Asphaltene Removal – The Effect of Ionic Liquid to Asphaltene Characteristics

by

Siti Sarah binti Marjunit

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

DECEMBER 2009

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CERTIFICATION OF APPROVAL

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Approved by,

____
(AP Dr Zakaria Man)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

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.

SITI SARAH BINTI MARJUNIT

ABSTRACT

Crude oil composes of asphaltene, along with saturates, aromatics and resins (SARA) compound. Changes of temperature and pressure during oil production lead to the precipitation, flocculation and aggregation of asphaltene. This condition has caused many problems faced by the oil and gas industry, especially during production, refining, storage and transportation. This project aims to enhance existing method in removing asphaltene (through dispersion) using n-heptane solvent by replacing the solvent used for the process with the ionic liquid, IL solvent. The IL solvents used are [EMIM] toluene sulfonate and [BMIM] hydrogen sulfate. Experiment in treating crude oil and asphaltene with IL were conducted and mixing effect observed and analyzed by comparing weight percent, carbon, hydrogen and sulfur content, and also molecular weight of asphaltene before and after treatment. The experiments were carried out in two phases - first phase is to treat crude oil directly with the IL and the next phase is to extract asphaltene prior to treat with the IL. From the experiments that were conducted, ionic liquid used [BMIM]HSO_4 shows potential in reducing asphaltene content. This interesting finding should be granted further analysis. In the other hand, [EMIM]tos is proven to increase the asphaltene weight percent, sulfur content and also molecular weight. This type of ionic liquid tends to cluster with asphaltene molecule, results in higher molecular weight compared to before treatment. If [EMIM]tos is going to be used in the industry, it is highly recommended to remove asphaltene that aggregates prior entering distillation column for fractionation.

ACKNOWLEDGEMENT

In the name of Allah, the Most Merciful, the Most Compassionate

In completing this dissertation, I am indeed indebted to many individuals. My respected supervisor, Dr Zakaria Man, and research officer; Nor Mona Yunus for their effort and time enlighten me with their wisdom and knowledge. To my beloved parents Marjunit Suhadi and Nasirah Muin, this project will be no avail without your strong support and endless love from the very beginning. I specially dedicate this piece of work to both of you. Not forgetting my dedicated lecturer, teacher from afar (Ms Ida Ruhidiba) and invariable companion course mates Jan 05 of Chemical Engineering Department. My dear close friends, especially Orie, Fara and WKW2482, I enjoy our partnership and company. My beloved siblings, Hailwa, Hajar and Hilmi, Last but not least I would like to credit R Symsul Amin Raja Kamrin for standing by me, through thick and thin. Although at first this project is close to impossible, these people afore mentioned made it happened through their unceasing encouragement, supports, helps, advices, critiques and comments, all of which have been invaluable to me in carrying out this dissertation. May Allah bless us all, Amen. Thank you.

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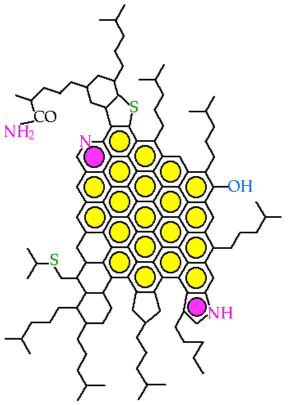
CHAPTER 1

INTRODUCTION

1.1 Background study

Crude oil contains saturated aliphatic hydrocarbons (known as paraffins), aromatics, resins and asphaltenes (SARA). Asphaltene is considered as the heaviest and most polar petroleum fractions and they form in shiny black solids. This component is soluble in aromatic solvents like benzene and toluene but insoluble in n-heptane. This is why, in the industry, asphaltene usually obtained by precipitation from n-heptane or n-pentane. Asphaltenes have high concentrations of sulfur, nitrogen, nickel and vanadium. Asphaltenes usually formed from brown to black amorphous solids with complex structures, involving carbon, hydrogen, nitrogen, oxygen and sulfur. Apshaltene basically formed of condensed aromatic nuclei associated with alicyclic groups. The particles are often surrounded by resins which are considered to add to dispersion stability. Below is an example of asphaltene molecular compound:



[1]

Figure 1: asphaltene molecular compound

[2]

Figure 2: Example of asphaltene

Asphaltene characteristic which has limited solubility and has no definite boiling point has led some problems in refining process. Current practice in the industry is removing asphaltene during deasphalting process, or processing vacuum residue by solvent extraction. Vacuum residue is the recovery from the first distillation of crude oil. Solvent that used normally are propane, butane and pentane (light paraffins). Major products recovered by deasphalter are asphalt and deasphalted oil (DAO). Asphalt, or bitumen is popularly used as road paving while DAO can be further processed to produce fuel oils.

[15] Until today, many refinery plants employ solvents such as n-pentane and n-heptane to eliminate asphaltene during deasphalting process. However, refining operators suffer high energy consumption of the process. Generally, refinery plants seek ways to eliminate or convert asphaltene to lighter material and something useful like bitumen used in road paving, because asphaltene contents like sulfur and nitrogen cause pollution problems; catalyst poisoning and corrosion during combustion.

Ionic liquids (IL) are salt that have inorganic cation and organic anion with melting point below 100ºC, low vapor pressure [3], less flammability and high ion content [4]. These characteristics made ionic liquid eligible and may be used to replace the organic solvent like n-heptane or toluene. Most of ionic liquid exist at room temperature with melting point below 25 ºC, which called room-temperature ionic liquid (RTIL). With currently increasing industry demand, study in ionic liquid has expanded into many fields, including, electrochemistry, catalysis, physical chemistry, and engineering.

1.2 Problem statement

Nowadays, trend in petroleum refining industry is to use heavy crude oil because the supply for light crude is already running out. However, heavy crude oil is more difficult to process compared to lighter crude oil due to its high content of heteroatoms, asphaltene and large amount of non-distillable hydrocarbons. [15] Asphaltene has created many hindrances in crude refining industry, for examples:

1. During production, asphaltene precipitates and blocking the tubing. Polar chemical compounds (N, S, O compounds) in asphaltene makes the rock wettable to hydrocarbon, thus limits its production.
2. Fouling of equipments (especially at heat exchanger) is also caused by this insoluble material. Currently, petroleum processors expect this problem and periodic shut down is planned for cleaning purpose that triggered high maintenance cost for the process.
3. Asphaltene create oil recovery plugging and pipeline deposition. It also oxidizes and cause storage problem due to sedimentation and plugging. If asphaltene exists during storage,
4. Polarity of crude oil might increase and caused asphaltene aggregation if asphaltene exist during storage. Sludge also may form faster if bacteria plague in the crude.
5. During hydrotreating (HDT) process, asphaltene also able to deactivate the catalyst since it is coke precursors.

Figure 3: A crude oil pipeline blocked by asphaltenes and waxes.

Figure 4: Fouling of heat exchanger caused by asphaltene precipitation

1.3 Objective

This project goal is to deliver new alternative and possible option in order to remedy problems that occured caused by asphaltenes. There are three main objectives of this project.

i. To **replace** the conventional solvent with suitable ionic liquid to treat crude oil
ii. To **reduce** the asphaltene content by means to reduce sulfur content
iii. To **control** precipitation of asphaltene in oil production

1.4 Scope of Study

Ionic liquids from [BMIM] HSO_4 and [EMIM] tos type will be mixed with crude oil sample. Some asphaltene properties and characteristic before and after mixing will be area of concern, which are molecular weight (MW), C, H and S content determination. Finally the observed mixing effects of crude oil and ionic liquid are translated and deduced into a meaningful result. The scope of this project only covers the effect of asphaltene behavior and not the process of implementing the findings.

CHAPTER 2
LITERATURE REVIEW

2.1 Asphaltene

Asphaltene generally defined as the material that is insoluble in n-pentane (or n-heptane) at a dilution ratio of 40 parts alkane to 1 part crude oil and re-dissolves in toluene [2]. Major fraction of asphaltene is from heteroatoms components (O, S, and N) and organometallic constituents (Ni, V, and Fe) in the crude oil. These properties cause them to interact readily with rock surfaces. Asphaltene cannot be distilled without thermal cracking. There is no specific molecular weight of asphaltene, since it has the tendency to self aggregate. However, Narve [5] predicted that asphaltene weight in between 500-2000 g/ mole while in [6], the molecular weight is said to be 1000- 100,000g/mole.

