EXTRACTION OF SULPHUR SPECIES USING DEEP EUTECTIC SOLVENT

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CHEMICAL ENGINEERING

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CERTIFICATION OF APPROVAL

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Approved by,

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(Dr Raihan Mahirah Binti Ramli)

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR, PERAK

September 2015

CERTIFICATION OF ORIGINALITY

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

AMIRUL AKMAL BIN MOHD SALLEH

ABSTRACT

The burning of fuel containing sulphur compound produce sulphur oxides (SO_2) and can be considered a major source of pollution. Therefore, many research has been conducted to reduce the sulphur content in the fuel to meet the regulation requirement. In this study, deep eutectic solvents (DES) are synthesized using choline chloride and glycerol. The prepared DES are characterized using density meter. Then, performance of the DES for deep desulphurization of model oil via liquid-liquid extraction are monitored. The performance DES indicated by the extraction efficiency by measure the concentration sulphur using gas chromatography. The extraction conducted by mixing n-dodecane containing sulphur as model oil and synthesized DES. The experiment conducted at room temperature, the mixture stirred at 400rpm for 3hrs. Lastly, the extraction efficiency of recycle DES without regeneration monitored. The parameters interested in the experiment are effect of initial concentration of model oil, volume ratio between model oil and DES and the molar ratio between glycerol and choline chloride. The density value for DES with molar ratio choline chloride: glycerol of 1:1, 1:2, 1:3 and 1:4 are 1.1545, 1.1980, 1.2050 and 1.2100 g/cm^3 respectively. The extraction efficiency decrease as the initial concentration increase. The highest extraction efficiency for DBT and BT are 78.68 and 75.33% at 50ppm. DBT has higher selectivity than BT therefore, DBT more easily to extract than BT. Extraction efficiency decrease as the volume model oil increases at fixed model oil volume. The extraction efficiency for DES: model oil volume ratio 1:5, 1:10, and 1:20 are 63.7%, 62.92% and 60.9% respectively. Then, extraction efficiency DES decreases after being recycle for two times. The extraction efficiency for no of cycle 1 and 2 are 60.4576 rand 55.9654 % respectively.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Diesel engines convert the chemical energy contained in the fuel into mechanical power. Diesel fuel is injected under pressure into the engine cylinder where it mixes with air and combustion occurs. The exhaust gases which are discharged from the engine contain several constituents that are harmful to human health and to the environment.

Diesel is widely used in highway transportation vehicles such as cars buses, trucks and lorry. Apart from that, non-highway transportation system also use diesel as fuel sources likes locomotives, marine vessel and plantation equipment. The reason is the diesel engines are 25-40% more fuel efficient than gasoline engines

Sulphur is one of the natural content in crude oil. Vitllasenor et al (2004) stated that the sulphur discharge result of fuel combustion can be considered a major source of pollution. The sulphur content for sweet crude oil is less tha 0.5% while for sour crude oil is higher than 0.5%. The sulphur compound in diesel fuels have higher molecular weight and larger ring sizes compared to the gasoline due to the differences in the boiling point. Most sulphur compounds in the diesel are alkalinated benzothiophene type and dibenzothiophene types such as 4, 6 – dimethylbenzothiophene and dibenzothiophene.

1.2 Problem Statement

The sulphur content in the diesel can lead to the air pollution. The burning of fuel containing sulphur compound produce sulphur oxides (SO_2). SO_2 is a colourless toxic gas, irritating with odour. SO_2 can be oxidised to produce sulphur trioxide (SO_3) which is the precursor of sulphuric acid, can cause acid rain to occur. Acid deposition result from the acid rain causes negative effect to soils, trees, animals, water human health and building. Concentration of the SO_2 in the exhaust gas is closely related to the sulphur content in the fuel. The higher the concentration sulphur species in the diesel fuel the higher the concentration SO_2 emitted to the air.

1.3 Objectives

The objectives of the study are:

1. To synthesize and characterise choline chloride-glycerol deep eutectic solvents (DES).

2. To investigate the performance of the DES for deep desulphurisation of model diesel via liquid-liquid extraction.

3. To recycle and regenerate the Deep Eutectic Solvents

1.4 Scope of Study

The first scope covers in the projects is synthesis of deep eutectic solvent using glycerol and choline chloride. Then, characterise of deep eutectic solvent using density meter is used for the study.

The study involves monitoring the performance of deep eutectic solvents in deep desulphurisation of model diesel via liquid-liquid extraction of model oil containing dibenzothiophene and benzothiophene as sulphur species in n-dodecane. The concentration of residual sulphur species will be measured using gas chromatography. Lastly, recycling and regenerate study of the deep eutectic solvents is conducted to minimise the waste produce in the process.

1.5 Relevancy of the Study

As the pollution becomes one of the major considerations by the human being in worldwide, the emission sulphur dioxide must be reduced. The amount of sulphur in the diesel must be reduced to minimise the impact to environment. For instance, European Nation has implemented new standards in 2009 for the sulphur content in the diesel Euro V which allow 10ppm of the sulphur content in the diesel. Many industrial companies especially in oil and gas start to find economical and more environmental friendly to remove the sulphur in their products to meet the stringent requirement.

Apart from that, the application deep eutectic solvents as desulphurisation solvents has been rarely reported and it is new process. Therefore, it can be alternative methods to replace conventional methods to remove sulphur from the diesel.

CHAPTER 2

LITERATURE REVIEW

Many countries introduced environmental regulations to reduce the sulphur content of diesel fuel to ultra-low levels in the range of 10–15 ppm. (Stanislaus et al. 2010) The purpose is to reduce harmful exhaust emissions from diesel engine and improve air quality. Breysse et al., (2003) stated that the new environmental regulations are beneficial for the environment, however to meet sulphur limit levels in diesel and other transportation fuels to a very low specifications give major operational and economic challenge for the petroleum refining industry.

According to Li et al. (2015) conventional methods which effectively remove sulphides, disulphides and light thiophenic sulphur compound is catalytic hydrodesulphurisation. The process required high pressure, high temperature and great amount of hydrogen consumption. Meanwhile, Wang et al. (2011) claim that hydrodesulphurisation is inefficient for refractory sulphur containing compounds likes 4, 6 Dimethyl Dibenzothiophene (4,6-DMDBT) and dibenzothiophene (DBT).

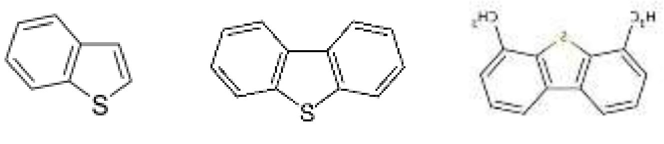

Figure 2.1 Molecular structure Bnzothiophene, Dibenzothiophene and 4, 6 Dimethyl Dibenzothiophene.

Li et al. (2015) proposed that, alternatives methods such as biodesulfurization, selective adsorption, extraction by ionic liquids and oxidative desulfurization to achieve deep desulphurisation.

