



# **Investigation of the Desulfurization of Petroleum Distillates using Novel Ionic Liquids**

*by*

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## **Declaration**

I declare that this dissertation is my own unaided work. It is being submitted to the degree of Masters of Science to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

.....

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09 May 2016

## **Abstract**

The use of fuels (from crude oil) in vehicles is responsible for one of the biggest environmental challenges; SO<sub>2</sub> emission. As a result most countries regulate their sulfur emissions, with the goal of getting to the use of 10 ppm sulfur fuels. These stringent fuel sulfur content requirements have resulted in intensive research being directed at alternative desulfurization technologies which will ensure the treatment of fuels to acceptable sulfur levels. Extractive desulfurization using ionic liquids (IL) may be considered as one of the most promising of these technologies and is the subject of the study presented in this work.

This study served two major purposes: (1) to investigate the capacity as well as key parameters which affect the extraction efficiency of the IL; 1-butyl-3-methylimidazolium octylsulfate as a solvent for deep extractive desulfurization of real Fluid Catalytic Cracking Unit (FCCU) diesel fuel samples collected from a typical South African Refinery, (2) to study/find suitable solvents for the regeneration of sulfur-loaded 1-butyl-3-methylimidazolium octylsulfate and the efficiency and effectiveness of the regenerated IL in the desulfurization of diesel fuel. 1-butyl-3-methylimidazolium octylsulfate was selected due to its properties i.e. good extractive ability for S-compounds and insolubility in fuel oils.

A 22.1% sulfur removal was achieved in the desulfurization of FCCU feed stream diesel fuel, while 96% sulfur removal was achieved for FCCU product stream diesel fuel. These results show that the IL is more effective in the selective removal of sulfur (S) from FCCU diesel product than from FCCU feed stream, suggesting that fuel sulfur content and stream composition affects the extraction efficiency and effectiveness of the IL. Based on thermodynamic considerations, hexane was selected as the most suitable solvent for the re-extraction of sulfur from spent IL. Regenerated IL was used for desulfurization of diesel and achieved highest sulfur removal of 95% and the IL was regenerated up to four times without appreciable decrease in efficiency. The results obtained herein show that ILs are effective in the desulfurization of real diesel oil samples when the sulfur concentration is not very high. Further studies on the recoverability of ILs as well as their environmental impact need to be done to support findings in this study.

# Table of Contents

List of Figures.....	v
List of Tables .....	viii
<b>Chapter 1</b>	<b>1</b>
1. Introduction .....	1
1.1. Background .....	1
1.2. Research Motivation.....	2
1.3. Research Aims and Objectives .....	3
1.4. Dissertation Outline.....	4
<b>Chapter 2</b>	<b>5</b>
2. Literature Review .....	5
2.1. Sulfur in fuel oils.....	5
2.2. Sulfur Regulation.....	7
2.2.1. Air pollution Background .....	7
2.2.2. Sulfur Emissions Background .....	8
2.2.3. Air Emissions Legislation .....	8
2.3. Conventional desulfurization process.....	12
2.4. Alternative and/or supplementary desulfurization processes .....	13
2.4.1. Biodesulfurization.....	14
2.4.2. Adsorptive Desulfurization (ADS) .....	14
2.4.3. Oxidative Desulfurization (ODS) .....	15
2.4.4. Extractive Desulfurization (EDS).....	15
2.4.5. Oxidative-Extractive Desulfurization .....	18
2.5. Ionic Liquids .....	18
2.5.1. Definition .....	18
2.5.2. Uses/Applications of Ionic Liquids.....	19
2.5.3. Structure of Ionic Liquids.....	20
2.5.4. Ionic Liquids as Solvents in Extractive Desulfurization .....	21
2.6. Diesel Sample .....	31
<b>Chapter 3</b>	<b>35</b>
3. Experimental.....	35
3.1. Feed Materials.....	35
3.2. Analysis Procedure .....	36
3.3. Equipment .....	37

<b>3.4.</b>	<b>Real diesel desulfurization .....</b>	<b>41</b>
<b>3.5.</b>	<b>Ionic Liquid regeneration .....</b>	<b>43</b>
<b>3.5.2.</b>	<b>Regeneration methods and experimental procedure .....</b>	<b>44</b>
<b>Chapter 4</b>		<b>46</b>
<b>4.</b>	<b>Results.....</b>	<b>46</b>
<b>5.</b>	<b>Discussion .....</b>	<b>62</b>
<b>6.</b>	<b>Conclusion and Recommendations .....</b>	<b>68</b>
<b>References</b>		<b>70</b>
<b>Appendices.....</b>		<b>77</b>
<b>Appendix A: Publications .....</b>		<b>77</b>
<b>Appendix B: List of Symbols .....</b>		<b>77</b>
<b>Appendix C: Ionic Liquids Acronyms and Names .....</b>		<b>78</b>
<b>Appendix D: H NMR and C NMR Spectroscopy Results .....</b>		<b>80</b>

## List of Figures

<b>Figure 1</b> Structures of typical aromatic sulfur compounds found in fossil fuels .....	<b>6</b>
<b>Figure 2</b> European Union Sulfur Emissions' Regulations Timeline .....	<b>10</b>
<b>Figure 3</b> Milestones in Sulfur Emissions from Vehicles in South Africa.....	<b>11</b>
<b>Figure 4</b> Relative reactivity of various organic sulfur compounds in HDS.....	<b>13</b>
<b>Figure 5</b> Extractive desulfurization process (Single Stage), IL = Ionic Liquid .....	<b>16</b>
<b>Figure 6</b> Extractive desulfurization process with solvent recovery .....	<b>17</b>
<b>Figure 7</b> Multistage extractive desulfurization process with solvent recovery.....	<b>17</b>
<b>Figure 8</b> Common cations of current ionic liquids .....	<b>20</b>
<b>Figure 9</b> Common anions of current ionic liquids .....	<b>21</b>
<b>Figure 10</b> IL Re-use without Regeneration (1) vs. with Regeneration (2) .....	<b>26</b>
<b>Figure 12</b> Adam ACBplus-1000 weighing balance .....	<b>37</b>
<b>Figure 13</b> Heidolph heater and magnetic stirrer (a), IKA C-MAG HS4 digital heater and magnetic stirrer (b).....	<b>37</b>
<b>Figure 14</b> The Airflow Specialist fume hood.....	<b>38</b>
<b>Figure 15</b> Heidolph Laborota 4000-efficient (a), KNF rotary evaporation pump (b).....	<b>39</b>
<b>Figure 16</b> Vismara V065 vacuum oven (a), Pall vacuum/pressure pump (b).....	<b>39</b>
<b>Figure 17</b> MARS microwave digester .....	<b>40</b>
<b>Figure 18</b> Thermo ICap 6200 ICP-AES.....	<b>40</b>
<b>Figure 19</b> A schematic diagram of the experimental setup.....	<b>42</b>
<b>Figure 20</b> Visual change in the diesel (FCC unit feed stream diesel) during the desulfurization process.....	<b>43</b>
<b>Figure 21</b> The ionic liquid as per different part of the study .....	<b>45</b>
<b>Figure 22</b> Sulfur removal from Vacuum Gasoil (FCC-Unit feed) using [BMIM][OctSO <sub>4</sub> ] at different extraction stages (Oil to IL ratio = 4:1, Initial sulfur content=4203ppm)...	<b>46</b>
<b>Figure 23</b> Sulfur removal from Vacuum Gasoil (FCC-Unit feed) using [BMIM][OctSO <sub>4</sub> ] different extraction stages (Oil to IL ratio=2:1; Initial sulfur content=4203 ppm)....	<b>47</b>
<b>Figure 24</b> Multistage extraction of sulfur from VGO, showing initial compositions and compositions after the 1st, 2nd, 3rd and 4th extraction stages .....	<b>47</b>

<b>Figure 25</b> Multistage Sulfur removal from Light Cycle Oil (FFC-Unit product) using [BMIM][OcSO <sub>4</sub> ] (Oil to IL ratio= 4:1, initial sulfur content=549.9 ppm, final sulfur content=32.93 ppm) .....	<b>48</b>
<b>Figure 26</b> Multistage extraction of Sulfur from Light Cycle Oil (FCC-Unit product), (Oil to IL ratio= 2:1, initial sulfur content=549.9 ppm, final sulfur content=27.60 ppm) .....	<b>48</b>
<b>Figure 27</b> Multistage extraction of sulfur from LCO, compositions in initial LCO and after the 1st, 2nd, 3rd and 4th extraction stages .....	<b>49</b>
<b>Figure 28</b> Extraction of sulfur from Light Cycle Oil at different extraction/residence times, (Oil to IL ratio=2:1, initial S content=549.9 ppm, S content after 30 min extraction time=46.89 ppm, S content in LCO after 90 minutes extraction time=243.89) .....	<b>50</b>
<b>Figure 29</b> Reusing of IL in the extraction of sulfur from LCO, (Oil to IL ratio 4:1, Initial S content = 549.9 ppm, 0 on the horizontal axis denotes fresh IL).....	<b>51</b>
<b>Figure 30</b> Reusing of IL, sulfur removal at each IL condition (Oil to IL ratio 4:1, Initial S content=549.9 ppm) .....	<b>51</b>
<b>Figure 31</b> Tie lines for the ternary system {Hexane(1) + Thiophene(2) + [BMIM][OcSO <sub>4</sub> ](3)} .....	<b>54</b>
<b>Figure 32</b> Thiophene distribution ratio for the ternary system {Hexane + Thiophene + [BMIM][OcSO <sub>4</sub> ] } where 2 refers to [BMIM][OcSO <sub>4</sub> ] ionic liquid and I refers to the Hexane phase .....	<b>55</b>
<b>Figure 33</b> Tie lines for the ternary system {Pentane(1) + Thiophene(2) + [BMIM][OcSO <sub>4</sub> ](3)} .....	<b>56</b>
<b>Figure 34</b> Thiophene distribution ratio for the ternary system {Pentane + Thiophene + [BMIM][OcSO <sub>4</sub> ] } where 2 refers to [BMIM][OcSO <sub>4</sub> ] ionic liquid and I refers to the Hexane phase .....	<b>57</b>
<b>Figure 35</b> Tie lines for the ternary system {Ethyl acetate(1) + Thiophene(2) + [BMIM][OcSO <sub>4</sub> ](3)} .....	<b>58</b>
<b>Figure 36</b> Thiophene distribution ratio for the ternary system {Ethyl Acetate + Thiophene + [BMIM][OcSO <sub>4</sub> ] } where 2 refers to [BMIM][OcSO <sub>4</sub> ] ionic liquid and I refers to the Hexane phase .....	<b>59</b>
<b>Figure 37</b> Efficiency of regenerated IL in removing S from LCO (Oil to IL ratio=2:1, Initial S content=549.9 ppm) .....	<b>60</b>

<b>Figure 38</b> Efficiency of regenerated IL in removing S from LCO (Oil to IL ratio=4:1, Initial S content=549.9 ppm) .....	<b>60</b>
<b>Figure 39</b> Efficiency of regenerated [BMIM][OcSO <sub>4</sub> ] at different oil/IL mass ratio (shows the ppm Sulfur in the fuel after each IL regeneration cycle) .....	<b>61</b>
<b>Figure 40</b> Mass fraction of thiophene in exit stream as a function of IL-to-Diesel ratio (S/F) and number of extraction stages (N) in the desulfurization of diesel using IL.....	<b>65</b>
<b>Figure 41</b> Mass fraction of dibenzothiophene in the exit stream as a function of IL-to-Diesel ratio (S/F) and number of extraction stages (N) in the desulfurization of diesel using IL .....	<b>65</b>
<b>Figure 42</b> Integration of the extractive desulfurization unit into an existing South African refinery scheme .....	<b>66</b>

## List of Tables

<b>Table 1 Properties of Typical S-compounds found in crude oil .....</b>	<b>6</b>
<b>Table 2 Typical Sulfur compounds and corresponding refinery streams .....</b>	<b>7</b>
<b>Table 3 Regeneration methods classified by separation mechanism .....</b>	<b>27</b>
<b>Table 4 CDU Products and their boiling range .....</b>	<b>32</b>
<b>Table 5 Ionic Liquid investigated in this study .....</b>	<b>35</b>
<b>Table 6 Diesel samples properties .....</b>	<b>35</b>
<b>Table 7 [BMIM][OcSO<sub>4</sub>] Critical properties and other scalar parameters .....</b>	<b>44</b>
<b>Table 8 Summary of key results in this section.....</b>	<b>49</b>
<b>Table 9 LLE Data, solute distribution ratio and selectivity for the ternary system {Hexane(1) + Thiophene(2) +[BMIM][OcSO<sub>4</sub>](3)} .....</b>	<b>53</b>
<b>Table 10 LLE Data, solute distribution ratio and selectivity for the ternary system { Pentane(1) + Thiophene(2) + [BMIM][OcSO<sub>4</sub>](3)}.....</b>	<b>55</b>
<b>Table 11 LLE Data, solute distribution ratio and selectivity for the ternary system {Ethyl Acetate(1) + Thiophene(2) + [BMIM][OcSO<sub>4</sub>](3)}.....</b>	<b>57</b>

# Chapter 1

## 1. Introduction

### 1.1. Background

Crude oil is the most widely used source of energy for the world, with 80% of the world's transportation fuels demand being met by crude oil products (Behmiri and Manso, 2014). Unfortunately crude oil is one of the biggest air pollutant source responsible for the emission of Carbon Dioxide (CO<sub>2</sub>), Particulate Matter (PM), Nitrogen Oxides (NO<sub>x</sub>) and Sulfur Dioxide (SO<sub>2</sub>). These air pollutants are responsible for some of the current environmental problems such as stratospheric ozone depletion and global climate change (Mukhopadhyaya and Forssell, 2005). Sulfur Dioxide (SO<sub>2</sub>) is a major cause of acid rain which results in acid deposition causing major ecological damage to both land and water systems. This sulfur compound is also known to restrict the use of advanced emission control technologies in vehicles such as catalytic converters (Song and Ma, 2003). In the wake of these concerns, new legislation has been passed in different countries to support the production of cleaner (low sulfur content) diesel and petrol. The Environmental Protection Agency (EPA) has set the USA standards at 15 ppm for both diesel and petrol as of 2006, in Europe the European Union standards regulate the emission of toxins from fuels, the EURO V/VI standards are the most stringent yet (in the world) setting the allowable sulfur content in fuels at 10 ppm as at 2009 (Deng, Wang and Wang, 2010). South Africa has also been tightening its legislation regarding fuel sulfur levels since 2004 at the inception of the National Environment Management Air Quality Act of 2004 (Naicker *et al.* 2012). Currently diesel and petrol fuels with sulfur levels of no more than 500 parts per million (ppm) are permissible. The National Department of Environmental Affairs plans to further reduce the permissible sulfur content of diesel and petrol, so as to bring South Africa's standards in line with those around the world (Benton, 2006). Due to these stringent fuel sulfur content requirements intensive research has been directed at alternative desulfurization technologies which will ensure the treatment of fuels to acceptable sulfur levels (Rang *et al.* 2006).

## 1.2. Research Motivation

Studies on the desulfurization of petroleum distillates abound, however Hydrodesulfurization (HDS) remains the major process currently employed in many refineries globally for the removal of sulfur compounds from crude oil. This process requires large quantities of hydrogen ( $H_2$ ) and the expensive Cobalt-Molybdenum catalyst; Zhang and Zhang (2002) reported that to reduce diesel sulfur content from 500 ppm to 50 ppm will require four times more Co-Mo catalyst or an increase in reaction temperature of  $38^\circ C$ . Other requirements include the use of additional infrastructure in the treatment facility (Liu *et al.* 2008). Moreover the increased severe operating conditions will induce undesired side reactions such as the saturation of olefins, which may result in a decrease in octane number of petrol and cetane number of diesel, thus the need to explore alternative desulfurization technologies. The significance of this research is to investigate the suitability of ionic liquids (ILs) as solvents for the extraction of sulfur compounds from fuels. In recent years ionic liquids have gained recognition as greener and safer solvents that can be applied in separation processes due to their unique properties such as negligible vapor pressure, thermal stability and high extraction capacity for various organic compounds and metal ions (Han and Row, 2010). Research by Wassercheid, Sudhakar and their co-workers investigated the suitability of ionic liquids as sulfur solvents; using mostly **halogen-containing** ionic liquids (Dharaskar *et al.* 2013). Chemically and thermally stable ionic liquids suitable for application in the extraction of S-compounds have also been reported, these ionic liquids contain an octylsulfate anion (Dharaskar, 2012). It has recently been discovered that halogen containing ionic liquids form hydrolysis products at elevated temperatures (Liu *et al.* 2008). Research is yet to be done on the applicability of the ionic liquids with an **octylsulfate anion** for the desulfurization of real fuel oils; the effects of key parameters which affect the extraction efficiency and effectiveness of ionic liquids as well as the regeneration of the ILs, a very important factor as the debate on the toxicology and biodegradability of IL is still ongoing. This gap sets forth the focus of this research; which is to investigate the suitability of alternative halogen-free ionic liquids as solvents in the desulfurization of petroleum distillates without the need of integrating substantial new equipment with existing refinery schemes.

### 1.3. Research Aims and Objectives

This research work is aimed at:

- Investigating the capacity of the IL, 1-butyl-3-methylimidazolium octylsulfate as a solvent for deep desulfurization of real FCC diesel fuel, specifically:
  - To determine whether extractive desulfurization can lower the 4000 ppm sulfur content of FCC diesel feed to allowable sulfur content of 10 ppm
  - To determine whether extractive desulfurization can lower the 450 ppm sulfur content of FCC diesel outlet to allowable sulfur contents 10 ppm
- Assessing ( at a conceptual/preliminary level) the possibility of incorporating an ionic liquid extractive desulfurization process within an existing South African refinery

The objectives are to:

- Determine the effects of key parameters; namely reaction time, IL to fuel mass ratio, number of extraction stages and reusability of the ILs on the extraction efficiency of the ionic liquid under investigation.
- Study the regeneration of the Sulfur-loaded IL (1-butyl-3-methylimidazolium octylsulfate) i.e. finding suitable solvents for the regeneration
- Study the efficiency and effectiveness of the regenerated IL

## **1.4.Dissertation Outline**

### **Chapter 1**

This chapter gives background information as well as motivation for the proposed research, furthermore the scope of the project and research objectives are explicitly and succinctly stated.

### **Chapter 2**

This chapter gives a review of literature to put things into perspective and provide background information on fuels desulfurization and ionic liquids. Firstly different desulfurization techniques are discussed highlighting their advantages as well as their shortcomings. Detailed discussion is also included on ionic liquids with emphasis on ionic liquids as solvents in extractive desulfurization and their regeneration.

### **Chapter 3**

In this chapter procedures for fuel desulfurization and ionic liquids regeneration are described in complete detail. A description of the equipment and instrumentation used is also provided.

### **Chapter 4**

All the results obtained in the experiments performed are presented in this chapter.

### **Chapter 5**

In this chapter the results presented in Chapter 4 are discussed.

### **Chapter 6**

Presented in this chapter are the conclusions and recommendations of this dissertation.

## Chapter 2

### 2. Literature Review

#### 2.1. Sulfur in fuel oils

Sulfur is the third most abundant element in fossil fuels; after carbon and hydrogen. Sulfur in crude oil occurs as either:

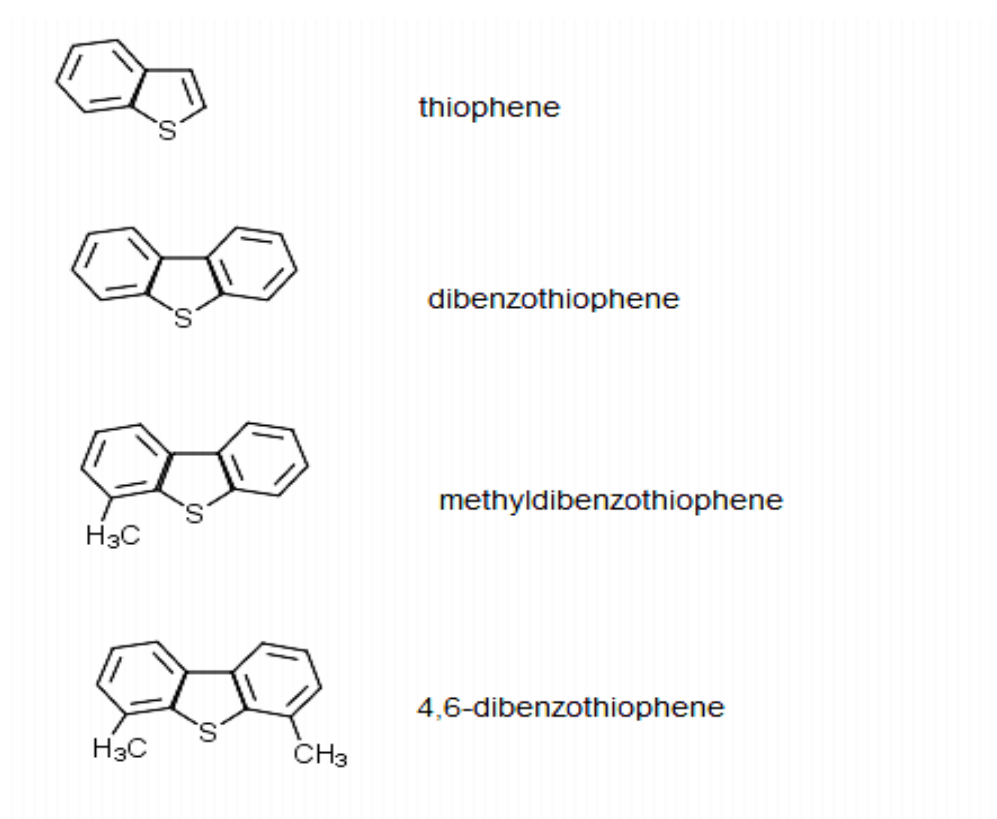
1. Elemental sulfur, which is found in trace amounts if present at all
2. Aliphatic organic S-compounds; mercaptans and thiols (R-SH), sulfides which are also known as thioethers (R-S-R), and disulphides (R-S-S-R). The aliphatic S-compounds are very reactive due in part to the sulfur being attached at the end of the molecules and to their low molecular weight and boiling point range; as given in Table 1 (Song, 2003). These S-compounds can be completely removed by Hydrodesulfurization (HDS).
3. Aromatic S-compounds; thiophenes, benzothiophenes (BTs) and their alkylated derivatives i.e. dibenzothiophene (DBT), methyl dibenzothiophene (MDBT), 4,6-dibenzothiophene (4,6-DMDBT) which have complex structures wherein the sulfur is contained within the molecule making them less reactive for HDS, as such cannot be completely removed by the process (Speight, 1998).

The removal of aromatic S-compounds (Figure 1) in crude oil/crude oil products to very low levels by HDS requires more knowledge on the heavy aromatic S-compounds and kinetic information on the compounds' reactivity. Characterizations of the S-compounds (Table 1) can give such information as well as first approach of their location, but due to the high boiling point range of these compounds characterization proves to be very challenging (Guibard *et al*, 2003).

