



UNIVERSITI  
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PETRONAS

## **Investigation of asphaltene under ionic liquid**

by

Abdelaziz Ibrahim El sayed

14694

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Petroleum)

May 2015

Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the  
Petroleum Engineering Programme  
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In partial fulfilment of the requirement for the  
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May 2015

## **CERTIFICATION OF ORIGINALITY**

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

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Abdelaziz Ibrahim Elsayed

## **Abstract**

Ionic Liquids are salts with melting temperature below 100 °C. They have fascinating characteristics that made them an eco-friendly replacement for volatile organic solvents. Over years, research has proven the capability of Ionic Liquids to extract heavy metals and organic compounds from water and organic solvents. Researchers have also been able to immobilize Ionic Liquid on Solid support to be used as a catalyst. This study investigates the dissolution of petroleum asphaltene with ionic liquid. The important parameters governing the ability of ionic liquids for dissolution of asphaltene are discussed. The ionic liquids based on the cations containing a conjugated aromatic core or the anions which are strong hydrogen bond acceptors are most effective, whereas the ionic liquids containing non-coordinating anions such as [BF<sub>4</sub>]<sup>-</sup> and [PF<sub>6</sub>]<sup>-</sup> are nonsolvents for asphaltene. Increase in the effective anion charge density enhances the ability of ionic liquids to break the extensive asphaltene associations and thus enhances the solubility of asphaltene in the ionic liquid. Temperature is found to play an important role on dissolution of asphaltene and the dissolution can be significantly improved by microwave heating.

## **ACKNOWLEDGEMENT**

The author wishes to take the opportunity to express his utmost gratitude to the individual that have taken the time and effort to assist the author in completing the project. Without the cooperation of these individuals, no doubt the author would have faced some minor complications throughout the course.

First and foremost the author's utmost gratitude goes to the author's supervisor, Dr. Pradip Chandra Mandal. Without his guidance and patience, the author would not be succeeded to complete the project. To the Final Year Research Project Coordinator, Dr. Asif Zamir for providing him with all the initial information required to begin the project.

To the entire technician staff in Petroleum Engineering department for helping with the materials and equipment.

The author would be pleased to thank all the lectures from UNIVERSITI TEKNOLOGI PETRONAS. That helped me and supported me all over the way.

Finally, my family who always supported me and always believed in me. To them I am grateful.



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# INTRODUCTION

## 1.1. Project Background

For Many years, crude oil has been the cheapest source of liquid fuels in many countries. With the increasing demand of the oil in our daily life a balance between the production economics and the demand should has been done and with the need of light oil the amount of heavy crude oil increase as a result of that. Basic processes for this are the so-called “cracking” processes in which relatively heavy hydrocarbons are broken down into smaller, lower boiling fractions.

The present trend in the petroleum industry shows an increasing demand for light products such as gasoline , jet fuel and diesel fuel. In order to meet the market demand, refineries convert a portion of their residual heavy oils into light fractions by destructive processes. This conversion also results in the production of moder heavy fuels, which contain concentration of sulfur, vanadium and asphaltenes (ASs) (Vasily Simanzhenkov,2003).

In the present market, there is less high quality crude oil but more bitumen with very high content of ASs. This is the reason why heavy bitumen and/or vacuum residues from petroleum refineries should be realized as an alternative feed for the production of liquid fuels.

ASs, Maltenes (MAs) and Coke are the main three compositions of the crude oil. MAs represent the fraction of asphalt that is soluble in n-alkane solvent such as pentane and heptane.

This project will focus on investigation of ASs under Ionic liquid by conducting the laboratory experiment. After done with the investigation, the heavy oil sample will undergo an extraction process to identify the percentage of MAs, ASs and coke.

## 1.2. Problem Statement

With the increasing demand for light crude oil products such as gasoline, jet fuel, propane, heating oil and diesel fuel and the need to meet the market demand it became a must that refineries convert a portion of their residual heavy oils into light fractions. This conversion results in the production of heavy fuels which contain greater concentration of ASs.

ASs are considered to be part of the bottom of the barrel. They constitute the non-volatile, high molecular weight fraction of petroleum. In addition to that they remain in the solid form in crude oil since ASs are non-soluble in heptane. The presence of ASs in crude oil causes problems for oil recovery, visbreaking processes and storage.

Many different methods have been used to solve the problems presented by ASs. Chemical treatments of ASs usually involve the use of aromatic-based cleaning fluids, such as toluene and xylene, to dissolve ASs precipitates and deposits. In order to improve the efficiency of ASs dissolution the cosolvents such as amine and sulfonic acid compounds have been added to aromatic solvents (Gonzalez, G., Middea, A., 2001).

Since the aromatic-based solvents are volatile and hazardous, it is important to develop new solvents for removal of ASs precipitates and deposits. In this project ionic liquids (ILs) will be used for dissolution of petroleum ASs.

### **1.3. Objective**

The objectives of this study are as the following:

- To Identify the suitable (IL) for the dissolution of heavy crude oil ASs in economic way.
- To extract the main three compositions of crude oil “MAs, coke and ASs”.
- To investigate ASs under suitable ionic liquid.

#### **1.4. Scope of Study**

The study is divided into 5 major parts as follows:

1. Literature Review: In the literature review stage, existing asphaltenes and ionic liquid are studied and identified. Methods and experiments by other researchers are the important highlights to be studied during this stage.
2. Experimental procedures: After identifying the asphaltenes physical properties and characteristic, experimental procedures will be selected for laboratory test. The suitable experimental procedures will be used in laboratory tests.
3. Laboratory Set Up: Tools and equipment to be used will be identified and familiarized prior to the laboratory tests to avoid any inaccurate result. Accuracy of equipment and chemicals used in the tests also will be checked in order to get accurate results.
4. Laboratory Tests: A series of laboratory tests will be performed in the laboratory that suites the experiment.
5. Analysis of Results: Results obtained from the laboratory tests will be analyzed and interpreted.

# LITERATURE REVIEW

## 2.1 Heavy Crude Oil

Heavy oil is that type of oil that cannot easily flow. It is called “heavy” because of it has density or specific gravity is higher than that of light crude oil. Heavy crude oil has API gravity approximately between 10 to 20, which means its production under normal reservoir conditions is not easy.

