EFFECT OF INHIBITORS ON ASPHALTENE PRECIPITATION

by

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CERTIFICATION OF APPROVAL

Effect of Inhibitors on Asphaltene Precipitation

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Approved by,

____

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TRONOH, PERAK

May 2013

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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MUHAMMAD ASYRAF BIN ISKANDAR

ABSTRACT

Asphaltene precipitation and its deposition along the production system and separation facilities cause a lot of problems in the Oil and Gas industry. It damages reservoir by reducing its permeability while also changing its wettability. Asphaltene precipitation also reduces well productivity where they clog production system and separation facilities. To overcome this issue, the prediction of asphaltene precipitation is important so that preventive measures could be taken before the deposition of the asphaltene precipitates becomes worse.

The prediction of the behaviour of asphaltene and its precipitation could be of assistance in finding the suitable inhibitors that could mitigate asphaltene precipitation. Inhibitors are widely used in the industry to prevent or stop asphaltene precipitation. However, inhibitors are sensitive to the crude oil system that they are put into. Besides that, inhibitor environment (neutral, acidic, basic) also plays very important role in determining the efficiency of the inhibitors in mitigating asphaltene precipitation. Hence, it is essential that the inhibitors used to prevent asphaltene precipitation are customized precisely to each reservoir system. This study focuses on finding the most suitable inhibitor to mitigate asphaltene precipitation, as well as analyzing all the possible effects of using the inhibitors.

ACKNOWLEDGEMENT

I would like to take this opportunity to express my deepest gratitude to my Final Year Project Supervisor, Associate Professor Dr. Muhannad Talib Shuker for his utmost support and guidance throughout the two (2) semesters of Final Year Project course. Besides that, I would like to thank all Graduate Assistant postgraduate students who have been extremely helpful in guiding me, especially Mr. Muhammad Ali Buriro, who has been a terrific mentor during the execution of my Final Year Project. Last but not least, millions of thank you goes to everyone who has been a part of my Final Year Project in Universiti Teknologi PETRONAS.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Asphaltenes are molecular substances that are frequently found in crude oil. They are typically found together with alkanes, aromatic hydrocarbons, and resins. Asphaltene molecules are very complex with relatively high molecular weight and they have a density of around 1.2 g/cc. Asphaltenes mainly contains carbon, hydrogen, nitrogen, oxygen, and sulphur. They are also widely defined as n-heptane (C_7H_{16}) insoluble, toluene ($C_6H_5CH_3$) soluble component of a carbonaceous material. Due to its insoluble nature to n-heptane, asphaltene molecules will precipitate when an excess of n-heptane is added to a crude oil system.

In the oil industry, asphaltenes are usually regarded as troublesome only when they are precipitated. The precipitated asphaltene could be deposited anywhere along the production system, from near wellbore region to production tubing, flow lines, and processing facilities such as separators. Asphaltene deposition that occurs at oil producing zones near the wellbore could cause a reduction in the permeability, as well as the change in wettability which will result in lower oil recoveries. Also, the deposition of asphaltene could cause choking and this restricts the tubing clearance, leading to the decline of production rate. Besides that, asphaltene precipitation can cause various operational problems, such as water-oil emulsion and higher oil viscosity. At the processing facilities, asphaltene precipitation can cause oil and water separation problems.

Asphaltenes can appear in solid coal-like form, or more sticky tar-like form. Asphaltenes deposits with more oil-like appearance indicate that the crude oil system contains more resins. The nature of the deposits depends highly on the crude oil composition and the conditions under which the precipitation occurs. In an oilfield operation, the crude oil of that field is usually characterized beforehand on its asphaltene content and also the solvency that the crude has for its asphaltenes.

However, asphaltene content is not directly related to asphaltene precipitation risk. A high-asphaltene content crude oil could be more stable than low-asphaltene content crude and vice versa.

In asphaltene studies, SARA analysis is an important tool. SARA refers to saturates, aromatics, resins, and asphaltene fractions of a crude oil. The saturate fraction consists of non-polar materials where they usually decrease asphaltene solubility. Aromatics are more polarizable and they increase asphaltene solubility. On the other hand, resins acts as a coating and provides a protective shield around the asphaltene molecules to prevent it from aggregating. By adding n-alkanes such as n-heptane, the protective shield will be removed and this will induce the precipitation of asphaltene. Asphaltene content can be determined using IP-143 method. Asphaltene fractions are extracted from a crude oil using n-heptane before they are extracted into toluene. Figure below shows the asphaltene stabilization-ability assessment by using SARA analysis.

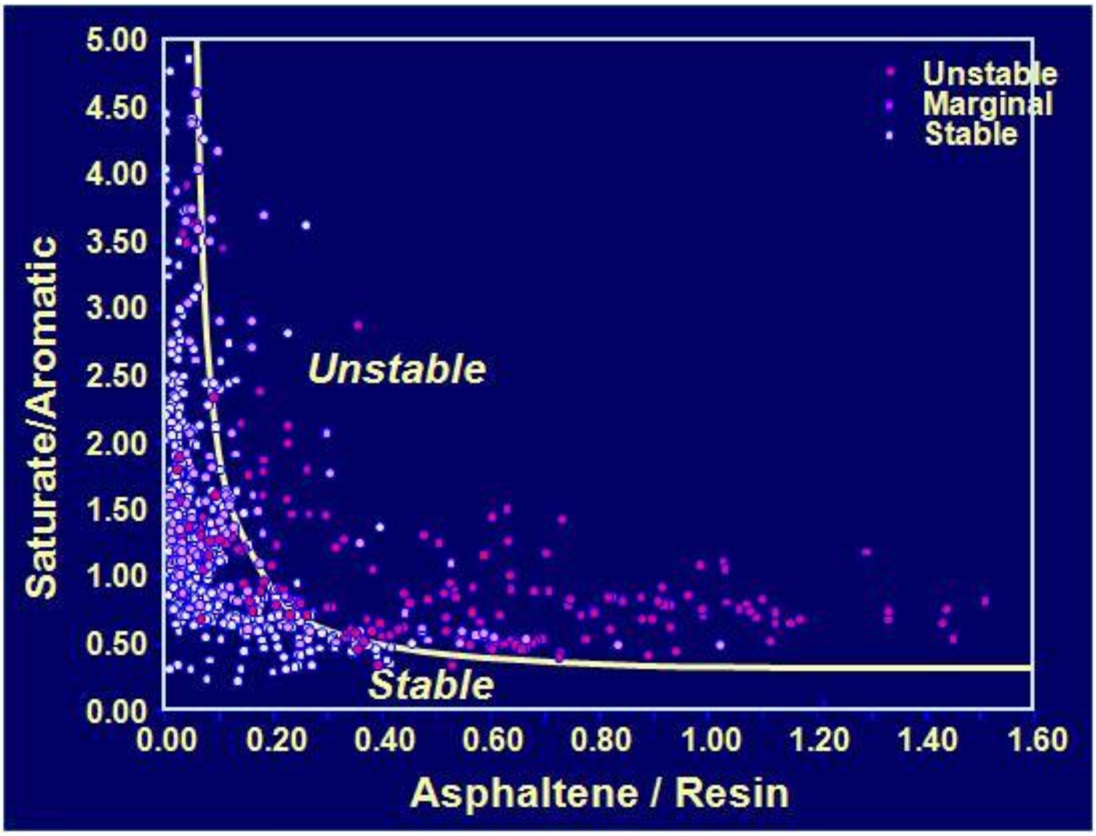

Figure 1 - Asphaltene stabilization assessment using SARA analysis

(Source: http://www.oilfieldwiki.com/wiki/Asphaltenes)

1.2 Problem Statement

Non-precipitated asphaltene are typically stable at original reservoir conditions. Resins are widely believed to be the element that holds down and stabilize the asphaltene in its original dispersed condition. During production, there are numerous factors that may induce the destabilization and ultimately the precipitation of asphaltene, such as the effect of temperature and pressure drop, effect of gas lift, effect of oxidation, change in chemical composition, and others. These factors are almost always inevitable during oil production where eventually, asphaltene precipitation will occur. Precipitation takes place when the crude loses its ability to keep the asphaltene particles dispersed.