**Table 1 Properties of Typical S-compounds found in crude oil**

<i>Name</i>	<i>Carbon Chain</i>	<i>Molecular Weight Range (g/mol)</i>	<i>Boiling Point Range (°C)</i>
Mercaptans	C1 - C5	48.11 - 90.16	6.2 - 98.46
Sulfides	C0 - C8	32.8 - 146.3	-60.7 - 185
Disulfides	C1 - C6	70.13 - 122.3	46.3 - 195
<i>Name</i>	<i>Molecular Formula</i>	<i>Molecular Weight (g/mol)</i>	<i>Boiling Point Range (°C)</i>
Thiophene	C <sub>4</sub> H <sub>4</sub> S	84.14	84
Benzothiophene	C <sub>8</sub> H <sub>6</sub> S	134.2	221
Dibenzothiophene	C <sub>12</sub> H <sub>8</sub> S	184.26	332 – 333

Structures of the unreactive organic sulfur compounds



**Figure 1 Structures of typical aromatic sulfur compounds found in fossil fuels**

In a petroleum refinery process different streams/products are composed of different sulfur compounds. The aliphatic organic S-compounds are more prevalent in petrol producing streams, diesel producing streams comprise mainly of the unreactive aromatic compounds and the most unreactive S-compounds are found in the heavy fuel oil as shown in Table 2.

**Table 2 Typical Sulfur compounds and corresponding refinery streams (Song, 2003)**

<i>Sulfur compounds</i>	<i>Refinery streams</i>	<i>Corresponding fuels</i>
Mercaptanes, RSH; sulfides, R <sub>2</sub> S; disulfides, RSSR; thiophene (T) and its alkylated derivatives, benzothiophenes	SR-naphtha FCC naphtha Coker naphtha	Gasoline (BP range: 25–225 °C)
Mercaptanes, RSH; benzothiophene (BT), alkylated benzothiophenes	Kerosene Heavy naphtha; Middle distillate	Jet fuel (BP range: 130–300 °C)
Thiophene, alkylated benzothiophenes; dibenzothiophene (DBT); alkylated dibenzothiophenes	Middle distillate; FCC LCO; Coker gas oil	Diesel fuel (BP range: 160–380 °C)
Greater than or equal to three-ring polycyclic sulfur compounds, including DBT, benzonaphthothiophene (BNT), phenanthro[4,5-b,c,d]thiophene (PT) and their alkylated derivatives and naphthothiophenes (NT)	Heavy gas oils; Vacuum gas oil; Distillation residues	Fuel oils (non-road fuel and heavy oils)

The refinery process streams are discussed in more detail in section 2.6.

Extensive studies have been carried out on the relative reactivities of these sulfur compounds for HDS and this will be discussed further when looking at HDS.

## **2.2. Sulfur Regulation**

### **2.2.1. Air pollution Background**

Air pollution a phenomenon caused by the emission of harmful substances; called air pollutants; into the atmosphere is known to cause global warming and health issues. As such governments of different countries are working to limit and/or in some cases to eliminate the emissions of these harmful substances (Welz *et al.*, 2009). Most countries have established national air quality

standards for the most common air pollutants namely; Carbon Monoxide (CO), Carbon Dioxide (CO<sub>2</sub>), Lead (Pb), Nitrogen Dioxide (NO<sub>2</sub>), Ozone, Particulate Matter (PM) and Sulfur Dioxide (SO<sub>2</sub>). The standards are maintained and adhered to by tracking the pollutants' emissions from the sources. There are two different types of emissions of air pollutants;

- (i) Point source emissions: refers to emissions from large stationary sources largely industrial facilities such as petroleum refineries, power plants/stations, chemical plants etc.
- (ii) Non-point source emissions: includes emissions released from stationary sources over a large widespread area as well as mobile sources such as motor vehicles (Blumberg *et al.*, 2003).

### **2.2.2. Sulfur Emissions Background**

Blumberg *et al.* (2003) in their article addressing the importance of reducing sulfur emissions stated that “it is impossible to reduce air pollution; especially from the transportation sector; without getting sulfur out of fuels.” Elemental sulfur is a very important component (feedstock) in the chemical industry and makes part of amino acids, co-enzymes and vitamins thus it is essential for plants and animals. However, the compound SO<sub>2</sub>; produced during the combustion of fuels; is highly toxic and of environmental concern, as such the reduction of its emissions into the atmosphere is a high priority globally (Welz *et al.*, 2003).

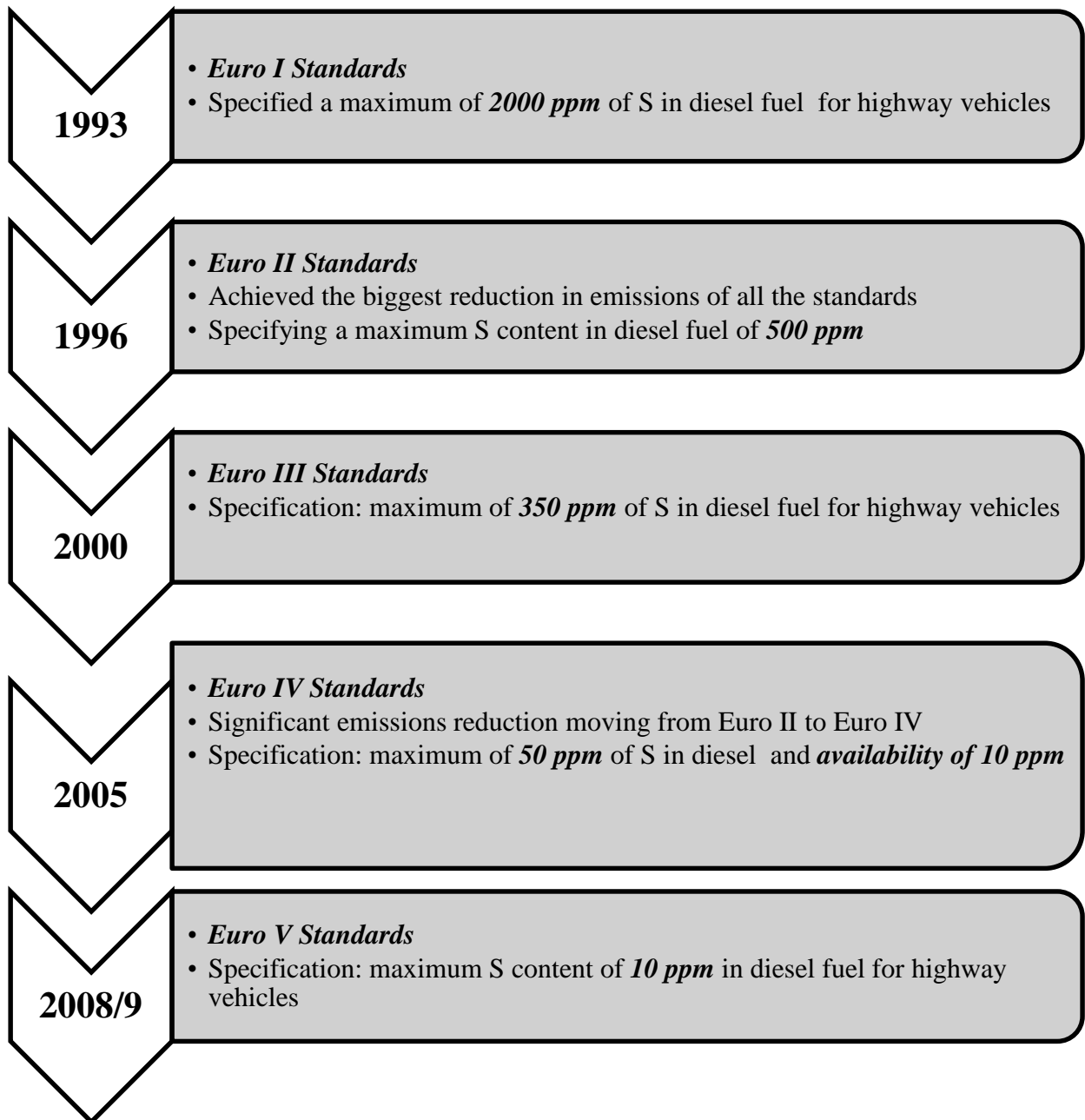
### **2.2.3. Air Emissions Legislation**

Vehicle emission reduction plight first surfaced in the 1970s leading to the passing of the first fuel specification regulations on the 31<sup>st</sup> of December 1970 in the US and 1972 in Japan. The said standards were for the regulation of lead content in petrol. The regulation came about as lead posed a problem in the control of other vehicle emissions; it poisoned new catalytic converters technologies (which required unleaded petrol) for controlling the products of incomplete combustion of fuels; CO, HC and NO<sub>x</sub>. Sulfur is another petroleum products constituent inhibiting the use of advanced technology in vehicles for the reduction of emissions, hence the quest for low sulfur fuels.

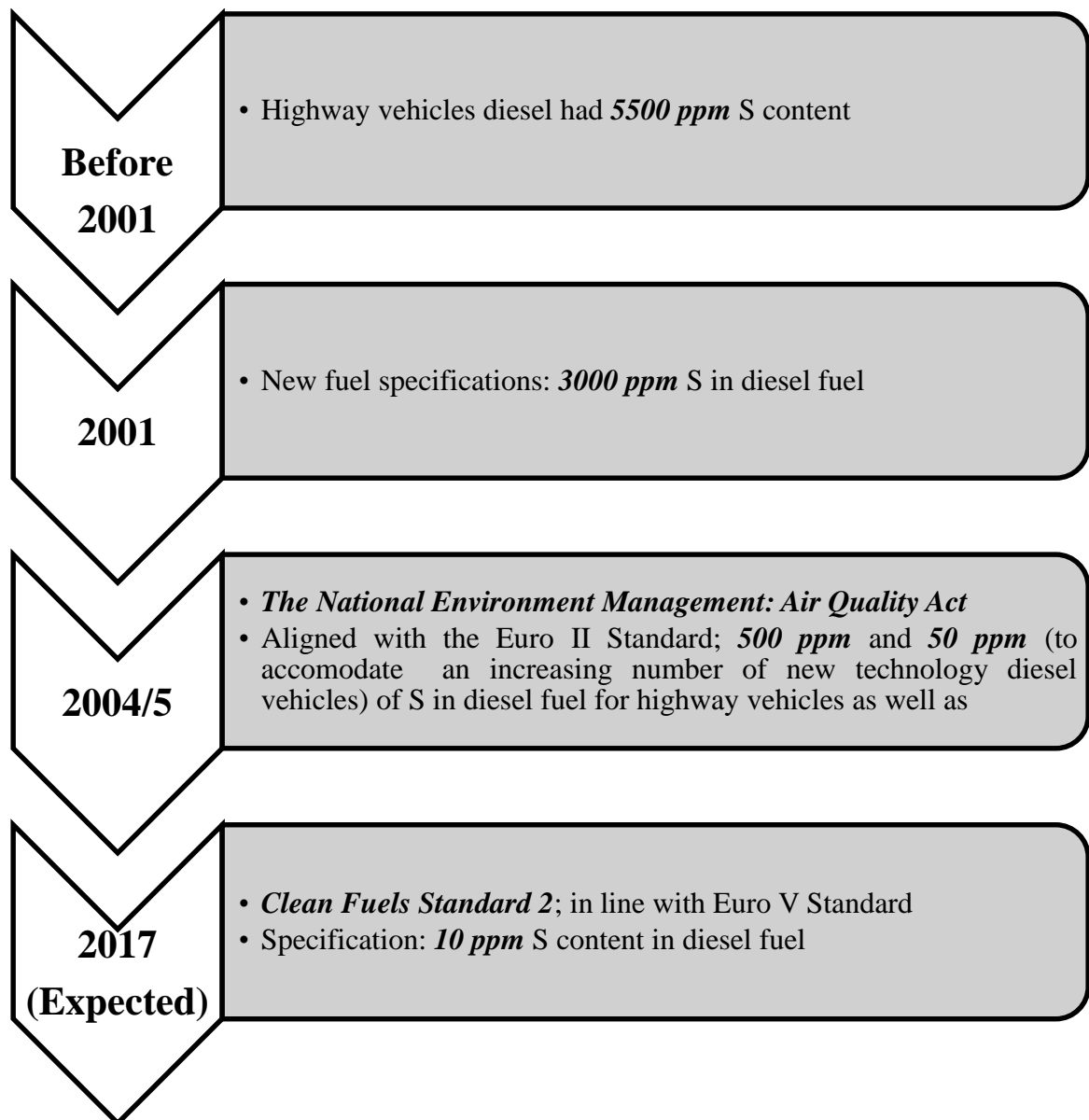
Most countries have passed fuel sulfur levels legislations; to regulate air emissions. Low sulfur fuels will enable the use of vehicles fitted with advanced catalytic technologies in addition to lower SO<sub>2</sub> emissions

**Sulfur Regulations per year per country for European countries and South Africa:**

The European emission standards regulating the air pollutant emissions from vehicles for countries in Europe are the most stringent yet, as such serves as a reference for the rest of the world. Figure 2 shows the Euro standards milestones, while Figure 3 shows South Africa's vehicle sulfur emissions regulations' timeline:



**Figure 2 European Union Sulfur Emissions' Regulations Timeline (Chambliss and Bandivadekar, 2015)**



**Figure 3 Milestones in Sulfur Emissions from Vehicles in South Africa (National Association of Automobile, 2007)**

### 2.3. Conventional desulfurization process

Hydrodesulfurization (HDS) is the most widely used chemical process for the removal of sulfur compounds from crude oil and refined crude oil products; such as petrol, diesel and fuel oils; during crude oil refining (Batista *et al.*, 2012). HDS consists of catalytic hydrotreating with Cobalt Molybdenum (Co-Mo/Al<sub>2</sub>O<sub>3</sub>), Nickel Molybdenum (Ni-Mo/Al<sub>2</sub>O<sub>3</sub>) or Nickel Tungsten (Ni-W/Al<sub>2</sub>O<sub>3</sub>) catalysts. During this catalytic process the organic sulfur compounds (S-compounds) are converted to hydrogen sulfide (H<sub>2</sub>S) and the corresponding hydrocarbons (Vrinat, 1983). Typical conditions for this reaction which takes place in high pressure reactors or vessels are as follows; high temperatures of 350°C and pressures of around 30 to 100 bars (Kumar and Banerjee, 2008). The H<sub>2</sub>S formed during the catalytic reaction is separated from the desulfurized fuels and then converted into elemental sulfur (S) usually by the Claus process (Eber *et al.*, 2004). The hydrodesulfurization process is unsuitable for ultra-deep desulfurization due to some of the S-compounds being unreactive for the process refer to Figure 4 which shows the reactivity of the various sulfur compounds in HDS as a function of their ring size and positions of alkyl substitutions on the ring. Kumar and Banerjee (2008) brought it forth that the reactivity of S-compounds for HDS depends strongly on the molecular structures of the compounds, the bigger the molecule the less reactive it is and from the figure it can be seen that the aliphatic S-compounds are more reactive than the aromatic ones and even with the aromatic ones reactivity decreases with an increase in the ring size and number of alkyl groups attached. The figure also shows that the diesel fraction constitute mainly the unreactive aromatic sulfur compounds thus the high focus on alternative desulfurization processes for diesel streams. The unreactive and refractory aromatic S-compounds present the most difficult challenges to the HDS processes as they require elevated temperatures and high quantities of H<sub>2</sub> as well as high reactivity and selectivity of the catalysts in use (Chu *et al.*, 2008). These severe operating conditions elevate process costs. The above mentioned requirements render HDS process uneconomical and unsafe. High temperatures also increase coke formation in the refining process and also lead to an increase in the deactivation rate of the catalyst. High pressures on the other hand cause increased side reactions i.e. saturation of olefins, which lowers octane numbers for petrol and cetane numbers for diesel fuel.

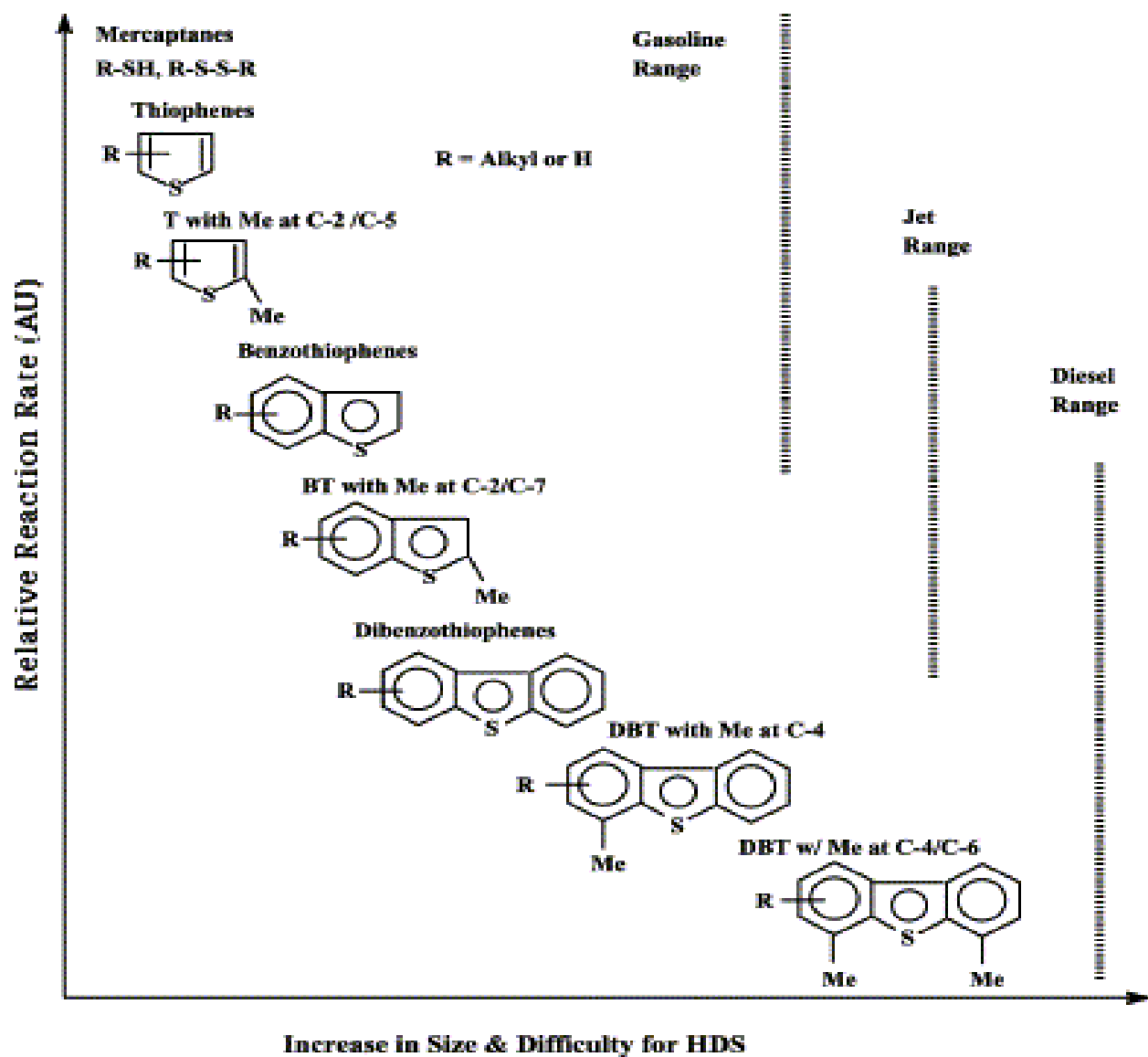


Figure 4 Relative reactivity of various organic sulfur compounds in HDS (Song, 2003)

## 2.4. Alternative and/or supplementary desulfurization processes

As gathered from the above discussion the HDS process may not enable the petroleum industry to meet standard allowable transportation fuels specification. Alternative desulfurization processes are therefore needed, preferably processes that do not require hydrogen as well as high

operating temperature and pressure (Eber *et al.*, 2004). A number of alternatives have been mentioned in the literature, these include adsorption, biodesulfurization, precipitation, oxidation and extraction. Whether considered separately or in combination with HDS all these processes may be viable alternative desulfurization techniques.

#### **2.4.1. Biodesulfurization**

Biodesulfurization also often referred to as microbial desulfurization is an environmentally friendly, biological process that can be used to remove sulfur from fuels (Soleimani *et al.*, 2007). Biodesulfurization processes employ microorganisms to remove sulfur atoms from organic S-compounds; without breaking down the carbon skeleton of the S-compounds (Mohebbi and Ball, 2008). The process principle as explained by Mohebbi and Ball (2008) is as follows; the refractory, organic S-compounds i.e. dibenzothiophene (DBT) and its alkylated derivatives ( $C_x$ -DBTs) are converted to non-sulfur compounds such as 2-hydroxybiphenyl (2-HBP) and sulphate. The biodesulfurization technology appears as a viable complementary process to HDS. For one it requires mild operating conditions (i.e. ambient temperature and pressure), thus saving energy costs. Further energy cost cuts are due to the fact that the biodesulfurization process reduces the need for hydrogen. Another advantage of the BDS process is that it is highly selective due to the involvement of biological catalysts i.e. enzymes (Soleimani *et al.*, 2007) and also does not produce any undesirable products. The biodesulfurization technology has also been found to generate only a fraction of the greenhouse gas emissions generated by HDS. This technology can only be applied as a complementary process due to the fact that it cannot do some of the things done by the HDS in addition to removing S-compounds e.g. induce saturation of some carbon-carbon double bonds and also improve the cracking characteristics of the material. Unfortunately the biodesulfurization technology has not as yet been shown to be economically viable on a commercial scale.

#### **2.4.2. Adsorptive Desulfurization (ADS)**

Adsorptive desulfurization (ADS) is currently the most commonly used HDS alternative method for achieving ultra clean fuels (Adeyi and Aberuaga, 2012). ADS is a mass transfer process wherein S-compounds are selectively adsorbed onto the surface of a solid adsorbent; intermolecular forces cause the S-compounds to bound to the adsorbent surface (Ma *et al.*,

2003). The greatest challenge with this technology is finding or developing suitable adsorbents. The adsorbent must be selective i.e. adsorb S-compounds, but leave the coexisting hydrocarbons untouched. Secondly as stated by Ma, Sun and Song (2003) the adsorbent should be easily regenerated without using hydrogen gas, to cut on process costs. There are a number of reports on adsorptive desulfurization using adsorbents such as activated carbon, metal exchanged zeolites, metal oxides and mesoporous materials (Dasgupta *et al.* 2013). Metal oxides have been found to show great potential due to their high reactivity towards S-compounds (Adeyi and Aberuagba, 2012). This technology has shown great potential, thus major research is being undertaken to develop the process and work on the possible regeneration of the adsorbents as there is no report on that aspect (Dasgupta *et al.* 2013).