In the north of Orinoco river in Venezuela the largest reserves of heavy crude oil in the world could be located , the oil reserves of Saudi Arabia have the same amount, but there are more than 30 countries are known to have resources.

Due to the density and specific gravity of the heavy oil production, transportation and refining always present special challenges compared to light crude oil. Usually, to facilitate the flow of the heavy oil a diluent is added at regular distances in the pipeline carrying it.

Heavy oil is dense and viscous due to the presence of high ratio of aromatics and naphthelenes to paraffines and high amounts of NSO's (nitrogen,sulfur, oxygen and heavy metals). Heavy oil has a high boiling point and molecular weight due to the high percentage of compounds with over 60 carbon atoms.

The high proportions of high molecular weight, non-paraffinic compounds and low proportions of volatile, low molecular weight compounds are the reason for the “heaviness” of heavy oil.

Two major types of heavy crude oil can be found :

- Those mostly found in North America (Canada), United states, South America (Venezuela, Colombia and Ecuador) and Middle East (Kuwait, Saudi Arabia) and in these the Sulfur percentage is over 1% (high sulfur crude oils) with aromatics and ASs.
- Those found in Western Africa (Chad), Central Africa (Angola) and East Africa( Madagascar) and in these the sulfur is less than 1% ( low sulfur crude oils) with aromatics, naphthenes and resins.

## 2.2 Asphaletene (ASs)

Asphaltene originally comes from the word “asphaltu” which means “to split”, and then the word was adopted by the Greeks to mean “firm”, “stable” or “secure”. ASs are poorly understood according to the complexity of its chemical structure and having no exact information about it. ASs are known for their insolubility in paraffin solvents (n-heptane) and solubility in aromatic solvents (toluene). After the cracking and visbreaking processes the ASs tend to stay in the heavy residues of crude oil.

There are problems related to the presence of ASs in the crude oil such as:

- the presence of ASs tends to lead to a problem with oil recovery . For example the fine particles of ASs will prevent the fluid in the pipeline to flow which means blocking the pipeline that connects the platform to the onshore terminal and In some cases it can get worse and ASs accumulate and stick onto the pipeline.
- ASs cause a problem in the storage of the crude oil due to sludge and plugging because of the further oxidation that happens among other things.
- During the visbreaking process the degraded ASs tend to represent another problem as they are small in size, more aromatic and less soluble in MAs which causes the formation of coke formation.
- The presence of ASs causes a problem of the transportation of the crude oil.

Due to the high viscosity of the ASs the time needed for the distillation of crude oil will increase. The complexity of structure of ASs is the main reason behind that. There is always a high amount of sulphur in ASs which means treatments are needed to refine it.

When the salt is found in the liquid state then it is called ionic liquid at room temperature. Lately the term has been limited to those salts which have boiling point less than 100 °C (212 °F) taking the boiling point of water as a reference point. The ionic liquid basic structure feature is the cation, which consists normally of bulk of organic structure with low symmetry. The widely used cations in ionic liquids are based on ammonium, sulfonium, phosphonium, imidazolium, pridinium, picolinium, pyrrolidinium, etc. The anion of ionic liquid may be organic or inorganic. For example, anions include  $[\text{CF}_3\text{SO}_3]^-$ ,  $[\text{PF}_6]^-$ ,  $[\text{SbF}_6]^-$ ,  $[\text{BF}_4]^-$ , alkyl sulfates, etc. (Geeranjali Singh, Anil Kumar, 2008). Figure 1 shows some typical cations and anions.

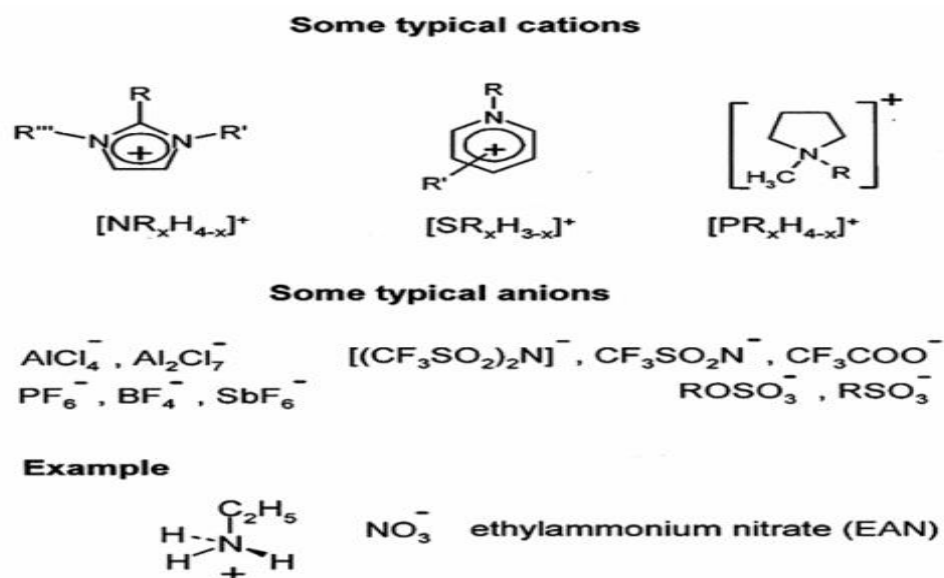


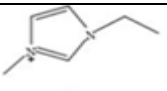
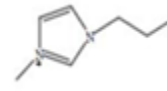


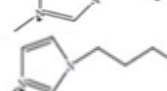
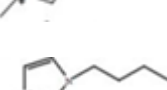

Figure 2.1 Some typical cations and anions that are commonly employed in synthesizing ionic liquids

The physic-chemical properties of ionic liquids are very important when you deal with ionic liquids as the presence of some impurities like water, organic solvents and chloride ions can alter their properties. One of the most significant physical properties is the melting point of the ionic liquid. The melting point depends on the structure and composition of the ionic liquid and the selection of both cation and anion. If the ionic liquid has a cation with low symmetry then the melting point is less than the one with high symmetry. Ionic liquids are generally denser than water and its density depends on the constituent cation and anion and it varies with the length of the N-alkyl chain on the imidazolium cation. It could be said that the density of the ionic liquid decreases with the increase in the bulkiness of the organic cation and it varies in the range between 1.05 to 1.35  $\text{gcm}^{-3}$  at ambient temperature.

