Oxidative Dusulfurization of Dibenzothiophene from Model Oil (dodecane) using [bmim][Cl] as an Extracting Agent

Mohd. Ridzhuan Bin Jinal

ABSTRACT

The oxidative desulfurization of dibenzothiophene (DBT) from model oil (in dodecane) was carried out using ionic liquid as the extractant and catalyst, and hydrogen peroxide in combustion as an oxidant. The ionic liquid used were 1-Butyl-3-Methylimidazolium Chlorine [bmim]Cl. The effect of the amount of hydrogen peroxide on oxidative desulfurization was first investigated without usage of ionic liquid at room temperature. The result indicate that greater amount of hydrogen peroxide yield higher desulfurization and the maximum desulfurization in this study were 17.32% removal at the molar ratio of hydrogen peroxide to S-content was 10:1. With the usage of ionic liquid and the molar ratio 10:1(hydrogen peroxide to S-content), the efficiency of sulfur removal from model oil was enhanced to 21.02% removal, it was increase significantly in term of sulfur removal and removal time. The mixing time was 300 minutes at room temperature. The result indicates the potential of ionic liquids as the extractant and catalyst for oxidative desulfurization of hydrocarbon fuels.

ACKNOWLEDGEMENT

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Thanks

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List of Abbreviations

ILs	Ionic Liquids
HDS	Hydrodesulfurization
ODS	Oxidative Desulfurization
USLD	Ultra-low-sulfur-diesel
ppm	parts per million
EPA	Environment Protecting Agency
EU	European Union
CAA	Clean Air Act
VOCs	Volatile Organic Compound
ACN	Acetonitrile
DMF	Dimethylformamide
[bmim]Cl	1-butyl-3-methylimidazolium chloride
DBT	Dibenzothiophene
H_2O_2	Hydrogen Peroxide
H_2	Hydrogen
H_2S	Hydrogen Sulfide
S	Sulfur
SOx	Sulfur Oxide

CHAPTER 1: PROJECT BACKGROUND

1.1 Background of studies

Desulfurization of transportation fuel, gas and diesel has attracted many researchers as sulfur affects the quality of petroleum-derived fuels and gives negative impact to the environment (Mohd Faisal, Atikah, Chong, & Shaharun, 2012). Through combustion of petroleum-derived fuel, sulfur is converted to sulfur oxide (SOx). The releasing of SOx in air promotes high air pollution index, contributing towards an acid-rain and smog (Palawec, Navarro, Campos-Martin, & Fierro, 2011). It also causes many serious diseases respiratory system such as lung cancer (Di-shun, Zhi-min, Fa-tang, & Hai-dan, 2009). Gas containing SOx also poisoning noble-metal catalysts irreversibly in automobiles and electrodes used (Li, Zhu, Wang, Zhang, Lu, & Yan, 2009) and this consequently promoting the emissions of CO, NO_X, and other particulates into the air (Yu, Zhao, Song, Asumana, Zhang, & Chen, 2011).

In order to achieve ultra-low-sulfur diesel (ULSD), it was imposed on oil refineries in many countries are being imposed to reduce the S content at a very low limit around 0.001%-0.002% by 2012 or in other word is “zero sulfur” (Dehkordi, Sobati, & Nazem, 2009). Many stringent environment legislations have been issued to limit the sulfur content of fuels (Xu, et al., 2009). EU legislation set upper limit of sulfur content in diesel in 10ppm & in by December 2006 and US Environment Protecting Agency (EPA) reduced the limit to 15ppm (Zhang, et al., 2010).

Sulfur-containing compounds and polyaromatic hydrocarbons present in diesel fuel are responsible for the particulates or soot in diesel (Palawec, Navarro, Campos-Martin, & Fierro, 2011). Alkylthiophene, benzothiophene (BT), dibenzothiophene (DBT) and its derivatives such as 4-6-dimethylthiophene (4-6-DMDBT) are difficult to be removed from the diesel due to the sterically hindered adsorption of these compounds on the catalyst surface in catalytic hydrodesulfurization (HDS) (Wang, Zhao, & Li, 2010).

Currently, HDS is the common method used in reducing sulfur-containing compounds from fuels in oil refineries. However, it is required to be operated under high operating condition which is leads to the increasing of operating cost and an investment cost on the reactor used (Di-shun, Zhi-min, Fa-tang, & Hai-dan, 2009).

In recent years, various alternatives deep desulfurization processes operated under moderate conditions without requiring H_2 have been extensively investigated by the researchers such as bio-desulfurization, selective adsorption, oxidative desulfurization (ODS), selective adsorption and ionic liquids (ILs) extraction desulfurization (Xu, et al., 2009). Among of these, ODS is the best alternative due to high rate of reactivity (easily converted to oxidation) rather that HDS process. It is currently receiving great attention as it avoids the use of hydrogen and allows the process to be conducted at ambient condition (atmospheric pressure and room temperature), high efficiency and selectivity (Mohd Faisal, Atikah, Chong, & Shaharun, 2012).

However, although ODS process is effective, it requires a large amount of volatile organic compound (VOCs) as reactant. By combining both ODS and ILs method, the efficiency of desulfurization is increased whereby ILs act as an extracting agent as well as catalyst (Wang, Zhao, & Li, 2010). Ionic Liquids are easy to handle because of non-volatility, non-flammability and high thermal stability. Also, ionic liquid can be recycling up to 6 times of usage (Zhang, et al., 2010). Thus, ionic liquids can be considered as the novel green solvent (Li, et al., 2009) for the extractive-oxidative desulfurization.

1.2 Problem Statement

At present, work in reducing the sulfur content in the conventional fuel, i.e. gasoline and diesel, at ultra-low-sulfur has attracted many interest of many researchers. In fact, many countries have imposed very stringent regulations for specification of sulfur content in fuel (Zapata, Pedraza, & Valenzuela, 2005). In USA, the current acceptable sulfur contain in highway diesel is less than 15 ppm as specified by the Clean Air Act (CAA) early 2000. Currently, in European Union (EU) country and Japan, it was imposed on oil refineries to reduce sulfur content in the range of 10-20 ppm (Palawec, Navarro, Campos-Martin, & Fierro, 2011). Currently, all refineries used hydro treating method, i.e. hydrodesulfurization (HDS), to reduce the sulfur contain in fuels. However, due to its high operating cost and investment cost, many alternatives for removal of sulfur from fuel such as bio-desulfurization, selective adsorption, oxidative desulfurization (ODS), selective adsorption and ionic liquids (ILs) extraction desulfurization are being studied laterally (Xu, et al., 2009). Among these alternative methods, ODS is the most promising process whereby uses the peroxide to enable the conversion of sulfur contain into molecule sulfoxide and sulfones (Mohd Faisal, Atikah, Chong, & Shaharun, 2012). It also can be performed at atmospheric pressure and operated at room temperature (Zapata, Pedraza, & Valenzuela, 2005). Studies have shown that the combination of ODS and ionic liquids (extracting agent and catalyst), had provide high degree of sulfur removal efficiency (Gao, Guo, Xing, Zhao, & Liu, 2010).

1.3 Objective

The main objectives of this work are:

a. To study the efficiency of oxidative desulfurization of DBT from dodecane (model oil) using [bmim]Cl as an extracting agent.
b. To study the following factor on the efficiency of desulfurization of DBT form dodecane (model oil) with different:
    i. mixing time
    ii. amount of oxidant (hydrogen peroxide)
    iii. amount of ionic liquid ([bmim]Cl)

1.4 Scope of Studies

In this study, the removal of DBT from dodecane using ODS and ionic liquid ([bmim]Cl) at room temperature was carried out. Generally, this piece of work was divided into two phases;

a. The first phase was the literature review whereby the student needs to study the related journals and come out with the proposal.
b. The second phase was experimental work. The experiment work was conducted based on the methodologies proposed (from the first phase). Data and result obtained from the experimental work was be analyzed in order to conclude this study.

CHAPTER 2: LITERATURE REVIEW

2.1 Desulfurization

Sulfur, identified by the chemical symbol S, is the seventeenth most abundant element on the earth. As a nonmetal, it is a poor conductor of electricity and heat. It also does not dissolve in water, but does dissolve in certain organic (carbon-containing) solvent (Stimola & Aubrey, 2007). Fossil fuels naturally contain sulfur. Crude oil contains on average 1.5% sulfur, which is set to rise by about 5% recently due to the use of lesser quality crudes. To achieve ultra-low-sulfur, all oil refineries throughout the world are being imposed to reduce the S content at a very low limit around 0.001%-0.002% by 2012 or in other word is “zero sulfur” (Zapata, Pedraza, & Valenzuela, 2005).

Desulfurization is the process of removing sulfur to prevent contamination. Currently, HDS is the common method used in oil refineries. However, it is difficult to remove sulfur from aromatic organic sulfur systems using HDS method. It requires the high operating condition, which leads to high investment as well as high operating cost (Di-shun, Zhi-min, Fa-tang, & Hai-dan, 2009).

2.2 Sulfur in Crude Oil

Crude oil is a complex mixture of an organic liquid. The crude oil comes from the reservoir, in which the sulfur is naturally reacting with the small amount of crude oil to form organosulfur. There were several type organosulfur compounds which have different physical-chemical properties such as aliphatic and aromatic sulfur compound (Zhu, et al., 2008).

