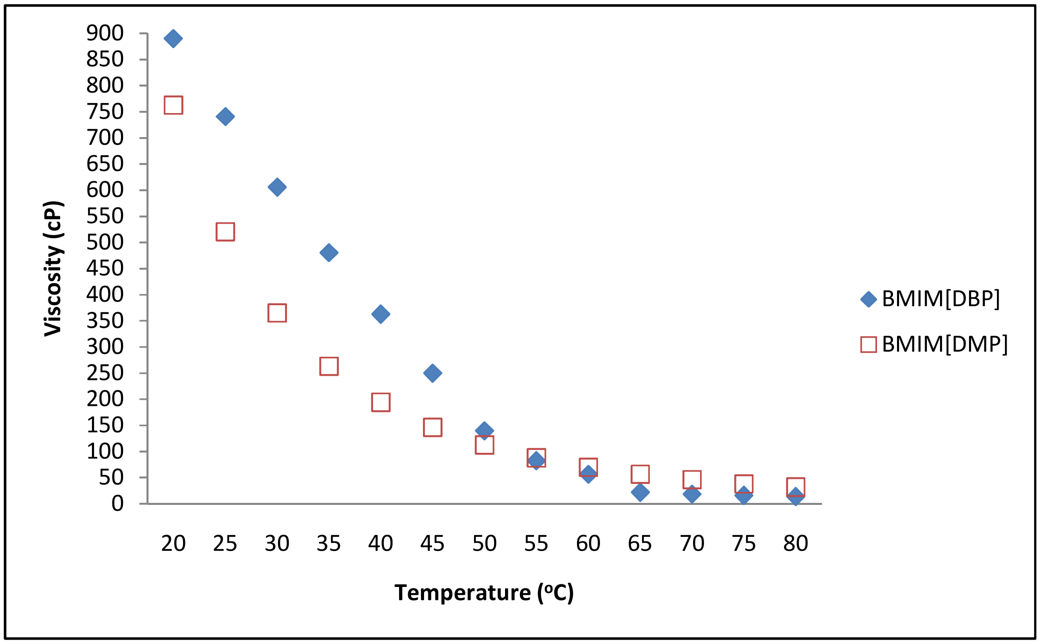


Figure 4.5 Viscosity of BMIM[DBP] and BMIM[DMP] versus temperature.

To observe the effect of the substituted alkyl chain length in the cation on viscosity, ILs with the same anion was compared. Ionic liquid MMIM[DMP], EMIM[DMP] and BMIM[DMP] have the same anion (DMP) but different alkyl length on the cation, methyl, ethyl and butyl, respectively. As can be seen in Figure 4.6, as the alkyl chain in the cation increases, the viscosity of the IL also increases. This can also be seen in ionic liquid EMIM[DEP], EEIM[DEP] and BEIM[DEP], having the same anion (DEP) but different length in the alkyl chain on the cation (Figure 4.7). As the alkyl chain increases from methyl, ethyl to butyl, the viscosity increase from 397.30, 491.91 and 604.69 cP, respectively. For ionic liquid BMIM[DBP] and BBIM[DBP], the same trend was also observed as can be seen in Figure 4.8. The viscosity of BMIM[DBP] was 889.87 cP compared to BBIM[DBP] with a viscosity of 1930.5 cP. Again the increase in viscosity is caused by increasing the alkyl length in the cation [124]. Data for viscosity can be seen in Appendix M.

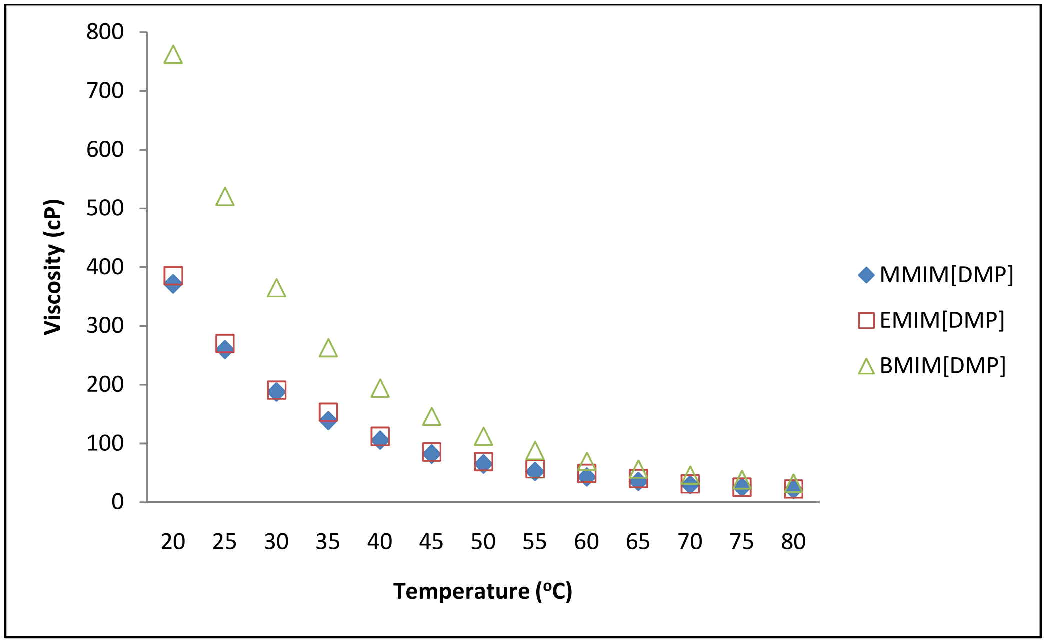


Figure 4.6 Viscosity of MMIM[DMP], EMIM[DMP] and BMIM[DMP] versus temperature

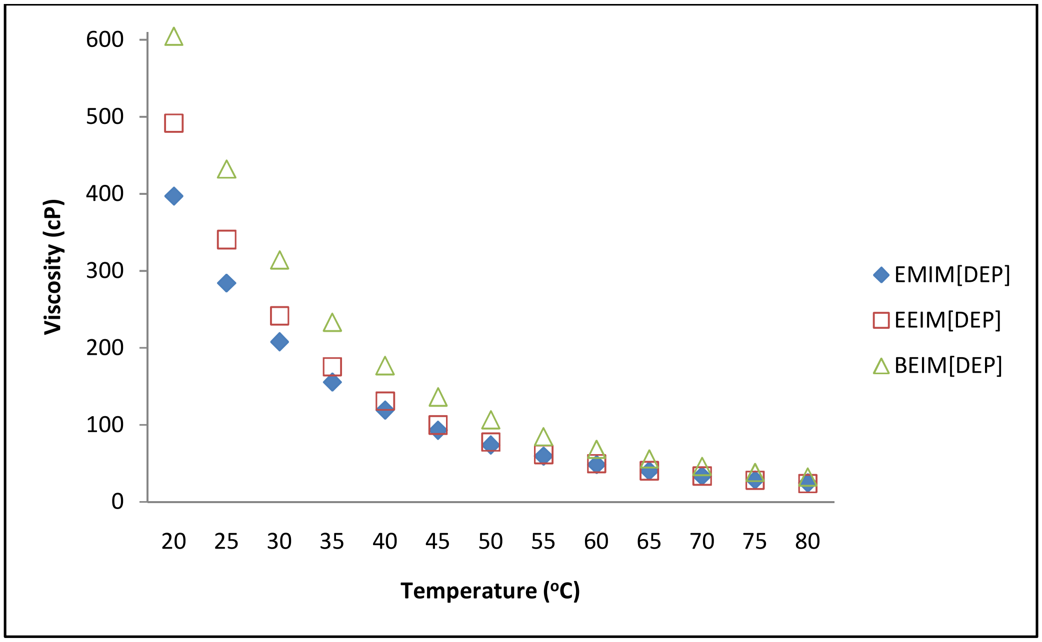


Figure 4.7 Viscosity of EMIM[DEP], EEIM[DEP] and BEIM[DEP]versus temperature

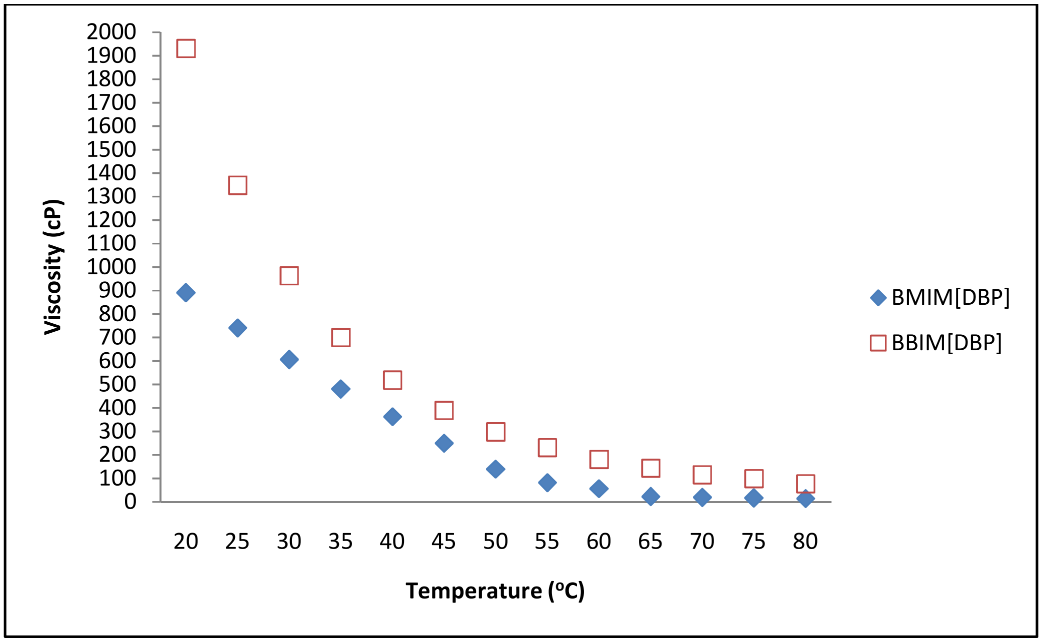


Figure 4.8 Viscosity of BMIM[DBP] and BMIM[DBP] against temperature

Viscosity describes a fluid's internal resistance to flow and may be thought of as a measure of fluid friction. Viscosity information is essential for the design of heat-transfer equipment, process piping, reactors, stripping columns, deodorizers, liquid–liquid extractors, distillation columns, crystallization equipment, and other units found in various chemical, oil, paint, clay, dairy and food industry. Because viscosity strongly affects flow behavior, it must be considered in engineering process calculations, analysis and design, being also an input for process simulation and optimization. Viscosity is an important physical property of ionic liquids. A low viscosity is generally desired to use IL as a solvent, to minimize pumping costs and increase mass transfer rates. However, the ionic liquids in this study showed an increases in sulfur removal when the viscosity increase. This may be due because of the increase in the alkyl chain length of the cation and anion. When the alky chain increase, the van der Waals forces also increases, increasing the sulfur removal. Even though high viscosity ionic liquids are not favorable because it increases industrial costs, the viscosity can be reduced with increase of temperature [122]-[125].

4.6 Density analysis

The density of ILs was measured with an Anton Paar, Oscillating U-tube density meter, (DMA 5000) from of 20 to 80°C with an uncertainty of $\pm$ 0.01°C. The apparatus was calibrated by measuring the density of Millipore quality water at regular intervals according to the supplier instructions. The calibrated apparatus was also verified using few pure organic liquids of known densities. The overall precision in experimental density measurements for all samples was found to be better than $\pm 2 \times 10^{-5}$ g.cm^{-3}.

The density of the eight ILs were measured from 20°C until 80°C, with a 5°C interval, as can be seen in Figure 4.9. The results for density at room temperature (20°C) are presented in Table 4.5. It can be seen that the densities of the ILs varied from 0.9741 to 1.2585 g.cm^{-3}. These results are in agreement with Valderrama and Zarricuet [125], who predicted that the densities of the ILs varies between 0.9 – 1.7 g.cm^{-3}. Data for density can be seen in Appendix N

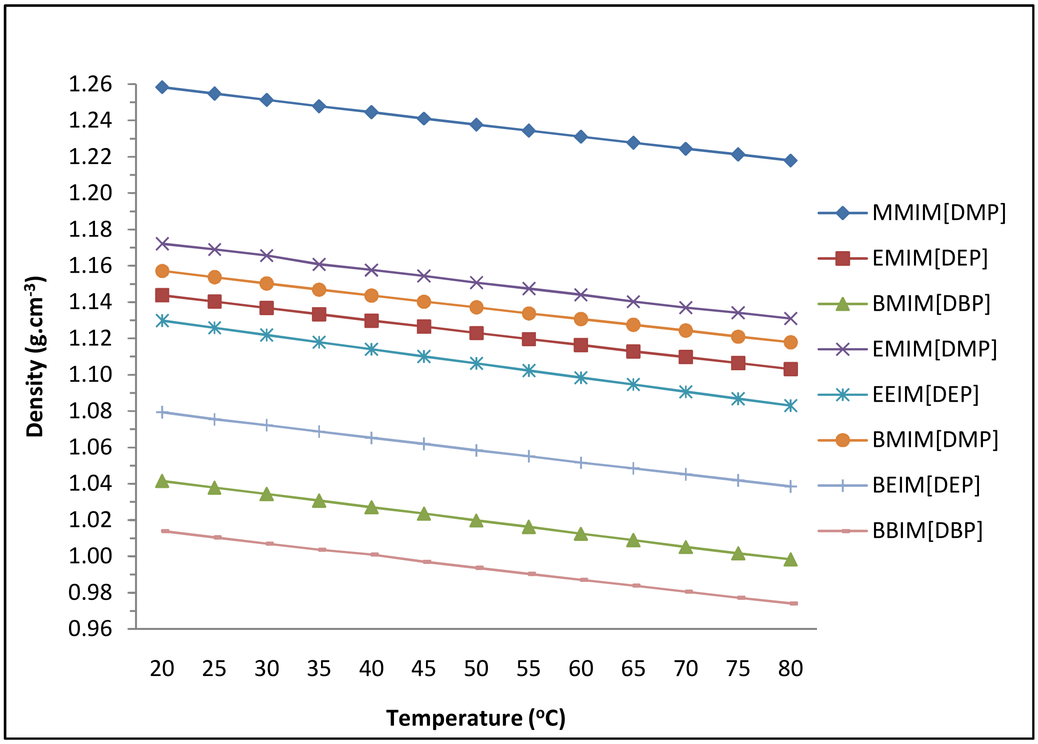


Figure 4.9 Plot of experimental density (ρ) values versus temperature (T) for all 8 ILs.

Table 4.5 Density data for imidazolium based phosphate ILs (at 20 °C)

Structure code	Density (ρ), g/cm^3
MMIM[DMP]	1.2585± 0.0001
EMIM[DEP]	1.1438± 0.0005
BMIM[DBP]	1.0415± 0.0004
EMIM[DMP]	1.1722± 0.0002
EEIM[DEP]	1.1298± 0.0003
BMIM[DMP]	1.1573± 0.0001
BEIM[DEP]	1.0793± 0.0004
BBIM[DBP]	1.0139± 0.0003

Several researchers have proven that the density decreases with increase in temperature. It was also agreed that the density of the ILs decreases with the increase of the alkyl chain in the cation or anion of the ILs. The fact that the longer alkyl chains have lower densities is most likely due to the alkyl chain interactions in each ionic liquid; the longer chains would allow for ordering of the ions which would lead to them being less dense because they can slide around each other more easily [124].

For the same cation, there were some changes in the density associated with changes in the side chains. For example, the IL EMIM[DEP] and EMIM[DMP] with the same cation EMIM, but different alkyl chain length in the anion (ethyl and methyl). When the substituted alkyl chain increased from methyl to ethyl as in EMIM[DMP] to EMIM[DEP], the density dropped from 1.1722 to 1.1438 g.cm^{-3}, respectively at 20°C. Similarly, for BMIM[DMP] and BMIM[DBP], the density decreased from 1.1573 to 1.0415 g.cm^{-3} respectively, when the side chain of the anion was changed from methyl to butyl. It can be seen that the ILs with the same cation but different length in the anion show a decreases in density with the increase in the alkyl chain in the anion, as can be seen in Figure 4.10. The results also indicate that the ILs follow a systematic behaviour [124], [126].

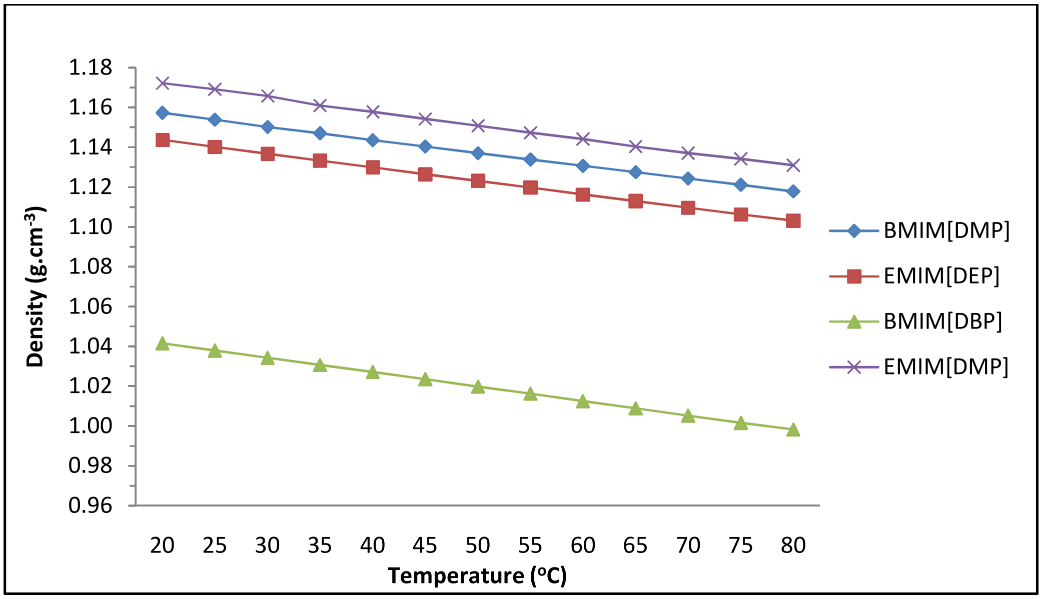


Figure 4.10 Density value versus temperature for IL BMIM[DMP], EMIM[DEP], BMIM[DBP] and EMIM[DMP]

The effect of the cation alkyl length chain on the density can also be observed for ILs having the same anion. IL MMIM[DMP], EMIM[DMP], and BMIM[DMP] have the same anion (DMP), but when the alkyl chain changed from methyl to ethyl and butyl in the cation, the density decreased from 1.2585 to 1.1722 and 1.1573 g.cm^{-3} (Figure 4.11). Similarly, for the IL BEIM[DEP], EEIM[DEP] and EMIM[DEP] having the same anion DEP but different alkyl groups at R in the cation (REIM), i.e., butyl, ethyl and methyl, a decrease in density can be seen when the length of the side chain in the cation is increased (Figure 4.12). The density of BEIM[DEP], EEIM[DEP] and EMIM[DEP] are 1.0793 to 1.1298 and 1.1438 g.cm^{-3}, respectively. This trend is also seen when IL BBIM[DBP] and BMIM[DBP] is compared as can be seen in Figure 4.13. As can be seen in the Table 4.4, the density of BBIM[DBP] having a butyl chain is 1.0139 g.cm^{-3} compared to 1.0415 g.cm^{-3} for BMIM[DBP] that has a methyl side chain. [124], [126].

