IDENTIFYING AND EVALUATING POTENTIAL INHIBITORS TO TREAT DOWNHOLE ASPHALTENE PRECIPITATION USING UV-VISIBLE SPECTROMETER

By

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CERTIFICATION OF APPROVAL

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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 person

MOHAMAD HAIKAL BIN NORDIN

ABSTRACT

The objectives of this study are to compare potential inhibitors in treating asphaltene precipitation and to evaluate the effectiveness in terms of amount of n-heptane required for precipitation to take place. Asphaltene can cause severe problem when it started to precipitate upon surplus presence of paraffin solvent that can plug wellbore, safety valves, flow line and so on. In addition, asphaltene can aggregate oil/water interfaces as it stabilize water-oil emulsion or at oil/solid interfaces. It is unfortunate for engineers since major part of reservoir fluid contains paraffin which precipitation will occur over time. Therefore, preventive or remedial solutions are required to cater this problem. The study covers the fundamental understanding of asphaltene precipitation mechanism, identifying potential inhibitors and evaluating the effectiveness through laboratory experiments. The study is organized into two stages which mainly cover a depth study of the subject and validating early inferences through experiments. The method used in the study is based on observing light absorbance using Shimadzu UV-visible double beam spectromter. Interpretation is done by observing light intensity difference between test cell and reference cell inside UV-visible spectrometer. Throughout early study in literature reviews, aromatic solvents and sulphonic acid derivative shows a great result in inhibiting asphaltene precipitation. Therefore, xylene and 1,3 benzenedisulfonic acid were chosen as main inhibitors with toluene as backup inhibitor to be studied. The effectiveness between these three inhibitors in inhibiting asphaltene precipitation was compared in this study.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

The most challenging part in oil and gas industry is to prevent and/or treat associated operational problems that lead to reduction of production. One of the common downhole problems is asphaltene precipitation which can cause trouble when it started to form solid material in oil production, transportation and processing. Engineers predicted the asphaltene precipitation will become apparent in Malaysia since most of the wells have been producing more than 20 years. Engineers are struggling to find potential solutions to overcome this before the problem becoming more serious; which this study has become an interest to all. By definition, asphaltene is a solid material that precipitates from crude oil, asphalt or bitumen upon surplus presence of low molar mass paraffin solvent. Normally, asphaltenes may be partly dissolved and/or partly suspended by resins in crude oil due to its range of molar mass distribution and compositions. Researches indicate that separated asphaltene from crude oil consists of three main components which are condensed aromatics, naphthenic molecules and polar molecules. However, there has been a dispute regarding the nature of asphaltene which some consider it to be solid phase while others consider it to be a highly viscous liquid. In addition; asphaltene stability is highly dependent on composition, pressure and temperature of the oil.

1.2 PROBLEM STATEMENT

In studying asphaltene precipitation, the asphaltene stability is the main factor that determines the seriousness of operational problems in production phase. The stability depends on the properties of asphaltene fraction and the solvent. Normally, asphaltene started to destabilize due to miscible gas or other solvent injection as well as pressure depletion. An unstable asphaltene can cause problem near wellbore when asphaltene started to form a separate phase that might plug the oil-bearing rock formation. Asphaltene can also aggregate oil/water interfaces as it stabilize water-in-oil emulsions and/or at oil/solid interfaces where it alters surface wetting properties. (Boer et al., 1995) concluded in his research that the problem tend to occur in light oils with small amounts of asphaltene compared to heavy oil with larger amounts of asphaltene fraction. This is because, light oil contains high saturates while having low aromatics and resins. Since major part of reservoir fluid contains paraffin, the tendency of asphaltene precipitation is quite frequent. Therefore, inhibitor is required in order to stabilize asphaltene micelles from agglomerating.

It is clearly that this problem needs to be resolved by first understanding the conditions that lead to asphaltene precipitation; so that preventive actions can be taken to avoid severe problems

1.3 OBJECTIVES AND SCOPE OF STUDY

1.3.1 Objectives

The main objectives of this study are:

1. To identify potential inhibitors in treating asphaltene precipitation
2. To compare inhibitors effectiveness

1.3.2 Scope of Study

The scope of this study is mainly to identify potential inhibitors and compare its effectiveness. However, it is compulsory to initially understand asphaltene precipitation formation since different inhibitors will behave differently from one another. The study involves identifying the main components or compositions of inhibitors that prevent asphaltene precipitation. The study is divided into two stages of which the first stage is generally on identifying the potential inhibitors while the second stage involves laboratory experiments to compare inhibitors effectiveness. As a result, a full report will be presented based on the understanding gained throughout the project.

1.4 FEASIBILITY OF PROJECT WITHIN SCOPE AND TIME FRAME

The time frame suggested for this project is within 29 weeks of study period; that are evenly divided to each dedicated scope of works. This project involves two stages which the weeks are divided into 14 weeks and 15 weeks. For the first stage, the scope is to identify potential inhibitors. First two weeks is devoted for selection of project topic. The project then proceeds with research work on topic and submission of preliminary report on week 6. Next, the research is continued and Interim report is submitted on week 12. As for the second stage, the study is delved into laboratory experiments to compare inhibitors effectiveness. The second stage involve submission of progress report in week 22, pre-EDX in week 25, submission of technical report in week 27 and ended with submission of project dissertation in week 29. The time frame provided will ease the smoothness of completing the project within the given period. In conclusion, the project is feasible to be accomplished within the scopes and time frame.

CHAPTER 2

LITERATURE REVIEW

2.1 CONDITIONS LEADING TO ASPHALTENE PRECIPITATION AND ITS MECHANISM

Based on literature readings of different scholars, asphaltene stability is highly dependent on three factors which are composition, temperature and pressure of the oil. It is believed that changes in reservoir condition such as pressure depletion, CO_2 flooding or natural gas flooding into the reservoir contributed towards asphaltene precipitation. (Hamami, 1999) stated in his study that pressure depletion alone can destabilize asphaltene and it is the main reason of asphaltene precipitation in wellbore tubular. As the reservoir pressure depleted below the bubble point pressure, gas bubble started to form. N-alkanes gases such as n-heptane can induce more destabilization of asphaltene micelles. (Hamami, 1999) added that the solubility of the asphaltene is moved by the paraffinic compound in the bulk oil. In a different literature by (Sahhaf, 2002), asphaltene micelles are initially stabilized by a layer of resin molecules adsorption around the asphaltene. The presence of a normal alkane solvent will disturb the equilibrium between the micelles and the bulk oil phase that leads to higher concentration of asphaltene monomers in the bulk phase. Based on colloidal model of asphaltene behavior; in an effort to restore thermodynamic equilibrium, resin molecules react to the addition of light hydrocarbon by desorbing from the surface of asphaltene. Asphaltene micelles are compelled to agglomerate in order to reduce its overall surface free energy due to desorption of the peptizing resins. Asphaltene particles will then detach as a discrete solid phase as agglomeration continues. These observations are comparable to (Pan and Firoozabadi, 1998, 2000) studies using thermodynamic micellization model for crudes.

Based on extensive researches, it is found that the asphaltene precipitation mainly arises and more serious in a reservoir with light crude with low asphaltene content comparing to heavy crude with high asphaltene content. According to (de Boer et.al, 1995) study, the most important parameter is in-situ density which mostly affects the crude oil solubility. The relative change in asphalt solubility in the crude per unit pressure drop is obseved to be highest for light crudes that are undersaturated with gas, that is normally consist of a small number of asphaltenes. Therefore, the probability that asphalt precipitate will be greatest for these light crudes.

2.2 METHOD IN IDENTIFYING ASPHALTENE PERCIPITATION

There are numerous methods in investigating asphaltene precipitation such as refractive index measurement (RI), power of transmitted light (PTL) using PVT cell as well as light absorbance using near-infrared (NIR) spectrometer. (Joshi et al, 2001) characterized asphaltene study into two main definitions which are “field asphaltene” and “lab asphaltene”. These two terms are characterized based on methodology used in investigating asphaltene precipitation. According to (Joshi et al, 2001), “lab asphaltene” is defined according to its solubility where asphaltene is insoluble in n-heptane or any other light alkanes while soluble in toluene. On the other hand, “field asphaltene” is defined as a material that precipitates from live crude oil as depressurization goes on. Generally, “lab asphaltene” investigation uses n-heptane to induce asphaltene whereas “field asphaltene” uses pressure reduction to induce onset precipitation. However, most of the time, “lab asphaltene” investigation is not enough to represent the whole reservoir condition as the pressure and temperature is based on ambient condition. All in all, even though the methods and models are different, the scholars have one objective in common which is to understand and treat the asphaltene precipitation Listed below are common methodologies used in investigating asphaltene precipitation.

2.2.1 Theoretical Analysis in Predicting Onset Asphaltene Precipitation Using Refractive Index (RI)

(Buckley et al, 1998) pointed out that prediction of the onset precipitation may be improved by measuring refractive index (RI) to characterize crude oils and their mixtures with precipitants and solvents. Reports in the literatures show that the onset precipitation occurs at constant solvent-to-precipitant ratios. In (Buckley et al, 1998) study, the theory is developed on the assumption that London dispersion forces dominate aggregation and precipitation of asphaltenes. A thermodynamics model is developed to estimate the heat of solution of asphaltene precipitation. This model is traditionally used to investigate asphaltene stability using its solubility as mentioned by (Victorov and Firoozabadi, 1996) and (Pan and Firoozabadi, 1998). In this model, the heat of asphaltene-crude oil (ΔH^M) is a function of the difference between the solubility parameter of the asphaltene (δ_a) and solvent that of the remaining components of the crude oil (δ_s).

$$\Delta H^M \infty (\delta_a - \delta_s)^2$$

The Flory-Huggins model describing the intermolecular interactions of asphaltene and solvent solubility

(Reference: Buckley et.al, 1998)

However, since the experiment is based on Flory-Huggins model, the accuracy of the terms is limited to single model only. The solubility parameter of the oil is then predicted by approximating the cohesive energy density from equation of state fit to live oil PVT data.