The pictures from Figure 2 and Figure 3 below show examples of a string of production tubing and heat exchanger at separation facilities clogged with asphaltene precipitate. It can be seen clearly that the solid asphaltene precipitates plugged the tubing clearance and this restricts the oil flow to a certain degree where production rate is at stake, while also causing separation difficulties at separation facilities.

Figure 2 - Production Tubing with asphaltene precipitate

(Source: http://www.oilfieldwiki.com/wiki/Asphaltenes)

Figure 3 - Damaged separation facility equipment due to asphaltene deposits

(Source: http://www.oilfieldwiki.com/wiki/Asphaltenes)

To counter this problem, various types of inhibitors were formulated to reduce or even completely stop the precipitation of asphaltene. Asphaltene inhibitors are usually set in a way that they mimic the stabilizing effect of a resin layer to prevent flocculation. However, asphaltene problems vary from area to area and field to field. Thus, a universally effective inhibitor that can be used in every case is quite impossible to have. Plus, the inhibitors itself are sensitive to the crude oil system that they are put into, as two different inhibitors may have two very different results for the same system they are used on.

Therefore, it is important that the inhibitors used to reduce or prevent asphaltene precipitation are customized precisely to each reservoir system so that they will not have a detrimental effect on the reservoir system later on.

1.3 Objective and Scope of Study

Inhibitors to mitigate asphaltene precipitation are being developed by service companies all over the world. There are various types of inhibitors, for example, inhibitors that directly prevent asphaltene flocculation and keeping them dispersed and stabilized in its original condition, and inhibitors that re-disperse asphaltenes that were already precipitated.

The efficiency of each inhibitor actually varies one from another, depending highly on the type of crude system they are used on. In general, asphaltene inhibitors are usually injected upstream of the precipitation location for optimal performance. To counter asphaltene problem near the wellbore region, there are cases of using inhibitor squeeze treatment but there are not many successful case studies of this method.

The practice of applying inhibitors may have adverse or harmful effects on the reservoir and production system in the future. This could mean a more severe decrease in the production rate after the initial treatment is successful; where the well could be highly producing only for a short time after it was treated, then the production rate declines rapidly.

Therefore, this study aims to find the most suitable inhibitor that can mitigate asphaltene precipitation in a specific crude system. Also, this project will focus on investigating all the possible effects of using the inhibitors, be it a positive or a negative effect, and also finding possible ways to counteract these negative effects, if any. Ultimately, this will contribute to an increase in the reservoir performance, where higher oil recovery is to be expected.

CHAPTER 2

LITERATURE REVIEW

2.1 Asphaltene Properties and Behaviour

Asphaltene was defined as the polyaromatic and high molecular weight hydrocarbon faction of crude oil that are generally characterized as insoluble in n-heptane or in n-pentane (Srivastava et al, 1993). They are believed to be a finely dispersed colloidal suspension in oil stabilized by resins adsorbed on their surface. On the other hand, resin was defined as the fraction of the deasphalted oil strongly adsorbed in surface-active materials and can only be desorbed by solvents such as the mixture of toluene and methanol (Buenrostro-Gonzalez et al, 2004). According to Koots and Speight (1975), asphaltenes and resins are aromatic hetero-compounds with aliphatic substitutions and they form the most polar fraction of the crude oil.

Asphaltene precipitation issue can be considered as quite a common problem in oil and gas industry, particularly in production and flow assurance sector all over the world. Their deposition during oil recovery operations have been well documented in the literature (Islam, 1994). This issue has been widely tackled by the practice of using inhibitors to reduce or stop the precipitation from occurring in the production system. Besides causing flow assurance problem in processing facilities, flocculated asphaltene also restricts pore throats in the reservoir and ultimately reducing the effective permeability of the formation. The figure below illustrates the choking of pore throats by flocculated asphaltene (Leontaritis et al, 1994)

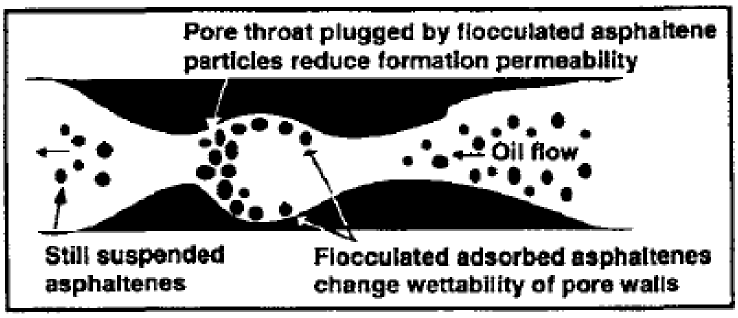

Figure 4 - Asphaltene flocculation near producing well

(Source: Leontaritis et al, 1994)

According to Leontaritis et al. (1994), asphaltene will be deposited only after they are flocculated. Hence, the most important measure to be taken is actually to prevent the flocculation before it happens. In fact, it is better to take preventive measures at an early stage, as early as during the drilling and well completion stages once the crude oil is known to inhibit asphaltenic properties. The prevention may not be possible for every case, thus the next step to be considered is to minimize asphaltene dropout after flocculation. If this is not achieved, there is a very high risk of permanent formation damage to occur at the near wellbore region.

Besides pore throat choking, the study by Leontaritis et al. (1994) also considers wettability reversal which could cause lower oil recoveries. This phenomenon usually happens with reservoir system with high polarity where the most polar and charged particles of the asphaltene attach to negatively-charged water-wet sands, which alters the oil wettability towards becoming more oil-wet. The observation is associated with reports done by Clementz (1982). This condition is irreversible in some cases. The figure below illustrates the wettability reversal due to asphaltene flocculation.

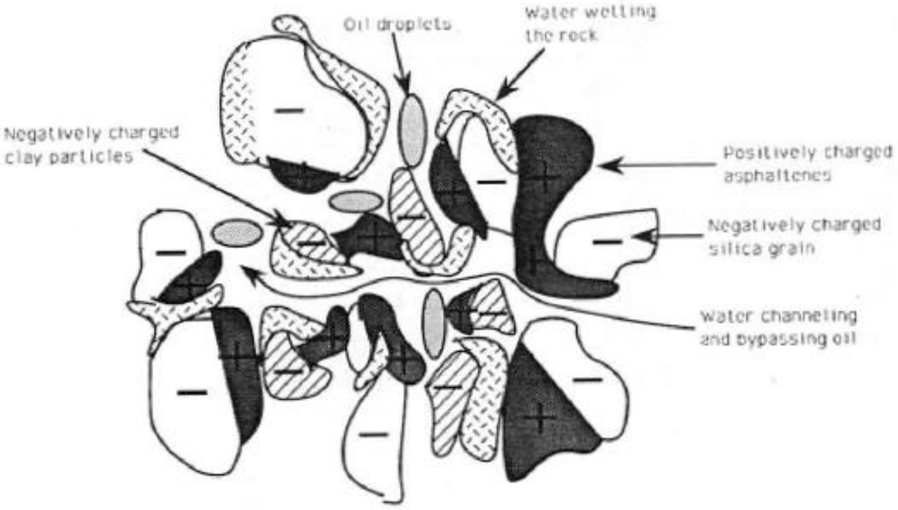

Figure 5 - Wettability changes due to asphaltene adsorption on the rock matrix

(Source: Leontaritis et al, 1994)

Asphaltene precipitation in reservoirs, wells, and facilities present a damaging effect on the oil production and also its economics. These solids that clog the tubing and production facilities contains carbon, hydrogen, oxygen, nitrogen, and sulphur usually remain in solution under reservoir temperature and pressure conditions. They precipitate when there is a drop on the temperature and pressure below the onset conditions (Andersen, 1994). The figure below shows the Asphaltene Precipitation Envelope where the red-coloured border is the onset condition where asphaltene precipitation is more likely to occur if there is pressure and temperature changes off these onsets.

