DEEP OXIDATIVE DESULPHURIZATION OF DIESEL USING IONIC LIQUID

By

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Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Technology (Hons)
(Chemical Engineering)

Sept 2011

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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Approved by,

(Mr Mohd Faisal Taha)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

SEPT 2011

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 of person.

(NURUL ATIKAH ABDULLAH)
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ABSTRACT

Environmental concern has driven the need to remove sulphur compound in fuel. Since, oxidative desulfurization is conducted under very mild reaction conditions, much attention has been recently devoted to this process. In this study sulphur compound in dodecane was oxidized by oxidizing agent. The correspond sulfone and sulfoxide are more soluble in ionic liquid and will not recombine with fuel. Thus, this ensures for better sulphur removal performance. The aim of this project is to study the potential of ionic liquid to remove sulphur in diesel. Three types ionic liquid and 5 different oxidant/sulphur ratio was used to determine the optimum system for oxidative desulphurization. The best oxidant: sulphur ratio is 5: 1, with 30% sluphur removal. The best ionic liquid is bmim octyl sulphate, with sulphur removal up to 70%. The best condition was then used to remove sulphur from diesel. Sulphur removal percentage of diesel was around 50%. Based on the result obtained, bmim octyl sulphate showed a good potential as axtractiong agent for sulphur removal from diesel.

ACKNOWLEDGEMENTS

First of all, I would like to thank my supervisor, Mr. Faisal B. Taha, and my co-supervisor, AP Dr Chong Fai Kait, for their guidance and inspiring motivation to work on this Final Year Project 2 (FYP 2). Without their contribution, I would not have managed to gain this much knowledge on the project. My sincere appreciation goes to Ms. Nur Aisyah, the Research Assistant who also working on this project. She has helped me a lot in terms of the research methods and the literatures related on the project. I would also like to thank my internal examiner, Dr. Moulay Rachid Baba who has been helping me out on the project during my FYP1. Without his views and advice, I would have not gotten a clear picture on the project like I have now. Finally, I would like to thank all my friends at Universiti Teknologi PETRONAS (UTP) especially my coursemates for giving me the moral support and sharing their knowledge with me.

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CHAPTER 1

PROJECT BACKGROUND

1.1 Background of Study

1.1.1 History of Gasoline[1]

In the late 19th Century the most suitable fuels for the automobile were coal tar distillates and the lighter fractions from the distillation of crude oil. During the early 20th Century the oil companies were producing gasoline as a simple distillate from petroleum, but the automotive engines were rapidly improved and required a more suitable fuel. Typical in mid-1920s, gasoline contained 40 - 60 octane. By the 1940s, catalytic cracking was introduced and gasoline compositions became consistent between brands during the various seasons.

The 1950s saw the start of the increase of the compression ratio, which lead to requirement of higher octane number fuels. Lead levels were increased, and some new refining processes such as hydrocracking , specifically designed to provide hydrocarbons components with good lead response and octane, were introduced. Minor improvements were made to gasoline formulations to improve yields and octane until the 1970s, where unleaded fuels were introduced to protect the exhaust catalysts and for environmental reasons as well. From 1970 until 1990 gasoline were slowly changed and improved. Later, Cleaner fuel with minimum lead and sulphur were used widely in the world.

1.1.2 Sulphur Reduction in Transportation fuel

Sulphur is a compound found naturally in crude oil. In refinery sulphur acts as a poison to after-treatment systems. It usually damage catalyst and produce off spec product. The low sulphur level in crude oil, reduce emissions of sulphur oxide and produce better engine performance. Sulphur compounds in fuels are a major source of pollution. On combustion, they are converted to sulphur oxides which, rise to sulphur oxyacids that contribute to acid rain. When sulphur is emitted into the air, its produce negative environmental and health effects. Sulphur emitted will react with water in the air to produce sulphuric acid which cause environmental damage to forests, crops, water supplies and contribute to acid rain. Industry and policymakers around the world have placed emphasis on reducing sulphur limits in fuels for decades now, but variations in those limits remained. [6]

Specification for vehicle fuel requires a large reduction of sulphur content for both gasoline and diesel. As for Malaysia, current diesel sulphur restriction is 1,000 to 10,000 ppm. As for gasoline, the sulphur limit is 1,500 to 2,000 ppm. [2]

1.2 Conventional Sulphur Removal Process

1.2.1 Hydrodesulphurization

The common industrial process to treat crude oil is hydrodesulphurization process (HDS). HDS is a process which light oil is heated, mixed with hydrogen and fed to a reactor packed with a palleted catalyst. Typical reactor temperature range is between 300°C to 380°C. At this temperature, the feed is expected to be fully or partially vaporized. Reaction pressure range between 15 to 90 bar depending on the difficulty of removing the sulphur. In this process, sulphur compound is converted into hydrogen sulfide and hydrocarbon. In production of light oil such a diesel, the feed and hydrogen mixture flow downward through the reactor passing around and through the particulate catalyst. Upon leaving the reactor the fuel and hydrogen mixture flow through a series of mechanical devices to separate and recycle the hydrogen, remove the generated H_2S and recovering the product. HDS catalyst will slowly lose activity during the operation. Therefore it musts be removed and replaced after few years of operation. [11]

1.2.2 Disadvantages of Hydrodesulphurization

This process is very costly. This is due to several reasons

- Use of metal catalyst such as Nickel/Molybdenum catalyst
- Critical operating condition(require high pressure and high temperature)

HDS is very effective in removing aliphatic sulphur compound such as thiol, sulfide, disulfide and so on. However, it is only slightly effective in removing aromatic sulphur compound such as thiophene, dibenzyl thiophene(DBT) and etc.

1.3 Problem Statement

In brief, HDS is quite costly and ineffective to remove aromatic sulphur compound such as thiophene, dibenzothiophene and etc. With the stated disadvantages of this conventional sulphur removal method, many technologies have been developed to encounter such problem. Recently, oxidative desulphurization by using oxidant such as peroxide acid combine with the extraction of ionic liquid is showed the potential to achieve low sulphur transportation fuel.

CHAPTER 2

LITERATURE REVIEW

2.1 Extractive Desulphurization

2.1.1 Ionic Liquid (IL)

Ionic liquids provide an important green alternative in removing such compounds by liquid–liquid extraction. Ionic liquid is the excellent substitute to other common solvent due to its property, such as designable, highly solvating, high-thermal stability, very low vapour pressure, low flammability, non corrosive, low toxicity and high viscosity [12]. Besides that, IL also have higher sulphur extracting ability and virtually immiscible with diesel, preventing cross contamination. Used IL can be recovered and regenerate.