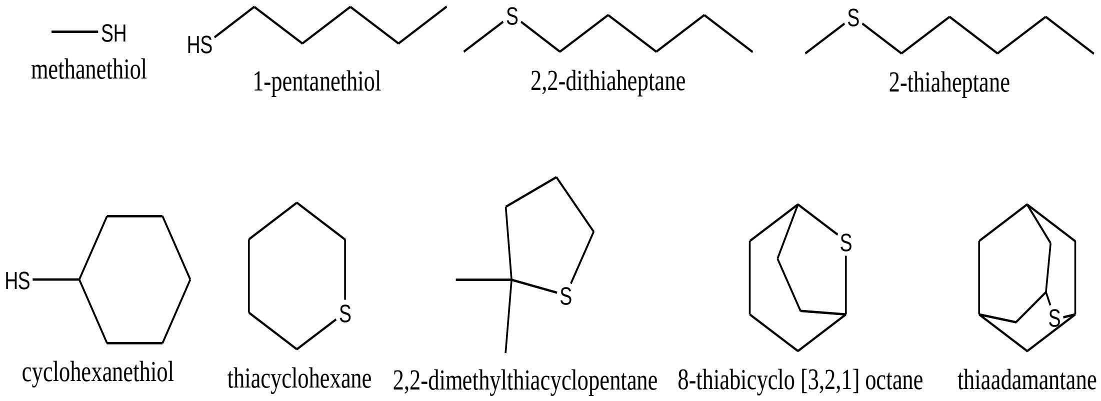
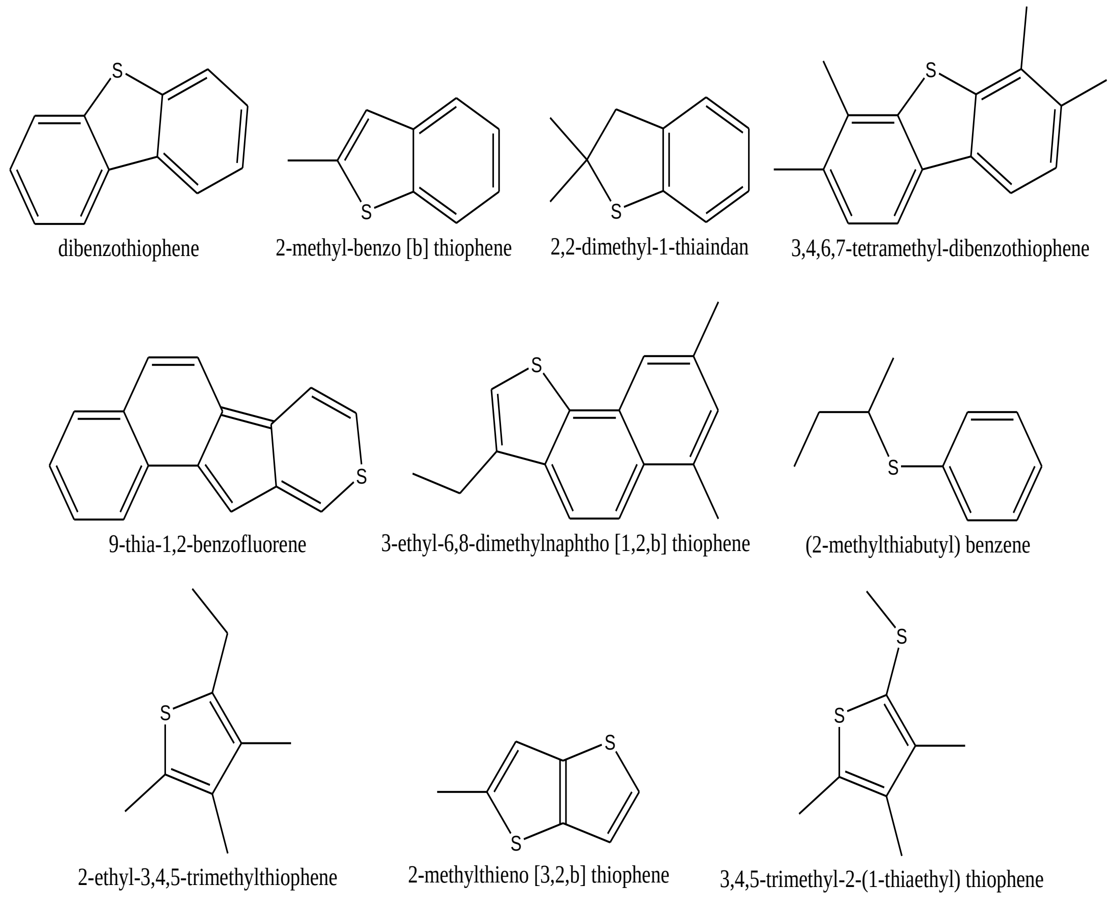


Figure 1: Example of aliphatic and cyclic sulfur compounds in petroleum

Figure 1 shows the examples of aliphatic and cyclic sulfur compounds in petroleum (Zhu, et al., 2008). These sulfur compounds can be easily removed from the crude oil through the conventional catalytic HDS.



dibenzothiophene

2-methyl-benzo [b] thiophene

2,2-dimethyl-1-thiaindan

3,4,6,7-tetramethyl-dibenzothiophene

9-thia-1,2-benzofluorene

3-ethyl-6,8-dimethylnaphtho [1,2,b] thiophene

(2-methylthiabutyl) benzene

2-ethyl-3,4,5-trimethylthiophene

2-methylthieno [3,2,b] thiophene

3,4,5-trimethyl-2-(1-thiaethyl) thiophene

Figure 2: Example of aromatic sulfur compound in petroleum

Figure 2 shows the examples of aromatic sulfur compounds in petroleum. In spite of aliphatic sulfur compound, aromatic sulfur compound is difficult to remove due to its sterically hindered structure (Mohd Faisal, Atikah, Chong, & Shaharun, 2012).

2.3 Hydrodesulfurization

Nowadays, HDS is the common method used in oil refineries to reduce the sulfur content in fuels. In HDS, the emission of sulfur oxides will be converted to hydrogen sulfide and sulfuric acid with the present of hydrogen and an active catalyst which is operated under high temperature and pressure (Palawec, Navarro, Campos-Martin, & Fierro, 2011). In HDS process, S-compounds react with H_2 and are catalytically converted into H_2S and subsequently oxidized into elemental S in the Claus process (Yu, Zhao, Song, Asumana, Zhang, & Chen, 2011).

Although HDS method is very efficient for removal of aliphatic sulfur compounds, but it has low reactivity towards aromatic heterocyclic sulfur compounds due to its sterically hindered structure of aromatic heterocyclic sulfur compound (Di-shun, Zhi-min, Fa-tang, & Hai-dan, 2009). An active catalyst used in HDS, typically a catalyst consisting of an alumina base impregnated with cobalt and molybdenum (Palawec, Navarro, Campos-Martin, & Fierro, 2011) is easily malfunctions due to the reaction with sulfur itself (Zhu, et al., 2008). The cost requirement to operate HDS is high due to high operating condition, high consumption of hydrogen and active catalyst, low process cycle life and expensive unit operations (Ito & Veen, 2006).

In HDS, the sulfur compound is classified into four groups depending on its reactivity towards HDS that are described by the pseudo-first-order rate constants. They are: (i) sulfur compound dominated by alkyl benzothiophenes (BTs); (ii) dibenzothiophenes (DBT) and alkyl dibenzothiophene (DBTs) without alkyl substitution at 4- and 6- position; (iii) alkyl DBTs with one only alkyl substituent either at 4- or 6- position; and (iv) alkyl substituents at 4- and 6- position (Palawec, Navarro, Campos-Martin, & Fierro, 2011).

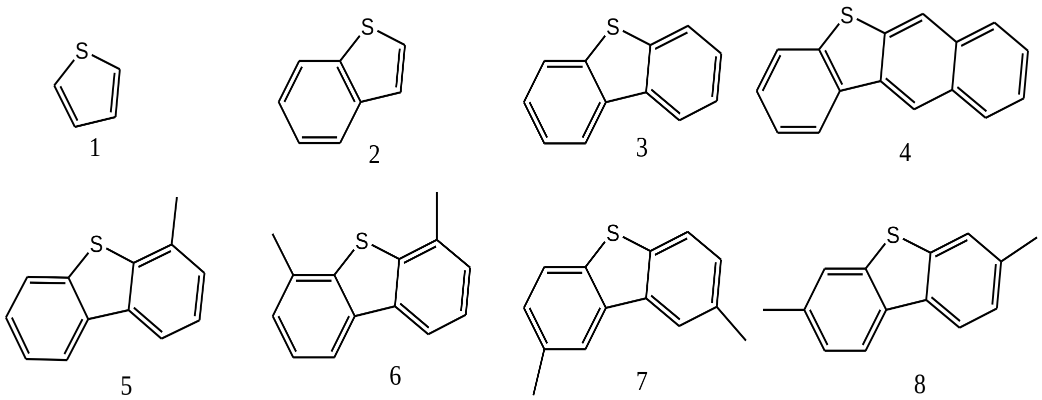


Figure 3: Type of sulfur compound in HDS process (1) thiophene; (2) benzothiophene; (3) dibenzothiophene; (4) benzo(b)naphtha 2,3-thiophene; (5) 4-methyl dibenzothiophene; (6) 4,6-dimethyl dibenzothiophene; (7) 2,8-dimethyl dibenzothiophene; and (8) 3,7-dimethyl dibenzothiophene

Figure 3 shows the structure of DBT and its derivatives. Among these thiol derivatives, DBT is the most difficult to remove by HDS (Palawec, Navarro, Campos-Martin, & Fierro, 2011).

DBT and alkyl DBTs hydrodesulfurization mainly precede *via* two parallel routes which is direct desulfurization (DDS) leading to the formation *of* biphenyl, and hydrogenation (HYD) leading to the formation of tetrahydrodobenzothiophene. Tetrahydrodobenzothiophene is further desulfurized to cyclohexylbenzene.

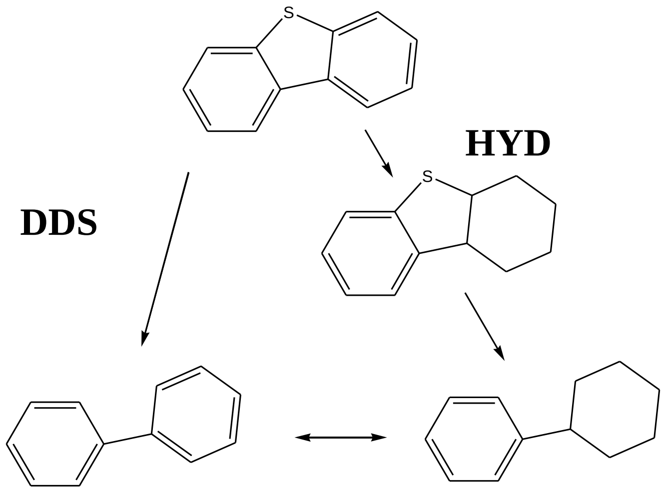


Figure 4: Direct and hydrogenation reaction pathways for hydrodesulfurization of 4,6-dimethyl dibenzothiophene.

However, the DDS route reduces the DBT's HDS reactivity and change the ratio between the rates of the two routes. HYD is more dominant in HDS with the present of catalyst (Palawec, Navarro, Campos-Martin, & Fierro, 2011).