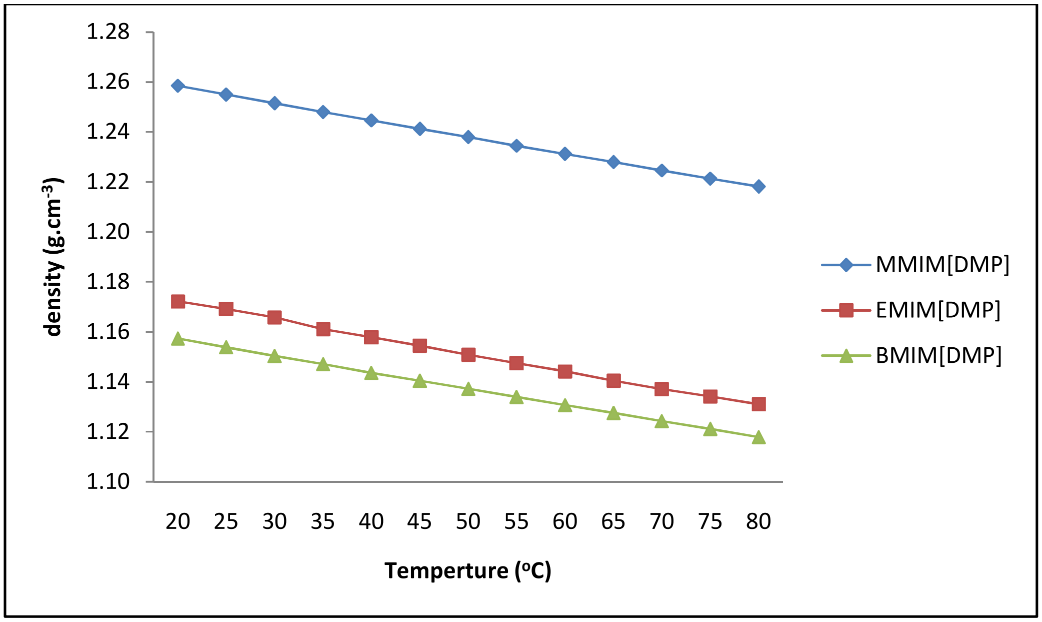


Figure 4.11 Density value versus temperature of IL MMIM[DMP], EMIM[DMP] and BMIM[DMP]

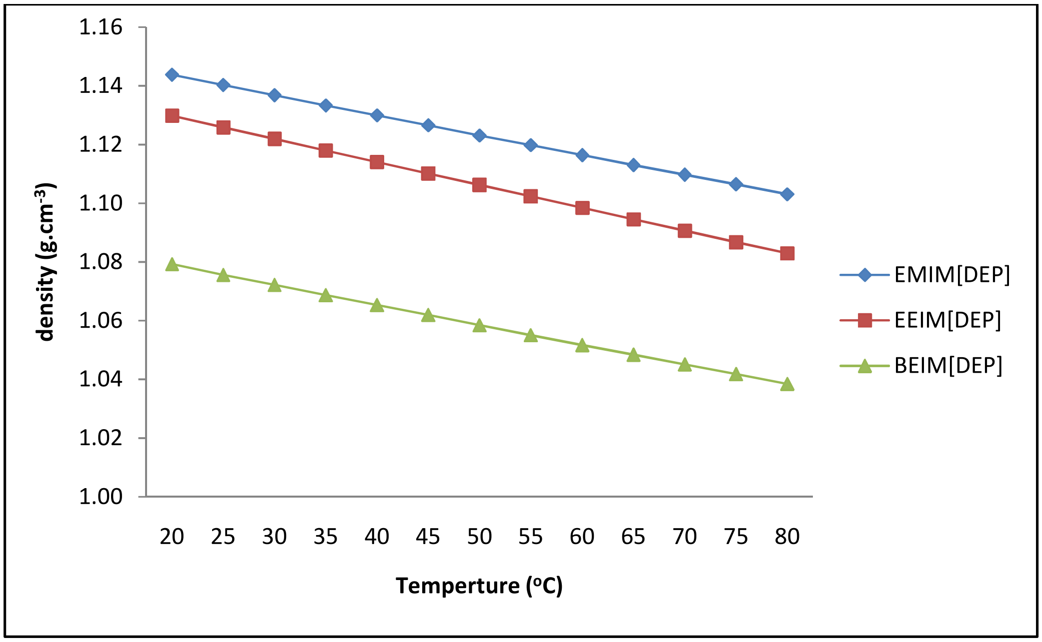


Figure 4.12 Density value versus temperature of IL EMIM[DEP], EEIM[DEP] and BEIM[DEP]

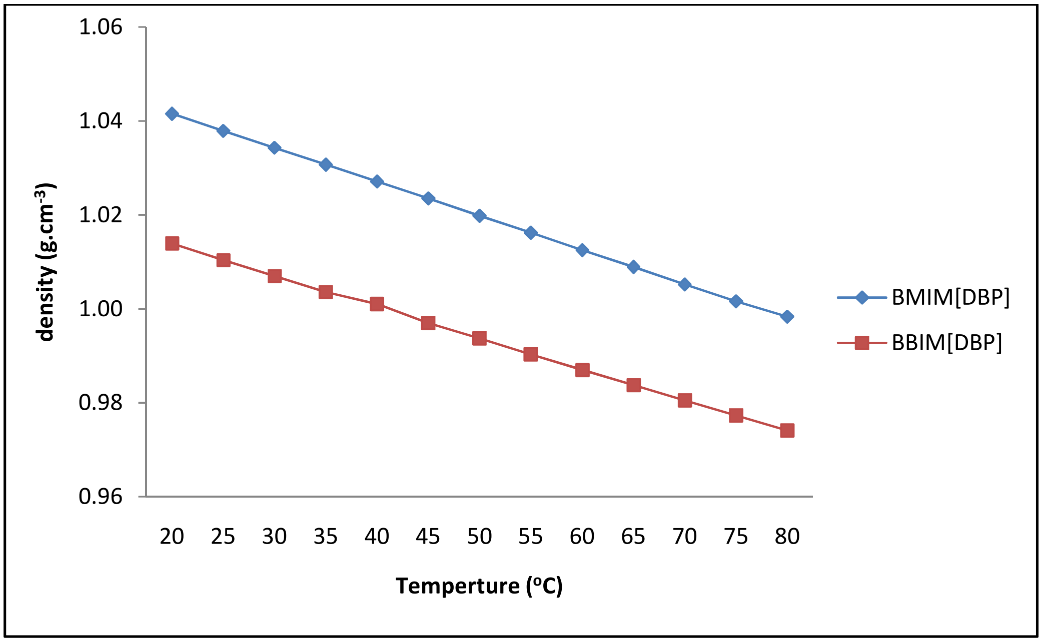


Figure 4.13 Density value versus temperature of IL BMIM[DBP] and BBIM[DBP]

The experimental results for the 8 ILs showed that the presence of long chain alkyl on the cation or anion, decreases the density of the IL, and this is seen in a systematic manners. Moreover, the density of the alkyl imidazoliums based phosphate

ILs are very close to one another. These results are in agreement with recent reports of Dunstan *et al*. [127] and Ahosseini and Scurto [128].

As can see in Figures above, the temperature and density show a linear correlation of more than 99.9%. Thus the linear equation can be used for calculating the density of any of the 8 ILs, at any temperature. Increasing the temperature from 20 to 80 °C did not show any significant decrease.

For example as seen in Figure 4.13, BBIM[DBP] showed a small density drop from 1.0139 g/cm^3 to 0.9741 g/cm^3 when the temperature was raised from 20 to 80 °C, a reduction of only 0.0398 g/cm^3. These results indicate that temperature variation has no considerable effect on the IL densities. The same observation was made by Valderrama and Zarricueta [129], in their study on the synthesis and properties of some ILs.

Optimal physical property for good sulphur removal is that the density difference of ionic liquid and the oil phase be large, in order for easy phase separation. Density of ionic liquid should also be low for easy mixing. When density is low the fluid flow of the system increases. BBIM[DBP] show a difference in density with model oil used (dodecane) of 0.2639 g/cm^3, and also has the lowest density compared to the other ionic liquids tested [129].

4.7 Water content

The water contents of ILs were investigated using a coulometric Karl Fischer titrator, DL 39 (Mettler Toledo), using Hydranal coulomat AG reagent (Riedel-de Haen). Each measurement was made in triplicate and the values are reported as an average with an accuracy of 5% [126].

The water contents of the dried ILs are found to be in the order of [MMIM[DMP]] > [EMIM[DEP]] > [EEIM[DEP]] > [EMIM[DMP]] > [BMIM[DBP]] > [BMIM[DMP]] > [BEIM[DEP]] > [BBIM[DBP]], respectively as shown in Table 4.6.

Table 4.6 Water content of dried IL.

Ionic liquid	Water impurities (ppm)
MMIM[DMP]	8230.189
EMIM[DEP]	6040.351
BMIM[DBP]	3165.638
EMIM[DMP]	4234.750
EEIM[DEP]	5591.762
BMIM[DMP]	1550.000
BEIM[DEP]	1461.833
BBIM[DBP]	1024.175

Although imidazolium based ionic liquids containing larger alkyl groups are not miscible with water, they will absorb some moisture from the air. The amount of water absorbed by the ionic liquid depends on the anion, and the length of the alkyl chain in the cation.

The absorption of water by the ionic liquids with the same anion showed that the cations with shorter alkyl chains tend to absorb more water than those with longer chains. This seems likely as a longer alkyl chain will make the ionic liquid more hydrophobic and also promote cation stacking interactions and hydrogen bonding within the liquid preventing the absorption of water into the system. The relatively low concentration of water absorbed in these samples can also be attributed to the larger anion, which can prevent the absorption of water. The presence of water may have a rather dramatic affect on the ionic liquid by lowering the ionic liquid reactivity. Water can also alter the physical properties of ionic liquid considerably. The presence of water reduces the viscosity. Thus, careful consideration must be given to the selected synthetic routes to ionic liquids, especially when physical parameters are to be determined [126], [128].

4.8 Ionic liquid selectivity

4.8.1 Model oil confirmation

Like the ILs, the model oil were analyzed by using CHNS analyzer to determine if the model oil were prepared correctly. The Table 4.7, below shows the results of S % for the all the model oils prepared. It can be seen that all the model oil were successfully prepared. See Appendix L

Table 4.7 CHNS results for the model oil prepared.

Model Oil	S(%)
0.1% DBT in dodecane	0.098 ± 0.01
0.1% BT in dodecane	0.102 ± 0.04
0.1% 3-MT in dodecane	0.107 ± 0.03
1.0% BT in dodecane	1.035 ± 0.03
2.0% BT in dodecane	2.012 ± 0.02
3.0% BT in dodecane	3.007 ± 0.01

4.8.2 ECODS

A combination of catalyst oxidative and extractive desulphurization (ECODS) using the eight imidazolium based phosphate ILs that were prepared previously to remove sulphur compound DBT from model oil. ECODS method was selected because the percentage of sulphur removal by extractive desulphurization (EDS) and oxidative desulphurization (ODS) are rather low. It has been reported that the combination of the two methods can increase the percentage of sulphur removal significantly.

The purpose of this step is to select three ILs from the eight ILs that have the highest percentage of sulphur removal and then to use these selected ILs for further analysis. All eight ILs were used to perform the ECODS method that was conducted at room temperature for 8 h in order for the reaction to reach equilibrium.

The model oil used was spiked with 1000 ppm of sulphur compound DBT. The amount of sulphur removed from the model oil phase into the IL phase was analyzed by the combustion method using CHNS. The percentage of removal from the model oil was determined by the following equation;

$$\% \text{ S removal} = \frac{[S]_i - [S]_f}{[S]_i} \times 100\%$$

$[S]_i$ is the initial sulphur content

$[S]_f$ is the final sulphur content after extraction

4.8.2.1 Effect of the length of the alkyl chain on extraction

Below shows the results of sulphur removal using the eight imidazolium based phosphate ILs. All of the ILs reached equilibrium after 5 to 7 h of interaction at room temperature. IL BBIM[DBP] showed the highest sulphur removal of 81 %. The second highest was BEIM[DEP] with a percentage of 75%, and the third was EEIM[DEP] with a removal of 74%, as can be seen in Figure 4.14.

Therefore for future analysis, BBIM[DBP], BEIM[DEP], and EEIM[DEP] were employed, as they displayed superior performance for sulphur removal among the eight ILs that were synthesized.

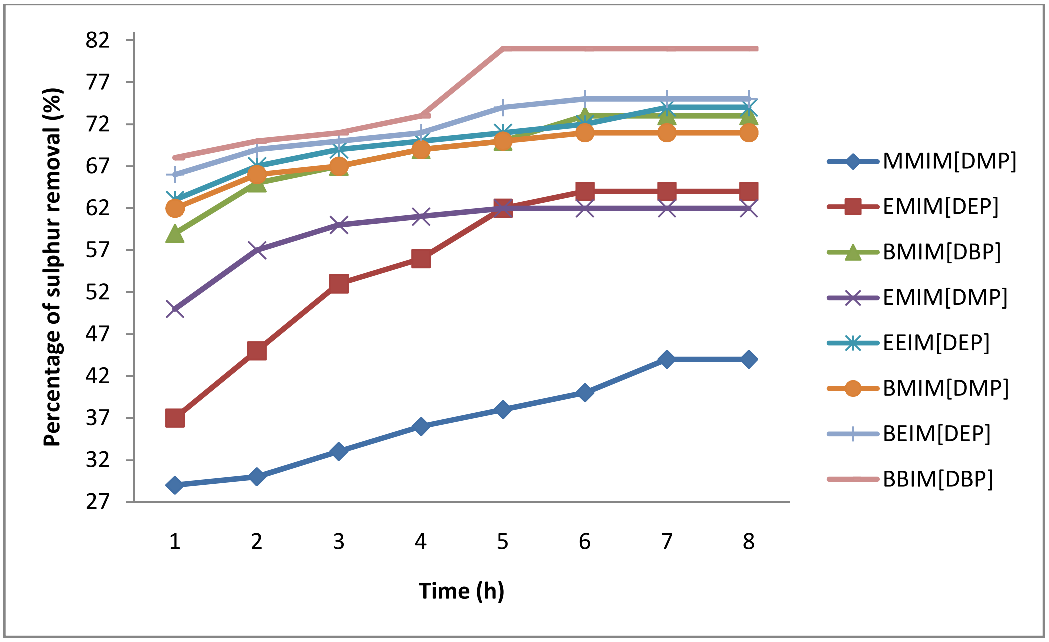


Figure 4.14 Percentage of sulphur removal using imidazolium-based-phosphate ILs at room temperature

The extractive desulphurization efficiency of ILs are related to their chemical properties such as the cation and anion structure, the size of the IL. Based on the data shown, with the same anions, imidazolium based ILs with the substitution of a longer alkyl group to the imidazolium ring, have higher desulphurization ability than that of imidazolium based ILs with a shorter alkyl chain. But when the cations of ILs are the same, the desulphurization ability of ILs connects with the chemical property of anion. The lone pair electron of the imidazole and the electron-donating ability of the alkyl substitution make the n-alkyl-imidazolium have higher polarizable aromatic π-electron density than imidazole. The strong affinity of the ILs for the aromatics sulphur compounds is related to the high polarity of the ILs. The mechanisms for the extraction of sulphur containing compounds with non-lewis-acidic ILs are because the formation of liquid clathrate compounds and the π-π interactions between aromatic structure of the extraction target and the imidazloe ring system [7], [18], [22].

Table 4.8 Sulphur removal percentage with different length of alkyl chain on anion and cation at room temperature

Ionic liquid $R_1R_2IM\text{-}R_3R_3PO_4$	R_1	R_2	R_3	Sulphur removal percentage (%)
MMIM[DMP]	methyl	methyl	methyl	44.0
EMIM[DEP]	ethyl	methyl	ethyl	64.0
BMIM[DBP]	butyl	methyl	butyl	73.0
EMIM[DMP]	methyl	ethyl	methyl	62.0
EEIM[DEP]	ethyl	ethyl	ethyl	74.0
BMIM[DMP]	methyl	butyl	methyl	71.0
BEIM[DEP]	ethyl	butyl	ethyl	75.0
BBIM[DBP]	butyl	butyl	butyl	81.0

Table 4.8 shows the changes in the extraction yield of dibenzothiophene with the length of alkyl chain of anion and cation groups. The ionic liquid EMIM[DEP] and EMIM[DMP] (Figure 4.15) have the same cation $EMIM^+$ but different alkyl group at R_3 in the anion $R_3R_3PO_4^-$. The percentage of sulphur removal for ethyl group was 64% when compared to a 62% with the methyl group. This can also be see for IL BMIM[DMP] and BMIM[DBP] in Figure 4.16. Both IL have the same cation ($BMIM^+$) but different length of the alkyl chain on the anion (methyl group and butyl group). IL BMIM[DMP] and BMIM[DBP] show sulphur removal of 71% and 73% respectively. This shows a higher extraction yield was observed for the ethyl group compared to the methyl group at R_3 for cation $EMIM^+$ and butyl group compared to methyl group at R_3 for cation $BMIM^+$ [19].

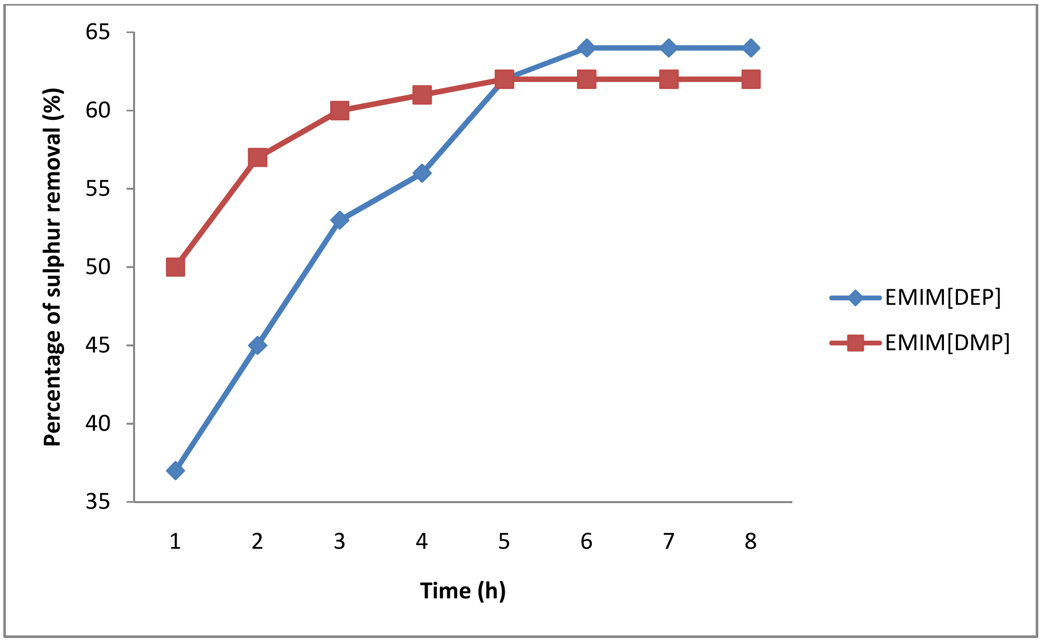


Figure 4.15 Percentage of sulphur removal of EMIM[DEP] and EMIM[DMP] versus time at room temperature

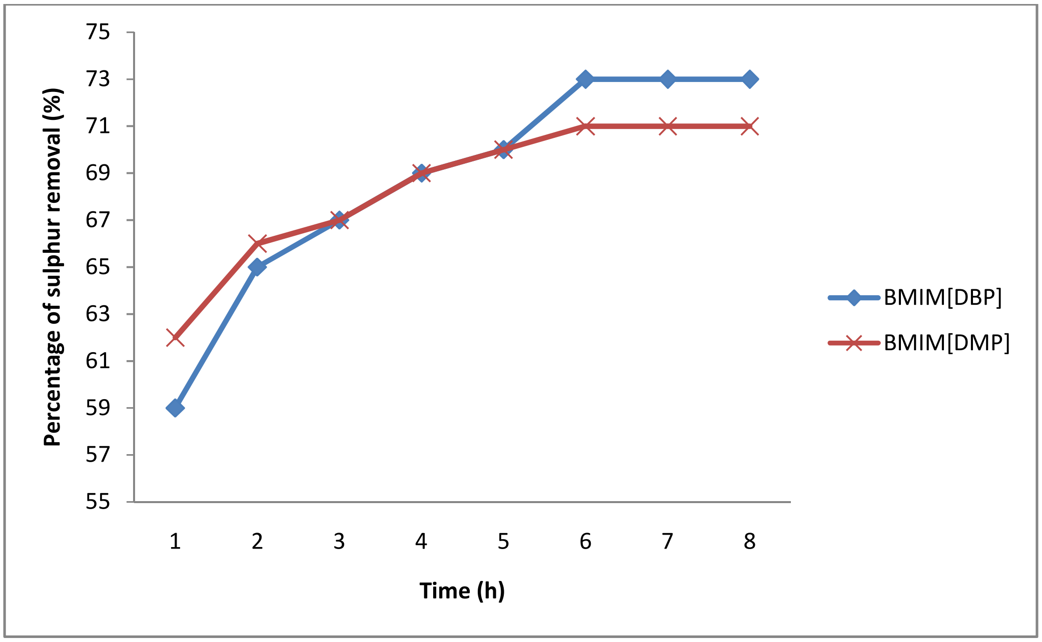


Figure 4.16 Percentage of sulphur removal of BMIM[DBP] and BMIM[DMP] versus time at room temperature

For a fixed anion group, the effect of the length of the alkyl chain of the group at R_2 in the alkyl imidazolium cation on the extraction yield was investigated. MMIM[DMP], EMIM[DMP], and BMIM[DMP] have the same anion $2MePO_4^-$ but different alkyl group at R_2, i.e., methyl, ethyl and butyl, respectively, in the cation (Figure 4.17). With these ILs, the extraction yield of dibenzothiophene was 44%, 62% and 71% for the methyl, ethyl, and butyl groups, respectively, at R_2; that is, the extraction yield increases with the length of the alkyl chain of the group at R_2. Similarly, for the ILs having the same anion $EtPO_4^-$ but different alkyl groups at R_2, i.e., butyl, ethyl and methyl, BEIM[DEP] with a percentage of 75% shows a higher extraction yield as compared to EEIM[DEP] and EMIM[DEP] with a percentage removal of 74% and 64% respectively, as can be seen in Figure 4.18. This trend can also be seen for IL having the same anion $BuPO_4^-$ but different alkyl group at R_2, where BBIM[DBP] shows a 81% sulphur removal compared to BMIM[DBP] with a removal of only 73% (Figure 4.19). The effect of the length of the alkyl chain of the group at R_2 on the extraction yield was more significant than that of the alkyl group at R_3. Holbery et al. [19] have observed that ILs form a liquid cluster consisting of a zigzag stacking structure of anions and cations. The increase in the extraction yield shown in table 4.8 may result from the increase in the extraction space because of the increase in the length of the alkyl chain [58].