Narve [5] also cited that resin molecules are responsible in stabilizing and expanding asphaltene aggregated, so the aggregate is an asphaltene-resin complex. Figure 3 shows model of an asphaltene aggregate stabilized by resin molecules. However, if the crude oil mixed with unfavorable solvent condition, larger asphaltene aggregates might form. Asphaltene aggregation increases as straight-chain aliphatic relative to aromatics in the solution increases. Mixing of crude oils from different sources during production or refining may cause such aggregation effects, and the consequences can be severe asphaltene deposition on all types of processing facilities

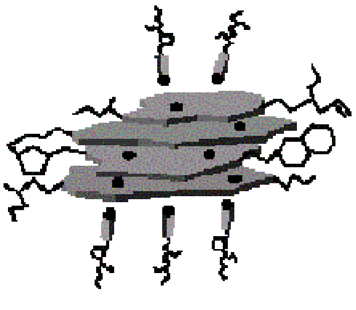


Figure 5: Resin stabilizing asphaltene aggregates. [5]

Dispersion of asphaltenic aggregates in heavy crude is solvated by resins and other aromatic compound. Asphaltenes were more soluble in crude oil than heptane-toluene solvent blends that imitate the crude composition. Yield of insoluble asphaltene is reduced due to its enhanced solubility, and more polar and aromatic structures were concentrated. Heat applied to the crude containing asphaltene can further lessen aggregation process and reduce equilibrium aggregates size. Precipitation process mainly depends on dispersion and π-π bonding interactions between asphaltene and solvent mixture. While precipitation controlled by weak dispersion forces, asphaltene aggregates due to strong polar and hydrogen bonding forces [13].

2.2 Study on Asphaltene for Heavy Oil Upgrading

In their study of Precipitation, Fractionation and Characterization of Asphaltene from Heavy and Light Crude Oil, Trejo et al. [15] quoted that their project is important in determining asphaltene characteristic, for designing more meaningful hydroprocessing catalyst for heavy oils. Asphaltene, as aforementioned, ignited numerous problems, including during HDT process. They cited that during the process asphaltene quality rather than quantity plays a key role in coke deactivation. So, they did the experimental study on both heavy crude and light crude in order to achieve the project objectives. They found that the least soluble asphaltene fraction has more complex structure than the other fractions. They also concluded that the amount of precipitated asphaltene has linear relationship with binary toluene/ n-heptane solvent volumetric ratio.

Miller et al. [17] separated asphaltene into two fractions. One fraction is associated with solution while the other fraction works vice versa, which means it does not associate with solution (non-colloidal). In other words, this will lead to agglomerates formation. The extracted asphaltene will not associate with solution, and thus classified as non-colloidal. Hence, this will result in smaller molecular size and lower weight. That is the reason why in the industry it is important to extract the asphaltene out of crude oil during refining process.

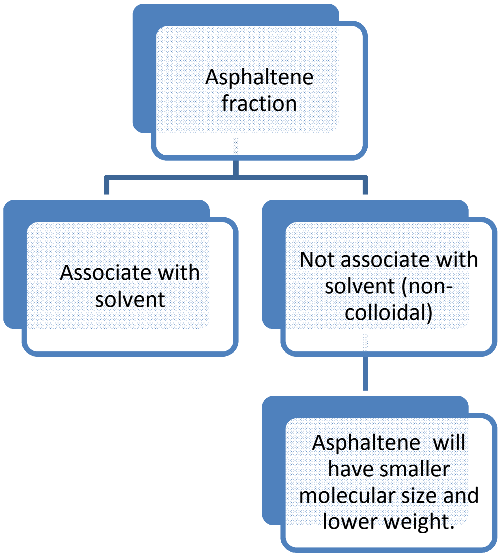


Figure 6: Schematic diagram of fractionation of asphaltene by Miller

Fractionation of asphaltene also has become the interesting subject to many researchers in order to find the easiest way to handle asphaltene problems. Kaminski et al. [20] proposed a fractionation procedure where the asphaltene dissolved in methylene chloride first. After that, sufficient amount of pentane is added to precipitate the first asphaltene, collected by filtration. They found that the high polarity fraction contains more metals and dissolve slowly and to lesser extend than the low polarity fractions. They conclude that unfractioned asphaltene behave as sum of their fractions, too.

Kokal [12] said that electrokinetic charges on asphaltene are dependent on the solution pH, ionic strength, ionic composition and the degree of hardness of the electrolyte solution. Asphaltenes are negatively charged in the neutral pH range. A charge reversal is observed at high pH values for solutions which contain multivalent cations. An increase in the ionic strength of the aqueous solution leads to a decrease in the charge of asphaltenes. However, it is possible to measure the electrophoretic mobility of asphaltenes in non-aqueous solvents with relatively high permittivity.

2.3 Ionic Liquid as New Solvent Alternative

Numerous studies have been made on ionic liquid since it has promising effect as solvents, electrolytes, heat storage, metal processing, performance additives and separation processes. nGimat Co. [7] has been promoting ionic liquid as ‘green solvents’ since it is less hazardous solvent option and more environmental friendly. Ionic liquids unique properties which can be tailored and designed easily to meet requirement have attracted studies in the recent years [3] and [4].

Ionic liquid successfully used as novel extractive solvents for deep desulfurization of diesel fuels, especially for the removal of the sulfur compounds intractable with common hydrodesulfurization techniques [8]. During the research, they used [C8Py][BF4] and [C8mim][BF4] as solvent and promising results were obtained. However, the sulfur-removal ability of an ionic liquid depends on its structure and size. It shows that as cation chain length longer, the higher absorption of S-compound can be obtained as mass ratio of ionic liquid/ diesel fuel increases, the desulfurization ability of the examined ionic liquids also increases.

Hong-fu et al. used ionic liquid in their research of Experimental Study on Using Ionic Liquids to Upgrade Heavy Oil [9]. In their study, they cited that viscosity reducing technology is vital in upgrading heavy oil, however the common method using aquathermolysis is somehow very expensive and need to be handled at very high temperature. At the end of the research work, ionic liquid used [(Et) NH] [AlCl] can reduce viscosity, average molecular weight, and asphaltene content while saturates, aromatics and resins in heavy oil increase. They also proved that transition metal modified ionic liquid has catalytic effects to upgrade heavy oil. There are more SARA data retrieved after treated with $[(Et)_3 NH][AlCl_4]\text{-}Ni^{2+}$ compared to be treated with non metal modified ionic liquid. The amount of ionic liquid used also can determine the successfulness of result. Since the key goal of their project is to reduce viscosity, they found that the more ionic liquid they use, the viscosity will reduced greatly. The research observed that reduced of viscosity and average molecular weight caused by breakup of C-S bonds. Organic sulfur reacts with metal ionic liquid to form complex and weaken C-S bonds.

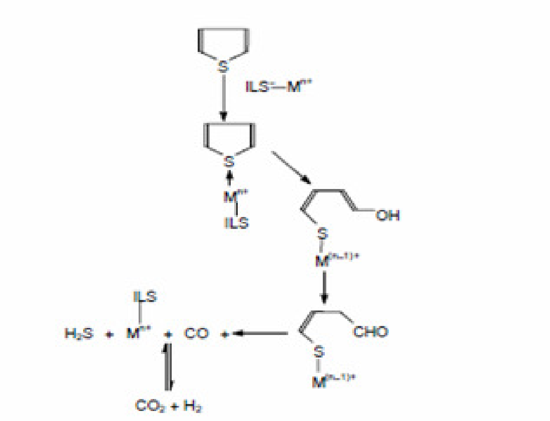


Figure 7: Example of reaction mechanism between ionic liquid and the heavy oil. [15]

In the other hand, Kumar et al, [18] in his works stressed that by 2010, petroleum industry is bound to produce ultra lowsulfur diesel (ULSD) containing a maximum of 15ppm sulfur. The removal of aromatic sulfur compounds from diesel oil is becoming increasingly difficult because of its resistance to hydrodesulfurization (HDS). Solvents like ionic liquid are proposed as new approach to remove sulfur by using liquid-liquid extraction. Kumar said that ionic liquids have higher sulfur extracting ability, virtually immiscible with diesel, and recovery and regeneration involves simple heating to recover the sulfur compounds. Kumar et al. use thiophene inside ionic liquid concluded that there is a competing effect between the sizes of cation of ionic liquid. Smaller size of cation has higher selectivity but lower capacity as it accommodates only thiophene molecules. So, the paper work highly recommends smaller size cation used to achieve the objectives.

