Bio Solvent EOR: Performance Assessment of Plant Extracts as Asphaltene Inhibitor

by

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13658

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

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(A.P. Dr Ismail bin Saaid)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
September 2014

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.

AMIRUL ASYRAF BIN ABDUL BASIR

ABSTRACT

Oil production, transportation and refinery are important processes for oil industry because this is where they make profit for their investment. However, change in pressure, temperature and CO_2 injection will affect the composition of hydrocarbon which will lead to the formation of asphaltene. Deposition of asphaltene in near wellbore region, production tubing and production facilities will cause severe effect in oil recovery process due to reduction in oil flow. Physical removal of asphaltene deposition is not a favorable option due to uneconomical and costly process. A more favorable option is to prevent the asphaltene from precipitation by using inhibitor. The main objective of this experiment is to examine the performance of green solvent as asphaltene inhibitor and compared with commercial inhibitor, Duo Benzene Sulphonic Acid (DBSA). Based on reported works, amphiphile and phenolic compound have the ability to inhibit asphaltene. Green plants that have those components are coconut, olive, palm, green tea, cinnamon and lemon grass. Different parameters are tested during deposit level test such as solvent type, concentration and contact time between oil and solvent. Then turbidity and Uv-Vis are used to analyze the data. Based on the experiments, coconut oil shows the best result in reducing asphaltene deposit level when compare with other green inhibitors. The green solvent can have the same performance as DBSA if high dosage of solvent is used.

ACKNOWLEDEMENT

First and foremost, I would like to praise the God for His blessing I managed to complete my Final Year Project. A special thanks to my supervisor, A.P. Dr. Ismail bin Saaid for his supervision and guidance throughout the FYP I and II.

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CHAPTER 1

INTRODUCTION

1.1 Background

In oil industry, asphaltene need to be monitored carefully because it can lead to a serious problem in tubing and pipelines. Pressure, temperature and composition are the root cause of unstable asphaltene precipitation. The change of temperature and pressure will affect the composition of crude oil which will weaken the strength of resin which hold the asphaltene molecule together. When the resin is weaken, asphaltene molecule will start to accumulate and precipitate due to its polar property.

Asphaltene that are precipitated and deposited near wellbore region, production tubing, flowlines and process facilities which can cause production drop, reservoir damage, tubing and piping clogging and increase in production and operational cost.

Chemical solvents treatment such as benzene, toluene, chlorate and xylene are widely used in dissolving asphaltene deposition problem. These chemicals are excellent asphaltene inhibitors but dangerous to the users that handling the chemicals and harmful to the environment because of their exceedingly low flash point and high acute toxicity.

Environmentally friendly inhibitor is used as alternative for commercially available chemical inhibitor. Vegetable oil is tested and proved to be a good asphaltene inhibitor due to their chemical nature which is compatible with crude oils. Thus, quality of crude oil is unaffected during production. Other than that, vegetable oil is chosen due to economical reason, which is lower cost of production than majority of commercial chemical inhibitor, easily available, environmental friendly, and ease of handling and operational application.

More so, green solvent is important alternative for toxic and non-biodegradable commercial inhibitor. Phenolic compound present in the plant have similar chemical structure as amphiphile. Amphiphile possess both hydrophilic and hydrophobic properties which can stabilized asphaltene molecule and act as artificial resin [1].

1.2 Problem Statement

Deposition of asphaltene near wellbore region, production tubing, flowlines and process facilities will affect well productivity. Physical removal of asphaltene deposition is not a favorable option due to uneconomical process. Chemical based asphaltene inhibitor is widely used in solving asphaltene problem. Chlorate, benzene, xylene, and toluene solvents are some examples of commercial chemical inhibitor in the market. However, these chemicals are toxic, non-biodegradable, flammable and pose harmful side effect to the people that handle the chemicals and environment. New biodegradable and environmental friendly asphaltene inhibitors that have high solubility rate need to be develop to provide alternative for existing inhibitors.