One of the most important properties of ionic liquid is viscosity especially if the ionic liquid is used as a solvent media during a chemical reaction. Huddleston J G, Visser A E (2001) have stated that if the ionic liquid viscosity is very high then it

is not suitable as solvent media as high viscous ionic liquids tend to reduce the diffusion rates of redox reactions. Table 2.1 shows some of the physical properties of the ionic liquids.

**Table 2.1: Physical properties of Ionic Liquids**

| Chemical formula  |  | Abbreviation  | Melting point, °C | Density (g mL <sup>-1</sup> ), 25 °C | Viscosity (cP), 25 °C | Molecular weight |
|---|--|---|-------------------|--------------------------------------|-----------------------|------------------|
| Cation  | Anion  |   |                   |                                      |                       |                  |
|    | [BF <sub>4</sub> ] <sup>-</sup>                                  | [EMIM][BF <sub>4</sub> ]                                  | 6                 | 1.248                                | 66                    | 197.8            |
|   | [PF <sub>6</sub> ] <sup>-</sup>                                  | [EMIM][PF <sub>6</sub> ]                                  | 58-62             | 1.373                                | 450                   | 256.13           |
|    | [BF <sub>4</sub> ] <sup>-</sup>                                  | [BMIM][BF <sub>4</sub> ]                                  | -82               | 1.208                                | 233                   | 225.80           |
|   | [PF <sub>6</sub> ] <sup>-</sup>                                  | [BMIM][PF <sub>6</sub> ]                                  | 10                | 1.373                                | 400                   | 284.18           |
|    | [Br] <sup>-</sup>  | [BMIM]Br  | 60                | 1.134                                | Solid                 | 218.9            |
|   | [Cl] <sup>-</sup>  | [BMIM]Cl  | 89                | 1.120                                | Solid                 | 146.5            |
|   | [CF <sub>3</sub> SO <sub>3</sub> ] <sup>-</sup>                  | [BMIM][CF <sub>3</sub> SO <sub>3</sub> ]                  | 16                | 1.290                                | 90                    | 260              |
|   | [(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N] <sup>-</sup> | [BMIM][(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N] | -4                | 1.420                                | 52                    | 487.9            |
|   | [NTfO <sub>2</sub> ] <sup>-</sup>                                | [BMIM][NTfO <sub>2</sub> ]                                | -8                | 1.404                                | 48                    | 433              |
|   | [BF <sub>4</sub> ] <sup>-</sup>                                  | [AMIM][BF <sub>4</sub> ]                                  | -88               | 1.231                                | 321                   | 240.02           |
|   | [BF <sub>4</sub> ] <sup>-</sup>                                  | [HMIM][BF <sub>4</sub> ]                                  | -82               | 1.075                                | 211                   | 254.08           |
|    | [PF <sub>6</sub> ] <sup>-</sup>                                  | [HMIM][PF <sub>6</sub> ]                                  | -61               | 1.304                                | 800                   | 312.00           |
|   | [BF <sub>4</sub> ] <sup>-</sup>                                  | [OMIM][BF <sub>4</sub> ]                                  | -79               | 1.11                                 | 440                   | 281.8            |
|    | [Cl] <sup>-</sup>  | [OMIM][Cl]  | 0                 | 1.000                                | 16000                 | 230.50           |
|   | [NTfO <sub>2</sub> ] <sup>-</sup>                                | [MPPyr][NTfO <sub>2</sub> ]                               | 0                 | 1.44                                 | 39                    | 416              |
|   | [HCOO] <sup>-</sup>  | BAF   | -10               | 0.99                                 | 11.5                  | 91               |
|  | [NTfO <sub>2</sub> ] <sup>-</sup>                                | [BMPPyrrol][NTfO <sub>2</sub> ]                           | -50               | 1.4                                  | 71                    | 422              |

Yansheng , Yufeng, Haibo , Chunming, Dejun and Yan performed several experiments to study Ionic liquids as solvents for petroleum asphaltenes to replace the aromatic based solvents. Ionic liquids containing N-alkylpyridium[N-alkyl-py]<sup>+</sup>, N-butylisoquinolinium[C<sub>4</sub>isoq]<sup>+</sup>, 1-butyl-3-methylimidazolium [BMIM]<sup>+</sup> cations in connection with [Cl]<sup>-</sup> anion are screened. Variations in cation alkyl-substituent from ethyl through butyl were investigated for the [N-alkyl-py][Cl] salts “[Netpy][Cl],

[Nprpy][Cl], and [Nbutpy][Cl] and the ionic liquids based on [BMIM]<sup>+</sup> were examined with range of anions.

The solubility of asphaltenes in ionic liquid was determined by using the rotary

evaporator technique and microwave. The table below shows the experimental results.