There is also study on the selection of the most suitable ionic liquid for the extraction of aromatic hydrocarbons from aromatic/ aliphatic mixtures by G. Wytze et al. [19]. Extractions of aromatics from mixed aromatic/aliphatic stream with ionic liquids are expected to require less process step since ionic liquid has negligible vapor pressure. In their study, they separate alkanes/ alkenes by using [OMIM]Cl, [BMIM]BF_4 or, [BMIM] octylsulfate, [HMIM]$PF_{6.}$ They found that environmental pollutants, like aromatic hydrocarbon can be extracted from aqueous solution with ionic liquid [BMIM] PF_6 and [OMIM] $PF_{6.}$ Other options of desulfurization of are to use [EMIM]AlCl4, [BMIM]AlCl4, and also [BMIM]BF4. However, they conclude that extraction of toluene/heptane using [BMIM]I_3 at room temp is very corrosive and should not be proceed. The most suitable ionic liquid for separation of aromatic hydrocarbons should be:

1) High solubility of aromatic hydrocarbons in the ionic liquid,
2) No or low solubility of aliphatic in the ionic liquid,
3) High separation factor and high distribution coefficient,
4) Simple recovery of the ionic liquid from extract and raffinate phase,
5) Fast mass transport from the feed phase to the IL phase.

Despite of that, ionic liquid also has some disadvantages. Their physical properties not always known, their viscosity usually higher than common solvent and last but not least, toxicity is not always known.

Up to date, researches are still going on to study on effect of ionic liquid to asphaltene derived from crude oil. Nonetheless, based on the literature review, ionic liquid behaviors are promising to replace solvent used in current technology. This project is relevant to design the best ionic liquid that has potential in replacing normal solvent used and will open the path in obtaining higher yield of fuel oil. Next, corrosion effect of ionic liquid onto equipment is going to be further studied.

CHAPTER 3
METHODOLOGY

A well planned methodology is designed to ensure that research went on smoothly. Theoretical study on behavior of ionic liquid, and also asphaltene are studied thoroughly prior to experimental works. Research scopes are mainly on chemical composition and physical properties of the sample. The project work are divided into two phase. 1^{st}, crude oil will be treated directly with ionic liquid at given temperature and condition. 2^{nd}, asphaltene will be derived prior to treat with ionic liquid.

Basically, the significance of experiment is to quantify asphaltene content of crude oil asphalt before and after being mixed with ionic liquid. Scopes of the analysis are on weight percentage of asphaltene, oil composition analysis and visual analysis. In determining asphaltene molecular weight in crude oil, Gel Permeation Chromatograph(GPC) method is employed, while to obtain asphaltene content inside the crude sample, the most common and widely used method will be used, which is ASTM D3279, set by American Society for Testing and Materials (ASTM). [16] Finally, ionic liquid used ([BMIM]HSO_4 and [EMIM]tos) will be determined whether suitable for crude oil treatment method depending on the results obtained.

As ratio of crude oil and n-heptanes higher, the more asphaltenes produced from crude oil. While for experiment of mixing process of crude oil and ionic liquids, it is assumed from previous study [10] that the best temperature for separating ionic liquid from crude oil is 80^0C.

GPC analysis is widely used to determine molecular weight of asphaltene inside crude. Separation based on the selective separation of polymer molecules, which penetrate the rigid gel structure constituting the stationary phase in the column. [25]. Gel Permeation Chromatography (GPC) is an attractive, relative to others such as ultra-centrifugation, fractional precipitation and alternative fractionation methods, because it is easy to obtain a qualitative chromatogram that relates directly to the molecular weight distribution of the macromolecules. When GPC is coupled with advanced detectors such as light scattering detectors and viscometers, determination of additional molecular parameters such as intrinsic viscosity (inverse molecular density), molecular size and long chain branching is possible. The principle of GPC operation is the separation of molecules based on their hydrodynamic radius (Rh) or volume (Vh), not molecular weight. This separation takes place in GPC/SEC columns which are packed with porous material such as polystyrene gels, glass beads, silica gels, etc. Because of their size, the larger molecules cannot fit into as many pores and elute faster through the porous packing than the smaller molecules. Figure below shows mechanism of gel permeation separation. The molar mass of a macromolecule is obtained by averaging the molar mass of the different chains by number (Mn) or by weight (Mw). [23]

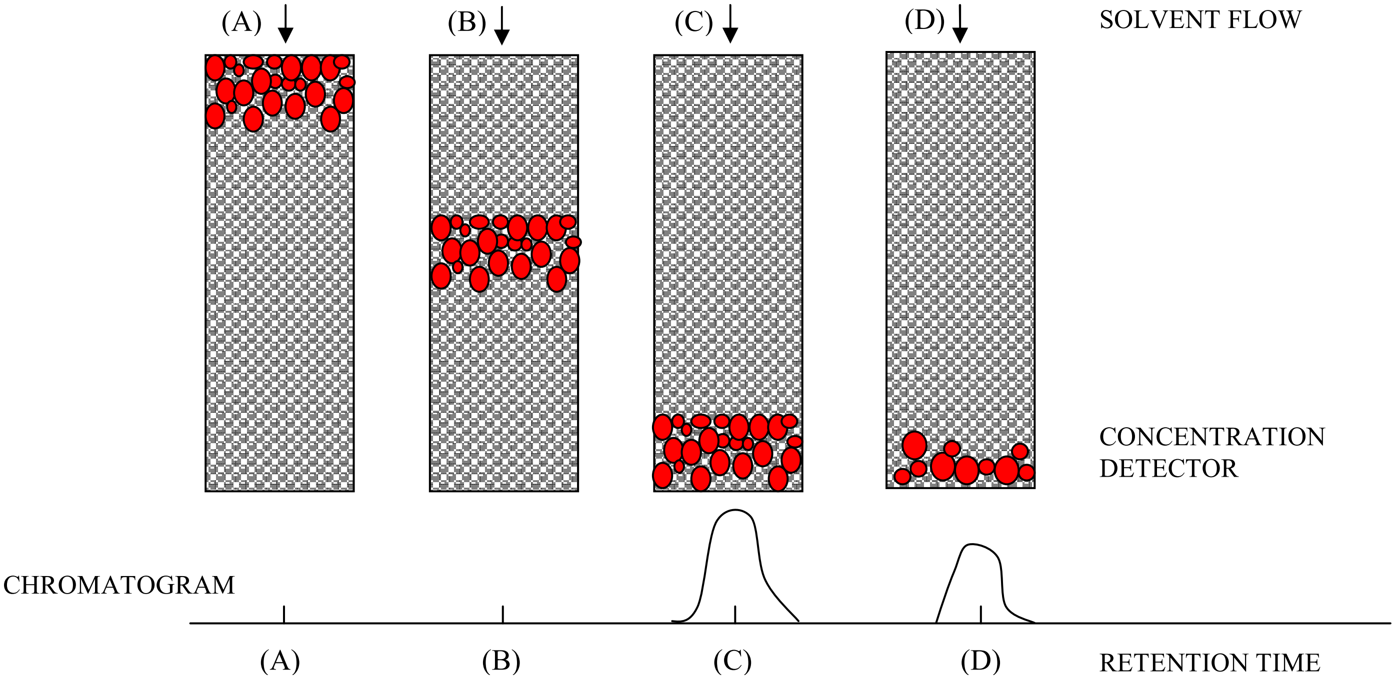


Figure 8: Mechanism of gel permeation separation.

ASTM method [16] used is the standard test method in determination of mass percent of asphaltene which is insoluble in n-heptane solvent. The method is applicable to all solid/ semi-solid petroleum asphalt containing crude petroleum that has been topped to a cut-point of 343ºC or higher.