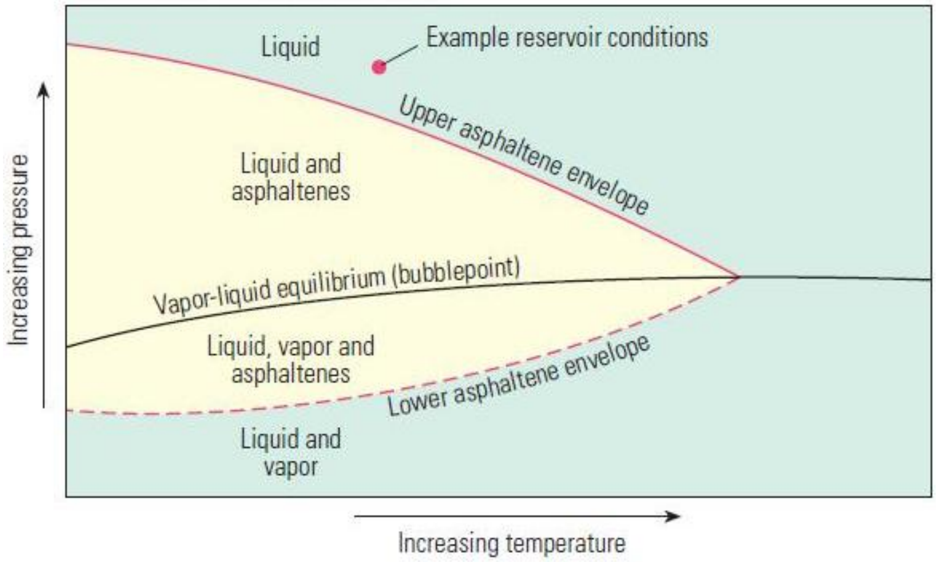

Figure 6 – Asphaltene Precipitation Envelope

(Source: http://www.oilfieldwiki.com/wiki/Asphaltenes)

Asphaltene precipitation is caused by several factors such as temperature and pressure change, chemical composition of the crude oil, mixing the oil with diluents, and the effect of acid stimulation (Kokal and Sayegh, 1995). Asphaltene composition and pressure changes effects are believed to be stronger than the effect of temperature. In fact, pressure drop alone can be the factor that destabilizes the asphaltene molecules in crude oils and is the major reason for asphaltene deposition in wellbore. Due to depressurization, the density of the crude oil decreases and this causes the interactions between asphaltenes to become stronger. Eventually, this will induce the precipitation of asphaltene molecules.

Based on the general Asphaltene Precipitation Envelope (APE) from Figure 3, the relationship between the pressure and temperature of the reservoir could be deduced. As studied by Bilheimer et al. (1949), there will be a consistent decrease in asphaltene precipitation as pressure increased. Lhioreau et al. (1967) validated this research in mixtures of crude oil and hydrocarbons from methane to n-heptane.

From APEs developed by Leontaritis and Mansoori (1988) for Primos crude oil, it was observed that as temperature increases, the onset pressure will decrease. This will require a bigger pressure change from the initial reservoir condition to initiate asphaltene precipitation. Asphaltene solubility will also increase in association with higher temperature reservoir, as proven by studies by Andersen (1994).

As mentioned before, crude oil with high asphaltene content does not necessarily cause asphaltene problems. For example, the Boscan crude oil in Venezuela contains around 17 weight percentage (wt %) of asphaltene, but there is no issue of asphaltene deposition whatsoever (Lichaa, 1977). On the contrary, the Hassi Messaoud oil, which contains only 0.1 wt % of asphaltene, has caused serious asphaltene deposition problems during recovery and processing (Haskett and Tartera, 1965).

2.2 Inhibitor

In some of the Marrat Jurassic wells from the West Kuwait and South East Kuwait area of producing zones, the asphaltene deposition in oil well tubing has a severe detrimental effect on the economics of oil production. Ghloum et al (2009) carried out studies on the inhibition effect of three commercial and three non-commercial inhibitors. Four crude oil samples were used to investigate the effect of these inhibitors by a series of titration tests using the PVT cell with the laser technique. The physical properties and chemical composition of the four crude oil samples and inhibitors were evaluated.

From the screening tests that were carried out on the inhibitors, it was revealed that the base-based inhibitors are more effective with most crude oils due to its high resin content. On the other hand, some other crude responds better to acid-based inhibitors because of their high polarity and compatibility with the asphaltene fraction. The study done by Ghloum et al (2009) indicates that the same inhibitor may have different effects on different crude oil sample, and vice versa.

The effectiveness of an inhibitor is primarily dependant on its chemical and structural characteristics. However, Chang and Fogler (1993) argue that the inhibitor ability to stabilize asphaltenes depends also on the solvent or dispersion medium. Rogel (2010) discusses that the efficiency of inhibitors correlates with the maximum amount of inhibitor adsorbed on asphaltenes. In general, it is widely accepted that inhibitors interact with asphaltenes, decreasing the size of aggregates and/or hindering further aggregation. However, it is not exactly clear how this interaction could drive the de-agglomeration (Barcenas et al, 2008).

As stated earlier, two different inhibitors may have very different results on hindering asphaltene precipitation for the same system. Inhibitors can have no effect at all; act as stabilizers, or even enhancing the flocculation of asphaltenes. Smith et al (2008) and Wang et al (2009) testify that the presence of acidic or basic groups in asphaltenes can have a significant effect on the performance of the inhibitors. Rogel (2002, 2008) has proposed a model on the basis of a molecular thermodynamic approach used for asphaltene aggregation. In this model, asphaltene aggregates are depicted as composed of an aromatic core which was formed by stacked aromatic sheets surrounded by aliphatic chains. Low solubility of the polyaromatic rings in the solvent is the driving force for the aggregation because of strong aromatic interactions. This model does not take other possible interactions between asphaltenes molecules into account, such as hydrogen bonding or acid-base interactions.

The aggregation behavior of asphaltenes in different solvents has been successfully predicted by using this model (Rogel, 2002/2004), as well as the effect of resin on asphaltene precipitation (Rogel, 2008; Sedghi & Goual, 2010). In the proposed model, the main element involves a detailed description of the free energy of formation of a complex. This complex is composed by an asphaltene aggregate and several inhibitors. The molecular changes produced by the assimilation of inhibitors in the asphaltene aggregate structure are taken into consideration. Particularly, the presence of the inhibitors has an effect on the interaction between asphaltene aggregates and the solvent. Besides that, the solubility and the self-aggregation of inhibitors impact the formation of the complex, as they resist the assimilation of the inhibitors in the complex structure. These factors are all considered in the model. Rogel (2010) argues that the proposed model is used to evaluate how different factors affect the performance of inhibitors.

The effect of inhibitors on aggregate size, as explained by Chang and Fogler (1994) is that the usage of inhibitors can develop smaller, similar sized or larger aggregates depending on experimental conditions. The decrease in asphaltene molecule number does not mean a decrease in the actual size of aggregates. As experimented by Rogel (2010), the inhibitor concentration affects the assimilation of the inhibitor in the asphaltene aggregates. As more concentrated inhibitor is set, more inhibitor molecules form part of the aggregate, thus the number of asphaltene molecules per aggregate decreases.

However, after reaching certain concentration, the inhibitor/asphaltene ratio remains constant. The addition of more inhibitor does not give any impact on the aggregate size any further. This gives the indication that there exists an optimum inhibitor concentration that could be used specifically for one type of crude system.

Besides that, experiments by Buriro & Shuker (2012) shows the effect of different inhibitors varies from one to another, depending on the crude oil system it was used on as well as the characteristics of the inhibitors themselves. Similar with experiments done by Rogel (2010), the optimum concentration of the inhibitor could be found to determine the most efficient inhibitor.

CHAPTER 3

METHODOLOGY

To achieve a satisfying result on the study of the “Effect of Inhibitors on Asphaltene Precipitation”, the author needs to read a lot of journals, articles, books, and other reading materials to find suitable materials for this project. Also, the author needs to consult the Supervisor regularly to discuss on the feasibility of conducting the project within the time frame and also the problems that is related to the topic area.