**Table 2.2 Solubility of petroleum asphaltenes in ionic liquids**

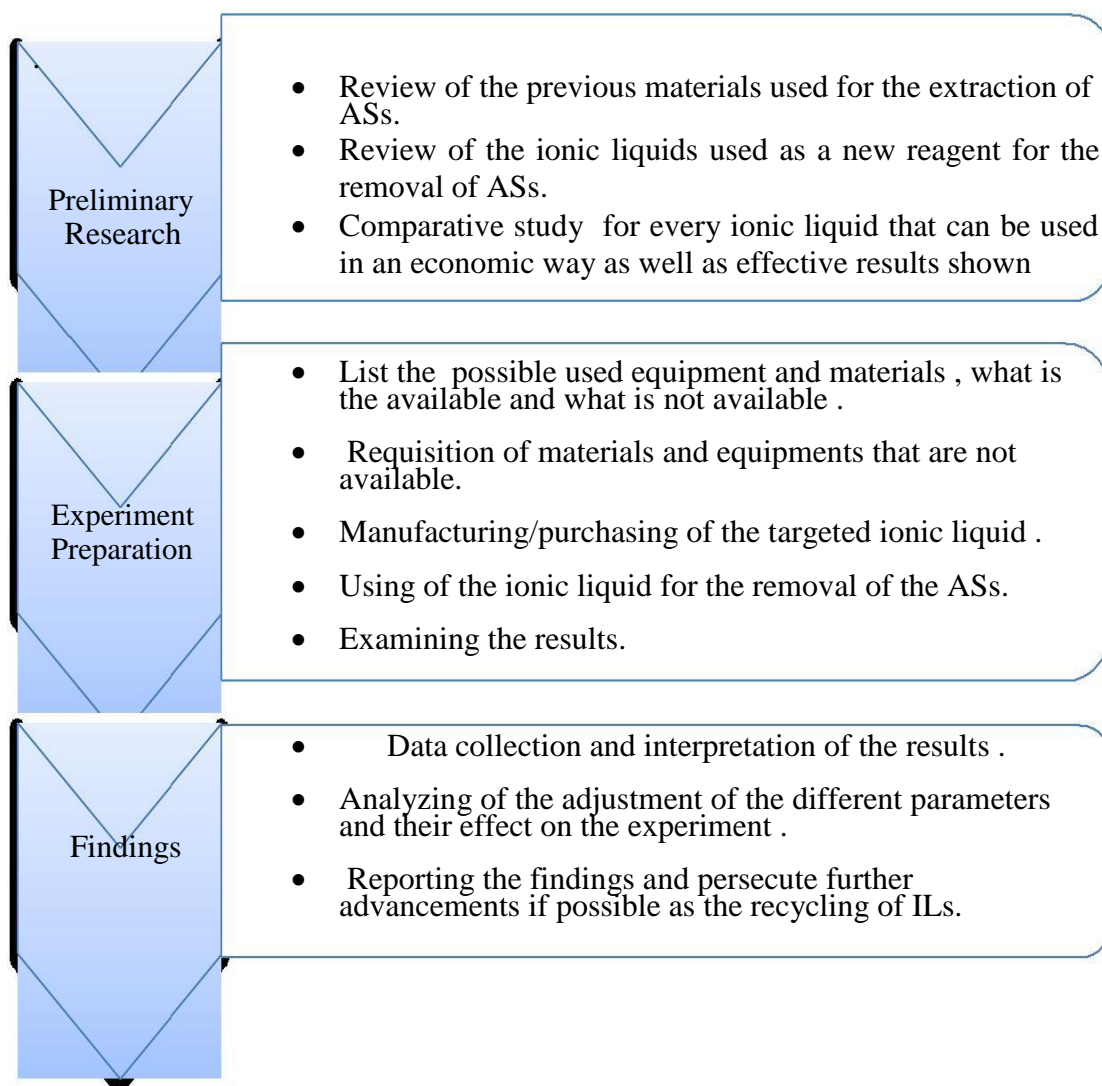
| Ionic Liquid              |                     |                   | Solubility (by mass) % |
|---------------------------|---------------------|-------------------|------------------------|
|                           | Heating temperature | Heating technique |                        |
| [C <sub>4</sub> isoq][Cl] | 50                  | Rotary evaporator | 15.2                   |
|                           | 80                  | Rotary evaporator | 26.9                   |
|                           | -                   | microwave         | 36.8                   |
| [Netpy][Cl]               | 135                 | Rotary evaporator | 16.2                   |
|                           | 150                 | Rotary evaporator | 22.8                   |
|                           | -                   | microwave         | 32.0                   |
| [Nprpy][Cl]               | 135                 | Rotary evaporator | 13.6                   |
|                           | 150                 | Rotary evaporator | 20.1                   |
|                           | -                   | microwave         | 29.5                   |
| [Nbupy][Cl]               | 135                 | Rotary evaporator | 10.3                   |
|                           | 150                 | Rotary evaporator | 18.0                   |
|                           | -                   | microwave         | 26.7                   |
| [BMIM][Cl]                | 80                  | Rotary evaporator | 8.5                    |
|                           | 135                 | Rotary evaporator | 15.6                   |
|                           | -                   | microwave         | 28.8                   |
| [BMIM][BF <sub>4</sub> ]  | 30                  | Rotary evaporator | Insoluble              |
|                           | 135                 | Rotary evaporator | Slightly soluble       |
|                           | -                   | microwave         | 2.5                    |
| [BMIM][PF <sub>6</sub> ]  | 30                  | Rotary evaporator | Insoluble              |
|                           | 135                 | Rotary evaporator | Insoluble              |
|                           | -                   | Rotary evaporator | Insoluble              |



# METHODOLOGY

## 3.1. Research Methodology

The research would be carried out through approximately eight months. The selection of the perfect ionic liquid at certain parameters would be defined to make it economic. Ionic liquids would then be synthesized with certain amounts. Purchase of crude oil, toluene and n-heptane would take place. Finally extraction of the ASs using the ionic liquids would be carried out, and would regenerate ionic liquids if possible. The flow of the study is illustrated in Figure 3.1 below:



**Figure 3.1 the flow of the project**

### 3.2. Gantt Chart

The Gantt chart for Final Year Project I and Final Year Project II are shown in Table 3.1 and Table 3.2 below:

Table 3.1: Gantt chart for FYP I

| Week  | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|----|----|----|----|----|
| Organizing the literature review              |   | ■ | ■ | ■ | ■ |   |   |   |   |    |    |    |    |    |
| Preliminary research work preparation         |   |   |   | ■ | ■ | ■ | ■ | ■ | ■ |    |    |    |    |    |
| Preparation of Extended proposal & submission |   |   |   |   | ■ | ○ |   |   |   |    |    |    |    |    |
| Proposal defense execution                    |   |   |   |   |   |   |   |   | ○ |    |    |    |    |    |
| Listing the materials & equipment required    |   |   |   |   |   |   |   |   |   |    | ■  | ■  | ■  |    |
| Preparation of Interim report & submission    |   |   |   |   |   |   |   |   |   |    |    |    | ○  |    |
| Finalizing the interim draft report           |   |   |   |   |   |   |   |   |   |    |    |    |    | ■  |