3.1 Process Flow

Phase I : Treat Crude Oil Directly with Ionic Liquid

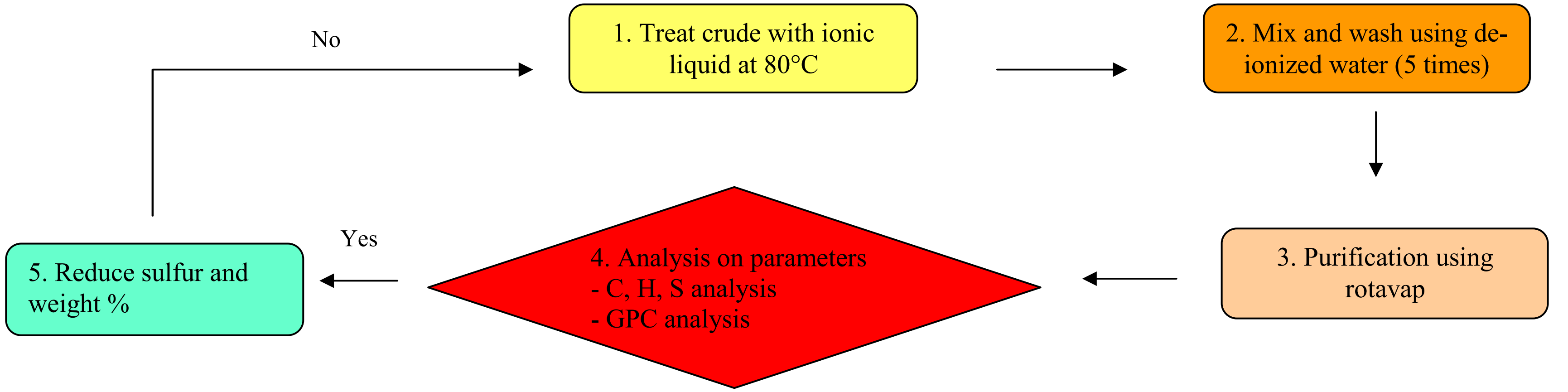


Figure 9: Flowchart of treating crude oil directly with ionic liquid

Phase II : Treat Asphaltene with Ionic Liquid

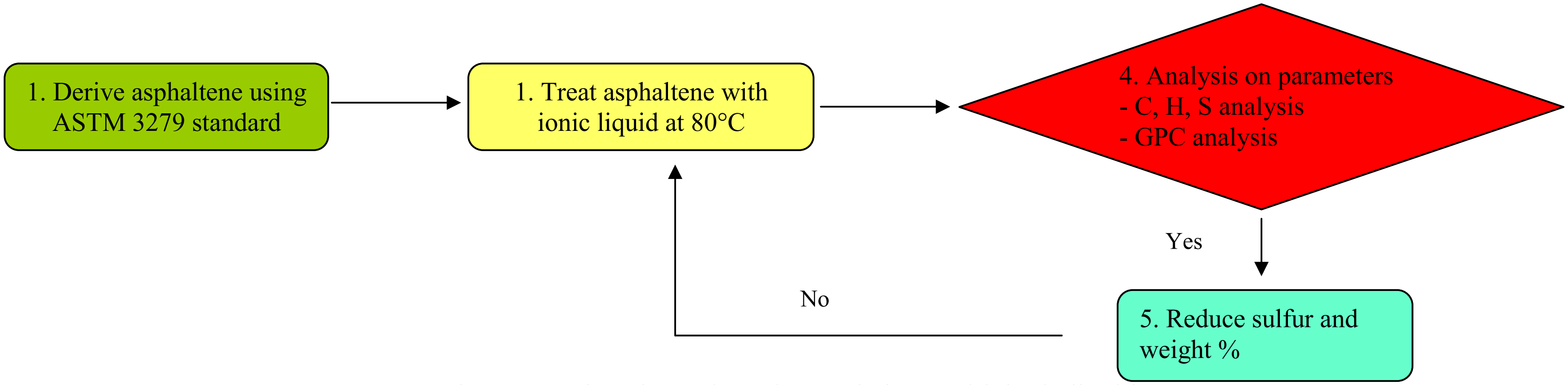


Figure 10: Flowchart of treating asphaltene with ionic liquid

3.1 Experiment 1: Solubility Test

Objective: To determine solubility of ionic liquid with solvent

Experiments:

1. **Materials:**

    1. pipette
    2. flask
    3. vortex rotary
    4. disposable syringe (for viscous BMIM HSO_4)

2. **Chemicals:**

    1. [BMIM]HSO_4
    2. [EMIM]tos
    3. Toluene
    4. n-heptane
    5. distilled water, H_2O
    6. THF

3. **Methodology:**

    1. Using 1:10 ratio, mix ionic liquid together with THF, n-heptane and toluene, for 30 minutes using vortex rotary.

3.2 Experiment 2: Determination of Asphaltene Contents in Crude Oil (ASTM D3279) [16]

Objective: To derive asphaltene from crude oil

1. **Reagent and Material:**
   - i. n-heptane, 100ml
   - ii. Ratawi Crude (1g transferred using disposable syringe)

2. **Apparatus**
   - i. Glass microfibre filters GF/O 32mm Whatman
   - ii. Erlenmeyer flask, of 250mL capacity adapted to reflux condenser
   - iii. Magnetic stirrer and magnetic stirrer hot plate.
   - iv. Gooch crucible
   - v. Filter pad, glass-fiber 32mm in diameter
   - vi. Filter flask, heavy wall with side tube
   - vii. Filter tube, 40 to 42mm inside diameter
   - viii. Rubber sleeve or adapter for holding Gooch crucible on the filter tube.

3. **Equipments:**
   - i. vacuum pump
   - ii. heating mantle
   - iii. weighing balance

Experimental Procedure. [9]

1. **Procedures:**

   - i. 1.0g for crude oil weighted in round bottom flask

   - ii. 100ml of n-heptane (in ratio 100ml of solvent/1g of sample) is added

iii. Round bottom flask is placed on the magnetic stirrer hot plate at 98 °C and secured under reflux condenser about 30minutes.

iv. Gooch crucible is placed in an oven at 107 °C for 15minutes and is allowed to cool in desiccators in 15minutes.

v. The Gooch crucible is weighted (initial weight).

vi. The flask is let warm at 50 °C on the hot plate.

vii. Mixture of crude oil and n-heptane is poured through the glass fiber filter using a gentle vacuum.

viii. The flask is controlled while transferring the final precipitation using spatula.

ix. The precipitate is washed with three portion of n-heptane about 10ml each.

x. The crucible is placed in 107°C for 15 minutes.

xi. The crucible is cooled in desiccators (15minutes) and weighted (final weight).

Calculation of asphaltene content (weight %):

$$\text{Weight, \%} = \frac{\text{(Final weight-Initial weight)}}{\text{g of sample}} \times 100\%$$

Data to collect:

1.Weight of sample: ___________g

2.weight of crucible + filter paper (initial): ___________g

3.weight of crucible + filter paper (final): ___________g

3.3 Experiment 3: Mixing and Washing Process of Crude Oil and Ionic Liquids

Objective: To observe the mixing effect between crude oil and ionic liquid.

1. **Reagent and Material**

   i. Crude Oil

   ii. [BMIM]HSO_4

   iii. [EMIM]tos

   iv. De-ionized water (DI water)

2. **Apparatus**

   i. Syringe,10ml
   ii. Plunges as a top cover of the syringe.