2.1.2 Sulphur Extraction by Ionic Liquid

Ionic liquid chosen for this project are 1-butyl-3-methyl imidazolium acetate (bmim acetate), 1-butyl-3-methyl imidazolium chloride (bmimCl), and 1-butyl-3-methyl imidazolium octyl sulfate (bmimOS).

Sulphur removal by using ionic liquid only applied liquid- liquid extraction technique. Liquid-liquid extraction is a mass transfer operation in which a solution which is brought into intimate contact with an immiscible or slightly immiscible liquid in order to achieve transfer of the solute from the feed to the solvent [8].

In this process, Ionic Liquid will be mixed with the model oil that contain sulphur. The mixture is stirred at suitable reaction temperature. A biphasic mixture will produced. The upper phase of the mixture is the oil phase and the bottom phase is the ionic liquid phase. Sulphur compound will dissolve in the ionic liquid phase. Ionic liquid that contained aromatic ring structure with large π bond will interact with DBT (sulphur compound). Sulphur compound will be extracted to the Ionic Liquid phase due to easily polarizes sulphur molecule [6].

Many ionic liquid has been used as extracting agent in extraction process such as B[mim]PF_6, pyridium based IL and Imidazolium IL and etc. As a general rule, ILs themselves, in the absence of oxidants, fail to provide a high degree of sulfur removal. Usually, sulphur removal percent varies within range of 10% to 40% (at room temperature) [6,11,12].

2.2 Oxidative Desulphurization

2.2.1 Organic Peracids

Oxidant is compound that can donate oxygen atom to sulphur in mechaptan such as sulfides, disulfides, thiophene . For example peroxy organic acid, hydroperoxide, nitrogen oxides peroxy salt and ozone.

Peracids are very powerful oxidizing agent and able to oxidize sulphur component. These compound are usually very reactive and corrosive. Thus, the reaction must be conducted in-situ. Usually, the amount of oxidizing agent use I a lot, that make the reaction not feasible economically. With that, addition of catalyst is important to oxidize sulphur compound more effectively. Most common catalysts used are transition of metal salt like tungsten salt, modified activated carbon, transition and strong acid like concentrated sulphuric acid [11].

In this study, a blank experiment was conducted to check the ability of bmim acetate to replace acetic acid in order to produce peroxy acid. If bmim acetate is capable to replace acetic acid, this reaction could be more feasible economicly. To verify the present of peroxy acid, Raman spectroscopy was used to check the existence of peroxy acid.

2.2.2 Hydrogen Peroxide

Hydrogen peroxide is the candidate as an oxidizing agent and it only gives water as by-product. Also it is cheap, nonpolluting, not strongly corrosive and commercially available.

2.2.2 Oxidation Process

Sulphur containing compound are oxidized using selected oxidant to form compound that can be preferentially exacted from fuel due to their increased relative polarity. Hydrogen Peroxide, H_2O_2 converts carboxylic acids (RCOOH) into peroxy acids (RCOOOH), which act as a strong oxidizing agent.

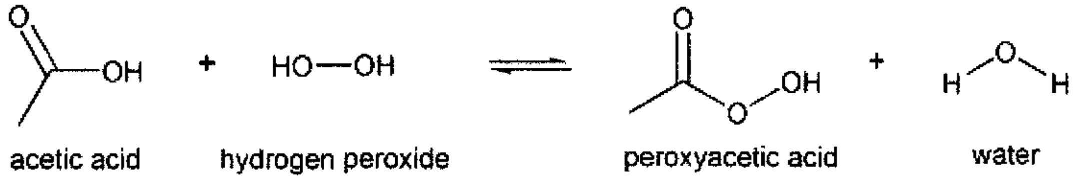


Figure 2.1: reaction of acetic acid and hydrogen peroxy

Usually, oxidative desulphurization is a two stage process of oxidation and liquid extraction of the oxidized sulphur compound. In the first stage, sulphur species in the feedstock (model oil) is oxidized into sulphoxides and sulphone [7].

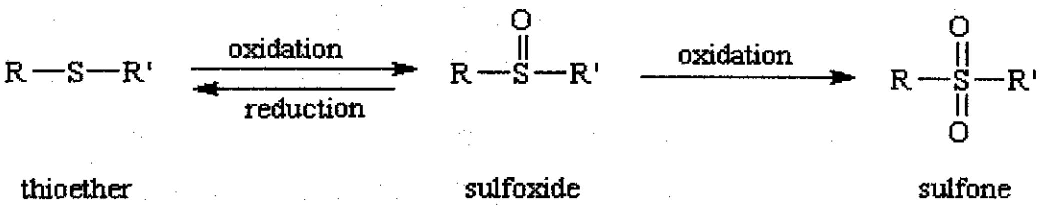


Figure 2.2: oxidation of sulphur compound

Sulphoxide and sulfone has higher polarity compared to the parental sulphide, and more preferentially extracted from the feed stock.

For the second stage, sulphone will be removed by the extraction of the selective polar solvent. Usually, solvent used are those boiling point below the initial boiling point of the feed-stock. Potential extractants are dimethylformamide (DMF) and acetonitrile.[7]

2.3 Combination of both Oxidative and Extractive Desulphurization

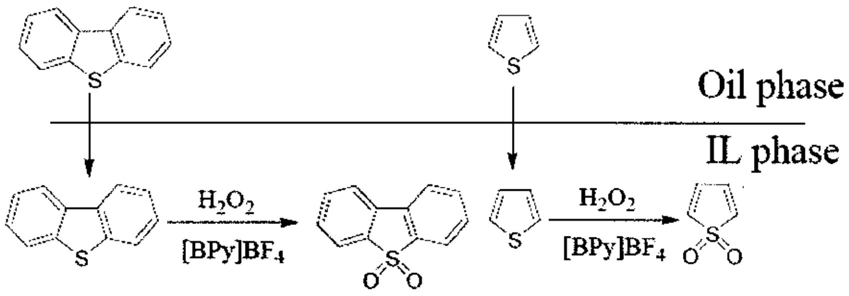


Figure 2.3: Desulphurisation Reactions

(Process of extraction- extraction of thiophene and DBT in model oil by IL-H2O2 system)