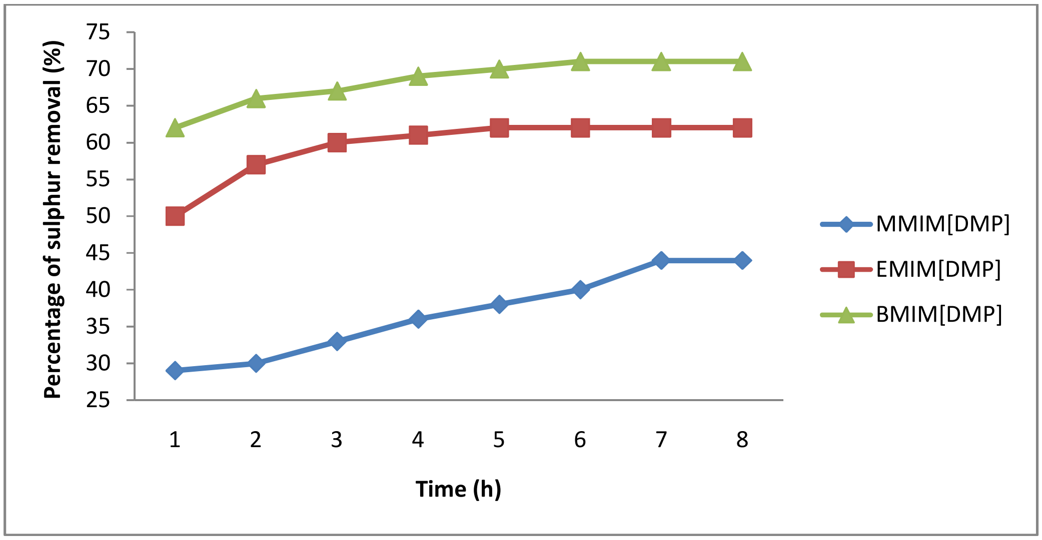


Figure 4.17 Percentage of sulphur removal of MMIM[DMP], EMIM[DMP] and BMIM[DMP] versus time at room temperature

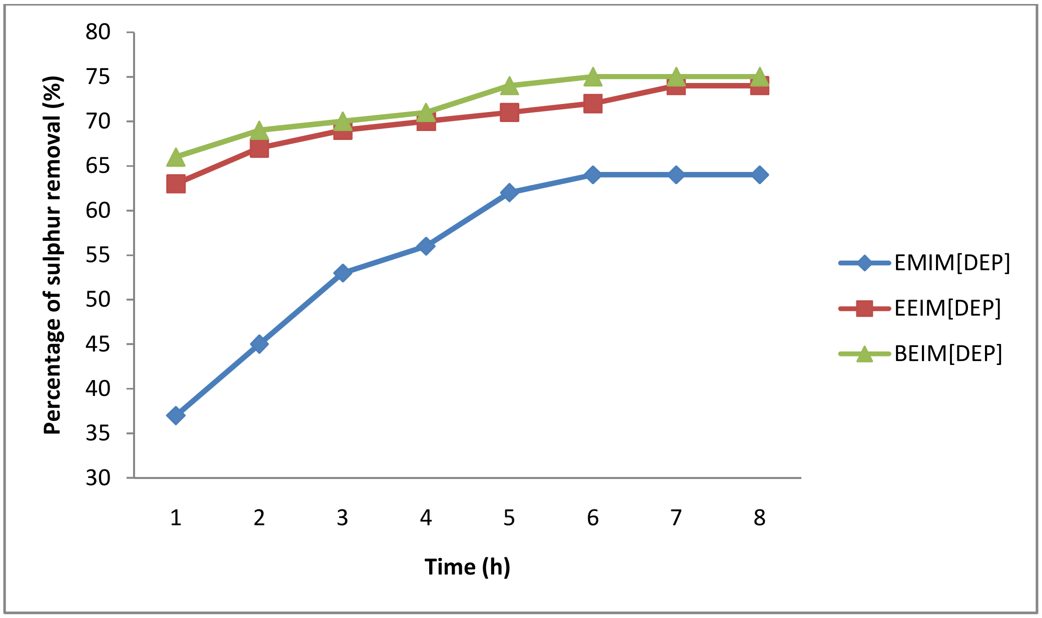


Figure 4.18 Percentage of sulphur removal of EMIM[DEP], EEIM[DEP] and BEIM[DEP] versus time at room temperature

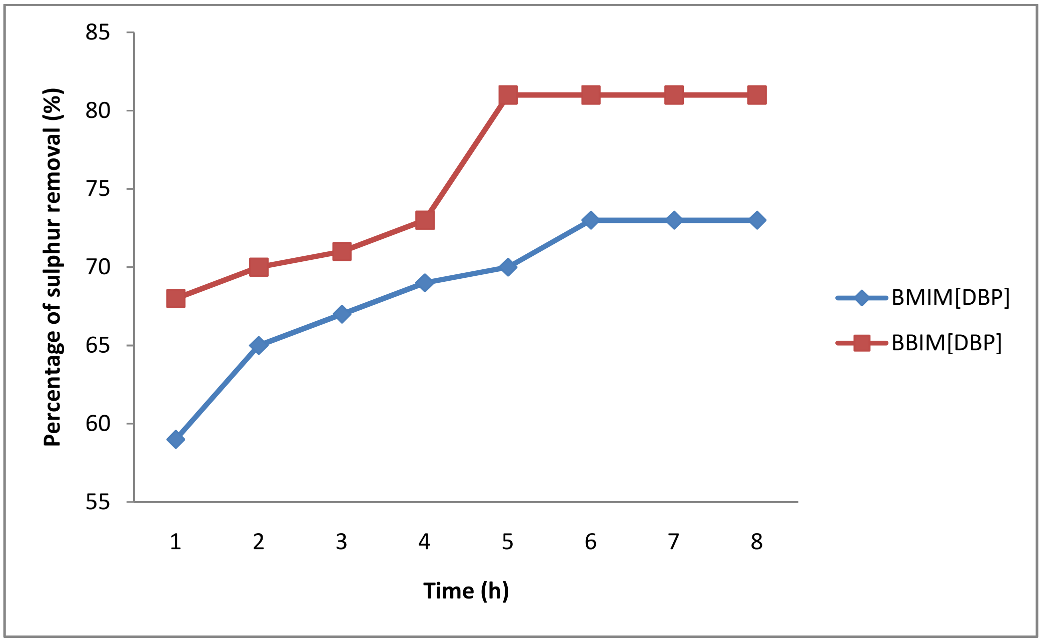


Figure 4.19 Percentage of sulphur removal of BMIM[DBP] and BBIM[DBP] versus time at room temperature

4.8.2.2 Possible Mechanism of the DBT ECODS

First, large numbers of DBT molecules were extracted from the model oil to the IL phase. Then the H_2O_2 in the IL phase decomposed to an oxidizing agent. Since IL consist of cation and anion and has lower dielectric, it may be excellent medium for the oxidizing agent. Finally, the DBT which is dissolved in the IL phase is oxidized by the oxidizing agent. Since the oxide products DBTO and $DBTO_2$ have higher solubility in the IL it will remain in the IL phase. The remaining DBT in the oil phase will be extracted from the oil phase to the IL phase and then oxidized. Therefore, continuous decrease in the concentration of DBT in model oil as observed during the process can be attributed to the large numbers of DBT molecules being continuously oxidized in the IL phase by the oxidizing agent [9]. Mechanism of ECODS process can be seen Figure 4.20

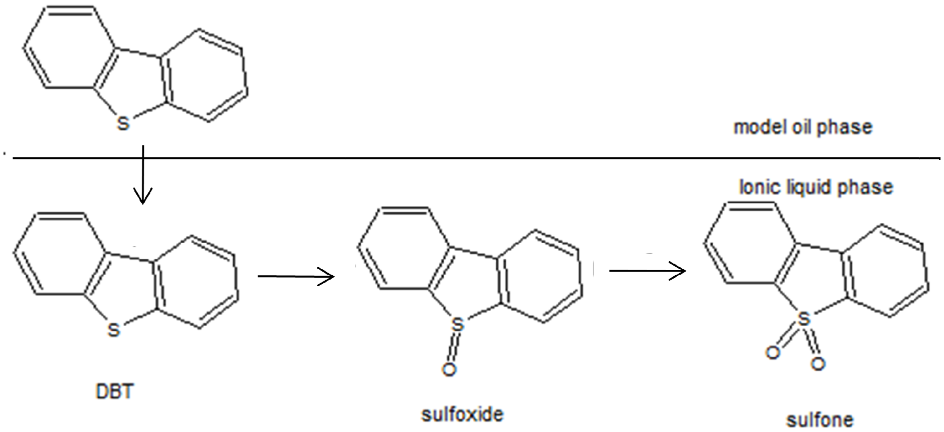


Figure 4.20 Mechanism of ECODS process

4.8.3 The effect of reaction temperature

The effect of temperature was also investigated. The treatment time was 6 h, this was the optimum time for equilibrium achieved at room temperature. 0.1277 ml of 30 wt % H_2O_2 [$(n_{\mathrm{H2O2}}/n_{S_{DBT}})$=4] and 0.00378 g of catalyst [$(n_{S_{DBT}}/n_{Cat})$=20] was added to 2 ml of IL.

10 ml of model oil that contained DBT as the sulphur compound with a percentage of 1000 ppm was added to the IL mixture. Figure 4.21 shows the results of sulphur removal using BBIM[DBP] ionic liquid at four different temperatures. At room temperature, the sulphur removal was 81.0%. When the temperature increased to 40°C, sulphur removal efficiency increased to 82.0 % The highest sulphur removal for BBIM[DBP] IL was 85.2% at 60°C and 70°C, revealing that the activity of the catalysts was enhanced with increase of temperature [130]. This behaviour is expected and can be explained by the increase in the oxidation reaction rate of sulphur containing compounds present in the model oil due to the strong dependent of reaction rate on the reaction temperature [60]. If the temperature is low, the IL is more viscous, with the temperature increase the viscosity of the ILs is lowered making the IL mobility. The exposure of IL with the model oil increases increasing the desulphurization rate of removal of sulphur [18].

However, 70°C was chosen instead of 60°C because the reaction had complete in 4 h, compared to 5 h for reaction to complete at 60°C. The sulphur removal was 83.0%, 82.0% and 81.0% at temperature 80°C, 40°C and room temperature respectively. However, as the reaction temperature increased from 70°C to 80°C, It showed a decrease in sulphur removal percentage. Caution must be exercised at temperature higher than 80°C which may lead to the oxidation of useful components of the fuel

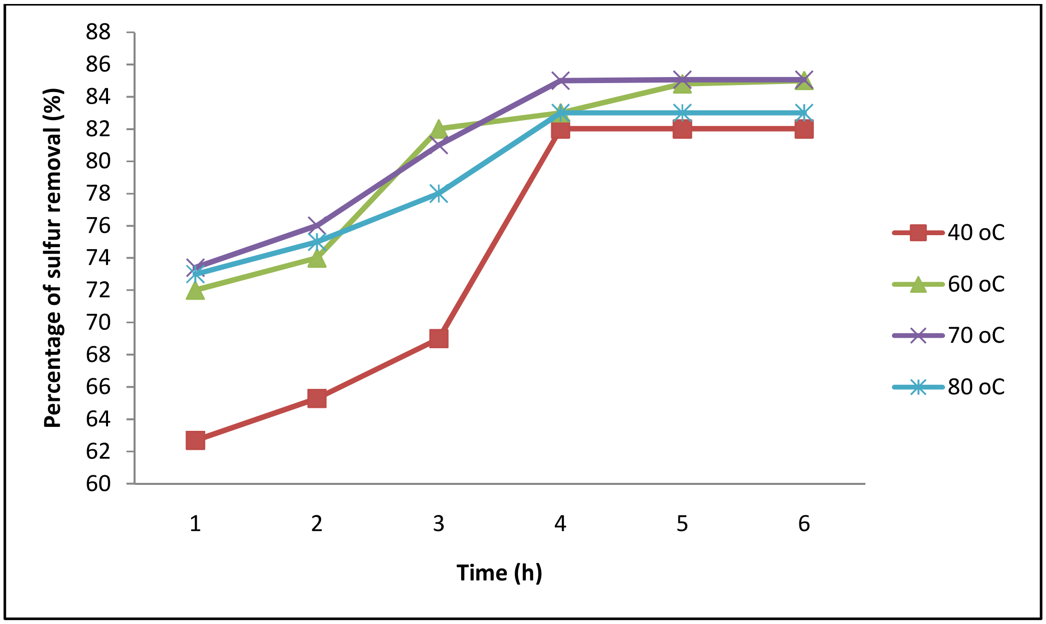


Figure 4.21 Effect of different temperature on the ECODS process using BBIM[DBP].

4.8.4 Effect of the amount of H_2O_2

As described above, the desulphurization system containing the catalyst, hydrogen peroxide, and IL BBIM[DBP], BEIM[DEP], and EEIM[DE] exhibited high catalytic activity. To study the effect of the amount of oxidizing agent on the oxidative properties, the desulphurization reaction under various H_2O_2/ sulphur molar ratios were carried out at 70°C for 4h. According to the stoichiometric reaction, 2 mol of hydrogen peroxide were consumed for every 1 mol of sulphur containing compound. The sulphur removal of different molar ratio of hydrogen peroxide and DBT had a strong influence on the reaction. As the molar ratio of hydrogen peroxide to sulphur increases from 2:1 to 4:1, the removal of sulphur from the model oil increased from 77.3% to 85.2% for IL BBIM[DBP], 71.8% to 79.1% for ionic liquid BEIM[DEP], and 70.5% to 78.2% for IL EEIM[DEP]. Further increase of the ratio did not show any improvement to the sulphur removal efficiency, as can be seen in Table 4.9. This showed that hydrogen peroxide have higher useful efficiency in the ECODS system, which may be because IL stabilized the hydrogen peroxide in the reaction [9], [10].

Note that the oxidant is usually used in excess of the stoichiometric ratio because of transport limitation on the two-liquid-phase reaction system, the unproductive (thermal) decomposition of hydrogen peroxide to water and oxygen, and possible parallel oxidation reactions such as oxidation of nitrogen containing compounds, which are present in the model oil. Thermal decomposition of hydrogen peroxide is strongly dependent on the temperature [60].

Table 4.9 Effect of the H_2O_2/Sulphur molar ratio on the reaction.

Ionic liquid	% S removal of different n_{H2O2}/n_s ratio		
	2:1	4:1	6:1
BBIM[DBP]	77.3	85.2	85.2
BEIM[DEP]	71.8	79.1	79.0
EEIM[DEP]	70.5	78.2	78.2

Reaction condition: T = 70°C, t = 4 hours, model oil = 10 ml, IL = 2 ml, [$(n_{S_{DBT}}/n_{Cat})$=20]

4.8.5 Effect of catalyst amount

The sulphur removal ability of molybdenum catalyst with different amounts was also investigated. In this experiment, the treating temperature was 70°C and treating time was 4 hours. Table 4.10 shows the results of sulphur removal using BBIM[DBP], BEIM[DEP], and EEIM[DEP] ILs with different amounts of catalyst. It can be shown that by increasing the amount of catalyst inside the ECODS system, the percentage of sulphur removal can also be increased. The sulphur content in the model oil decreased from 1000 ppm to 149.8 ppm when the ration of DBT to catalyst was 20:1 for IL BBIM[DBP]. This showed sulphur removal percentage of 85.2% compared to 60.0%, 65.4%, 72.0% and 74.9% for catalyst ratio of 100:1, 80:1, 60:1 and 40:1, repectively. When comparing IL BEIM[DEP] and EEIM[DEP], the same trend was seen. When increasing the catalyst ratio from 100:1 to 20:1 there was a significantly increase from 54.4% to 79.1% for BEIM[DEP] and 53.2% to 78.2% for EEIM[DEP]

However the increase of the catalysts amount from 20 to 10 led to no notable improvement of the sulphur removal. Thus, the catalysts amount of 20 was enough to remove sulphur from the model oil with a percentage of 85.2% for BBIM[DBP], 79.1% for BEIM[DEP] and 78.2% for EEIM[DEP] [24].

Table 4.10 Effect of DBT/Catalyst molar ratio

Ionic liquid	% S removal of different $n_{S_{DBT}}/n_{Cat}$ ratio				
	100:1	80:1	60:1	40:1	20:1
BBIM[DBP]	60.0	65.4	72.0	74.9	85.2
BEIM[DEP]	54.4	59.2	66.1	68.5	79.1
EEIM[DEP]	53.2	55.1	62.7	65.2	78.2

Reaction condition : T = 70°C, t = 4 hours, model oil = 10 ml, IL = 2 ml, [($n_{H2O2}/n_{S_{DBT}}$)=4]

This experiment clearly demonstrated that the amount of catalyst was a main factor in the reaction activity.

4.8.6 Effect of type of sulphur species in model oil

The selectivity to the organic sulphur exhibited by the IL BBIM[DBP] was investigated. Below show the percentage of sulphur removal for three different model oils using BBIM[DBP], BEIM[DEP] and EEIM[DEP] ILs in the ECODS process. The model oils used were model oil containing DBT, BT and 3-MT with 1000 ppm concentration.

Table 4.11 Effect of different sulphur compounds for ECODS process

Ionic liquid	S% removal of different sulphur compounds		
	DBT	BT	3-MT
BBIM[DBP]	85.2	58.1	34.9
BEIM[DEP]	79.1	52.2	32.8
EEIM[DEP]	78.2	50.2	31.1

Reaction condition : T = 70°C, t = 4 hours, model oil = 10 ml, IL = 2 ml, [($n_{H2O2}/n_{S_{DBT}}$)=4], [($n_{S_{DBT}}/n_{Cat}$)=20]

The removal of 3-MT was only 34.9% when compared to the removal of DBT and BT, which showed a percentage of 84.5% and 58.1% of sulphur removal for BBIM[DBP]. BEIM[DEP] and EEIM[DEP] showed the same trend as can be seen in Table 4.11.

BT exhibited a lower reactivity when compared to DBT, which was attributed to the significantly lower electron density on the sulphur atom BT. For DBT the difference in the electron density on the sulphur was very small (5.758). Steric hindrance of the methyl of the substrate became an obstacle for the approach of the sulphur atom to the catalystic active species in IL is another factor. Because of these two factors, the reactivity of sulphur compounds in the ECODS system decreases in the order of DBT>BT>3-MT, which is opposite to the HDS activity [20]. This property is of practical significance, suggesting that DBT and BT sulphur compounds can be extracted efficiently by the HDS process. Therefore, the ECODS could be used at least as a complementary process for HDS. It has also been reported that the stronger selective extraction of dibenzothiophene results from the formation of liquid clathrate due to the π-π interaction between the unsaturated bonds of aromatic sulphur compound on the thiophene ring with the imidazolium ring of the IL [22], [61]. In general, the IL shows significant π-π interaction with the aromatic ring. Therefore, the small extraction yield of 3-MT may be due to the interaction of the ILs exhibit strong selectivity to thiophenic sulphur in organic sulphur. Figure 4.22 shows the percentage of removal of different sulphur species [58].

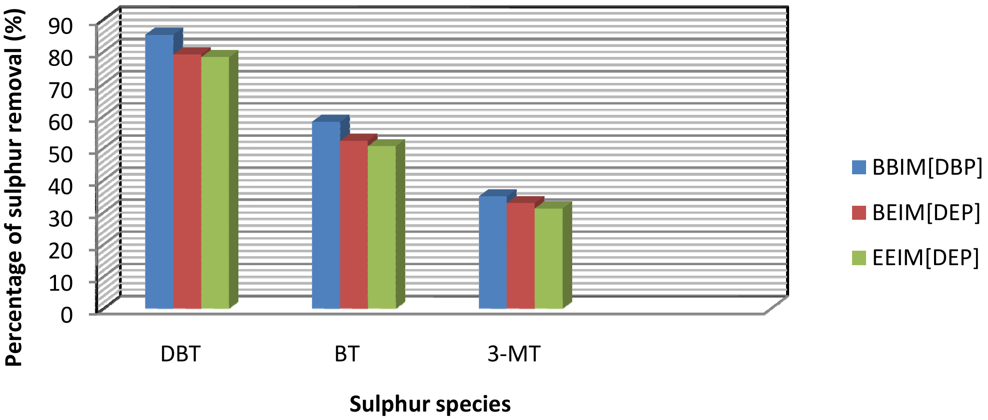


Figure 4.22 Percentage of sulphur removal for different sulphur species

4.8.7 Effect of initial sulphur concentration

0.1277 ml of 30 wt % H_2O_2 [$(n_{\mathrm{H2O2}}/n_{S_{DBT}})$=4] and catalyst [$(n_{S_{DBT}}/n_{Cat})$=20] was added to 2 ml of IL BBIM[DBP], BEIM[DEP] and EEIM[DEP]. 10 ml of model oil that contained BT as the sulphur compound with different percentage, that is 1%, 2% and 3% was added to the IL mixtures. The mixtures was stirred vigorously for 4 h at a temperature of 70°C. After the reaction was complete the mixture was centrifuge and the upper layer was withdrawn and analyzed with CHNS**.** As can be seen in Table 4.12, with the increase of BT percentage, the percentage of sulphur removal decreases. For IL BBIM[DBP], the sulphur removal decreased from 30.1% to 16.5%, when the sulphur percentage was increased from 1% to 3%. This was also seen for IL BEIM[DEP] and EEIM[DEP], with a decrease of 22.1% to 10.2% and 20.9% to 8.20% respectively.

Table 4.12 Effect of different percentage of sulphur (BT)

Ionic liquid	S% removal of different percentage of BT		
	1%	2%	3%
BBIM[DBP]	30.1	22.7	16.5
BEIM[DEP]	22.1	13.4	10.2
EEIM[DEP]	20.9	10.5	8.20

Reaction condition : T = 70°C, t = 4 hours, model oil = 10 ml, IL = 2 ml, , [$(n_{\mathrm{H2O2}}/n_{S_{BT}})$=4], [$(n_{S_{BT}}/n_{Cat})$=20]

4.8.8 Product Identification

The GC-MS spectra of DBT and oxidized DBT are shown in Figure 4.22 (a) and Figure 4.22 (b) respectively. The molecular mass of DBT was determined to be 184.15 which is close to the calculated value of 184.26. The oxidized product was found to have a mass of 216.03 giving a difference mass of 32 units. This additional 32 unit mass corresponds to the mass of two oxygen atoms.