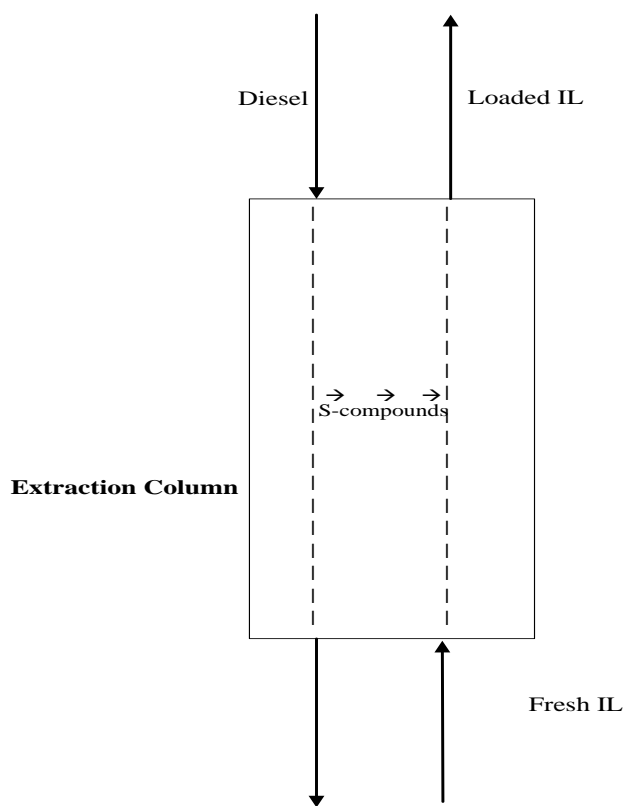
#### **2.4.3. Oxidative Desulfurization (ODS)**

ODS is a new technology which is being considered for deep desulfurization of fuels. In this process an oxidant is reacted with the divalent organic S-compounds found in fuels at low temperatures (<93°C) and low pressures (<6.8 atm) in the presence of a catalyst to form the corresponding hexavalent sulfur known as sulfoxides and sulfones, which can be removed by either solvent extraction or adsorption (Gatan *et al.*, 2004). This technology is able to remove those S-compounds which are unreactive to the HDS process i.e. thiophenes and its alkylated derivatives. The other S-compounds i.e. thiols, thioethers and disulfides are reactive for HDS, are not easy to remove by the ODS process as they oxidize slowly. It is for this reason that the ODS technology can only be used as a complementary process to the HDS. Main disadvantage of this process is high process costs, which are due to the sulfone separation unit of this process (Gatan *et al.*, 2004). Research is ongoing to develop this viable alternative technology to the HDS.

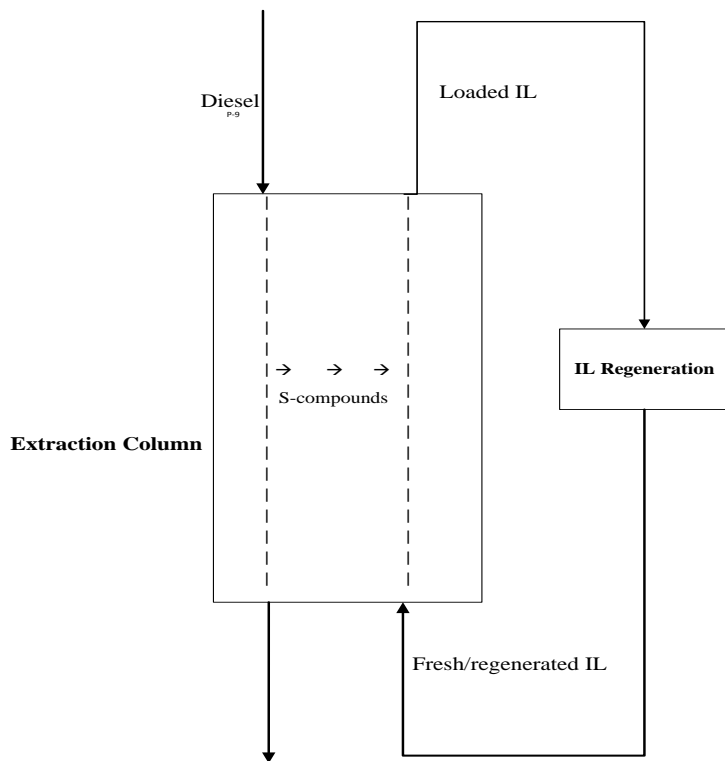
#### **2.4.4. Extractive Desulfurization (EDS)**

EDS is a liquid-liquid extraction process and is the most widely studied alternative desulfurization technology. Liquid-liquid extraction process; also referred to as solvent extraction process; is concerned with the removal of one or more components from one liquid; called the feed; through contact with another liquid; called the solvent; to produce an extract and a raffinate, the latter being the stripped liquid phase while the former is the solvent-rich phase. The driving force for this process is solubility, the components to be removed preferentially

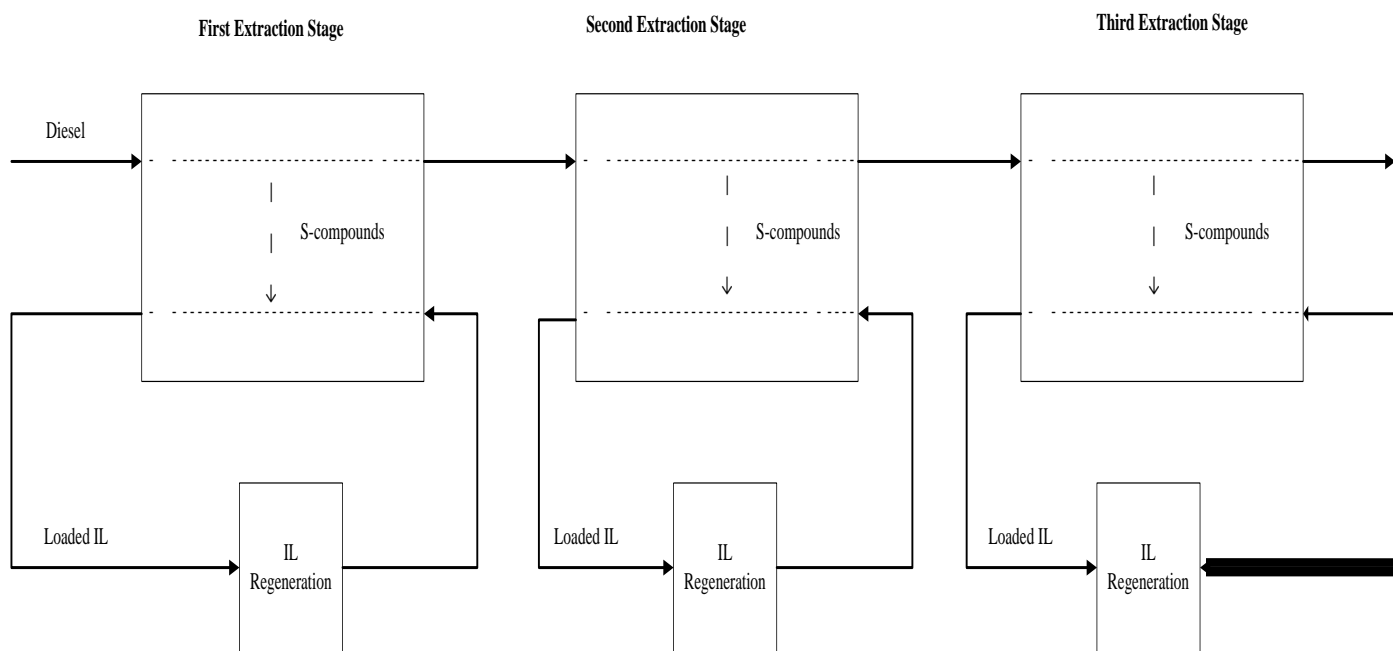
migrates to the liquid where they have the greatest solubility. Following from this in an EDS process sulfur compounds are removed from fuels by contacting the fuel with a suitable solvent (Rodriguez-Cabo *et al.* 2013); extraction can be conducted either in a single stage or multistage process as depicted in Figures 5, 6 and 7. The fact that S-compounds are more soluble than other fuel constituents in an appropriate solvent is the backbone of the EDS technology. EDS has a number of advantages over the conventional HDS technology. Firstly this process does not require severe operating conditions; it operates at ambient pressure and temperature. Secondly there is no H<sub>2</sub> consumption and a need of expensive catalysts, thus the process is economical.



**Figure 5 Extractive desulfurization process (Single Stage), IL = Ionic Liquid**



**Figure 6 Extractive desulfurization process with solvent recovery**



**Figure 7 Multistage extractive desulfurization process with solvent recovery**

### **2.4.5. Oxidative-Extractive Desulfurization**

This is a desulfurization process combining oxidative and extractive desulfurization techniques. The process comprises of two stages, the first stage involves the oxidation of fuel oils by a suitable oxidant at ambient conditions (Xu *et al.*, 2012). This is followed by extraction of organosulfur compounds with solvents (ionic liquids). The oxidative process/stage serves to improve the solubility of the organosulfur compounds in the ionic liquids employed in the succeeding stage i.e. the extractive stage (Rodriguez-Cabo *et al.*, 2013). Oxidation makes it much easier to extract the organic sulfur compounds. There are a number of oxidants being used and researched for this process with the main oxidant being hydrogen peroxide ( $\text{H}_2\text{O}_2$ ). Other oxidants that have been reported are sodium hypochlorite ( $\text{NaClO}$ ), acetic acid ( $\text{CH}_3\text{COOH}$ ) and ozone ( $\text{O}_3$ ) (Li *et al.*, 2012). Efficient oxidation of the organosulfur compounds takes place in the presence of catalysts and numerous viable catalysts have been studied. These include polyoxometalate (POMs) catalysts, which achieve high oxidation yields, but are expensive and difficult to recycle (Rodriguez-Cabo, 2013). Other solid catalysts such as  $\text{V}_2\text{O}_5$  have also been found to be difficult to handle. Research is ongoing to enhance and improve this viable yet difficult to handle and recycle oxidative-extractive desulfurization process.

## **2.5. Ionic Liquids**

### **2.5.1. Definition**

Ionic liquids are organic salts which are liquids below  $100^\circ\text{C}$  (the boiling point of water) with an additional feature of a wide span of temperatures between the melting and the boiling point, a feature shared with traditional molten salts (Wassereich and Welton, 2003). Traditional volatile organic compounds (VOCs) are the media of choice for industrial processes; such as extraction and organic chemicals synthesizing processes which require solvents. However, these solvents are one of the major air pollutants giving rise to health and environmental concerns. Due to these concerns environmental bodies; such as the EPA and European Union; have put regulations in place to manage and eliminate the emission of these compounds. Research on ionic liquids has garnered momentum as they are seen as possible replacements for VOCs due to their suitable properties. Ionic liquids possess the following desirable properties:

- Negligible vapour pressure due to the strong ionic interactions within these substances, this feature has the advantage of emission reductions
- Non-flammability
- Good thermal stability over a large temperature range
- Mechanical and electrochemical stability
- Good ionic and electrical conductivity as well as a wide electrochemical window
- Non-toxic and environmentally benign
- Relatively moderate surface tensions
- Designable nature i.e. their properties can be changed to meet specific demands by altering their ionic structures

Further research on ILs is being undertaken looking mainly at the major concerns which are cost and biodegradability of these solvents (Mohammad and Inamuddin, 2012).

### **2.5.2. Uses/Applications of Ionic Liquids**

Initially ionic liquids were used solely for specialized electrochemical applications; as solvents and electrolytes; due to their conductivity. However, the desirable properties of ionic liquids have attracted rising interest for a diverse range of applications. Now, in addition to the use in electrochemical devices ionic liquids have been found to be promising solvents to replace volatile organic substances in chemical sensing and many chemical processes i.e. in organic reactions such as esterification, isomerization etc. and many coupling reactions as well as in extraction processes (Khupse and Kumar, 2010). The polarity of ILs enables them to solubilize both organic and inorganic compounds (Anderson *et al.*, 2006). Application of ILs in organic reactions has been mainly as both solvents and catalysts for the Friedel-Crafts alkylation process. In contrast to the traditional solvents and acid catalysts used in this process; ILs require mild reaction conditions, are able to achieve high conversions and product selectivities and most importantly allow for easy recovery and reuse of the catalyst systems (Mohammad and Inamuddin, 2012). ILs have also been studied as possible solvents in the removal of H<sub>2</sub>S via absorptive processes. Preliminary results show that ILs are capable of absorbing H<sub>2</sub>S from gas streams and selectively separating H<sub>2</sub>S from CO<sub>2</sub>. Currently amine solvents are used for the removal of H<sub>2</sub>S in gas streams in the oil and gas and electric power industries unfortunately their use is highly energy intensive “due to the heat requirements for the reverse reaction”

(Mohammad and Inamuddin, 2012). Other uses include; as high-performance lubricants with better antiwear capabilities than conventional lubrication oils due to very good tribological properties, ILs have also found application in the formation of different types of multicomponent reactions (Mohammad and Inamuddin, 2012).

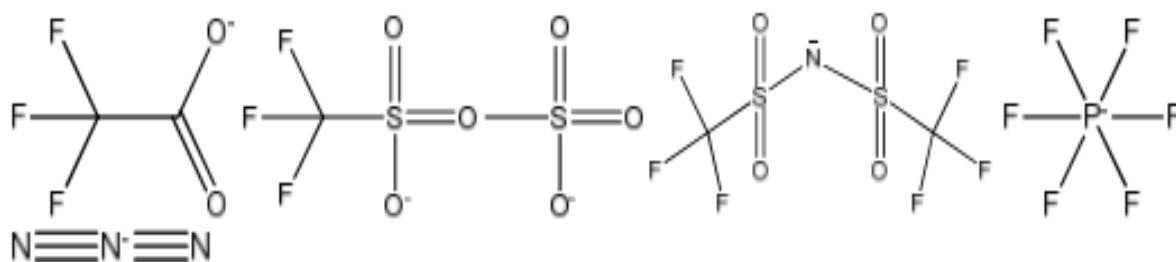
### 2.5.3. Structure of Ionic Liquids

Most ionic liquids are comprised of a heterocyclic organic cation and an inorganic polyatomic anion, with special feature of a delocalized charge (Wassercheid and Welton, 2003). The cation and anion constituents of ionic liquids determine properties such as melting point, viscosity, surface tension and solubility of other materials in the ionic liquids. More research still needs to be done to determine the effect of anion/cation, substitution patterns etc on the properties of ionic liquids (Casal, 2010). The designable nature of ionic liquids allows for their synthesis to get specific properties per process needs. There are numerous possible cation and anion choices which results in the formation of ionic liquids (Wassercheid and Welton, 2003); the most common are shown in Figure 8 and 9. It has even been estimated there to be one trillion ( $10^{18}$ ) accessible ionic liquids (Seddon and Holbrey, 1999). The most common organic cations used in the synthesis of ionic liquids are imidazolium-, pyridinium-, pyrrolidinium-, ammonium-, phosphonium- and quinolium-based (Omar *et al.*, 2014). While some of the most common anions of current ionic liquids are trifluoroacetate, trifluoromethanesulfonate or triflate, bis{(trifluoromethyl)sulfonyl}imide, octylsulfate, hexafluorophosphate and dicyanamide (George *et al.*, 2011).



**Figure 8 Common cations of current ionic liquids (Casal, 2010)**

From left to right; 1,3-dialkylimidazolium, 1-alkylpyridinium, 1,1-dialkylpyrrolidinium, tetraalkylammonium and tetraalkylphosphonium (Casal, 2010).



**Figure 9 Common anions of current ionic liquids (Casal, 2010)**

From left to right; trifluoroacetate, trifluoromethanesulfonate or triflate, methanesulfonate or mesylate, bis{(trifluoromethyl)sulfonyl}amide, hexafluorophosphate and dicyanamide (Casal, 2010).

#### 2.5.4. Ionic Liquids as Solvents in Extractive Desulfurization

##### Viable Ionic Liquids

Ionic liquids provide a greener alternative to the traditional volatile organic solvents. In addition to the earlier mentioned properties ionic liquids exhibit other properties which render them as ideal extractive desulfurization solvents (Dharaskar *et al.* 2013). The properties are:

- Good extractive ability for S-compounds more especially thiophene and its alkylated derivatives
- Insolubility in oil and/or oil products
- Recoverability from S-compounds
- Reusability
- Recycling ability
- Catalyst solubility

##### Methods for determining viable ILs for EDS

Two methods have been applied in determining the suitability of ILs as solvents in extractive desulfurization. The first of these methods is the use of liquid-liquid equilibrium (LLE) data. The most important parameter to consider when choosing a solvent for extraction purposes is solubility. The best solvent is one into which S- and N-containing compounds distribute preferentially and has very low or no interaction with the hydrocarbons found in fuels. Ternary LLE data allows for the determination of the capacity of ILs as solvents for extractive

desulfurization, the data quantifies the solubility of fuel constituents in ILs. There are different techniques that can be used to obtain LLE data i.e. continuous measurements, titration method and the most common method is based on the direct analysis of the phases, the method of equilibrium cell (Casal, 2010). With the method of equilibrium cell LLE data for IL systems is obtained by introducing an IL, a hydrocarbon and a solute, which can be an S-containing compound such as thiophene for desulfurization experiments or N-containing compound pyridine for denitrogenation investigations; into a temperature controlled jacketed glass cells or round bottom flasks. The reactor contents are stirred for 2 hours to get a good contact between the phases and then allowed to settle down for a minimum of 4 hours to achieve phase splitting. Samples of both layers are taken with a syringe for compositions analysis with an adequate analytical method e.g. gas chromatography. From the determined compositions ternary diagrams can be drawn to graphically represent the results. In all the reported work the ILs' solvent extraction capacity was evaluated by calculating the S- and N-containing compounds' distribution ratio,  $\beta$  which quantifies the distribution of a solute between the immiscible phases in a ternary mixture and solvent selectivity,  $S$  which is the ratio of the distribution ratios of the two solutes at hand, it describes the effectiveness of the separation of the two solutes. The two quantities are given by the following equations;

$$\beta = \frac{(x_1)^I}{(x_1)^{II}} \quad \text{Equation 1}$$

$$S = \frac{(x_1)^I \cdot (x_2)^{II}}{(x_1)^{II} \cdot (x_2)^I} \quad \text{Equation 2}$$

Where subscripts;

*I*-is the solute which can be an S- or an N-containing compound

*2*-is a hydrocarbon.

While superscripts;

*I*-refers to the IL phase

*II*- refers to the hydrocarbon phase

And lastly  $x$  is the molar composition of component indicated as subscript, in the phase indicated as superscript (Casal, 2010).

LLE data results as well as  $\beta$  and  $S$  values by Alonso *et al.* (2007) for the IL, [C<sub>8</sub>MIM][BF<sub>4</sub>] showed that S-containing compounds distribute preferentially in the IL phase rather than in the hydrocarbon phase. However, other reported work showed that for some ionic liquids the unwanted effect of co-extraction of aromatic hydrocarbons occurs, leading to a decrease of diesel cetane number. Kędra-Królik and co-workers investigated the possible use of some ILs namely; [EMIM][SCN], [DMIM][MP] and [TEMA][MeSO<sub>4</sub>]. The measured ternary LLE data showed very low interaction/extraction of the hydrocarbon matrix of the fuel by the ILs and high selectivity for S-containing compounds, the highest capacity for fuel desulfurization exhibited by [EMIM][SCN].

The second method is Conductor-like Screen Model (COSMO) along with its extension to Real Solvents (COSMO-RS), which is a Continuum Solvation Model. Continuum Solvation Models are quantum mechanical calculations methods widely used in quantum chemistry to approximate the chemical equilibria between different liquid phases i.e. the effect of solvents on other species in a mixture (Klamt and Schüürmann, 1993). With the COSMO method the solute molecule's dielectric screening energy is evaluated within a cavity, which is often referred to as the solvent accessible surface (SAS) (Klamt and Schüürmann, 1993; Rzepa and Suñer, 1993). Unfortunately from a theoretical perspective this method is unjustifiable. COSMO-RS is an extension of COSMO beyond the dielectric approximation and uses COSMO calculations to compute the chemical potentials of almost any solute molecules in any mixture. Klamt *et al.* (1998) give more details on these models. In the case of extractive desulfurization, COSMO and COSMO-RS have been used to predict the efficiency and effectiveness of ILs in the extraction of unreactive and refractory sulfur compounds found in fuel oils. Kumar and Banerjee (2009) used COSMO-RS to screen 264 possible cation-anion combinations for extractive desulfurization studies and to also predict LLE data for about 15 ternary systems, which involved the most promising of the screened ILS. The predicted LLE data was compared with reported experimental LLE data, the method is quite good in predicting LLE data as the percent deviation; from experimental data; in root mean square deviation for all systems was found to be ~8%.

#### **Best structure of ionic liquids suitable for extraction**

The most commonly studied ionic liquids are those with the imidazolium-based cation. This is due to their desirable physical properties as well as ease of synthesis (Casals, 2010). Continuum

Solvation models have been used to determine suitable cations for the most efficient ionic liquid for desulfurization. Kumar and Banerjee (2009) reported on the use of Continuum Solvation models to predict the efficiency and effectiveness of certain ionic liquids, more specifically the cations constituting these ionic liquids. The two researchers found that smaller size cations have the highest selectivity, but low capacities. Selectivity is the ratio of the mole fraction of S-compounds in the IL rich phase to the mole fraction of the S-compounds in the oil rich phase. While capacity refers to the maximum amount of the oil species that can be dissolved in the IL (Chu *et al.*, 2008). Smaller size cations should always be used for desulfurization because low capacity means that it will extract S-compounds only and leave out the hydrocarbons. The results from the research also indicated that imidazolium-based cations have higher selectivities than all the other ionic liquids. This is because thiophenic molecules have a five-membered ring structure similar to the imidazolium-based cations structures. It is for this reason that the most commonly used and the most investigated ionic liquids are composed of the 1-alkyl-3-methylimidazolium cations ( $C_nC_1I_m$ ). Holbrey *et al.* (2007) reported contradictory results to those attained by Continuum Solvation models. The research investigated the extraction of dibenzothiophene from dodecane using a range of ionic liquids with varying cation classes i.e. imidazolium, pyridinium and pyrrolidinium and a range of anion types (Holbrey *et al.*, 2007). The results showed that the desulfurization ability of the ionic liquids by cation are in this order methylpyridinium  $\geq$  pyridinium  $\approx$  imidazolium  $\approx$  pyrrolidinium and there was an insignificant change with anion type (Holbrey *et al.*, 2007).