Oxidative –Extractive Desulphurization is a sulphur removal method that involves both ionic liquid and oxidation process. In brief, the desulphurization process is achieved when peroxy acid is added to the extraction system whereby peroxy acid is used to oxidize sulphur component into correspond sulfone which were extracted by the ionic liquid.[6]

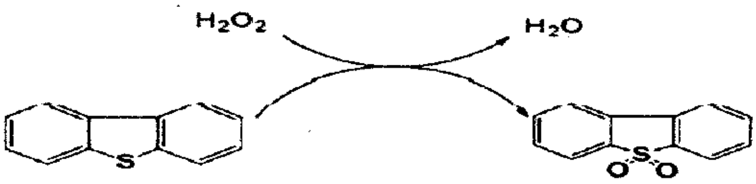


Figure 2.4 : Oxidation of dibenzyl thiophene

Hydrogen peroxide dissolved in the ionic liquid and decomposed into hydroxyl radical in the system. Hydroxyl radical oxidized dibenzylthiophene(DBT) into correspond sulfoxide. Since the polarity of sulfoxide is high, it is remained in the ionic liquid phase.

Various studies showed that oxidative desulphurization using ionic liquid has more effective sulphur removal as compared to extractive sulphur removal alone [6].

CHAPTER 3

METHODOLOGY

3.1 Ionic Liquid

In this project, commercial ionic liquid was used due to time constraint.

3.2 Model Oil

Weigh 5.00g of dibenzyl thiophene(DBT) and place in 200mL volumetric flask. Add dodecane until reach volume graduation mark to produce 200mL solution. Stir the mixture by using magnetic stirrer at 400rpm. After all DBT is dissolved, take 0.5mL of model oil sample. Determine the initial sulphur content by using Gas Chromatography.

3.3 Oxidant

Mix Hydrogen Peroxide acetic acid and sulphuric acid with the molar ratio of H_2O_2/S – 1:1 mol/mol, H_2SO_4/S - 1:1 and CH_3COOH/S – 2:1 mol/mol. Varies molar ratio of H_2O_2/S from 1:1, 2:1, 3:1, 4:1 and 5:1 [7].

3.4 Experiment Procedures

3.4.1 To determine the best H_2O_2/S ratio(Oxidative desulphurization).[7]

3.4.1.1. For 1:1 H_2O_2/S molar ratio, measure 0.0145mL of Hydrogen Peroxide(30%), 0.054mL of acetic acid and 0.025mL of concentrated sulphuric acid by using fisher 10µL - 100µL micro pipette.

3.4.1.2. Place the measured chemical into 25mL of two neck round bottom flask.

3.4.1.3. Measure 20mL of model oil using measuring cylinder and add into the three neck round bottom flask.

1.4 Objective and Scope of Study

This project was conducted to achieve the following objectives.

1. To study the possibility of using ionic liquid to remove sulphur from diesel.
2. To determine the optimum amount of hydrogen peroxide and acetic acid mixture for oxidation sulphur species
3. To determine the best ionic liquid to combined with hydrogen peroxide and acetic acid.

To achieve the goal of this study, experimental work was conducted to study the effectiveness of oxidative desulphurization by using peroxy acid as oxidant and several ionic liquids such as bmim acetate, bmim chloride and bmim octyl sulfate.

3.4.1.4. Set magnetic stirer's at 400rpm.

3.4.1.5. Take 0.5mL sample by using 1mL syringe at each 10min, 20min, 30min, 1hour, 2hour, 3hour, 4hour and 5hour.

3.4.1.6. Centrifuge sample at 25 x 1000 rpm for 5minutes.

3.4.1.7. Determine sulphur content in each sample by using Gas Chromatography.

3.4.1.8. Repeat step 1 until 6 by using 0.0289mL, 0.0434mL, 0.05786mL and 0.07233mL of hydrogen peroxide, for 2:1, 3:1, 4:1 and 5:1 molar ratio.

3.4.1.9. Determine the best H_2O_2/S ratio by plotting graph of sulphur removal versus time.

3.4.2 Oxidative desulphurization(substitute acetic acid with BmimAc)

3.4.2.1. Measure hydrogen peroxide and sulphuric acid according to the best H_2O_2/S molar ratio.

3.4.2.2. Measure 0.1775mL of bmim acetate and place it in the two neck round bottom flask follow by hydrogen peroxide and sulphuric acid.

3.4.2.3. Add 20mL of model oil and set magnetic stirrer at 400rpm.

3.4.2.4. Take sample at 10min, 20min, 30min, 1hour, 2hour, 3hour, 4hour and 5hour.

3.4.2.5. Centrifuge sample and test with Gas chromatography.

3.4.2.6. Check sample using Raman spectroscopy to check the present of peroxy acid.

3.4.3 Oxidative and Extractive desulphurization.

3.4.3.1. Measure hydrogen peroxide, acetic acid and sulphuric acid according to the best H_2O_2/S ratio.

3.4.3.2. Place 20mL of Bmim Acetate into 50mL of three neck bottom round flask follow with hydrogen peroxide, acetic acid and sulphuric acid.

3.4.3.3. Add 20mL of model oil and set magnetic stirrer at 400rpm.

3.4.3.4. Take sample at 10min, 20min, 30min, 1hour, 2hour, 3hour, 4hour and 5hour.

3.4.3.5. Centrifuge sample and test with Gas chromatography

3.4.3.6. Repeat step 2-5 by using bmim chloride and bmim octyl sulfide.

3.4.3.7. Determine the best ionic liquid by plotting graph of percentage sulphur removal versus time.

3.4.4 Oxidative and Extractive desulphurization on Diesel.

3.4.4.1. Measure hydrogen peroxide, acetic acid and sulphuric acid according to the best H_2O_2/S ratio.

3.4.4.2. Place 10gram of the best Ionic Liquid in 50mL of three neck bottom round flask follow with hydrogen peroxide, acetic acid and sulphuric acid.

3.4.4.3. Add 10gram of Diesel and set magnetic stirrer at 400rpm.

3.4.4.4. Take sample at before extraction and after 5hour.

3.4.4.5. Determine the best Ionic liquid by plotting graph of percentage sulphur removal versus time.

3.4.4.6. Repeat step 1 to 5, but reducing the amount Ionic liquid to 5gram.

3.2 Instrument/Tools:

3.2.1 Density Meter

Density Meter used is model Anton Paar DMA 5000M. 4mL of model oil is injected. Temperature is set at the range of 20°C to 40°C. After the process is done, hexane is injected. Hexane is the solvent for dodecane. After that, ethanol is injected to dissolve hexane. The right solvent need to be used to clean the density meter.