1.3 Objectives

The objectives are:

- To screen and identify potential asphaltene inhibitor from green resources
- To characterize properties of extracted inhibitor
- To compare the performance of green solvents to commercially available inhibitors

1.4 Scope of Study

Final Year Project focused on acquiring knowledge regarding conceptual understanding on asphaltene and inhibitor. Theory and knowledge can be obtained from previous studies, research papers and reference books. Furthermore, further study on green solvent is needed to determine the criteria in order to be chosen for the project. The criteria are:

- Environmental friendly and bio degradable
- Have amphiphile and phenolic compound

The green solvents that have been identified based on the criteria:

1. Lemon grass
2. Green tea leaves
3. Cinnamon
4. Palm methyl ester
5. Methyl ester oleate
6. Coconut oil
7. Olive oil

1.5 Relevancy and feasibility

Asphaltene inhibitor study is relevant to petroleum engineering student because the presence of asphaltene in crude oil will affect well productivity if not properly managed. Asphaltene deposited near wellbore region, production tubing, flowlines and process facilities can cause production drop, reservoir and equipment damage, tubing and piping clogging. Physical removal of asphaltene deposition will take time and cost which eventually will increase the production and operational cost. Prevention is another alternative for solving asphaltene problem. For that, asphaltene study needs to be conduct to identify the factors leading to asphaltene deposition especially during WAG injection. This will greatly help student to achieve deeper understanding on maintaining well productivity by applying theoretical and practical knowledge obtained from classes, laboratory work and practical experience. Within the 14 weeks of Final Year Project, many task related to research work, lab, equipment and chemical confirmation are completed within the timeframe. To get better understanding on the project, consultation with supervisor is conducted every week while research paper can be obtained from the library. Centrifuge, chemicals and lab equipment are all available in the university. Amphiphile and phenolic plants can be found within Malaysia. The availability of the equipment, chemical and sample help to make the study feasible.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to asphaltene

The structure of crude oil (physical and chemical) during production and transportation will affect the formation of suspended solid phase or precipitation such as asphaltene, resin and wax. Asphaltene are dark to brown amorphous solid with no definite melting point. Furthermore, asphaltene do not crystallize and thus the individual component is difficult to determine [2]. The composition of asphaltene is difficult to determine because the molecules are extremely complex containing thousands of atoms. Hence, characterized asphaltene based on their individual molecules is not possible [3]. In the crude oil composition, asphaltene are considered the most polar molecules and the heaviest which are primarily consist of carbon, hydrogen and heteroatoms (nitrogen, oxygen and sulfur). Asphaltene are soluble in xylene, toluene and benzene (aromatic solvents) but insoluble in heptane, pentane and hexane (light saturated hydrocarbon).

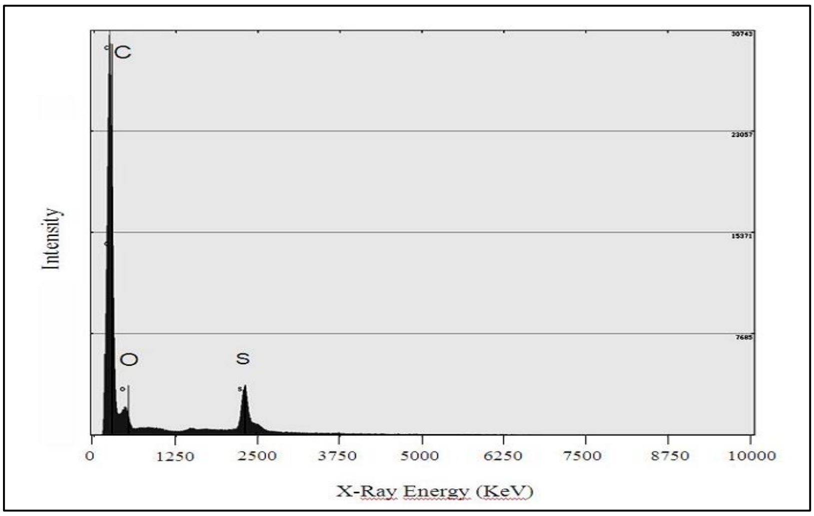

FIGURE 2.1. Asphaltene Composition from EDS Spectrum [4]