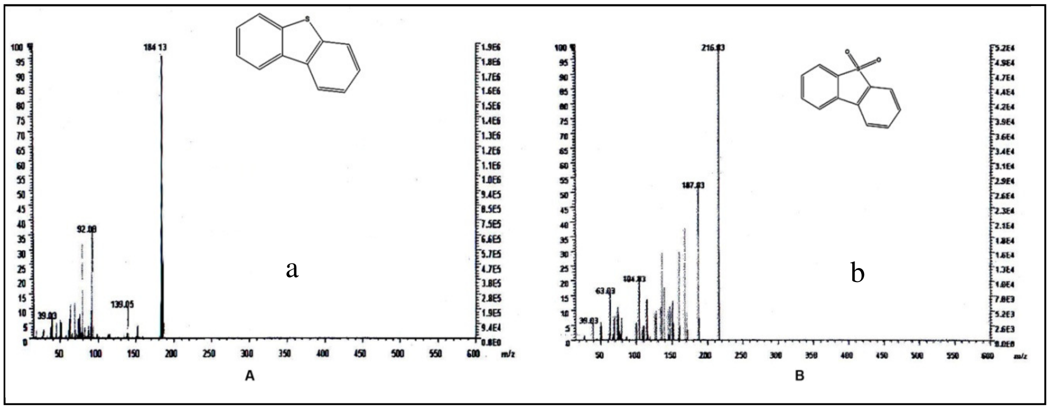


Figure 4.22 GC-MS spectra for DBT (a) and oxidized DBT (b).

The above analytical results indicate that the following compound was formed during the oxidation process. This identification of the products has helped in sulfone speciation. This work will help study the oxidation of different DBT derivatives that exist in crude oil. It gives an indication that all hindered sulphur compounds can be oxidized and converted to their corresponding sulfones. Reviewing the reaction of organic sulphur compounds indicated that organic sulfides could undergo the oxidation process to give either sulfoxides or sulfones.

On the basis of the above analysis, the ECODS process of DBT can be proposed. In a combination of extraction and oxidation, DBT was oxidized in the IL as it was extracted from the oil phase. Therefore, a continuous decrease in the concentration of DBT in the oil phase was observed for each solvent during the oxidation process. In these desulphurization processes, DBT can be oxidized to its sulfoxide and sulfone, which keep in the IL phase due to their high polarities [10].

4.8.9 Influence of different desulphurization system for model oil

The sulphur removal efficiency for different reaction systems are listed in Table 4.13. The catalyst and H_2O_2 could dissolve in the BBIM[DBP], BEIM[DEP], and EEIM[DEP] IL, and a biphasic system was formed, where the upper layer was the oil phase and the bottom layer was the IL phase, along with the catalyst and the hydrogen peroxide. Table 4.13 shows the results.

Table 4.13 Sulphur removal efficiency of different desulphurization system in model oil

	S% removal of different desulphurization systems			
Ionic liquid	EDS[1]	ODS[2]	ODS[3]	ECODS[4]
BBIM[DBP]	68.4	65.8	55.2	85.2
BEIM[DEP]	62.0	59.1	50.9	79.1
EEIM[DEP]	60.8	56.5	48.8	78.2

1 Condition: T = 70°C, t = 4 h, model oil = 5 mL, IL = 1 mL,

2 Condition: T = 70°C, t = 4 h, model oil = 5 mL, IL = 1 mL, $[(n_{\mathrm{H2O2}}/n_{S_{DBT}})$=4]

3 Condition: T = 70°C, t = 4 h, model oil = 5 mL, IL = 1 mL, catalyst $[(n_{S_{DBT}}/n_{Cat})$=20]

4 Condition: T = 70°C, t = 4 h, model oil = 5 mL, IL = 1 mL, $[(n_{\mathrm{H2O2}}/n_{S_{DBT}})$=4] and catalyst $[(n_{S_{DBT}}/n_{Cat})$=20]

Interestingly, with the addition of BBIM[DBP], the removal of DBT in the model oil could reach a percentage 85.2% with stoichiometric amount of H_2O_2. This demonstrates that the IL plays a vital role in the ECODS system. DBT was extracted into the IL phase and was oxidized in the IL. The process was also superior to simple extraction (EDS) with IL that showed a percentage of 68.4% sulphur removal or the oxidation process (ODS), that removed 65.8% of sulphur. This can also be seen for IL BEIM[DEP] and EEIM[DEP] showing a sulphur removal percentage to only 79.1% and 78.2% for the ECODS process. This is compared to only 62.0% for BEIM[DEP] and 60.8% for EEIM[DEP] for the EDS process and 59.1% for BEIM[DEP] and 56.5% for EEIM[DEP] for the ODS process. This experiment clearly indicates that a combination of extraction and catalytic oxidation can remove DBT from model oil more efficiently.

4.8.10 Sulphur removal from crude oil

In order to determine the efficiency of ECODS for desulphurization, crude oil was used. The initial concentration of sulphur in the crude oil was 43000 ppm. After extraction the concentration dropped to 35776 ppm. The amount of sulphur removed was 16.8% [10]. This suggests that the sulphur removal from crude oil is more difficult than that using model oil because of the co-extraction of aromatic compounds from the crude oil. Crude oil contains more heteronuclear compounds than model oil, such as nitrogen-containing compounds and sulphur-containing aromatic compounds, which decreases the sulphur removal ability of BBIM[DBP] ionic liquid.

Because of the steric effect of the alkyl groups in the aromatic rings, methylthiophene, methylbenzothiophene, methyldibenzothiophene, etc, sulphur containing compounds in crude oil are extracted less than that in model oil [18].

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Based on the results in the previous chapter, it can be proven that the best IL is BBIM[DBP]. The catalyst oxidation and extraction desulphurization (ECODS) was found to be a promising approach for the reduction of sulphur with a total removal of 85.2%. This was achieved at low temperature, 70^oC and atmospheric pressure, with 0.00378 g of sodium molybdate dehydrate [$(n_{S_{DBT}}/n_{Cat})$=20] and 0.1277 ml of 30% wt H_2O_2 [$(n_{\mathrm{H2O2}}/n_{S_{DBT}})$=4]. The direct extraction of model oil without any oxidation has resulted in about 68.4% sulphur removal. However such direct extraction has a great impact on removing significant amount of other aromatic hydrocarbons species. ODS process showed a removal of 65.8% with the presence of H_2O_2 and 55.2% removal with the presence of only catalyst.

It can also be seen that increasing the alkyl chain on the cation and anion effects the properties of the IL and also helps in the sulphur removal percentage. When the alkyl chain on the cation increases the desulphurization ability also increases.

The reactivity of the sulphur compounds in the ECODS process is also investigated in this research and it was found that the reactivity of sulphur compounds in the ECODS system decreases in the order of DBT>BT>3-MT.

In conclusion, it can be concluded that the best IL in this research was BBIM[DBP] using the ECODS process.

5.2 Recommendations

The findings in this study is very interesting and worth investigating further. In order to enhance the understanding of ECODS process, the following studies are recommended:

- Use other types of ILs in the ECODS process to see the efficiency.
- Apply different types of catalyst to optimize the ECODS process.
- Regenerate the IL used in the ECODS process.
- Since not much report available in ECODS process, it is important to optimize the parameters for the sulphur removal.

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APPENDIX A

[CALCULATION FOR SYNTHESIS OF IONIC LIQUID]

$$\text{Mol} = \frac{\text{Mass (g)}}{\text{M. W}} \tag{1}$$

$$\text{Density} = \frac{\text{Mass (g)}}{\text{Volume (dm}^3\text{)}} \tag{2}$$

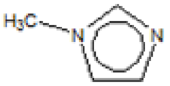
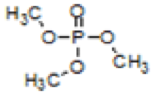
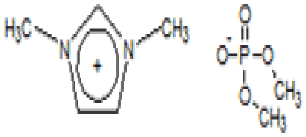
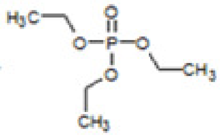
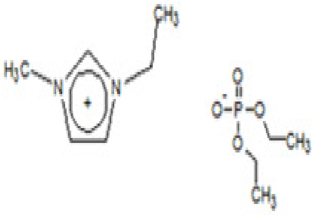
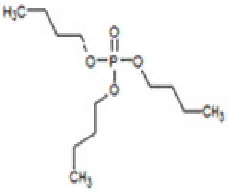
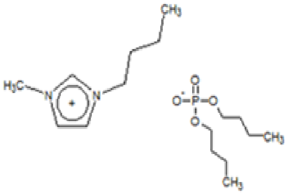
Mole ratio (n-alkylimidazole:trialkylphosphate) = 1:1

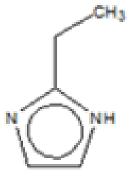
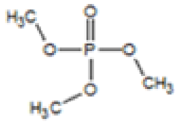
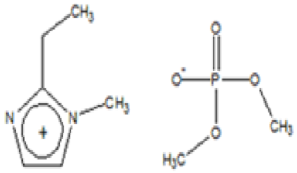
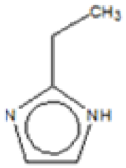
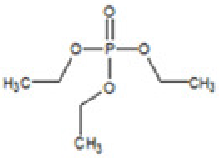
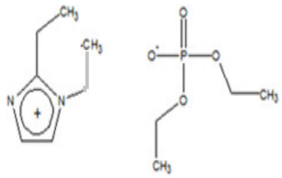
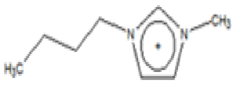
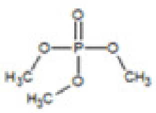
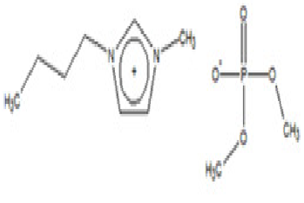
Table A.1 The molecular weight and density of reactants for the synthesis of ILs

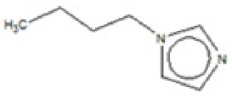
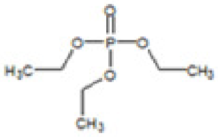
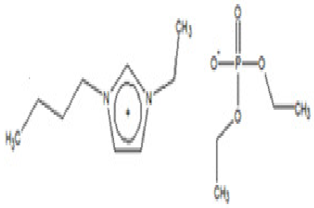
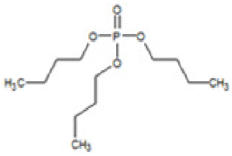
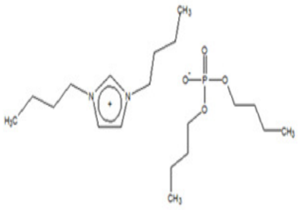
Mole of reatants	Molecular weight (g mol^{-1})	Density (g dm^{-3})
1-methylimidazole	82.11	1.030
2-ethylimidazole	96.13	-
1-butylimidazole	124.19	0.950
Trimethylphosphate	140.08	1.212
Triethylphosphate	182.16	1.069
Tributylphosphate	266.32	0.978

APPENDIX B

[THE IMIDAZOLIUM BASED PHOSPHATE IONIC LIQUIDS]

Amount of starting material (cm^3)		Condition	Ionic liquid synthesized
Alky imidazole	Trialkyl phosphate		
1-methylimidazole 39.86 cm^3 (0.5 mol) 	Trimethylphosphate 57.79 cm^3 (0.5 mol) 	100°C 72 h	1-methyl-3-methyl-imidazolium dimethylphosphate (MMIM[DMP]) 
1-methylimidazole 31.89 cm^3 (0.4 mol) 	Triethylphosphate 68.19 cm^3 (0.4 mol) 	100°C 48 h	1-methyl-3-ethyl-imidazolium diethylphosphate (EMIM[DEP]) 
1-methylimidazole 39.22 cm^3 (0.3 mol) 	Tributylphosphate 81.78 cm^3 (0.3 mol) 	110°C 72 h	1-methyl-3-butyl-imidazolium dibutylphosphate (BMIM[DBP]) 

Amount of starting material (cm^3)		Condition	Ionic liquid synthesized
Alky imidazole	Trialkyl phosphate		
2-ethylimidazole 38.45 g (0.4 mol) 	Trimethylphosphate 46.23 cm^3 (0.4 mol) 	90^{o}C 72 h	1-ethyl-3-methyl-imidazolium dimethylphosphate (EMIM[DMP]) 
2-ethylimidazole 28.84 g (0.3 mol) 	Triethylphosphate 51.17 cm^3 (0.3 mol) 	80^{o}C 96 h	1-ethyl-3-ethyl-imidazolium diethylphosphate (EEIM[DEP]) 
1-butylimidazole 58.83 cm^3 (0.45 mol) 	Trimethylphosphate 52.01 cm^3 (0.45 mol) 	65^{o}C 72 h	1-butyl-3-methyl-imidazolium dimethylphosphate (BMIM[DMP]) 

Amount of starting material (cm^3)		Condition	Ionic liquid synthesized
Alky imidazole	Trialkyl phosphate		
1-butylimidazole 45.75 cm^3 (0.35mol) 	Triethylphosphate 59.70 cm^3 (0.35 mol) 	95^{o}C 72 h	1-butyl-3-ethyl-imidazolium diethylphosphate (BEIM[DEP]) 
1-butylimidazole 52.30 cm^3 (0.4 mol) 	Triethylphosphate 59.70 cm^3 (0.4 mol) 	85^{o}C 6 days	1-butyl-3-butyl-imidazolium dibutylphosphate (BBIM[DBP]) 

APPENDIX C

[PREPARATION OF MODEL OIL]

Preparation of 1000 ppm DBT in Dodecane

Molecular Formula (DBT) = $C_{12}H_8S$
Molar Mass DBT = 184.26 g/mol
1000 mg S /L
1000 ml solution ↔ 1000 mg S
250ml solution ↔ 250 mg S

184.26 g DBT ↔ 32.00 g S
184.26 mg DBT ↔ 32.00 mg DBT
32.00 mg S ↔ 184.26 mg DBT
250 mg S ↔ (250 mg S /32.00) x 184.26

250 ml solution ↔ 1439.53 mg DBT

99.5% DBT ↔ 1439.53 /(99.5%)
↔ 1446.76 mg DBT
↔ 1.44676 g DBT

n = mv = = 1.439.53/184.26
mg/mm = 7.812 mmol

Preparation of 1000 ppm BT in Dodecane

Molecular Formula (BT) = C_8H_6S
Molar Mass BT = 134.20 g/mol
1000 mg S/L
1000 ml solution ↔ 1000 mg S
25 ml solution ↔ 25 mg S

134.20 g BT ↔ 32.00 g S
134.20 mg BT ↔ 32.00 mg BT
32.00 mg S ↔ 134.20 mg BT
25 mg S ↔ (25 mg S/32.00) x 134.20

25 ml solution ↔ 104.844 mg BT

97% BT ↔ 104.844 /(97%)
↔ 108.09 mg BT
↔ 0.10809 g BT

Preparation of 1000 ppm 3-MT in Dodecane

Molecular Formula (3-MT) = C_5H_6S
Molar Mass 3-MT = 98.16 g/mol
1000 mg S/L
1000 ml solution ↔ 1000 mg S
25 ml solution ↔ 25 mg S

98.16 g 3-MT ↔ 32.00 g S
98.16 mg 3-MT ↔ 32.00 mg 3-MT
32.00 mg S ↔ 98.16 mg 3-MT
25 mg S ↔ (25 mg S/32.00) x 98.16

25 ml solution ↔ 76.688 mg 3-MT

99% 3-MT ↔ 76.688 /(99%)
↔ 77.46 mg 3-MT
↔ 0.07746 g 3-MT

Preparation of 10000 ppm BT in Dodecane (1%)

Molecular Formula (BT) = C_8H_6S
Molar Mass BT = 134.20 g/mol
10000 mg S/L
1000 ml solution ↔ 10000 mg S
25 ml solution ↔ 250 mg S

134.20 g BT ↔ 32.00 g S
134.20 mg BT ↔ 32.00 mg BT
32.00 mg S ↔ 134.20 mg BT
250 mg S (250 mg S/32.00) x 134.20

25 ml solution ↔ 1048.44 mg BT

97% BT ↔ 1048.44 /(97%)
↔ 1080.9 mg BT
↔ 1.0809 g BT

Preparation of 20000 ppm BT in Dodecane (2%)

Molecular Formula (BT) = C_8H_6S
Molar Mass BT = 134.20 g/mol
20000 mg S/L
1000 ml solution ↔ 20000 mg S
25 ml solution ↔ 500 mg S

134.20 g BT ↔ 32.00 g S
134.20 mg BT ↔ 32.00 mg BT
32.00 mg S ↔ 134.20 mg BT
500 mg S ↔ (500 mg S/32.00) x 134.20

25 ml solution ↔ 2096.875 mg BT

97% BT ↔ 2096.875 /(97%)
↔ 2162 mg BT
↔ 2.162 g BT

Preparation of 30000 ppm BT in Dodecane (3%)

Molecular Formula (BT) = C_8H_6S
Molar Mass BT = 134.20 g/mol
30000 mg S/L
1000 ml solution ↔ 20000 mg S
25 ml solution ↔ 750 mg S

134.20 g BT ↔ 32.00 g S
134.20 mg BT ↔ 32.00 mg BT
32.00 mg S ↔ 134.20 mg BT
750 mg S ↔ (750 mg S/32.00) x 134.20

25 ml solution ↔ 3145.3 mg BT

97% BT ↔ 3145.3 /(97%)
↔ 3242.6 mg BT
↔ 3.2426 g BT

APPENDIX D

[CALCULATION FOR ECODS PROCESS]

Preparation of 1000 ppm DBT in Dodecane

Molecular Formula (DBT) = $C_{12}H_8S$
Molar Mass DBT = 184.26 g/mol
1000 mg S/L
1000 ml solution ↔ 1000 mg S
250ml solution ↔ 250 mg s

184.26 g DBT ↔ 32.00 g S
184.26 mg DBT ↔ 32.00 mg DBT
32.00 mg S ↔ 184.26 mg DBT
250 mg S ↔ (250 mg S/32.00) x 184.26

250 ml solution ↔ 1439.53 mg DBT

99.5% DBT ↔ 1439.53 /(99.55%)
↔ 1446.76 mg DBT
↔ 1.44676 g DBT

n = mv = mg/mm = 1.43953/184.26
= 7.812 mmol

Mass of catalyst used for [$(n_{S_{DBT}}/n_{Cat})$=20]

$$n_{S_{DBT}} = \frac{(1000 \text{ mg/L})(10 \times 10^{-3})}{32.00}$$

Volume of model oil = 10ml

= 0.3125 mmol

$n_{S_{DBT}}/n_{Cat}$ = 20
n_{Cat} = 0.3125/20
0.015625 mmol

Mass of Cat = 0.015625 x 241.95 M.W. Cat = 241.95 mg/mmol
= 3.78 mg
= 0.00378 g

Volume of 30 % H_2O_2 used for [($n_{\mathrm{H2O2}}/n_{S_{DBT}}$)=4]

$n_{\mathrm{H2O2}}/n_{S_{DBT}}$ = 4

n_{H2O2} = 4 x 0.3125
1.25 mmol

Mass of H_2O_2 = 1.25 x 34.01
= 42.5125 mg

M.W H_2O_2 = 34.01 mg/mmol

Volume of H_2O_2 = $\frac{42.5125 \times 10^{-3}\ \mathrm{g}}{1.11\ \mathrm{g\ mL^{-1}}}$
= 0.038299 mL

Density of H_2O_2 = 1.11 g $\mathrm{mL^{-1}}$

30% H_2O_2 = 0.038299/ 0.3
= 0.1277 mL

APPENDIX E

[CALCULATION FOR EFFECT OF THE AMOUNT OF H_2O_2]

Volume of 30 % H_2O_2 used for [($n_{\mathrm{H2O2}}/n_{S_{DBT}}$)=2]

$n_{\mathrm{H2O2}}/n_{S_{DBT}}$ = 2

n_{H2O2} = 2 x 0.3125
0.625 mmol

Mass of H_2O_2 = 0.625 x 34.01   M.W H_2O_2 = 34.01 mg/mmol
= 21.256 mg

Volume of H_2O_2 = $\frac{21.256 \times 10^{-3}\ \mathrm{g}}{1.11\ \mathrm{g\ mL^{-1}}}$ Density of H_2O_2 = 1.11 g mL^{-1}
= 0.01915 mL

30% H_2O_2 = 0.019149/ 0.3
= 0.063853mL

Volume of 30 % H_2O_2 used for [($n_{\mathrm{H2O2}}/n_{S_{DBT}}$)=4]

$n_{\mathrm{H2O2}}/n_{S_{DBT}}$ = 4

n_{H2O2} = 4 x 0.3125
1.25 mmol

Mass of H_2O_2 = 1.25 x 34.01   M.W H_2O_2 = 34.01 mg/mmol
= 42.5125 mg

Volume of H_2O_2 = $\frac{42.5125 \times 10^{-3}\ \mathrm{g}}{1.11\ \mathrm{g\ mL^{-1}}}$ Density of H_2O_2 = 1.11 g mL^{-1}
= 0.038299 mL