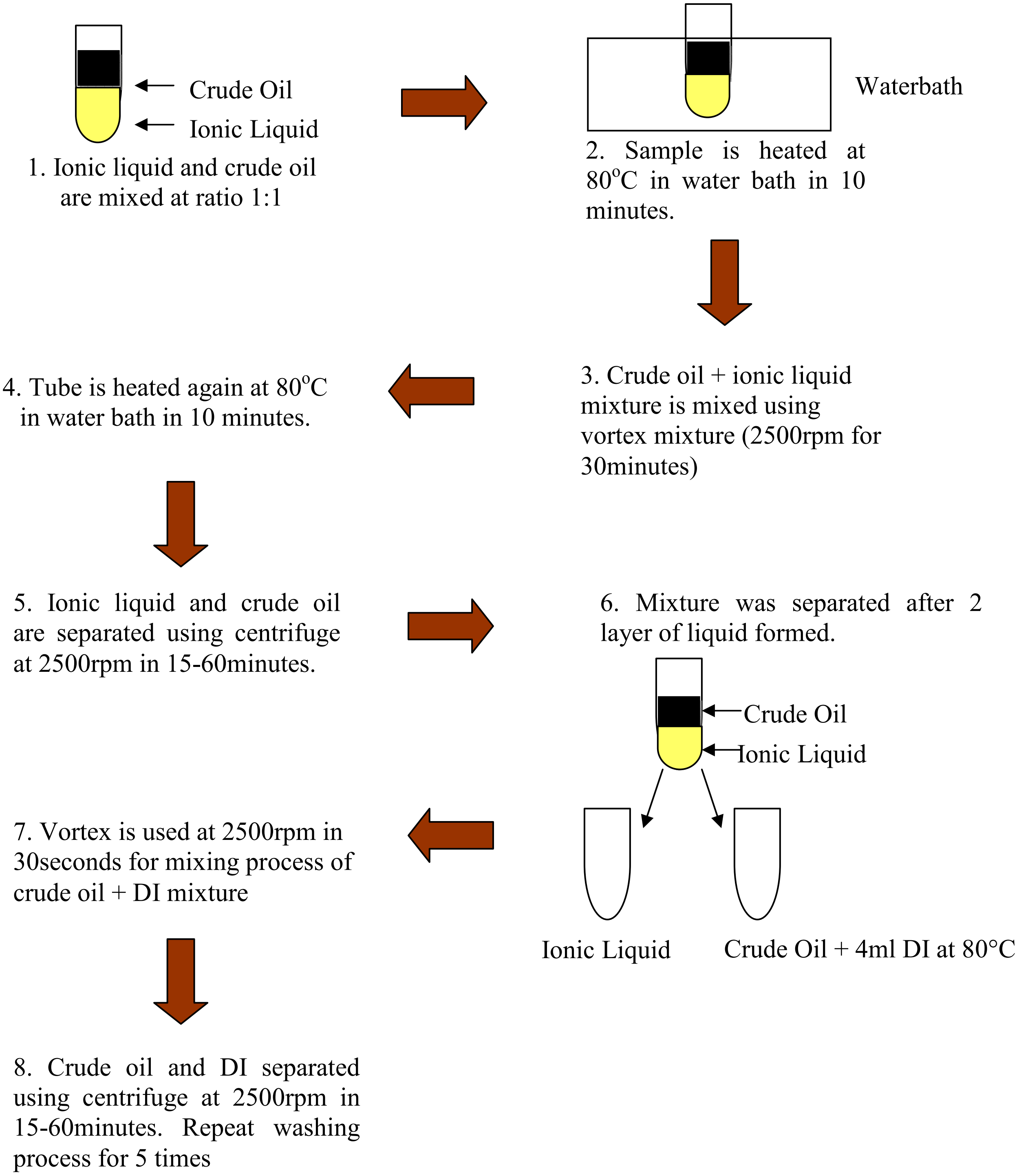
3. **Equipment**

   i. Waterbath

   ii. Vortex

   iii. Centrifuge

4. Procedures:



1. Ionic liquid and crude oil are mixed at ratio 1:1

2. Sample is heated at 80^{o}C in water bath in 10 minutes.

3. Crude oil + ionic liquid mixture is mixed using vortex mixture (2500rpm for 30minutes)

4. Tube is heated again at 80^{o}C in water bath in 10 minutes.

5. Ionic liquid and crude oil are separated using centrifuge at 2500rpm in 15-60minutes.

6. Mixture was separated after 2 layer of liquid formed.

7. Vortex is used at 2500rpm in 30seconds for mixing process of crude oil + DI mixture

8. Crude oil and DI separated using centrifuge at 2500rpm in 15-60minutes. Repeat washing process for 5 times

3.4 Experiment 4: Determination of Asphaltene Yield

Objective: To determine asphaltene yield (solidified asphaltene)

1. **Reagent and Material**
   i. Asphaltene from Experiment 1
   ii. Toluene
   iii. N-heptane
2. **Apparatus**
   i. Petri dish
   ii. 100ml beaker
   iii. Round bottom flask, Eyela 100ml
3. **Equipment**
   i. Rotavap
   ii. Vacuum Oven
   iii. Filtration Pump
   iv. Centrifuge
4. **Procedures:**
   i. Asphaltene contained in gooch crucible is dissolved in a beaker using toluene.
   ii. Beaker covered using petri dish, and left for 24 hours
   iii. Gooch filtered using filtration pump with gentle vacuum applied and washed with toluene
   iv. The dissolved solution purified using rotavap machine

v. The remaining asphaltene left inside the round bottom flask is titrated using n-heptane.
vi. An empty test tube weighed. Solution form step v is transferred inside the test tube.
vii. Mixture centrifuged at 2500rpm, for 30minutes.
viii. n-heptane is separated from the glass
ix. Glass containing asphaltene is put inside oven for about 15 minutes, at 107°C
x. Dried asphaltene is weighed

Total weight = Empty test tube (g) – Dried asphaltene inside test tube (g)

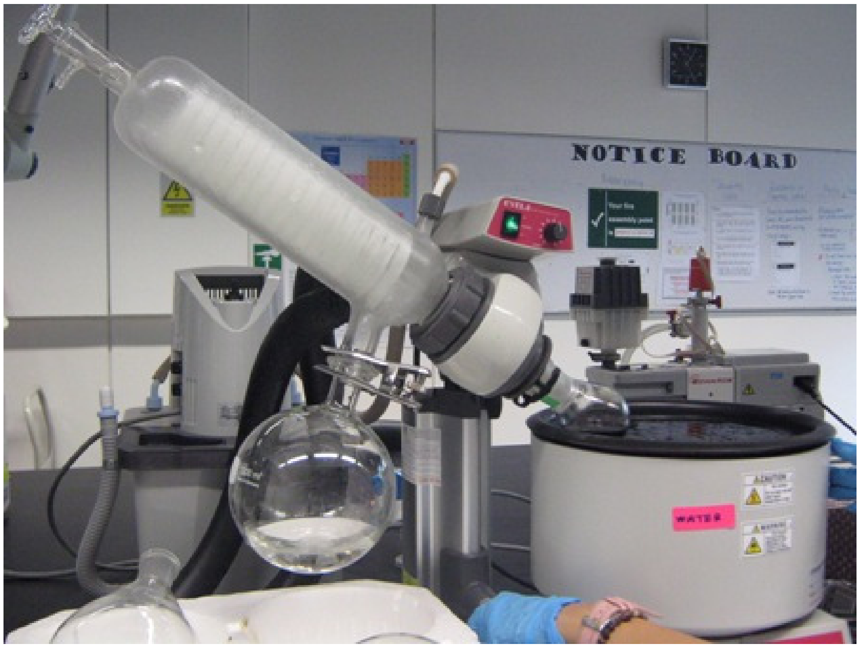


Figure 11: Apparatus assembly of rotavap process

3.5 Experiment 5: CHS Analysis (Carbon, Hydrogen, and Sulfur Content) of Asphaltene Derived From Crude Oil Treated with Ionic Liquid

Objective: To determine Carbon, Hydrogen and Sulfur Content

1. **Equipment:**

   i. Weighing balance Sartorius
   ii. CHNS-932 machine (using Helium, Oxygen, purified air)

2. **Methodology:**

   i. Sample is prepared
   ii. Helium, Oxygen and compressed air are set to 40psi
   iii. Ambient monitor is checked for proper values
   iv. CO_2 , Hydrogen and Sulfur IR cells monitored between 7.5-9.2 volts
   v. Oxi. furnace temperature is set to 1000^{o}C
   vi. Red. furnace temperature is set to 650^{o}C
   vii. Run leak check if necessary (gas must be in Analyzed position before a leak check can be performed)
   viii. ‘Manual’ mode is selected to load sample individually
   ix. Gas switch is set to ‘Analyze’ position
   x. Furnace temperature is waited until stable
   xi. 5 blank analyzes and 5 blank samples are run.

3.6 Experiment 6: Gas Permeation Chromatography (GPC) Analysis

Objective: To determine molecular weight of asphaltene

1. **Apparatus:**
   1. Gooch Crucible
   2. Filter funnel
   3. Filter flask with trap
   4. Tweezer
   5. Parafilm
   6. Vials (28ml, 2 inch)
   7. Syringe
   8. Pipette and bulb
   9. Water Pump
   10. Syringe filter (advanter, nylon 0.2μm)

2. **Chemical:**
   1. Asphaltene derived from crude oil with ionic liquid
   2. THF, Lichrosolv, Merck

3. **Equipment:**
   1. Weighing balance, Mettler Toledo
   2. Oven
   3. Spa systems, water

4. Methodology:

1. Standard solutions are prepared as follows

Vial	MW	Concentration, g/v%	x gram/10ml THF
1	370,9890	0.25	0.025
2	474,18200	0.25	0.025
3	890,44200	0.25	0.025
4	2770,120000	0.20	0.020
5	6520,177000	0.20	0.020

Table 1: Standard solution composition for GPC analysis

2. A calculated amount of THF is added to make 0.25% g/v solution of asphaltene in THF.
3. 2ml of solution in 5 is taken out and filtered using microfibre filter (Advantec, 0.2µm size)
4. GPC separations are performed on a Waters Model GPC (1100 series) equipped with refractometer and UV detector(λ = 350nm)
5. THF is used as mobile phase
6. Flow rate is set to 0.3ml/minutes
7. Injection volume is set to 50ml
8. Calibration curve for GPC column constructed from standard solution in table above
9. GPC conducted at ambient temperature while the refractometer maintained at 40°C

3.7 Experiment 7: Treating Asphaltene with Ionic Liquid [26]

Objective: To quantify effect of dispersants (ionic liquid) on the amount of aspahaltene remaining in solution after flocculation with n-heptane.