3.2.2 Gas Chromatography (GC)

Gas Chromatography used is equipped with a flame photometric detector (GC-FPD). All sample are tested using the same standard.

3.2.3 Centrifuge

2 sample of model oil is inserted in the centrifuge equipment. The sample need to parallel to each other. The machine is set at 25 x 1000rpm for 5 minutes.

CHAPTER 4

RESULTS AND DISCUSSION

3.1 Oxidative Desulphurization

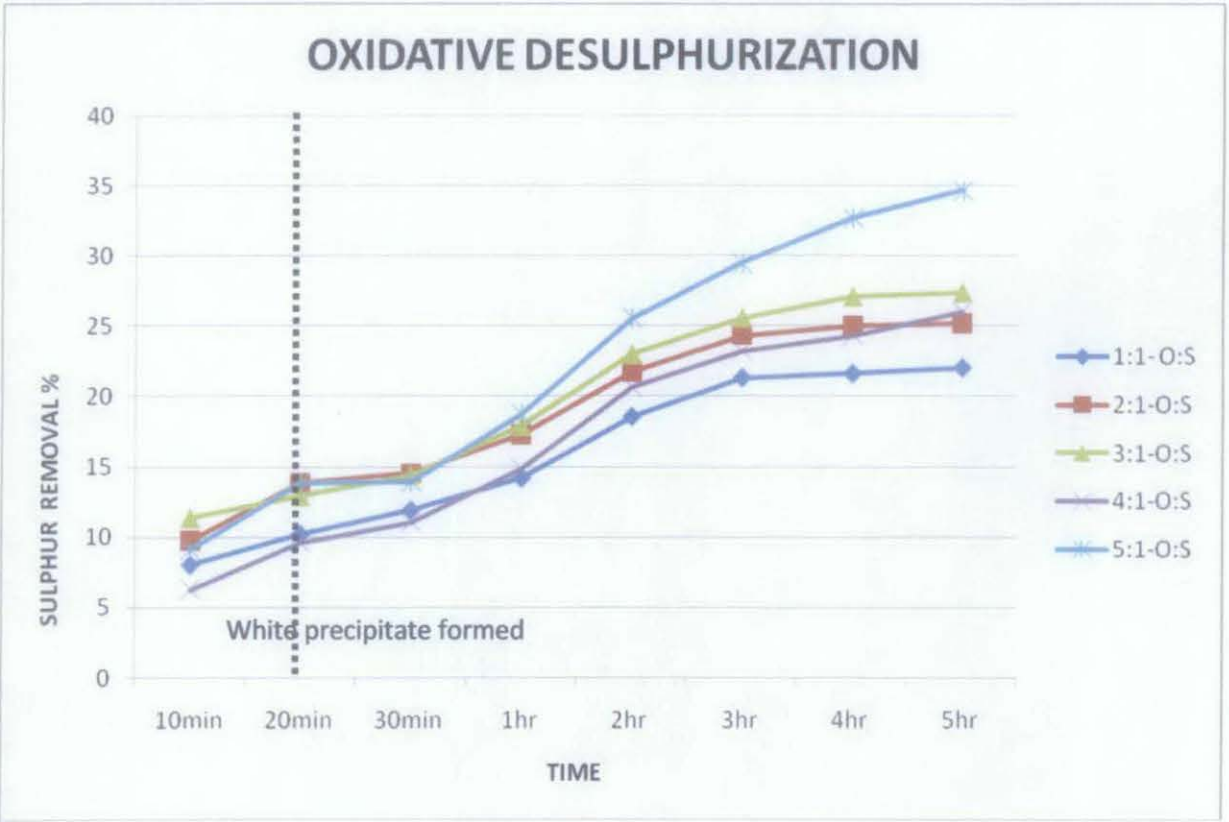
Initial sulphur content: 3.680ppm

TABLE 4.1 : Oxidative Desulphurization Data

Time.	H_2O_2/S molar ratio (ppm)				
	1:1	2:1	3:1	4:1	5:1
10min	3.384	3.321	3.261	3.45	3.346
20min	3.304	3.169	3.205	3.328	3.281
30min	3.241	3.145	3.149	3.274	3.227
1hr	3.158	3.044	3.021	3.134	3.083
2hr	2.997	2.88	2.834	2.922	2.895
3hr	2.896	2.785	2.738	2.827	2.764
4hr	2.885	2.761	2.683	2.786	2.654
5hr	2.87	2.753	2.672	2.724	2.57

TABLE 4.2: Percentage of Sulphur Removal

Time.	H_2O_2/S molar ratio				
	1:1	2:1	3:1	4:1	5:1
10min	8.04	9.75	11.38	6.25	9.07
20min	10.22	13.88	12.90	9.57	10.84
30min	11.90	14.53	14.42	11.03	12.309
1hr	14.18	17.28	17.09	14.84	16.22
2hr	18.56	21.73	22.98	20.60	21.33
3hr	21.30	24.32	25.59	23.18	24.89
4hr	21.60	24.97	27.09	24.29	27.88
5hr	22.01	25.19	27.39	25.98	30.16



Graph 4.1 : Oxidative Desulphurization

Observation:

White precipitate formed after 20 min of mixing in each experiment.

Discussion:

According to the stoichiometric reaction, 2 mol of hydrogen peroxide was consumed for every 1 mol of sulfur-containing compound. Based on the results, the higher the amount of hydrogen peroxide used, the higher sulphur removal percentage. As the molar ratio of H_2O_2 and DBT increased from 1:1 to 5:1, the removal of DBT from the model oil increased from 20% to 30%. The best sulphur removal was obtained when the molar ratio of H_2O_2 : S was 5:1, followeed by 3:1, 4:1, 2:1 and 1:1. In general, greater amount of hydrogen peroxide would give greater sulphur removal. This could be due to sulphone and sulphoxide produced from sulphur oxidation that was easily dissolved in ionic liquid as compared to parental sulphur as they have higher polarity.