30% H_2O_2 = 0.038299/ 0.3
= 0.1277 mL

Volume of 30 % H_2O_2 used for $[(n_{\mathrm{H2O2}}/n_{S_{DBT}})\text{=}6]$

$n_{\mathrm{H2O2}}/n_{S_{DBT}}$ = 6

n_{H2O2} = 6 x 0.3125

1.875 mmol

Mass of H_2O_2 = 1.875 x 34.01 M.W H_2O_2 = 34.01 mg/mmol

= 63.7688 mg

Volume of H_2O_2 = $\frac{63.7688 \times 10^{-3}\ \text{g}}{1.11\ \text{g mL}^{-1}}$ Density of H_2O_2 = 1.11 g mL^{-1}

= 0.05745 mL

30% H_2O_2 = 0.05745/ 0.3

= 0.1915 mL

APPENDIX F

[CALCULATION FOR EFFECT OF THE CATALYST AMOUNT]

Mass of catalyst used for [($n_{S_{DBT}}/n_{Cat}$)=10]

$n_{S_{DBT}}$ = $\frac{(1000\ \text{mg/L})(10 \times 10^{-3})}{32.00}$ Volume of model oil = 10ml
= 0.3125 mmol

$n_{S_{DBT}}/n_{Cat}$ = 10
n_{Cat} = 0.3125/10
= 0.03125 mmol

Mass of Cat = 0.03125 x 241.95 M.W. Cat = 241.95 mg/mmol
= 7.561 mg
= 0.007561 g

Mass of catalyst used for [($n_{S_{DBT}}/n_{Cat}$)=20]

$n_{S_{DBT}}$ = $\frac{(1000\ \text{mg/L})(10 \times 10^{-3})}{32.00}$ Volume of model oil = 10ml
= 0.3125 mmol

$n_{S_{DBT}}/n_{Cat}$ = 20
n_{Cat} = 0.3125/20
= 0.015625 mmol

Mass of Cat = 0.015625 x 241.95 M.W. Cat = 241.95 mg/mmol
= 3.78 mg
= 0.00378 g

Mass of catalyst used for [($n_{S_{DBT}}/n_{Cat}$)=40]

$n_{S_{DBT}}$ = $\frac{(1000 \text{ mg/L})(10 \times 10^{-3})}{32.00}$ Volume of model oil = 10ml

= 0.3125 mmol

$n_{S_{DBT}}/n_{Cat}$ = 40

n_{Cat} = 0.3125/40

= 0.0078125 mmol

Mass of Cat = 0.0078125 x 241.95 M.W. Cat = 241.95 mg/mmol

= 1.8903 mg

= 0.0018903 g

Mass of catalyst used for [($n_{S_{DBT}}/n_{Cat}$)=60]

$n_{S_{DBT}}$ = $\frac{(1000 \text{ mg/L})(10 \times 10^{-3})}{32.00}$ Volume of model oil = 10ml

= 0.3125 mmol

$n_{S_{DBT}}/n_{Cat}$ = 60

n_{Cat} = 0.3125/60

= 0.0052083 mmol

Mass of Cat = 0.0052083 x 241.95 M.W. Cat = 241.95 mg/mmol

= 1.2602 mg

= 0.0012602 g

Mass of catalyst used for [($n_{S_{DBT}}/n_{Cat}$)=80]

$n_{S_{DBT}}$ = $\frac{(1000\ \text{mg/L})(10 \times 10^{-3})}{32.00}$ Volume of model oil = 10ml

= 0.3125 mmol

$n_{S_{DBT}}/n_{Cat}$ = 80

n_{Cat} = 0.3125/80

= 0.0039063 mmol

Mass of Cat = 0.0039063 x 241.95 M.W. Cat = 241.95 mg/mmol

= 0.94512 mg

= 0.00094512 g

Mass of catalyst used for [($n_{S_{DBT}}/n_{Cat}$)=100]

$n_{S_{DBT}}$ = $\frac{(1000\ \text{mg/L})(10 \times 10^{-3})}{32.00}$ Volume of model oil = 10ml

= 0.3125 mmol

$n_{S_{DBT}}/n_{Cat}$ = 100

n_{Cat} = 0.3125/100

= 0.003125 mmol

Mass of Cat = 0.003125 x 241.95 M.W. Cat = 241.95 mg/mmol

= 0.756094 mg

= 0.000756094 g

APPENDIX G

[CALCULATION FOR EFFECT OF TYPES OF SULPHUR SPECIES IN MODEL OIL]

Preparation of 1000 ppm DBT in Dodecane

Molecular Formula (DBT) = $C_{12}H_8S$
Molar Mass DBT = 184.26 g/mol
1000 mg S/L
1000 ml solution ↔ 1000 mg S
250 ml solution ↔ 250 mg S

184.26 g DBT ↔ 32.00 g s
184.26 mg DBT ↔ 32.00 mg DBT
32.00 mg S ↔ 184.26 mg DBT
250 mg S ↔ (250 mg S/32.00) x 184.26

250 ml solution ↔ 1439.53 mg DBT

99.5% DBT ↔ 1439.53 /(99.55%)
↔ 1446.76 mg DBT
↔ 1.44676 g DBT

n = mv = = 1.43959/184.26
mg/mm = 7.812 mmol

Preparation of 1000 ppm BT in Dodecane

Molecular Formula (BT) = C_8H_6S
Molar Mass BT = 134.20 g/mol
1000 mg S/L
1000 ml solution ↔ 1000 mg S
25 ml solution ↔ 25 mg S

134.20 g BT ↔ 32.00 g s
134.20 mg BT ↔ 32.00 mg BT
32.00 mg S ↔ 134.20 mg BT
25 mg S ↔ (25 mg S/32.00) x 134.20

25 ml solution ↔ 104.844 mg BT

97% BT ↔ 104.844 /(97%)
↔ 108.09 mg BT
↔ 0.10809 g BT

Preparation of 1000 ppm 3-MT in Dodecane

Molecular Formula (3-MT) = C_5H_6S
Molar Mass 3-MT = 98.16 g/mol
1000 mg S/L
1000 ml solution ↔ 1000 mg S
25 ml solution ↔ 25 mg S

98.16 g 3-MT ↔ 32.00 g s
98.16 mg 3-MT ↔ 32.00 mg 3-MT
32.00 mg S ↔ 98.16 mg 3-MT
25 mg S ↔ (25 mg S/32.00) x 98.16

25 ml solution ↔ 76.688 mg 3-MT

99% 3-MT ↔ 76.688 /(99%)
↔ 77.46 mg 3-MT
↔ 0.07746 g 3-MT

APPENDIX H

[CALCULATION FOR EFFECT OF DIFFERENT INITIAL
SULPHUR CONCENTRATION]

Preparation of 10000 ppm BT in Dodecane (1%)

Molecular Formula (BT) = C_8H_6S
Molar Mass BT = 134.20 g/mol
10000 mg S/L
1000 ml solution ↔ 10000 mg S
25 ml solution ↔ 250 mg S

134.20 g BT ↔ 32.00 g S
134.20 mg BT ↔ 32.00 mg BT
32.00 mg S ↔ 134.20 mg BT
250 mg S (250 mg S/32.00) x 134.20

25 ml solution ↔ 1048.44 mg BT

97% BT ↔ 1048.44 /(97%)
↔ 1080.9 mg BT
↔ 1.0809 g BT

Preparation of 20000 ppm BT in Dodecane (2%)

Molecular Formula (BT) = C_8H_6S
Molar Mass BT = 134.20 g/mol
20000 mg S/L
1000 ml solution ↔ 20000 mg S
25 ml solution ↔ 500 mg S

134.20 g BT ↔ 32.00 g s
134.20 mg BT ↔ 32.00 mg BT
32.00 mg S ↔ 134.20 mg BT
500 mg S ↔ (500 mg S/32.00) x 134.20

25 ml solution ↔ 2096.875 mg BT

97% BT ↔ 2096.875 /(97%)
↔ 2162 mg BT
↔ 2.162 g BT

Preparation of 30000 ppm BT in Dodecane (3%)

Molecular Formula (BT) = C_8H_6S
Molar Mass BT = 134.20 g/mol
30000 mg S/L
1000 ml solution ↔ 20000 mg S
25 ml solution ↔ 750 mg S

134.20 g BT ↔ 32.00 g s
134.20 mg BT ↔ 32.00 mg BT
32.00 mg S ↔ 134.20 mg BT
750 mg S ↔ (750 mg S/32.00) x 134.20

25 ml solution ↔ 3145.3 mg BT

97% BT ↔ 3145.3 /(97%)
↔ 3242.6 mg BT
↔ 3.2426 g BT

Mass of catalyst used for [($n_{S_{DBT}}/n_{Cat}$)=20] (for BT 1 %)

$$n_{S_{DBT}} = \frac{(10000 \text{ mg/L})(10 \text{ x } 10^{-3})}{32.00}$$ Volume of model oil = 10ml

$= 3.125$ mmol

$n_{S_{DBT}}/n_{Cat} = 20$

$n_{Cat} = 3.125/20$
$= 0.15625$ mmol

Mass of Cat = 0.015625 x 241.95 M.W. Cat = 241.95 mg/mmol
= 37.80 mg
= 0.0378 g

Volume of 30 % H_2O_2 used for [($n_{H2O2}/n_{S_{DBT}}$)=4] (for BT 1 %)

$n_{H2O2}/n_{S_{DBT}}$ = 4

n_{H2O2} = 4 x 3.125
= 12.5 mmol

Mass of H_2O_2 = 12.5 x 34.01 M.W H_2O_2 = 34.01 mg/mmol
= 425.125 mg

Volume of H_2O_2 = $\frac{425.125 \times 10^{-3}\ g}{1.11\ g\ mL^{-1}}$ Density of H_2O_2 = 1.11 g mL^{-1}
= 0.38299 mL

30% H_2O_2 = 0.38299/ 0.3
= 1.277mL

Mass of catalyst used for [($n_{S_{DBT}}/n_{Cat}$)=20] (for BT 2 %)

$n_{S_{DBT}}$ = $\frac{(20000\ mg/L)(10 \times 10^{-3})}{32.00}$ Volume of model oil = 10ml
= 6.250 mmol

$n_{S_{DBT}}/n_{Cat}$ = 20

n_{Cat} = 6.25/20
= 0.3125 mmol

Mass of Cat = 0.3125 x 241.95 M.W. Cat = 241.95 mg/mmol
= 75.60 mg
= 0.07560 g

Volume of 30 % H_2O_2 used for [($n_{\mathrm{H2O2}}/n_{S_{DBT}}$)=4] (for BT 2 %)

$n_{\mathrm{H2O2}}/n_{S_{DBT}}$ = 4

n_{H2O2} = 4 x 6.250
= 25 mmol

Mass of H_2O_2 = 25 x 34.01 M.W H_2O_2 = 34.01 mg/mmol
= 850.25 mg

Volume of H_2O_2 = $\frac{850.25 \times 10^{-3}\ \mathrm{g}}{1.11\ \mathrm{g\ mL^{-1}}}$ Density of H_2O_2 = 1.11 g mL^{-1}
= 0.76600 mL

30% H_2O_2 = 0.76600/ 0.3
= 2.553mL

Mass of catalyst used for [($n_{S_{DBT}}/n_{Cat}$)=20] (for BT 3 %)

$n_{S_{DBT}}$ = $\frac{(30000\ \mathrm{mg/L})(10 \times 10^{-3})}{32.00}$ Volume of model oil = 10ml
= 9.375 mmol

$n_{S_{DBT}}/n_{Cat}$ = 20

n_{Cat} = 9.375/20
= 0.46875 mmol

Mass of Cat = 0.46875 x 241.95 M.W. Cat = 241.95 mg/mmol
= 113.41 mg
= 0.1134 g

Volume of 30 % H_2O_2 used for [($n_{\mathrm{H2O2}}/n_{S_{DBT}}$)=4] (for BT 3 %)

$n_{\mathrm{H2O2}}/n_{S_{DBT}}$ = 4

n_{H2O2} = 4 x 9.375
= 37.5 mmol

Mass of H_2O_2 = 37.5 x 34.01 M.W H_2O_2 = 34.01 mg/mmol
= 1275.375mg

Volume of H_2O_2 = $\frac{1275.375 \times 10^{-3}\ \mathrm{g}}{1.11\ \mathrm{g\ mL^{-1}}}$ Density of H_2O_2 = 1.11 g $\mathrm{mL^{-1}}$
= 1.14899 mL

30% H_2O_2 = 1.14899/ 0.3
= 3.8300 mL

APPENDIX I

[CALCULATION FOR DESULPHURIZATION PROCESS WITH CRUDE OIL]

Mass of catalyst used for [($n_{S_{DBT}}/n_{Cat}$)=20] (for BT 3 %)

$n_{S_{DBT}}$ = $\frac{(43000 \text{ mg/L})(10 \times 10^{-3})}{32.00}$ Volume of model oil = 10ml

= 13.4375 mmol

$n_{S_{DBT}}/n_{Cat}$ = 20

n_{Cat} = 13.4375/20

= 0.671875 mmol

Mass of Cat = 0.671875 x 241.95 M.W. Cat = 241.95 mg/mmol

= 162.560 mg

= 0.16256 g

Volume of 30 % H_2O_2 used for [($n_{H2O2}/n_{S_{DBT}}$)=4] (for BT 3 %)

$n_{H2O2}/n_{S_{DBT}}$ = 4

n_{H2O2} = 4 x 13.4375

= 53.75 mmol

Mass of H_2O_2 = 53.75 x 34.01 M.W H_2O_2 = 34.01 mg/mmol

= 1828.0375 mg

Volume of H_2O_2 = $\frac{1828.0375 \times 10^{-3} \text{ g}}{1.11 \text{ g mL}^{-1}}$ Density of H_2O_2 = 1.11 g mL^{-1}

= 1.6469 mL

30% H_2O_2 = 1.6469/ 0.3

= 5.4896 mL

APPENDIX J

[^{1}H NMR and ^{13}C NMR RESULTS]

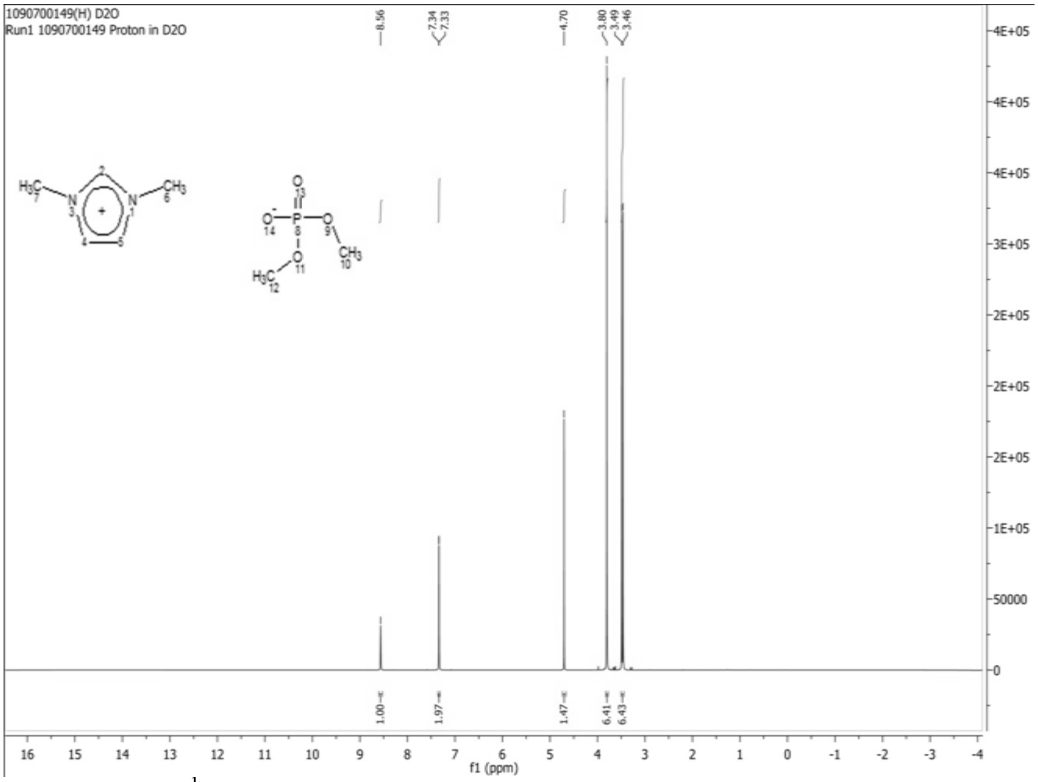


Figure J.1 ^{1}H NMR for 1-methyl-3-methyl-imidazolium dimethylphosphate (MMIM[DMP])

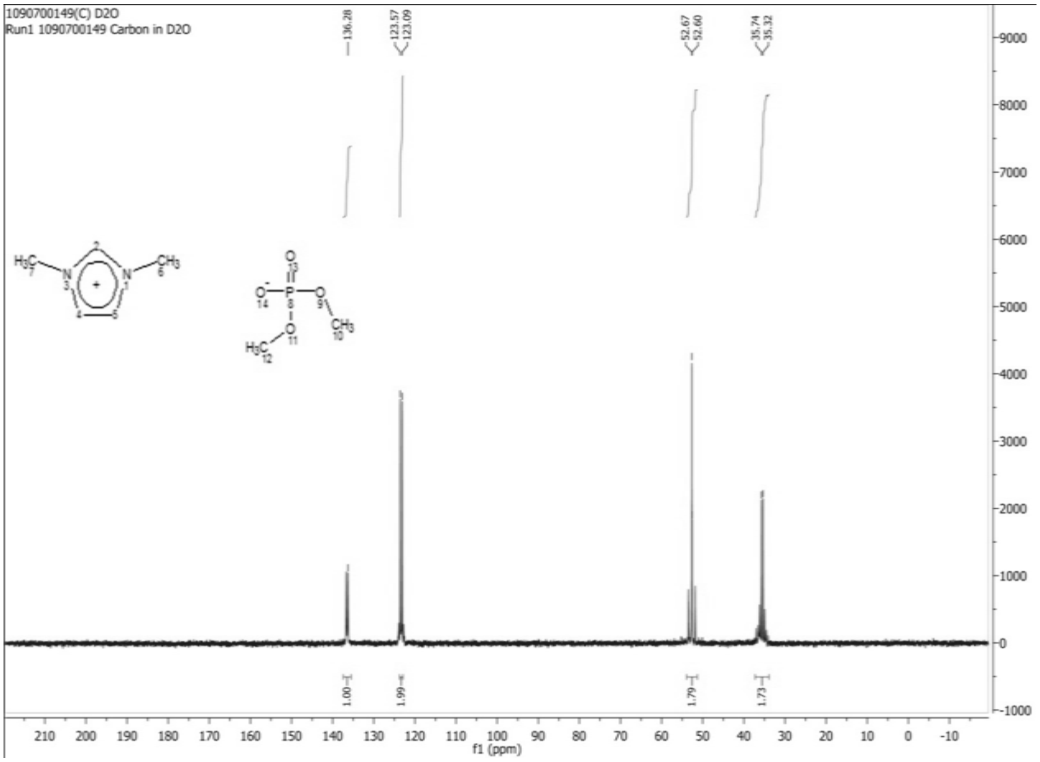


Figure J.2 ^{13}C NMR for 1-methyl-3-methyl-imidazolium dimethylphosphate (MMIM[DMP])

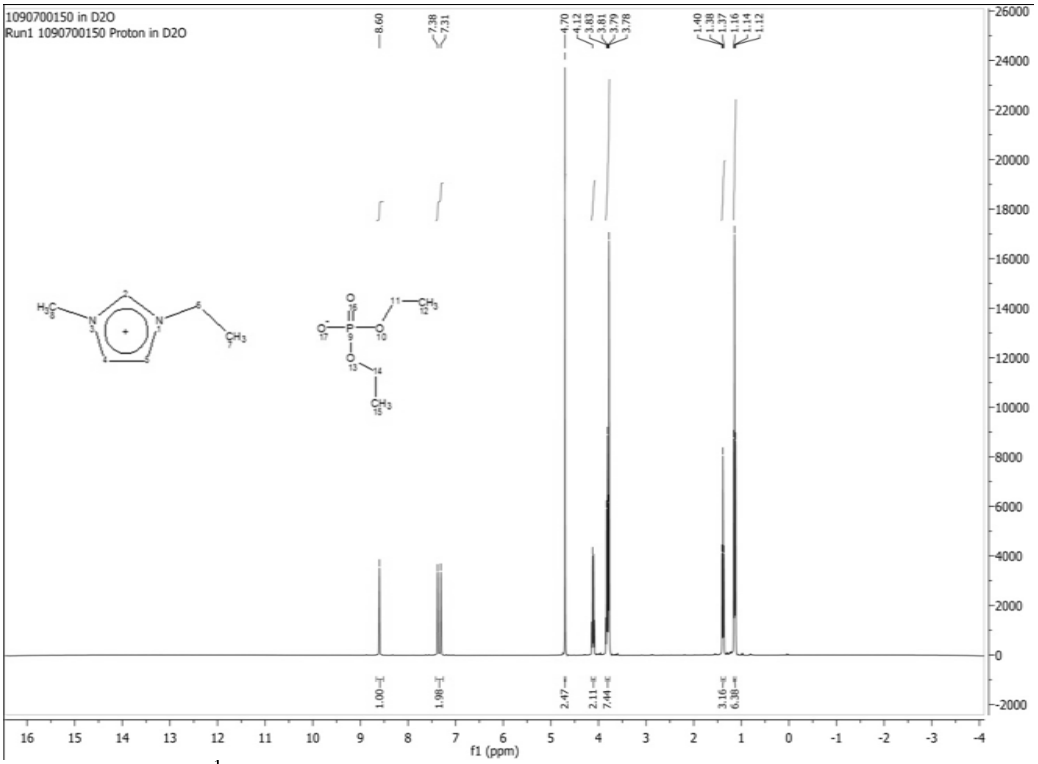


Figure J.3 ^{1}H NMR for 1-methyl-3-ethyl-imidazolium diethylphosphate (EMIM[DEP])