#### **Research on ILs as solvents in extractive desulfurization**

The use of ionic liquids as solvents in fuel desulfurization was first reported by Wassercheid and co-workers in 2001 and their work has been followed by several publications on the topic. In that first publication the group investigated the desulfurization of model diesel fuel, with a sulfur content of 500 ppm, using 1-butyl-3-methylimidazolium chloride ([BMIM]Cl/ $AlCl_3$ ) and 1-ethyl-3-methylimidazolium chloride with  $AlCl_3$  ([EMIM]Cl/ $AlCl_3$ ) as well as a mixture of two trialkylammonium methanesulfonate salts. After one extraction stage/step [BMIM]Cl/ $AlCl_3$  was found to be the most efficient of the investigated ionic liquids, with close to 50% S removal (Bösmann *et al.*, 2001). The results inspired further research into ionic liquids as solvents in extractive desulfurization. Imidazolium-based ionic liquids with different anions were investigated; the anions included,  $[PF_6]^-$ ,  $[CF_3SO_3]^-$ ,  $[BF_4]^-$ ,  $Cl^-$ ,  $[MeSO_4]^-$ ,  $[MeSO_3]^-$  and

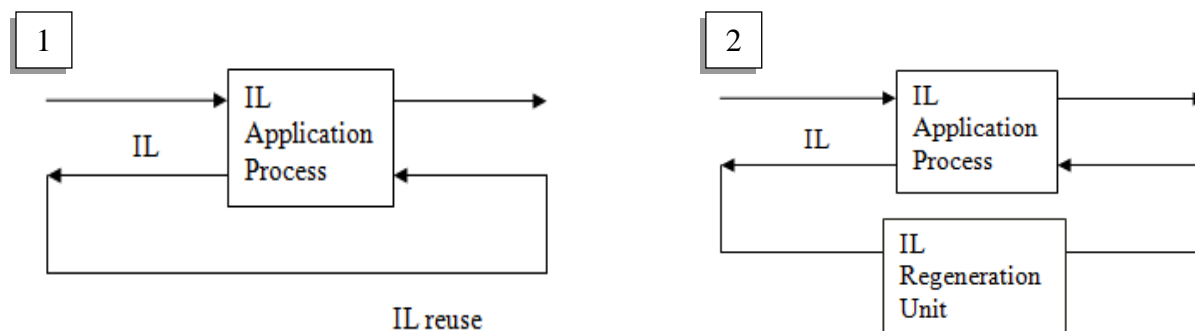
[OcSO<sub>4</sub>]<sup>-</sup> (Bösmann *et al.*, 2001). The anion [OcSO<sub>4</sub>]<sup>-</sup> showed the most potential in the removal of DBT; a sulfur compound; in model diesel. Dharaskar *et al.* (2012) reported on the investigation of ionic liquids with the following anions; Cl<sup>-</sup>, Br<sup>-</sup>, [BF<sub>4</sub>]<sup>-</sup>, [BF<sub>6</sub>]<sup>-</sup> and [PF<sub>6</sub>]<sup>-</sup>. The team further investigated other parameters which affect the efficiency and effectiveness of ionic liquids such as temperature, oil/IL mass ratio, number of extraction stages etc. and achieved highest S removal of 77.15% with the Cl<sup>-</sup> anion. Several other authors studied the use of Cl<sup>-</sup>, [BF<sub>4</sub>]<sup>-</sup> and [PF<sub>6</sub>]<sup>-</sup> anions and ILs containing these anions showed high efficiency for organic S-compounds extraction, unfortunately ionic liquids with halogen-based anions cannot be applied to large scale processes due to their possible toxicity and hydrolysis instability; i.e. form corrosive and toxic hydrolysis products such as HCl and HF (Wasserscheid and Welton, 2003). A preliminary study by £ber and co-workers has shown that the ionic liquid 1-butyl-3-methylimidazolium octylsulfate can be applied for the extraction of real fuel oils. There is a need for further research to determine the extraction, partition coefficients of S-compounds real fuels (£ber *et al.*, 2004).

#### **Ionic Liquid selection for the current study**

In choosing appropriate solvent for this study, the main properties considered were good extractive ability for the non-reactive organic S-compounds and insolubility of the solvents in fuel oils and their constituents. The ionic liquid 1-butyl-3-methylimidazolium octylsulfate was proven to be a suitable solvent through screening experiments with model diesel, giving the highest (53% higher than the second highest) sulfur partition co-efficient out of the five studied ILs (£ber *et al.*, 2004; Bösmann *et al.*, 2001). Kumar and Banerjee's COSMSO-RS results showed 1-butyl-3-methylimidazolium octylsulfate to be a viable solvent in extractive desulfurization. In this work this ionic liquid will be investigated further to establish its capacity as a solvent for deep desulfurization of real diesel fuel as well as its reusability and regeneration, including the screening and application of suitable solvents for the regeneration process.

### 2.5.5. Regeneration of Ionic Liquids

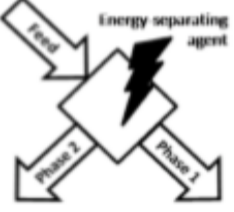
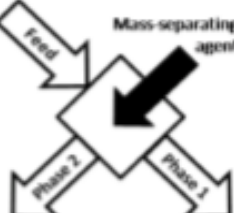
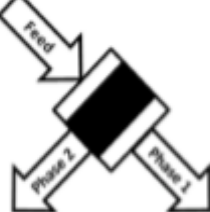
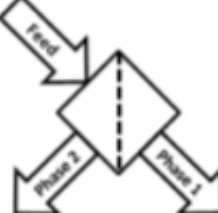
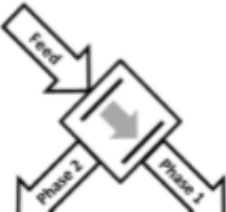
There is a lack of knowledge on the economic, social and ecological impact of ILs on the environment and human health (Mohammad and Inamuddin, 2012). This is as a result of much of the research on ILs being concentrated/directed at their synthesis, measurement of their properties and new application fields and little on their re-usability, regeneration and recoverability, toxicity and biodegradability (Fernández *et al.*, 2011). Due to the high ILs production costs, extension of their lifetime in any form is essential, thus the need to study their reusability (without regeneration) and their regeneration; setting forth one of the core objectives of this work. Figure 10 shows IL application processes with IL reuse and IL regeneration options. In theory the re-use (without regeneration) of ILs is the optimum cost cutting method for extending the lifetime of ILs in their industrial application, however in practice/reality ILs can be re-used to a certain extent or until a threshold concentration is reached above which there is noticeable degradation or inefficiency of the ILs as solvents, thus the need for the study of regeneration operations which will supplement the re-use of ILs.



**Figure 10 IL Re-use without Regeneration (1) vs. with Regeneration (2)**

Fernández *et al.* (2011) reported on several regeneration techniques which can be used and in some cases have been used for different purposes (i.e. regeneration of ILs applied in different processes). Table 3 (Fernández *et al.*, 2011) outlines these techniques and the most viable operations for the regeneration of ILs used in the desulfurization process are discussed.

**Table 3 Regeneration methods classified by separation mechanism adapted from Fernandez et al. (2011)**

Separation by	Scheme	Examples
Phase Creation		Vacuum distillation, crystallization
Phase Addition		Liquid-liquid extraction, supercritical CO <sub>2</sub> , salting-out
Solid Agent		Adsorption, ion exchange
Barrier		Nanofiltration, pervaporation
Force Field		Decantation, centrifugation, use of magnetic fields

Of all the processes given in the table two re-extraction processes have been identified as viable methods for the regeneration of ILs; due to their efficiency and cost effectiveness; by Liu *et al.* (2008), Gabrić *et al.* (2013) and others.

**(i) Vacuum Distillation**

Vacuum distillation/evaporation is appropriate for the regeneration of ILs, due to one of the properties of ILs; nonvolatility. The method was tested in a pilot plant at the University of Twente (The Netherlands). IL was regenerated by distillation after being used as a solvent in the extraction of toluene from a toluene-heptane mixture. The IL was regenerated and reused for 6 months without noticeably decrease in efficiency (Fernández *et al.*, 2011). Thus it proved worthwhile to study vacuum distillation as an IL regeneration method for the desulfurization process. Gabrić and co-workers in their study of the “Extraction of S- and N-compounds from a mixture of Hydrocarbons by Ionic Liquids as Selective Solvents” investigated the regeneration of the selected ILs using vacuum evaporation. It was found that for model diesel oil, after regeneration the ILs were not totally purified due to the high boiling points of the S-compounds found in diesel oil (Gabrić *et al.*, 2013). Another disadvantage associated with this method is the high investment costs and further high energy costs when in operation.

**(ii) Liquid Liquid Extraction**

This is the simplest method of removing solutes form ILs. ILs are washed with a solvent then dried off at high vacuum. The key challenge with liquid liquid extraction is finding a suitable solvent; a great start is the knowledge that ILs tend to be immiscible with non-polar organic solvents, so alkanes and other non-polar organic compounds such as diethyl ether and ethyl acetate can be used to extract sulfur from ILs. Polar or dipolar solvents e.g. chloroform, acetonitrile and methanol have been reported to be totally miscible with all ILs (Wassercheid and Welton, 2003). Supercritical CO<sub>2</sub> is another viable solvent (Fernández *et al.*, 2011). There are numerous reports in literature on the use of LLE for regeneration of ILs used in the desulfurization of model diesel oil, one such study found that the purity of the ILs were retained after extraction with a promising solvent and drying at high vacuum for 4 hours (Liu *et al.*, 2008), thus it is worthwhile to study this method for desulfurization of real diesel oil.

As mentioned a very important factor in using this regeneration method is the determination or selection of suitable solvents. The following are important criteria used in solvent selection (for liquid liquid extraction processes) (Prat *et al.*, 2013):

- Distribution ratio ( $\beta$ ) and Selectivity (Separation factor,  $S$ ) as defined by Equations 1 and 2 in section 2.5.4
- Insolubility of solvent in the feed material
- Recoverability, a solvent that can be regenerated for reuse is always desirable as it is cost efficient and has less environmental impact
- Chemical stability, solvent must be unreactive towards feed material and not breakdown when vigorously mixed
- Availability and cost
- Others include; density, thermal stability, toxicity and viscosity

LLE data is the most appropriate method for solvent selection as it gives an idea of the solubility degree of involved substances. For the determination of LLE data for IL systems, knowledge of the physical and physicochemical properties of the IL are required. The required physical and physicochemical parameters include critical properties, ideal gas heat capacity equation coefficients, liquid heat capacity equation co-efficients, heat of vaporization equation co-efficients and Antoine vapor pressure equation co-efficients/constants. A number of authors have reported on different methods for determining IL parameters and Group contribution methods are the most widely used. Group contribution methods calculate properties of a substance by summing up the contributions of certain defined groups of molecules, including the number of times each group occurs in the substance (Valderrama and Sanga, 2008).

#### • **Critical Properties**

The critical properties of most substances can be determined directly by experimental methods as described by Friedman *et al.* (1951). Due to their thermal instability at temperatures approaching  $T_b$ , ILs critical properties are difficult to determine experimentally (Valderrama *et al.*, 2008). There are a number of critical properties estimation methods presented in literature and among these methods the Group contribution approach has been proven to be most accurate in the estimations. The Lydersen method was the very first one of these Group Contribution methods to be reported. The method was for the calculation of critical temperature  $T_c$ , critical pressure  $P_c$

and critical volume  $V_c$  for 43 defined structural groups. The critical properties are given as follows;

$$T_c = \frac{T_b}{A_L + \sum n_i \Delta T_L - (\sum n_i \Delta T_L)^2} \quad \text{Equation 3}$$

$$P_c = \frac{M}{(C_L + \sum n_i \Delta P_L)^2} \quad \text{Equation 4}$$

$$V_c = E_L + \sum n_i \Delta V_L \quad \text{Equation 5}$$

The Joback and Reid method is an extension of the Lydersen method with more supported properties, new parameters and slightly modified equations.

$$T_c = \frac{T_b}{A_J + B_J \sum n_i \Delta T_J - (\sum n_i \Delta T_J)^2} \quad \text{Equation 6}$$

$$P_c = \frac{1}{(C_J + D_J N - \sum n_i \Delta P_J)^2} \quad \text{Equation 7}$$

$$V_c = E_J + \sum n_i \Delta V_J \quad \text{Equation 8}$$

Most recently Alvarez and Valderrama proposed a modified Lydersen-Joback-Reid method. “The method considers the equations of Lydersen for the critical pressure and critical volume and the equations of Joback-Reid for the normal boiling temperature and the critical temperature (Valderrama and Robles, 2007).”

$$T_b = 198.2 + \sum n \Delta T_{bM} \quad \text{Equation 9}$$

$$T_c = \frac{T_b}{A_M + B_M \sum n \Delta T_M - (\sum n \Delta T_M)^2} \quad \text{Equation 10}$$

$$P_c = \frac{M}{[C_M + \sum n \Delta P_M]^2} \quad \text{Equation 11}$$

$$V_c = E_M + \sum n \Delta V_M \quad \text{Equation 12}$$

$$\omega = \frac{(T_b - 43)(T_c - 43)}{(T_c - T_b)(0.7T_c - 43)} \log \left[ \frac{P_c}{P_b} \right] - \frac{(T_c - 43)}{(T_c - T_b)} \log \left[ \frac{P_c}{P_b} \right] + \log \left[ \frac{P_c}{P_b} \right] - 1 \quad \text{Equation 13}$$

The modified Lydersen-Joback-Reid method has been used by Valderrama and Robles to calculate the critical properties of ILs. To measure the accuracy of the method in the estimation

of critical properties for ILs, the liquid density of the ILs was estimated from a generalized correlation using exclusively the calculated normal boiling temperatures and the calculated critical properties. The average deviation was found to be 1.6% and the average absolute deviation was 5.2%, thus the calculated critical properties and normal boiling temperatures are accurate.

$$\rho_L = \left(0.01256 + \frac{0.9533M}{V_c}\right) \left[\left(\frac{0.0039}{M} + \frac{0.2987}{V_c}\right) V_c^{1.033}\right] \varphi \quad \text{Equation 14}$$

$$\text{Where } \varphi = -\left[\frac{1-T_R}{1-T_{bR}}\right]^{\frac{2}{7}} \quad \text{Equation 15}$$

- **Vapor Pressure (Antoine Equation Constants)**

Valderrama and Sanga (2008) developed equations for the estimation of Antoine equation constants using critical properties and constant  $C = 43$ ;

$$A = \text{Log}(P_c) * \frac{T_c - 43}{T_c - T_b} \quad \text{Equation 16}$$

$$B = \text{Log}(P_c) * (T_c - 43) * \frac{(T_b - 43)}{(T_c - T_b)} \quad \text{Equation 17}$$

## 2.6. Diesel Sample

For this study the FCC-unit feed and diesel product were chosen due to the HDS not being capable of reducing the sulfur content to 10ppm in these petroleum fractions. A look at the diesel path in a refinery shows that diesel producing streams contain S-compounds which are unreactive for the HDS process, thus the need for an alternative desulfurization process, which will ensure compliance with government regulations on fuel sulfur content.

### Crude Oil Refining:

In an oil/petroleum refinery process, crude oil is taken in as a feedstock to produce a wide range of different products, according to product specifications, that depend on the country, local regulations and even the seasonality (Maple, 2000). The oil goes through a number of process operations to achieve these specifications, as shown in Figure 11 below. The first processing steps in crude oil refining are distillation processes;

- **Crude Distillation Unit (CDU)**

This is the first processing step in any refinery process operation; follows the de-salter unit. In this unit the crude oil is separated into different fractions according to boiling point range as follows;

**Table 4 CDU Products and their boiling range**

<b>Fraction</b>	<b>Product Name(s)</b>	<b>Boiling range (°C)</b>
Light distillates	LPG (Propane+Butane)	(-41)-(-1)
Middle distillates	Naphtha	80 – 150
	Kerosene	150 – 250
	Light Gasoil (LGO)	250 – 350
	Heavy Gasoil (HGO)	350 – 370
Heavy Distillates	Long Residue	370 +

The LGO and HGO are fed to the HDS for treatment to produce in-spec diesel. These fractions are composed of thiophene, dibenzothiophene and alkylated dibenzothiophene organic S-compounds as shown in Table 2.

- **Vacuum Distillation Unit (VDU)**

This unit separates the heaviest product from the CDU; the Long Residue into Vacuum Gasoil (VGO), which will be treated in another unit to produce diesel and Short Residue (SR); an extremely heavy and viscous residual material.

The two distillation units, CDU and VDU collectively give a Gasoil (diesel) yield of 24.8% woc (Maple, 2000).

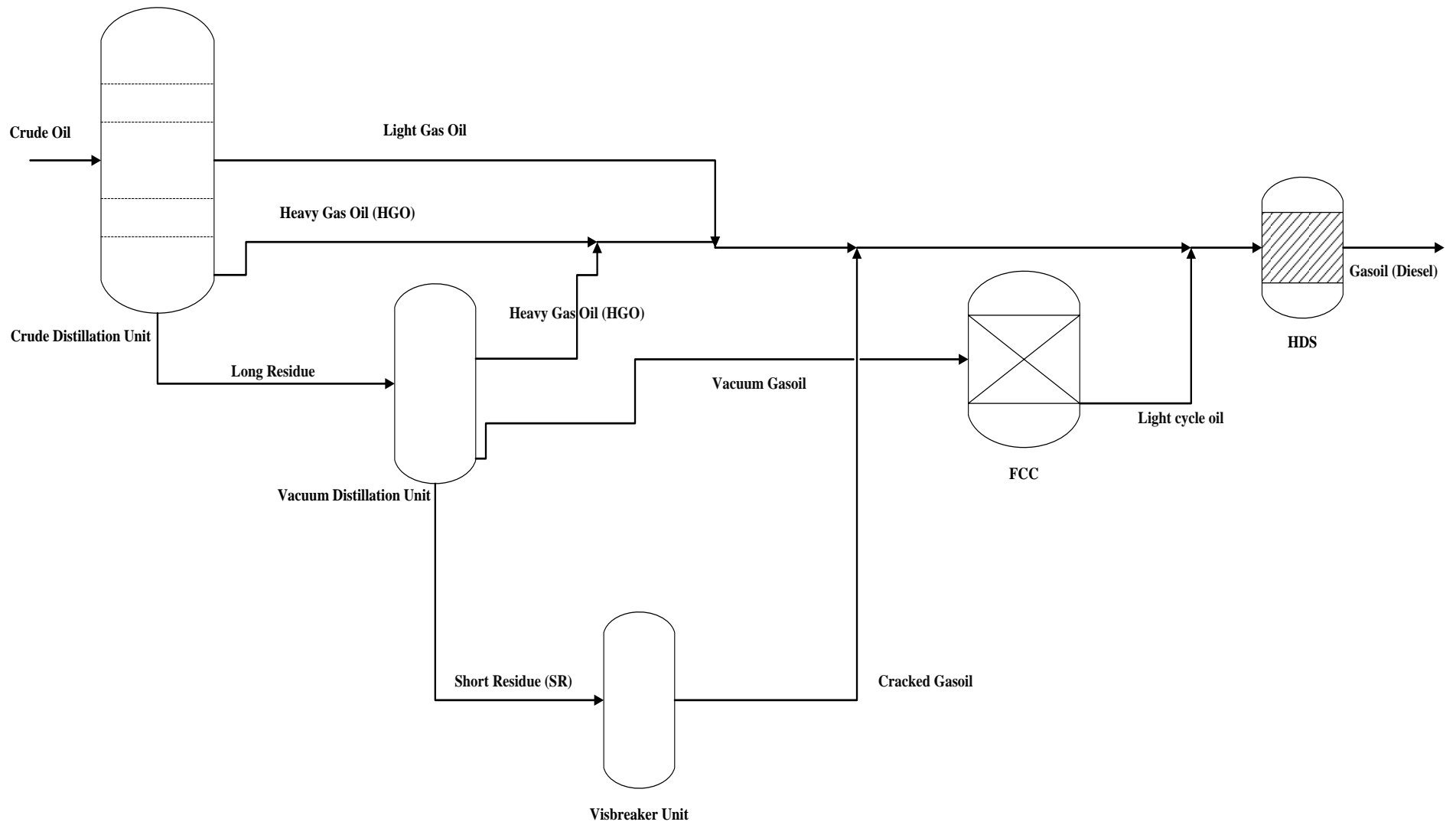
What follows from the distillation units are residue conversion units which upgrade residues by producing distillates, by reducing the amount of residue to be blended away and by making the remaining residues easier/cheaper to blend (Parkash, 2003).

- **Visbreaking Unit (VBU)**

This unit takes in the short residue stream from the VDU upgrades it to produce a number of distillates of interest for this study being Cracked Gasoil which will be blended with the LGO stream to the HDS process.

- **Fluid Catalytic Cracking Unit (FCCU)**

The FCCU improves the total refinery Gasoil (diesel) yield to 27.8% wco and collectively with the VBU brings the total Gasoil yield to 28.7% wco (Maple, 2000). This unit converts VGO into a number of fractions of focus in this study being Light Cycle Oil (LCO), which is a high sulfur content fraction containing the unreactive (refer to Figure 4) alkylated benzothiophenes, DBT and alkylated DBT organic sulfur compounds.



**Figure 11 Diesel path/streams in the refinery process**

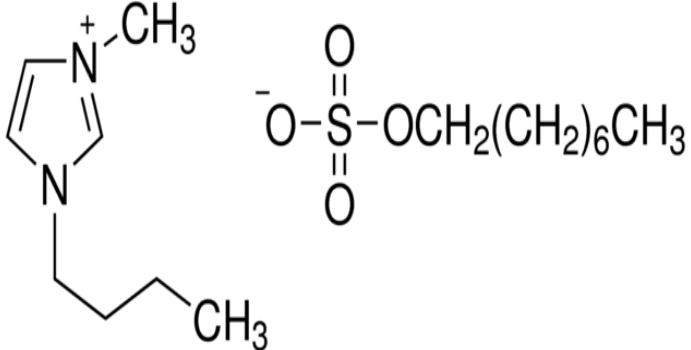
## Chapter 3

### 3. Experimental

#### 3.1. Feed Materials

The structure of the IL chosen is shown in Table 5

**Table 5 Ionic Liquid investigated in this study**

<b>Name</b>	1-butyl-3-methylimidazolium octylsulfate
<b>Acronym</b>	[BMIM][OcSO <sub>4</sub> ]
<b>Molecular Formula</b>	C <sub>16</sub> H <sub>32</sub> N <sub>2</sub> O <sub>4</sub> S
<b>Molecular Weight (g/mol)</b>	348.5
<b>Molecular Structure</b>	

This study focused on the desulfurization of VGO and LCO whose properties are presented in Table 6

**Table 6 Diesel samples properties**

<b>Property</b>	<b>FCC Unit Feed Diesel</b>	<b>FCC Unit Product Diesel</b>
Sulfur content (ppm)	4203	549.9
Cetane Index	46.0	
Density @ 15°C (kg/m <sup>3</sup> )	820.0	
Polycyclic aromatic hydrocarbons, wt%	2.1	
Ignition Point, °C	>55	
Kinematic Viscosity @40°C, mm <sup>2</sup> /s	3.98	

### 3.2. Analysis Procedure

The ICP-AES (inductively coupled plasma-atomic spectrometry) was used for sulfur analysis. ICP-AES is an analytical technique which operates on the principle that “excited electrons emit energy at a given wavelength as they return to ground state” (Basic overview of ICP-AES, 2013). Prior to analysis in an ICP-AES, the diesel samples were treated into a solution by microwave digestion.