Table 3.2: Gantt chart for FYP II

| Week                                 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|--------------------------------------|---|---|---|---|---|---|---|---|---|----|----|----|----|----|
| Experimentation & interpretation     | ■ | ■ | ■ | ■ | ■ | ■ |   |   |   |    |    |    |    |    |
| Submission of progress report        |   |   |   |   |   |   | ○ |   |   |    |    |    |    |    |
| Data analysis and reporting          |   |   |   |   |   |   |   | ■ | ■ | ■  | ■  | ■  |    |    |
| Pre-SEDEX                            |   |   |   |   |   |   |   |   |   | ○  |    |    |    |    |
| Draft final report submission        |   |   |   |   |   |   |   |   |   |    | ○  |    |    |    |
| Dissertation submission (Soft bound) |   |   |   |   |   |   |   |   |   |    |    | ■  |    |    |
| Viva                                 |   |   |   |   |   |   |   |   |   |    |    |    | ○  |    |
| Dissertation submission (Hard bound) |   |   |   |   |   |   |   |   |   |    |    |    |    | ○  |

|   |                |
|---|----------------|
| ○ | Deliverability |
| ■ | Work Progress  |

### **3.3 Experimental procedures**

#### **3.3.1 Extraction procedures under standard room condition :**

Extracting the ASs was according to the ASTM D-3279 method.

Chemicals :

- 1- Crude oil/ heavy oil.
- 2- N-heptane.
- 3- Toluene.

Apparatus and materials

- 1- Round bottom flask
- 2- filter papers
- 3- Electronic balance
- 4- Funnels
- 5- Bakers

The procedures for determining the asphaltenes content in the crude oil “not-treated” in standard condition :

- i- 1 g of crude oil was weighed in the 25ml baker using the electronic balance
- ii- N-heptane was added to the crude oil with a proportion of 1:15 from crude oil and n-heptane respectively.
- iii- The mixture was shaken/stirred for better mixing and dilution
- iv- The filter paper “whatman #1” was weighed using the electronic balance and the weight was recorded
- v- Using the filter paper and a funnel the mixture of the crude/heavy oil was filtered in a bottom round flask. The insoluble portion of that mixture in the n-heptane “asphaltenes and coke” will be collected on the filter paper.



**Figure 3.2 filtering the mixture after adding n-heptane**

- vi- After filtering the mixture the filter paper was put in the oven for 2-3 mins to dry
- vii- Then the filter paper with the insoluble part “ASs and coke” was weighed and recorded.
- viii- Knowing the weight of the filter paper the weight of asphaltenes + coke was known
- ix- Toluene was used to wash the filter paper carefully. Asphaltene is soluble in toluene so the insoluble portion would be coke.
- x- Using the oven for 2-3 mins the filter paper was dried.
- xi- The electronic balance was used to weigh the filter paper.

After these procedures, the weight for each Maltenes, Asphaltenes and coke could be calculated using the next formulas:

Weight of coke: “weight of filter paper + coke” – “the weight of the filter paper”

Weight of asphaltenes: “weight of filter paper + ASs+ coke” – “weight of filter paper + coke”

Weight of Maltenes: “weight of crude oil” – “weight of ASs+coke”

The percentage of each component could be calculated from the next formulas :

Percentage of maltenes: “weight of MAs /weight of crude oil” \* 100%

Percentage of asphaltenes: “weight of ASs /weight of crude oil” \* 100%

Percentage of coke: “weight of coke /weight of crude oil” \* 100%

### **3.3.2 Treating the crude oil with ionic liquid for 10,30 and 60 mins**

Experimental parameters:

The mixture of the crude oil and the 1-ethyl-3-methylimidazolium chloride ionic liquid were tested at different temperatures 70, 80, and 90 °C for different time 10, 30 and 60 minutes.

The chemicals:

- 1- Crude oil
- 2- 1-ethyl-3-methylimidazolium chloride ionic liquid
- 3- N-heptane
- 4- Toluene

Apparatus and materials

- 1- Measuring tube
- 2- Funnels
- 3- Whatman filter paper
- 4- Round bottom flask
- 5- Electronic balance

Procedures of mixing the ionic liquid and crude oil at 70 °C:

- i- 2 ml of the 1-ethyl-3-methylimidazolium chloride were added to a 1 g of crude oil in the round bottom flask
- ii- The mixture was stirred for better dilution
- iii- The flask was put in the oven at the specific temperature 70 °C for 10 minutes.
  
- iv- The filter paper was weighed using the electronic balance.
- v- After heating the mixture ionic liquid was separated from the crude oil
- vi- The crude oil was mixed with n-heptane and stirred for better dilution.

- vii- The mixture was filtered using filter paper and funnel
- viii- The filter paper was dried in the oven for 2-3 minutes.



**Figure 3.2 Asphaltenes + coke on filter paper**

- ix- The filter paper with the insoluble portion in the n-heptane was weighed.
- x- The insoluble portion in the n-heptane was washed by toluene
- xi- The filter paper was then dried in the oven for 2-3 minutes and then weighed.



**Figure 3.3 filter paper after being washed with toluene**

- xii- Results are recorded the same way in the first experiment.