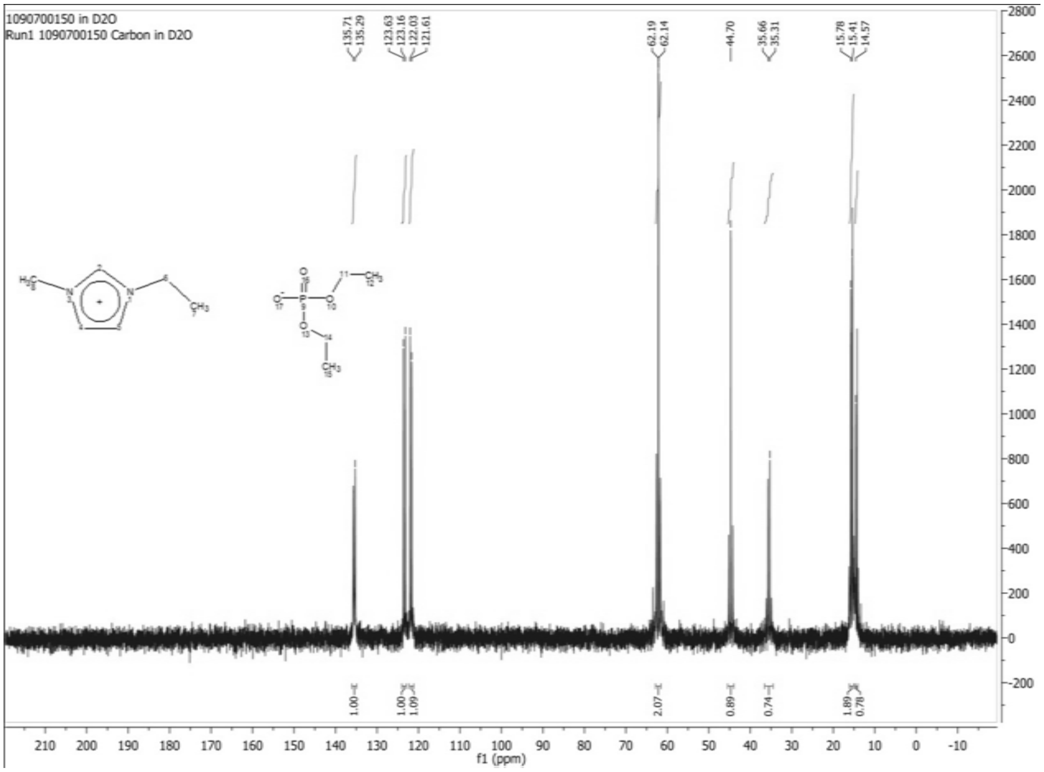


Figure J.4 ^{13}C NMR for 1-methyl-3-ethyl-imidazolium diethylphosphate (EMIM[DEP])

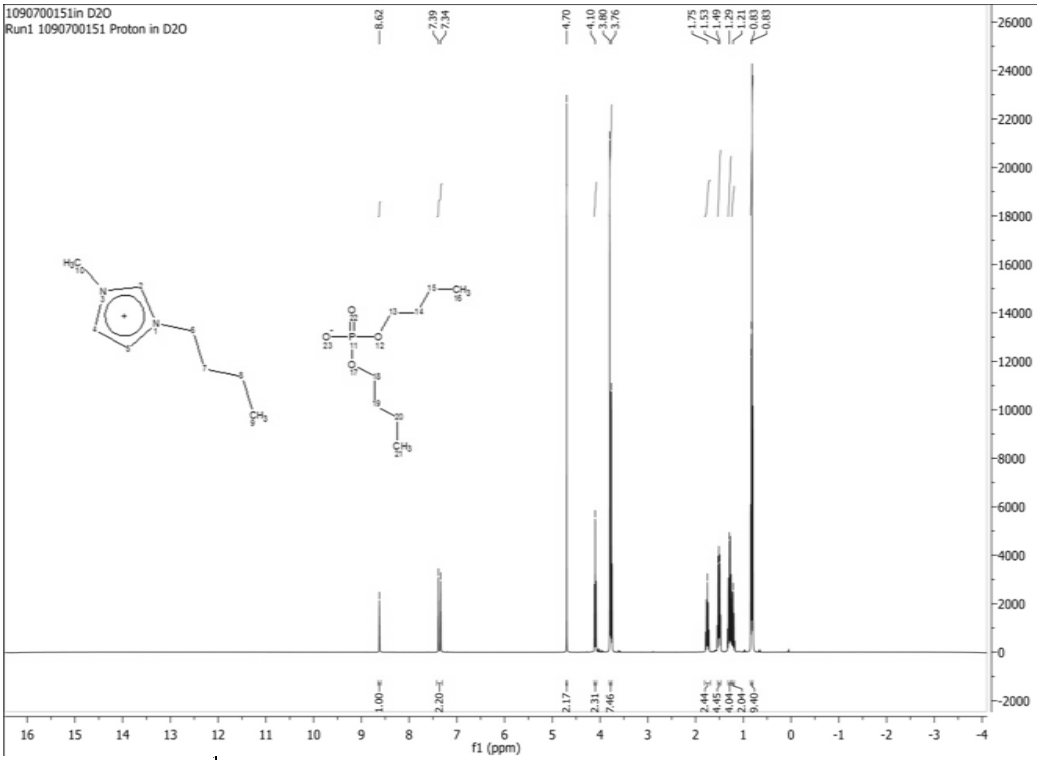


Figure J.5 ^{1}H NMR for 1-methyl-3-butyl-imidazolium dibutylphosphate (BMIM[DBP])

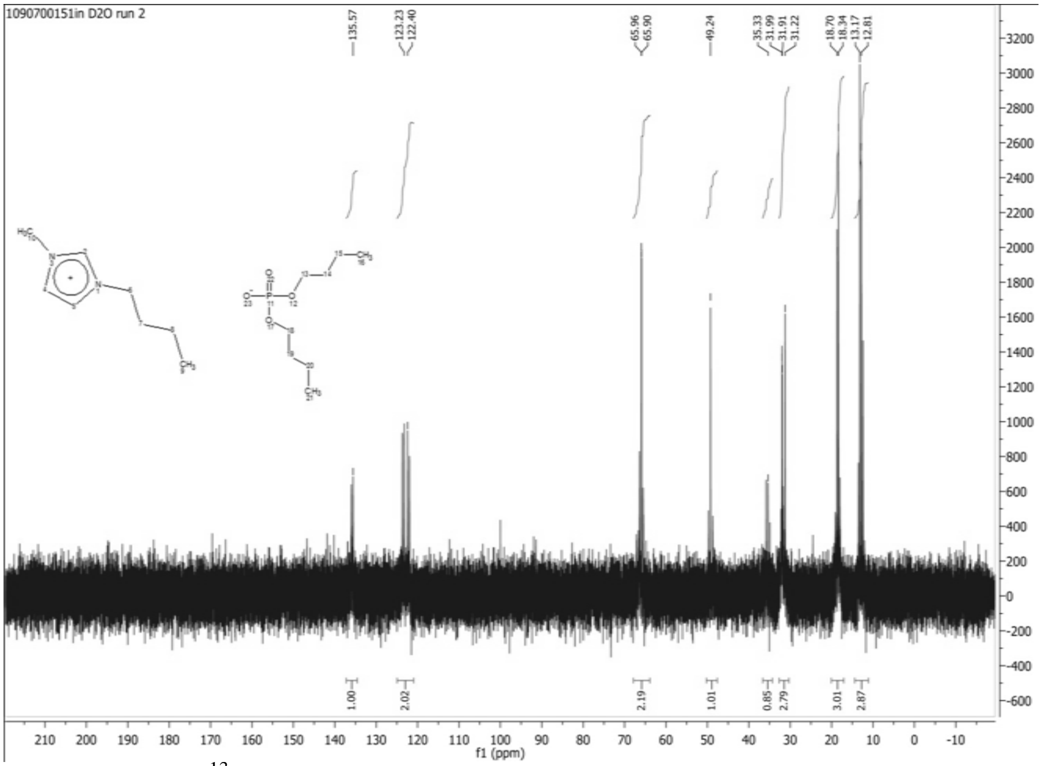


Figure J.6 ^{13}C NMR for 1-methyl-3-butyl-imidazolium dibutylphosphate (BMIM[DBP])

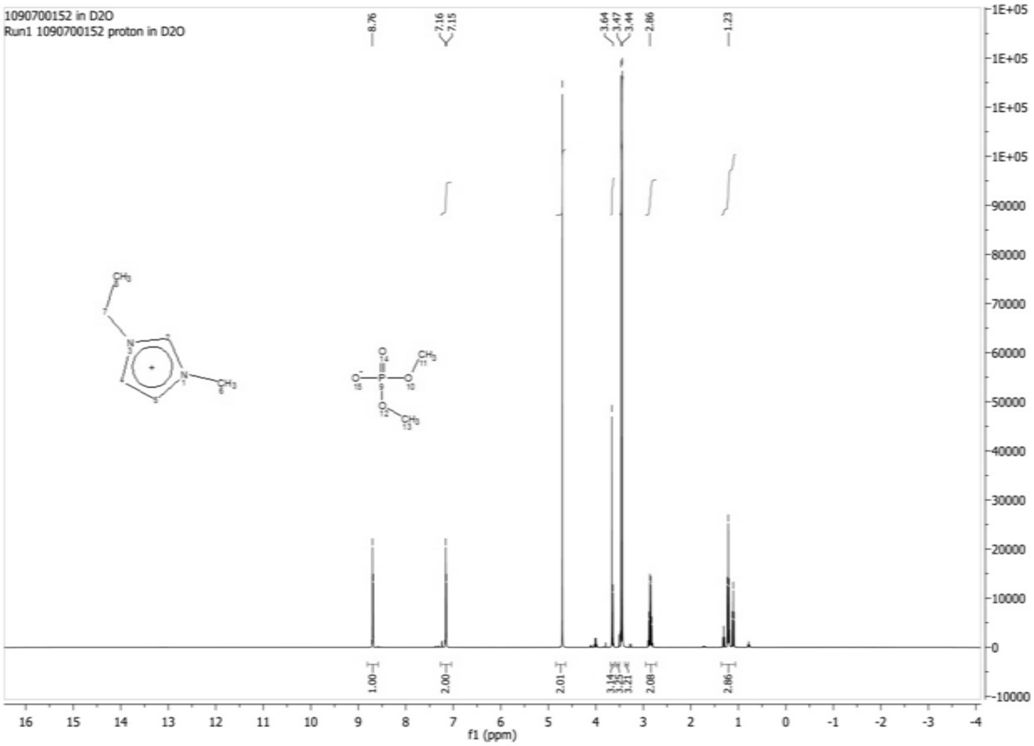


Figure J.7 ^{1}H NMR for 1-ethyl-3-methyl-imidazolium dimethylphosphate (EMIM[DMP])

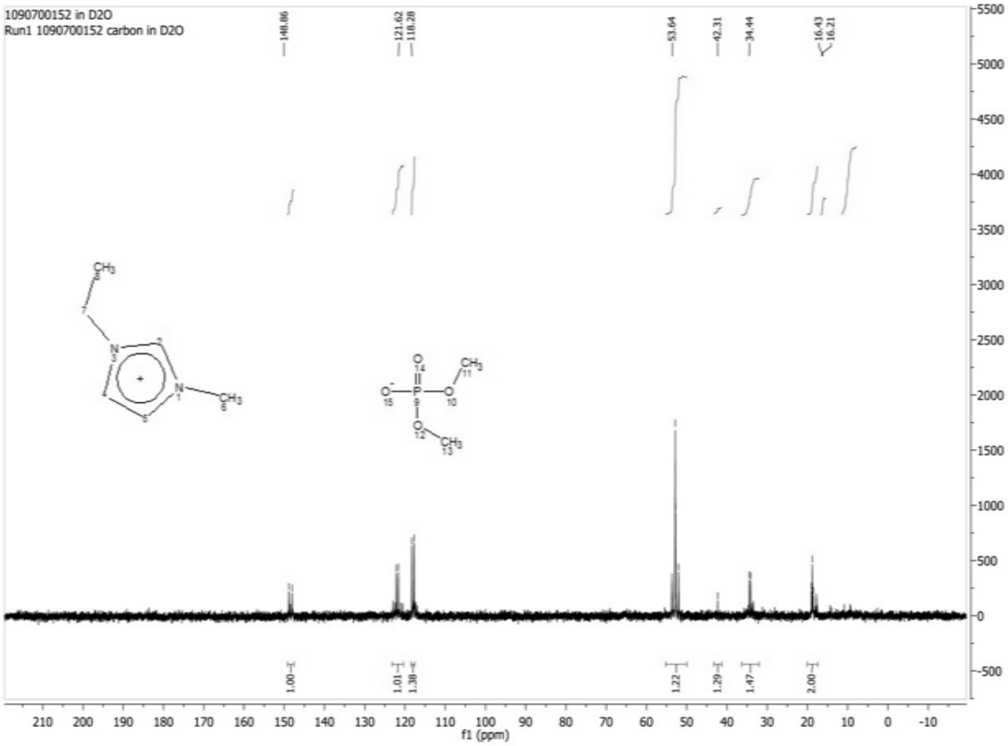


Figure J.8 ^{13}C NMR for 1-ethyl-3-methyl-imidazolium dimethylphosphate (EMIM[DMP])

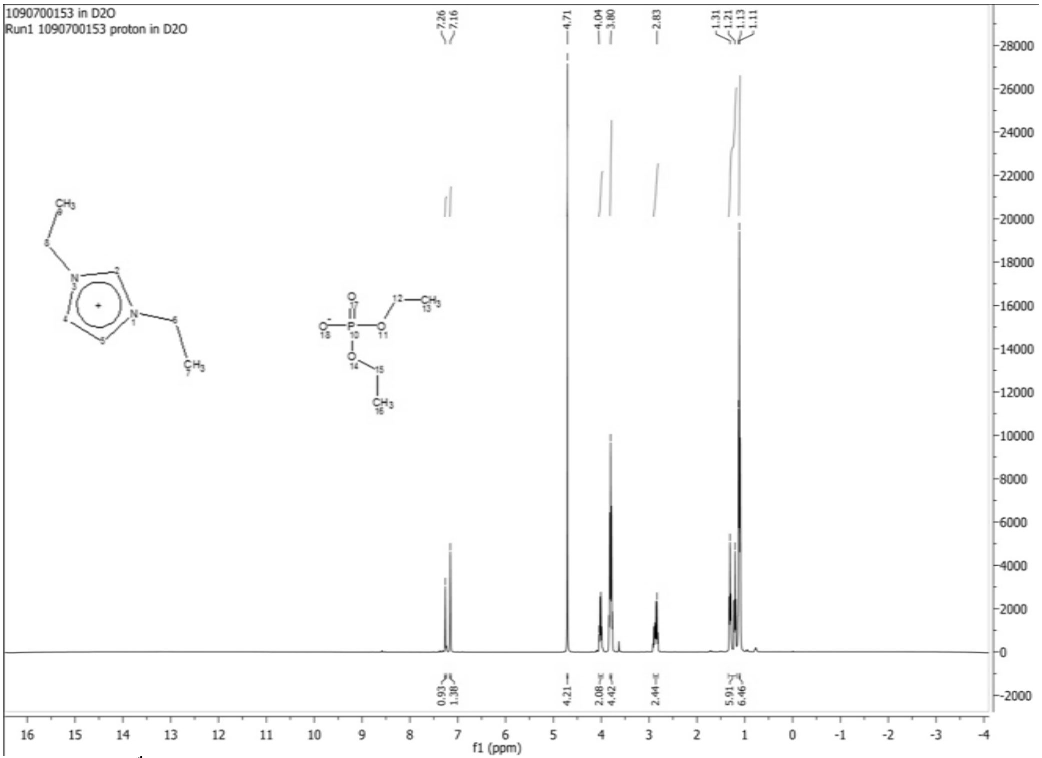


Figure J.9 ^{1}H NMR for 1-ethyl-3-ethyl-imidazolium diethylphosphate (EEIM[DEP])

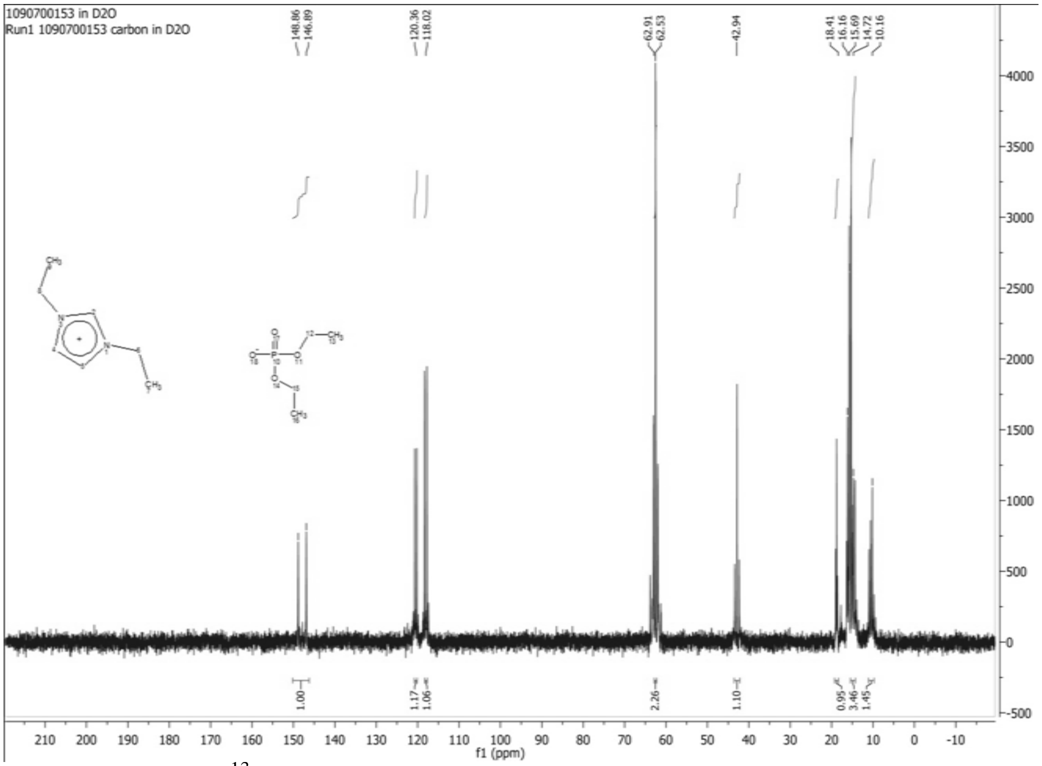


Figure J.10 ^{13}C NMR for 1-ethyl-3-ethyl-imidazolium diethylphosphate (EEIM[DEP])

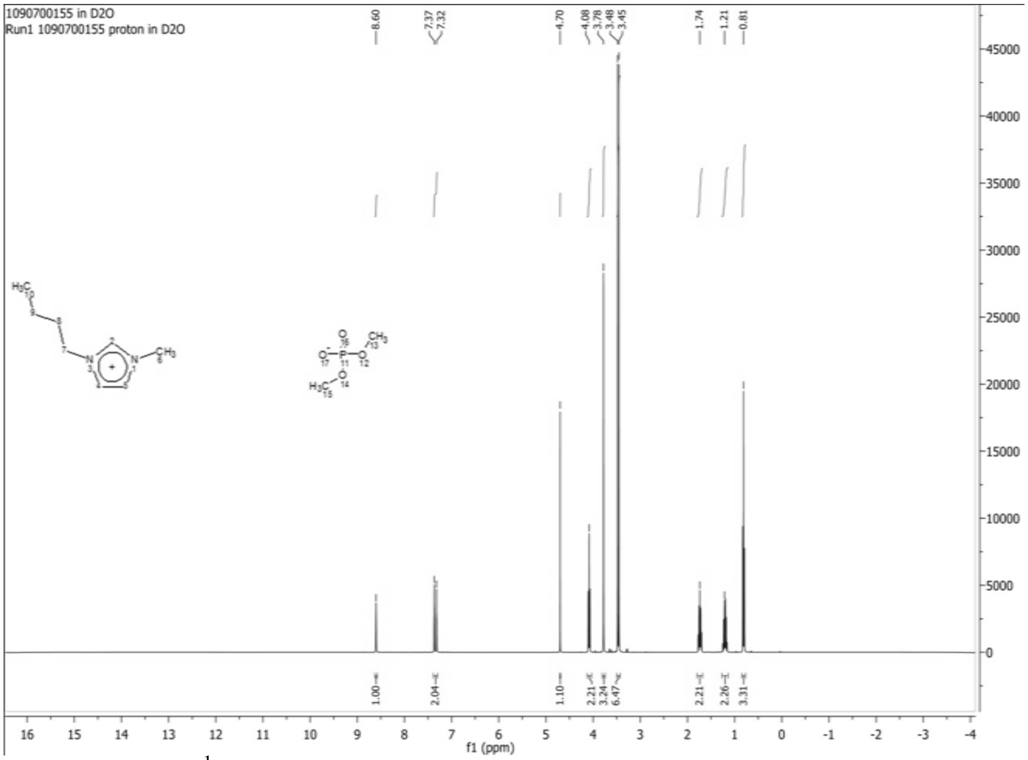


Figure J.11 ^{1}H NMR for 1-butyl-3-methyl-imidazolium dimethylphosphate (BMIM[DMP])