The refractive index (RI) of crude oil samples was measured using Abbe refractometer with sodium lamp to measure light refraction as light passed through the crude sample. First, the sample is sandwiched into a thin layer of illuminating prism and refracting prism. Then, a light source (Sodium lamp) is beamed into the illuminating prism which the bottom surface is fixed so that each point on the surface can be thought of as generating light rays travelling in all directions. A detector is positioned on the back side of the refracting prism so that a light and dark region of refracted light can be observed. The refraction angle of each sample can then be determined.

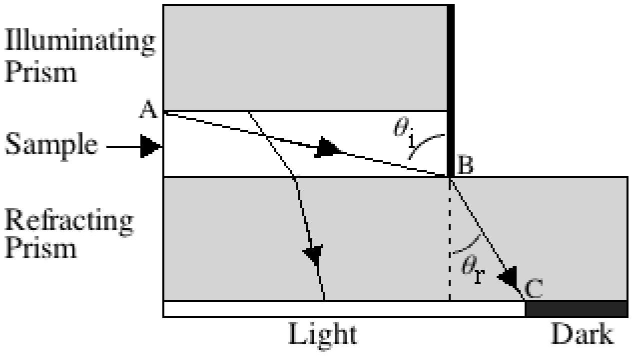


Figure 1: Cross section of Abbe refractometer

(Source: http://www2.ups.edu/faculty/hanson/labtechniques/refractometry/theory.htm)

(Buckley et al, 1998) pointed out that London dispersion interaction shows that solubility parameters of some hydrocarbons are depending on RI which the density can be precisely calculated by using Clausius-Mossotti or Lorenz-Lorenz equation over pressure range of interest. However, the detail explanation of equation of state (EOS) will not be covered in this literature study. (Buckley et al, 1998) found out that RI of crude oil or asphaltene can be estimated even if it is too opaque to be measured directly. He added that polar interactions are not essential for asphaltene precipitation and aromatic character of resin governs in solvating properties of the resins. The abovementioned methodology is used to investigate "lab asphaltene" as stated by (Joshi et.al, 2001).

2.2.2 Theoretical Analysis in Predicting Onset Asphaltene Precipitation Using Power of Transmitted Light (PTL)

In the research of (Hamami, 1999), the behavior of asphaltene can be examined by utilizing fully visual PVT cell with laser-based particle system. By using this method, asphaltene stability envelope can be obtained through a series of isothermal pressure depletion. Hamami found that induced asphaltene precipitation is a highly reversible process by pressure depletion. The study proves the reversibility of the asphaltene precipitation and flocculation process with a slower pace compared to the precipitation itself.

The experiment done by (Hamami, 1999) requires an incident laser which is mounted in front of PVT cell so that light passes high pressure sample chamber before reaching light detector probe. The interpretation is done by observing light transmission plot which indicates amount of light received by detector as function of pressure during depletion or repressurization cycles. Power of transmitted light (PTL) is used to refer amount of light that successfully passes through oil sample and captured by fiber optic cable. A relationship can be established through any changes in PTL. PTL is inversely proportional to density; any increment in PTL shows decrease in density. Since density and pressure is proportional to each other, a drop in density shows a pressure drop as well. PTL is also inversely proportional to particle size which as particle size increases or particles become tighter (gas condense into liquid), PTL will decrease. The results are recorded based on the PTL captured in light detector probe as pressure, temperature and/or composition is manipulated.

This method allows researchers to investigate onset asphaltene precipitation at the reservoir condition since samples are taken directly from the bottom of the well and preserved to its sampling pressure. According to (Buenrostro-Gonzales, 2004), by using this method; Pressure-Temperature (PT) diagram of onset precipitation can be drawn. This PT diagram of asphaltenic fluid is called asphaltene precipitation envelope (APE) where the asphaltene stability boundaries is localized. This method also has the capability of investigating asphaltene precipitation by using thermodynamic model. A detail description is given in (Wu et.al, 1998, 2000).

2.2.3 Theoretical Analysis in Predicting Onset Asphaltene Precipitation Using Near Infrared (NIR) spectrometer

The usage of spectrometer in measuring light absorbance of material has already been widely used in other industries and it is now a great interest to researchers in laboratory studies of crude oils and petroleum asphaltene. UV spectrometer allows scholars to observe and determine the onset of solid precipitation. However, as according to (Andersen, 1999), the dark nature of the original oil make it difficult to measure directly the onset precipitation. Therefore, near infrared (NIR) spectroscopy is used to accurately measure asphaltene onset precipitation which is explained by (Leontaritis, 1997 and Fuhr, 1991) in their studies. (Kyeongseok, 2001) uses near-IR probe which enable the light absorbance reading to be measure directly in the solution of oil and inhibitor. While in different study, (Evdokimov and Losev, 2007) use double beam UV-Visible spectrophotometer that measure light absorbance difference between test sample and reference sample. Both methods utilize wavelength of between 1200nm and 2400nm in order to have near infrared region (NIR). Onset precipitation can be observed once the light absorbance of a mixture started to increase when titrated with n-heptane or other n-alkanes. Both studies by (Kyeongseok, 2001; Evdokimov and Losev, 2007) proved that inhibitor effectiveness can be evaluated by using this method.

2.3 CURRENT SOLUTIONS PROPOSED TO OVERCOME ASPHALTENE PRECIPITATION

There are many practices done to overcome asphaltene precipitation by either remedial or preventive steps. The current remedial practices are such as cutting the deposit using wireline tools, washing tubing with solvent and chemical injection through tubing on the deposit. However, the remedial actions is far too costly, time consuming and cumbersome. Therefore, a proactive and preventive action should be taken at the first place.

2.3.1 Mechanical method

In the study by (Haskett, 1965); asphaltene precipitation can be largely controlled by producing oil at low wellhead pressure. The wellhead pressure is kept low to ensure the bottomhole pressure is above the bubble point pressure in order to stabilize asphaltene by minimizing liberated gas. Based on Haskett findings, asphaltene deposit is repeptized as the wellhead pressure reduced. However, he found out that as the well closed, liberated gas started to reabsorbed which then created excess of light hydrocarbon and later causes immediate precipitation. He then suggested, bottomhole choke to be set deeper in tubing which has an advantage in combating asphaltene problems since there will be no deposition above the choke. He concluded that since the practice is implemented, there is significant reduce number of tubing washing in Hassi Messaoud field, Algeria which indicates the practice is proven to be effective in overcoming asphaltene precipitation. The drawback of this method is in difficulty to keep maintaining the wellhead pressure above bubble point pressure since reservoir pressure will sooner or later depleted over time.

2.3.2 Chemical method

Most of the literature reviews chemical method as a good method in inhibiting precipitation to occur either by maintaining precipitates micelles in suspension or by stabilizing asphaltene against precipitation. Different methods and models were used to study the effect of inhibitors against asphaltene precipitation. Listed below are the literature reviews.

2.3.2.1 Effect of organic additives to the Onset of Asphaltene Precipitation

Even though it is believed that chemical method can be too costly, (Kyeongseok, 2001; Sahhaf, 2001) found out that organic additives have an impact on delaying onset asphaltene precipitation. Kyeongsook did several experiments using different types of organic additives such as toluene, aromatics solids, n-alkane compounds, separated asphaltene and polar and non-polar solids on light crude oil using near-IR spectroscopy.

Light absorbance reading was observed as the mixture of crude and inhibitor were titrated with n-heptane at a constant rate. By examining plot of absorbance reading and amount of titrated n-heptane, the onset can be easily determined. Based on the results obtained, addition of toluene and aromatics solids such as phenanthrene and naphthalene manage to delay onset asphaltene precipitation. (Kyeongseok, 2001) added that additional amount of toluene has significant effects in delaying onset precipitation. Meanwhile, addition of solid n-alkanes compounds and separated asphaltene into oil can accelerate asphaltene precipitation. On contrary, addition of polar and non-polar solids showed that precipitation was governed by non-polar compound. Kyeongsook concluded that complex occurrence of dissolved asphaltene precipitation is simply controlled by solubility.

2.3.2.2 Effect of sulphonic acid group to the Onset of Asphaltene Precipitation

In screening crude oils for asphalt precipitation and selection of inhibitors study (de Boer et.al, 1995); de Boer found that there are three main parameters that govern the tendency of asphaltene precipitation. The parameters are the extent which crude is undersaturated with gas, density of crude at reservoir condition and saturation with asphalt at downhole condition. In his experiment, ultrasonic back scattering is used in order to examine influence of different inhibitors towards asphaltene precipitation. A degree of supersaturation is required for asphaltene to precipitate which is normally caused by pressure drop during production. Supersaturation is highly dependent on the time taken, temperature, turbulence and medium. De Boer found out that supersaturation is highest when depressuring lightest crude which explains the question of low amount of asphaltene with high C1-C3 content has the highest tendency for asphaltene to precipitate. Supersaturation gives a strong driving force of precipitation that crude almost surely precipitate.

In his experiment, de Boer found a good composition of inhibitor that will stabilize asphaltene against precipitation by using aliphatic alcohol partial ester of phosphorous acid unlike other inhibitors that only keep asphaltene particle in suspension as small unit. He also tested several inhibitors such as alkyl-aryl salicylic acid, sulphonic acid and disulfonic acid of alkylated aromatics. It is believed that the effect of the compounds resulted from partial protonation of asphaltene and subsequent attachment of negatively charged alkyl phosphorous acid residue. The thesis was confirmed by testing C-18 sulphonic acid with a replacement of H+ ion with triethanolamine and tributylamine group that manage to neutralize acidic group. It is found that the replacement manage to invalidate inhibitor activity. This observation is comparable to (Gonzalez and Middea, 1991) that polarity has a crucial role in stabilizing asphaltene.