- Specified operating parameters;
  - Microwave power level - 1600W, 100%
  - Ramp time (time take to heat the sample from 20°C to 185 °C) - 25 min
  - Pressure - 800 psi
  - Temperature - 215°C
  - Hold time/cool down time ( time that the sample spend in the microwave under above conditions) - 15min
- Sample is weighed out into the microwave vessel and then 5mL HNO<sub>3</sub> and 2mL HCl added into the vessel
- The filled microwave vessel is then left to stand open for 20 minutes to predigest and then sealed and heated in the microwave as per above specifications
- After the digestion, 43 g of deionized water is added to the digested sample to make up 50 mL
- The digested sample is then analysed for Sulfur using the ICP-AES
- The ICP-AES results were corrected for the dilution factor as per digestion procedure

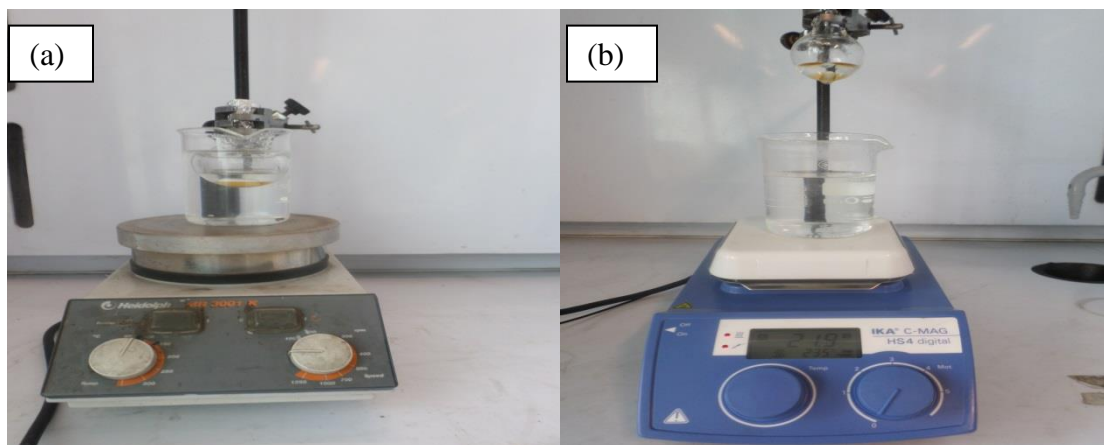
### 3.3.Equipment

All weighing conducted for the experiments was carried out on an Adam ACBplus-1000 balance with an accuracy of  $\pm 10^{-2}$  g shown in Figure 12



**Figure 12 Adam ACBplus-1000 weighing balance**

For all the extraction experiments the Heidolph MR 3001 K heater and magnetic stirrer plate as well as the IKA C-MAG HS4 digital heater and magnetic stirrer plate with temperature control were used (Figure 13).



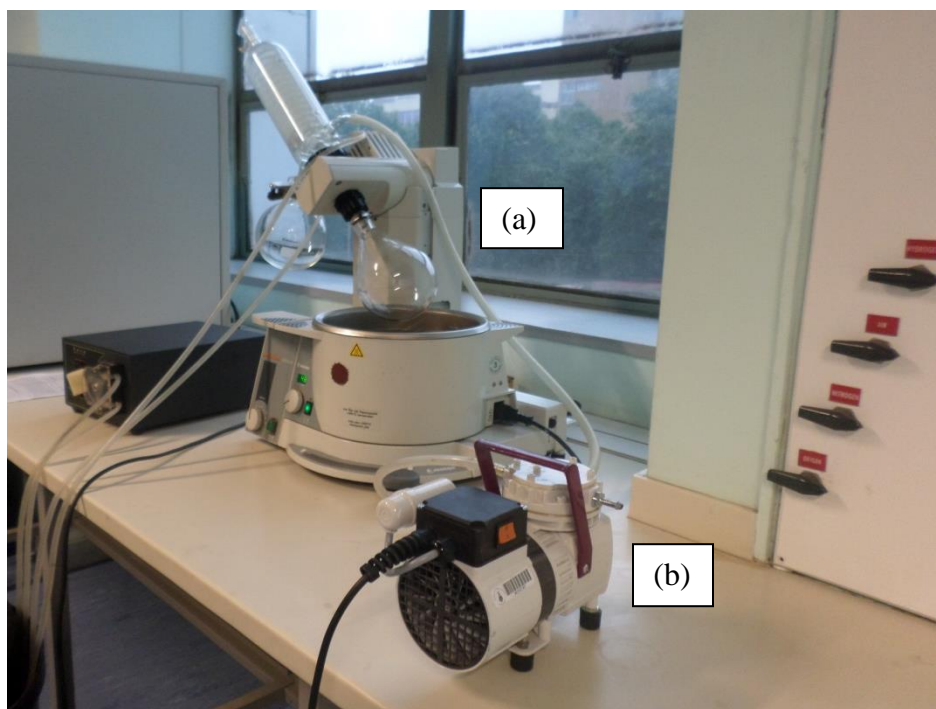
**Figure 13 Heidolph heater and magnetic stirrer (a), IKA C-MAG HS4 digital heater and magnetic stirrer (b)**

The experiments were conducted in a fume hood due to the hazardous and toxic nature of the chemicals used in the experiments (Figure 14).

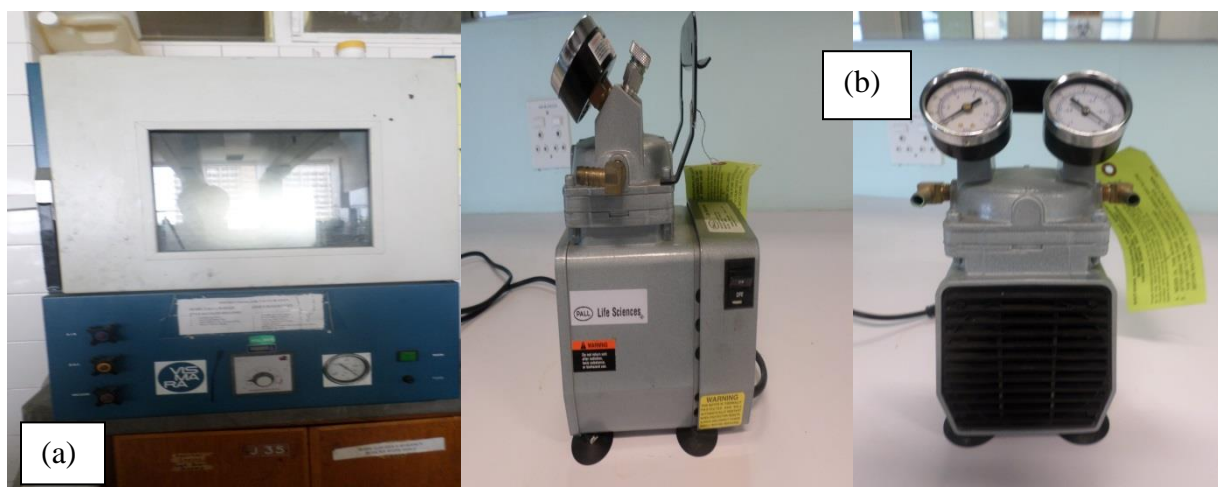


**Figure 14 The Airflow Specialist fume hood**

The S-compounds were re-extracted from ILs by evaporation, the Heidolph Laborota 4000-efficient connected to a KNF rotary evaporation pump was used for this purpose (Figure 15). The ILs was then dried off in a Vismara V065 vacuum oven connected to a Pall vacuum/pressure pump (Figure 16). The regenerated IL was characterized by H and C NMR.



**Figure 15 Heidolph Laborota 4000-efficient (a), KNF rotary evaporation pump (b)**



**Figure 16 Vismara V065 vacuum oven (a), Pall vacuum/pressure pump (b)**

After each extraction experiment samples were taken and analyzed for S composition using ICP-OES (Figure 18), the samples were first prepared for analysis by microwave digestion (Figure 17).



**Figure 17 MARS microwave digester**



**Figure 18 Thermo ICap 6200 ICP-AES**

The ICP-AES instrument was calibrated using NIST (National Institute of Standards and Technology, Gaithersburg MD, USA) traceable standards to quantify selected elements. A NIST-traceable quality control standard of a separate supplier than the main calibration standards were analysed to verify the accuracy of the calibration before sample analysis.

### **3.4. Real diesel desulfurization**

#### **3.4.1. Objective**

Much research has been conducted to investigate ionic liquid as solvents in the extractive desulfurization of model fuel oils. This part of the experiment aims to broaden the research knowledge by investigating the industrial application of this process. To achieve this, real diesel fuel was desulfurized with the chosen ionic liquids. The experiment was divided into two parts to investigate the efficiency of ionic liquids in different samples of diesel; one with a higher sulfur content of 4000 ppm and the other with lower sulfur content; 450 ppm. Furthermore the reusability as well as the efficiency of regenerated ionic liquids was investigated in addition to the investigation of core parameters efficiency and effectiveness of ionic liquids as solvents in extractive desulfurization namely; number of extraction stages and reaction time.

#### **3.4.2. Experimental procedure**

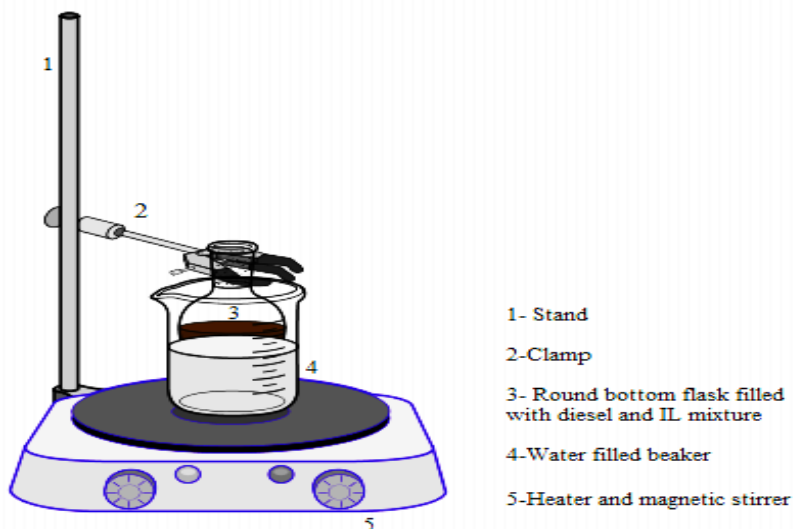
##### ***Chemicals***

Two different samples of real diesel fuel were obtained from Natref, SA. Both samples were from the fluid catalytic cracking unit (FCC) with the first sample being from the unit charge/feed and the second sample; which has a lower S content; was from the FCC unit discharge/product. Some properties have been mentioned in Table 6 in section 3.1.

Ionic liquid; 1-butyl-3-methylimidazolium octylsulfate (with a purity of  $\geq 95\%$ ) was purchased from Sigma-Aldrich, SA and used as received without further purification.

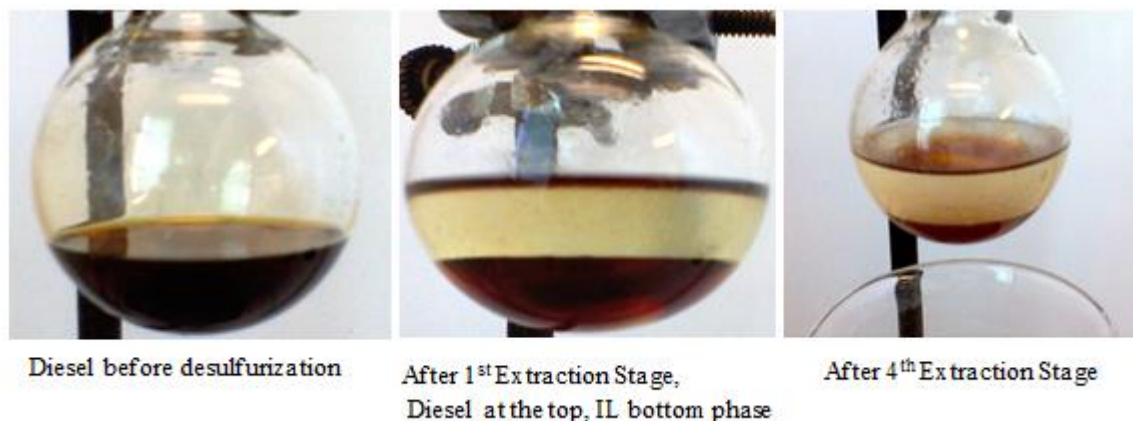
##### ***Procedure***

The two liquids; diesel and ionic liquid; were fed into 50 mL round bottom flasks and placed in temperature controlled water baths as illustrated by Figure 19.



**Figure 19 A schematic diagram of the experimental setup**

Ionic liquid was added to the flasks in a 4:1 mass ratio. The ratios used were as those used by *£ber et al.* (2004) in the prior study of the desulfurization of model diesel oil using [BMIM][O<sub>c</sub>SO<sub>4</sub>]. The flask contents were stirred for 30 minutes to get good contact between the phases. After the mixture was allowed to settle for 30 minutes to obtain phase splitting and settling, samples of the upper layer; the raffinate were withdrawn and analyzed by ICP-AES. For the experiments investigating the reusability of the ionic liquid, the bottom phase which is the loaded IL phase was fed; together with fresh diesel oil; into a round bottom flask and allowed to be in contact as explained above. When investigating the optimum number of extraction stages after the first stage the remaining diesel oil phase was fed to the second stage with fresh ionic liquid. Microwave digestion was used to prepare the diesel samples prior to analyzing for sulfur and content using ICP-AES for each extraction experiment as outlined in Analysis Procedure.



**Figure 20 Visual change in the diesel (FCC unit feed stream diesel) during the desulfurization process**

Figure 20 shows the change in the FCCU feed stream diesel during the different stages of the desulfurization process.

### **3.5. Ionic Liquid regeneration**

This part of the study is two-fold;

- (i) Part 1: the aim was to evaluate (screen) the ability of different solvents for the re-extraction of sulfur from loaded IL using thermodynamic criteria. For this purpose LLE data of [IL+Thiophene+Solvent] systems were determined and discussed in terms of  $\beta$  (distribution ratio) and  $S$  (selectivity), to understand the solubility of the involved components in each other.
- (ii) Part 2: suitable solvents were used in the regeneration of loaded IL and the efficiency of the regenerated IL was studied i.e. the extraction ability of regenerated IL was studied and compared with that of fresh IL and reused (without regeneration) IL.

#### **3.5.1. LLE Data**

Aspen Plus was used for the determination of LLE data for selected ternary systems. For this purpose the UNIFAC (**U**niversal **q**uasi-chemical **F**unctional group **A**ctivity **C**oefficients) thermodynamic model was chosen as the Base Method. Like the UNIQUAC and NRTL thermodynamic models, UNIFAC is an activity coefficient model, but more thermodynamically consistent than the two due to its use of functional groups present on the molecules making up the liquid mixture to calculate activity coefficients. The UNIFAC method has become widely

used for predicting liquid-phase activity co-efficients (LLE data) in cases where little or no relevant experimental information is available (Gmehling *et al.* 2002), like in the case of ILs.

When using thermodynamic models for mixtures containing ILs, the substances' critical properties and other physical properties are required. The critical properties given in Table 7 were calculated from the modified Lydersen-Joback-Reid properties estimation method given by equations 9-13 in *section 2.5.5* with a deviation of 2.3% as measured by calculating the IL density using equation 14 and equation 15 (Valderrama and Robles, 2007) also in *section 2.5.5*.

**Table 7 [BMIM][OcSO<sub>4</sub>] Critical properties and other scalar parameters**

<i>Name</i>	<i>Symbol</i>	<i>Value</i>
Normal Boiling Point	T <sub>b</sub> (K)	895.7
Molecular Weight	M <sub>w</sub>	348.5
Acentric Factor	ω	0.7042
Critical Temperature	T <sub>c</sub> (K)	1189.8
Critical Pressure	P <sub>c</sub> (bar)	20.2
Critical Compressibility Factor	Z <sub>c</sub>	0.2509
Critical Volume	V <sub>c</sub> (cm <sup>3</sup> /mol)	1116.7

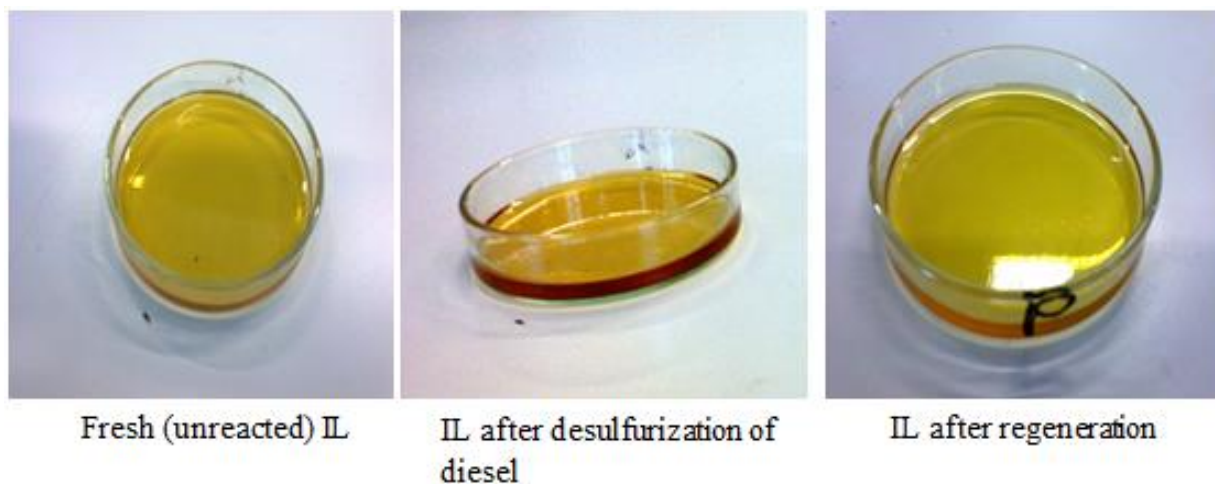
The vapor pressure properties i.e. Antoine's equation constants were calculated from the equations developed by Valderrama and Sanga (2008); equation 16 and equation 17 (*section 2.5.5*). The calculated Antoine constants for [BMIM][OcSO<sub>4</sub>] are; A-5.09, B-4340.27 and C-43.00.

### **3.5.2. Regeneration methods and experimental procedure**

After each desulfurization experiment the solvent-rich phase was kept to recover the ionic liquids. The S-containing ILs were regenerated by dissolution with a suitable solvent and dried-off by vacuum evaporation at 100°C for 10 hours for the clear separation of the ionic liquid and solvent. Vacuum evaporation is an appropriate method due to the negligible vapour pressure of ionic liquids and the volatility of components present in the ionic liquids, but as mentioned earlier the method cannot remove the high boiling unreactive S-compounds present in diesel fuel, hence the need to first treat the loaded IL with a solvent. The low boiling hydrocarbon hexane

was used as a solvent, as it has been reported to be promising re-extraction media for S-compounds containing ILs and was proven to be a suitable solvent from the LLE data.

The extraction performance of the regenerated ILs was investigated and compared with results obtained for fresh ILs. The same procedure described in 3.5 was followed and after each experiment the IL was regenerated, this was done up to 4 times; 4 regeneration cycles. Figure 21 shows the IL at different stages in the experimental work.



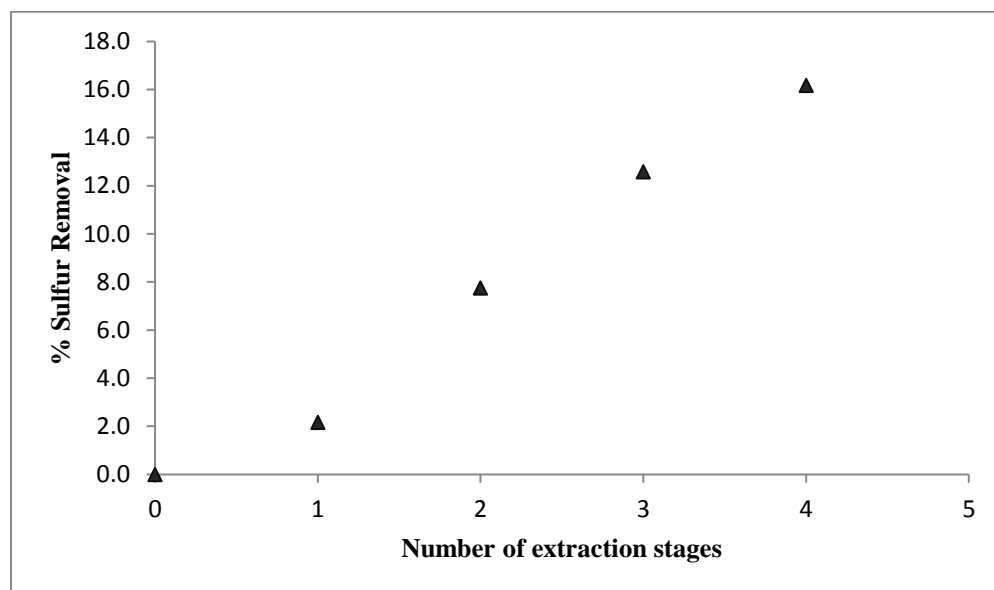
**Figure 21 The ionic liquid as per different part of the study**

## Chapter 4

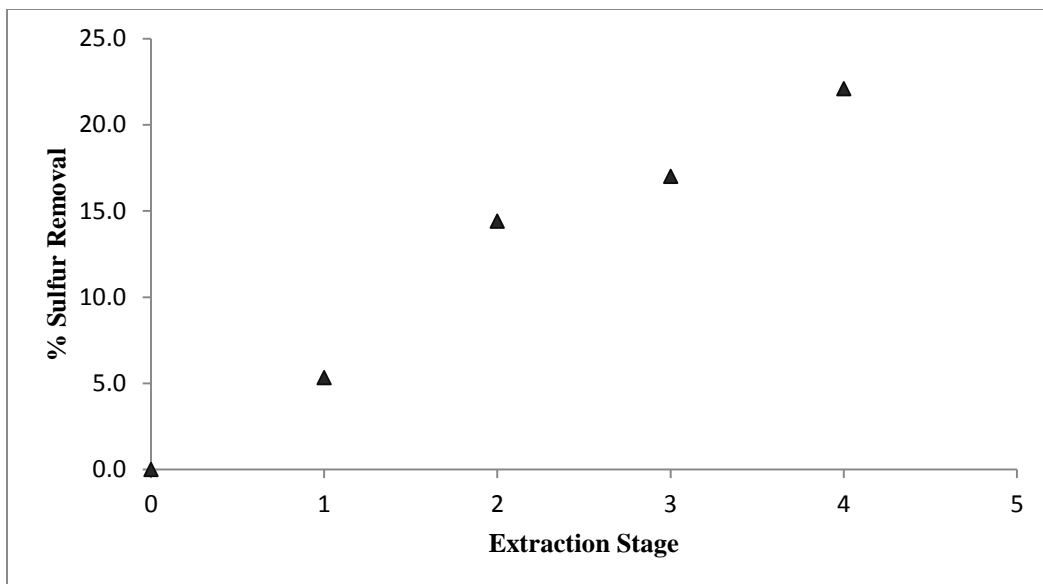
### 4. Results

#### 4.1. Effect of Sulfur content/concentration as well as oil and IL ratio on desulfurization of diesel

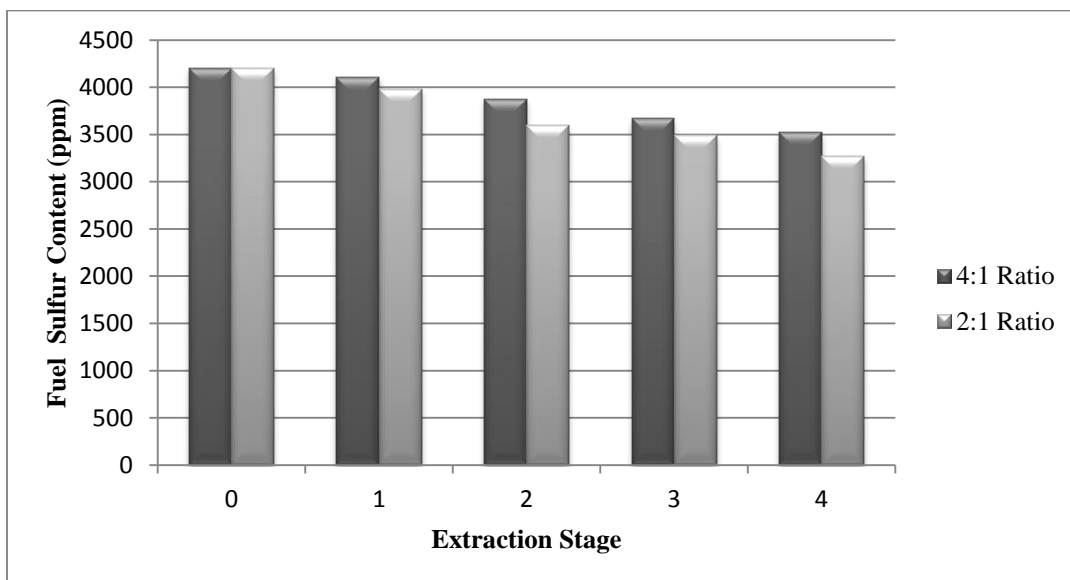
The capacity of the IL, 1-butyl-3-methylimidazolium octylsulfate as a solvent for the deep desulfurization of Vacuum Gasoil and Light Cycle Oil; FCC-Unit feed and product respectively was studied. The effect of IL/Oil mass ratio on the extraction efficiency of ILs was also studied. Figures 22-27 show the effect of sulfur content as well as Oil to IL ratio on the desulfurization of diesel distillates.