## Chapter 4 Results and discussion

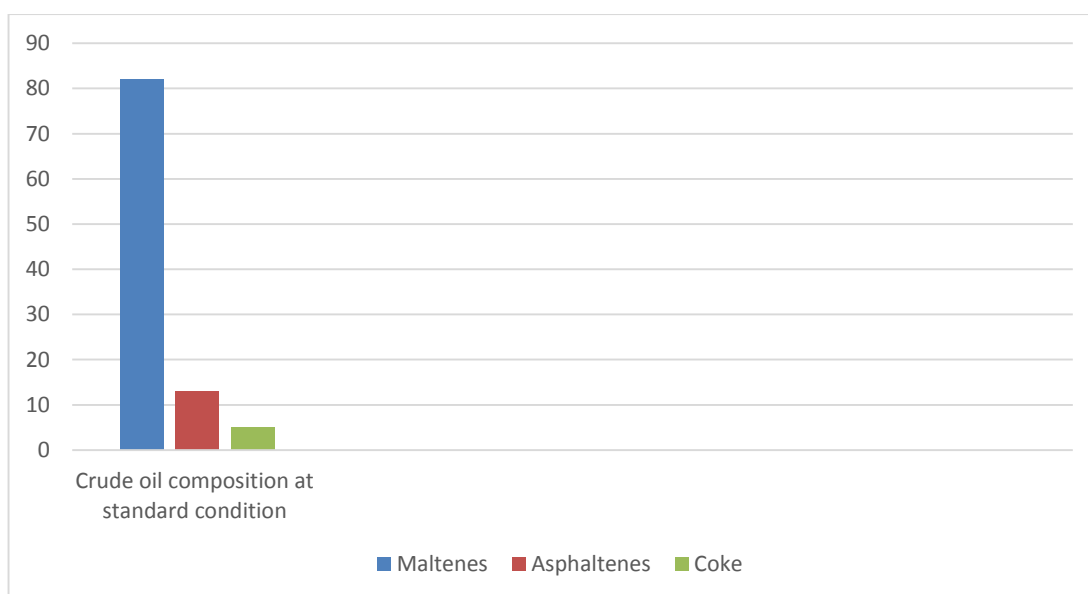
### 4.1 results

#### 4.1.1 Determination of the asphaltenes percentage in the crude oil at standard condition.

There was no effect of the pressure or the temperature on the percentage of the composition of the heavy oil as the experiment was done in the room temperature and pressure. Table show the results

**the ASs content at standard condition**

| Component    | Weight "g" | Percentage % |
|--------------|------------|--------------|
| Crude oil    | 1.034      | -            |
| Filter paper | 0.474      | -            |
| Coke         | 0.051      | 4.94         |
| Asphaltenes  | 0.134      | 12.95        |
| Maltenes     | 0.849      | 82.1         |



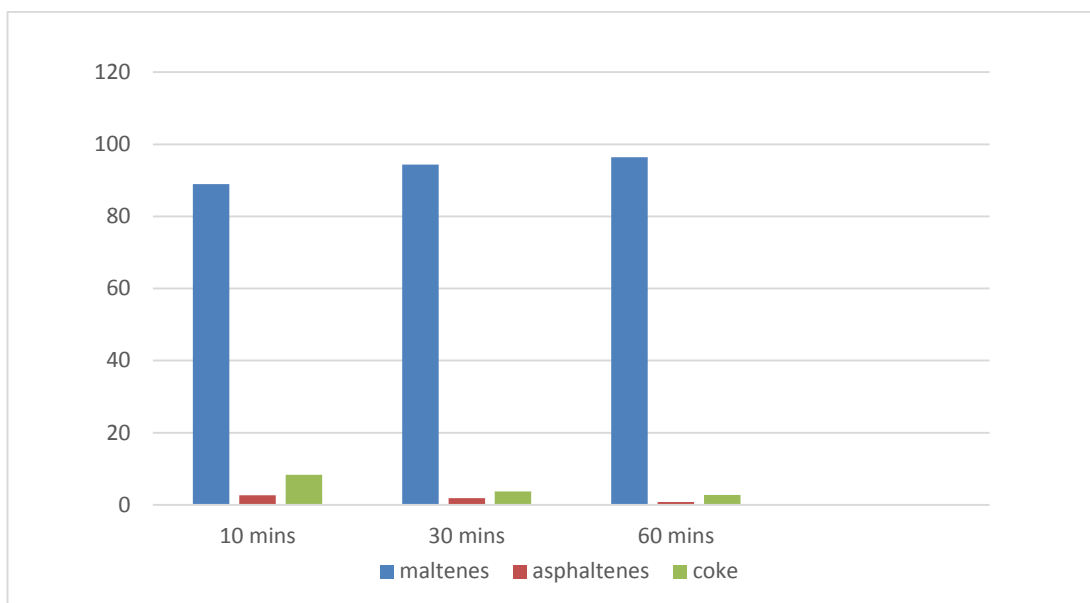
**Figure 4.1 Weight percentage of crude oil composition at standard conditions**

#### 4.1.2 Determination of crude oil composition after being treated with 1-ethyl-3-methylimidazolium chloride at different temperatures and for different time :

At 70 °C

**Table 4.2 the ASs content at 70°C with ionic liquid**

|      | 100 mins | 30 mins | 60 mins  |
|------|----------|---------|----------|
| ASs  | 2.703 %  | 1.872 % | 0.803 %  |
| MAs  | 88.91%   | 94.401% | 96.4509% |
| Coke | 8.386%   | 3.725%  | 2.745%   |