1. **Apparatus:**
    i. Glass bottle, 30ml
    ii. Gooch crucible
    iii. Filter pad, glass-fiber 32mm in diameter
    iv. Filter flask, heavy wall with side tube
    v. Filter tube, 40 to 42mm inside diameter
    vi. Rubber tubing or adapter for holding Gooch crucible on the filter tube.
    vii. Cylindrical measurement, 100ml

2. **Chemical**
    i. Toluene
    ii. N-heptane
    iii. Ionic liquid, [EMIM] tos, [BMIM]HSO_4

3. **Equipment**
    1. Waterbath Julabo SWW Model
    2. vacuum pump
    3. weighing balance, Sartorius CP 2P Model

4. Methodology

i. 3 sets of toluene solution containing 0.0025g asphaltene and 10ml toluene solution are prepared and stored in glass jar.
ii. 20 ml n-heptane is added to the solution to achieve n-heptane/toluene ratio of 2.
iii. 1 set of solution will be control experiment, while the other two will be added 0.01g ionic liquid, [EMIM]tos, [BMIM]HSO_4 added into the glass bottle respectively.
iv. The solutions are stirred for 24 hours using Waterbath Julabo SWW Model at 200rpm
v. Solutions are filtered trough glass-fiber 32mm in diameter using filter pump, and apparatus assembled similar to ASTM D3279 method.
vi. Weight of asphaltene is measured using CHNS balance, Sartorius CP 2P Model.
vii. Results between solution treated with ionic liquid and control experiment are compared.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Experiment 1: Solubility Test

Result

Ionic Liquid	**n-heptane**	**Toluene**	**THF**	**H_2O**
[BMIM]HSO_4	×	×	×	√
[EMIM] tos	×	×	×	√

√ = soluble; × = insoluble

Table 2: Solubility test result

Discussion

Experiments shows that ionic liquid used, [BMIM]HSO_4 and [EMIM]tos are not soluble in other solvent such as n-heptane, toluene, THF. However, these IL are dissolved in water, so water can be used to remove IL from IL-crude mixture in Experiment 4.

4.2 Experiment 2: Determination of Asphaltene Contents in Crude Oil (ASTM D3279)

Results

Ratawi Crude Samples	**Untreated Crude**	**Crude Oil + [EMIM] toluenesulfonate**	**Crude oil + [BMIM] HSO_4**
Weight of sample, g	1.07	1.0541	n/a
Weight of crucible + filter paper (initial), g	33.05	25.89	n/a
Weight of crucible + filter paper (final), g	33.08	25.92	n/a
Asphaltene content (wt %): $\frac{\text{final weight-initial weight}}{\text{sample weight(g)}} \times 100\%$	2.12	2.22	n/a

Table 3: Asphaltene content from treated ratawi crude oil

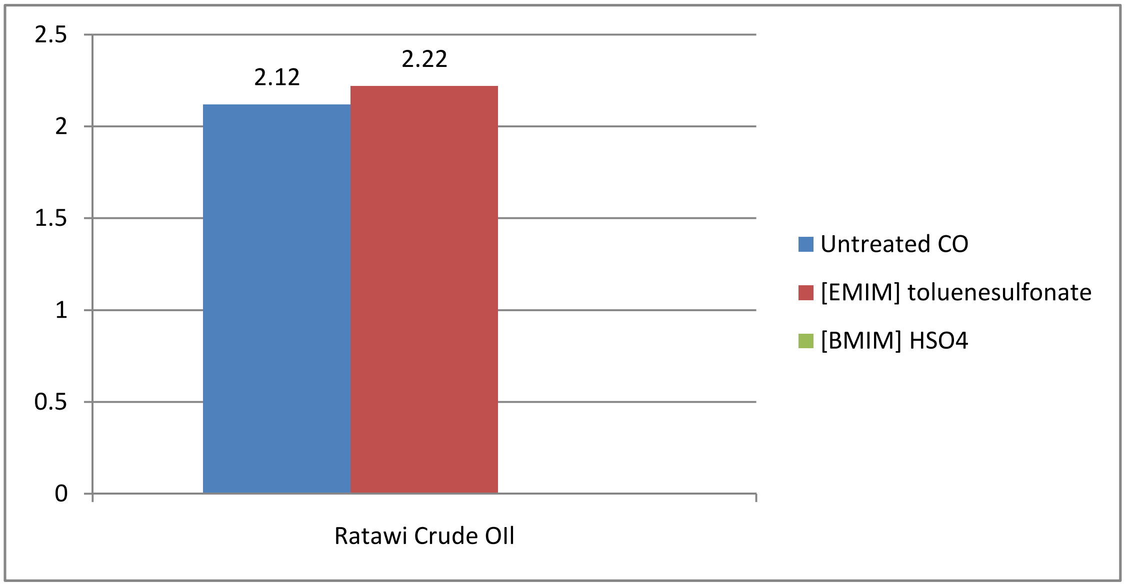


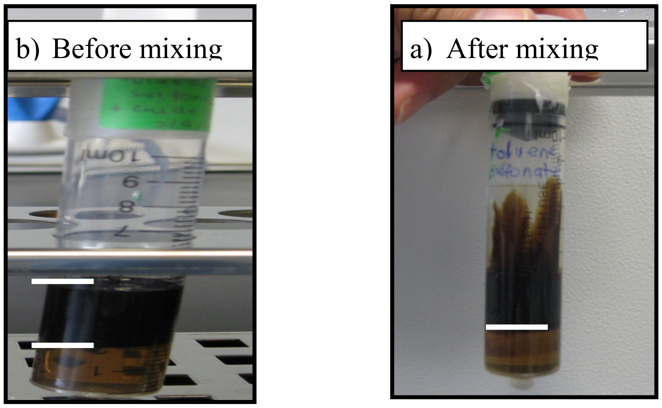
Figure 12: Bar chart based from the result of asphaltene weight % derived from crude oil

Discussion

Asphaltene precipitation occurred when temperature, pressure, and chemical composition of crude oil are changed. As n-heptane being added to the crude oil, **destabilization of micelle happened, resulting from dissolution of the resins and lead to aggregation**. This behaviour subsequently leads to precipitation of asphaltene. This method is used since this the **standard method and it would be easier to compare the results with other experiment alike**. From table 3, comparing between crude treated with IL and untreated crude sample, there are **increase by 4.71% of asphaltene content**. This is **due to self-association of asphaltene particles and asphaltene micelles with ionic liquid particles**. Sudden increases of asphaltene content occurred.

4.3 Experiment 3: Mixing and Washing Process of Crude Oil and Ionic Liquids (Visual Observation)

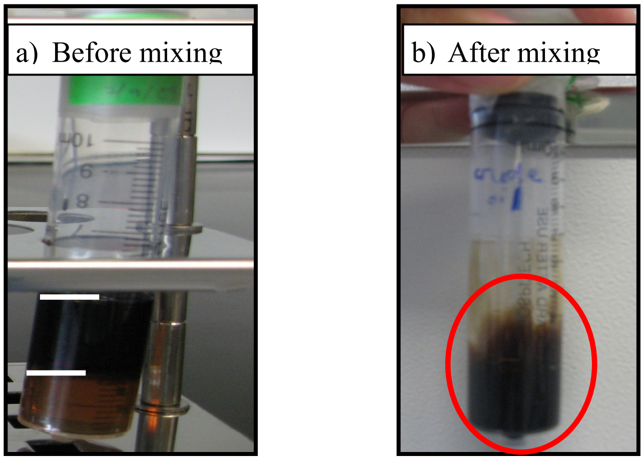
Results



b) Before mixing

a) After mixing

Figure 13: Crude oil sample with [EMIM] [tos] before and after mixing. White lines show initial level of crude oil and ionic liquid. **After centrifuged, ionic liquid level turned to initial level.**



a) Before mixing

b) After mixing

Figure 13: Crude oil sample with [BMIM]HSO_4 before and after mixing. The **sample failed to separate after centrifuged.**

Discussion

From picture, **crude oil mixed with [BMIM] HSO_4 did not separate.** During mixing, **increased temperature caused anion size of this IL increase, and effect in higher density (on account of higher molecular mass)**. Experiment also showed that **[BMIM] HSO_4 associate very well with crude oil at 80°C temperature** that it can't be separated anymore. Experiment to determine the best separation temperature for [BMIM] HSO_4 was not conducted prior to mixing experiment. So, it can be deduced that **[BMIM] HSO_4 has different ideal separation temperature** compared to other ionic liquid.