2.4 Oxidative Desulfurization

Sulfur removal by oxidative process aims to promote a reaction which is considered green rather than HDS by forming oxidized sulfur species. The general process consists of three parts: peroxide supply, sulfone generation and sulfone separation (Mohd Faisal, Atikah, Chong, & Shaharun, 2012). The initial part comprises the peroxide storage and handling facilities. In the second phase, the fuel mixed with the oxidant and catalyst and the oxidation of sulfur to sulfoxide and further continue to sulfone occurs in this section (Wang, et al., 2010). In this process, the physical-chemical properties significantly change as the conversion complete. The process is shown in figure 5:

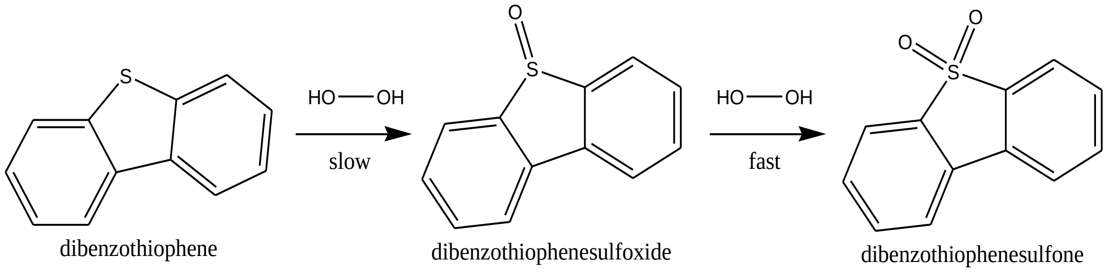


Figure 5: Simplified scheme showing the oxidation of DBT. The oxidant donates O-atomto the DBTmolecule present in the organic phase to form first sulfoxide and then sulfones (these oxidized compounds accumulate mainly in the polar phase).

Sulfones are polar molecules and they are easily separated by way of adsorption on a solid adsorbent or by solvent extraction using extracting agent (Palawec, Navarro, Campos-Martin, & Fierro, 2011)such as dimethylformamide (DMF) and acetonitrile (ACN) for the third phase. DMF and ACN are the most selective low-boiling solvent for use in treating middle distillate fractions. The separation of sulfones is radically reduce the cost of diesel dearomatization and desulfurization since they do not require hydrogen and are carried out at atmospheric pressure, and comparatively at low temperature (Toteva, Georgiev, & Topalova, 2009).

2.5 Oxidation Agent (Hydrogen Peroxide)

An oxidizing agent is the element or compound that participated in an oxidation-reduction (redox) reaction. The main concept of this oxidizing agent is to gaining an electron then enables it to be reduced. The oxidizing agent available for oxidative desulfurization are O_2, O_3, H_2O_2, F_2, halogen, sulphuric acid, acetate, nitric acid, tert-butyl hydroperoxide (Zhang, et al., 2010), peroxydisulfuric acid, hypochlorite, permanganate (Wang, et al., 2010), nitrous oxide, silver oxide, osminum oxide,valadium oxide (Dehkordi, Sobati, & Nazem, 2009) and potassium superoxide (Cun, et al., 2011).

Among of these oxidizing agents, the most suitable oxidant is H_2O_2 which has high efficiency toward oxidative desulfurization, easy to handle, cheap in pricing, non-polluting towards environment, not strongly corrosive in reaction and commercially available everywhere (Zhang, et al., 2010).

2.6 Ionic Liquids

Room temperature ionic liquids (ILs) are the new type of environmentally friendly solvent has been widely investigated by the researchers due to their properties (Xu, et al., 2009). Ionic liquid is an organic salt (Yansheng, et al., 2011) with melting point around ambient temperature, are entirely composed of cation and anion. They have some novel and desirable properties such as non-volatility, excellent solubility for organic/inorganic compounds, good thermal/chemical stability and non-flammability (Toteva, Georgiev, & Topalova, 2009). Ionic liquid recently gained recognition as environmentally benign alternative solvents applicable in other separation, synthesis, electrochemistry and catalyst (Li, et al., 2009).

Ionic liquids also show good extraction ability for aromatic sulfur-containing compounds and are immiscible with aliphatic liquids such fuels (Toteva, Georgiev, & Topalova, 2009). However, the extraction efficiency with ionic liquid show low reactivity (~50%) due to its same polarity among alkyls, aromatics and sulfur compound in fuels (Li, et al., 2009).

In extraction with ODS and ionic liquid, the organosulfur compounds are separated by distillation and the solvent then is recycled. The advantage in this extractive desulfurization is its application at low temperature and low pressure (Palawec, Navarro, Campos-Martin, & Fierro, 2011). There are several types of ionic liquid that can be used as an extracting agent in extractive desulfurization, such as; (i) imidazolium-based ionic liquid, (ii) pyridium-based ionic liquid and (iii) lewis and bronsted acidic ionic liquids or redox ionic liquids.

The structure and size of the cation and anion of an ionic liquid can affect the reactivity. Imidazolium-based ionic liquids are most favorable as extracting agent in ODS process due to its higher polarity rather than pyridium-based ionic liquid and redox ionic liquid which could contribute to higher desulfurization in fuels (Ito & Veen, 2006).

The studies shown that, 1-butyl-3-methylimidazolium chloride (shown in Figure 6) could remove sulfur by itself due to high negativity of chlorine ion, thus 1-butyl-3-methylimidazolium chloride could be used as the extracting agent in desulfurization (Zhang, et al., 2010).

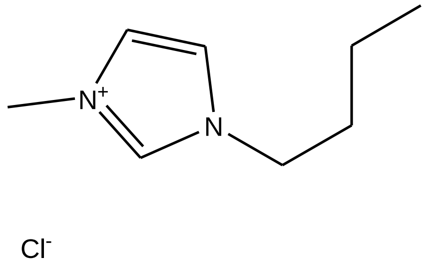


Figure 6: 1-butyl-3-methylimidazolium chloride structure.

2.7 Oxidative Desulfurization using Ionic Liquid as an Extractive Agent

Studies have shown that the efficiency of sulfur removal could be enhanced through the combination of oxidative desulfurization and ionic liquid (Mohd Faisal, Atikah, Chong, & Shaharun, 2012).

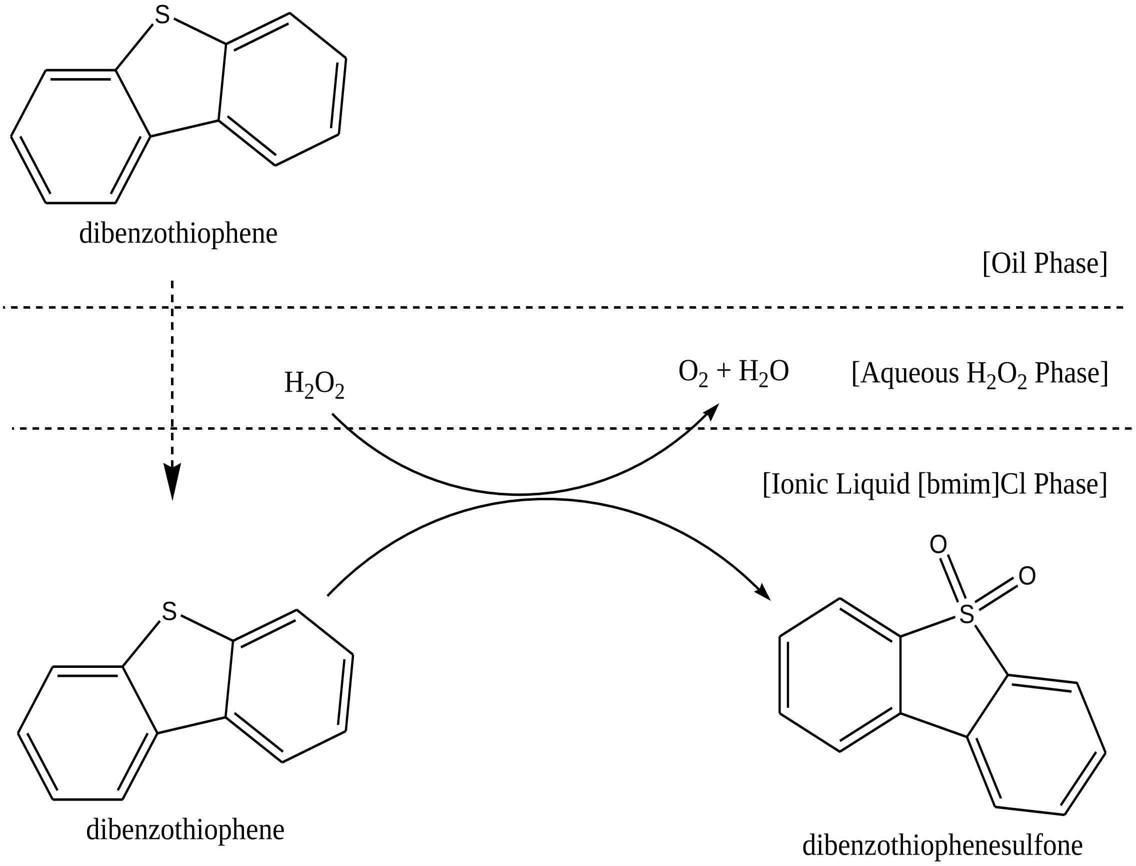
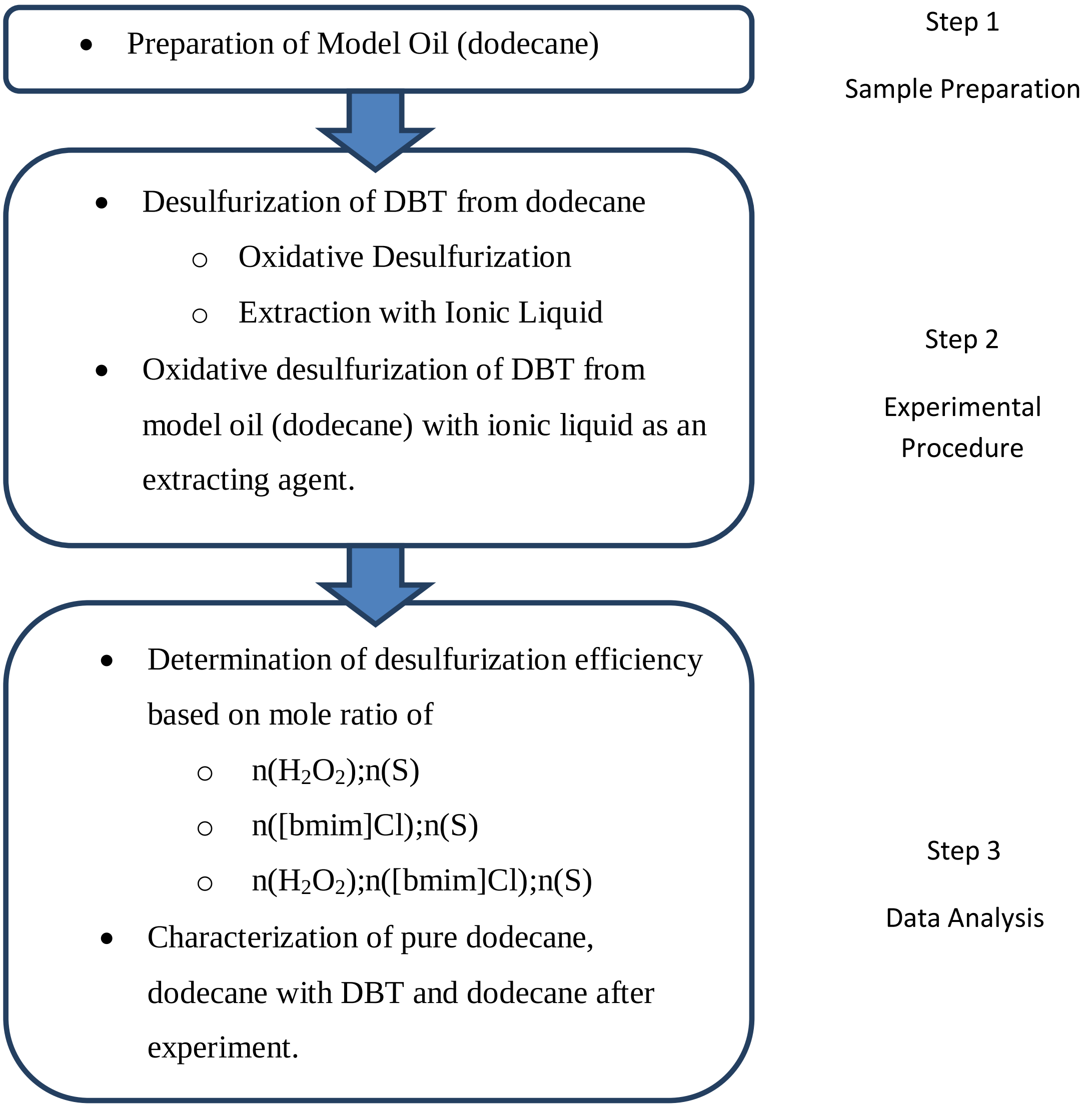