De Boer used sonic detection technique in order to monitor the effects of potential inhibitors by measuring back scattering of ultrasonic waves of particles. It is done by measuring energy reflected from particle as a result from short burst of emitted acoustic energy to the liquid and converts it to read-out signal. There are few findings de Boer stated in his result of experiment that C-18 sulphuric acid indicates better activity compared to salicylic acid compound and phosphoric acid. He also found certain component such as C-16 alkyl diphenyl-oxide di-sulphonic acid can cause severe destabilization due to its strong polarity. (Chang and Fogler, 1994) observed that a strong acid group might cause asphaltene to self-percipitate beyond a certain concentration. Therefore, the application of acidic group has its optimum concentration to be effective. The activity of inhibitor is not only dependant on properties of acidic head but also aliphatic or aromatics tail of inhibitor. Result indicates increase in pressure or temperature; will both reduce amount of inhibitor required to prevent deposition. A new inhibitor has been selected which is oil-soluble surfactant that had optimum activity at 1300 ppm during titration. It is considered success as it is proved to be effective at a concentration as low as 70ppm in field test in Alberta, Canada.

2.3.2.3 Thermodynamic Micellization Model for Asphaltene Precipitation Inhibition

In the study (Pan and Firoozabadi, 2000); they try to explain inhibition mechanism for both aromatic solvents and oil-soluble amphiphiles by using thermodynamic micellization model. The model shows how aromatic solvents are concentrated in the micellar shell and the interfacial tension (IFT) between asphaltene micellar core and shell is reduced as the micelles becomes more stable. A mixture of a small amount of an oil-soluble amphiphiles with crude achieves high micellar stability. They found out that amphiphiles work the same as resin species of the crude by coadsorb onto the micellar core with resins with higher adsorption enthalpy than resins which is very effective inhibitors. The model allows them to predict the amount required for amphiphiles to inhibit the precipitation. The model is based on Gibbs free energy with different compounds being included such as micelle, aromatic solvent, asphaltene monomer, resin monomer and so on.

(Pan and Firoozabadi, 2000) found out that aromatic solvent can stabilize asphaltene micelles through a reduction of the interfacial tension between the asphaltene core and the shell. Interfacial tension is the main key for aromatic solvents to inhibit asphaltene precipitation. On the other hand, adsorption enthalpy is the most important parameter for amphiphile which may be gained by calculating the heat of adsorption of an amphiphile in the liquid asphaltene. They concluded that an effective amphiphiles usually has a strong polar head to effectively inhibit asphaltene precipitation.

2.4 CRITICAL ANALYSIS OF LITERATURE

Based on the two findings of mechanical and chemical methods; both have their own pros and cons. Mechanical method is a cost effective and consume less time since no injection or well shut down is required. However, the constraint is in maintaining low wellhead pressure throughout the production as the reservoir pressure started to deplete below its bubble point. A low wellhead pressure can also cause back pressure to the surface facilities. (Garcia, 2001) added that it is difficult to maintain high well pressure to guarantee solubilized asphaltene because of inconvenience in gas injection due to absence of gas resources near the reservoir. On the other hand, there have been a lot of additives presented in the literature using different kind of methods. Based on different literatures, most researchers agreed that aromatic solvents have proven to inhibit asphaltene precipitation. The scholars concur that asphaltene stability is the main key to inhibit precipitation depending on different parameters. However, chemical method is too costly since regular injection is needed and in some study, the inhibitors are not tested in live well yet. Table below summarize key points of the literatures.

2.4.1 Methodology in investigating asphaltene precipitation

Methodology	**Refractive Index (RI)**	**Power of Transmitted Light (PTL)**	**Near Infrared (NIR) spectrometer**
Apparatus Involved	Abbe Refractometer	PVT cell	UV visible spectrometer
Data Measured	Refracted angle	Light transmission	Light absorbance reading
Procedure of experiment	1. Sample is sandwiched into thin layer of illuminating prism and refracting prism 2. Light is beamed to illuminating prism so as to generate light rays into the sample 3. Detector at the back of refracting index will measure refracted light	1. Sample is placed inside PVT cell with laser mounted in front 2. Light is beamed through sample towards detector 3. Detector measure amount of light successfully passes through sample in term of PTL	UV detector probe 1. UV probe is immersed into sample and light absorbance is measured directly Double beam spectrometer 1. Light absorbance difference is measured between test cell and reference cell inside UV spectrometer
Observation	Decrease in RI reading shows asphaltene started to precipitate	Decrease in PTL reading shows solid particle(asphaltene) absorbs most of light transmitted	Increase in absorbance reading shows that most light is absorbed by particle (asphaltene) inside sample
Drawback	Difficult to measure refracted angle since it depends on user’s eye to assess it	Difficult to inject inhibitor into PVT cell. Normally, inhibitor is pre-mixed with sample before placed inside cell	Difficult to measure crude sample light absorbance since it is opaque and will disturb reading consistency

Table 1: Methodology used in asphaltene precipitation studies

2.4.2 Current preventive solutions in inhibiting asphaltene precipitation

Keypoint	**Mechanical Method**	**Chemical Method**		
	Haskett	Kyeongsook	De Boer	Pan and Firoozabadi
Additives	None	1.Touluene 2.Aromatic Solids 3. N-alkane compound	1.Alkyl-aryl salicyclic acid 2.Sulphonic acid 3.Disulphonic acid of alkalyted aromatics	1. Aromatic Solvents 2.Amphiphiles
Method	Producing by keeping wellhead pressure below bubble point pressure	Near-IR spectoscropy	Ultrasonic Back Scattering	Thermodynamic Micellization Model
Findings	1. Asphaltene deposits repeptized as pressure of wellhead decrease 2. Setting bottomhole choke deeper has advantage in preventing asphaltene problem since no deposition above choke	1.Addition of toluene, phenanthrene and naphthalene (aromatic solids) manage to delay onset precipitation 2. Addition of solid n-alkanes compound and separated asphaltene into oil can accelerate precipitation	1.C-16 alkyl dophenyl-oxide disulphonic acid can cause severe destabilization 2.C-18 indicates better activity compared to salicyclic acid and phosphorous acid 3.Oil-soluble surfactant had optimum activity 4.Inhibitor depends on properties of acidic head and aliphatic or aromatics tail	1. Aromatic solvents stabilize asphaltene micelles through reduction of asphaltene core and shell interfacial tension 2.Adsorption enthalpy is an important parameter 3.Amphiphiles require strong polar head to inhibit asphaltene
Drawback	1.Reservoir pressure will deplete over time 2.Can cause backpressure to surface facilities	Time consuming and not cost effective due to continuous injection		

Table 2: Current preventive solutions in inhibiting asphaltene precipitation

CHAPTER 3

RESEARCH METHODOLOGY

3.1 ANALYZING ASPHALTENE PRECIPITATION USING UV-VISIBLE SPECTROMETER BY MEASURING LIGHT ABSORBANCE

The application of UV spectroscopy in investigating asphaltene precipitation has become widespread and common in laboratory studies. UV spectrometer allows the asphaltene precipitation to be studied in the Near-Infrared (NIR) region by adjusting the desired wavelength. Fuhr et.al and Kyeongsook suggested that the most essential information is obtained at a wavelength of 1600 nm. However, the complexity of using crude oil in UV spectrometer remains as the major problem due to its opaque and high absorption characteristics (Evdokimov, 2007). Most of researchers suggested that the crude need to be diluted with toluene in order to appropriately detect the precipitation. Conversely, a different approach is used in this experiment since toluene is identified as one of the inhibitors contrary as to dilutant. N-hepthane is used as solvent in the blank solution (reference) so that any amount of n-hepthane titrated into the crude will not affect the light absorbance reading. Therefore, any changes in reading are mainly due to solid presence (precipitated asphaltene) absorbance. Asphaltene precipitation can be observed by plotting the light absorbance over amount of n-hepthane titrated. A UV light is beamed through the crude sample and the absorbance is measured at the detection probe. A decrease of light intensity at the detection probe indicates that most of the light has been absorbed by solid or precipitate in the sample. According to Beer-Lambert law, a decrease in light intensity will give higher reading of absorbance. The law will be further discussed in chapter 4.

3.2 EXPERIMENT OVERVIEW

The experiment conducted involves a total of 5 runs; first run of crude oil without any inhibitor in UV spectrometer, second and third run of crude oil with inhibitor A at two different amounts while fourth and fifth run of crude oil with inhibitor B at two different amounts. The first run is set as a reference for comparison between the two inhibitors. The amount is made variable so as to see the effect of inhibitor amount over precipitation by observing the light absorbance. The Dulang crude oil sample was chosen to be investigated and was obtained from laboratory. To recent, there is no potential asphaltene precipitation studies been done on Dulang crude oil sample. N-heptane is used as to disturb the asphaltene stability in crude oil to induce precipitation. Therefore, the amount is set constant for all runs at 200mL with a rate of 5mL/min. Most of the experiment setting conducted is based on (Kyeongsook, 2001) except using different equipment which is double beam spectrometer.

3.3 INHIBITORS SELECTION AND PREPARATION

Xylene and 1,3-benzenedisulfonic acid are two main inhibitors used in this experiment. Xylene is an aromatic compound which consists of three isomers of dimethylbenze unlike toluene that is mono-substituted benzene that is widely used as inhibitor in the industry. On the other hand, 1,3-benzenedisulfonic acid was chosen as one of the inhibitor because sulfonic acid was found to be an effective inhibitor by (Boer, 1995) while a composition of benzene and sulfonic acid were shown to be effective as according to (Sahhaf et.al, 2001). Xylene (99.9% purity) is obtained from laboratory while 1, 3-benzedisulfonic acid is prepared in advance. Toluene is used as a backup inhibitor to be studied in case of failure of either xylene or 1,3 benzenedisulfonic acid in mixing well with crude oil.

1M solution of 1, 3 benzenedisulfonic acid was prepared by mixing 282.2 grams (MW: 282.2 g/mol) with a distilled water in a 1L flask under a constant stirring for around 30 minutes. Since 99.9% purity of n-hepthane and xylene are available, the solutions are ever ready to be used in the experiment.