Li et al. (2009) stated many organic solvents like dimethyl sulfoxide, acetonitrile and 1-methyl-2-pyrrolidinone have been used as extractive solvents in deep desulphurisation. However, the main concerns are that they are highly flammable and volatile which can lead to fire hazards and air pollution.

2.1 Ionic Liquid

Rodriguez- Cabo et al. (2014) reported that besides conventional organic solvents, ionic liquid has also been used to extract sulphur in diesel and gasoline. Ionic liquid are salts which entirely composed of ions with low melting temperature normally less than 100^0 C. Many ionic liquids are thermally and chemically stable. They also exist in liquid states over wide range of temperature. They have negligible vapour pressure under normal condition. Therefore, it can be recovered easily to avoid losses to atmosphere with pollution effect.

Despite of the advantages, ionic liquids also have their own drawbacks as stated by Mohd Zaid et al., (2015). Ionic liquids are quite difficult to synthesize and extremely expensive. The main requirements for the new solvents are low in cost, high solute solubility, environmental compatibility and easily synthesize.

2.2 Deep Eutectic Solvents

Zhang et al (2012) stated the new type of ionic liquid is known as Deep Eutectic Solvents (DES). DES generally composed of two or three component that is capable of self-association normally through hydrogen bond interaction to form eutectic mixture, Mjalli et al. (2014).

The first discovery of eutectic solvent through a mixture of urea and choline chloride with molar ratio 2:1 and melting point $133^{o}C$ and $302^{o}C$, respectively (Abo-Hamad et al., 2015). The mixture melts at $12^{o}C$.

Deep Eutectic Solvents are considered as environmental friendly solvents and the advantages over conventional ionic liquids solvents includes non-toxicity, non-reactivity with water and biodegradable (Shahbaz et al., 2015). The two component of DES are environmental friendly and abundant in nature such as choline chloride. Choline chloride well known as B4 vitamin. Therefore, DES considered as environmental friendly.

Apart from that, DES can be synthesized easily in high purity at low cost in contrast to ionic liquids which are very expensive and difficult to handle. A DES can be synthesized easily by thermal mixing of an ammonium salt such as choline chloride with hydrogen-bond donor such as urea and glycerol at specified stoichiometric ratio.

Shahbaz et al. (2012) claim that the synthesized DES gave lower freezing point to their constituting component. The melting point of the Deep Eutectic Solvents tabulated in the Table 2.1.

Table 2.1 Melting Point of Deep Eutectic Solvents

First Component	First Component Melting Point (°C)	Second Component	Second Component Melting Point (°C)	DES molar ratio 1st:2nd	DES freezing point (°C)	Reference
Choline Chloride	302-305	Glycerol	20	1:2	25	(Shahbaz, Mjalli, et al., 2012)
Choline Chloride	302-305	Glycerol	20	1:3	20	(Shahbaz, Mjalli, et al., 2012)
Choline Chloride	302-305	Glycerol	20	1:4	20	(Shahbaz, Mjalli, et al., 2012)
Choline Chloride	302-305	Thiourea	170-176	1:2	69	(Shahbaz, Mjalli, et al., 2012)

2.3 Application Deep Eutectic Solvent

Hayyan et al. (2012) stated that the physical properties of d-fructose based DES indicated that this type of fluids has a practical potential use in many industrial application involving reactions, pharmaceutical applications and as solvent in extraction process for instances separation of fructose from monosaccharide mixtures.

DES was also introduced in many industrial application as alternatives to ionic liquid such as the synthesis of zeolite analog (Copper et al., 2004), removal of excess glycerol from biodesel fuels (Hayyan et al., 2010), solvent extraction of aromatics from naphtha (Kareem et al., 2012) and synthesis nano-particles (Liao et al..2008).

Oliveira et al. (2013) proposed that one of the current ways to overcome separation of azeotropic mixture is to use other types of processes, such as liquid–liquid extraction. Liquid–liquid extraction processes have been emerging as appealing alternatives because they do not require high amounts of energy, volatile organic compounds or high pressures.

In a research, DES are tested as extraction solvents in the liquid–liquid separation of azeotropic mixtures (Oliveira et al., 2013). Three different DES, all based on choline chloride, were used for the liquid–liquid separation of an azeotropic mixture of heptane + ethanol at 25°C. The obtained data show that DES surpass the performance of existing extraction solvents, leading to an increase in efficiency and a reduction in energy consumption of the overall process.

Although DES has been successfully applied in many application, the studies related to the usage of DES as solvent in desulphurization has been hardly reported. In a research stated that DES can be successfully used as desulphurisation fuels solvents. Tetrabutyl ammonium chloride-based DES give the highest extraction efficiency in the best conditions. The extraction efficiency of tetrabutyl ammonium chloride as hydrogen bond acceptor and polyethylene glycol s hydrogen bond donor can reach 82.83%. The extraction efficiency DES is higher than ionic liquid (Li et al., 2013).

Extractive desulphurisation using model oil containing dibenzothiopehene and thiophene was conducted using $FeCl_3$-based deep eutectic solvents. DES effectively remove sulphur from the fuels. Extraction efficiencies are 64% and 44% for dibenzothiophene and thiophene respectively. Apart from that, DES was also tested with commercial diesel and the sulphur contents lowered. Overall extraction using commercial diesel fuel is 32% (Gano et al., 2015).

2.4 Choline chloride-glycerol deep eutectic solvents

Choline chloride is an organic compound and a quaternary ammonium salt.Choline chloride made up from choline cation and chloride as anion. The other name is 2-hydroethyl-trimethyl ammonium hydroxide. Choline chloride mass produce and use as chicken feed additives. Apart from that, choline chloride is non toxic biodegradable. Glycerol is colourless, odourless, viscous liquid. Glycerol is widely use in pharmaceutical formulations. Glycerol contain three hydroxyl group. It is non toxic. Mixing glycerol and choline chloride thermally produce deep eutectic solvents.

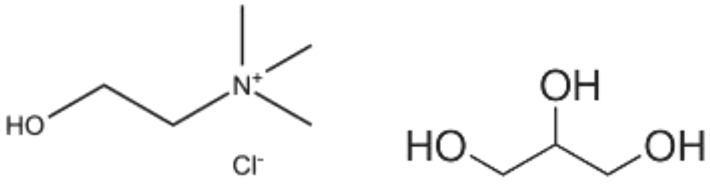

Figure 2.2 Molecular structure choline chloride and glycerol

2.5 Liquid-liquid Extraction

(Shakirullah et al., 2010) defined that liquid-liquid extraction is extensively used in the purification of organic compounds, and the same is very helpful in removing the unwanted sulphur compounds from the petroleum hydrocarbons.