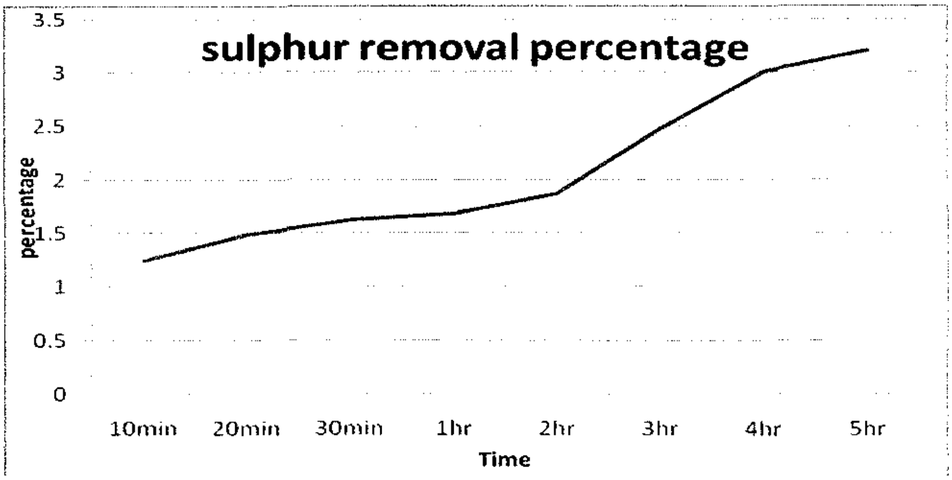
White precipitate appeared in the liquid-phase after 20 minutes of desulphurization. Work done by Xinrui Zhou and friend, also used DBT as their sulphur compound [13]. In that study, MS and NMR were used to confirm the chemical structure of the precipitate. Based on their results, white precipitate is $DBTO_2$. Since sulphur compound used in this experiment is the same as used by Xinrui Zhou and friend, the white precipitate produced in this experiment could also be $DBTO_2$ [13].

3.2 Blank experiment

Table 4.3: Blank experiment data

H_2O_2:S	5:1
10min	3.634
20min	3.625
30min	3.620
1hr	3.618
2hr	3.611
3hr	3.589
4hr	3.569
5hr	3.562

H_2O_2:S	Percentage removal
10min	3.634
20min	3.625
30min	3.620
1hr	3.618
2hr	3.611
3hr	3.589
4hr	3.569
5hr	3.562



Graph 4.2: sulphur removal performance in blank experiment

Discussion:

Sulphur removal percentage was low. Thus, this shows that COOH- in bmim acetate was not capable to react with hydrogen peroxide to produce peroxy acid. Thus, bmim acetate only suitable to act as an extractor rather than an oxidant. The COOH- ions in bmim acetate could act as oxidant, if excess amount of Bmim Acetate was used.

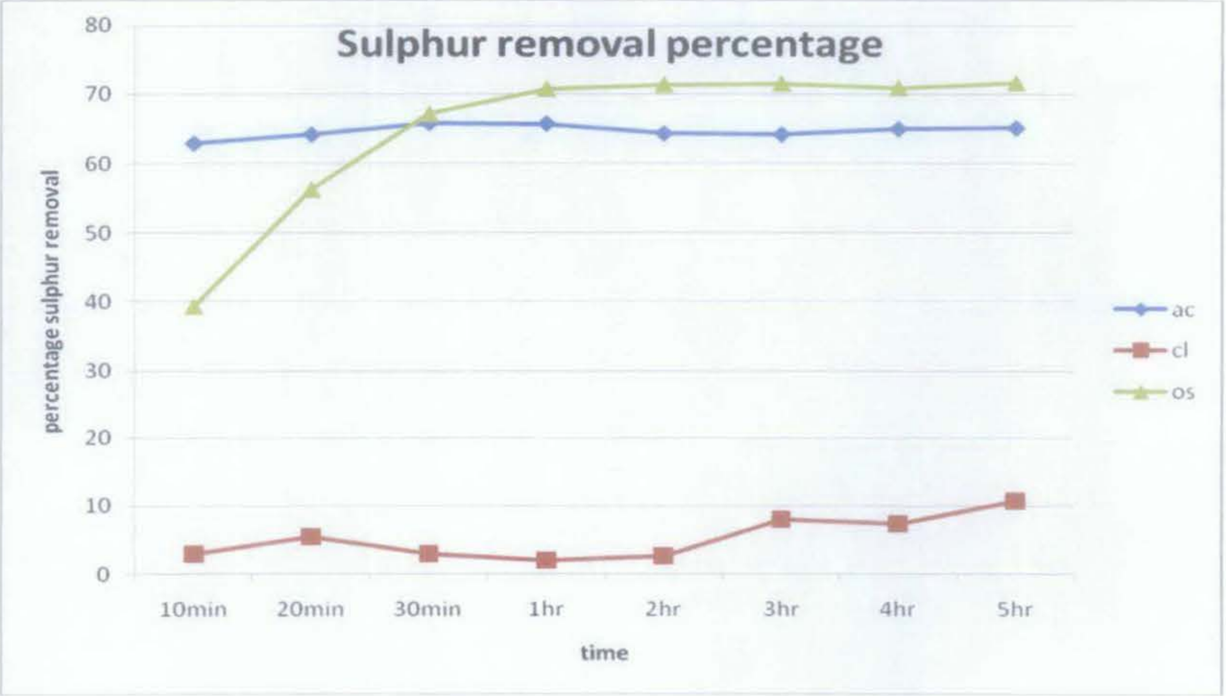
3.3 Oxidative and Extractive desulphurization