Figure 7: Oxidative desulfurization process of DBT in model oil (dodecane) using ionic liquid as an extracting agent.

Figure 7 shows the mechanism of sulfur removal using combination of ODS and ionic liquids. DBT that present in model is extracted into ionic liquid phase and then oxidized by hydrogen peroxide. The extraction occurs due to the high ability of ionic liquid to extract DBT from dodecane into ionic liquid phase. Then, the extracted DBT further oxidized with hydrogen peroxide to form high polar sulfoxide and sulfone and they are remains in ionic liquid phase (Di-shun, Zhi-min, Fa-tang, & Hai-dan, 2009).

CHAPTER 3: METHODOLOGY

3.1 Research Methodology and Project Activities



- Preparation of Model Oil (dodecane)

Step 1

Sample Preparation

- Desulfurization of DBT from dodecane
  - Oxidative Desulfurization
  - Extraction with Ionic Liquid
- Oxidative desulfurization of DBT from model oil (dodecane) with ionic liquid as an extracting agent.

Step 2

Experimental Procedure

- Determination of desulfurization efficiency based on mole ratio of
  - n(H_2O_2);n(S)
  - n([bmim]Cl);n(S)
  - n(H_2O_2);n([bmim]Cl);n(S)
- Characterization of pure dodecane, dodecane with DBT and dodecane after experiment.

Step 3

Data Analysis

Figure 8: Simplified experimental methodology

Figure 8 shows the summary of experimental procedure for the oxidative desulfurization of DBT from model oil (dodecane) using ionic liquid as an extracting agent.

3.2 Experimental Procedure

The procedures are divided into several parts. They are (a) preparation of model oil, (b) desulfurization of DBT from model oil, (c) oxidative desulfurization of DBT from model oil with ionic liquid.

a) Preparation of model oil

1. Model oil is prepared by spiking certain amount of DBT into 50 ml of dodecane in glass beaker. (Before spiking with certain amount of DBT, 1.5 mL of pure dodecane is taken to be analysed using Raman Spectroscopy)
2. This mixture was stirred at 400.00 rpm at the room temperature for 15 minutes. Small amount of the model oil containing DBT was analysed using gas chromatography in order to determine the initial amount of DBT.
3. Model oil containing DBT (1000ppm of S-content) was characterized using Raman Spectroscopy.

Table 1: Calculation of different concentration of S-content in DBT

S-content in DBT (ppm)	Dodecane (mL)	BDT 97%(g)
0	50.00	0.000
100	50.00	0.030
200	50.00	0.059
400	50.00	0.118
600	50.00	0.178
800	50.00	0.237
1000	50.00	0.296

b) Desulfurization of DBT from Model Oil

i. Oxidative desulfurization of DBT from model oil (without [bmim]Cl)

1. A certain amount of freshly prepared H_2O_2 was added into model oil (dodecane with S-content of DBT 1000ppm) with molar ratio n(H_2O_2);n(S), 2:1 in two-neck glass flask.
2. The mixture was stirred at 400 ppm on hot plate at room temperature.
3. Small amount of sample was taken for interval times of 10min, 20min, 30min, 1hr, 2hr, 3.5hr and 5hr. Each sample was analysed using gas chromatography to determine the sulfur content.
4. The same procedures were applied for other molar ratios of peroxide and S-content in DBT in the model oil; 2:1, 4:1, 6:1, 8:1 and 10:1

Table 2: Calculation of different molar ratios of H_20_2:S-content

Mole ratio H_20_2:S-content	Dodecane (mL)	H_2O_2 (g)	H_20_2 30% (g)
2:1	50.00	0.109	0.365
4:1	50.00	0.219	0.729
6:1	50.00	0.328	1.094
8:1	50.00	0.437	1.458
10:1	50.00	0.547	1.823

ii. Extractive desulfurization of DBT from model oil with [bmim]Cl

1. A certain amount of freshly prepared [bmim]Cl was added into model oil (dodecane with S-content of DBT 1000ppm) with molar ratio n([bmim]Cl);n(S), 1:1 in two-neck glass flask.
2. The mixture was stirred at 400ppm on hot plate at room temperature.
3. Small amount of sample was taken for interval times of 10min, 20min, 30min, 1hr, 2hr, 3.5hr and 5hr. Each sample was analysed using gas chromatography to determine the sulfur content.
4. The same procedures were applied for other molar ratio of [bmim]Cl and S-content in DBT in the model oil; 1:1, 0.8:1, 0.6:1, 0.4:1 and 0.2:1

Table 3: Calculation of different molar ratio of [bmim]Cl:S-content

Mole Ratio [bmim]Cl:S-content	Dodecane (mL)	[bmim]Cl (g)
1:1	50.00	0.281
0.8:1	50.00	0.225
0.6:1	50.00	0.168
0.4:1	50.00	0.112
0.2:1	50.00	0.056

c) Oxidative desulfurization of DBT from model oil (dodecane) using [bmim]Cl as an extracting agent

From (b) results, the best ratio of n(H_2O_2);n(S) and n([bmim]Cl);n(S) were taking into account to be further studies by combining both ODS method and ionic liquid as the extracting agent and catalyst. The experimental procedures are as follow;

1. A certain amount of freshly prepared H_2O_2 and [bmim]Cl was added into model oil (dodecane with S-content of DBT 1000ppm) with molar ratio n(H_2O_2);n([bmim]Cl);n(S), 10:1:1 in two-neck glass flask.
2. Small amount of sample was taken for interval times of 10min, 20min, 30min, 1hr, 2hr, 3.5hr and 5hr. Each sample was analysed using gas chromatography to determine the sulfur content.
3. Sample was taken from 1000ppm of S-content to be analyzed using Raman Spectroscopy after 5hr of interval time.

Table 4: Calculation of different molar ratio of H_2O_2:[bmim]Cl:S-content

Mole Ratio (H202:[bmim]Cl:S-content)	dodecane (mL)	H202 30% (g)	[bmim]Cl (mL)
Amount	50.00 mL	1.823 g	0.281 mL
mole			

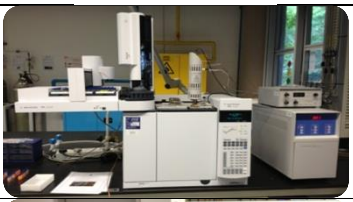
3.3 Chemical Used

Table 5: Chemical used

Chemical	Amount
Dodecane	900.00 mL
Dibenzothiophene, 97%	4.177 g
Hydrogen Peroxide, 30%	10.572 mL
Ionic Liquid, [bmim]Cl	1.123 g
Ethyl Acetate	400.00 mL

3.4 Instrument Used

Table 6: Instrument used

Instrument	Figure	Purpose
Hot Plate		To stirring the model oil at 400rpm
Gas Chromatography-SCD		To analyse the sample
DXR SMARTRAMAN Spectrometer		To analyse the sample

3.5 Experimental Setup

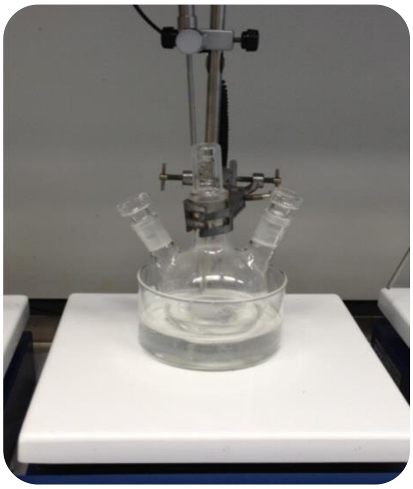


Figure 9: Experimental setup

3.6 Gantt Chart

NO	1st SEM (week) DETAIL	1	2	3	4	5	6	7	🟨	8	9	10	11	12	13	14
1	Selection of Project Title	🟦	🟦	🟦					🟨							
2	Preliminary Research Work and Literature Review			🟦	🟦	🟦	🟦	🟦	🟨							
3	Submission of Extended Proposal Defence							🟦	🟨							
4	Preparation for Oral Proposal Defence							🟦	🟨							
5	Oral Proposal Defence Presentation								🟨	🟦						
6	Detailed Literature Review								🟨	🟦	🟦	🟦	🟦	🟦		
7	Preparation of Interim Report				🟦	🟦	🟦	🟦	🟨	🟦	🟦	🟦	🟦	🟦		
8	Submission of Interim Draft Report								🟨					🟦	🟦	
9	Submission of Interim Final Report								🟨						🟦	

NO	2nd SEM (week) DETAIL	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	**Preparing the Chemical and Equipment for Experimental Work**	■	■						🟥							
2	**Preparing and Characterization of Sample from Model Oil using DXR SMARTRAMAN spectrometer and Gas Chromatography FID/SCD**		■						🟥							
3	**Oxidative Desulfurization Experimental Work**		■	■	■	■			🟥							
4	**Extractive Desulfurization Experimental Work**				■	■	■	■	🟥							
5	**Trial and Error**	■	■	■	■	■	■	■	🟥	■	■	■	■			
6	**Oxidative Desulfurization using Ionic Liquid as an Extracting Agent Experimental Work**					■	■	■	🟥	■						
7	**Analytical Data Analysis**		■	■	■	■	■	■	🟥	■	■	■	■	■	■	
8	**Submission of Progress Report**								🟥	■						
9	**Submission of Dissertation Report**								🟥						■	

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Results

a) Qualitative Analysis

Qualitative analysis was conducted using DXR SMART RAMAN spectrometer located in Ionic Liquid Laboratory. The results obtained from this analysis are showing the differences of the S-content before and after extraction.