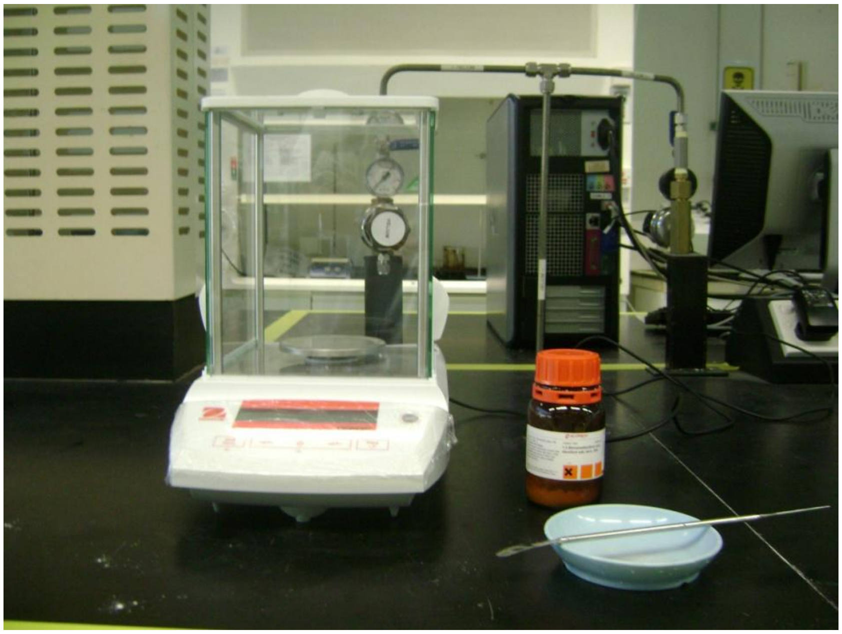


Figure 2: 1, 3 benzenedisulfonic acid preparation

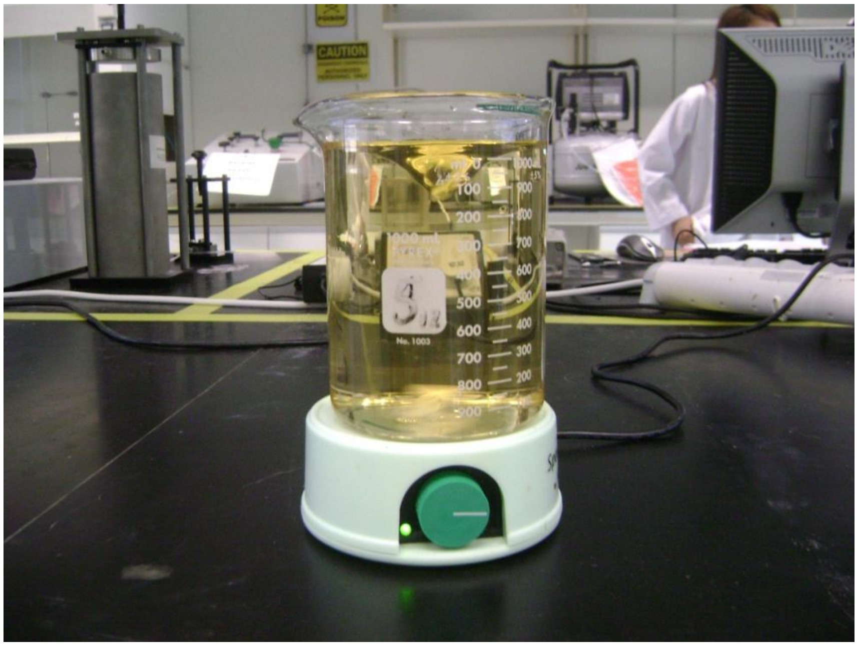


Figure 3: 1, 3 benzedisulfonic acid solution

3.4 EXPERIMENT PROCEDURES

N-heptane is injected in both cell container (reference and sample) and placed inside the spectrometer. The UV spectrometer is operated to analyze both absorbances reading to be equal and as close to zero value. Wavelength baseline is set in range between 1200 nm to 2000 nm. As soon as baseline reading is completed, the 1600 nm wavelength is set as test wavelength where any changes in absorbance (between reference and sample) is observed at 1600 nm wavelength. Next, the setting is calibrated by pressing autozero in the UVProbe software.

Then, the sample cell is taken out and n-heptane is dried out from the cell. The crude sample is then injected into the cell and placed inside the UV spectrometer. Absorbance reading can be obtained directly since the light is continuously transmitted in the spectrometer. The steps are repeated with different sample titrated with different amount of n-heptane. The steps mentioned are similar to all five runs. All of the experiments were conducted in a room temperature at average of 26°C.

3.5 PROJECT ACTIVITIES

The layout of this project is as in diagram below:

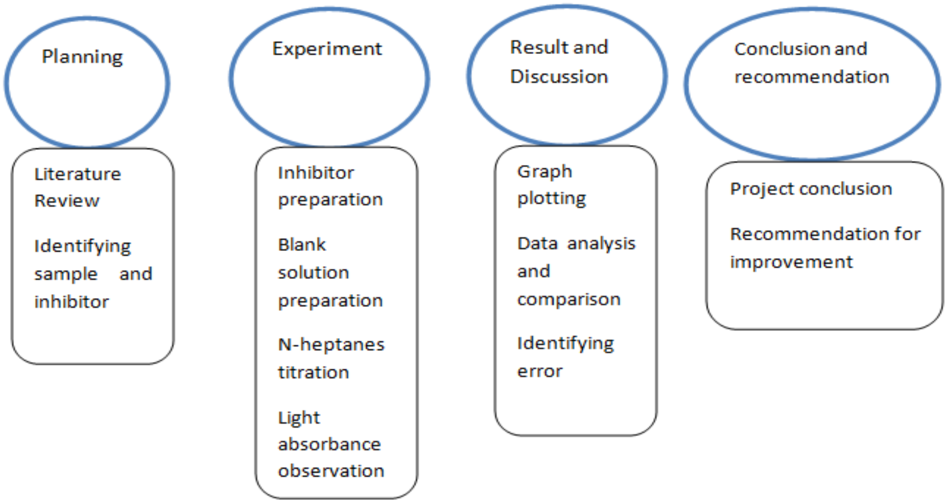


Figure 4: Project layout

3.5.1 Gantt Chart

No	Detail/Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	
1	Selection of topic	▨	▨						**Mid-Semester Break**								
2	Preliminary Research Work			▨	▨	▨	▨										
3	Submission of Preliminary Report							▨									
4	Project Work Continue									▨	▨	▨	▨	▨			
5	Submission of Interim Draft report														▨		
6	Submission of Interim Report															▨	▨

No	Detail/Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Project Work Continues	▨	▨	▨	▨	▨	▨	▨	**Mid-Semester Break**								
2	Submission of progress report									▨							
3	Project Work Continues									▨	▨	▨	▨	▨			
4	Pre-EDX												▨				
5	Submission of Draft Report													▨			
6	Submission of Dissertation (Soft Bound)														▨		
7	Submission of technical paper														▨		
8	Oral presentation															▨	
9	Submission of project																▨

	Dissertation (Hard Bound)																▨

Table 3: Project Gantt chart

3.5.2 Tools Required

The UV spectrometer used in this experiment is based on UV Shimadzu 3150 double beam spectrometer with a capability of measuring range of wavelength from 190nm to 3200nm with a slit width of 2 nm. The spectrometer is equipped with software, UVProbe to display the absorbance reading. Two cell containers are used to contain blank solution and crude sample which are then placed between light source and detector. However by using double spectrometer, it is contrary to other experimental procedure whereby a direct titration of n-hepthane can be done simultaneously while measuring light absorbance. Therefore, experimental setup is done as per figure 3 for n-hepthane titration into crude sample. After a constant stirring, an amount of 1 mL mixture is took out and injected into the cell which is then placed in the UV spectrometer for measuring light absorbance.

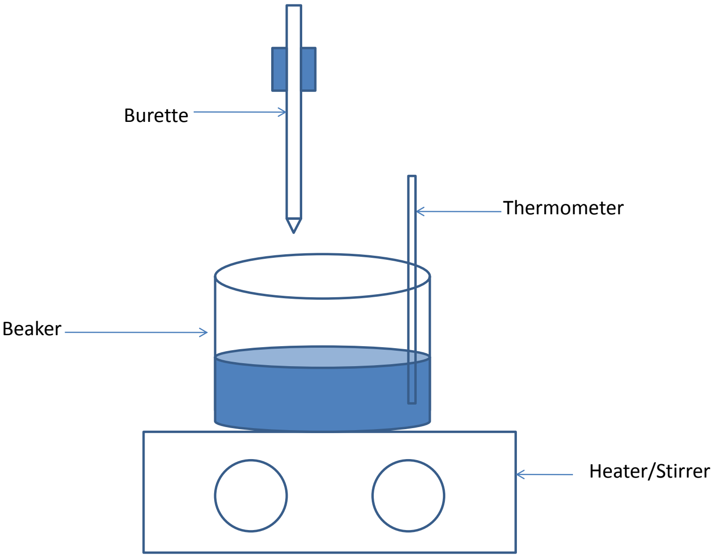
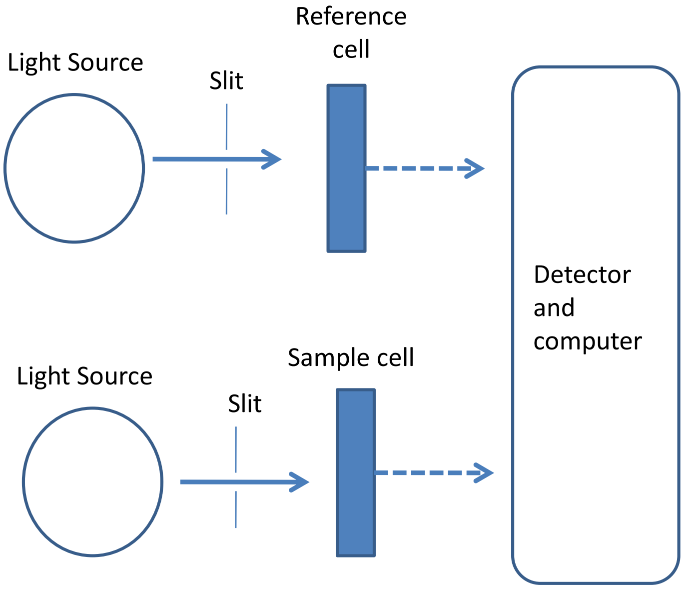