Table 4.4 : Oxidative- Extractive desulphursation data

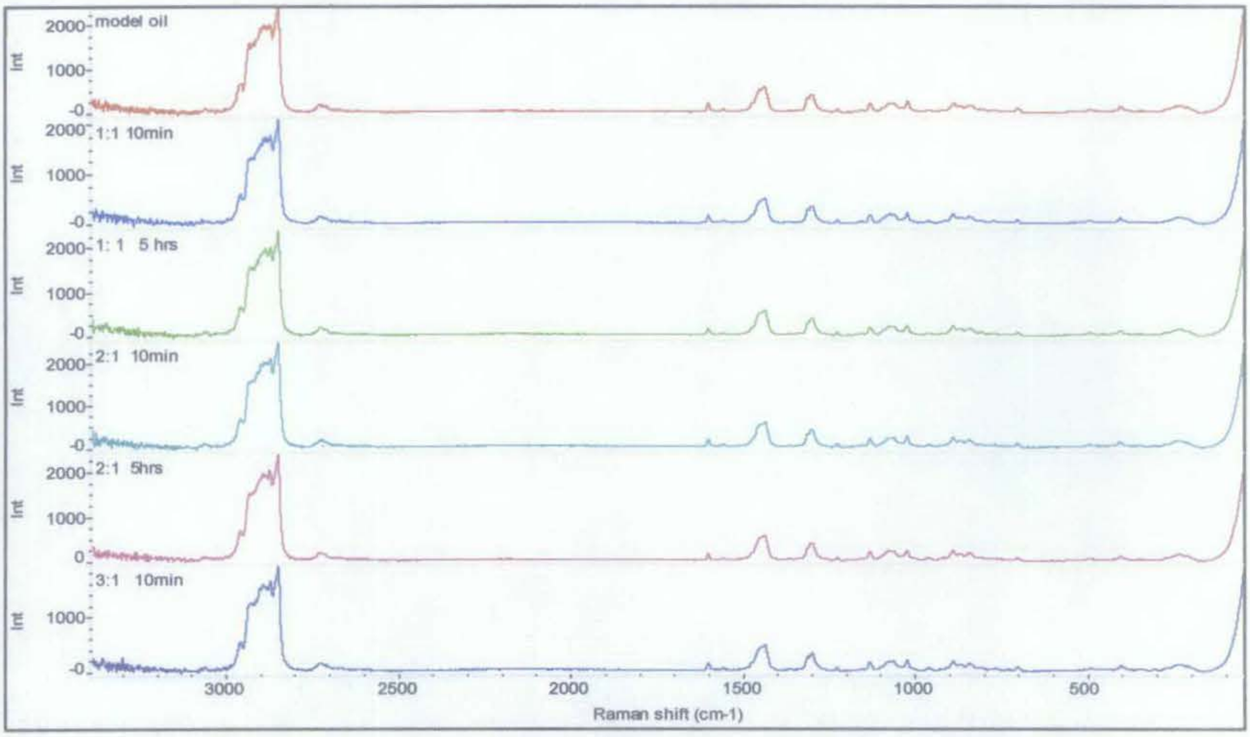
Time	Sulphur percentage(%)		
	Bmim Acetate	Bmim Chloride	Bmim Octyl Sulfate
10min	1.3654	3.571	2.233
20min	1.31974	3.479	1.611
30min	1.25884	3.573	1.21
1hr	1.26311	3.607	1.078
2hr	1.314	3.582	1.055
3hr	1.319	3.389	1.049
4hr	1.29	3.411	1.072
5hr	1.285	3.2882	1.045

Table 4.4 : Oxidative- Extractive desulphursation data

Time	Sulphur removal percentage		
	Bmim Acetate	Bmim Chloride	Bmim Octyl Sulfate
10min	62.89	1.98	39.31
20min	64.1	2.66	56.2
30min	65.79	2.907	67.1
1hr	65.67	2.962	70.7
2hr	64.29	5.46	71.33
3hr	64.16	7.309	71.49
4hr	64.94	7.907	71.60
5hr	65.08	10.64	71.86



Graph 4.3 : Oxidative- Extractive Desulphurization



Graph 4.4 : Model Oil Structure- Raman Spectroscopy

Discussion:

Based on the results obtained, the best ionic liquid for maximum DBT removal was bmim octyl sulfide, followed by bmim acetate and bmim chloride. Among these three ILs studied, the most suitable for desulfurization of diesel fuel was found to be bmim octyl sulfate which is fairly highly reactive toward sulfur, poorly soluble in fuel, and does not affects other properties of the fuel.

In this experiment, three processes take place. First, the extraction of sulfur-compounds by IL from the dodecane. Second, the carboxylic acid group (−COOH) in acetic acid reacts with H_2O_2 in acidic environments, and a peroxycarboxylic acids group (−COOOH) with oxidation functions will be generated. Third, the group (−COOOH) oxidized sulfur compounds to the corresponding sulfones, then sulfones is extracted into the IL.

Raman Spectroscopy result (graph 4.4) show that model oil structure does not change after desulphurization process takes place. This proves that ionic liquid and oxidant does not destroyed dodecane structure.

3.3 Application on Diesel

Result

Table 4.5: Initial sulphur reading

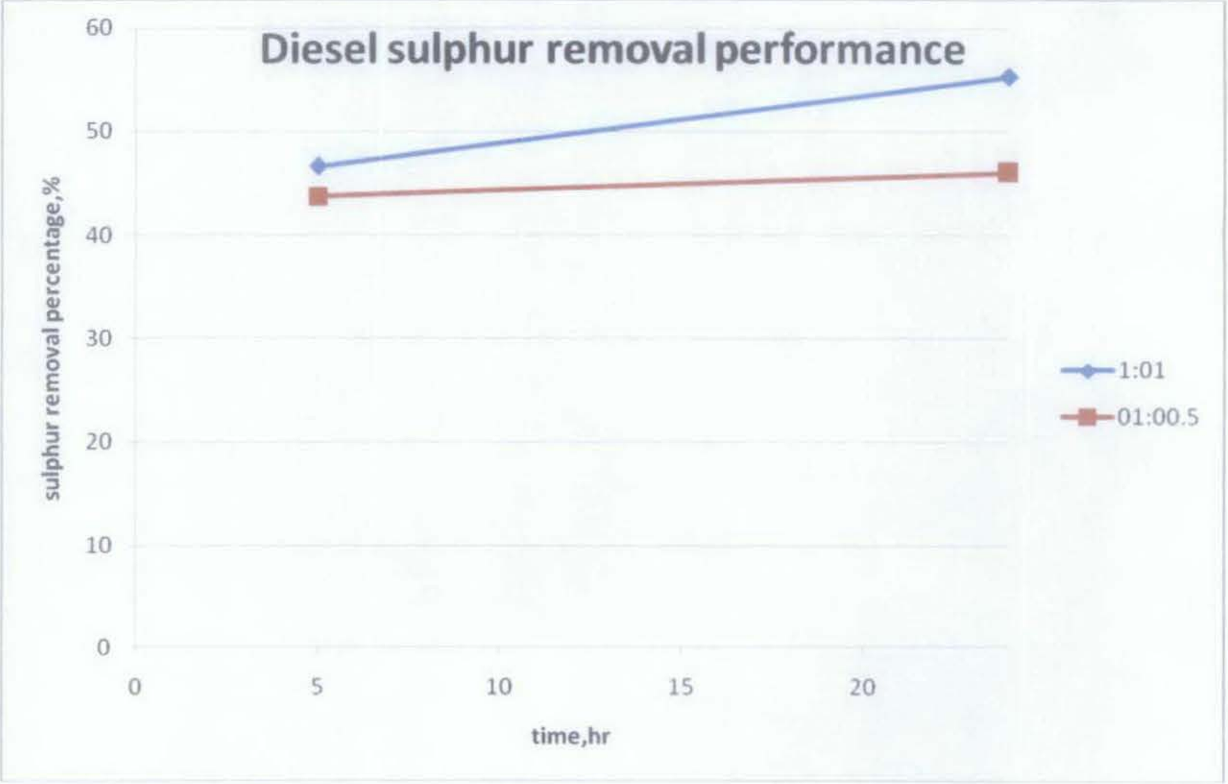
No	Reading (w/w)
1	1.195
2	1.018
3	0.993
4	0.993
Average	1.0498