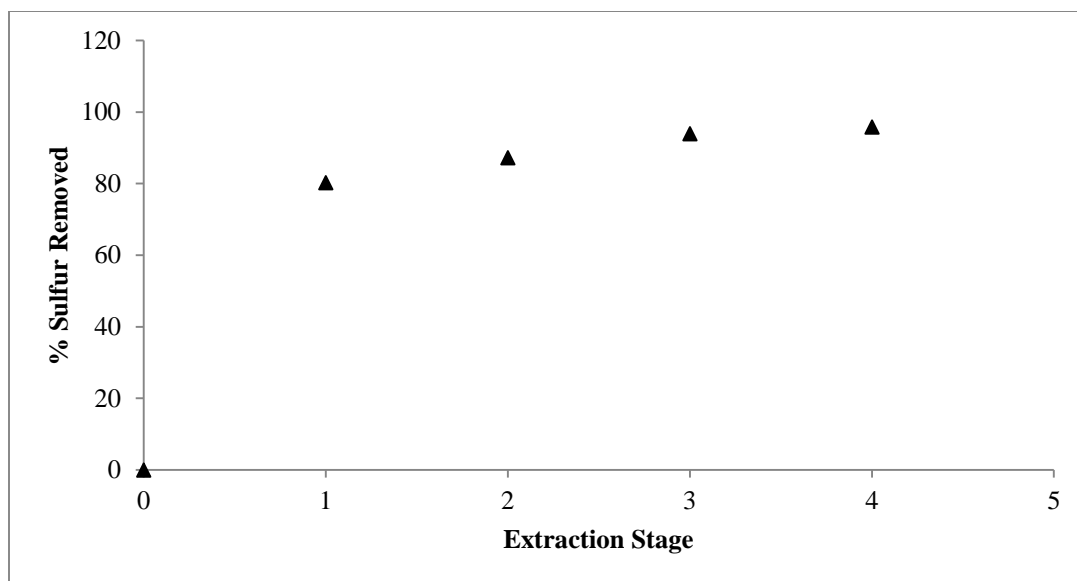
**Figure 22 Sulfur removal from Vacuum Gasoil (FCC-Unit feed) using [BMIM][OctSO4] at different extraction stages (Oil to IL ratio = 4:1, Initial sulfur content=4203ppm)**



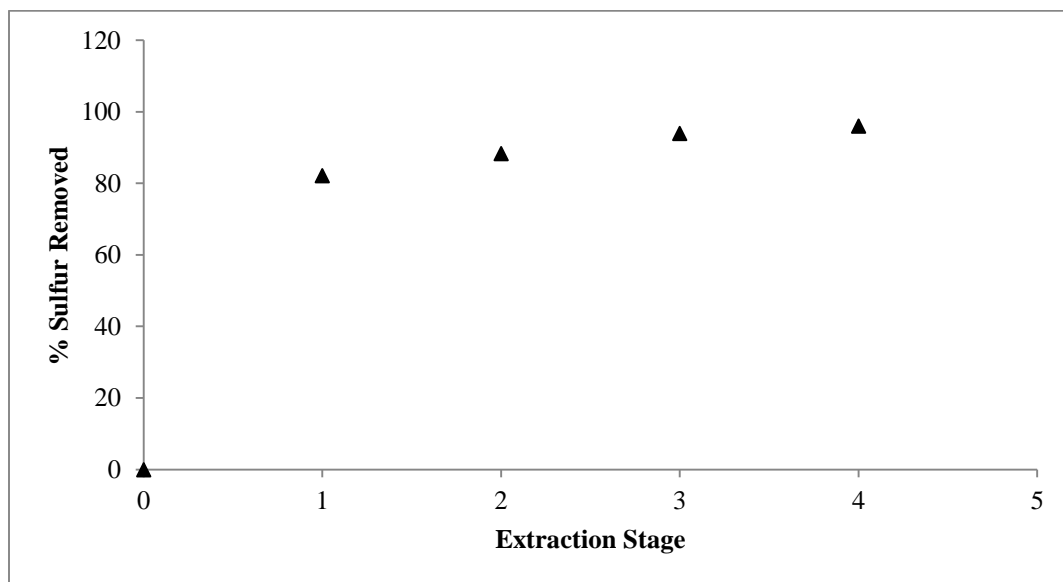
**Figure 23 Sulfur removal from Vacuum Gasoil (FCC-Unit feed) using [BMIM][OctSO<sub>4</sub>] different extraction stages (Oil to IL ratio=2:1; Initial sulfur content=4203 ppm)**



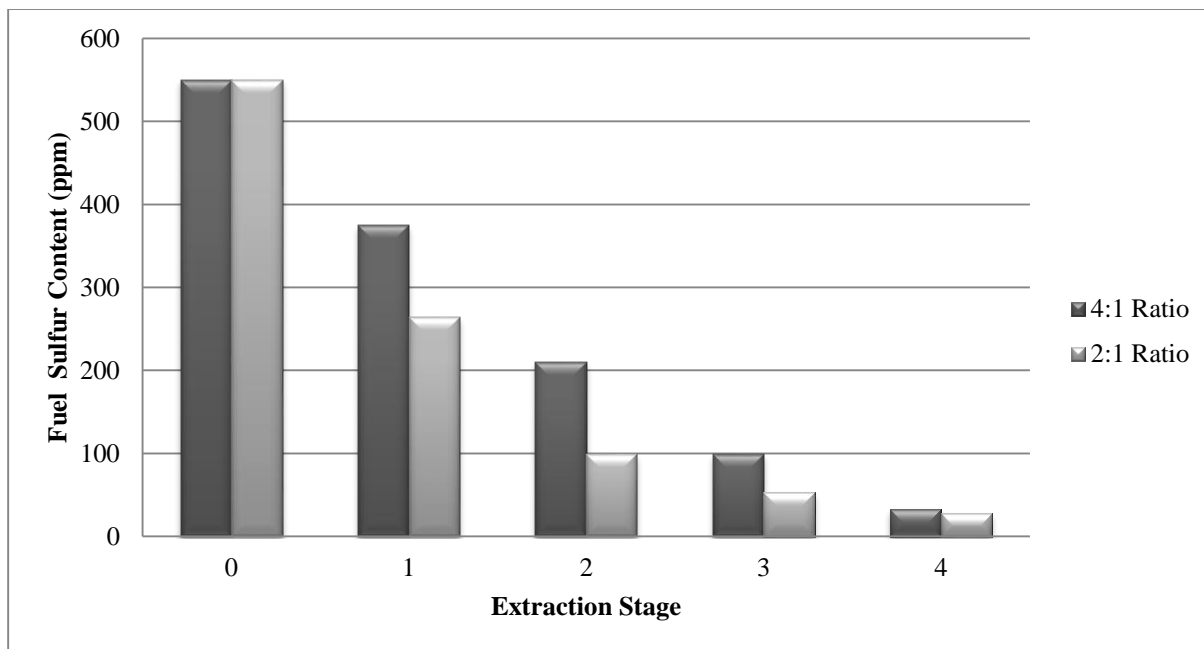
**Figure 24 Multistage extraction of sulfur from VGO, showing initial compositions and compositions after the 1st, 2nd, 3rd and 4th extraction stages**



**Figure 25 Multistage Sulfur removal from Light Cycle Oil (FFC-Unit product) using [BMIM][OcSO<sub>4</sub>] (Oil to IL ratio= 4:1, initial sulfur content=549.9 ppm, final sulfur content=32.93 ppm)**



**Figure 26 Multistage extraction of Sulfur from Light Cycle Oil (FCC-Unit product), (Oil to IL ratio= 2:1, initial sulfur content=549.9 ppm, final sulfur content=27.60 ppm)**



**Figure 27 Multistage extraction of sulfur from LCO, compositions in initial LCO and after the 1st, 2nd, 3rd and 4th extraction stages**

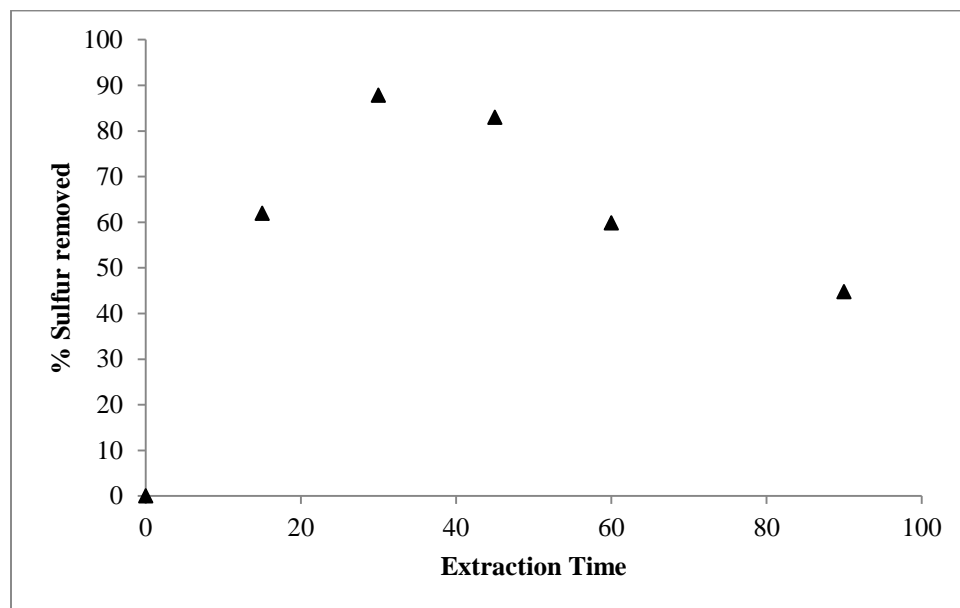
**Table 8 Summary of key results in this section**

<b>Final diesel Sulfur content and % removed after 4 extraction stages</b>		
	<b>4:1 mass ratio</b>	<b>2:1 mass ratio</b>
<b>VGO</b>	3274 ppm	3274.3 ppm
	16.20%	22.10%
<b>LCO</b>	32.93 ppm	27.6 ppm
	95.80%	96.01%

Table 8 shows the results for both diesel samples at different mass ratios, in terms of extraction efficiency (%) and final S content in the samples.

## 4.2. Effect of reaction time on sulfur removal

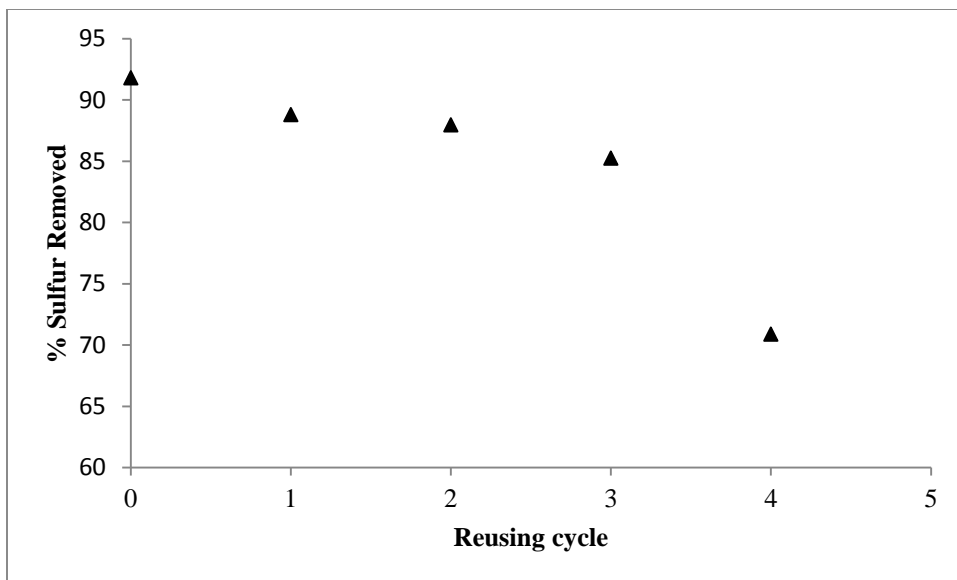
Residence/extraction/stirring time is one of the core parameters affecting the removal of sulfur from petroleum distillates. To study the effect of extraction time and to determine the optimum extraction time, extraction experiments were stopped in defined time intervals i.e. 15, 30, 45, 60 and 90 minutes and Figure 28 shows the removal of Sulfur at the different defined extraction times.



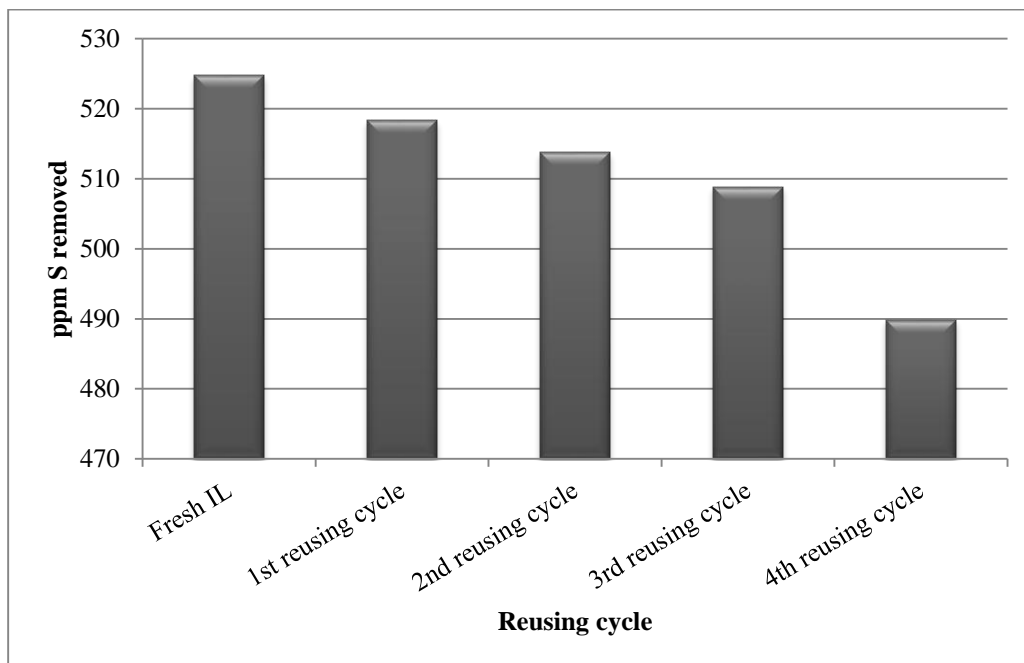
**Figure 28 Extraction of sulfur from Light Cycle Oil at different extraction/residence times, (Oil to IL ratio=2:1, initial S content=549.9 ppm, S content after 30 min extraction time=46.89 ppm, S content in LCO after 90 minutes extraction time=243.89)**

## 4.3. Extraction efficiency of used IL (Reusability of IL without regeneration)

Given the high cost of IL liquids; for industrial application it is important to be able to re-use the IL. Thus the extraction efficiency of used IL was investigated.



**Figure 29 Reusing of IL in the extraction of sulfur from LCO, (Oil to IL ratio 4:1, Initial S content = 549.9 ppm, 0 on the horizontal axis denotes fresh IL)**



**Figure 30 Reusing of IL, sulfur removal at each IL condition (Oil to IL ratio 4:1, Initial S content=549.9 ppm)**

From Figures 29 and 30 above it can be seen that the IL efficiency only started dropping significantly after the 3<sup>rd</sup> reusing cycle. More details are discussed in section 5.3.

## 4.4. Ionic Liquid Regeneration

As reported in literature ILs can be reused until a threshold concentration is reached above which there is a noticeable decrease in extraction efficiency. Thus in addition to its reuse the regeneration of 1-butyl-3-methylimidazolium octylsulfate was also studied. First suitable solvents for the re-extraction of sulfur compounds from the IL were studied using thermodynamic criteria, Aspen plus was used for this purpose and then the distribution ratio and selectivity were calculated. The second part of the study focused on the efficiency of the regenerated IL; the sulfur loaded 1-butyl-3-methylimidazolium octylsulfate was washed with a suitable solvent and then dried off at high vacuum and then used again in the desulfurization of diesel fuel.

### 4.4.1. LLE Data

An investigation of the suitability of selected solvents; namely hexane, pentane, ethyl acetate and diethyl ether; for the re-extraction of organic S-compounds from spent/loaded ILs was undertaken. To this end Aspen Plus was employed to obtain LLE data for the following ternary systems; to get an idea of the solubility degree among the components in each system

- {Hexane + Thiophene + [BMIM][OcSO<sub>4</sub>]}
- {Pentane + Thiophene + [BMIM][OcSO<sub>4</sub>]}
- {Ethyl Acetate + Thiophene + [BMIM][OcSO<sub>4</sub>]}

Tables 10-12 show the compositions of the tie lines for the studied ternary systems as well as the values of Solute Distribution Ratio ( $\beta$ ) and Solvent Selectivity (S) which were calculated according to the following equations;

$$\beta = \frac{(x_1)^I}{(x_1)^{II}}$$

$$S = \frac{(x_1)^I \cdot (x_2)^{II}}{(x_1)^{II} \cdot (x_2)^I}$$

Where subscripts;

1-is the solute/S-compound thiophene

2-is the IL

While superscripts;

I-refers to the solvent phase

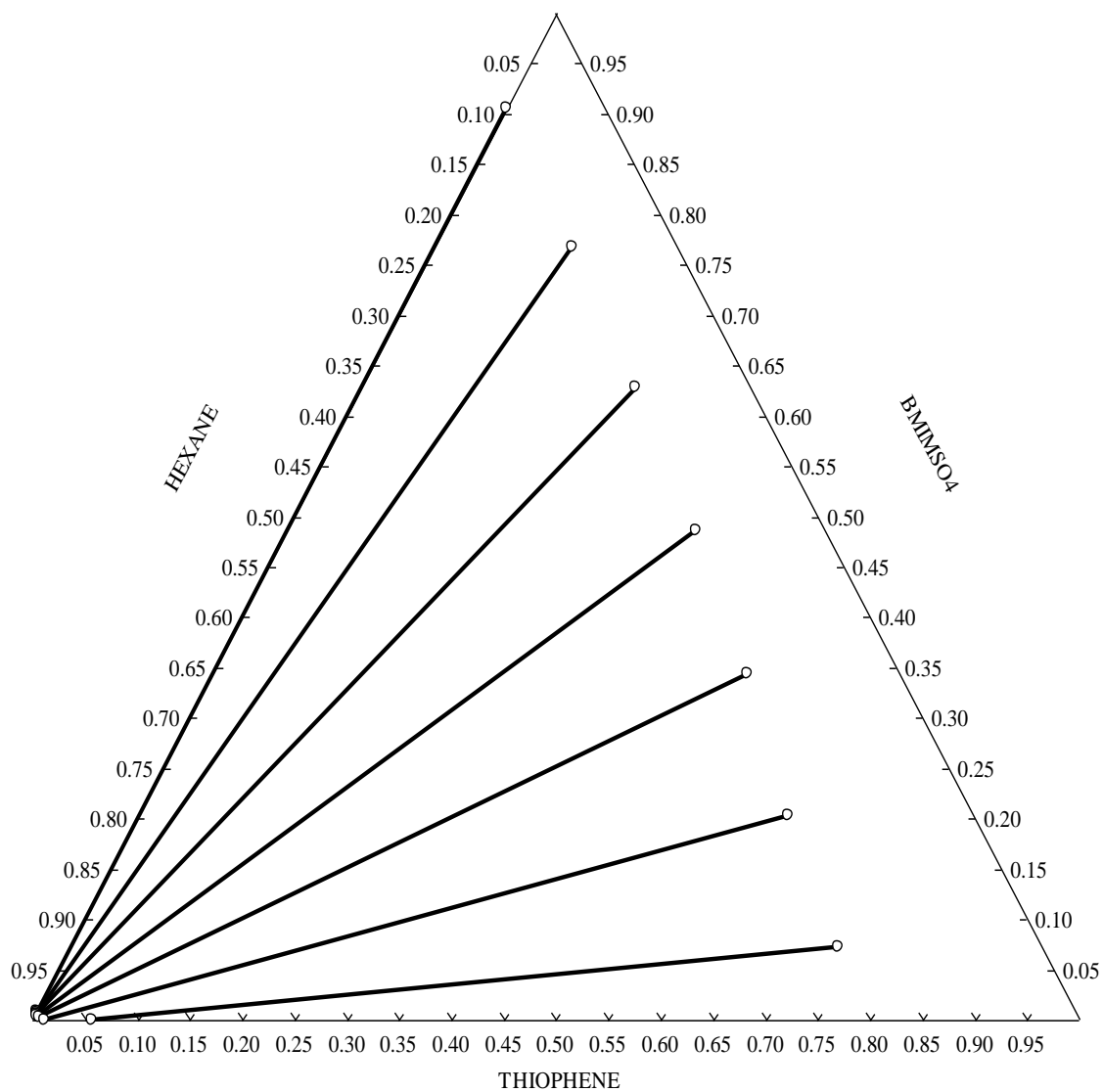
II- refers to the IL phase

$x$  is the molar composition of component indicated as subscript, in the phase indicated as superscript.