Besides conducting preliminary research on the topic, data gathering by conducting relevant experiments should also be done to ensure that the author met the timeline of the project, which will be around 9 months divided into 2 semesters. The suggested commencement of project (acquiring result and conducting analysis) is scheduled to be carried out during FYP 2; however, it is advisable to begin early so that a few initial observations could be recorded.

The project timeline of FYP 1 is illustrated in the table below.

Table 1 - FYP 1 Project Timeline

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Selection of Project Topic	■	■						Mid-semester break							
2	Preliminary Research Work		■	■	■	■										
3	Submission of Extended Proposal						●									
4	Proposal Defence									■	■					
5	Project work continues											■	■	■		
6	Submission of Interim Draft Report														●	
7	Submission of Interim Report															●

● Suggested milestone

■ Process

The project timeline for FYP 2 is illustrated in the table below.

Table 2 - FYP 2 Project Timeline

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-SEDEX											●					
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)																●

3.1 Research Methodology and Project Activities

After finding relevant materials and information on the properties of asphaltene as well as what inhibitors could do to them, it is important that the author understands the concept of asphaltene precipitation and inhibitors' effect in general before proceeding with the next step of this project.

The author will have to determine a solid objective of the study while also identifying the methods or experiments that will be used in the project. Relevant theories should also be developed in this process to prove the relationship of the early findings of the study.

When the method or experiments have been determined, the author will need to perform data gathering and conduct these experiments to prove or support the theory that has been developed. Subsequently, the analysis of the result is significant to complete the study. The Research Methodology and Project Activities are depicted in the diagrams below.

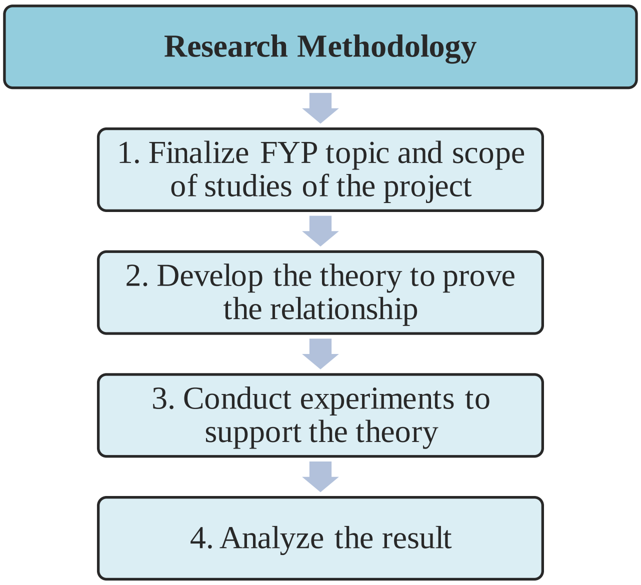

Figure 7 - Research Methodology

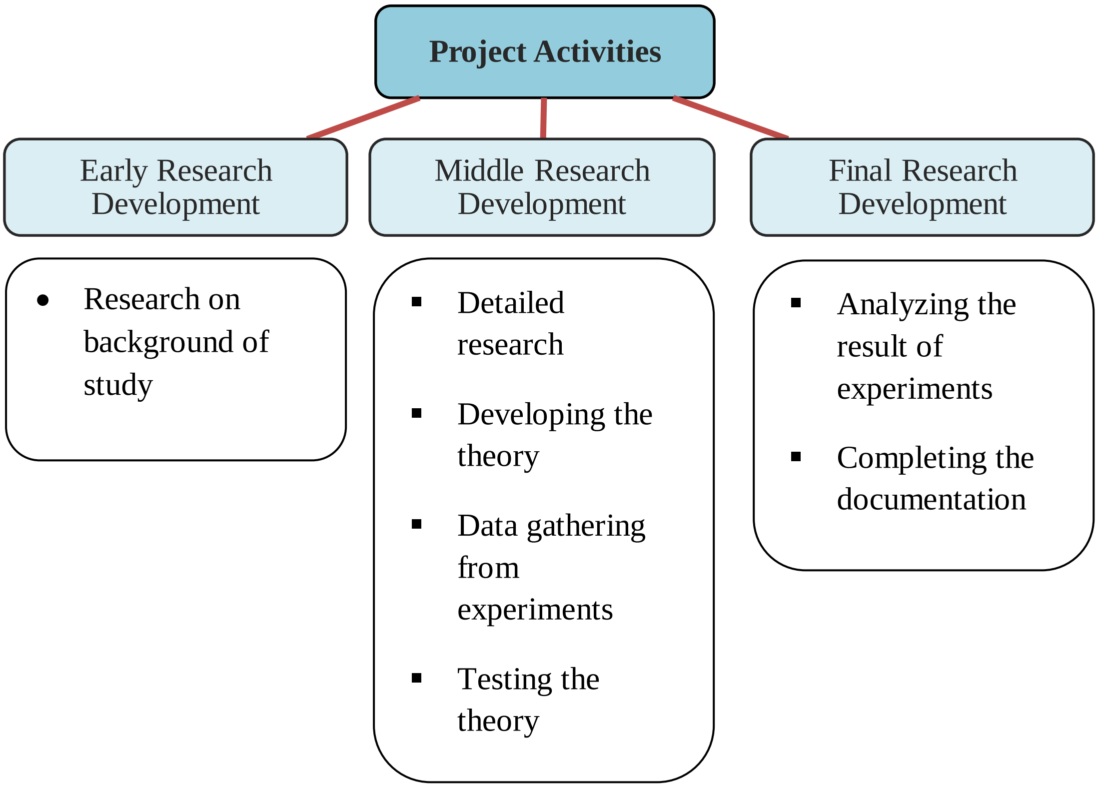

Figure 8 - Project Activities

3.2 Equipment/Materials/Chemical Required

In this project, the author will focus on using Flock Point Analysis (Titration Test), in which the precipitation of asphaltene will be observed using the digital optical microscope to observe the asphaltene flocculation.

All materials including crude oil samples and chemicals such as toluene, n-heptane, ethanol, acidic buffer solution and basic buffer solution were obtained beforehand to ensure smooth process of this project. Six inhibitors, which are referred to as I-1, I-2, I-3, I-4, I-5, and I-6 will be used in this experiment. The inhibitors will be mixed in the acidic, basic, and neutral group to test the efficiency of each group in stabilizing the asphaltene molecules.

Three different dead crude oil samples will be used in this experiment, where the main objective is to determine the most suitable inhibitor to act as peptizing agent for the asphaltene particles. The crude oil samples were referred to as Sample X1, X2, and X3.

3.3 Methods/Experiment Used

Firstly, the preparation of the crude oil samples is needed. 1 gram (gm) of each crude oil will be mixed with 3 ml of toluene, where the mixture will be left overnight to stabilize the asphaltene molecules in the crude oil. IP-143 method was used to measure the stabilized asphaltene content of all the crude oil samples as shown in the table below.

Table 3 - Asphaltene Content Weight Percentage

Crude Oil Sample	Method	Asphaltene Weight Percentage, %
X1	IP-143	0.3
X2	IP-143	8.0
X3	IP-143	14.0

Similarly, the inhibitors will be prepared accordingly to classify it into three different polar groups, which are acidic, basic, and neutral group. 1 gm of each inhibitor was mixed with 5 cc of respective solutions to prepare the abovementioned groups. The mixed solutions of the inhibitors were classified in the table below.