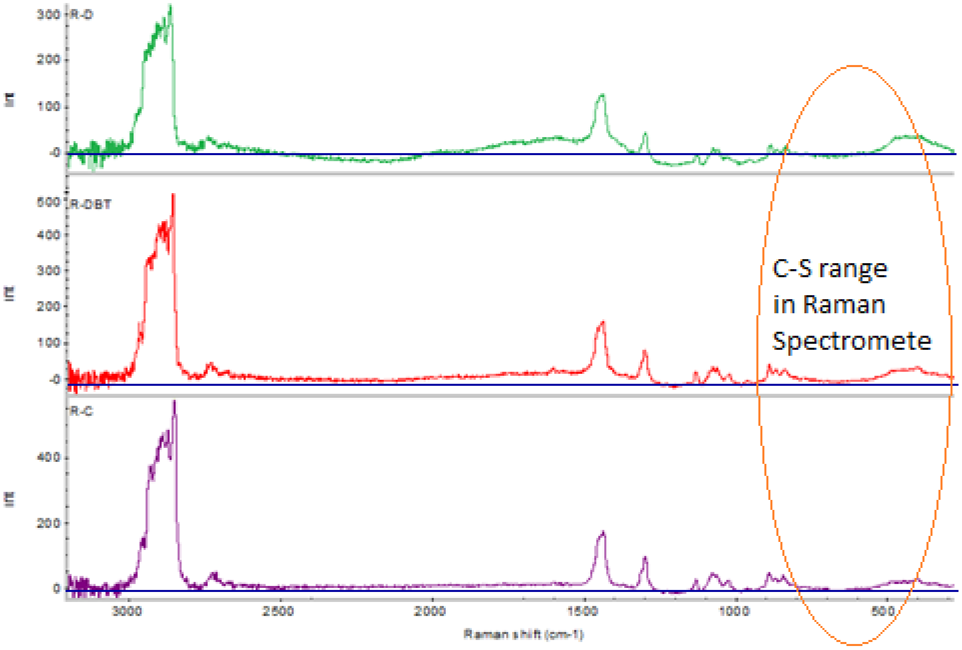


Figure 10: DXR SMART RAMAN spectra

R-D *= Pure Dodecane;*
R-DBT *= Pure Dodecane with DBT (1000ppm S-content);*
R-C *= Dodecane after Oxidative Desulfurization using Ionic Liquid*

As shown by the Raman Spectra (**Figure** 10), organosulfur (C-S) only exist at the range 200 – 700 nm^{-1}. Since S-content is too low, the peak is in this range is small due to the domination of dodecane. The Raman Spectra also proved that oxidant and [bmim]Cl did react with dodecane.

b) Quantitative Result

Quantitative analysis was carried out using GC-FID/SCD (Gas Chromatography – Flame Ionization Detector/Sulfur Chemiluminescene Detector). Basically GC-SCD is used for the quantitative determination of various sulfur organic species like hydrogen sulfide, mercaptans, thiophenes, benzothiophenes & sulfides in hydrocarbon samples. It is a very sensitive and useful technique to characterize crude oils of different origin. Sulfur speciation is essential during oil catalytic processing in the refineries. **Figure** 11 shows the example of data obtained for this project from gas chromatography;

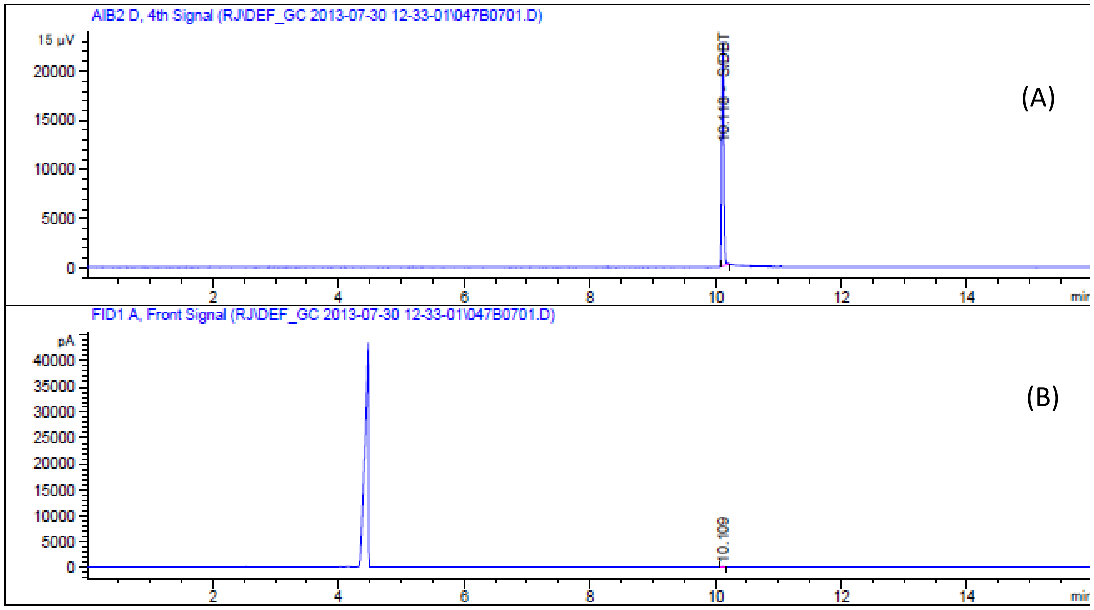
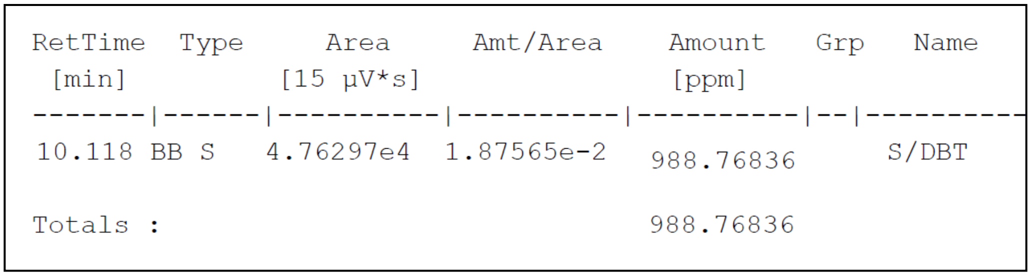


Figure 11: Example of raw data collected from sample A2-10min.

From **Figure** 11, (A) represents the Sulfur Chemiluminescene Detector data, in which the peak for sulfur is shown at 10min residence time and (B) represents the Flame Ionization Detector data, in which the peak for hydrocarbon (dodecane) is shown at 4.3min residence time, small peak for sulfur at 10min residence time.

From **Figure 11**, the data is given as below;



```
RetTime   Type       Area       Amt/Area      Amount    Grp    Name
 [min]           [15 µV*s]                    [ppm]
-------|------|----------|----------|----------|--|----------
10.118  BB  S    4.76297e4   1.87565e-2    988.76836        S/DBT

Totals :                                   988.76836
```

Others data samples are attached in Appendix C.

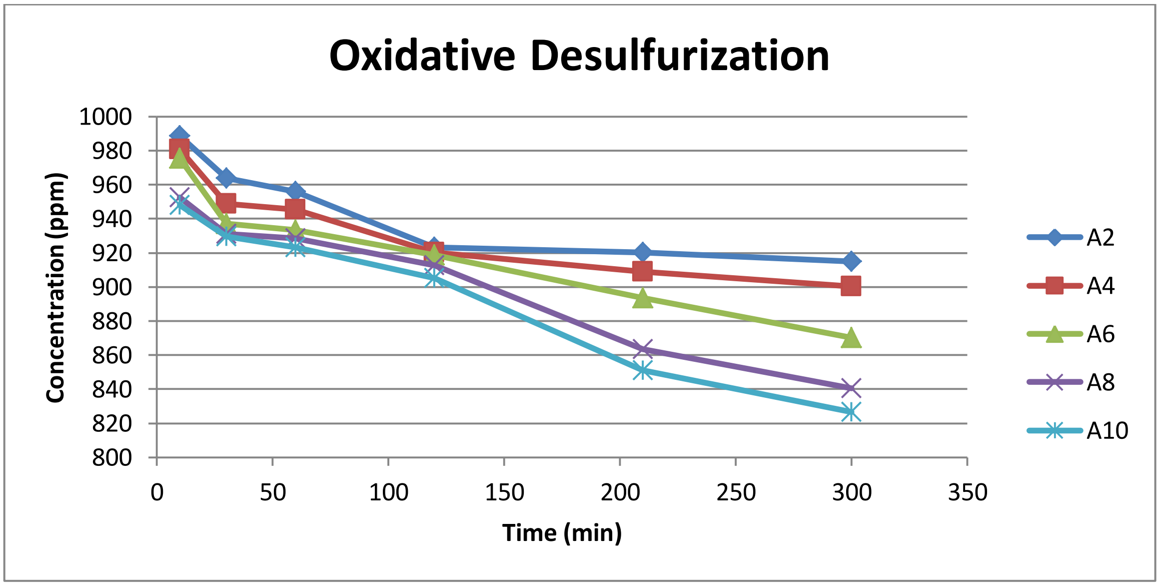


Figure 12: Oxidative Desulfurization Raw Data in different H_2O_2:S-content ratio

Figure 12 is shown the oxidative desulfurization data for different H_2O_2:S-content ratio, whereas for A2, A4, A6, A8 and A10 H_2O_2:S-content ratio given as 2:1, 4:1, 6:1, 8:1 and 10:1 respectively.