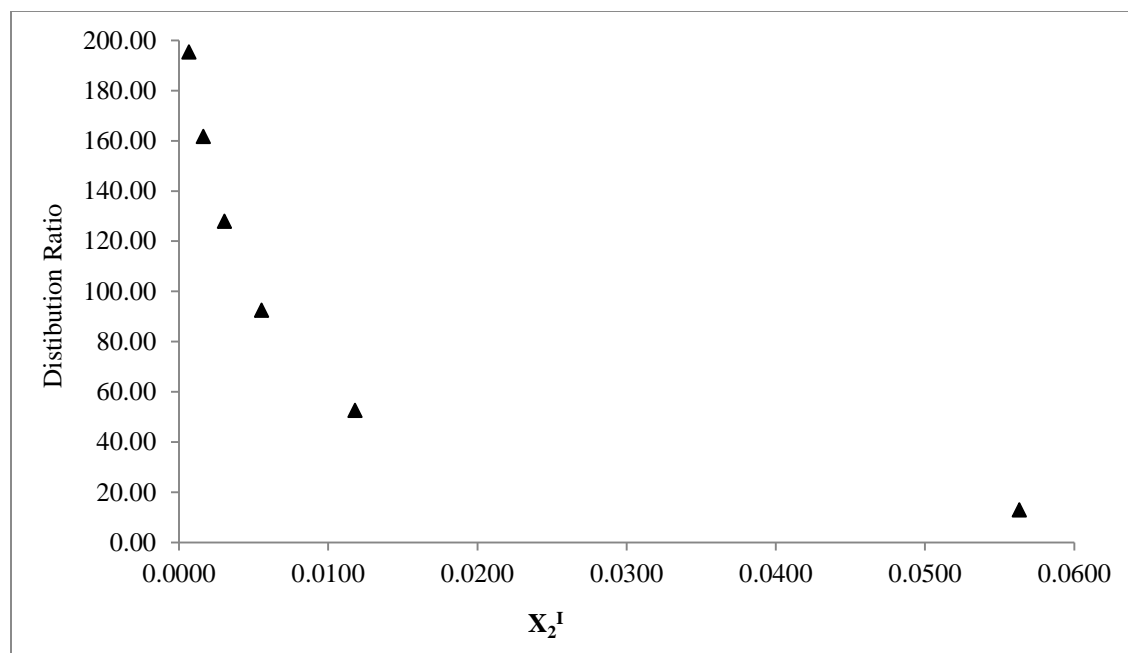
Figures 31, 33 and 35 provide graphical representation of these tie lines.

**Table 9 LLE Data, solute distribution ratio and selectivity for the ternary system {Hexane(1) + Thiophene(2) +[BMIM][OcSO4](3)}**

Hexane -rich phase			IL-rich phase			$\beta$	S
$X_1^{II}$	$X_2^{II}$	$X_3^{II}$	$X_1^I$	$X_2^I$	$X_3^I$		
0.91	0.00	0.09	0.0082	0.0000	0.9918		
0.77	0.13	0.10	0.0073	0.0007	0.9921	195.36	178,93
0.63	0.26	0.11	0.0060	0.0016	0.9923	161.67	394,49
0.49	0.39	0.12	0.0045	0.0031	0.9925	127.91	705,93
0.34	0.51	0.14	0.0026	0.0055	0.9919	92.57	1379,55
0.20	0.62	0.18	0.0007	0.0118	0.9875	52.69	5092,31
0.07	0.73	0.19	0.0000	0.0563	0.9437	13.04	



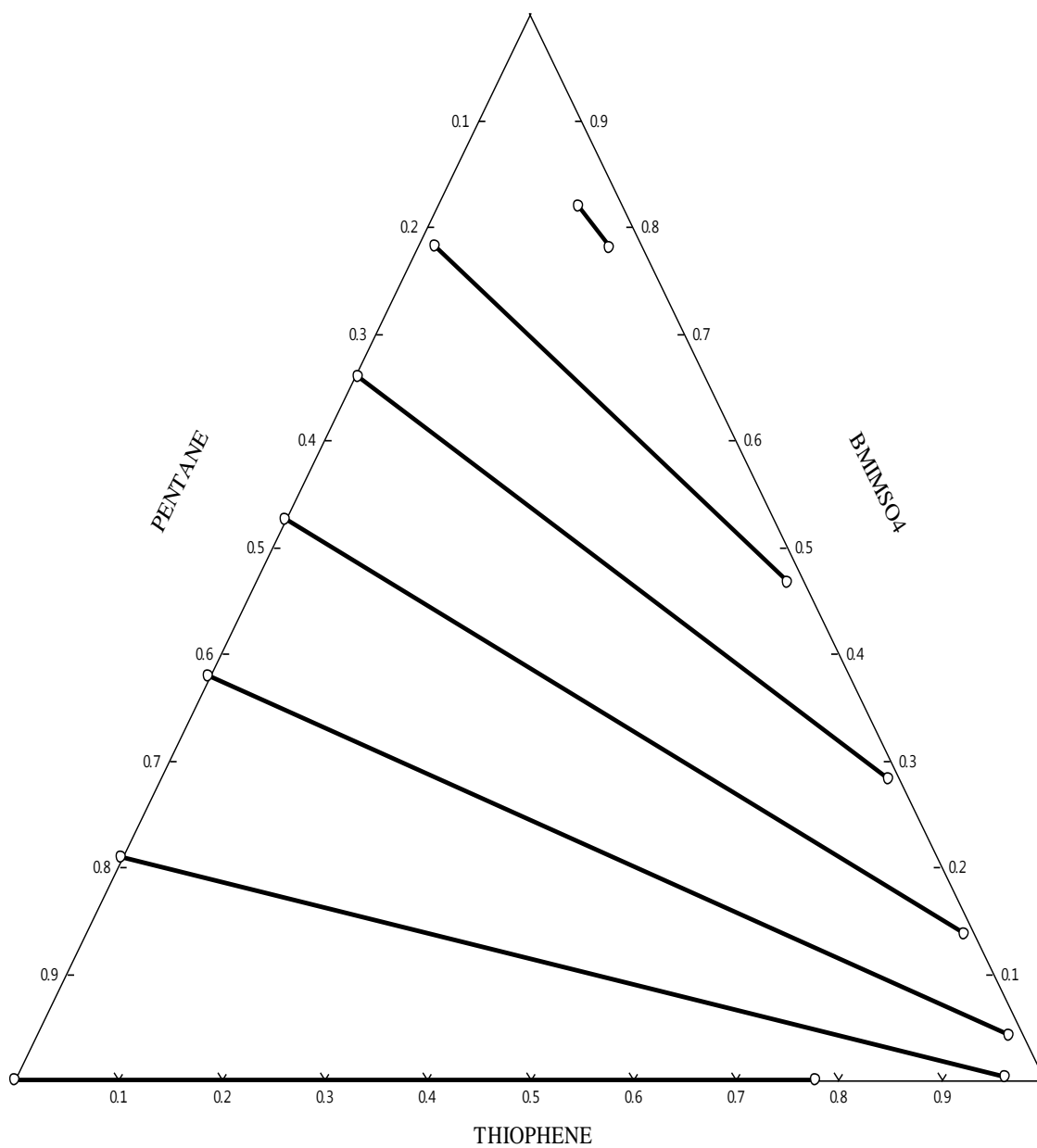
**Figure 31 Tie lines for the ternary system {Hexane(1) + Thiophene(2) + [BMIM][OcSO4](3)}**



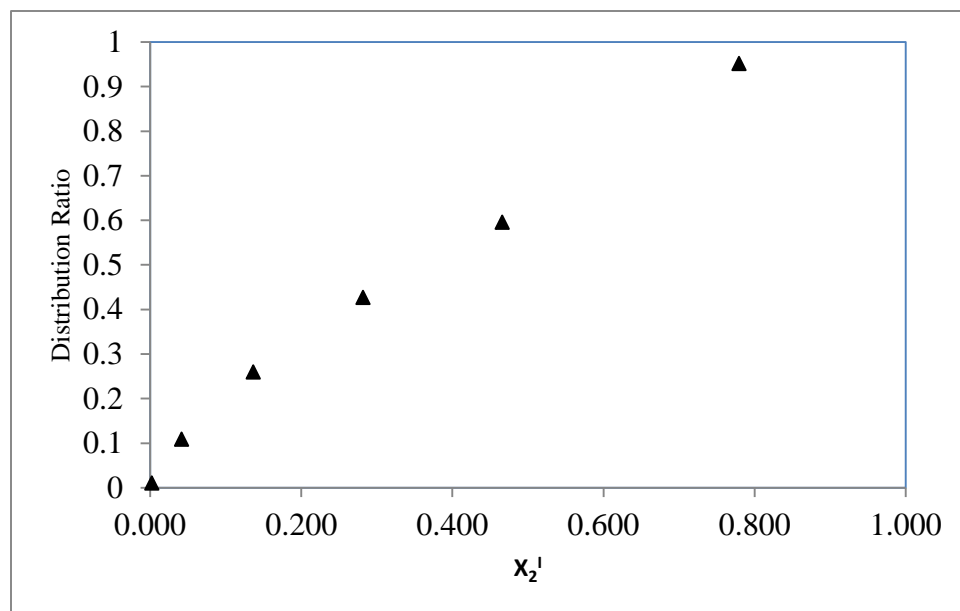
**Figure 32 Thiophene distribution ratio for the ternary system {Hexane + Thiophene + [BMIM][OcSO4]} where 2 refers to [BMIM][OcSO4] ionic liquid and I refers to the Hexane phase**

**Table 10 LLE Data, solute distribution ratio and selectivity for the ternary system { Pentane(1) + Thiophene(2) + [BMIM][OcSO4](3)}**

Pentane-rich phase			IL-rich phase			$\beta$	S
$X_1^{II}$	$X_2^{II}$	$X_3^{II}$	$X_1^I$	$X_2^I$	$X_3^I$		
1.000	0.000	0.000	0.221	0.000	0.779		
0.791	0.209	0.000	0.036	0.002	0.961	0.010563	4.369372
0.621	0.379	0.000	0.013	0.041	0.946	0.109074	0.185507
0.473	0.526	0.001	0.008	0.137	0.856	0.259668	0.06498
0.336	0.659	0.005	0.010	0.282	0.708	0.427036	0.070219
0.200	0.782	0.018	0.014	0.466	0.520	0.596016	0.117828
0.042	0.819	0.140	0.031	0.779	0.190	0.952106	0.779908



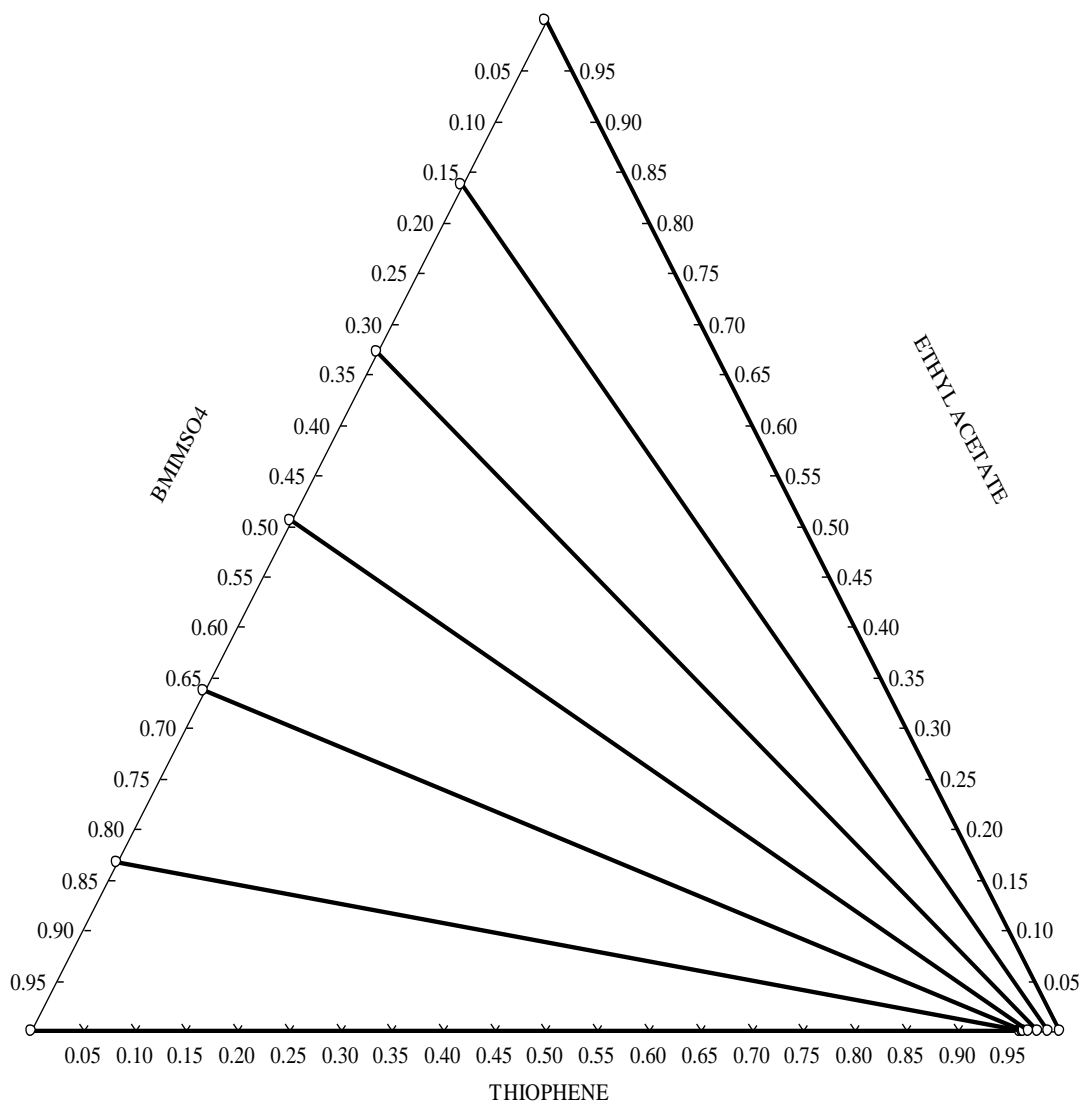
**Figure 33 Tie lines for the ternary system {Pentane(1) + Thiophene(2) + [BMIM][OAcSO4](3)}**



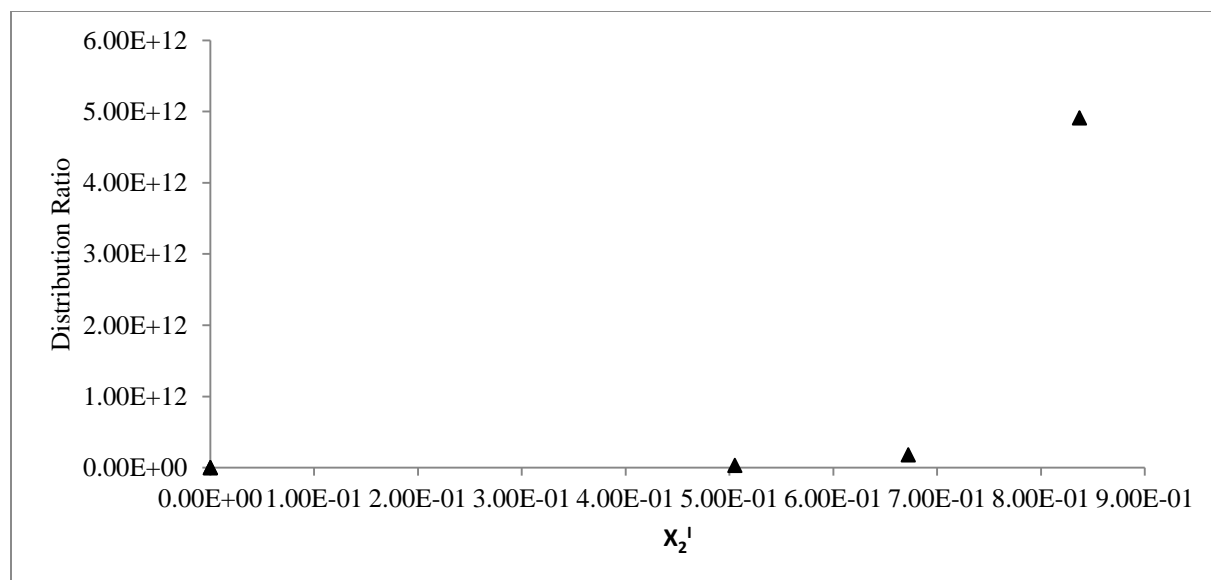
**Figure 34 Thiophene distribution ratio for the ternary system {Pentane + Thiophene + [BMIM][OcSO4]} where 2 refers to [BMIM][OcSO4] ionic liquid and I refers to the Hexane phase**

**Table 11 LLE Data, solute distribution ratio and selectivity for the ternary system {Ethyl Acetate(1) + Thiophene(2) + [BMIM][OcSO4](3)}**

Ethyl Acetate -rich phase			IL-rich phase			$\beta$	S
$X_1^{II}$	$X_2^{II}$	$X_3^{II}$	$X_1^I$	$X_2^{II}$	$X_3^I$		
0.5594	0.0000	0.4406	0.0396	0.0000	0.9604		
0.5435	0.0002	0.4563	0.0367	0.0000	0.9633	1.68E-07	1.26E+07
0.5323	0.0002	0.4675	0.0347	0.0000	0.9653	1.27E-07	1.63E+07
0.4987	0.0003	0.5010	0.4947	0.5051	0.0002	1.72E+03	1.99E-07
0.4277	0.0004	0.5720	0.3275	0.6723	0.0002	1.87E+03	1.54E-07
0.2907	0.0004	0.7089	0.1626	0.8372	0.0002	1.91E+03	1.28E-07
0.0000	0.0005	0.9995	0.0000	0.9998	0.0002	1.87E+03	1.08E-07



**Figure 35 Tie lines for the ternary system {Ethyl acetate(1) + Thiophene(2) + [BMIM][OcSO4](3)}**



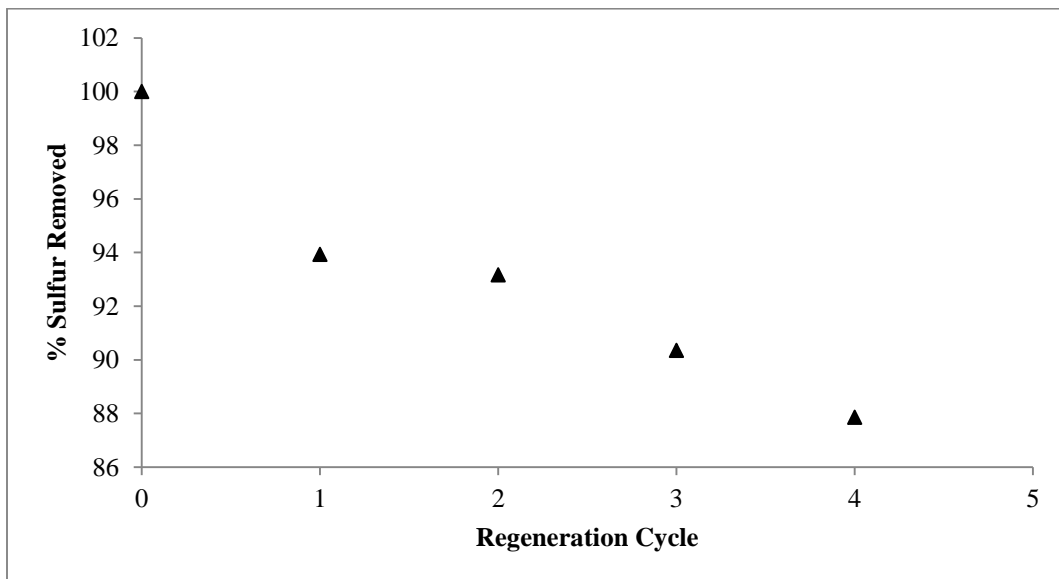
**Figure 36 Thiophene distribution ratio for the ternary system {Ethyl Acetate + Thiophene + [BMIM][OcSO<sub>4</sub>]}** where 2 refers to [BMIM][OcSO<sub>4</sub>] ionic liquid and I refers to the Hexane phase

From the above results it can be seen that of the three (pentane, hexane and ethyl acetate) solvents thiophene distributes most preferentially in hexane than in the IL, hence hexane was chosen as the more suitable solvent. For more details refer to discussion section 5.4.

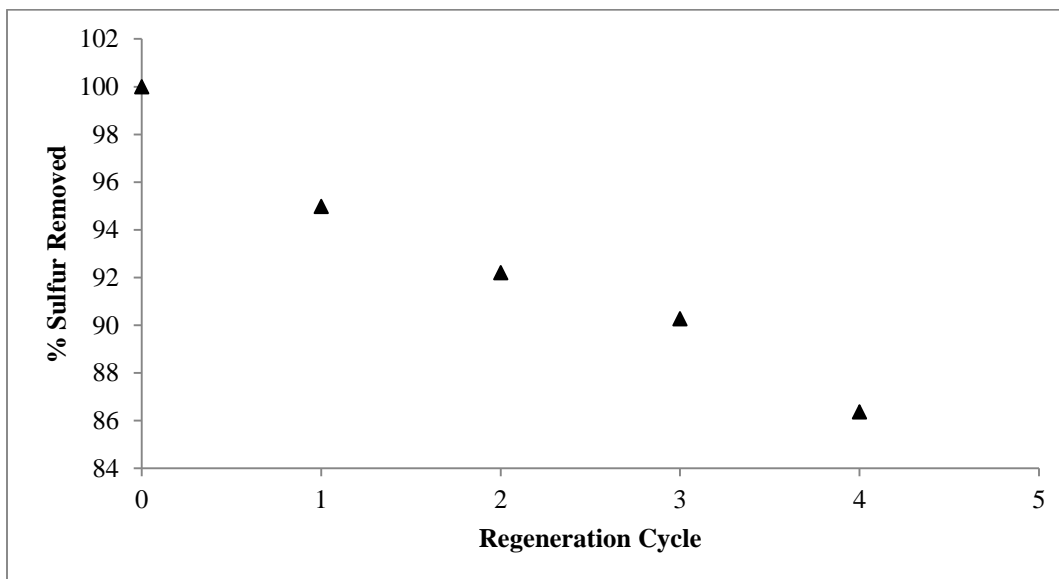
#### 4.4.2. Efficiency of regenerated [BMIM][OcSO<sub>4</sub>]

[BMIM][OcSO<sub>4</sub>] was regenerated by means of an extraction process with hexane as a solvent and vacuum for drying. The purity of the IL was analyzed by H NMR and C NMR spectroscopy and it was verified that its purity was relatively retained as can be seen by the results in Appendix C. From the comparison of the H and C NMR results for pure/unreacted IL, loaded IL and regenerated IL it can be seen that the S-compounds were removed to an extent from the loaded IL, however the IL was not totally purified. The regeneration of ILs used in the desulfurization of real diesel oil is much harder than for model diesel oil due to the contained aromatic S-compounds and complex diesel composition.