Table 4 - Mixed Solution of Inhibitors

Inhibitor	Acid Group	Basic Group	Neutral Group
I-1	1 gm + 5 cc acid buffer solution	1 gm + 5 cc basic buffer solution	1 gm + 5 cc ethanol
I-2	1 gm + 5 cc acid buffer solution	1 gm + 5 cc basic buffer solution	1 gm + 5 cc ethanol
I-3	1 gm + 5 cc acid buffer solution	1 gm + 5 cc basic buffer solution	1 gm + 5 cc ethanol
I-4	1 gm + 5 cc acid buffer solution	1 gm + 5 cc basic buffer solution	1 gm + 5 cc ethanol
I-5	1 gm + 5 cc acid buffer solution	1 gm + 5 cc basic buffer solution	1 gm + 5 cc ethanol
I-6	-	-	Natural

For each experiment, the prepared crude oil samples will be titrated with n-heptane, which is a precipitant that can destabilize the asphaltene molecules. This will lead to the flocculation of asphaltene molecules thus inducing asphaltene precipitation.

This process is performed by adding a certain amount of n-heptane gradually in the crude oil system. The magnification power to observe the asphaltene particles were fixed at 10x magnification. In room temperature, 1 cc of n-heptane will be added into the crude oil system and the mixture will be stirred using magnetic stirrer for 10 minutes while the beaker is sealed with aluminum foil. If there is no occurrence of asphaltene precipitation after 10 minutes, additional 1 cc of n-heptane will be added immediately. This procedure will be repeated until the asphaltene molecules are precipitated. This would then be regarded as the Asphaltene Flocculation Point (AFP). Increment of 1 cc of n-heptane will be added until all the asphaltene molecules are precipitated, and here, the amount of n-heptane used will be recorded to establish a base line of the blank crude oil sample.

Once the base line of the blank crude oil sample is determined, another sample of the same prepared crude oil system will then be mixed well with the mixed inhibitor solution with a known concentration. After allowing the mixture to stabilize, it will then be titrated with n-heptane once more to determine the new Asphaltene Flocculation Point (AFP). The amount of n-heptane used until all asphaltene molecules are destabilized and precipitated will be recorded again. This time, it is expected that a higher amount of n-heptane will be required to induce the precipitation of the asphaltene molecules.

The higher the AFP index, the more stable the asphaltene molecules are. The greater amount of n-heptane required indicates more stable asphaltene and more efficient inhibitor. This shows that the inhibitor has successfully prevented the precipitation of asphaltene, where previously at the same rate of mixed n-heptane in the blank crude oil sample, there is occurrence of asphaltene precipitation. Then, the effect of different inhibitors will be tested with the same crude oil sample and the best inhibitor will be determined.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Data Gathering and Analysis

Data gathering and analysis were done accordingly for each experiment of different samples of crude oil and inhibitors used. The results will be shown in figures and diagrams in this section of the report. The following results show the crude oil samples X1, X2, and X3 titrated with a certain amount of n-heptane to establish the initial asphaltene aggregation or flocculation point. The observation from the digital microscope can be illustrated in the figures below.

Figure 9 - Titration Test for Crude Oil X1

2 cc 6 cc 7 cc

Figure 10 - Titration Test for Crude Oil X2

2 cc 6 cc 8 cc

Figure 11 - Titration Test for Crude Oil X3

2 cc 5 cc 10 cc

Figure 9, 10, and 11 show the titration test results of crude oil X1, X2, and X3 respectively. As observed by using digital optical microscope, the asphaltene molecules started to aggregate and flocculate after 7 cc of n-heptane added in crude oil sample X1 in Figure 9. Sample X2 requires 8 cc of n-heptane as seen in Figure 10. Figure 11 shows asphaltene behavior of crude oil sample X3, where the asphaltene molecules started to flocculate at 10 cc of n-heptane added. Figure below shows graphical representation of the amount of n-heptane needed to induce the precipitation of asphaltene in all three crude oil samples X1, X2, and X3. This amount is regarded as the base line for each of the crude oil samples.

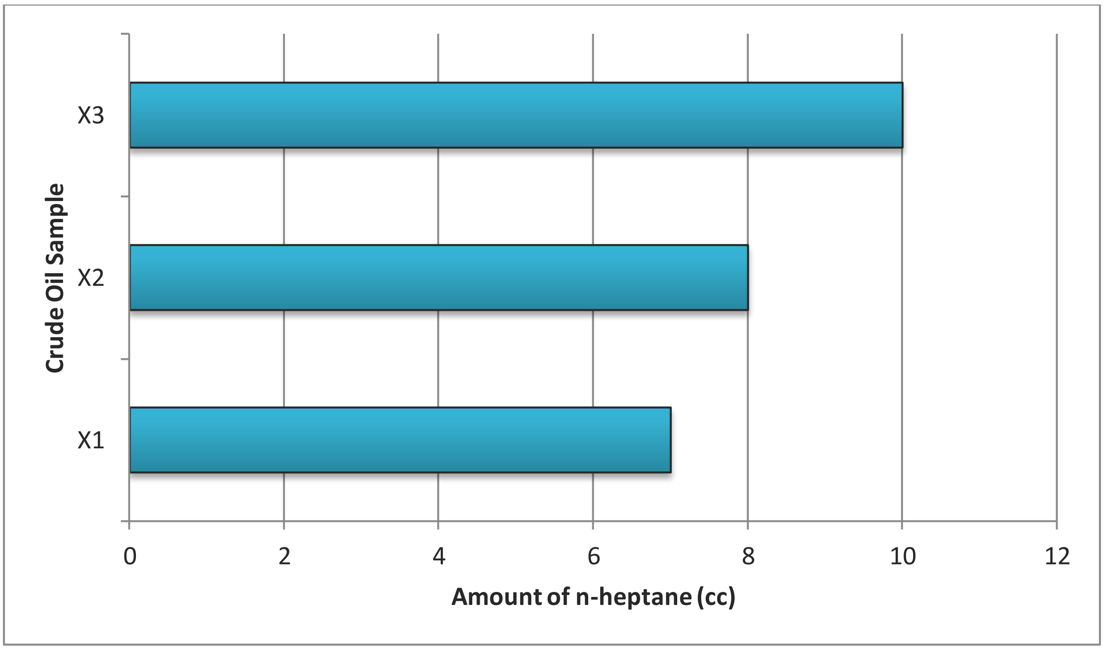

Figure 12 - Base line determination of n-heptane

4.2 Results and Discussion

These three (3) crude oil samples X1, X2, and X3 were then mixed with six different inhibitors, where each of them is refined into three different groups which are acidic, basic, and neutral group. For neutral case analysis, the graphical representation is shown in figures below for each samples of crude oil.

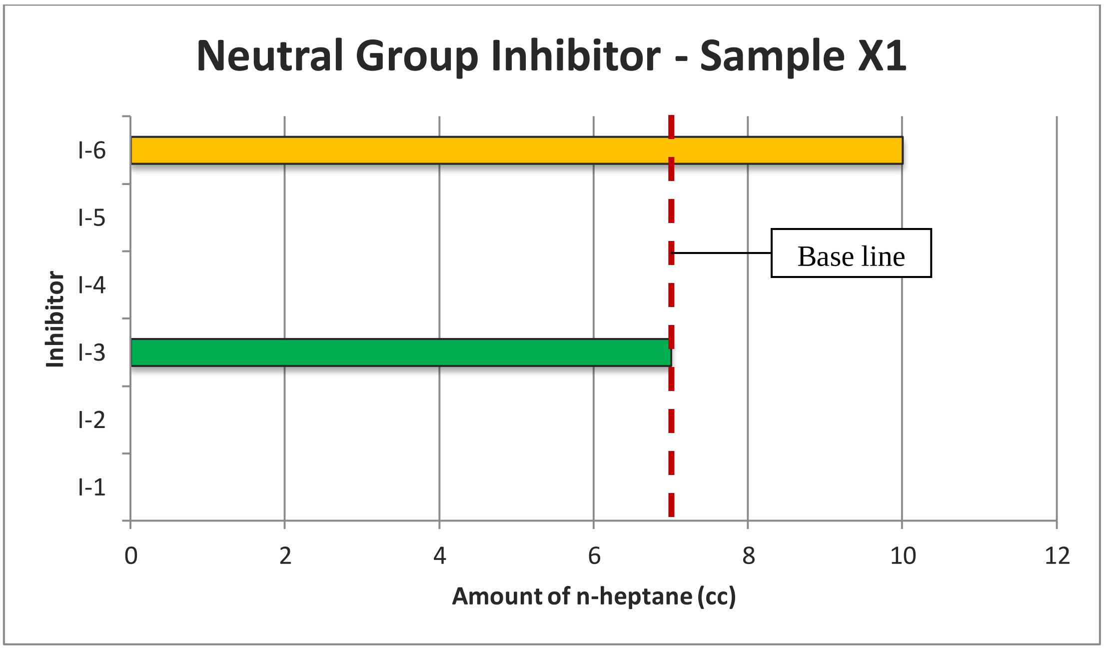

Figure 13 - n-heptane required for sample X1 (Neutral Case)