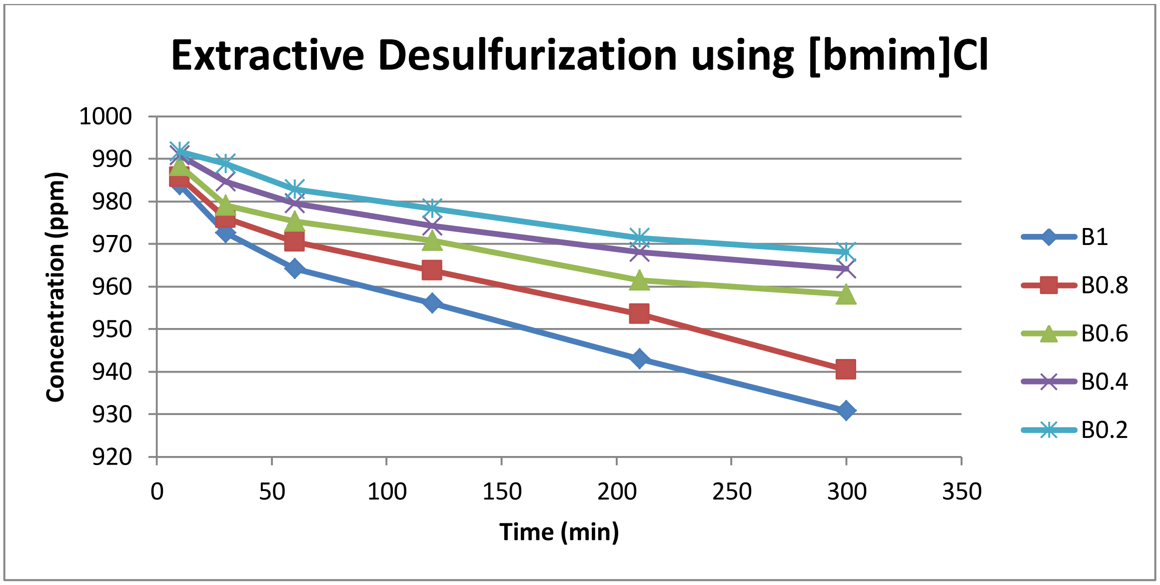


Figure 13: Extractive Desulfurization using [bmim]Cl Raw Data in Different [bmim]Cl:S-content ratio

Figure 13 is shows the extractive desulfurization using [bmim]Cl data for different [bmim]Cl:S-content ratio, whereas for B1, B0.8, B0.6, B0.4 and B0.2 [bmim]Cl:S-content ratio given as 1:1, 0.8:1, 0.6:1,0.4:1 and 0.2:1 respectively.

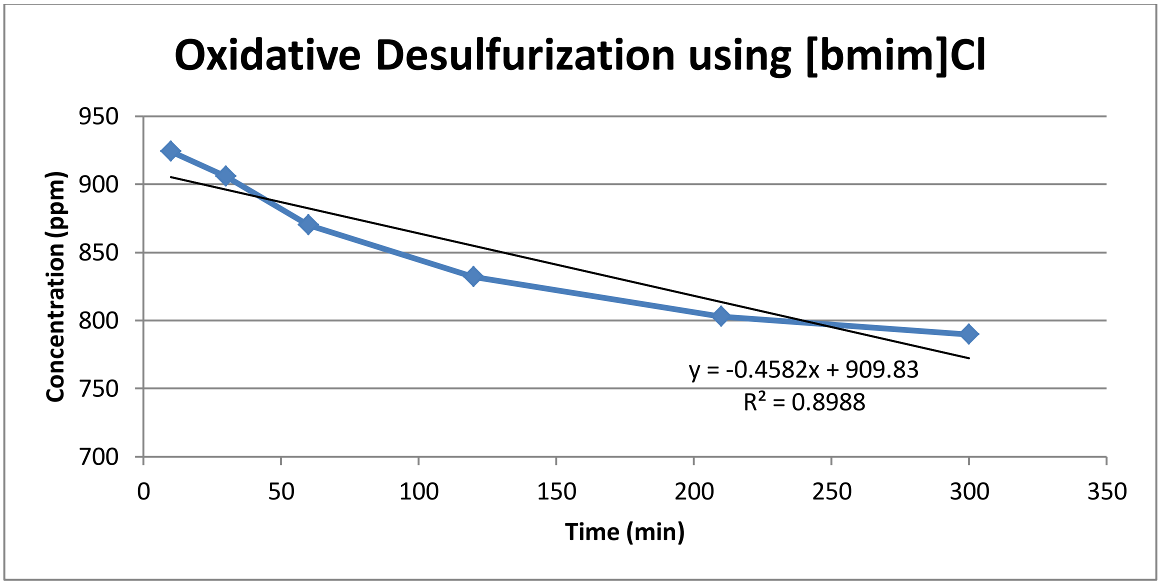


Figure 14: Oxidative Desulfurization using [bmim]Cl with ratio H_2O_2:[bmim]Cl:S-content (10:1:1)

The desulfurization goes deeper as the time goes by. However, at time 210min, the desulfurization become lesser and it shown that its approach its desulfurization limits.

4.2 Discussion

The objective of parts (a) experiment was to select the suitable concentration of S-content to be treated using oxidative desulfurization, extractive desulfurization using ionic liquid and also the combination of both methods. Thus for this project, the selective S-content concentration is 1000ppm due to its maximum value of the S-content in a normal reservoir. The experiment is run from 100ppm up to 1000ppm to help in calibration in analytical analysis part later.

For the experimental work part (b).i on the oxidative desulfurization, the desulfurization takes places based on the reaction of oxidant (hydrogen peroxide) and sulfur, where DBT is converted to its oxidized state (dibenzothiophenesulfone). In this state, the SO_2 from dibenzothiphenesulfone will be removed.

The calculation of sulfur removal (efficiency of sulfur removal) can be determined using the following equation;

$$Sulfur\ Removal, \% = \frac{Initial\ S\ content - Final\ S\ content}{Initial\ S\ content}\ x\ 100\%$$

From **Figure 12**, the raw data is being extracted to shown how much sulfur removal (%). This can be shown as below;

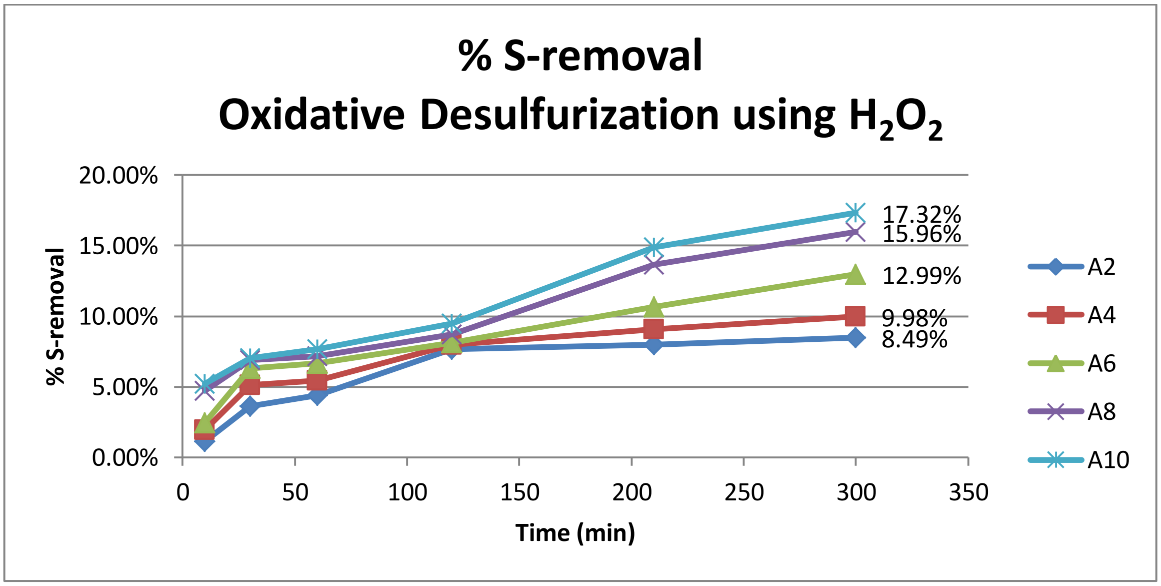


Figure 15: % S-removal in Oxidative Desulfurization using H_2O_2 for different S-content molar ratio

Figure 15 shows % S-removal using H_2O_2 for different S-content molar ratio. The highest S-removal (%) was shown by sample A10, 17.32% whereby the ratio of H_2O_2:S-content given as 10:1. It was followed by sample A8, A6, A4 and A2 whereby the % S-removal was 15.96%, 12.99%, 9.98% and 8.49% respectively. These result showed that the higher molar ratio of hydrogen peroxide to S-content leads to better oxidative desulfurization. Thus, it was decided to use the molar ratio of hydrogen peroxide to S-content as 10:1.

For experimental work of part (b).ii, desulfurization using ionic liquid was carried out using [bmim]Cl. The desulfurization may occur when the chlorine ion react with S-compound in DBT which enable it to remove S-compound from DBT. This is due to the high negativity of chlorine ion in [bmim]Cl.