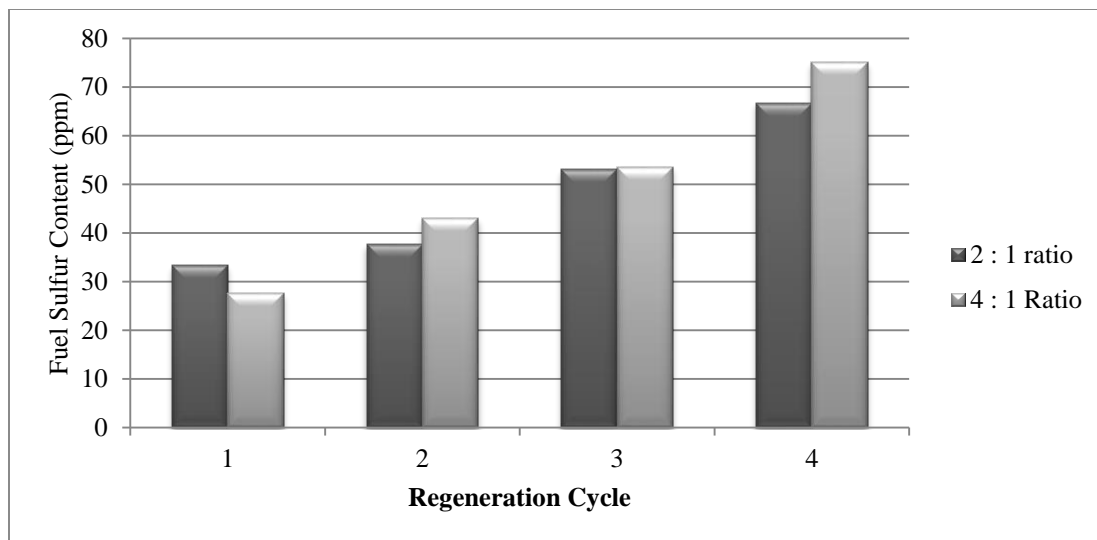
The efficiency in the extraction of sulfur from diesel fuel of the regenerated IL was studied and the results of this are shown in Figures 37 - 39.



**Figure 37 Efficiency of regenerated IL in removing S from LCO (Oil to IL ratio=2:1, Initial S content=549.9 ppm)**



**Figure 38 Efficiency of regenerated IL in removing S from LCO (Oil to IL ratio=4:1, Initial S content=549.9 ppm)**



**Figure 39 Efficiency of regenerated [BMIM][OcSO<sub>4</sub>] at different oil/IL mass ratio (shows the ppm Sulfur in the fuel after each IL regeneration cycle)**

## **Chapter 5**

### **5. Discussion**

#### **5.1. Effects of sulfur content/concentration as well as oil/IL mass ratio on the desulfurization of diesel using IL**

It was shown in the refinery configuration discussion (Figure 11) that the HDS unit can be placed before the FCCU or after the FCCU in a petroleum refinery, hence the extractive desulfurization process was investigated/tested on VGO and LCO (the FCCU feed and diesel product streams). From Figures 22-27 and Table 9 it can be seen that the extractive desulfurization method is much more efficient in removing sulfur from the less sulfur containing LCO (549.9 ppm) than VGO which contains 4203 ppm sulfur. This is largely due to the complex chemical composition of the VGO including more unreactive different types of organic sulfur compounds as given in Table 2. Treating VGO (the higher sulfur containing sample) to acceptable sulfur levels will require much more extraction stages, high volumes of IL and more energy which all translates to high processing costs.

Figures 22-27 also show the effect of diesel oil to IL mass ratio on the extraction efficiency. Generally a higher mass ratio will result in higher extraction efficiencies; however from a financial point of view smaller mass ratios are appropriate as an extractive desulfurization process employing higher mass ratios will require higher volumes of IL and even much higher volumes of solvents for the regeneration of the IL. Furthermore, it is shown from Figures 22-27 that multistage extraction is necessary for the reduction of oil sulfur content to allowable levels. Comparing the results presented in these figures mentioned above it can be seen that the reduction of sulfur to considerably negligible amount is more possible through the increase of the number of extraction stages than increasing the oil/IL mass ratio.

#### **5.2. Effect of reaction time on the desulfurization of diesel using IL**

Initially the amount of sulfur removed increased with an increase in the stirring time. In Figure 28, 30 minutes of stirring time was required to obtain a higher sulfur removal of 87.84%, however; the sulfur removal decreased to 44.74% when the stirring was extended to 1h30. Excessive lengthening of stirring time decreases the extractive ability of ILs. Based on the above a stirring time of 30 minutes was used in performing all other experiments in this study. In

general a short extraction time is desired for industrial application for low production costs and more importantly high production yields.

### **5.3. Efficiency of used/spent IL in extracting sulfur from diesel**

Due to the high cost of IL, it is necessary to be able to recover the solvent for reuse. The IL [BMIM][O<sub>2</sub>CSO<sub>4</sub>] can be reused (without being regenerated) up to three times without significant drop in efficiency in the extraction of sulfur from diesel as shown in Figure 29. Results in Figure 29 are consistent with results reported by Dharaskar *et al.* (2013) on the extraction of sulfur from model diesel oil, where it was found that ILs with the imidazolium cation can be reused three times without significant decrease in activity. For real diesel oil it was found that the IL was still able to remove sulfur on the 4<sup>th</sup> reusing cycle but at lower efficiency i.e. ~71% sulfur removed compared to 92% achieved when using fresh IL. The presence of S-compounds in the used IL decreases the efficiency and effectiveness of the IL for the desulfurization of diesel fuel.

### **5.4. IL regeneration and the efficiency of regenerated IL in desulfurization of diesel**

The preliminary choice of the solvents for the regeneration of ILs was based on the knowledge that ILs tend to be immiscible with non-polar organic solvents such as alkanes ( i.e. pentane and hexane) and other non-polar organic compounds such as ethyl acetate (Wassercheid and Welton, 2003). These solvents theoretically met one of the criteria (insolubility) used in solvent selection as stated in section 2.5.5. In terms of material purchase cost, pentane and ethyl acetate are less costly; however thermodynamic considerations as shown in Figures 31-36 and Tables 9-11, present hexane as the most suitable solvent. As previously stated in the experimental section, the LLE data of ternary systems (comprised of the selected solvents) will help determine the degree of solubility of the components through the evaluation of solute distribution ratios  $\beta$  and selectivities (S) for all the solvents. In this respect the solvent rank as follows: Hexane >> Pentane > Ethyl Acetate. large scale industrial application require high  $\beta$  values as they translate to low solvent requirements (consumption) for the re-extraction of sulfur compounds from the IL and high selectivity values which imply few number of equilibrium stages in the regeneration process (Rodriguez-Cabo, 2010). The low  $\beta$  values for Pentane and ethyl acetate indicate that

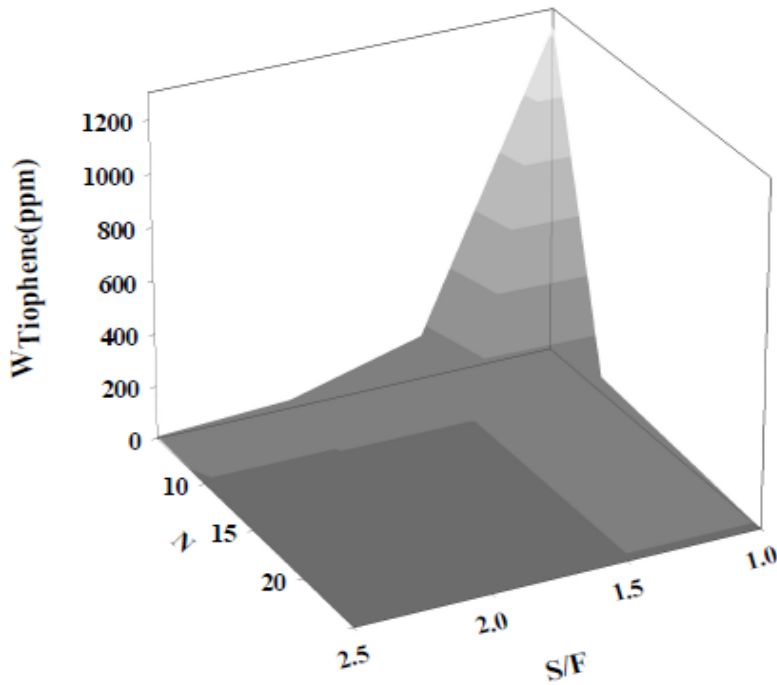
large quantities will be required. From the LLE data, hexane was found to be the most suitable solvent and was used in the regeneration of the IL.

Furthermore, from the solute distribution ratios ( $\beta$ ) values in Table 10 it can be seen that the S-compound thiophene distributes preferentially in hexane than in the IL, more so at low concentration (Figure 32). The phase diagram for this system (Figure 31) indicates that the re-extraction of thiophene from [BMIM][O<sub>2</sub>SO<sub>4</sub>] is possible with little cross-solubility of the IL in hexane. While the ternary system containing pentane (Figure 33) shows that the thiophene distribution in the pentane system is more in the IL phase at low Thiophene concentrations and nearly equal between the IL phase and pentane phase at higher thiophene concentrations.

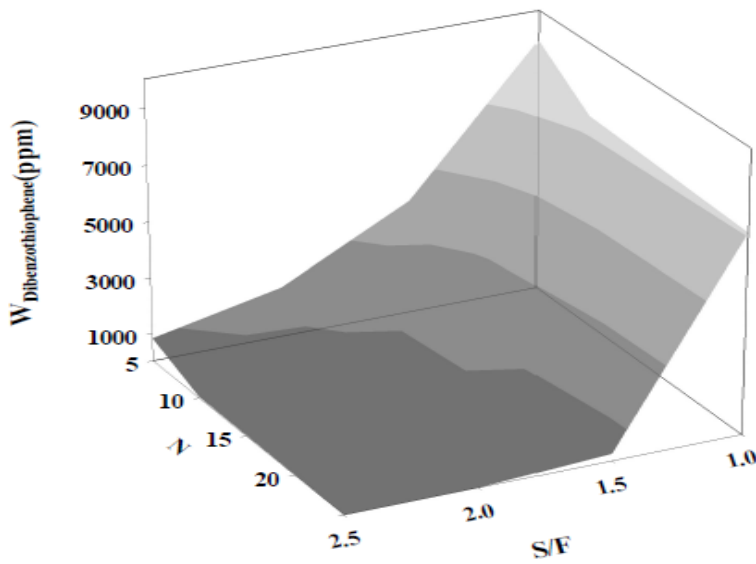
Another important parameter to consider is the co-extraction of the IL. The results for ethyl acetate and pentane indicate that some IL will be co-extracted with thiophene. Even with hexane it is likely that there may be some IL co-extraction (Table 9) which may give rise to IL loss in the regeneration process but at a much lower extent than when using ethyl acetate or pentane.

## 5.5. Simulation

Bösmann et al. (2001) and Casal (2010) did an extraction column simulation using Aspen Plus; to assess the possibility of achieving 10 ppm diesel sulfur content through extractive desulfurization with ionic liquids. The diesel feed was specified as per model diesel oil studied by Casal (2010) and Dharaskar (2012) in their respective papers. The feed (diesel) composition was as follows; 26% n-Heptane, 26% n-Dodecane, 26% n-Hexadecane, 10% Toluene, 3% Thiophene, 6% Pyridine and 3% Dibenzothiophene. The IL (solvent) mass flow and the extractive equilibrium stages (N) were varied to get an IL-to-diesel (solvent-to-feed, S/F) ratio. The simulation results are presented in Figure 40 and 41 below; concentration of the sulfur compounds; thiophene and dibenzothiophene, in the raffinate (diesel phase/stream) is plotted against the IL-to-diesel ratio and the number of equilibrium stages. It was found that for the more refractory S-compound close to 25 stages at a ratio of 2 will be required to achieve the required 10 ppm sulfur content in diesel.



**Figure 40** Mass fraction of thiophene in exit stream as a function of IL-to-Diesel ratio (S/F) and number of extraction stages (N) in the desulfurization of diesel using IL (Casal, 2010)



**Figure 41** Mass fraction of dibenzothiophene in the exit stream as a function of IL-to-Diesel ratio (S/F) and number of extraction stages (N) in the desulfurization of diesel using IL (Casal, 2010)

### 5.6. Preliminary Integration of Ionic Liquid based EDS into existing refinery network

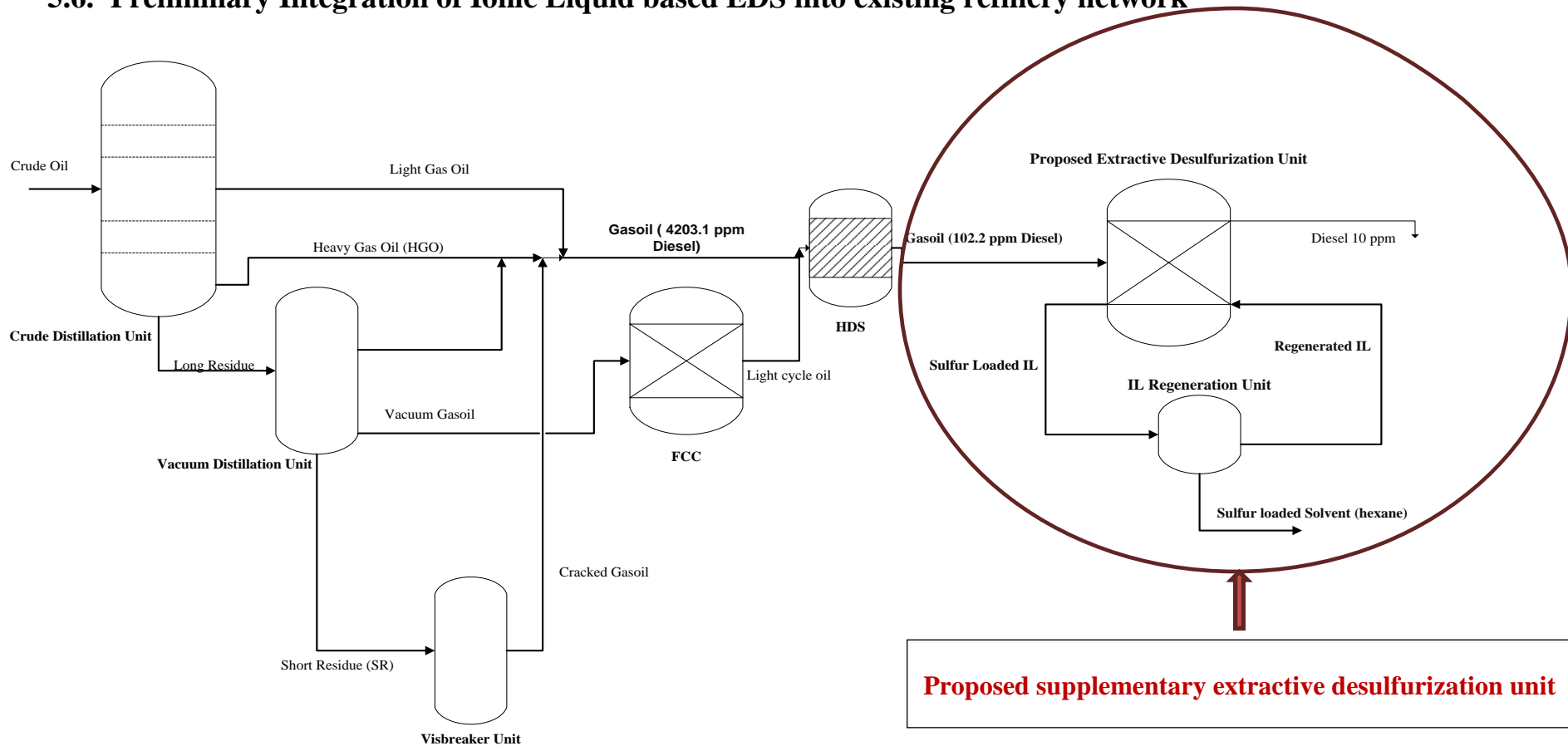


Figure 42 Integration of the extractive desulfurization unit into an existing South African refinery scheme

Based on the results in this work, a preliminary petroleum refinery configuration incorporating EDS (extractive desulfurization) into an existing refinery scheme is proposed by Figure 42 above where the EDS unit is placed after the conventional HDS unit.

In this conceptual configuration (Figure 42) gasoil from the conventional HDS is routed to a multistage EDS unit and treated with IL. Aspen simulations (using model diesel oil) done by Bösmann *et al.* (2001) and Casal (2010) independently revealed that 10 stages will be required at an IL to diesel mass ratio of 2 to treat the model diesel oil to thiophene level of 10 ppm and 25 stages to get the more refractory S-compound dibenzothiophene to 10 ppm. For real diesel oil as in this study more stages may be required due to the presence of even more refractory sulfur compounds. No operational challenges are anticipated with the incorporation of this unit into an existing refinery as it is positioned at a refinery exit stream (not an intermediate between existing units). The incorporation of EDS unit will introduce two new solvents into the refinery namely the IL and hexane. The main challenge with the use of solvents is their environmental impact. From the results obtained on the recoverability of the IL, the system can be set-up in a way that the IL is reused (without being regenerated) 3 times within the column before being routed to the regeneration unit. It was found that the IL can be regenerated up to 4 times before being discarded. Work by Dharaskar (2012) has shown that that in addition to the removal of sulfur ILs also remove the undesired nitrogen compound pyridine from diesel. An extra separation process will be required for the recovery of hexane (IL regeneration solvent) and sulfur. A challenge posed by the use of hexane is the loss of IL through co-extraction with S-compounds. This later point falls outside the scope of this dissertation.

## Chapter 6

### 6. Conclusion and Recommendations

#### 6.1. Conclusion

This work has assessed the extraction efficiency as well as the regeneration of the IL (1-butyl-3-methylimidazolium octylsulfate) in the desulfurization of the FCC entering and exiting samples collected from a typical South African refinery. The FCC (Fluid Catalytic Cracking) unit feed samples contained about 4000 ppm of S-compounds, while the exiting stream contained about 450 ppm. The IL was found to be effective in the selective removal of S from FCC diesel product than from the FCC feed stream. These results suggest that fuels sulfur content and stream composition affects the extraction efficiency and effectiveness of IL, and it may be preliminary advisable to have the desulfurization unit after the FCCU rather than before in a refinery network (as shown in Figure 42) where it may be cost effective to run in terms of energy and IL consumption. For industrial application low oil/IL mass ratios are recommended due to the high IL costs and multistage extraction is the more cost effective option to achieving low sulfur levels in diesel fuel.

The reusability (without and with regeneration) of [BMIM][OcSO<sub>4</sub>] was also evaluated and suitable solvents for the regeneration of the ionic liquid were identified i.e. hexane was found to be the most suitable solvent for the re-extraction of S-compounds from IL in terms of the solute distribution ratio. The results obtained herein show that ILs are effective in the desulfurization of real diesel oil samples collected from the refinery and extractive desulfurisation may be a viable supplementary technology to meet future needs for low sulfur diesel especially when the sulfur concentration is not very high in the treated samples.

## 6.2. Recommendations

To further explore the viability of the possible integration of the EDS unit in a refinery it is recommended that:

- More studies are done on the recoverability of ILs as well as their environmental impact to fully certify extractive desulfurization as an environmentally benign process. It was shown that the IL can be regenerated 4 times before noticeable drop in efficiency, so the need for discarding of the IL will occur at some point in the process.
- The degree of contamination of the regeneration solvent (hexane) by the IL be studied
- Study the possible separation methods for the sulfur loaded solvent, looking specifically at the prospects of integrating the separation within the refinery

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## Appendices

### Appendix A: Publications

Sefoka, R.E. and Mulopo, J. (2016), Assessment of the desulfurization of FCC Vacuum Gasoil and Light Cycle Oil Using Ionic Liquid 1-butyl-3-methylimidazolium octylsulfate. Submitted for review at International Journal of Industrial Chemistry.

### Appendix B: List of Symbols

#### Abbreviations

IL – Ionic Liquid

COSMO - Conductor-like Screen Model

COSMO-RS – Conductor-like Screen Model with an extension of Real Solvent

wco - weight on crude

wt - weight

#### Symbols

$\beta$  – solute distribution ratio

S – solvent selectivity

x – molar composition of component indicated by subscript

$n_i$  – number of times a group appears in the molecule

$T_b$  – normal boiling temperature

$T_c$  – critical temperature

$P_c$  – critical pressure

$V_c$  – critical volume

$\omega$  – acentric factor

$\Delta T_L$  – contribution to the critical temperature in the Lydersen method

$\Delta P_L$  - contribution to the critical pressure in the Lydersen method

$\Delta V_L$  – contribution to the critical volume in the Lydersen method

$M_w$  – molecular mass

$A_L, C_L$  and  $E_L$  – constants in the Lydersen method equations

$N$  – number of atoms in the molecule

$\Delta T_J$  – contribution to the critical temperature in the Joback and Reid method

$\Delta P_J$  - contribution to the critical pressure in the Joback and Reid method

$\Delta V_J$  – contribution to the critical volume in the Joback and Reid method

$A_J, B_J, C_J, D_J$  and  $E_J$  – constants in the Joback and Reid method equations

$\Delta T_M$  – contribution to the critical temperature

$\Delta P_M$  - contribution to the critical pressure

$\Delta V_M$  – contribution to the critical volume

$A_M, B_M, C_M, D_M$  and  $E_M$  – constants in the modified Lydersen-Joback-Reid method

$\rho_L$  - liquid density

$T_R$  – reduced temperature

$T_{bR}$  – reduced temperature at normal boiling point

## Appendix C: Ionic Liquids Acronyms and Names

Acronym	Name
[BMIM][O <sub>2</sub> CSO <sub>4</sub> ]	1-butyl-3-methylimidazolium octylsulfate
[C <sub>8</sub> MIM][BF <sub>4</sub> ]	1-octyl-3-methylimidazolium tetrafluoroborate
[EMIM][SCN]	1-ethyl-3-methylimidazolium thiocyanate
[TEMA][MeSO <sub>4</sub> ]	tris(2-hydroxyethyl)methylammonium methylsulfate
[DMIM][MP]	1,3-dimethylimidazolium methylphosphonat
[BMIM]Cl/AlCl <sub>3</sub>	1-butyl-3-methylimidazolium chloride
[EMIM]Cl/AlCl <sub>3</sub>	1-ethyl-3-methylimidazolium chloride



# Appendix D: H NMR and C NMR Spectroscopy Results