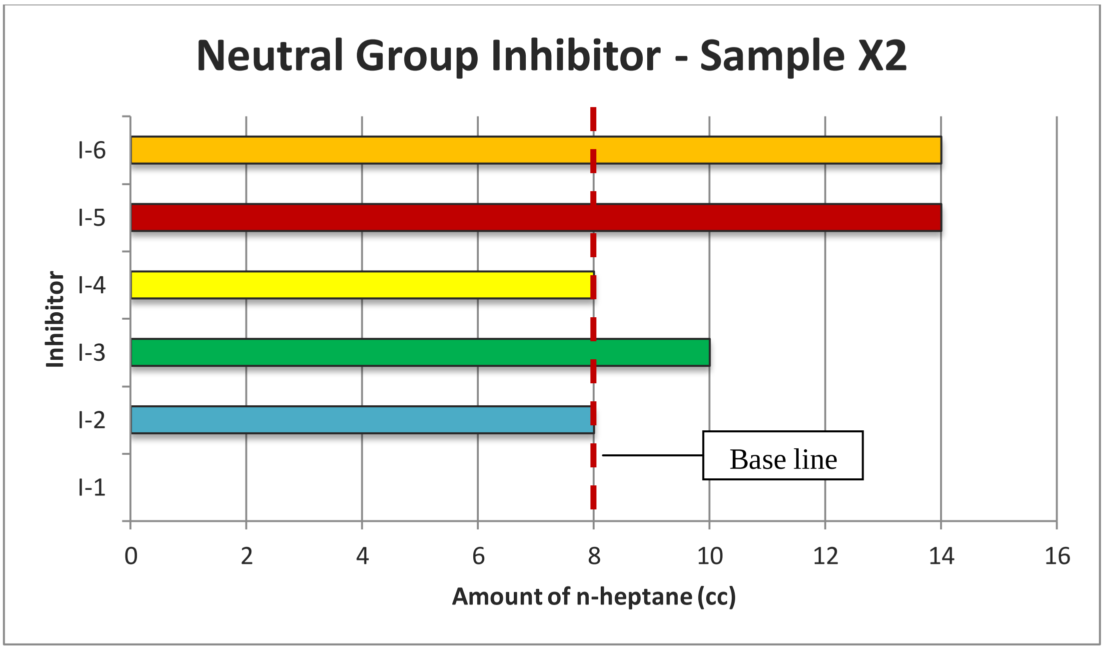

Figure 14 - n-heptane required for sample X2 (Neutral Case)

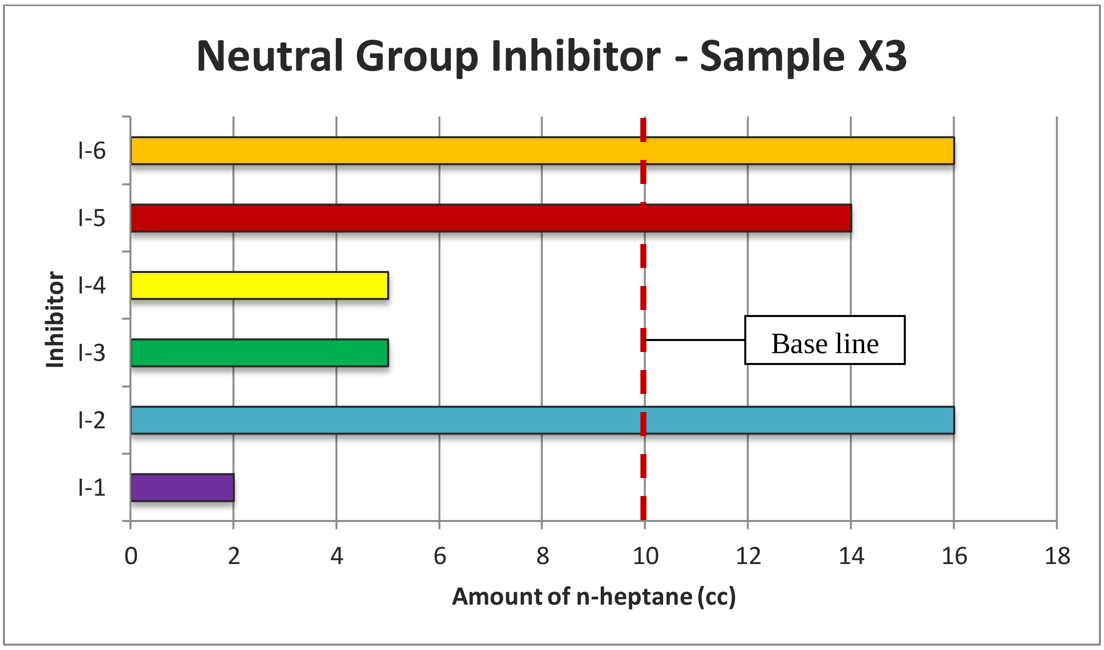

Figure 15 - n-heptane required for sample X3 (Neutral Case)

Based on the graphical representation of results above, the inhibitors I-1, I-2, I-4, and I-5 were not miscible in the crude oil sample X1.The inhibitors were deposited in a solid phase at the bottom of the beaker, hence rendering it unable to react with the crude oil. However, inhibitor I-3 and I-6 demonstrated effective peptizing power, where they are able to hold the asphaltene molecules in its dispersed form, making them harder to precipitate. Inhibitor I-3 is not effective as it requires 7 cc of n-heptane before asphaltene started to precipitate, the same amount as the base line for sample X1. Inhibitor I-6 however proved to be quite effective as only after 10 cc addition of n-heptane did the asphaltene molecules are precipitated.

For sample X2, all inhibitors were miscible except inhibitor I-1. Based on Figure 14, inhibitor I-5 and I-6 shows better performance than the others as they are able to hold the asphaltene precipitation until after 14 cc of n-heptane added. This far exceeds the base line for crude oil sample X2 which is only at 8 cc of n-heptane.

In crude oil sample X3, all six inhibitors are miscible to the crude oil. Inhibitors I-1, I-3, and I-4 are not very effective in sample X3. They actually sped up the precipitation process of the asphaltene molecules where the base line is at 10 cc. However, inhibitor I-2 and I-6 is effective where they require up until 16 cc of n-heptane before the asphaltene molecules are aggregated.

For acidic case analysis, all the inhibitors except inhibitor I-6 were mixed with crude oil samples X1, X2, and X3. Inhibitor I-6 is only used on neutral environment case, as shown in the mixed solution of inhibitor Table 4 before. The results of acid group inhibitors are shown below.