From **Figure 13**, the raw data is being extracted to shown how much sulfur removal (%). This can be shown as below;

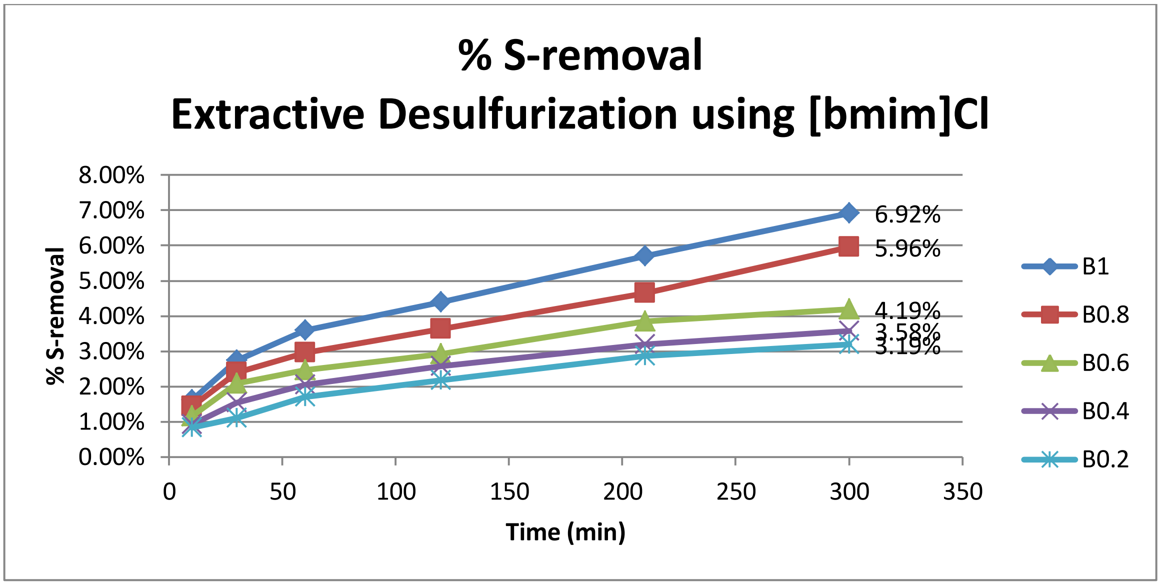


Figure 16: % S-removal in Extractive Desulfurization using [bmim]Cl for different S-content molar ratio

Figure 16 shows % S-removal using [bmim]Cl for different S-content molar ratio. The highest S-removal (%) was shown by sample B1, 6.92% whereby the ratio of [bmim]Cl:S-content given as 1:1. It was followed by sample B0.8, B0.6, B0.4 and B0.2 whereby the % S-removal was 5.96%, 4.19%, 3.58% and 3.19% respectively. These result showed that the higher molar ratio of ionic liquid to S-content leads to better oxidative desulfurization. Thus, it was decided to use the molar ratio of [bmim]Cl to S-content as 1:1.

The result showed that the efficiency of sulfur removal from dodecane could be improved with the combination of oxidant (H_2O_2) and ionic liquid ([bmim]Cl).

For the experimental work of part (c), the desulfurization was proposed using the combination H_2O_2 as an oxidant ionic liquid, [bmim]Cl as an extracting agent. In order to enhance the desulfurization, the highest ratio of hydrogen peroxide and [bmim]Cl was used.

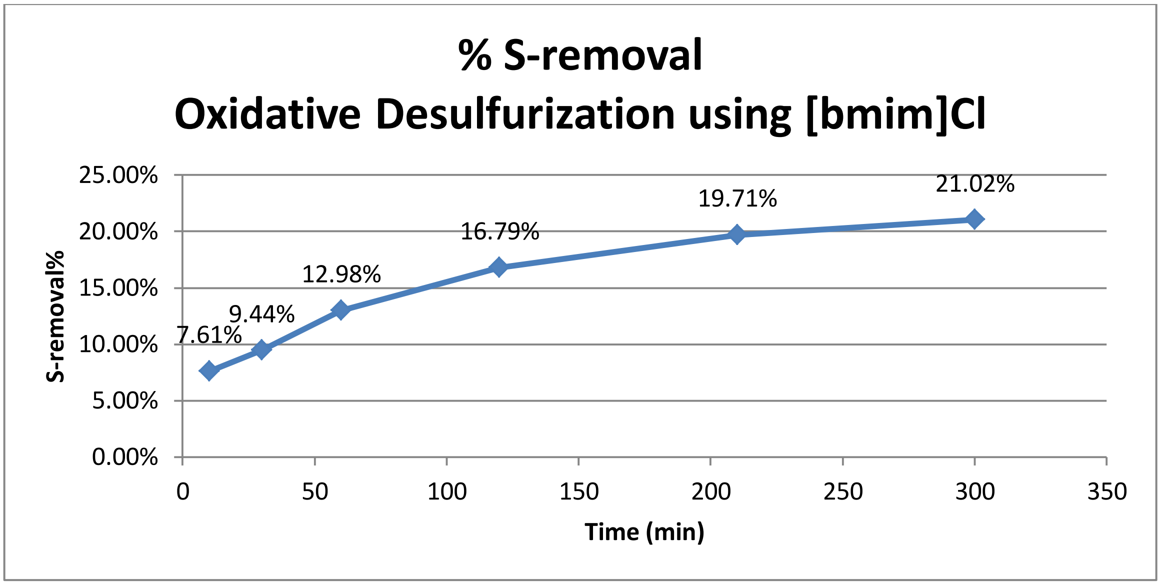


Figure 17: % S-removal in Oxidative Desulfurization using [bmim]Cl with ratio H_2O_2:[bmim]Cl:S-content (10:1:1)

From **Figure 17**, it was found that the highest S-removal (%) was 21.02% with interval time of 300min@5hours.

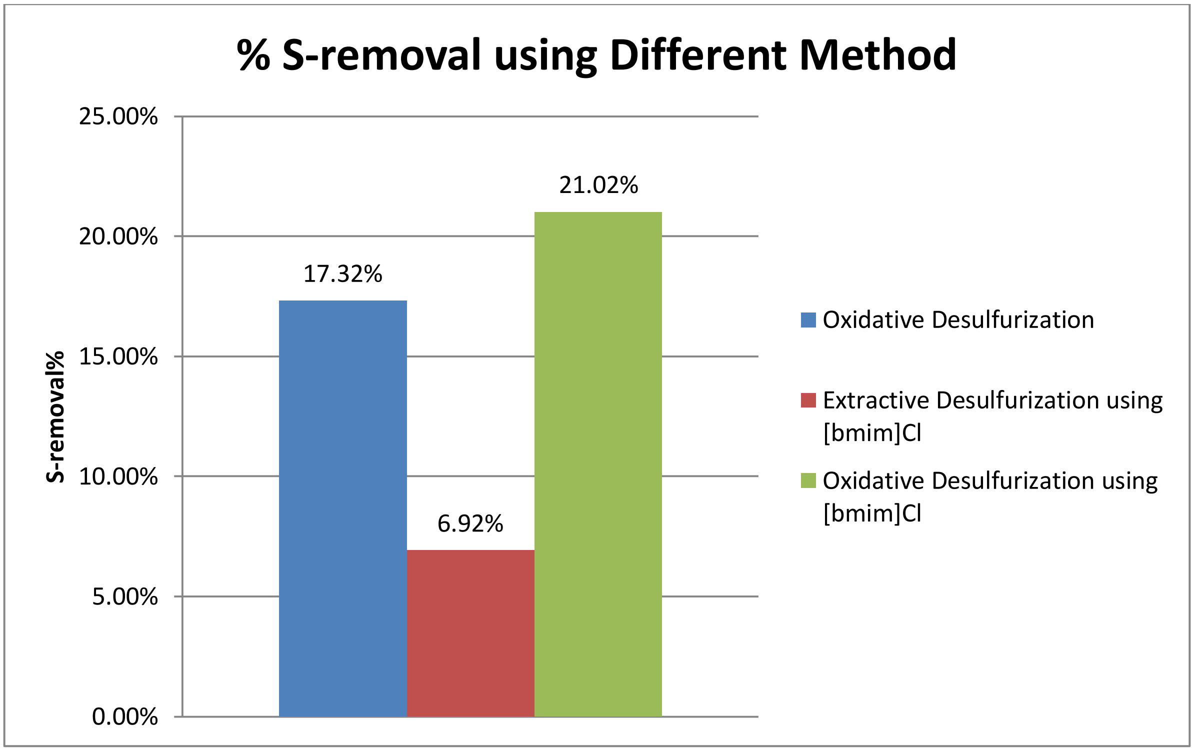


Figure 18: S-removal (%) in Different Method

Figure 18 shows the value of S-removal (%) using three different method, i.e, (i) oxidative desulfurization using hydrogen peroxide, (ii) extractive desulfurization using [bmim]Cl and (iii) oxidative desulfurization using hydrogen peroxide and [bmim]Cl. From here, its show that the highest s-removal are 21.02%, which is the oxidative desulfurization using hydrogen peroxide and [bmim]Cl. It proved that the efficiency of S-removal was increased using oxidative desulfurization with the combination of [bmim]Cl as an extracting agent.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The usage of [bmim]Cl ionic liquids has improved oxidative desulfurization of DBT from model oil significantly at room temperature compared to the system without ionic liquid. With [bmim]Cl ionic liquid, the efficiency of DBT removal was increased about 30%, i.e. from 17.32% removal (without [bmim]Cl to 21.02% removal. In addition, the ionic liquid played a role as the catalyst for ODS process.

5.2 Recommendation

a) Used other types of ionic liquids in extractive desulfurization, eg. [bmim][Ac].
b) Applying high molar ratio of oxidant (Hydrogen peroxide) and ionic liquids to S-content.
c) Used acetic acid as the solvent for Oxidative Desulfurization.

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APPENDICES

Appendix A – MSDS (Material Safety Data Sheet)

Product Name	Dodecane, 99%	Dibenzothiophene, 99%	Hydrogen Peroxide, 30%	1-butyl-3-methylimidazolium chloride, 99%
CAS#	112-40-3	132-65-0	7722-84-1	79917-90-1
Chemical Name	Dodecane	Dibenzothiophene	Hydrogen Peroxide	1-butyl-3-methylimidazolium chloride
Density	0.75 g/cm^3	1.25 g/cm^3	1.45 g/cm^3	1.08 g/cm^3
Chemical Formula	C12-H16	C12-H8-S	H2-02	C8-H15-Cl-N2
Physical State	Liquid	Powder	Liquid	Solid
Molecular Weight	170.34 g/mol	184.26 g/mol	34.01 g/mol	174.67 g/mol
Odour	Mild Aliphatic Hydrocarbon	Odourless	Odourless	Odourless
Colour	Colourless	Yellow to Green	Colourless	Colourless to slightly yellow
Boiling Point	216.3°C @760mmHg	332°C @760mmHg	108°C @760mmHg	65°C
Melting Point	-9.6°C	97°C	-33°C	Not Available
Volatility	Not Available	Not Available	Not Available	Absorb moisture
Stability	Stable	Stable under normal temperature and pressure	Stable, Contain a stabilizer	Hygroscopic

Appendix B – Calculation

Calculation of different concentration of DBT in model oil

To get 1000ppm of S-content in 50mL of model oil (dodecane), we need to calculate the amount of DBT, 97% used in term of grams; it can be shown in this equation;

$$X\ gram\ of\ DBT = \frac{(1000ppm)(50mL)(MW_{DBT})}{(1000000)\left(\frac{MW_S}{97\%}\right)}$$

Where the MW_{DBT} = 184.26 g/mol and MW_S = 32.065 g/mol, thus;

$$X\ gram\ of\ DBT = \frac{(1000ppm)(50mL)(184.26g/mol)}{(1000000)\left(\frac{32.065\ g/mol}{97\%}\right)} = 0.296\ gram\ of\ DBT$$

Other concentration can be shown below;

S-content in DBT (ppm)	dodecane(mL)	BDT 97%(g)
0	50.00	0.000
100	50.00	0.030
200	50.00	0.059
400	50.00	0.118
600	50.00	0.178
800	50.00	0.237
1000	50.00	0.296

Calculation for different molar ratio in experiment (b)

Since the S-content concentration chosen is 1000ppm in each 50mL of model oil (dodecane), thus the DBT required are 0.296 gram of DBT.