4.4 Experiment 4: Determination of Asphaltene Yield

Result

Crude Sample	**A**	**B**	**C**	**D**
Weight asphaltene, g	11.559	11.7054	11.6002	11.6421
Weight of maltene, g	11.541	11.6028	11.5372	115322
Yield (weight of maltene – weight of asphaltene),g	0.1557	0.1026	0.0630	0.1099

Table 4: Asphaltene yield for untreated crude oil

Discussion

Asphaltene yield will be used for further analysis (GPC, CHNS) and also other experiment, which is to treat asphaltene directly with ionic liquid.

4.5 Experiment 5: CHS Analysis

Result

	Crude Oil		Asphaltene	
Wt %	**Untreated Oil**	**Treated with [EMIM]tos**	**Untreated Oil**	**Treated with [EMIM]tos**
C/H	4.0707	3.8615	8.5665	9.2454
Sulfur	2.219	1.812	7.743	8.283

Table 5: Comparison of weight % and sulfur content between asphaltene and crude oil

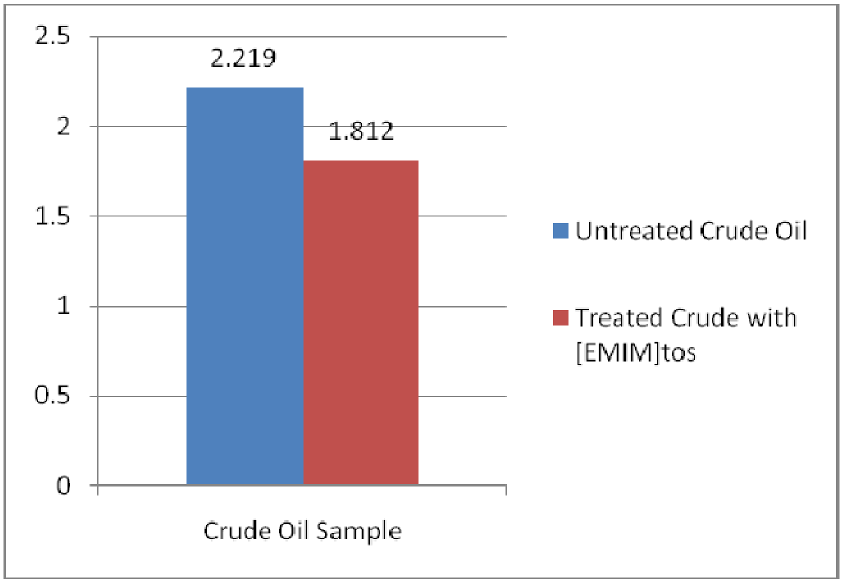


Figure 15: Bar chart based on the result of sulfur content for crude oil sample

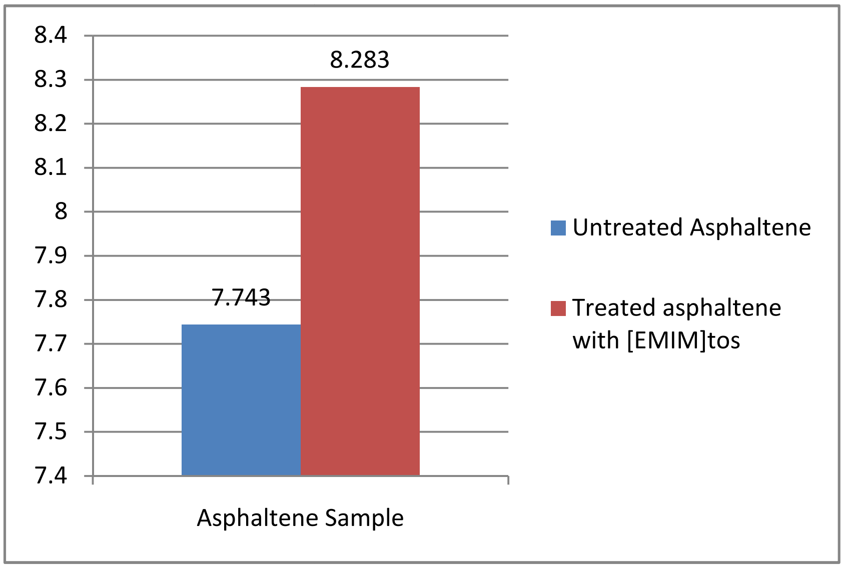


Figure 16: Bar chart based on the result of sulfur content for asphaltene sample

Discussion

There are two steps involved for this analysis. First, **to do analysis for crude oil treated with ionic liquid, and the next analysis is for asphaltene treated with [EMIM]tos. Crude oil sample recorded that sulfur decreased** from 2.2190 to 1.8120 wt%. This shows that **[EMIM]tos used can reduce sulfur content of crude oil**. However, **asphaltene showed increased sulfur content when treated directly with [EMIM]tos**. This also proved that with the **existence of other compound (SAR) in crude oil** during treatment of crude oil with [EMIM]tos, **[EMIM]tos tend to associate and cluster with other molecules** rather than asphaltene alone , and results in lower weight percent and sulfur content in samples.

4.6 Experiment 6: Gas Permeation Chromatography (GPC) Analysis

Result

	Untreated Asphaltene	**Treated Asphaltene with [EMIM] tos**
Mn	5629.00	4184.00
Mw	7215.00	7451.00

Table 6: Result for GPC analysis

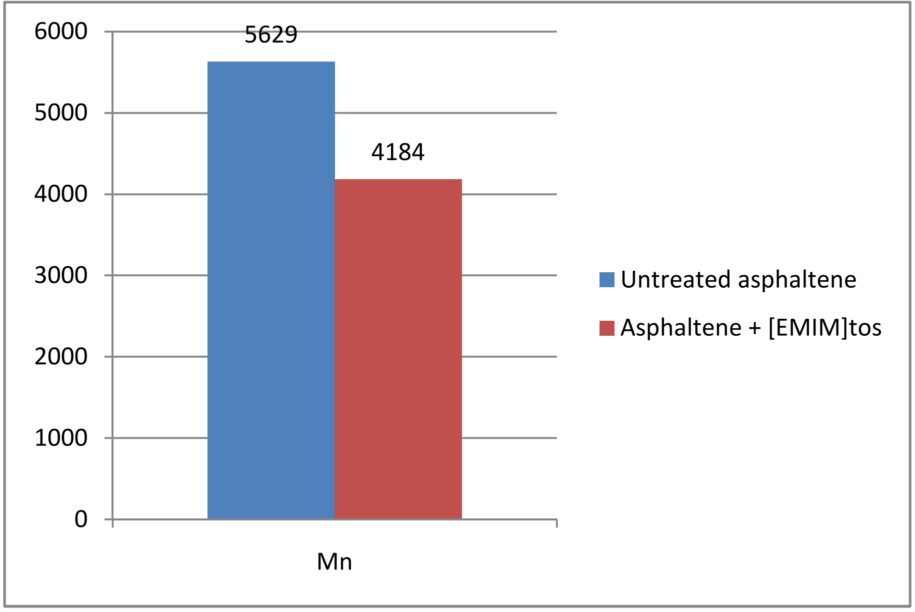


Figure 17: Bar chart based on the result of molecular number (Mn) for asphaltene sample

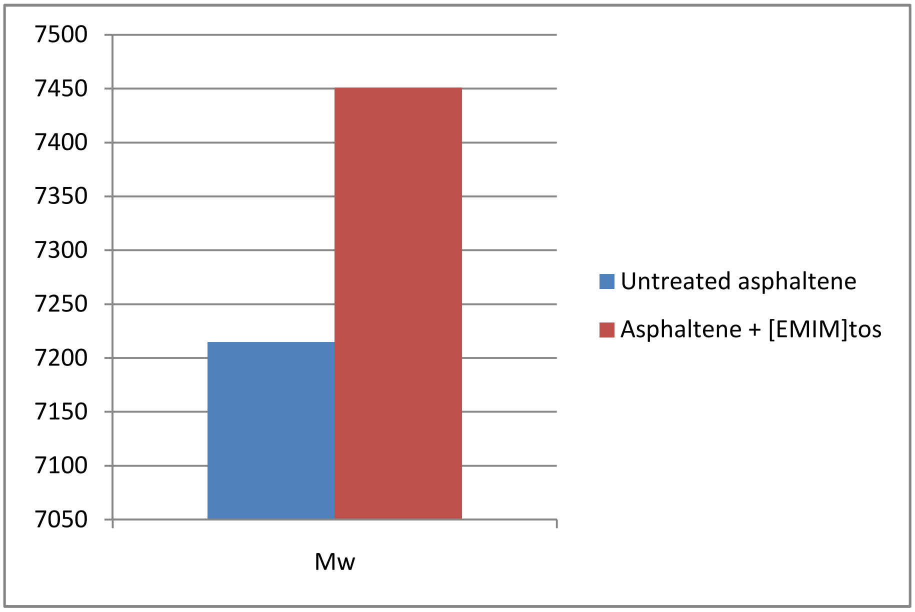


Figure 18: Bar chart based on the result of molecular weight (MW) for asphaltene sample