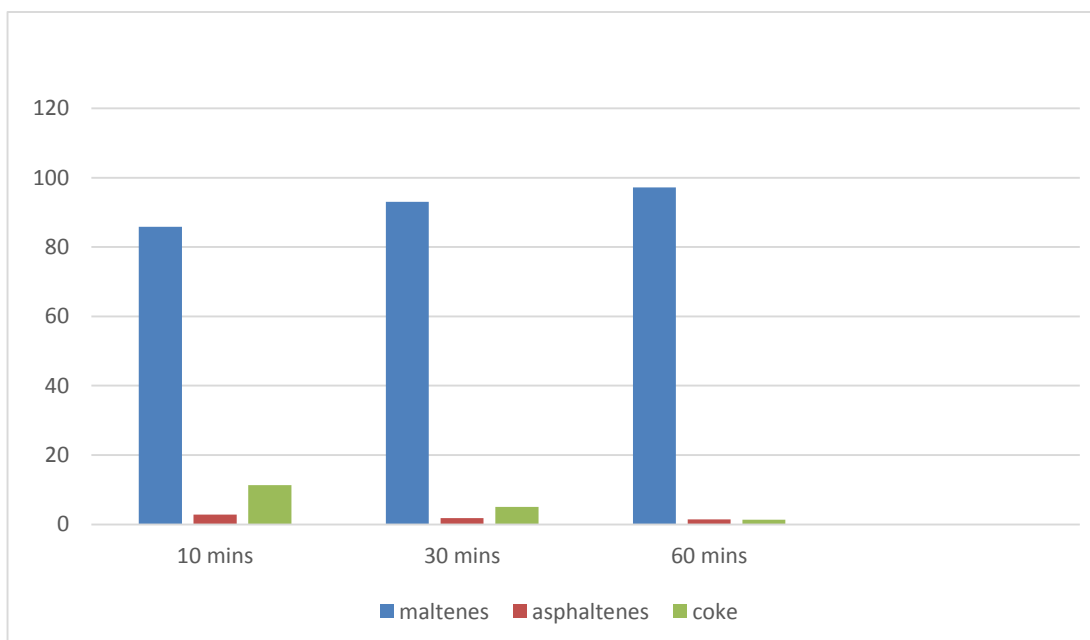


**Figure 4.2 Weight percentage of crude oil composition at 70 °C with ionic liquid**

At 80 °C

**Table 4.3 the ASs content at 80°C with ionic liquid**

|      | 10 mins | 30 mins | 60 mins |
|------|---------|---------|---------|
| ASs  | 2.856%  | 1.87%   | 1.45%   |
| MAAs | 85.81%  | 93.046% | 97.15%  |
| Coke | 11.32%  | 5.08%   | 1.39%   |



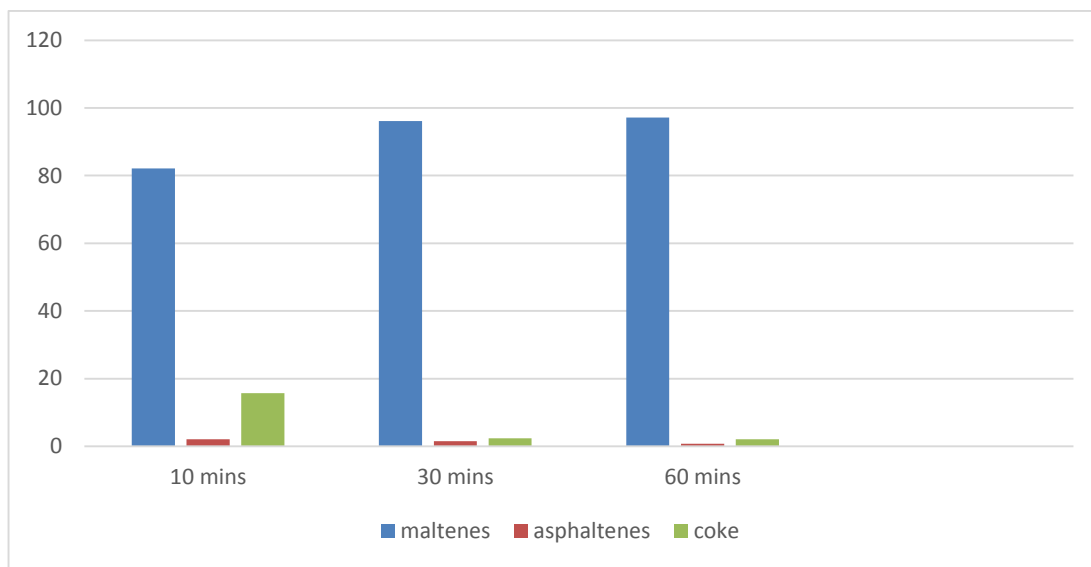
**Figure 4.3 Weight percentage of crude oil composition at 80 °C with ionic liquid**



At 90 °C

**Table 4.4 the ASs content at 90°C with ionic liquid**

|      | 10 mins | 30 mins | 60 mins |
|------|---------|---------|---------|
| ASs  | 2.11%   | 1.47%   | 0.7707% |
| MAs  | 82.159% | 96.12%  | 97.154% |
| Coke | 15.73%  | 2.39%   | 2.075%  |



**Figure 4.4 Weight percentage of crude oil composition at 90 °C with ionic liquid**

## **4.2 Discussion**

### **4.2.1 Extraction under standard room condition**

According to Watanabbe,2010 heavy oil contain 90% MAs and 10% ASs and from the experiment it was found that the crude used contain 82.1% MAs, 12.95% ASs and 4.94 coke which shows the values are different from the one used in the literature. To start the experiment , the heavy crude oil was weighed and mixed with n-heptane with the proportion of 1:15 (LIU Yansheng,HU Yufeng, SUN Yan, 2005) the mixture was stirred for better dilution according to the ASTM D-3279. N-heptane is one of the solvents for the crude oil maltenes which means after filtering the mixture only asphaltenes and coke would be left on the filter paper.

The maltenes were dissolved by the n-heptane and the filter paper was put in the oven to dry and to make sure the n-heptane is completely evaporated. This is important to make sure only the fine particles of ASs and coke were left on the filter paper to avoid any error in the weight measurement. Then the filter paper with the fine particles was washed with toluene. Knowing that ASs are soluble in the toluene then any fine particles on the filter would be coke. The ASs percentage could be calculated from the equations in appendix and it was 12.95%. The coke percentage in the crude oil is 4.94% which is higher than that from the literature review which is said to be very less and could be negligible (Eng et al., 2008). That means the crude oil we are dealing with is very heavy according to the high amount of ASs and coke

### **4.2.2 Determiation of asphaltenes content in the crude oil after treating with 1-ethyl-3-methylimidazolium chlorid :**

The amount of ASs in the heavy crude oil has been determined at different temperatures 70 , 80 and 90 °C . from the results it's observed that at the standard condition the ASs content wasn't affected with the ionic liquid before using the ionic liquid it was 12.95% while after mixing with the ionic liquid the percentage is 12.497 the difference is almost negligible while the maltenes and coke content were affected in different ways the coke content was increased from 4.94% to 10.209% and the MAs content decreased from 82.1% to 77.29%.