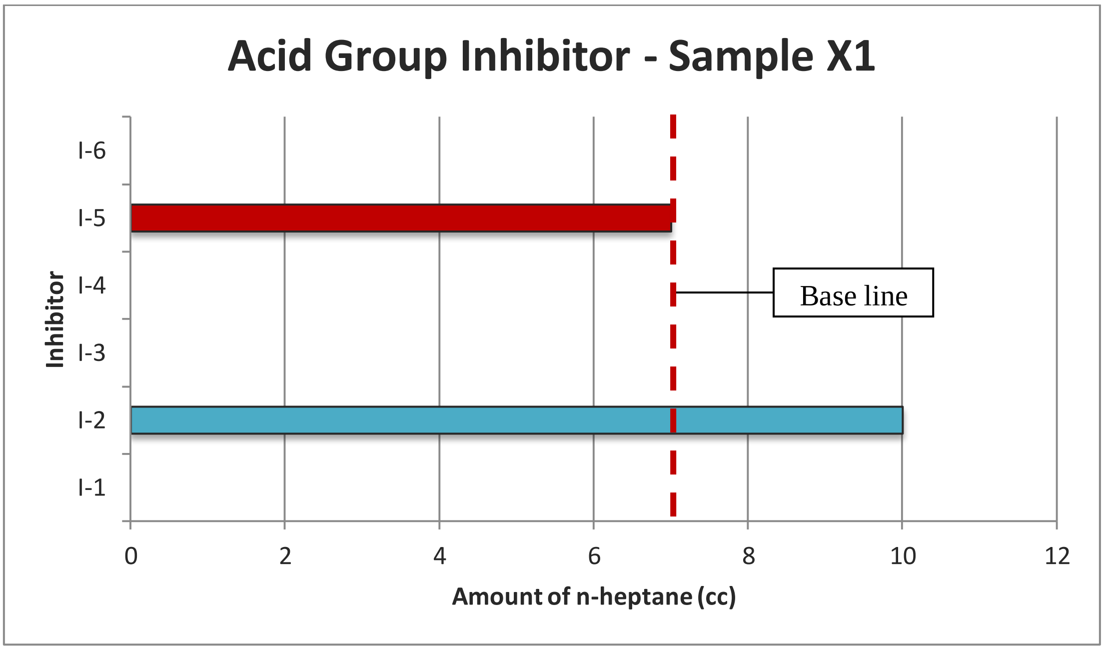

Figure 16 - n-heptane required for sample X1 (Acid Case)

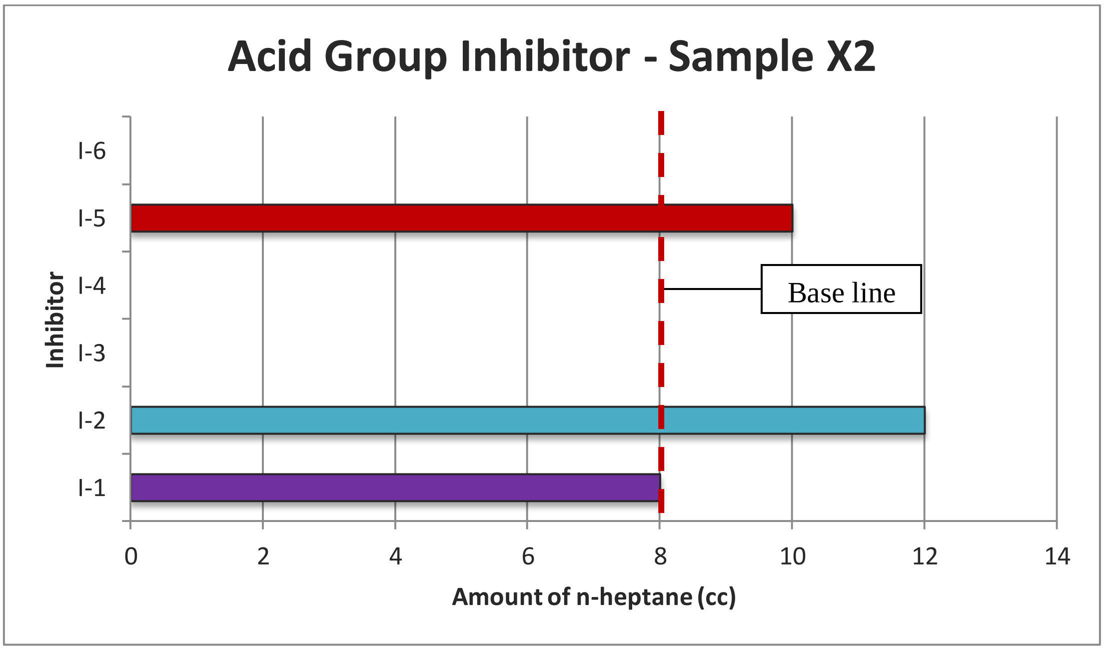

Figure 17 - n-heptane required for sample X2 (Acid Case)

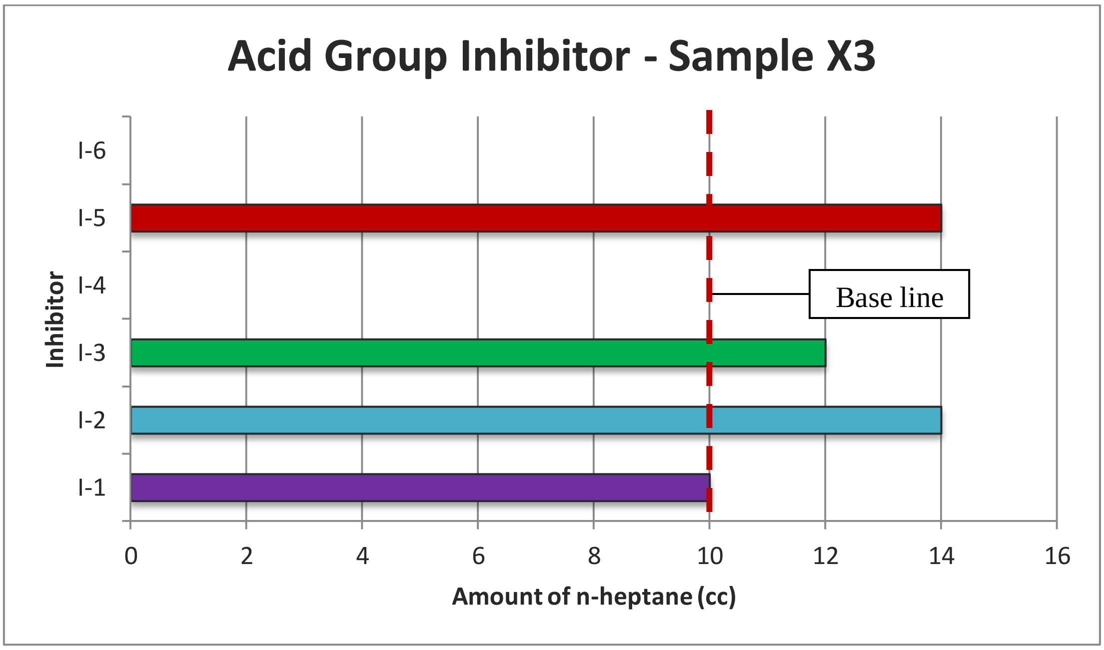

Figure 18 - n-heptane required for sample X3 (Acid Case)

Based on the graphical representation of the result above, for all crude oil samples, inhibitor I-6 does not show any results as it is only used in neutral condition case. For crude oil sample X1, inhibitors I-1, I-3, and I-4 are not miscible with the crude oil. The same condition is seen as per previous neutral case, where the inhibitors are deposited in a solid phase at the bottom of the beaker. However, inhibitor I-2 and I-5 shows good results, particularly inhibitor I-2. The mixed crude oil and inhibitor solution required 10 cc of n-heptane, higher than the base line for crude sample X1 of 7 cc of n-heptane.

Inhibitors I-3 and I-4 does not react with the crude oil sample X2 as shown in Figure 17. In this case, inhibitor I-2 is the most effective of the remaining inhibitors as it recorded a reading of 12 cc n-heptane required. This is higher than the base line for crude oil sample X2 with 8 cc of n-heptane.

In sample X3, the base line is at 10 cc of n-heptane. All five inhibitors are miscible except inhibitor I-4. Based on Figure 18, inhibitor I-2 and I-5 show better performance than other inhibitors with 14 cc of n-heptane volume required, while inhibitor I-1 and I-3 illustrate average performance with 10 cc and 12 cc n-heptane volumes respectively.

For basic case analysis, a different scenario is encountered. The mixing of basic group inhibitor with all the crude oil samples is mostly incompatible. None of the inhibitor was miscible with crude oil sample X1. For crude oil sample X2 and X3, the results were illustrated in figures below.