Liquid-liquid extraction is transferring solute in feed solution to solvent. The mechanism for liquid-liquid extraction is feed contains a component (solute) which is to be removed. Then, solvent is added into the feed. Solvent is immiscible with feed and solute is soluble in both phase feed and solvents. Solute is transfer from the feed to solvent. Solute distributes itself between the feed and solvents so that the ratio of concentration solute in feed to the concentration solute in the solvent remains constant at constant temperature. After extraction process feed and solvents are called raffinate and extract respectively. The mechanism of liquid-liquid extraction illustrated in Figure 2.3.

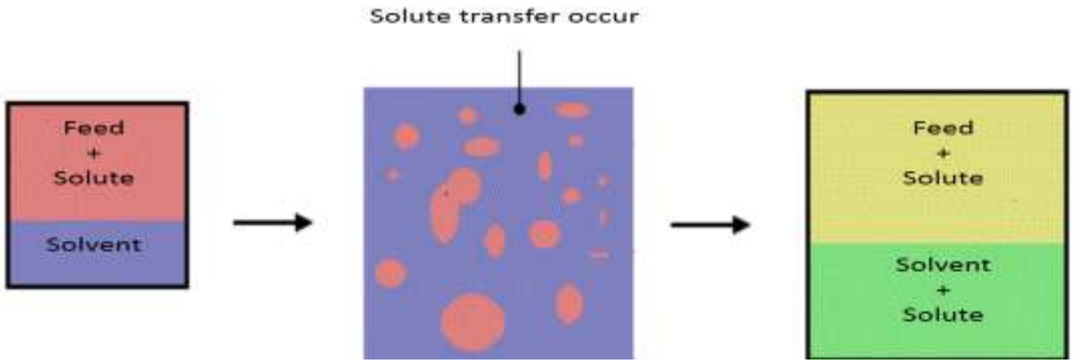

Figure 2.3 Mechanism of Liquid-Liquid extraction

It is assumed that the molecular state of the substance is same as in both solvents. If C_A is the concentration in the layer A and C_B is the concentration in the layer B, then at constant temperature:

$$C_A/C_B = \text{Constant} = k \quad (1)$$

The constant k is termed as the distribution or partition coefficient. As very rough approximation the distribution coefficient may be measured equal to the ratio of the solubility in the two solvents. Organic sulphur compounds are mostly soluble in the polar solvents; besides the solvents having affinity for the sulphur compounds can be more helpful in their extraction.

Liquid-liquid extraction is one of method can be apply in the deep desulphurisation process. (Gabri et al., 2013) The major advantage of extraction is its operating conditions which are low temperatures and pressures at ambient conditions and consequently conservation of significant amount of energy.

The process involves mass-separating agent, special care must be taken when selecting a proper solvent. However, liquid-liquid extraction generates organic waste which requires disposal.

In order to minimize that waste, the solvent should be recyclable, reusable, and re-generable solvents commonly used in industry are volatile organic compounds that exhibit high-vapour pressure. Additionally, volatile organic solvents are flammable and are of varying toxicity, depending on their nature, so the major task of many researchers is to find a way of replacing VOCs with environmentally friendly, so-called green solvents. This is not a simple problem, because one cannot simply replace one solvent with another. One possible solution is replacement of organic solvents with deep eutectic solvents. Deep eutectic solvents are very good solvents for a wide range of organic, inorganic, and polymeric compounds. Owing to their negligible vapour pressure, deep eutectic solvents are considered as green solvents. But even if deep eutectic solvents are not responsible for air pollution, their impact on complete ecosystem is still unexplored.

2.6 Desulphurisation via liquid-liquid extraction

Many studies has been conducted by the researches all ove the world to study the effectiveness of liquid-liquid extraction to remove sulphur from fuel. Swapnil et al. (2013) $FeCl_3$-based ionic liquid can be use as extrant to remove dibenzothiophene from liquid fuel. [Bmim]Cl/$FeCl_3$ show the best ability for desulphurisation process. The removal of dibenzothiophene from liquid fuel was 75.6% with single stage extraction. The condition are 30minutes and 30^oC. [Bmim]Cl/$FeCl_3$ can be used without regeneration and the extraction efficiency is 47.3%. Therefore, huge energy can be save because ionic liquid does not required to regenerate for every extraction.

In a study, 1-butyl-3-methylimidazolium thiocyanate [C_4mim][SCN] has shown highest extraction efficiency of 66.1%. The extraction is conducted to investigate the extraction efficiency of dibenzothiophene from dodecane. [C_4mim][SCN] can be reused without regeneration with extraction efficiency of 41.9%. Apart from that, the optimum extraction duration is 30mins before liquid-liquid equilibrium between dodecane and model oil containing dibenzothiophene achieved (Wilfred et al., 2012).

Apart from that, Dharaskar et al. (2013) stated that,1-butyl-3-methylimidazolium chloride ([Bmim]Cl) show 77.15% sulphur removal from model oil. The extraction conditions are temperature at 30^oC and duration of 90mins. Dodecane is use as model oil and dibenzothiophene is used as sulphur species. Extraction efficiency of

[Bmim]Cl after has been re-used three times and without regeneration decrease to 44.31%.

Sulphur removal by $[Et_3NH]Cl-FeCl_3$-Cucl from model oil containing thiophene could reach 96.56% at 50^oC for 50mins. After, 5 time has be re-used without regeneration $[Et_3NH]Cl-FeCl_3$-Cucl still can reach 95.02% extraction efficiency. (Haojie et al., 2014).

Table 2.2 Summary of Desulphurisation via liquid-liquid extraction previous study

Model Fuel	Solvents	Percentages Removal (%)	References
Dibenzothiophene + liquid fuel	$[Bmim]Cl/FeCl_3$	75.6	(Swapnil et al., 2013)
Dibenzothiophene + dodecane	$[C_4mim][SCN]$	66.1%	(Wilfred et al., 2012).
Dibenzothiophene + dodecane	[Bmim]Cl	77.15	(Dharaskar et al., 2013)
Thiophene+liquid fuel	$[Et_3NH]Cl-FeCl_3$-Cucl	96.56	(Haojie et al., 2014).

CHAPTER 3

METHODOLOGY

3.1 Project Process Flow

The process flow for the project is divided into five parts. The first part started with synthesis of choline chloride-glycerol deep eutectic solvent. Then, the resultant solvents was characterised. Next, experiment was conducted to monitor the performance of deep eutectic solvents in deep desulphurisation via liquid-liquid extraction. Lastly, recycle and regenerate the deep eutectic solvent. The Schematic overview process flow can refer to Figure 3.1 in the Appendices section.

3.2 Gantt Chart and Key Milestones

The Gantt Charts is for period of 28 weeks. The Gantts Charts show the starts and the finish date elements in the project. Gantts Charts starts with selection of project topic on the first week and finish with the submission of project dissertation on week 28.

Key milestones for the project are highlighted in the Gantts Charts. There seven milestone in the project which are submission of extended proposal, proposal defence, submission of interim final report, submission of progress report, submission of dissertation and technical paper, viva and finally submission of project dissertation on week 28. Please refer Figure 3.2 in the appendices section for more detail on Gantts Charts and milestones.