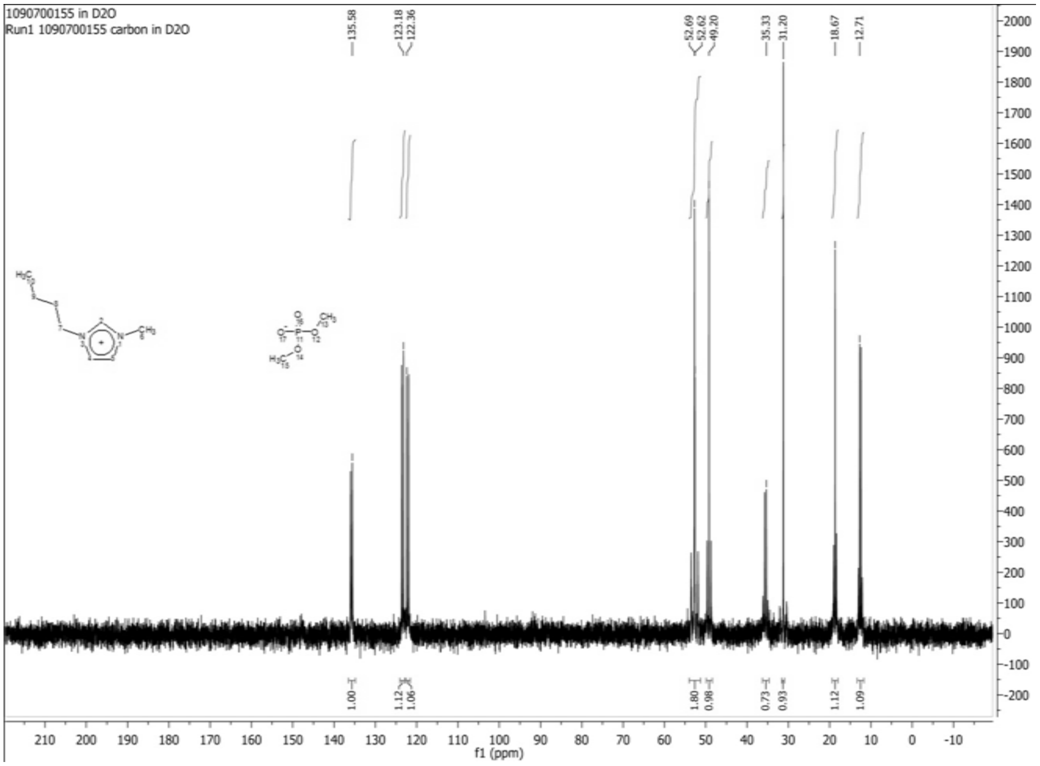


Figure J.12 ^{13}C NMR for 1-butyl-3-methyl-imidazolium dimethylphosphate (BMIM[DMP])

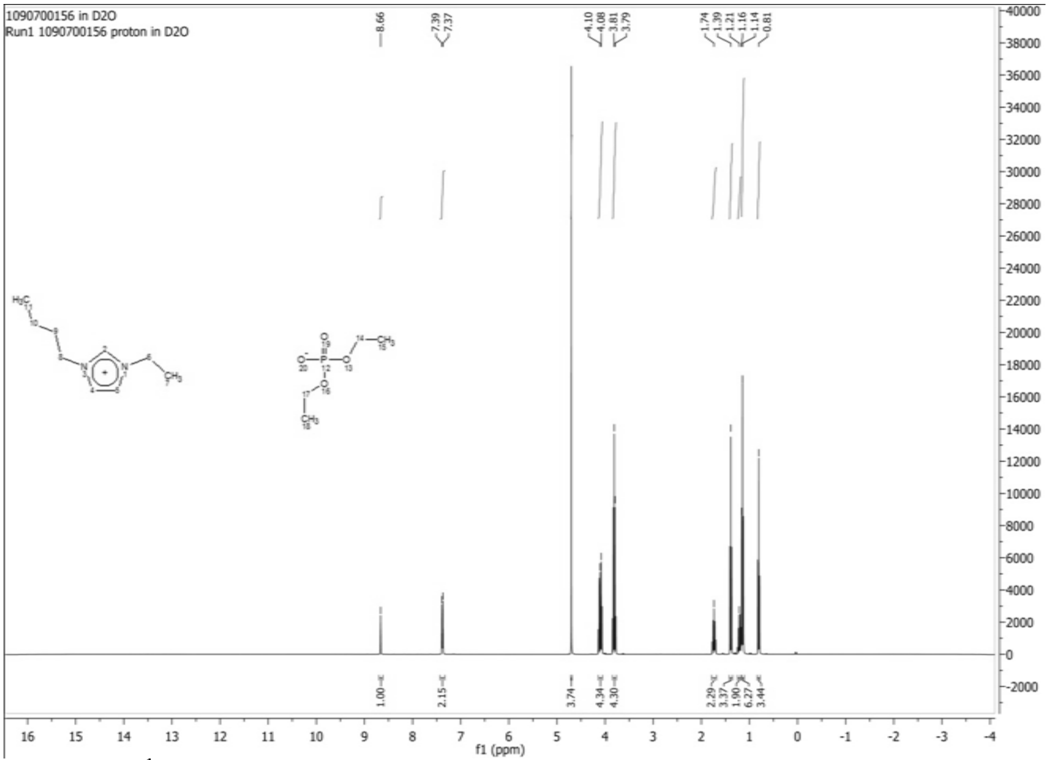


Figure J.13 ^{1}H NMR for 1-butyl-3-ethyl-imidazolium diethylphosphate (BEIM[DEP])

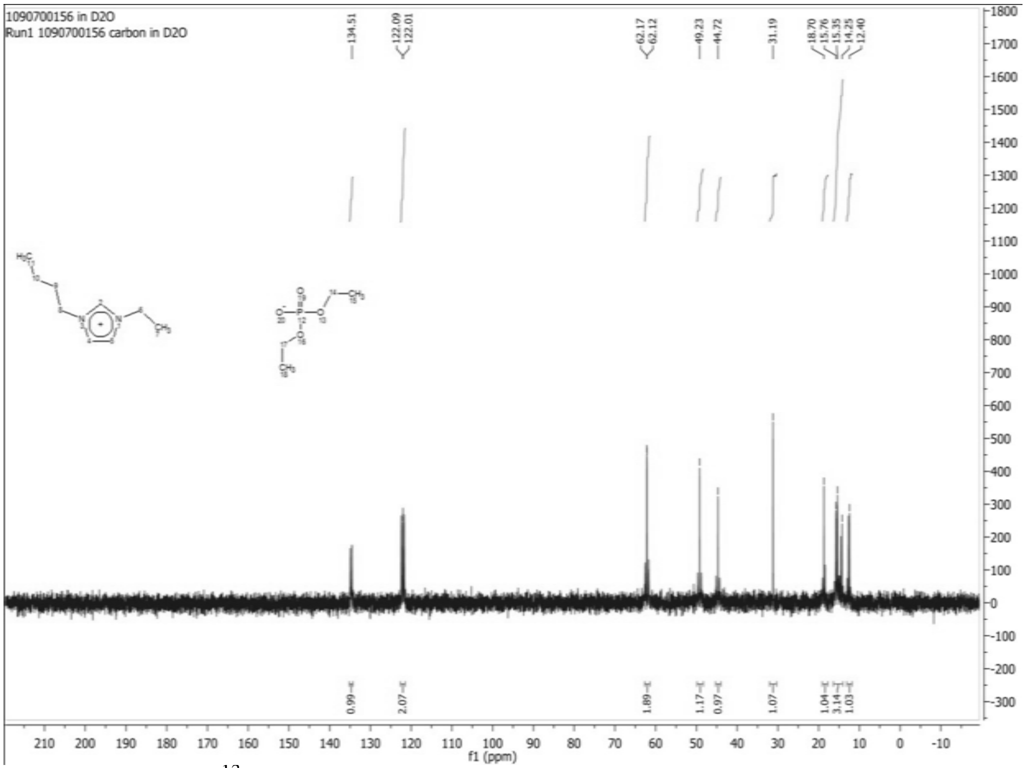


Figure J.14 ^{13}C NMR for 1-butyl-3-ethyl-imidazolium diethylphosphate (BEIM[DEP])

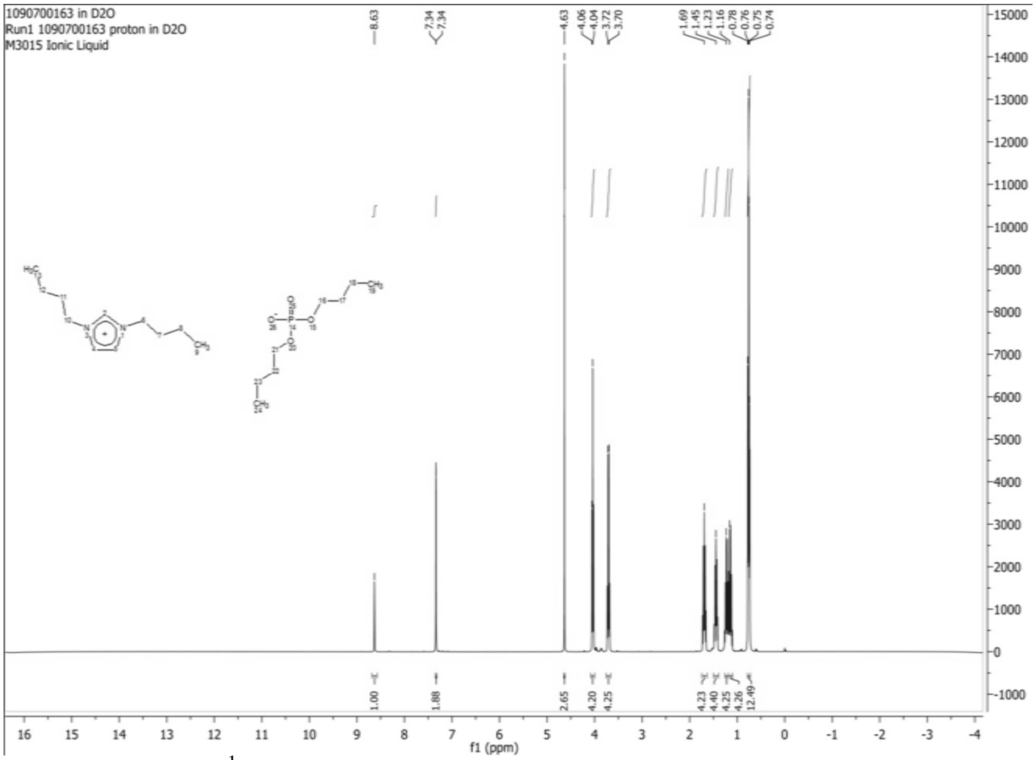


Figure J.15 ^{1}H NMR for 1-butyl-3-butyl-imidazolium dibutylphosphate (BBIM[DBP])

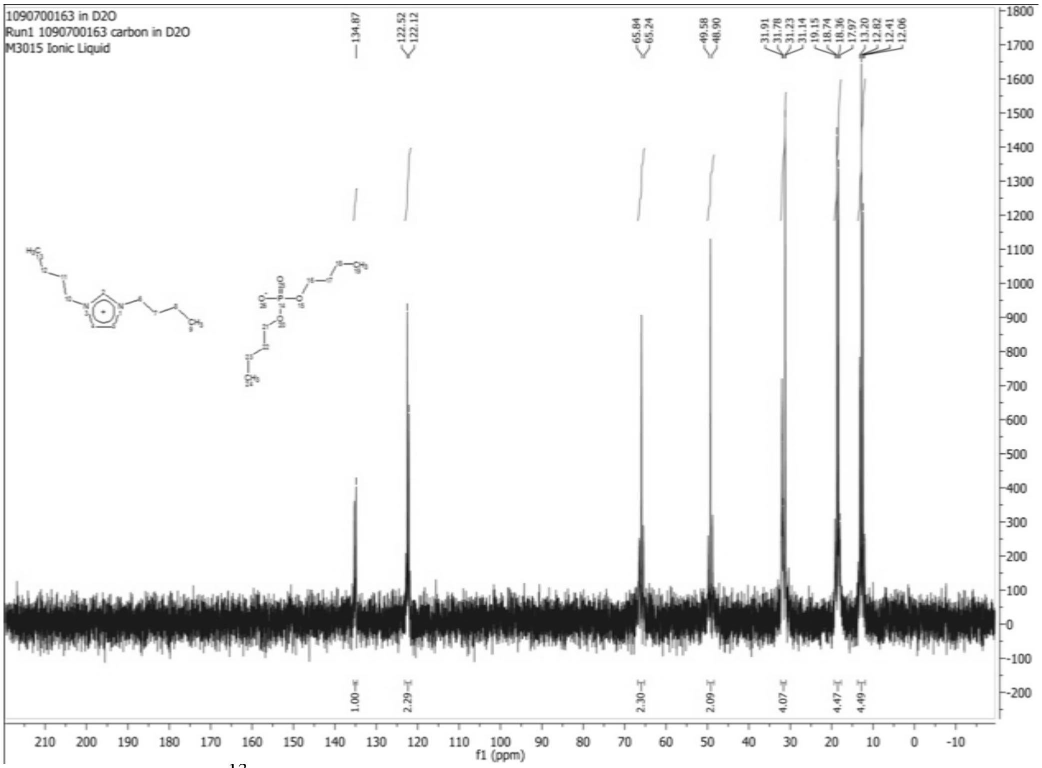


Figure J.16 ^{13}C NMR for 1-butyl-3-butyl-imidazolium dibutylphosphate (BBIM[DBP])

APPENDIX K

[DSC RESULTS]

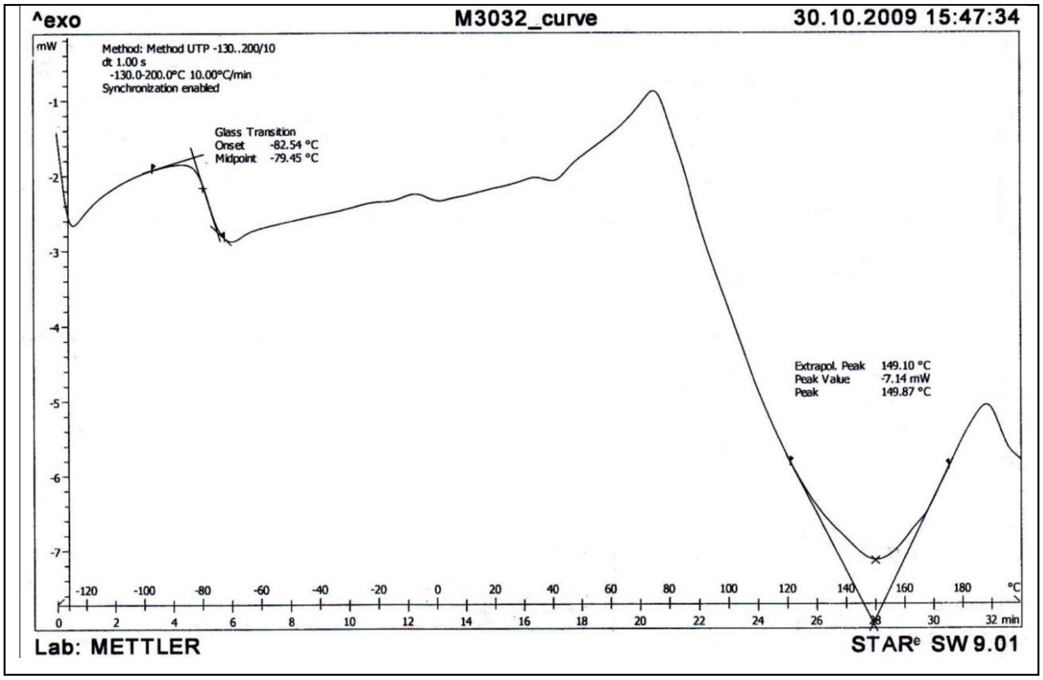


Figure K.1 DSC for 1-methyl-3-methyl-imidazolium dimethylphosphate (MMIM[DMP])

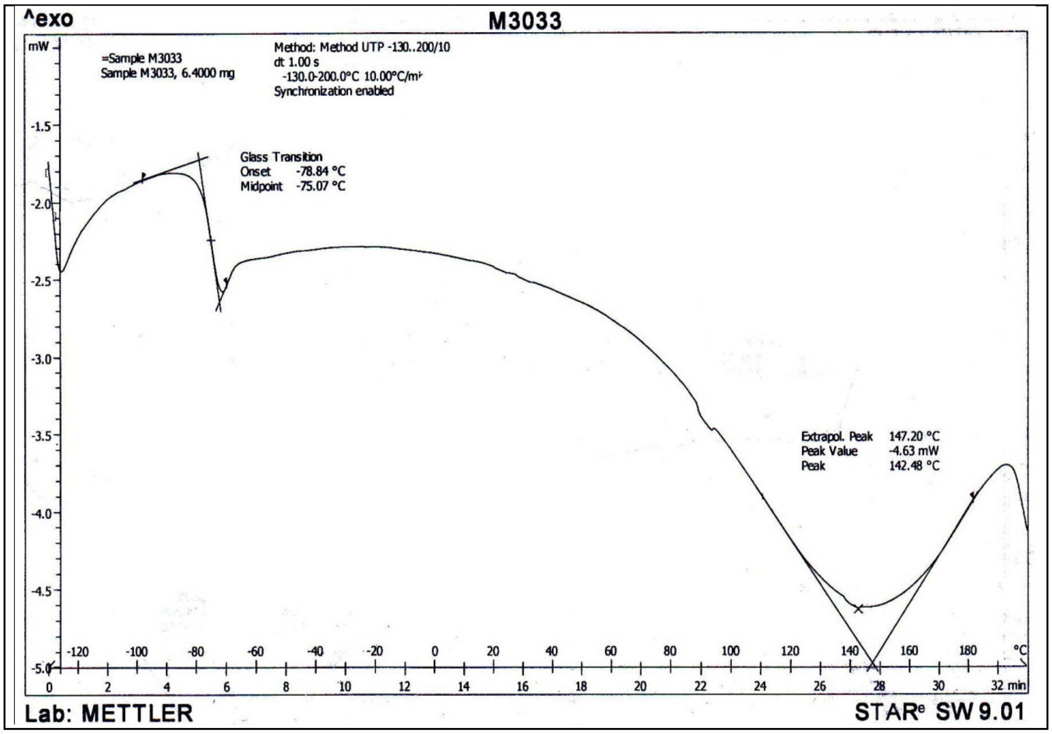


Figure K.2 DSC for 1-ethyl-3-methyl-imidazolium diethylphosphate (EMIM[DEP])

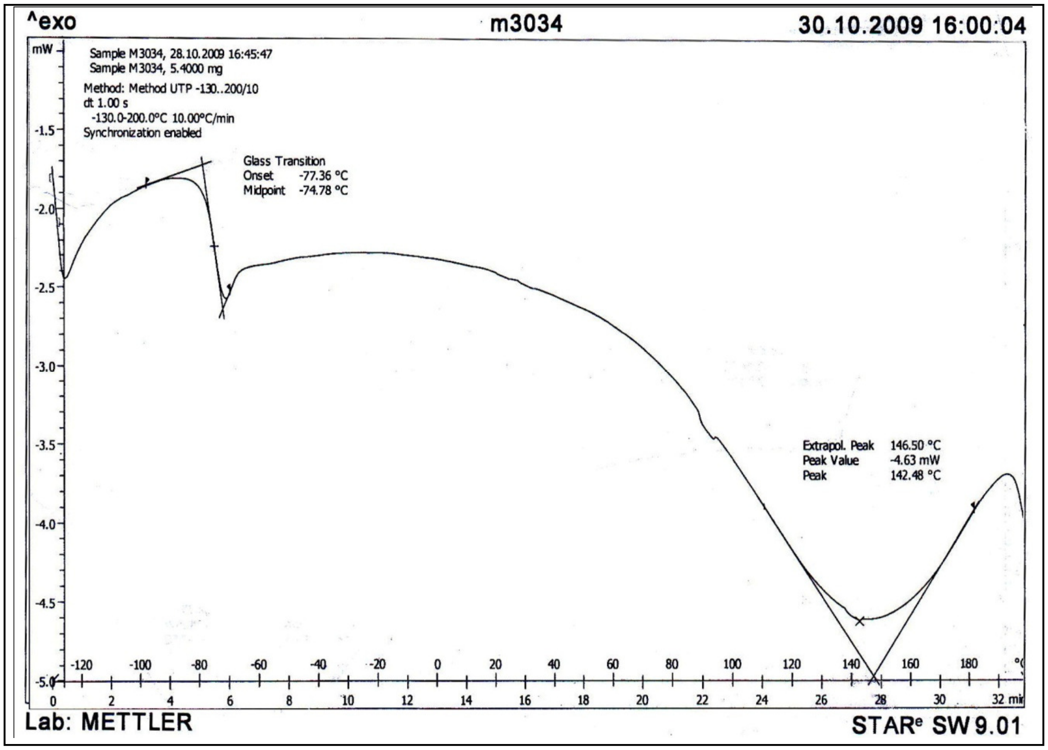


Figure K.3 DSC for 1-butyl-3-methyl-imidazolium dibutyllphosphate (BMIM[DBP])