Table 4.6: Data at Diesel: Ionic Liquid mass ratio is 1:1

No	5hr	1day
1	0.57	0.466
2	0.532	0.456
3	0.579	0.471
4		0.484
Average	0.56	0.469
Removal percentage	46.62	55.29

Table 4.7: Data at Diesel: Ionic Liquid mass ratio is 1:0.5

No	5hr	1day
1	0.543	0,591
2	0.609	0.484
3	0.699	0.575
4	0.593	0.617
Average	0.591	0.617
Removal percentage	43.7	46.01



Graph 4.5: Diesel performance

Disscusion:

Sulphur removal in diesel showed promising results with up to 50% removal. Diesel performance was expected to be lower than model oil due to diesel complex structure including the presence of impurities and various sulphur compound.

Since, ionic liquid was capable to remove sulphur from diesel, another experiment was conducted to minimize the amount of ionic liquid used. For practical considerations, and taking in account the high cost of ILs , the ratio of model oil to Ionic Liquid was reduced to 1:0.5. Based on the results obtained, as the amount of ionic liquid was reduced by halves, sulphur removal percentage was found to be decrease.

CHAPTER 5

CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

Based on the results obtained from this study, It can be can conclude that:

- Sulphur removal efficiency increase with the incresing of Oxidant : Sulphur molar ratio.
- bmim octyl sulphate is the best ionic liquid for sulphur removal compared to bmim acetate and bmim chloride.
- bmim octyl sulphate show a good potential as extracting agent of sulphur removal from diesel.

5.2 Future work.

Since ionic liquid is non- volatile and has low vapor pressure, it can be recycle. Ionic liquid can be regenerated by washing it with other solvent. Based on literature review, some IL can be recycled up to 3 times without a significant decrease in catalytic activity [6,12].

Higher sulphur removal percentage could be obtained by introducing temperature to the system. Based on literature review, optimum temperature for sulphur removal is around 30°C to 50°C. Thus, another project can be implement to operate at these mild temperature [6].

Appendices

Project Milestone

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12
1	Preparation of model oil								Mid Semester Break				
2	Progress report submission												
3	Conduct oxidative experiment												
4	Conduct blank experiment												
5	Conduct oxydative and extractive experiment												
6	Test sample												
7	Submission of Interim Report												
8	Oral Presentation												

Table A1: Project Milestone

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The format of references for the respective sources is as follows

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Attachment

Bil	Article	Method	Preparation	Chemical Reaction
1	**Photochemical Oxidation- ionic Liquid Extraction Coupling technique in Deep Desulphurisation of light oil** Year: 2007 Location: China Dishun Zhao, Ran Liu, Jianlong Way and Baoyou Lin	Coupling technique by combining photochemical oxidation and ionic liquid extraction **IL**: [Bmim]PF$_6$ **Objective**: • To determine the effectiveness of this method on light oil. • Determine the feasibility of recycle ionic liquid.	1. Prepare IL [Bmim]PF$_6$. 2. Prepare Model oil (1000πg/ml S). 3. Prepare actual light oil with sulphur content of 3240πg/mL. 4. Prepare photochemical reaction appratus. 5. Mix model oil(10ml) with [Bmim]PF$_6$(10ml) by using magnetic stirer with 2.0ml H_2O_2 (30%). 6. Mix actual light oil(10mL) with 3.0mL H_2O_2 (30%) 7. Mixture is added to asilex test tube and exposed to UV radiation. 8. Determine suphur content by observing Gas chromatography.	The reaction is a triphasic reaction system. **Result 1:** a. Extraction by using[Bmim]PF$_6$ DBT removal: 50.5% b. Using [Bmim]PF$_6$ and H_2O_2 without UV radiation DBT removal:51.7% c.Using water solvent H_2O_2 with the present of UV radiation DBT removal: 22.1% d. Using both [Bmim]PF$_6$ and H_2O_2 in the present of UV radiation DBT removal: 99.5%

2	**Deep desulphurization of fuel by using Liquid-Liquid extraction using Ionic Liquid** Location: Mexico Likhanoza N.V., R. Martinez Palou, D. Guzman Lucero, and Flores- Orpeza E.A	**Method:** Extractive desulphurization of IL **Objective(s):** To evaluate the effect of molecular array of 17 IL compound on their efficiency for removing sulphur from fuels. **IL:** Heterocyclic cation based, like imidazolium and pyridonium.	**Procedure:** 1. **Ionic Liquid Syntesis** Ionic liquid is syntesis. Purity and its composition was confirmed by NMR spectra. 2. **Sampling** Model diesel is prepared by adding equivalent thiophene and benzothiophene into mixture of hexane/heptane (1:1) with sulphur content of 500 ppm. CN sulphur content is 1600ppm and NG sulphur content is 210ppm. 3. **Extraction Desulphurization** desulphurization is conducted in 100ml glass vial. IL is added at room temperature. Mass ratio of IL to fuel s 1:10. The mixture is stirred for 15 min, and left in rest for 30 min . 4. **Analysis sulphur content of the fuel** total sulphur is determine in an Antex 9000S equipment at standard procedure ASTM-D 5453-05 by using Ultraviolet Flurescence .	**Result:** • Aluminates and ferrates type anions show excellence performance for deep desulphurization • Ratio higher than 1:1 of halogen as anion/MXn on methatesis reaction is prefered.