3.3 Chemicals

n-dodecane was purchased from Merck, DBT (≥98%) and BT (≥97) were purchased from Acros. Glycerol and choline-chloride (≥97) was bought from Sigma–Aldrich. All the chemicals were used without further purification.

Table 3.1 List of Chemical and properties

Chemicals	Molecular weight (g.mol^{-1})	Melting point (°C)	Boiling point (°C)	Density (g/cm^{3})
n-dodecane	170.34	-10	214-218	0.750
Dibenzothiophene	184.26	97-100	332	1.252
Benzothiophene	134.2	32	221	1.15
Glycerol	92.09	17.8	290	1.261
Choline Chloride	139.62	302		1.1

3.4 Deep Eutectic Solvents Synthesis

(Hayyan et al., 2012) and (Mjalli et al., 2014) suggested the prior to use the chemicals were dried in a vacuum oven to eliminate the moisture.

Deep Eutectic Solvents can be prepared by mixing of choline chloride and glycerol in a molar ratio of 1:1, 1:2, 1:3 and 1:4. 100mL of glycerol was measured and added into the beaker. Then, choline chloride was weighed using electronic weighing balance and added into the beaker. The amount of choline chloride added for each molar ratio are tabulated in Table 3.2. Next, the mixture stirred at 400rpm and heated at 80°C for 2 hours. The calculation for the mass choline chloride needed can be refer in Appendix C.

Table 3.2 Mass of choline chloride and volume glycerol for different molar ratio

Molar Ratio Choline Chloride : Glycerol	Volume Glycerol (mL)	Mass Choline Chloride (g)
1:1	100	197.0801
1:2	100	98.5536
1:3	100	65.6988
1:4	100	49.2736

3.5 Deep Eutectic Solvents Characterisation

DES was characterized using DMA500M Anton Paar Density Meter. Density measurement is carried out at 298.15 K. The density of water (degassed bi-distillated) was measured at 298.15 K to check the density meter adjustment.

3.6 Model Oil Preparation

The model oil was prepared with different concentration of sulphur species which are 50, 100, 200, 300 and 400 part per million. The sulphur species used in the experiment are benzothiophene and dibenzothiophene. The model oil prepared by dissolving solid dibenzothiophene (DBT) and benzothiophene in deodecane. The amount of dibenzothiophene and benzothiophene needed to prepare 100mL of model oil containing different concentration sulphur species tabulated in the Table 3.3 and Table 3.4 respectively. The detail calculation for the amount dibenzothiophene and benzothiophene can be refer to Appendix D and Appendix E respectively.

Table 3.3 Mass Of Dibenzothiophene needed for each Sulphur Concentration

Concentration of sulphur (ppm)	Mass of Dibenzothiophene (mg)
50	29.367
100	58.755
200	117.510
300	176.255
400	235.010

Table 3.4 Mass Of Benzothiophene needed for each Sulphur Concentration

Concentration of sulphur (ppm)	Mass of Benzothiophene (mg)
50	21.616
100	43.235
200	86.469
300	129.703
400	172.938

3.7 Liquid-Liquid Extraction of sulphur species

3.7.1.1 Selectivity of Sulphur Species on Extraction

The concentration of sulphur species in the model oil are 300ppm. The DES and model oil are mixed at 1:5 volume ratio are mixed and stirred at 400 rpm. Sample from n-dodecane (model oil) layer were taken out and analysed for sulphur content. The sample are taken every 30 min for 3 hours. The samples analysed using gas chromatography.

Shimadzu GC-2010 gas chromatography (SGE BP1 capillary column, 30 m × 0.25 mm, 0.25 μm film thickness) with flame ionization detector was used to determine the concentration of DBT remained in the dodecane layer before and after desulfurization. The carrier gas was nitrogen, with a column flow rate of 1.39 $\mathrm{ml \cdot min^{-1}}$. The injector temperature was held at 593.15 K, and temperature in detectors was fixed at 603.15 K. The injection volume was 1 μl with a split ratio of 1:50. The oven temperature was from 323.15 K to 373.15 K with a ramp of 5 $\mathrm{K \cdot min^{-1}}$, to 593.15 K at 20 $\mathrm{K \cdot min^{-1}}$.

3.7.1.1.1 Effect of Model Oil Concentration on DBT and BT extraction

DES and model oil of with different initial concentration mixed at 1:5 volume ratios. The initial concentrations of model oil prepared are 50, 100, 200 and 300 ppm of sulphur. The amount of DBT and BT can be refer to Table 3 and Table 4 respectively. The mixture stirred at 400 rpm. Sample from n-dodecane (model oil) layer were taken out and analysed for sulphur content. The sample was taken every 30 min for 3 hours. The samples were analysed using gas chromatography.

3.7.1.2 Effect of DES: Model Oil Volume Ratio on DBT extraction

DES and n-dodecane with 300ppm of DBT was mixed at 1:5, 1:10 and 1:20 volume ratio. The volume of DES fixed at 4mL for each volume ratio.The mixture was stirred at 400 rpm. Samples from n-dodecane layer were taken out and analysed for sulphur content. The experiment conducted for 3 hours and the sample taken every 30 minutes. The sample analysed using gas chromatography.

3.7.1.3 Effect of Choline Chloride: Glycerol Molar Ratio on DBT extraction

Choline chloride and Glycerol with molar ratio of 1:1, 1:2, 1:3 and 1:4 prepared. Please refer Section 3.4.1. The DES and n-dodecane with 300ppm DBT mixed at 1:5 volume ratio. The mixture was stirred at 400 rpm. Samples from n-dodecane layer were taken out and analysed for sulphur content. The experiment conducted for 3 hours and the sample taken every 30 minutes. The sample analyse using gas chromatography.

3.8 Deep Eutectic Solvent Performance

The performance of the DES can be monitored by calculating the desulphurisation efficiency of sulphur species DBT or BT in the model oil. The desulphurisation DBT and BT can be calculate by the equation (2) and (3) respectively

$$\text{Desulphurisation efficiency of DBT (\%)} = \frac{[\mathrm{DBT}]_\mathrm{i} - [\mathrm{DBT}]_\mathrm{f}}{[\mathrm{DBT}]_\mathrm{i}} \times 100\% \qquad (2)$$

Where $[\mathrm{DBT}]_\mathrm{i}$ is the initial concentration of Dibenzothiophene while $[\mathrm{DBT}]_\mathrm{f}$ is the final concentration of Dibenzotiophene.

$$\text{Desulphurisation efficiency of BT (\%)} = \frac{[\mathrm{BT}]_\mathrm{i} - [\mathrm{BT}]_\mathrm{f}}{[\mathrm{BT}]_\mathrm{i}} \times 100\% \qquad (3)$$

Where $[\mathrm{BT}]_\mathrm{i}$ is the initial concentration of Benzothiophene while $[\mathrm{BT}]_\mathrm{f}$ is the final concentration of Benzotiophene.