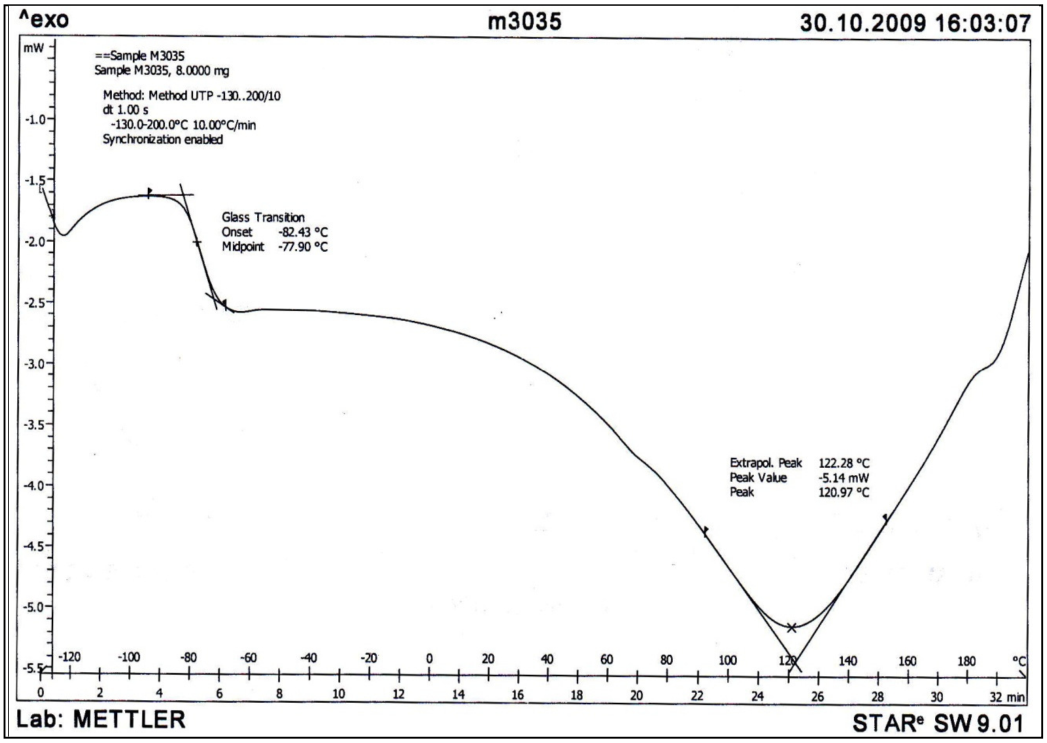


Figure K.4 DSC for 1-methyl-3-ethyl-imidazolium dimethylphosphate (EMIM[DMP])

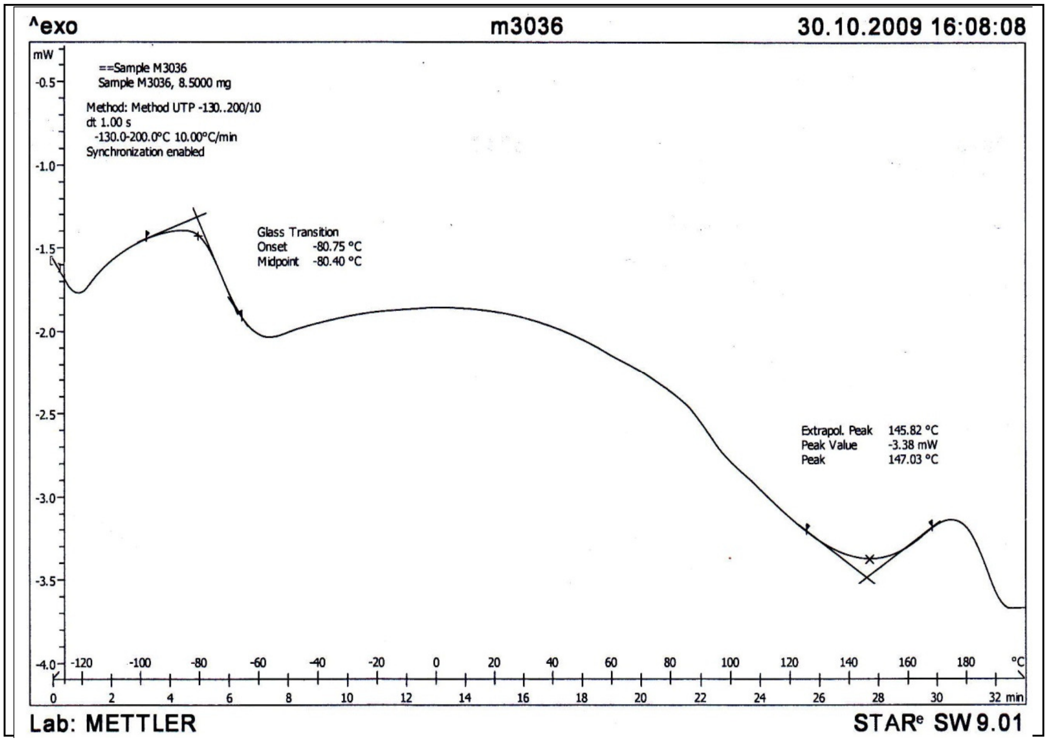


Figure K.5 DSC for 1-ethyl-3-ethyl-imidazolium diethylphosphate (EEIM[DEP])

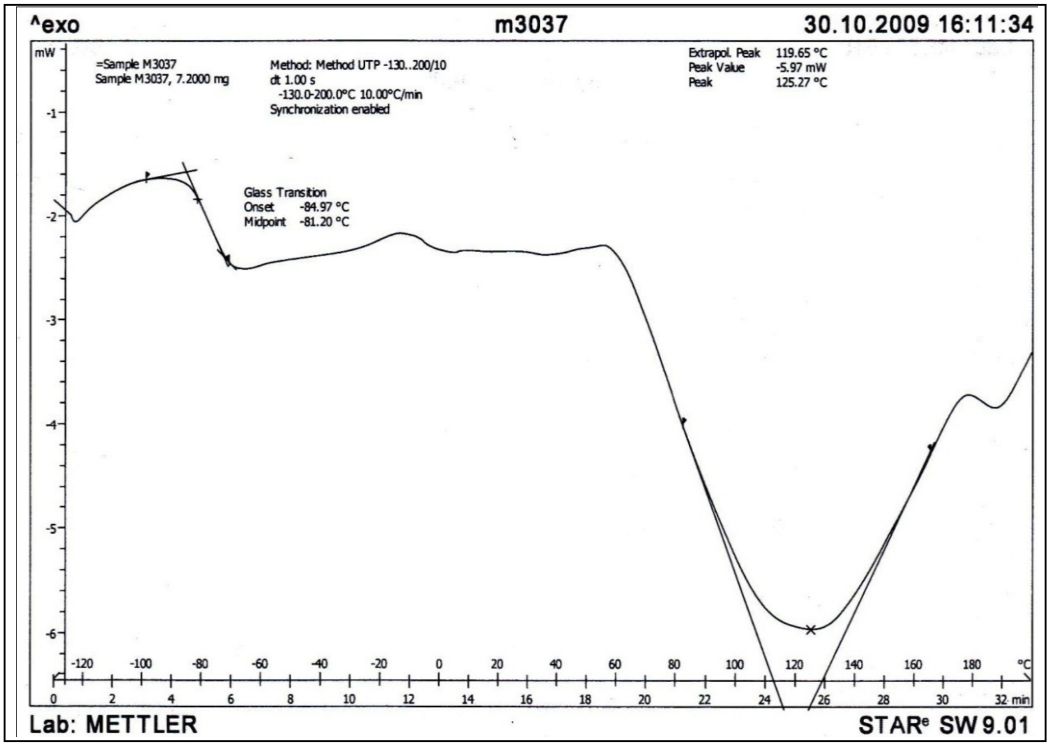


Figure K.6 DSC for 1-methyl-3-butyl-imidazolium dimethylphosphate (BMIM[DMP])

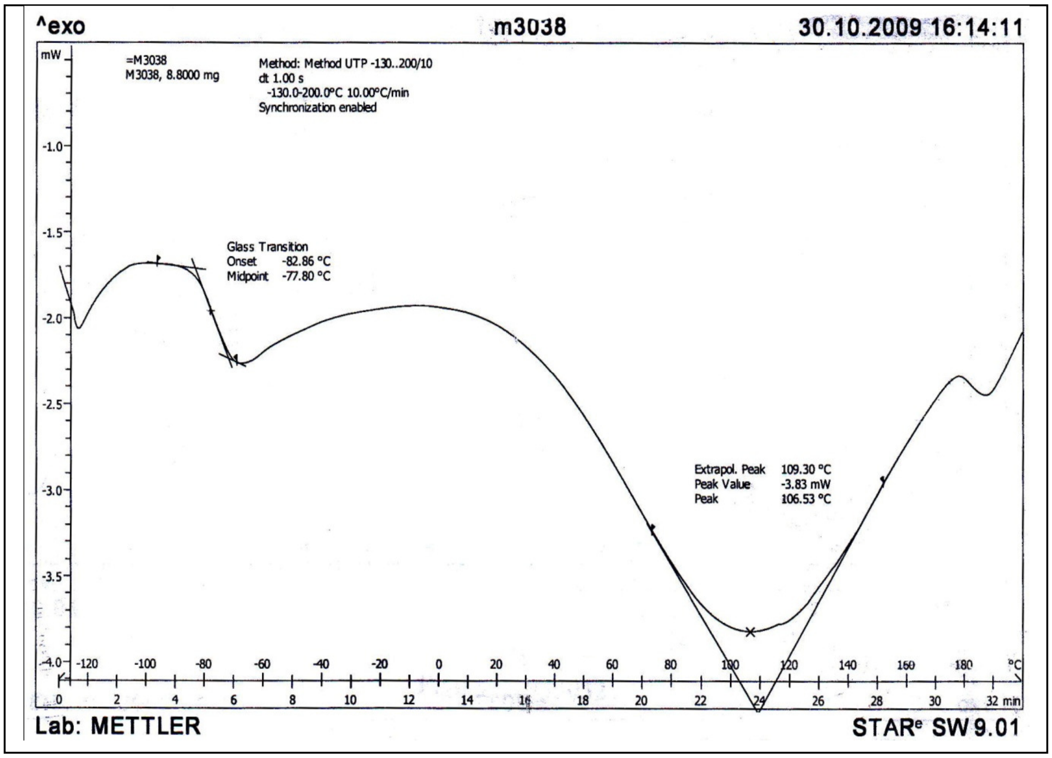


Figure K.7 DSC for 1-ethyl-3-butyl-imidazolium diethylphosphate (BEIM[DBP])

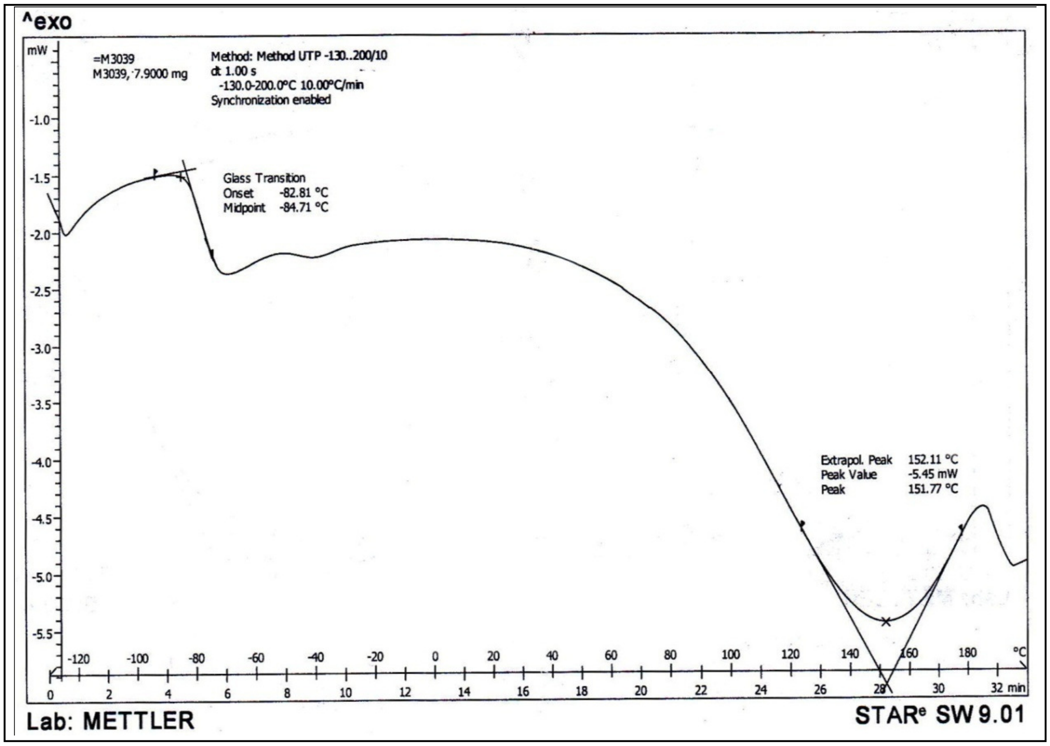


Figure K.8 DSC for 1-butyl-3-butyl-imidazolium dibutylphosphate (BBIM[DBP])

APPENDIX L

[CHNS DATA]

Table L.1 CHNS data for the ionic liquids prepared

IL		C (%)	H (%)	N (%)	S (%)
MMIM[DMP]	Experimental	37.78 ± 0.02	6.81 ± 0.01	12.37 ± 0.04	0.00 ± 0.00
	theoretical	37.84	6.76	12.61	0.00
EMIM[DEP]	Experimental	45.50 ± 0.04	7.98 ± 0.05	10.77 ± 0.01	0.00 ± 0.00
	theoretical	45.45	7.95	10.61	0.00
BMIM[DBP]	Experimental	55.23 ± 0.02	9.58 ± 0.02	8.03 ± 0.03	0.00 ± 0.00
	theoretical	55.17	9.48	8.05	
EMIM[DMP]	Experimental	40.62 ± 0.05	7.23 ± 0.02	11.90 ± 0.01	0.00 ± 0.00
	theoretical	40.68	7.20	11.86	0.00
EEIM[DEP]	Experimental	47.52 ± 0.03	8.21 ± 0.05	10.08 ± 0.04	0.00 ± 0.00
	theoretical	47.48	8.27	10.07	0.00
BMIM[DMP]	Experimental	45.62 ± 0.03	7.97 ± 0.01	10.70 ± 0.05	0.00 ± 0.00
	theoretical	45.45	7.96	10.61	0.00
BEIM[DEP]	Experimental	51.10 ± 0.01	8.85 ± 0.05	9.24 ± 0.06	0.00 ± 0.00
	theoretical	50.98	8.82	9.15	0.00
BBIM[DBP]	Experimental	73.50± 0.04	12.82± 0.05	9.12± 0.05	0.00 ± 0.00
	theoretical	73.79	12.62	9.06	0.00

Table L.2 CHNS data for model oils prepared

Model Oil	C (%)	H (%)	N (%)	S(%)
0.1% DBT in dodecane	80.72 ± 0.02	9.66 ± 0.01	0.167 ± 0.04	0.098 ± 0.01
0.1% BT in dodecane	78.46 ± 0.04	10.54 ± 0.03	0.281 ± 0.01	0.102 ± 0.04
0.1% 3-MT in dodecane	77.90 ± 0.02	11.88 ± 0.01	0.261 ± 0.02	0.107 ± 0.03
1.0% BT in dodecane	77.41 ± 0.04	10.84 ± 0.01	0.281 ± 0.01	1.035 ± 0.03
2.0% BT in dodecane	79.16 ± 0.01	10.77 ± 0.02	0.150 ± 0.02	2.012 ± 0.02
3.0% BT in dodecane	78.55 ± 0.02	10.63 ± 0.01	0.211 ± 0.03	3.007 ± 0.01

APPENDIX M

[VISCOSITY DATA]

Table M.1MMIM[DMP] viscosity data.

Temp [°C]	Viscosity [mPa·s]
20.00	371.33
25.00	259.95
30.00	187.29
35.00	138.74
40.00	105.27
45.00	81.730
50.00	64.686
55.00	52.115
60.00	42.638
65.00	35.387
70.00	29.743
75.00	25.287
80.00	21.696

Table M.2 EMIM[DEP] viscosity data.

Temp [°C]	Viscosity [mPa·s]
20.00	397.30
25.00	284.19
30.00	207.71
35.00	155.48
40.00	118.94
45.00	92.784
50.00	73.614
55.00	59.335
60.00	48.518
65.00	40.178
70.00	33.660
75.00	28.500
80.00	24.358

Table M.3 BMIM[DBP] viscosity data.

Temp [°C]	Viscosity [mPa·s]
20.00	889.87
25.00	740.46
30.00	605.40
35.00	480.56
40.00	362.49
45.00	249.45
50.00	139.61
55.00	82.159
60.00	56.439
65.00	21.984
70.00	18.477
75.00	15.679
80.00	13.411

Table M.4 EMIM[DMP] viscosity data.

Temp [°C]	Viscosity [mPa·s]
20.00	385.50
25.00	270.02
30.00	190.51
35.00	153.21
40.00	112.01
45.00	85.391
50.00	69.228
55.00	56.834
60.00	49.276
65.00	40.294
70.00	31.225
75.00	25.375
80.00	22.597

Table M.5 EEIM[DEP] viscosity data.

Temp [°C]	Viscosity [mPa·s]
20.00	491.91
25.00	340.69
30.00	241.56
35.00	175.52
40.00	130.91
45.00	99.849
50.00	77.680
55.00	61.514
60.00	49.508
65.00	40.423
70.00	33.448
75.00	27.993
80.00	23.677

Table M.6 BMIM[DMP] viscosity data.

Temp [°C]	Viscosity [mPa·s]
20.00	762.47
25.00	520.19
30.00	364.92
35.00	262.85
40.00	193.92
45.00	146.07
50.00	112.23
55.00	87.768
60.00	69.762
65.00	56.274
70.00	46.012
75.00	38.089
80.00	31.891

Table M.7 BEIM[DEP] viscosity data.

Temp [°C]	Viscosity [mPa·s]
20.00	604.69
25.00	432.46
30.00	314.28
35.00	233.43
40.00	176.82
45.00	136.23
50.00	106.68
55.00	84.795
60.00	68.329
65.00	55.743
70.00	45.991
75.00	38.348
80.00	32.304

Table M.8 BBIM[DBP] viscosity data.

Temp [°C]	Viscosity [mPa·s]
20.00	1930.5
25.00	1347.9
30.00	962.12
35.00	699.93
40.00	518.07
45.00	389.85
50.00	297.72
55.00	230.51
60.00	180.80
65.00	143.48
70.00	115.20
75.00	93.447
80.00	76.540

APPENDIX N

[DENSITY DATA]

Table N.1 MMIM[DMP] density data.

Temp [°C]	Density [g/cm^3]
20.00	1.2585
25.00	1.2549
30.00	1.2514
35.00	1.2480
40.00	1.2446
45.00	1.2412
50.00	1.2379
55.00	1.2345
60.00	1.2312
65.00	1.2279
70.00	1.2246
75.00	1.2213
80.00	1.2181

Table N.2 EMIM[DEP] density data.

Temp [°C]	Density [g/cm^3]
20.00	1.1438
25.00	1.1403
30.00	1.1368
35.00	1.1333
40.00	1.1299
45.00	1.1265
50.00	1.1231
55.00	1.1198
60.00	1.1164
65.00	1.1130
70.00	1.1097
75.00	1.1064
80.00	1.1031

Table N.3 BMIM[DBP] density data.

Temp [°C]	Density [g/cm^3]
20.00	1.0415
25.00	1.0379
30.00	1.0343
35.00	1.0307
40.00	1.0271
45.00	1.0235
50.00	1.0198
55.00	1.0162
60.00	1.0125
65.00	1.0089
70.00	1.0052
75.00	1.0016
80.00	0.9983

Table N.4 EMIM[DMP] density data.

Temp [°C]	Density [g/cm^3]
20.00	1.1722
25.00	1.1691
30.00	1.1658
35.00	1.1610
40.00	1.1578
45.00	1.1544
50.00	1.1504
55.00	1.1474
60.00	1.1442
65.00	1.1404
70.00	1.1370
75.00	1.1342
80.00	1.1310

Table N.5 EEIM[DEP] density data.

Temp [°C]	Density [g/cm^3]
20.00	1.1298
25.00	1.1258
30.00	1.1219
35.00	1.1179
40.00	1.1140
45.00	1.1101
50.00	1.1062
55.00	1.1023
60.00	1.0985
65.00	1.0946
70.00	1.0907
75.00	1.0868
80.00	1.0830

Table N.6 BMIM[DMP] density data.

Temp [°C]	Density [g/cm^3]
20.00	1.1573
25.00	1.1538
30.00	1.1503
35.00	1.1470
40.00	1.1436
45.00	1.1404
50.00	1.1371
55.00	1.1339
60.00	1.1307
65.00	1.1275
70.00	1.1243
75.00	1.1211
80.00	1.1179

Table N.7 BEIM[DEP] density data.

Temp [°C]	Density [g/cm^3]
20.00	1.0793
25.00	1.0756
30.00	1.0722
35.00	1.0687
40.00	1.0653
45.00	1.0619
50.00	1.0585
55.00	1.0551
60.00	1.0517
65.00	1.0484
70.00	1.0451
75.00	1.0418
80.00	1.0385

Table N.8 BBIM[DBP] density data.

Temp [°C]	Density [g/cm^3]
20.00	1.0138
25.00	1.0104
30.00	1.0070
35.00	1.0036
40.00	1.0010
45.00	0.9970
50.00	0.9937
55.00	0.9903
60.00	0.9870
65.00	0.9838
70.00	0.9805
75.00	0.9773
80.00	0.9741