Figure 5: Experimental Setup

Figure 6: Shimadzu 3150 UV double beam spectrometer



- •Detector will detect difference in light intensity passed through both cells
- •Computer will generate the absorbance result based on the light intensity difference

Figure 7: Components of UV spectrometer

CHAPTER 4

RESULTS AND DISCUSSION

4.1 DATA GATHERING

4.1.1 Light absorbance reading per amount of n-heptane titrated in crude oil without any addition of inhibitor

Amount of heptanes (mL)	Min reading (abs)	Max reading (abs)	Average (abs)
0	0.032	0.048	0.040
5	0.034	0.049	0.042
10	0.036	0.052	0.044
15	0.033	0.049	0.041
20	0.032	0.049	0.041
25	0.030	0.046	0.038
30	0.031	0.046	0.039
35	0.035	0.049	0.042
40	0.028	0.045	0.037
45	0.026	0.044	0.035
50	0.020	0.036	0.028
55	0.024	0.039	0.032
60	0.023	0.038	0.031
65	0.020	0.038	0.029
70	0.024	0.039	0.032
75	0.018	0.036	0.027
80	0.016	0.035	0.026
85	0.010	0.029	0.020
90	0.013	0.031	0.022
95	0.010	0.025	0.018
100	0.012	0.027	0.020
105	0.014	0.026	0.020
110	0.020	0.029	0.025
115	0.025	0.037	0.031
120	0.028	0.039	0.034
125	0.028	0.043	0.036
130	0.036	0.047	0.042
135	0.038	0.045	0.042

140	0.041	0.051	0.046
145	0.047	0.054	0.051
150	0.043	0.053	0.048
155	0.051	0.062	0.057
160	0.053	0.066	0.060
165	0.049	0.060	0.055
170	0.050	0.059	0.055
175	0.052	0.063	0.058
180	0.051	0.065	0.058
185	0.054	0.065	0.060
190	0.054	0.068	0.061
195	0.051	0.062	0.057
200	0.053	0.070	0.062

Table 4: Light absorbance reading for pure crude oil

4.1.2 Light absorbance reading per amount of n-heptane titrated in crude oil with 100ml of xylene

Amount of heptanes (mL)	Min reading (abs)	Max reading (abs)	Average (abs)
0	0.029	0.039	0.034
5	0.027	0.038	0.033
10	0.031	0.040	0.036
15	0.030	0.042	0.036
20	0.030	0.040	0.035
25	0.033	0.039	0.036
30	0.035	0.046	0.041
35	0.036	0.048	0.042
40	0.038	0.051	0.045
45	0.032	0.046	0.039
50	0.028	0.042	0.035
55	0.026	0.038	0.032
60	0.031	0.040	0.036
65	0.036	0.042	0.039
70	0.033	0.041	0.037
75	0.028	0.045	0.037
80	0.025	0.046	0.036
85	0.021	0.038	0.030
90	0.018	0.037	0.028

95	0.012	0.035	0.024
100	0.019	0.035	0.027
105	0.021	0.032	0.027
110	0.023	0.033	0.028
115	0.018	0.031	0.025
120	0.013	0.028	0.021
125	0.015	0.031	0.023
130	0.005	0.019	0.012
135	0.000	0.015	0.008
140	-0.004	0.007	0.002
145	-0.001	0.008	0.004
150	0.008	0.019	0.014
155	0.015	0.024	0.020
160	0.021	0.029	0.025
165	0.025	0.032	0.029
170	0.033	0.041	0.037
175	0.038	0.043	0.041
180	0.043	0.051	0.047
185	0.036	0.048	0.042
190	0.033	0.042	0.038
195	0.036	0.046	0.041
200	0.036	0.044	0.040

Table 5: Light absorbance reading for crude oil + 100 ml of xylene

4.1.3 Light absorbance reading per amount of n-heptane titrated in crude oil with 150ml of xylene

Amount of heptanes (mL)	Min reading (abs)	Max reading (abs)	Average (abs)
0	0.031	0.042	0.037
5	0.033	0.042	0.038
10	0.035	0.044	0.040
15	0.029	0.041	0.035
20	0.031	0.045	0.038
25	0.032	0.047	0.040
30	0.036	0.050	0.043
35	0.038	0.051	0.045
40	0.031	0.046	0.039

45	0.035	0.047	0.041
50	0.037	0.052	0.045
55	0.032	0.045	0.039
60	0.045	0.057	0.051
65	0.047	0.056	0.052
70	0.032	0.048	0.040
75	0.025	0.034	0.030
80	0.019	0.035	0.027
85	0.018	0.029	0.024
90	0.026	0.037	0.032
95	0.021	0.034	0.028
100	0.029	0.040	0.035
105	0.015	0.027	0.021
110	0.013	0.025	0.019
115	0.009	0.021	0.015
120	0.015	0.029	0.022
125	0.002	0.015	0.009
130	-0.003	0.013	0.005
135	0.002	0.018	0.010
140	0.005	0.020	0.013
145	0.004	0.018	0.011
150	0.012	0.029	0.021
155	0.019	0.034	0.027
160	0.025	0.037	0.031
165	0.031	0.045	0.038
170	0.037	0.049	0.043
175	0.034	0.048	0.041
180	0.031	0.045	0.038
185	0.038	0.044	0.041
190	0.043	0.051	0.047
195	0.049	0.057	0.053
200	0.052	0.064	0.058

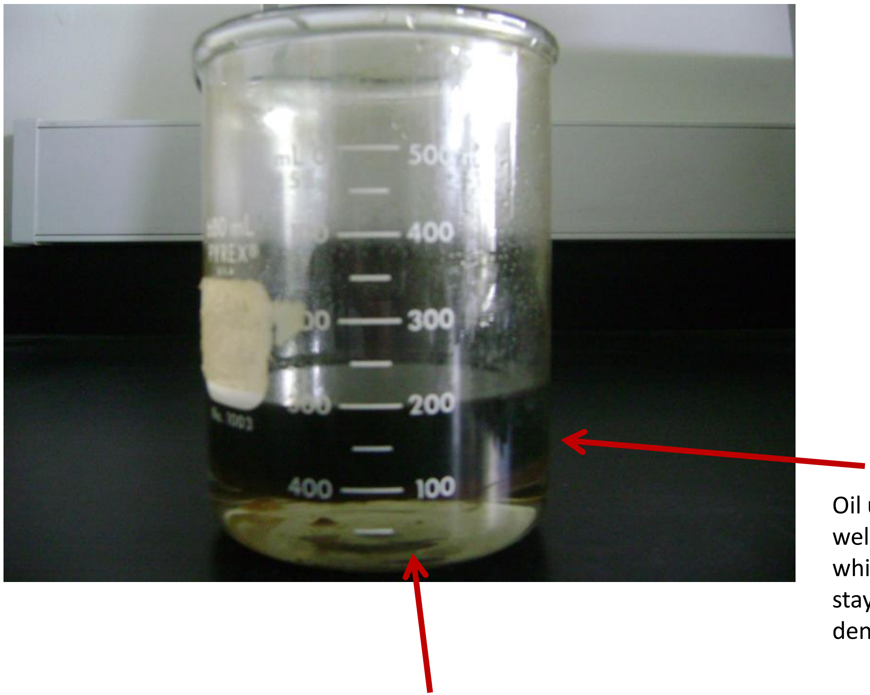
Table 6: Light absorbance reading for crude oil + 150 ml of xylene

4.1.4 Light absorbance reading per amount of n-heptane titrated in crude oil with 100ml of 1,3 benzenedisulfonic acid

Amount of heptanes (mL)	Min reading (abs)	Max reading (abs)	Average (abs)
0	1.603	2.283	1.943
5	1.623	2.159	1.891
10	1.649	2.337	1.993
15	1.634	2.195	1.915
20	1.620	2.283	1.952
25	1.457	2.195	1.826
30	1.489	2.337	1.913
35	1.496	2.218	1.857
40	1.319	2.217	1.768
45	1.453	2.202	1.828
50	1.480	2.146	1.813
55	1.613	2.007	1.810
60	1.616	2.092	1.854
65	1.667	2.119	1.893
70	1.472	2.292	1.882

Table 7: Light absorbance reading for crude oil + 100 ml of 1,3 benzenedisulfonic acid

The experiment was not continued since the prepared 1,3 benzenedisulfonic acid did not manage to properly solve into the crude oil as in figure 8. There were two layers of immiscible fluid could be observed which indicates that 1,3 benzendisulfonic acid was not a good solvent. The absorbance reading was taken to demonstrate disturbance in absorbance reading due to improper mixing.



Oil unable to mix
well with solvent
which causes it to
stay on top due to
density difference

1,3 benzenedisulfonic
acid resided on the
bottom of the mixture

Figure 8: Mixture of crude oil and 1,3 benzenedisulfonic acid

Since the experiment conducted using 1,3 benzenedisulfonic acid does not achieved the criteria of a good solvent which is be able to miscible with oil, the study of inhibitor precipitation is continued by using toluene as a backup plan. Similarly to xylene, toluene was also added with 100mL and 150mL into the crude and absorbance reading was observed.