3.9 Recycling and Regenerate

Deep Eutectic Solvent and dodecane were mixed at 1:5 volume ratio. The mixture was stirred at 400rpm for 3 hours at room temperature. After 3hrs, the mixture was left to settle for 10 min. Then, dodecane was sampled out from the mixture for analysis. The separated DES layer was reused for two times using the same parameters. Gas Chromatography was used to determine the concentration of DBT remained in the n-dodecane layer before and after desulfurization.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterisation DES

The density of DES will be increase as the glycerol molar fraction of glycerol increases. In the study by Shahbaz et al. (2011) also showed the same trend for the density of DES. Based on data obtained from DMA500M Anton Paar Density Meter, the density value for DES with molar ratio choline chloride: glycerol of 1:1, 1:2, 1:3 and 1:4 are 1.1545, 1.1980, 1.2050 and 1.2100 g/cm^3 respectively.

4.2 Effect of extraction time on BT extraction

The experiment was conducted to determine the effect of time on BT extraction from model oil containing benzothiophene as sulphur species. The study is conducted at room temperature. . The DES molar ratio choline chloride and glycerol is 1:2 and volume ratio DES: model oil is 1:5. The extraction duration is 3hr and sample taken every 30min.

Based on Figure 4.1, the extraction happened very quickly. It can be observed the efficiency extraction increase very drastically for the first 30 mins. The extraction equilibrium achieve in 30 min. After the equilibrium achieve, the extraction efficiency only slightly changed.

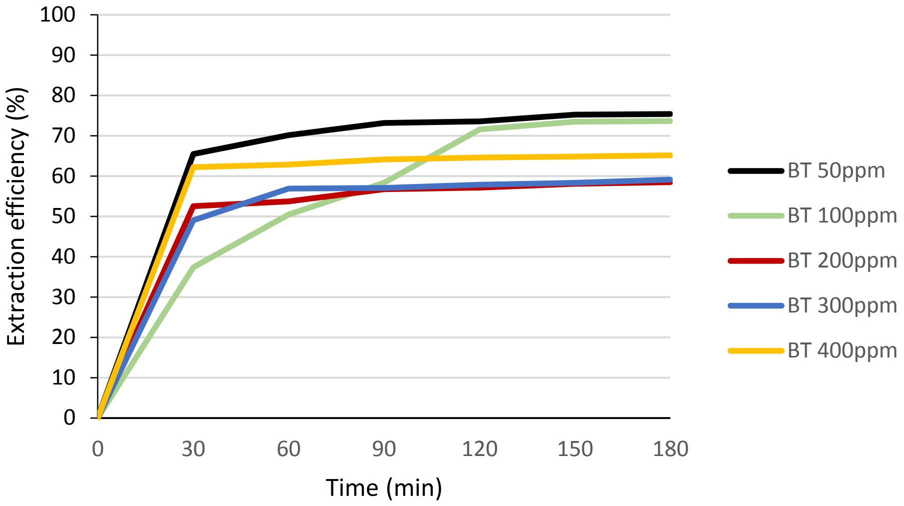

Figure 4.1 Effect of extraction time on BT extraction efficiency [Room temperature, DES molar ratio choline chloride and glycerol is 1:2, stirring speed at 400rpm and volume ratio DES: model oil is 1:5]

4.3 Effect of extraction time on DBT extraction

The effect of extraction time on DBT extraction was studied. In the experiment, the parameter fixed are DES molar ratio choline chloride and glycerol is 1:2, volume ratio DES: model oil is 1:5, extraction time 3hr and at room temperature.

Based on Figure 4.2, the equilibrium is achieved at 30mins. After the equilibrium between model oil and DES achieved the extraction efficiency do not show significant change. Wilfred et al. (2012) also stated that the optimum extraction time for the desulphurisation efficiency are 30mins. After 30mins, the extraction efficiency does not make significant increase.

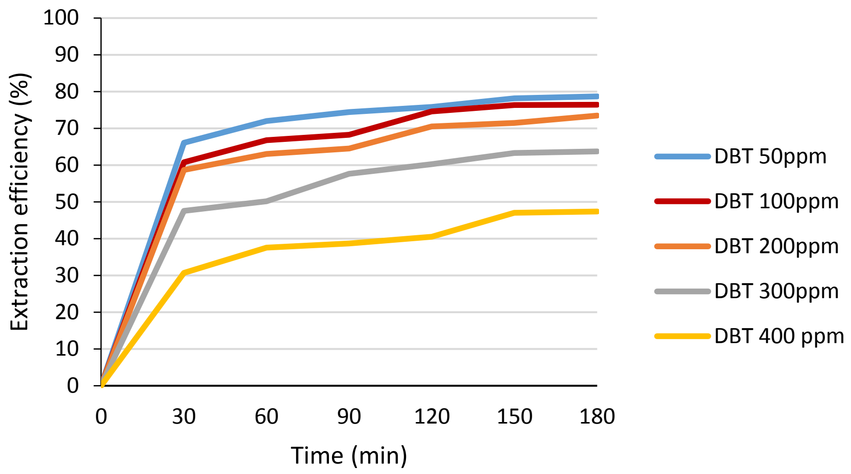

Figure 4.2 Effect of extraction time on DBT extraction efficiency [Room temperature, DES molar ratio choline chloride and glycerol is 1:2, stirring speed at 400rpm and volume ratio DES: model oil is 1:5]

4.4 Selectivity of Sulphur Species on Extraction

Apart from that, the selectivity of sulphur species is conducted. The experiment is to determine which sulphur species has higher reaction rate. The parameter fixed for the experiment were 300ppm of suphur, DES molar ratio choline chloride and glycerol was 1:2, volume ratio DES: model oil was 1:5, extraction time 3hr and at room temperature. The extraction is conducted for 3hrs and sample taken every 30mins.