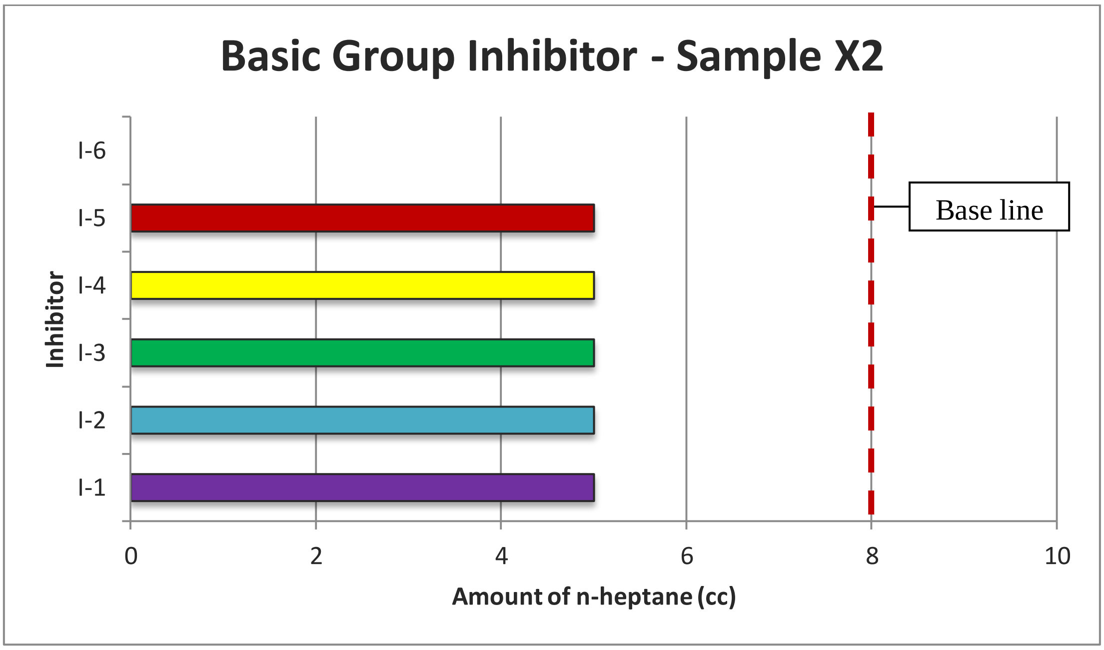

Figure 19 - n-heptane required for sample X2 (Basic Case)

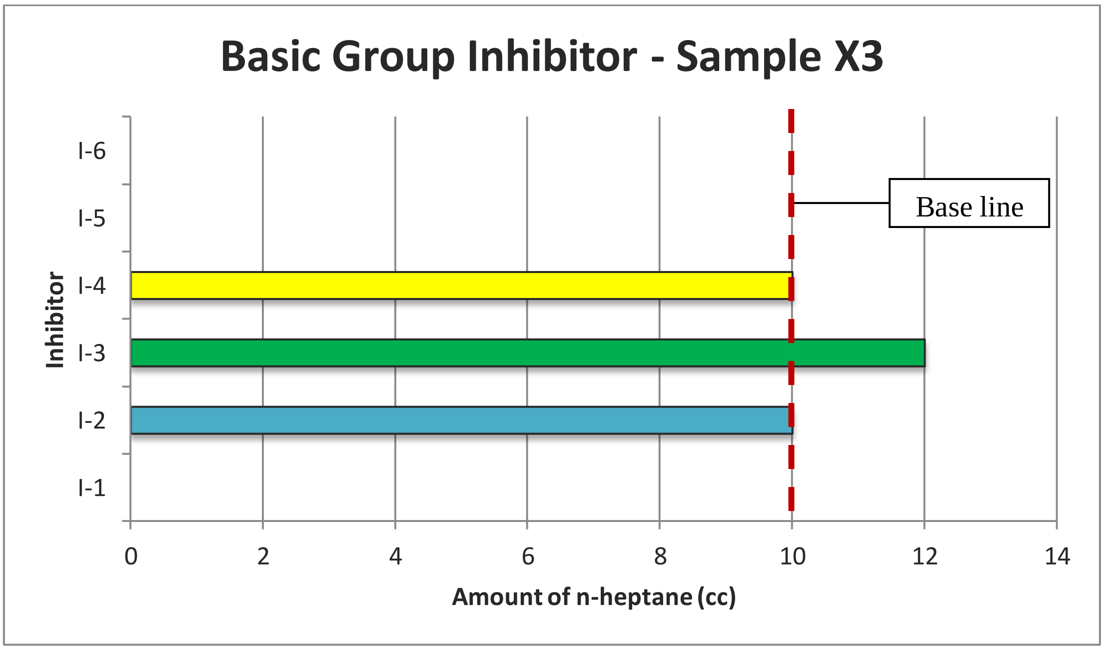

Figure 20 - n-heptane required for sample X3 (Basic Case)

Based on Figure 19 and Figure 20, the results for basic group inhibitors were not very stimulating. For sample X2, all inhibitors do not show peptizing properties, where they are not even reaching the base line for crude oil sample X2 required at 8 cc n-heptane volume.

In crude oil sample X3, inhibitors I-1 and I-5 are not miscible with the crude oil. Inhibitors I-2 and I-4 both possess equal properties in basic environment where they are able to produce average result of 10 cc n-heptane, the same value as the base line for crude oil sample X3. However, inhibitor I-3 is the most effective peptizing agent is crude sample X3 where it requires 12 cc of n-heptane before the asphaltene molecules are precipitated.

Based on the experiments, it can be observed that inhibitor I-2 from acidic group has effective inhibiting power to slow down or delay the precipitation of asphaltene molecules. Inhibitor I-6 from neutral group also showed effective functionality on all three crude oil samples.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The importance of using an efficient inhibitor is evident as proven by the results of the experiments. An effective inhibitor can delay or slow down the process of asphaltene precipitation to a great extent. The precipitation of asphaltene is widely regarded as an inevitable process where sooner or later, a drop in pressure and temperature or a sudden change in the chemical composition of the oil molecules will ultimately cause the asphaltene molecules to precipitate or flocculate.

The environment of the inhibitor plays a vital role in ensuring an effective adsorption of the inhibitor on asphaltene components. This is why three environmental groups, namely neutral, acidic, and basic group were chosen to be experimented with the inhibitors. The environment can determine the miscibility of the inhibitors with the crude oil samples as seen in the results of the experiment. Also, by manipulating the environment of the inhibitors, ineffective inhibitors which actually sped up the aggregation process of asphaltene rather than slowing it down could be sorted out.

In future, it is recommended that more inhibitors could be tested and experimented to find the most effective inhibitors. A universally-effective inhibitor that can mitigate asphaltene precipitation in all types of crude oil system is quite impossible to find, hence it would be better to find as many effective inhibitors as possible which will react specifically to a certain type of crude oil. Despite all this, environmentally friendly inhibitors should also be developed in an attempt to preserve and decontaminate the crude oil with many impurities.

5.2 Recommendation

In future, it is suggested that the analysis of the asphaltene study will include not only qualitative analysis, but also quantitative analysis. The exact percentage of asphaltene molecules reacting with the n-heptane before it is precipitated should be found out by using relevant software. This will enhance the feasibility of this study for future reference.

Besides that, more crude oil samples and also inhibitors should be tested for their properties and behaviour. This is important to maximize the options of using various types of inhibitors to different types of crude oil system. As what the author has reported in this paper, crude oils are very sensitive to additives like inhibitors. Also, inhibitors with different environmental group (neutral, acidic, basic) will have different reactions to a specific crude oil. Hence, it is a good idea to evaluate and experiment as much crude oils and inhibitors as possible to increase the possibility to find the most suitable and efficient mixture of crude and inhibitor. Ultimately, the prevention of asphaltene precipitation could be prevented and this will mitigate its deposition near wellbore, in the production system, and also at the separation facilities.

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