4.1.5 Light absorbance reading per amount of n-heptane titrated in crude oil with 100ml of toluene

Amount of heptanes (mL)	Min reading (abs)	Max reading (abs)	Average (abs)
0	0.027	0.040	0.034
5	0.028	0.038	0.033
10	0.030	0.045	0.038

15	0.025	0.043	0.034
20	0.028	0.043	0.036
25	0.030	0.047	0.039
30	0.034	0.049	0.042
35	0.035	0.052	0.044
40	0.033	0.051	0.042
45	0.036	0.053	0.045
50	0.030	0.049	0.040
55	0.031	0.049	0.040
60	0.028	0.045	0.037
65	0.025	0.046	0.036
70	0.024	0.044	0.034
75	0.019	0.042	0.031
80	0.016	0.039	0.028
85	0.020	0.041	0.031
90	0.024	0.046	0.035
95	0.015	0.040	0.028
100	0.012	0.037	0.025
105	0.018	0.039	0.029
110	0.014	0.036	0.025
115	0.005	0.025	0.015
120	0.008	0.029	0.019
125	0.006	0.027	0.017
130	0.003	0.021	0.012
135	0.010	0.032	0.021
140	0.014	0.030	0.022
145	0.020	0.033	0.027
150	0.024	0.037	0.031
155	0.030	0.039	0.035
160	0.027	0.040	0.034
165	0.040	0.051	0.046
170	0.042	0.053	0.048
175	0.048	0.060	0.054
180	0.044	0.058	0.051
185	0.045	0.058	0.052
190	0.049	0.061	0.055
195	0.052	0.063	0.058
200	0.055	0.068	0.062

Table 8: Light absorbance reading for crude oil + 100 ml of toluene

4.1.6 Light absorbance reading per amount of n-heptane titrated in crude oil with 150ml of toluene

Amount of heptanes (mL)	Min reading (abs)	Max reading (abs)	Average (abs)
0	0.031	0.042	0.037
5	0.033	0.042	0.038
10	0.035	0.044	0.040
15	0.029	0.041	0.035
20	0.031	0.045	0.038
25	0.032	0.047	0.040
30	0.036	0.050	0.043
35	0.038	0.051	0.045
40	0.031	0.046	0.039
45	0.035	0.047	0.041
50	0.037	0.052	0.045
55	0.032	0.045	0.039
60	0.045	0.057	0.051
65	0.047	0.056	0.052
70	0.032	0.048	0.040
75	0.025	0.034	0.030
80	0.019	0.035	0.027
85	0.018	0.029	0.024
90	0.026	0.037	0.032
95	0.021	0.034	0.028
100	0.029	0.040	0.035
105	0.015	0.027	0.021
110	0.013	0.025	0.019
115	0.009	0.021	0.015
120	0.015	0.029	0.022
125	0.002	0.015	0.009
130	-0.003	0.013	0.005
135	0.002	0.018	0.010
140	0.005	0.020	0.013
145	0.004	0.018	0.011
150	0.012	0.029	0.021
155	0.019	0.034	0.027
160	0.025	0.037	0.031
165	0.031	0.045	0.038
170	0.037	0.049	0.043

175	0.034	0.048	0.041
180	0.031	0.045	0.038
185	0.038	0.044	0.041
190	0.043	0.051	0.047
195	0.049	0.057	0.053
200	0.052	0.064	0.058

Table 9: Light absorbance reading for crude oil + 150 ml of toluene

4.2 DATA ANALYSIS

4.2.1 Beer-Lambert Law

The law is regularly used in a quantitative way to determine the linear relationship between absorbance and concentration of an absorbing species in a solution. The relationship can be defined as:

$$A = \log \frac{I_o}{I}$$

In UV spectrometer, the incoming light is detected by detector which then converted into a current. The greater the current, the higher intensity of the light is recorded. The intensity of light passing through the reference cell is referred as I_o while I is given for the intensity of light passing through the sample cell. Theoretically, when I is less than Io, some of the light has already been absorbed in the sample. This difference in intensity will be converted into absorbance reading, A which is generated by the computer. In most cases, the absorbance reading ranges from 0 to 1, which 0 indicate no light been absorbed at all while 1 indicates highest absorbance. A simple relationship can be define when most of the light is absorbed by the sample, the intensity of light detected become lower. Hence, the absorbance reading, A will give a higher reading.

4.2.2 Data Justification

As discussed in the previous chapter, crude oil has an opaque characteristic that the absorbance reading is not constant at each second. Therefore, a minimum and maximum reading of absorbance is recorded so that the average reading can be calculated. Based from the tables above, it is apparent that the absorbance reading for all runs at each amount of n-heptane is very low with less than 0.1. It is contrary to literatures (Kyeongsook, 2001) where most of the average reading is around 0.4-0.85. At some points, the reading shows a negative value of absorbance which is erroneous in this experiment. This is probably because of the usage of n-heptane as the blank solution (reference cell) where the absorbance might be low at a wavelength of 1600 nm.

The titration rate used in this experiment is also differing from other literature where 5mL/min is considered high rate. There has been a lot of argument that some researchers stated that using high rate of injection can lower the asphaltene precipitation (Kyeongsook, 2001) while (Andersen, 1999) observed a quicker onset precipitation. Since only one rate of injection is used in this experiment, the variation could not be observed.

The experiment concluded that the blend of 1,3 benzenedisulfonic acid with crude was a failure and replaced with toluene as another potential inhibitor . There is a general pattern in all graphs, where there is an increase in the beginning, followed by a large decrease and a sudden increase afterwards. The pattern is quite similar to Kyeongsook’s finding with a slight different with an increase at the beginning. The pattern can be observed in figure 9-13:

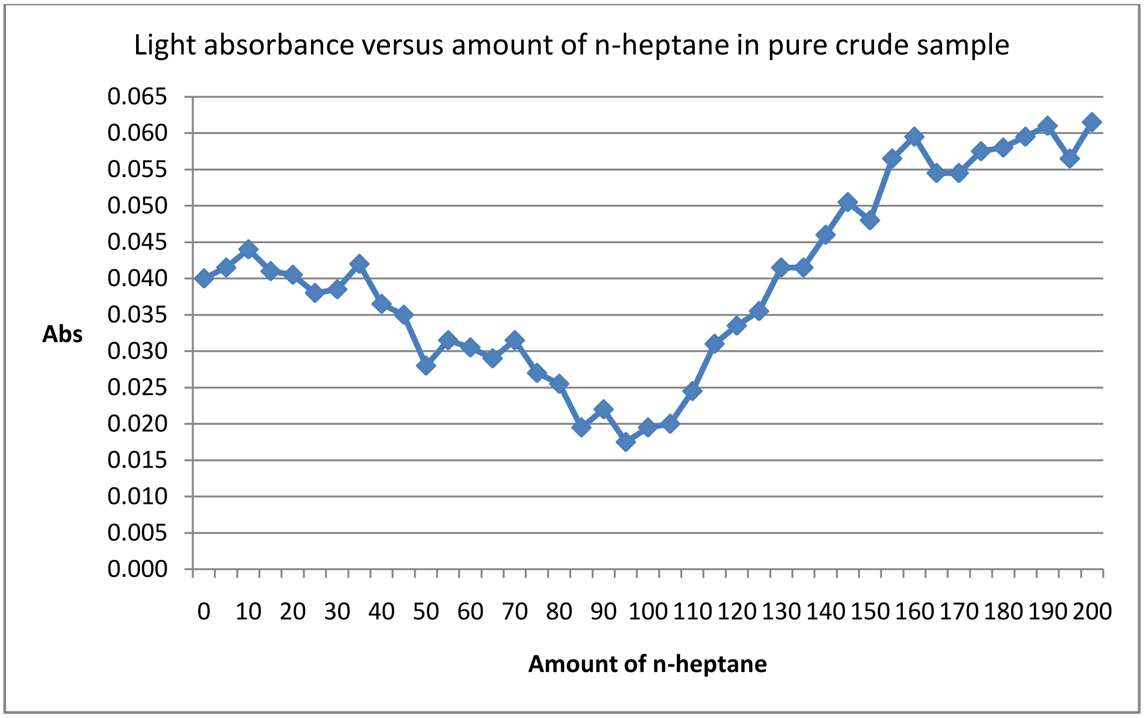


Figure 9: Light absorbance versus amount of n-heptane in pure crude sample

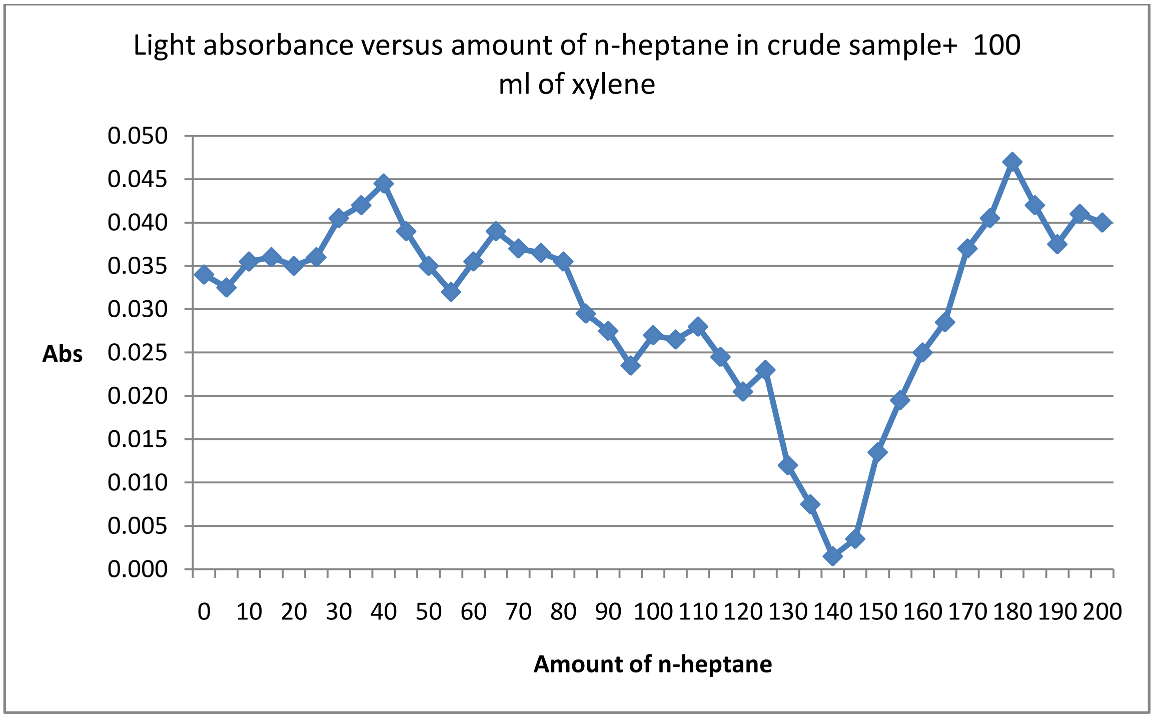


Figure 10: Light absorbance plot in crude sample + 100 ml of xylene

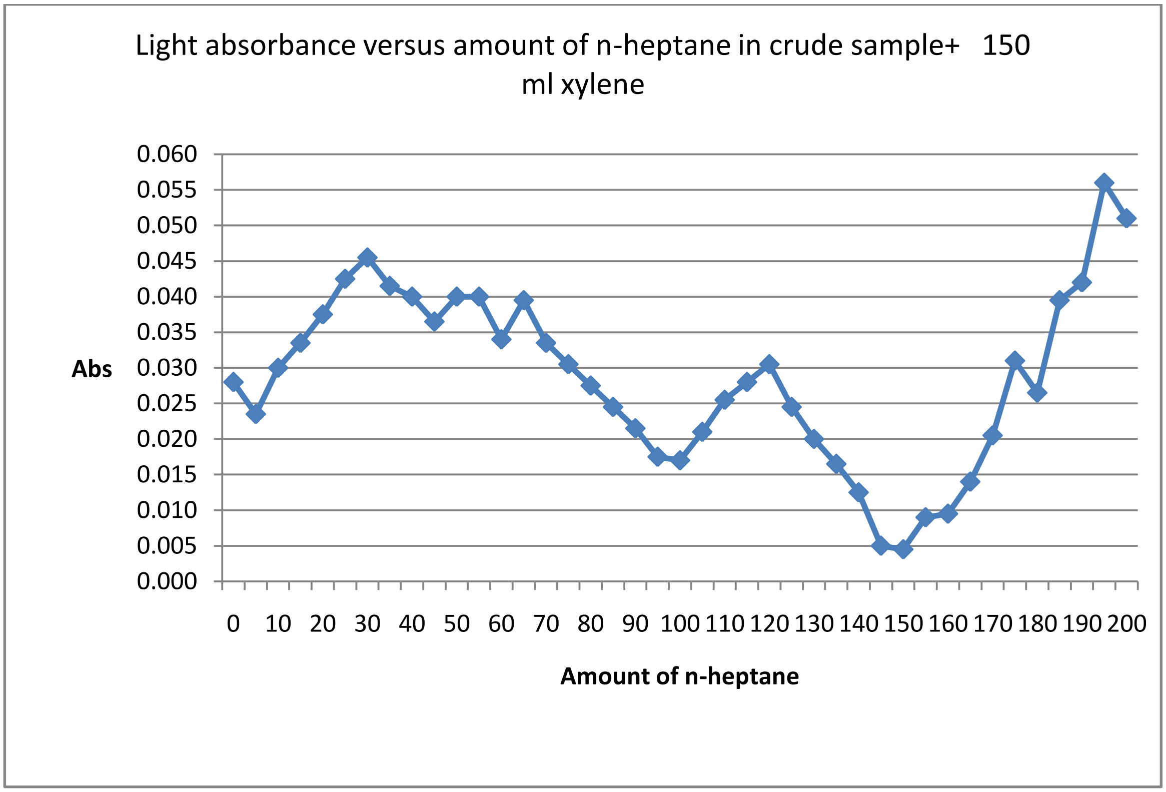


Figure 11: Light absorbance plot in crude sample + 150 ml xylene

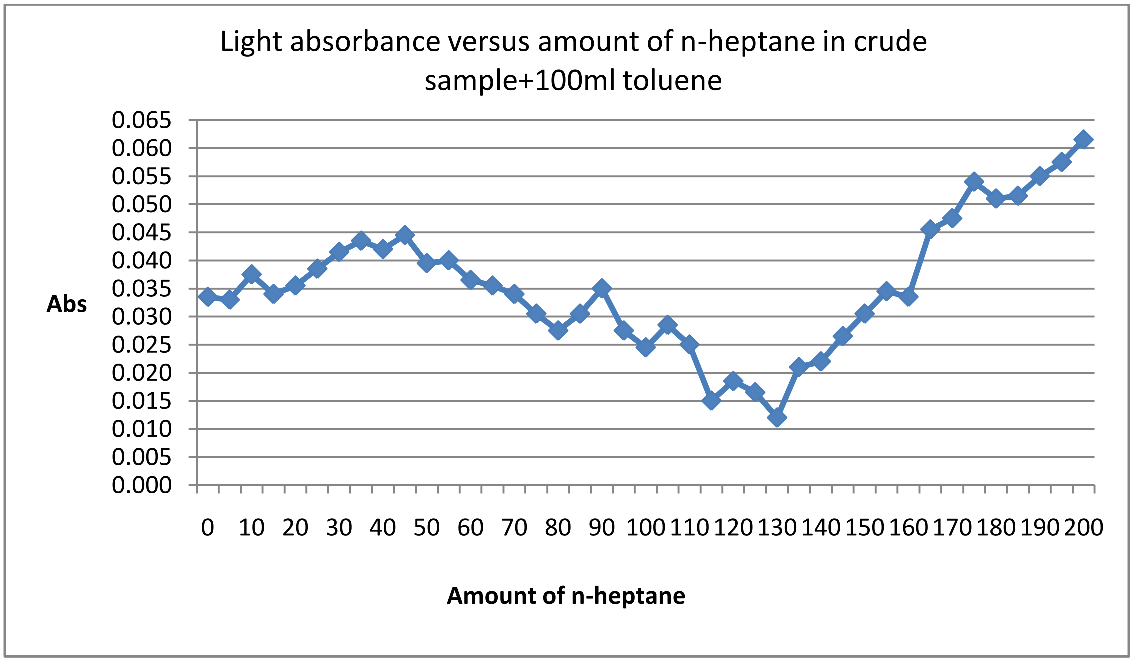


Figure 12: Light absorbance plot in crude sample+ 100 ml toluene

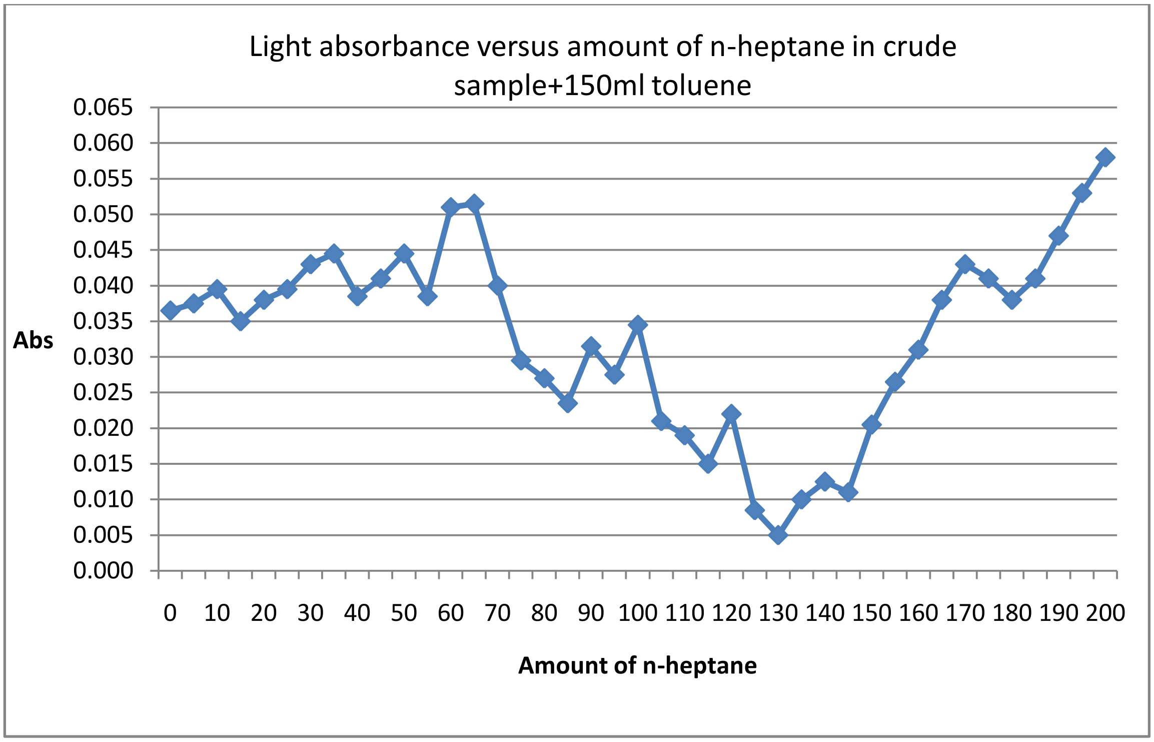


Figure 13: Light absorbance plot in crude sample+ 150 ml toluene

All the graphs share some similarities as well as differences. First, the discussion will be regarding the similarity followed by the differences. It is clear that there is a slight increase in absorbance in the early stage followed by a great decrease and ended with an increase slightly higher than the earlier increment. The initial small increment is probably due to high difference in concentration between crude sample and n-heptane in the reference sample. The decrease in absorbance in the middle stage indicates that dilution process of crude with n-heptane started to arise. The minimum in absorbance indicates the point of onset precipitation where asphaltene started to separate from oil and precipitate. The increase in absorbance shows that most of the light is absorbed by the asphaltene particle. This measurement allows researchers to find the point of onset precipitation. These observations are comparable to Kyeongsook's finding.