Based on Figure 4.3, the extraction efficiency DBT and BT almost the same for the first 30mins which are 47.53 and 49.03% respectively. At time 60mins the extraction efficiency BT is higher than DBT. The extraction efficiency BT and DBT are 59.11% and 50.20% respectively. At 90mins of extraction, the extraction efficiency BT and DBT are the same at 57%. During the duration 90mins to 180mins the extraction efficiency DBT is higher than BT. The overall efficiency for DBT and BT are 63.7% and 59.4% respectively. It show that, DBT has higher selectivity for extraction compare to BT. In a study, the removal of DBT is higher than BT for single stages extraction (Dharaskar et al., 2013)

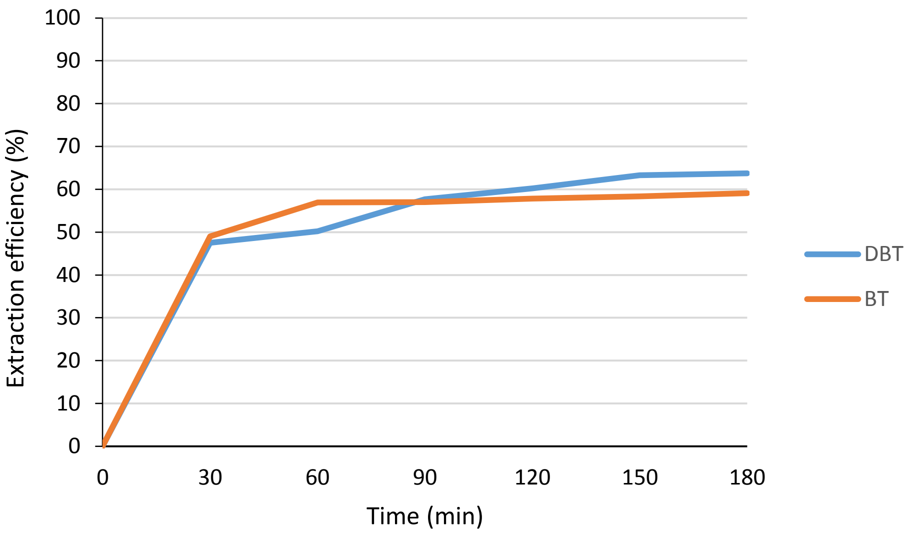

Figure 4.3 Selectivity of sulphur species on extraction [300ppm sulphur, room temperature, DES molar ratio choline chloride, stirring speed at 400rpm and glycerol is 1:2 and volume ratio DES: model oil is 1:5]

4.5 Effect of Model Oil Concentration on DBT and BT extraction

The effect of model oil concentration on DBT and BT extraction were studied. It is to determine the efficiency of the DES to extract sulphur from the model oil as the sulphur content in model oil increase. The constant parameter for this experiment are conducted at room temperature, the ratio DES molar ratio choline chloride: glycerol 1:2 and volume ratio DES: model oil 1:5.

Based on Figure 4.4, the as the initial concentration of sulphur either DBT or BT in the model oil, the extraction efficiency reduce. The ability of DES to extract sulphur species decrease at higher concentration. The highest efficiency observed at 50ppm either DBT or BT. The highest extraction efficiency for DBT and BT are 78.68% and 75.33% respectively. While the lowest extraction efficiency at 300ppm. The extraction efficiency for DBT and BT are 63.70% and 59.12% respectively. As the model oil concentration increase the amount of sulphur extracted from model oil into DES increase, the empty space in between the DES molecule become more concentrated therefore the extraction efficiency decrease.

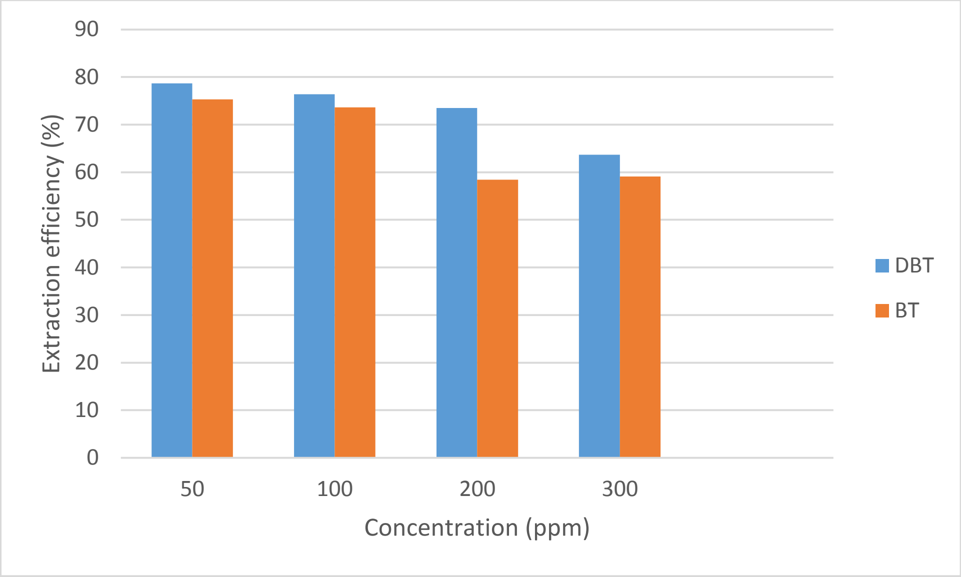

Figure 4.4 Effect of Model Oil Concentration on DBT and BT extraction [Room temperature, DES molar ratio choline chloride and glycerol is 1:2, stirring speed at 400rpm, extraction duration 3hrs and volume ratio DES: model oil is 1:5]

4.6 Effect of DES: Model Oil Volume Ratio on DBT extraction

The effect of DES model oil volume ratio on DBT was investigated. In this experiment, the parameter fixed are the concentration DBT in model oil 300ppm, DES molar ratio choline chloride: glycerol was 1:2 and at room temperature. The amount of DES use is 4mL. The sample for analysis taken every 30mins for 3hrs.

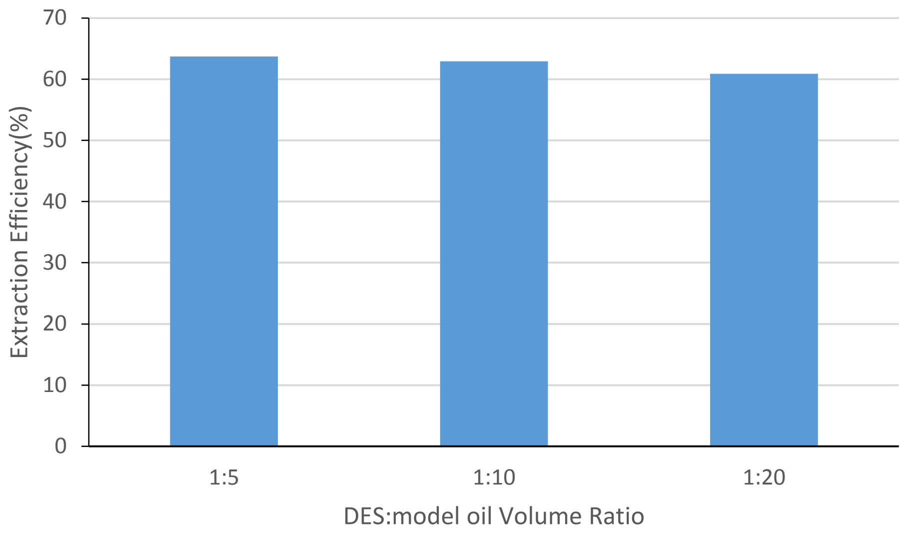

Figure 4.5 Effect of DES: model oil volume ratio [Room temperature, DES molar ratio choline chloride and glycerol is 1:2, stirring speed at 400rpm, extraction duration 3hrs and DBT as sulphur concentration at 300ppm]

Based on the Figure 4.5, the extraction efficiency of sulphur was decreasing as the volume model oil increase. The extraction efficiency for the DES: model oil ratio 1:5, 1:10 and 1:20 are 63.7, 62.92 and 60.9 respectively.