For part (b).i, in order too calculate molar ratio of H_2O_2, 30% to S-content, 2:1, we need to calculate the right amount of hydrogen peroxide in terms of gram; it can be shown in this equation;

$$X\ gram\ of\ H_2O_2 = \frac{(ratio)\left(MW_{H_2O_2}\right)(mass\ of\ BDT)}{(30\%)(MW_{DBT})}$$

Where the MW_{H2O2} = 34.0147 g/mol, thus;

$$X\ gram\ of\ H_2O_2, 30\% = \frac{(2)(34.0147 g/mol)(0.296\ g)}{(30\%)(184.26\ g/mol)} = 0.365\ gram\ of\ H_2O_2, 30\%$$

Other molar ratio can be shown below;

Molar ratio H_2O_2:S-content	dodecane (mL)	H2O2, 30% (g)
2:1	50.00	0.365
4:1	50.00	0.729
6:1	50.00	1.094
8:1	50.00	1.458
10:1	50.00	1.823

Same thing for part (b).ii, the equation can be applied too.

Where the $MW_{[bmim]Cl}$ = 174.67 g/mol, thus;

Mole Ratio [bmim]Cl:DBT	dodecane (mL)	[bmim]Cl (g)
1:1	50.00	0.281
0.8:1	50.00	0.225
0.6:1	50.00	0.168
0.4:1	50.00	0.112
0.2:1	50.00	0.056

Sulfur removal (%) calculation

The equation is given as below;

$$Sulfur\ Removal, \% = \frac{(Initial\ Sulfur\ Concentration - Final\ Sulfur\ Concentration)}{Initial\ Sulfur\ Concentration}$$

Since, the initial sulfur concentration is already fixed to 1000ppm, thus;

$$Sulfur\ Removal, \% = \frac{(1000\ ppm - Final\ Sulfur\ Concentration)}{1000\ ppm}$$

The final value of the sulfur concentration can be gained from GC-FID/SCD analytical analysis

Below shown the others calculation for each sample in term of sulfur removal, %

Time (min)	A2	S-rem.%	A4	S-rem.%	A6	S-rem.%	A8	S-rem.%	A10	S-rem.%
10	988.77	1.12%	980.80	1.92%	975.390	2.46%	952.685	4.73%	947.922	5.21%
30	963.90	3.61%	948.65	5.13%	937.130	6.29%	931.046	6.90%	929.559	7.04%
60	955.89	4.41%	945.50	5.45%	933.380	6.66%	928.491	7.15%	923.154	7.68%
120	923.33	7.67%	920.25	7.97%	918.847	8.12%	912.761	8.72%	905.121	9.49%
210	920.35	7.97%	909.10	9.09%	893.445	10.66%	863.490	13.65%	850.949	14.91%
300	915.12	8.49%	900.23	9.98%	870.144	12.99%	840.442	15.96%	826.776	17.32%
Time (min)	B1	S-rem.%	B0.8	S-rem.%	B0.6	S-rem.%	B0.4	S-rem.%	B0.2	S-rem.%
10	983.92	1.61%	985.69	1.43%	988.390	1.16%	990.796	0.92%	991.768	0.82%
30	972.56	2.74%	976.05	2.40%	979.130	2.09%	984.654	1.53%	988.897	1.11%
60	964.15	3.58%	970.49	2.95%	975.380	2.46%	979.501	2.05%	982.892	1.71%
120	956.12	4.39%	963.76	3.62%	970.847	2.92%	974.251	2.57%	978.325	2.17%
210	942.95	5.71%	953.49	4.65%	961.445	3.86%	968.100	3.19%	971.345	2.87%
300	930.78	6.92%	940.44	5.96%	958.144	4.19%	964.234	3.58%	968.123	3.19%
Time (min)	C	S-rem.%								
10	923.92	7.61%								
30	905.56	9.44%								
60	870.15	12.98%								
120	832.12	16.79%								
210	802.95	19.71%								
300	789.78	21.02%								

Appendix C – Analytical Analysis

DXR SMARTRAMAN Spectrometer

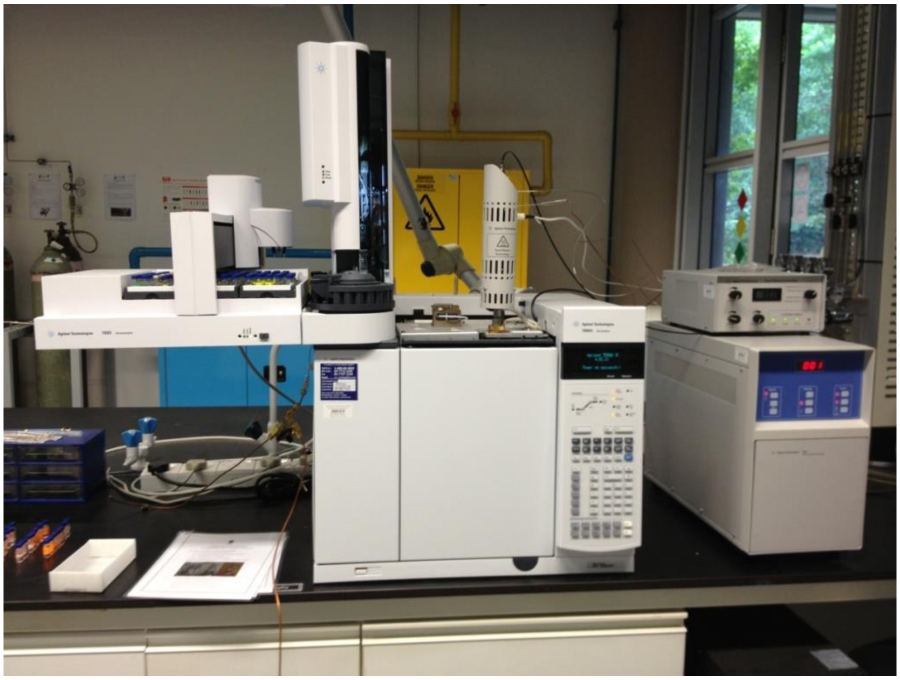
Top showing DXR SMARTRAMAN Spectrometer located in PETRONAS IONIC LIQUID CENTRE. Parameter used for laser are 783nm which purposely to detect the present of hydrocarbon and sulfur. However, since the S-content in the model oil (dodecane) is low, thus, the spectra didn't show a good result in term of quantitative analytical analysis. Thus, the result obtained can only be used as qualitative analytical analysis for this project.

Gas Chromatography – Flame Ionization Detector/Sulfur Chemiluminescene Detector

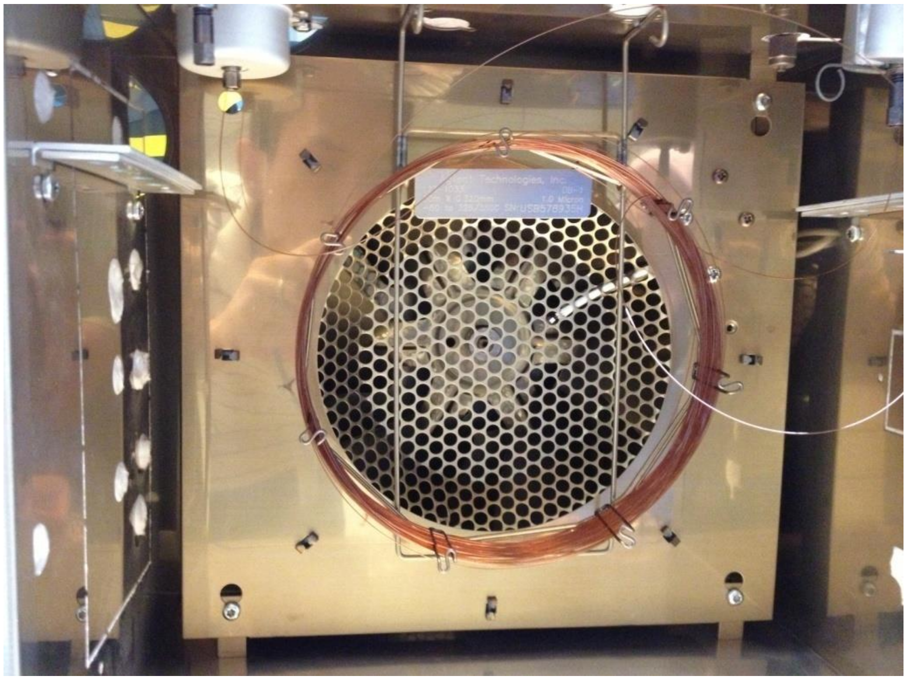
Parameter

Inlet Temperature = 340^0C
Split = 100:1
Flow (helium) = 2mL/min
Column = 30m X 320µm X 1µm + 5m guard column (DB-1 column)
Oven Temperature = 140 – 250^0C (10^0C/min, holding time 5min)
FID Detector Temperature = 250^0C
SCD Detector Temperature = 800^0C

Gas Chromatography – Flame Ionization Detector/Sulfur Chemiluminescene Detector



Top showing Gas Chromatography – Flame Ionization Detector/Sulfur Chemiluminescene Detector (GC–FID/SCD) located in PETRONAS IONIC LIQUID CENTRE.



Top Showing the column used in this GC analysis, (DB-1 column)