3	**Oxidative Desulphuriation(ODS) of Thiophene Catalyzed by $(C_4H_9)_4NBr.2C_6H_{11}$ NO coordinated ionic liquid.** Location: China Year: 2008 Zhao, Zhimin Sun, Fatang Li, Ran Liu and Haidan Shan	**Method:** ODS of thiophene with hydrogen peroxide/ acetic acid using quaternary ammonim coordinated ionic liquid(catalyst). **Objective:** • To remove thiophene from n-octane.	**Procedure** • Prepare $(C_4H_9)_4NBr.2C_6H_{11}$ NO coordinated ionic liquid (0.05mol TBAB and 0.1mol caprolactam were stirred in a 3 necked flask at 90°C for 15 min.when the mixture is clear, it is continue to stirred for 15 min. Then IL is dried in vacuum at 120°C for 2h. Colourless liquid is form and it is tested by using NMR and FTIR) • Prepare model oil • 18ml of model oil is put in reactor, heated to 40°C. • 2ml of H_2O_2, 4ml of acetic acid and 0.2g IL is added to the reactor. • Mixture is stirred for 30 min. • Sulfur content is analyzed by using GC	**Result:** • **Oxidation mechanism** ○ MS- comfirm the presence of sulfoxide an dsulfone in water phase. ○ $BaCl_2$- white deposit appear and not dissolve when HCl is dropped. • **Effect amount of IL to desulphurization.** ○ When IL amount increase up to 0.2g, rate of desulphurizaton increase significantly. ○ When IL amount exceed 0.2g, desulphurization rate did not increase remarkably • **Effect amount of H_2O_2 on desulphurization.** ○ Optimal amount of H_2O_2 is 30wt% 2mL H_2O_2.
4	**Oxidative Desulphurization of Fuel Oil by Pyridium-Based Ionic Liquid**	**Method:** ODS of thiophene and dibenzothiophene by using $[BPy]BF_4$ and hydrogen peroxide	**Procedure:** • $[BPy]BF_4$ is prepared • Model oil is prepared by dissolving thiophene (0.525g) in n-octane (500mL) and DBT (0.920g) in 500mL n-	**Result:** • **Effect of extractive desulphurization on model oil.** ○ At 30°C for 15 min, it shows that that IL has better

	Location: Tianjin,China Year : 2009 Dishun Zhao, Yanan wang and Erhong Duan	**Objective:** To study the effect of ODS by • The presence of oxidant • Manipulate amount of oxidant (peroxide) • Manipulate temperature	octane. • 10mL of model oil, 10 ml of ionic liquid and certain amount of hydrogen peroxide is added to 50mL flask. • The mixture is stirred for 30 min at reaction desired temperature. • Concentration of sulphur is determine by using microcoulometric detector (WK-2D) and GC	extracting ability to remove DBT compared to thiophene. This is dur to the presence of benzene ring in DBT. • **Effect of Oxidant amount** o The presence of hydrogen peroxide increase desulphurization rate if thiophene from 44.5% to 69.8% and DBT from 47.2% to 74%. o Optimal ratio by volume of H_2O_2 to IL is 0.4:1 o No visible change to desulphurization rate when the ratio is higher • **Effect of reaction temperature** o Reaction temperature is varies from 30°C to 65°C o When temperature is increase from 30 to 50°C, desulphurization reached maximum value. o When temperature is higher than 55°C, desulphurization rate decrease appreciably, this is due to H_2O_2 decompose to H_2O at high temperature.

5	**Oxidative desulphurization of light cycle oil (LCO) monitoring by FTIR spectrocopy** Location: Bulgaria Year: 2008/09 Vesislava Toteva, Anton Georgiev and Lilian Topalova	**Method:** Oxidative desulphurization with extractant by DMF **Objective:** • To study the effect of temperature on oxidation rate. • To study the effect of oxidation time on sulfone yield. • To determine maximum oxidant amount for maximum sulphur removal.	**Procedure:** • 100ml LCO was treated with 5.5ml H_2O_2, 2.0ml CH_3COOH and 1.0ml H_2SO_4. • The separated acid phase is was separated by using funnel and later discarded. • the upper oil layer is analyzed by using FTIR. • Oxidation temperature, oxidation time and quantity of oxidant is monitored. • To determine the consumption of oxidant for maximum sulphur removal, different amount of hydrogen peroxide is used.	**Result:** • Oxidation temperature o Temperature used is 20,50 and 90°C. o Maximum absorption is at 50°C. o Temperature above 80°C are not recommended. • Oxidation time o Maximum S adsorbent at 120 min • Oxidant consume o Max sulphone produce when H_2O_2/S is 3:1
6	**Halogen-free IL in naphtha desulphurization and their recovery** Year: 2010 Location: Mexico	**Method:** Extractant desulphurization using halogen free IL **Objective:** To determine the most effective IL for sulfur removal	**Procedure:** • Synthesis IL • Mix naphtha with IL • Shake the mixture vigorously • Determine the final Sulphur concentration	**Result:** • 1-Octyl-3-methyl imidazolium acetate has the highest sulphur removal rate. • 1-Octyl-3-methyl imidazolium acetate can be recover until 3 cycle

		IL involved: Imidazole, pyridium, isoquinoline and tertiary based IL	Recovering and recycling ▪ Heat IL @ 78°C ▪ Wash IL with solvent(ether) ▪ Eliminate solvent under vacum cond.	

Table A3: Journal Summary

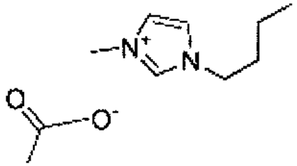
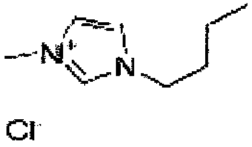
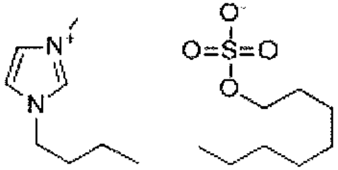
Ionic Liquid	**Structure**
Bmim Acetate	
Bmim Cl	
Bmim OS	

Table A4: Ionic Liquid Structure

Ionic Liquid	**Moisture Content**
Bmim Acetate	0.78%
Bmim Cl	1.63%
Bmim OS	0.69%

Table A5: Ionic Liquid Moisture Content

Figure A1: Experiment Set Up, Sampling, Centrifuge Sample, Gas Chromatography (anti clockwise)

Figure A2: White precipitate formed in oxidizing desulphurization