To apply desulphurisation extraction using DES in industry, the dosage is very important. The optimum volume ratio between DES and model oil are determine. Based on previous study conducted by Haoijie et al. (2014), sulphur extraction efficiency increase as the ratio DES/model oil increase. For the experiment DES volume fixed at 4mL for every experiment and the volume of model oil varied. Therefore, the DES/model oil ratio increases as volume of model oil decrease. DBT had more contact opportunities with DES at higher DES/model oil ratio or at lower volume of the model oil.

4.7 Effect of Choline Chloride: Glycerol Ratio on DBT extraction

The influence of DES molar ratio choline chloride: glycerol also studied. The parameter kept constant for this study are the concentration of DBT in model oil

300ppm, volume ratio DES: model oil was 1:5 and at room temperature. The sample for analysis was taken every 30mins for 3hrs.

Based on the Figure 4.6, as the choline chloride: glycerol molar ratio increase the extraction efficiency shows the decreasing pattern. The DES with higher density, will have lower specific volume as specific volume define as:

$$\text{specific volume} = \frac{1}{\text{density}} \qquad (4)$$

DES with lower specific volume has less free space between ions to be filled by DBT molecules. The lower the molecules DBT can fill between the free space of the DES the lower the extraction efficiency. Wilfred et al., (2012) in the study stated the reason is lower density DES might also result a higher chance for the cations to interact with the electron-rich sulphur compound.

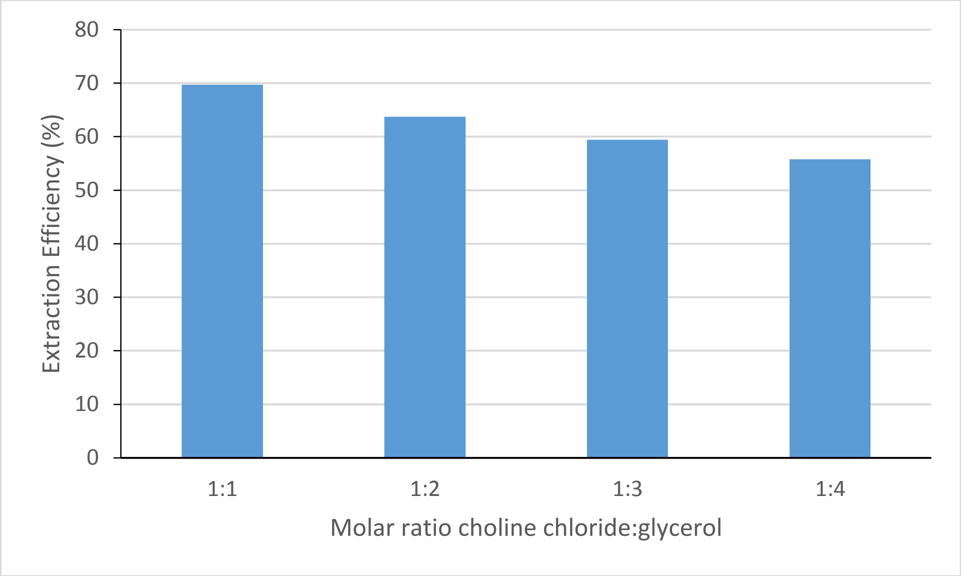

Figure 4.6 Effect of choline chloride: glycerol ratio [Room temperature, volume ratio DES: model oil was 1:5, stirring speed at 400rpm, extraction duration 3hrs and DBT as sulphur concentration at 300ppm].

4.8 Recycling and regeneration

The extraction efficiency of the DES after being reused was investigated. The parameter fixed for this study are the concentration sulphur DBT in model oil

300ppm, volume ratio DES: model oil was 1:5, the molar ratio choline chloride : glycerol is 1:2 and at room temperature. The sample for analysis taken after 3hrs.The DES re-used after the first extraction and the second cycle conducted using the same parameter.

The extraction of DES decrease after has being used for two times as shown in Figure 4.7. The extraction efficiency for no of cycle 1 and 2 are 60.4576 and 55.9654% respectively. Reuse of DES without regeneration is very important to reduce the cost to generate new DES after every extraction.

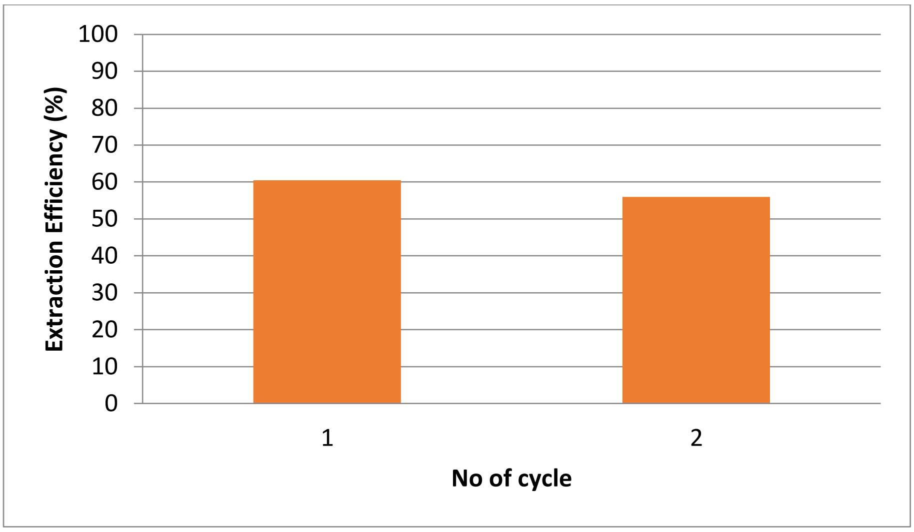

Figure 4.7 Recycling DES without regeneration [Room temperature, volume ratio DES: model oil was 1:5, choline chloride: glycerol 1:2, stirring speed at 400rpm, extraction duration 3hrs and DBT as sulphur concentration at 300ppm].

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

DES can be alternatives solvents for desulphurisation process. The advantages of DES over conventional ionic liquids are can be easily synthesis at high purity and low cost of material can be used to synthesis DES. Apart from that, it is also environmental friendly solvents.

The performance DES for desulphurisation process measured by determine the extraction efficiency. As the concentration of the sulphur in the model oil increase the extraction efficiency decrease. DBT has higher selectivity compare to BT. The extraction efficiency also can be influence by the molar ratio between choline chloride: glycerol, the higher the no of mole of glycerol to the no of mole choline chloride extraction efficiency decrease. Apart from that, the volume ratio DES: model oil, the high extraction efficiency shown as the volume. The extraction efficiency of DES decrease as after recycled for two times.