At 70 °C the amount of ASs content after being treated with the 1-ethyl-3-methylimidazolium chloride has been reduced significantly to 1.872 % after 10 minutes heating while the MAs content has increased to be 94.401 % which means the ionic liquid has successfully reduced the ASs and coke content after 10 minutes heating. The best results at 70 °C were obtained when the mixture was heated for 60 minutes. The ASs content has been reduced to be 0.803 % which means temperature is playing a great role in affecting the ASs content as well as the time of heating the more you heat the mixture the more the particles tend to break down and get separated from the crude oil.

When heating the mixture to 80 °C the ASs content has been reduced to 1.45% after 10 minutes while the MAs has increased to be 97.15% which means 10 minutes were enough to break down the asphaltene bonds and building up new ones with the MAs. After 60 minutes of heating the ASs content was 1.87% while the coke percentage went up to be 5.08 the justification for that is the ionic liquid has been attracted to the coke ions forming new bonds and increasing it in the weight.

The other temperature the mixture has been tested at was 90 °C. when the mixture has been heated for 10 minutes the ASs content went down to be 2.11 % while the coke percentage went up to be 15.73% which means there is some sort of bonding between the ionic liquids and the coke in the crude oil. When the mixture was heated for 30 and 60 minutes the results were much better and much appealing as the ASs content went down to be 1.47% and 0.7707 % respectively which means at high temperature and when increasing the time of heating the ASs content is decreasing and the same goes for the coke content.

## **CHAPTER 5**

### **CONCLUSION AND RECOMMENDATIONS**

#### **5.1 Conclusion**

From this experiment we can conclude that the more amount of heavy crude oil used the more ASs content could be found in the crude oil. And the asphaltenes content in the sample used was about 12.49 % of the heavy crude oil composition and according to the literature the amount of asphaltenes in the typical heavy crude oil is between 10-15 % which means the crude oil used just fits in the same category.

According to the literature review the imidazolium cation has been proven to be a great dissolvent especially for the crude oil asphaltenes as the ionic liquid is attacking the bond in the asphaltenes and break it down which leads to decrease the asphaltenes content in the crude oil which means less problem in the oil recovery, transportation and storage .

1-ethyl-3-methylimidazolium chloride as ionic liquid has been successful as a solvent agent for the asphaltenes in the heavy crude oil .From the results of the treated crude oil the best temperature to mix the 1-ethyl-3-methylimidazolium chloride with the crude oil is 90 °C as the results got from this temperature were consistent.

Temperature and the time of heating play a great role in determining the amount of ASs in the crude oil when using 1-ethyl-3-methylimidazolium chloride as a solvent. The asphaltenes content was decreasing by increasing the temperature from 70 up to 90 as shown in the results.

## **5.2 Recommendations**

After the 1-ethyl-3-methylimidazolium chloride has already been proven to successful in the lab it's now the time to perform more experiments including other parameters to determine the ability of applying this in the field and getting results. The amount of both crude oil and the ionic liquid should be experimented to figure out the best proportion between them. The amounts of crude oil and ionic liquid should be varied to determine the best proportion. And finally a CHNS analyzer should be used for more accurate results.

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# APPENDECIES

## Appendix A

### NuGenTec® n-heptane

#### First-aid measures

**After inhalation:** In case of unconsciousness place patient stably in side position for transportation.

**After skin contact:** Immediately wash with water and soap and rinse thoroughly.

**After eye contact:** Rinse opened eye for several minutes under running water.

**After swallowing:** Give large amounts of water. If symptoms persist consult doctor.



|            |   |
|------------|---|
| HEALTH     | 1 |
| FIRE       | 3 |
| REACTIVITY | 0 |

Danger

**Hazard statements:**  
Highly flammable liquid and vapour. May be fatal if swallowed and enters airways. Very toxic to aquatic life. Very toxic to aquatic life with long lasting effects. Causes skin irritation. May cause drowsiness or dizziness.

**Precautionary statements:**  
Keep away from heat/sparks/open flames/hot surfaces. - No smoking. Use explosion-proof electrical/ventilating/lighting equipment. IF SWALLOWED: Immediately call a POISON CENTER or doctor/physician. IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower. Store locked up. Dispose of contents/container in accordance with local/regional/national/international regulations.



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 888-996-8436 or 707-820-4080 for product information

## Appendix B

|   |   |                               |  |  |
|---|---|-------------------------------|--|--|
| <b>PRODUCT IDENTIFIER</b><br>(CAS # 108-88-3) |   | <b>TOLUENE</b>                |  | <b>REFERENCE</b><br>TO123421                             |
| <b>HEALTH</b> <b>2</b>                        | <b>WARNING !</b><br>Flammable solid. May ignite in moist air. Reacts violently with water. Corrosive material. Causes burns to the skin and eyes. May cause severe burns of mouth and throat. May be fatal if swallowed. May cause lung injury - effects may be delayed. May cause sensitization by skin contact.   |                               |  |  |
| <b>FLAMMABILITY</b> <b>3</b>                  | <b>PRECAUTION:</b><br>Keep away from heat, sparks and flame. Avoid contact with water. Keep away from incompatibles. Use with adequate ventilation. Keep container tightly closed. Handle in accordance with good industrial hygiene and safety practices. Do not swallow. Do not breathe dust. Avoid contact with eyes, skin and clothing. Wash thoroughly after handling. Wear protective goggles, full face shield, impervious boots, gloves and apron.  |                               |  |  |
| <b>REACTIVITY</b> <b>0</b>                    | <b>FIRST AID:</b><br>If inhaled, remove from contaminated atmosphere. For skin contact, flush with water for at least 15 minutes, while removing contaminated clothing. Launder clothing before reuse. For eye contact, flush with running water for at least 20 minutes. If ingested, do not induce vomiting. Have victim rinse mouth with water, then let victim drink water or milk. Never give anything by mouth if victim is unconscious. For all cases, obtain medical attention immediately. |                               |  |  |
| <b>PERSONAL PROTECTION</b> <b>J</b>           | <b>REFER TO SAFETY DATA SHEET</b>   |                               |  |  |
| <b>PERSONAL PROTECTIVE EQUIPMENT</b><br>      |   | <b>GHS HAZARD SYMBOLS</b><br> |  | <b>SHIPPING DESCRIPTION</b><br><b>TOLUENE</b><br>UN 1294 |

ICC GHM6P