Discussion

The molar mass of asphaltene is obtained by averaging the molar mass of the different chains by number (Mn) or by weight (Mw). **Asphaltene treated with [EMIM]tos showed higher Mw than untreated asphaltene.** This is due to **[EMIM]tos that unable to dissolve asphaltene and associate with asphaltene molecule.** However, **untreated asphaltene shows higher number than treated asphaltene**. This proved that **less asphaltene will result in higher molecular weight in single molecule** rather than more asphaltene which has lower molecular weight for single molecule. It can be deduced that **[EMIM]tos managed to reduce number of mol exist in asphaltene, but increase asphaltene molecular weight.**

4.7 Experiment 7: Treating Asphaltene with Ionic Liquid

Result

Solution Mixture	**Weight (initial), mg**	**Weight (final), mg**	**Weight (final-initial)**
Asphaltene + Toluene + n-heptane (control experiment)	137.650	150.620	12.97
Asphaltene + Toluene + n-heptane + [EMIM] tos	111.817	168.221	56.404
Asphaltene + Toluene + n-heptane + [BMIM]HSO_4	141.801	146.535	4.743

Table 7: Differences in asphaltene weight (g) when treated with ionic liquid

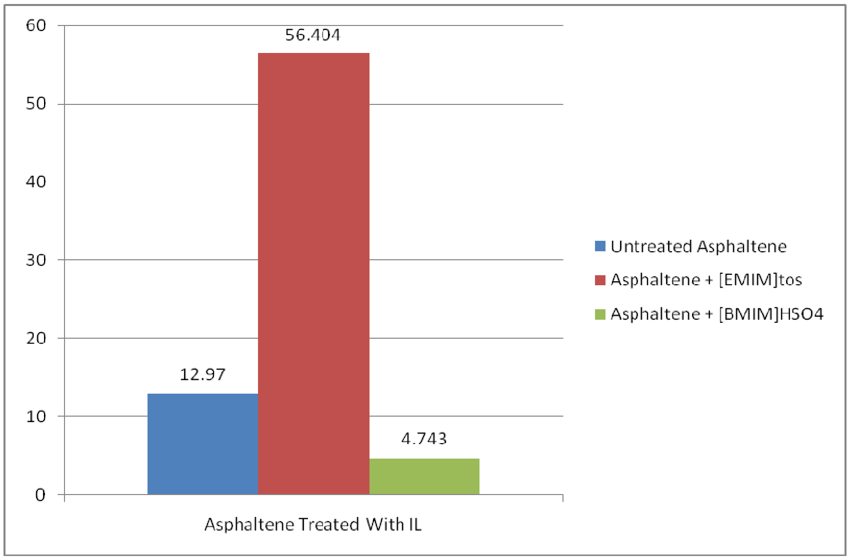


Figure 19: Bar chart based on the weight (g) for asphaltene sample treated with IL

Discussion

These results support the outcome from Experiment 5. There are **increments in weight (g) of precipitate of asphaltene when it is directly treated with [EMIM]tos**. The reason behind this is because **[EMIM]tos associated very well with asphaltene molecules**, and caused aggregation happened. However, although there showed some **decrease for sample treated with [BMIM]HSO_4**, we **cannot compare the result** with earlier experiment since this type of ionic liquid can't be separated at 80°C. For this experiment, it is **recommended to wash the sample with DI water prior to weigh** it so comparison will be more accurate.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

The experiment method should be improvised to obtain better results and reduce potential error that occurred. Some opportunity for study improvements are:

1. **In experiment 3 during mixing process of crude oil with ionic liquid**, the sample should be vortex and centrifuged directly so there will be no change in temperature and condition during separating the ionic liquid with crude oil. In the other hand,
2. **For experiment 7 in treating asphaltene with ionic liquid**, the balance used is located quite far from the location where experiment conducted. This might result in change of sample weight and other error. So, it is recommended to locate the equipment nearby the experiment location.
3. It is recommended **to study the best separation temperature for [BMIM]HSO$_4$ and crude oil prior to treat crude oil** with this type of ionic liquid. The might be some differences in between [BMIM]HSO$_4$ and other type of ionic liquid.
4. Use ionic liquid that has lower/ no amount of sulfur.

From the experiments that were conducted, ionic liquid used [BMIM]HSO4 shows potential in reducing asphaltene content. This interesting finding should be granted further analysis. In the other hand, [EMIM]tos is proven to increase the asphaltene weight percent, sulfur content and also molecular weight. This type of ionic liquid tends to cluster with asphaltene molecule, results in higher molecular weight compared with before treatment. If this ionic liquid used in the industry, it is highly recommended to remove asphaltene that aggregates prior entering distillation column for fractionation.

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APPENDIX:

Experiment 1

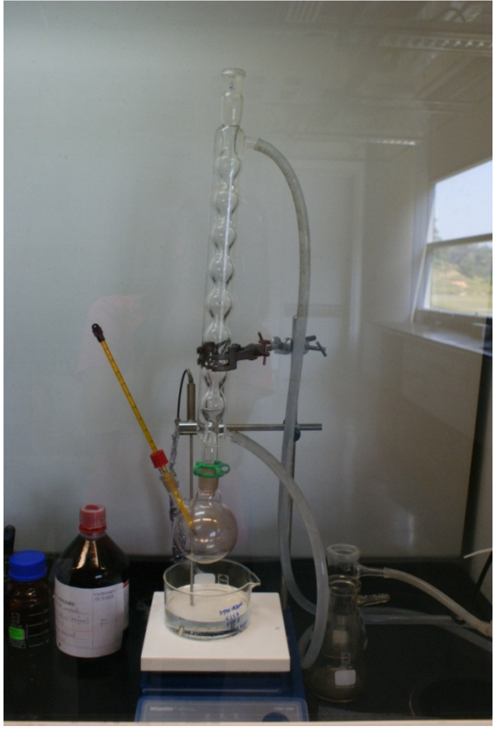

Figure 20: Assembly of apparatus for dispersing

Figure 21: Assembly of filtration apparatus. [16]

Figure 22: Gooch crucible is placed in an oven for drying purposes at 107^{0}C for 15minutes

Experiment 2

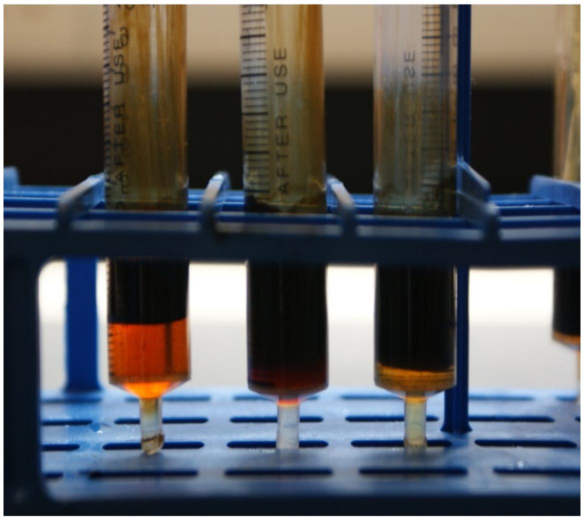

Figure 23: Crude oil mixed with IL

Figure 24: Asphaltene derived from crude oil

Results for Experiment 5

1. For crude oil

Wt%	**Untreated Crude**	**Crude Treated with [EMIM]tos**
Carbon	45.0633	36.62
Hydrogen	11.07	9.4833
Sulfur	2.219	1.812

Table 8: Result for CHS analysis of crude oil

2. For asphaltene

Wt %	**Untreated asphaltene**	**Asphaltene Treated with [EMIM]tos**
Carbon	67.17	72.5767
Hydrogen	7.841	7.85
Sulfur	7.743	8.283

Table 9: Result for CHS analysis of asphaltene

3. For maltene

Wt %	**Untreated Maltene**	**Maltene Treated with [EMIM]tos**
Carbon	59.29	47.96
Hydrogen	9.037	6.305
Sulfur	3.163	1.443

Table 11: Result for CHS analysis of maltene