As for the differences, it is obvious that the addition of inhibitors manage to delay the precipitation process. In figure 9, the minimum point is around 90 mL of n-heptane titrated with pure crude oil with no inhibitor. Whereas in figure 10 the minimum point is at 140 mL and 145 mL in figure 11 with addition of 100ml and 150ml of xylene respectively. In addition, toluene shows similar affect in delaying asphaltene precipitation which is indicated in figure 12 and figure 13. The minimum point is around 130ml correspondingly. Even though the absorbance readings are varied between the runs, the common trend allows the point of precipitation to be identified. There is no great effect on adding the amount of inhibitor into the crude oil which an addition of 50 mL of xylene can only delay onset precipitation by 5 mL of n-heptane titrated. In contrast, additional of extra 50mL of toluene shows no effect at all. These observations are contrary to literature where additional amount of inhibitor does prolong the onset precipitation with a greater result. The type of crude and its composition are also contributing factors for the results obtained. Based on the data gathered, it is evident that xylene has greater effect in delaying asphaltene precipitation compared to toluene.

4.2.3 Potential errors in experiment

There are a lot of potential errors that might contribute to inaccuracy since there is a lot of a changes made in this experiment converse to literatures. The most possible reason of a small reading of light absorbance is due to usage of n-heptane as a blank solution. This is because only a pure solvent that is able to permit the light passed through can be chosen as a reference sample. In addition, the practice of using a crude sample diluted with toluene as a reference sample would only produce other inaccuracy. This is because the effectiveness of inhibitor could not be measured against a stable crude oil. Therefore, n-heptane is chosen as a blank solution since it has a characteristic of a pure solvent and the increment of n-heptane amount will not contribute towards a light absorbance difference.

Moreover, there is a potential error in absorbance reading due to solid particles stick onto the cell surface. As mentioned in the previous chapter, the test sample is removed and injected with another amount of sample into the same cell. Without a good cell cleaning, the solid will stick onto the surface even after the sample is completely removed. Therefore, acetone is used as a cleaning agent to remove any precipitate stick on the cell surface.

Another potential error is the preparation of 1, 3 benzenedisulfonic acid. The result of using this inhibitor was totally in opposition to other literature findings. Since the amount was not disclosed in other literature, there is a probability of a certain concentration that will mix well with the crude. A simple test was conducted by mixing 5 mL of 1,3 benzenedisulfonic acid with crude but the result shows no difference at all. It is probably due to the preparation stage where the 1,3 benzenedisulfonic powder was diluted into a distilled water. A depth study or perhaps a complex method is needed in order to prepare the exact solution.

Furthermore, human error contributes towards the inaccuracy of the experiment. Mainly, it is the inability to observe the exact light absorbance reading. Since the reading kept on changing each second, it is quite impossible to identify the exact value. Hence, by recording the minimum and maximum reading, the error can be reduced by taking the average reading.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 RELEVANCY TO OBJECTIVES

This report broadly covers the fundamentals in identifying and evaluating potential inhibitors to treat downhole asphaltene precipitation. In defining the objectives, the background of the study and the problems were clearly studied and described in the early stage. Hence the objectives of the study are clearly categorized based on the problems stated. In order to further understand the mechanism of asphaltene precipitation formation; lots of literatures were studied particularly in investigating parameters governing the precipitation. Extensive researches in literature were also done mainly in finding out list of potential inhibitors and the methodology used done by other scholars.

Based on the information gathered; xylene, 1, 3 benzenedisulfonic acid and toluene were chosen as the potential inhibitor to be studied using UV spectrometer. The experiments were conducted to measure the inhibitors effectiveness by observing the amount of n-heptane needed for the asphaltene onset precipitation. Nevertheless, the main criteria for a good inhibitor is the ability to mix well with the crude oil which 1, 3 benzenedisulfonic acid failed to fit this criterion. On the other hand, xylene and toluene showed a good result by delaying the onset precipitation. Nonetheless, the result shows that there is no significant effect in delaying onset precipitation by adding more amount of inhibitor into the crude oil. Therefore, the experiments manage to accomplish the objectives which are to identify potential inhibitors and evaluate its effectiveness by observing the amount n-heptane required to induce onset precipitation.

5.2 RECOMMENDATION

In order to produce a better result for this experiment, a single beam spectrometer or UV detector probe should be used instead of double beam spectometer. This is to reduce the inaccuracy of using n-heptane as a blank solution since the applicability is yet to be studied in depth. In addition, the equipment has a capability to give a better persistence and stable result compared to double beam spectrometer. Furthermore, a better solvent should be used to replace n-heptane mainly because n-heptane produces very low absorbance reading. Inaccuracy caused by solid attachment on the cell surface could also be reduced by using UV detector probe since it requires no cell and absorbance reading can measure directly.

Even though 1,3 benzenedisulfonic acid was mainly chosen due to its sulfonic characteristics and has a single benzene ring, the result shows a disappointment in mixing well with the crude. Therefore, it is recommended that other potential inhibitors particularly sulfonic acid derivatives should be exploited in investigating delaying effect of asphaltene precipitation.

It should be noted that the study is mainly based on laboratory condition which is less accurate to present the whole reservoir condition. Therefore, a deep study using PVT cell should be used to simulate reservoir condition that allow researchers to examine the mechanism in downhole condition as well as understanding the phase behavior of asphaltene precipitation. As for that reason, there are still rooms of improvements that can be made for continuous expansion of this study.

REFERENCES

[1]Al-Sahhaf, T., Fahim, M., & Elkilani, A. (2001). Retardation of asphaltene precipitation by addition of toluene,resins,deasphalted oil and surfactants. *Fluid Phase Equilibria* , 1045-1057.

[2]Aske, N., kallevik, H., Johnsen, E. E., & Sjoblom, J. (2002). Asphaltene Aggregation from Crude Oil and Model System Studied by High Pressure NIR Spectroscopy. *Energy&Fuel* , 1287-1295.

[3]Buckley, J., Hirasaki, G., Liu, Y., Drasek, V., Wang, J.-X., & Gill, B. (1998). Asphaltene precipitation and solvent properties of crude oils. *Petroleum Science and Technology* , 251-285.

[4]Buckley.J.S, H. D.-X. (1998). Asphaltene Precipitation and solvent properties of crude oils. *Petroleum Science and Technology* , 251-258.

[5]Buenrostro-Gonzalez, E., Lira-Galeana, C., Gil-Villegas, A., & Wu, J. (2004). Asphaltene Precipitation in Crude: Theory and Experiment. *American Institute of Chemical Engineers* , 2552-2570.

[6]Castillo, J., Hung, J., Fernandez, A., & Mujica, V. (2000). Nonlinear optical evidence of aggregation in asphaltene-toluene solutions. *Elsevier* , 1239-1243.

[7]D.Deo, K. O. (2002). Effect of Organic Additives on the Onset of Asphaltene Precipitation. *Energy&Fuel* , 694-699.

[8]De Boer, R., Leerlooyer, K., Eigner, M., & Van Bergen, A. (1995). Screening of Crude Oils for Asphalt Precipitation:Theory,Practice and the selection of inhibitors. *SPE Production & Facilities* , 55-61.

[9]Evdokimov, I. N., & Losev, A. P. (2007). Potential of UV Visible Absorption Spectroscopy for Characterizing Crude Petroleum Oils. *Oil and Gas Business* .

[10]Garcia, M. d., & Chiaravallo, N. (2001). Asphaltene Deposition Control in Lake Maracaibo Crude Oil Production. *Society of Petroleum Engineer* .

[11]Hammami.A. (1999). Asphaltene Precipitation from Live Oils:An Experimental Investigation of Onset Conditions and Reversibility.

[12]Hanson, J. (2006, January 11). *Refractrometry*. Retrieved April 13, 2012, from Chemistry Lab Technique: http://www2.ups.edu/faculty/hanson/labtechniques/refractometry/theory.htm

[13]Haskett, C. (1965). A Practical Solution to the Problem of Asphaltene Deposits-Hassi Messaoud Field,Algeria. *Society of Petroleum Engineering* , 387-391.

[14]Hirschberg, A., deJong, L., Schipper, B., & Meijer, J. (1984). Influence of Temperature and Pressure on Asphaltene Flocculation. *Society of Petroleum Engineers* , 289-293.

[15]Joshi, B. N., Mullins, O. C., Jamaluddin, A., Creek, J., & McFadden, J. (2001). Asphaltene Precipitation from Live Crude Oil. *Energy&Fuel* , 979-986.

[16]McCain, W. (1990). *The properties of petroleum fluids-2nd edition.* Oklahoma: PennWell Publishing Company.

[17]Ostlund, J., Nyden, M., Auflem, H. I., & Sjoblom, J. (2003). Interactions between Asphaltene and Napthanic Acid. *Energy&Fuel* , 113-119.

[18]Pan, H., & Firoozabadi, A. (2000). Thermodynamic Micellization Model for Asphaltene Precipitation Inhibition. *AIChE Journal* , 416-426.

[19]Pedersen, K. S., & Christensen, P. (2007). *Phase Beahavior of Petroleum Reservoir Fluids.* Parkway NorthWest: Taylor&Francis.

[20]Salager, J. (2002). Surfactants types and uses. Los Andes, Venezuela.

[21]Solomons, T. (1997). *Fundamental of organic chemistry-5th edition.* John Wiley & Sons Inc.

[22]Wang, J. (2000, October 18). Asphaltene:A general introduction. New Mexico.

[23]Wasan, D. (n.d.). *Introduction to surface active agents (SAA)*. Retrieved December 18, 2011, from Dr Kishor Wasan Laboratory: http://www.wasanlab.com/pharm/saa.html