5.2 Recommendation

For the further study on deep desulphurisation using DES, another parameter can be consider is the optimum temperature for the extraction to occur. In a study by Wilfred et al. the optimum temperature is at 30^{o}C. However the efficiency of the desulphurisation is slightly decrease as the temperature increase. The desulphurisation efficiency at 30^{o}C almost the same with at room temperature. To run the extraction process at higher temperature required higher energy consumption. Therefore, it is expected the extraction does not required higher temperature and can be conducted at room temperature. It also can save energy.

Apart from that, the desulphurization using DES still new and rarely been reported in any literature. The desulphurisation can be expand by performing photooxidative-extraction using metal doped-TiO as photocatalyst. Photooxidative reaction utilise abundant sunlight source in the Earth. The photocatalyst can be suspending in the model oil containing DBT and photooxidation can be conduted under halogen lamp. Titanium oxides (TiO_2) can be used as photocatalyst to oxidise DBT to DBT sulfone ($DBTO_2$). However, TiO_2 cannot fully utilise the solar energy as the ultra violet radiation intensity is not very high in the solar energy reaches the Earth. In order to improve the performance of TiO_2 under visible enhance the performance is by metal doping. The metal use as dopant is usually transition metal such as iron, copper. Then, $DBTO_2$ can be extracted from the model oil using DES via liquid-liquid extraction process. Sulfone can be easily extracted from model oil compare to DBT and BT.

Then, the experiment can be conducted by using actual diesel. In the actual diesel, there are many other non-aromatics sulphur components such as thiol sulphide which DES night not extract them effectively. Therefore, the expected desulphurisation efficiency is lower than the extraction efficiency using model oil. Apart from that, the data experiment conducted using real diesel is more realistic than model oil.

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APPENDICES

A. Overview Process Flow

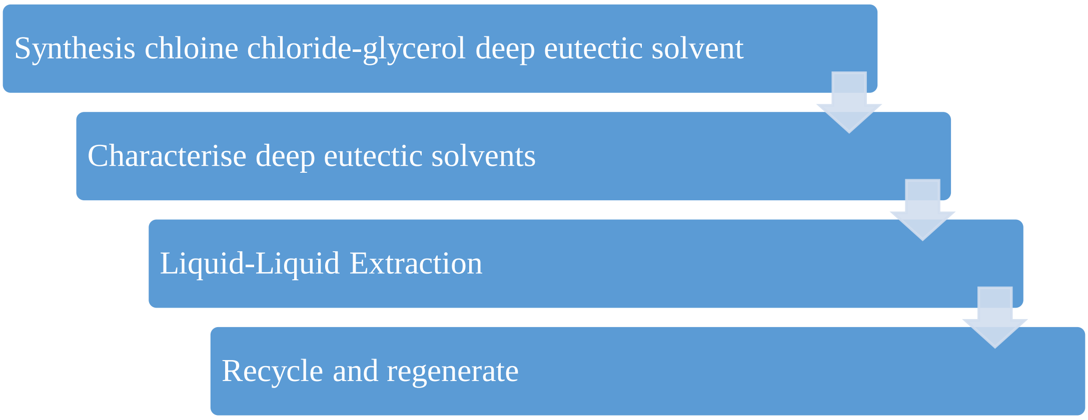

Figure 3.1 Overview Process Flow

B. Gantt charts and key milestones

No	Details	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
1	Selection of Project Topic	🟦	🟦																										
2	Preliminary Research Work		🟦	🟦	🟦	🟦	🟦																						
3	Submission of Extended Proposal							☒																					
4	Proposal Defence									☒																			
5	Project Work Continues								🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦			
6	Submission of Interim Final Report													☒															
7	Submission of Progress Report																					☒							
8	Submission of dissertation and Technical paper																										☒		
9	Viva																										☒		
10	Submission of Project Dissertation-Hard Bound																												☒

☒ Key milestones 🟦 Gantt Charts

Figure 3.2 Gantt Charts and milestones

C. Amount of Glycerol and Choline Chloride

The calculation based on molar ratio Choline Chloride: Glycerol 1:2.

The volume of Glycerol 100mL

$$\text{Volume} = \frac{\text{mass}}{\text{density}}$$

$$\text{mass} = \text{density} \times \text{volume}$$

$$\text{mass} = 1.261\frac{\text{g}}{\text{mL}} \times 100\ \text{mL}$$

$$\text{mass} = 126.1\ \text{g}$$

$$\text{No of mol} = \frac{\text{mass}}{\text{molar mass}}$$

$$\text{No of mol} = \frac{126.1\ \text{g}}{92.09\ \text{g/mol}}$$

$$\text{No of mol glycerol} = 1.3693$$

Molar ratio Choline chloride: Glycerol is 1: 2.

$$\therefore\ \text{No of mol choline chloride} = \frac{\text{no of mol glycerol}}{2}$$

$$\text{No of mol choline chloride} = \frac{1.3693}{2}$$

$$\text{No of mol choline chloride} = 0.6847\ \text{mol}$$

$$\text{Mass of choline chloride} = \text{no of mol} \times \text{molar mass}$$

$$\text{Mass of choline chloride} = 0.6847\ \text{mol} \times 139.62\frac{\text{g}}{\text{mol}}$$

$$\text{Mass of choline chloride} = 95.5987\text{g}$$

D. Calculation amount of Dibenzothiophene needed to dissolve in dodecane

Calculation shown based on 300 ppm sulphur in dodecane

Molecular weight Sulphur = 32 g/mol

Molecular weight Dibenzothiophene = 184.26 g/mol

Molecular Formula Dibenzothiophene = $C_{12}H_8S$

To produce 300 ppm sulphur from the Dibenzothiophene

300ppm = 300 mg/L

Hence, in 100mL containing 30mg sulphur

32.00g Sulphur in every 184.26 g Dibenzothiophene

$$\text{Dibenzothiophene required} = \frac{30\text{mg} \times 184.26\text{ g}}{32.00\text{ g}} = 172.73\text{ mgDBT}$$

The purity of Dibezothiophene used is 98%

$$\text{The amount of Dibenzothiophene} = \frac{172.73}{0.98} = 176.255$$

E. Calculation amount of Benzothiophene needed to dissolve in dodecane

Calculation shown based on 200 ppm sulphur in dodecane

Molecular weight Sulphur = 32 g/mol

Molecular weight Benzothiophene = 134.2 g/mol

Molecular Formula Benzothiophene = C_8H_6S

To produce 200 ppm sulphur from the Benzothiophene

200ppm = 200 mg/L

Hence, in 100mL containing 20mg sulphur

32.00g Sulphur in every 134.2 g Benzothiophene

$$\text{Dibenzothiophene required} = \frac{20\text{mg} \times 134.2\text{ g}}{32.00\text{ g}} = 115.163\text{ mg BT}$$

The purity of Benzothiophene used is 97%

$$\text{The amount of Dibenzothiophene} = \frac{115.163}{0.97} = 118.725\text{ mg BT}$$