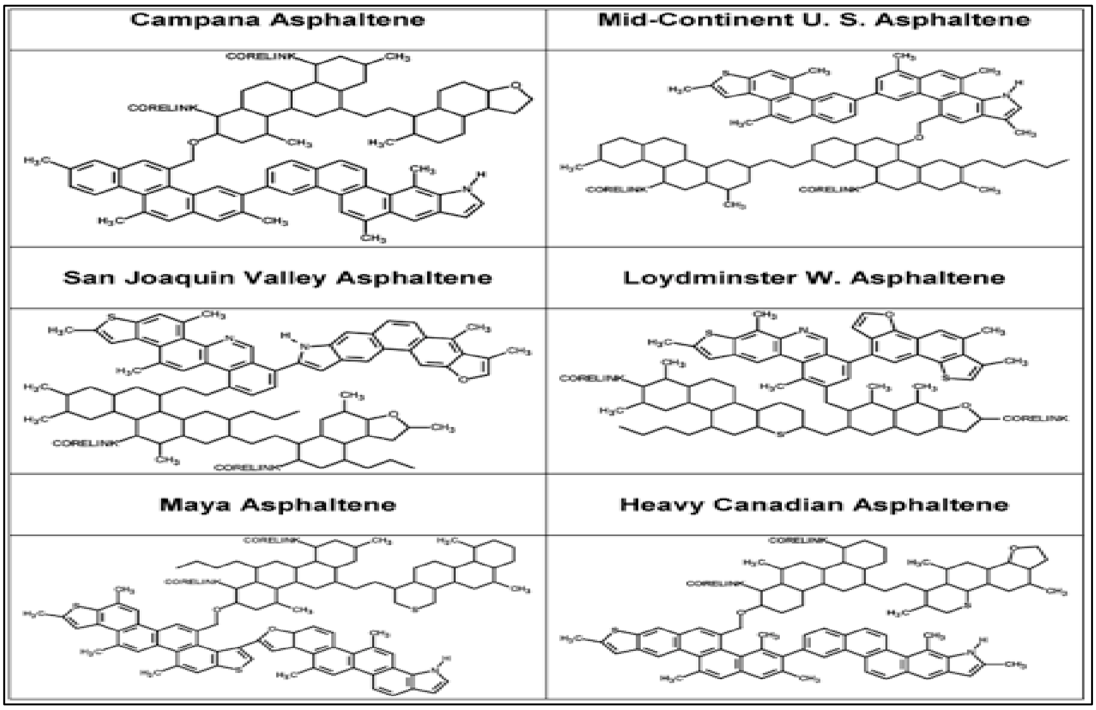

FIGURE 2.2. Different Composition of Asphaltene from Crude Oil around the World [5]

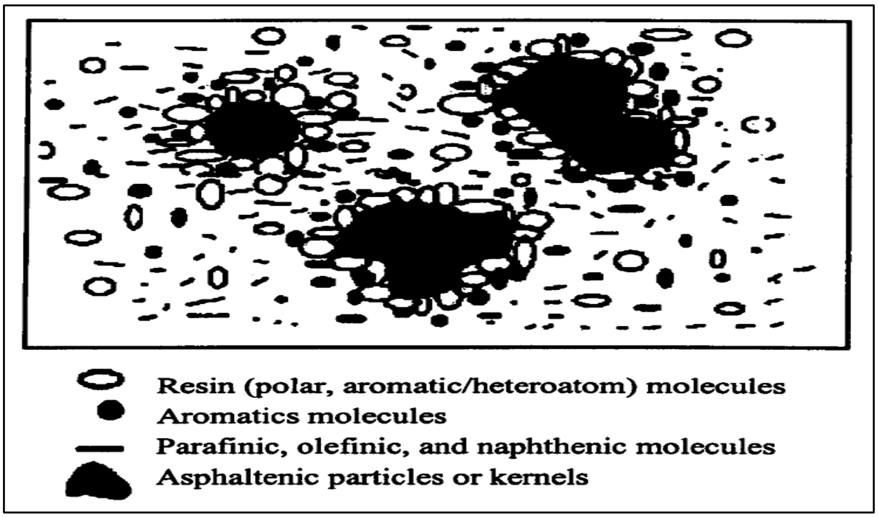

FIGURE 2.3. Asphaltene-Resin Micelle [6]

Asphaltene is polar molecule which tend to attract each other. As the molecule aggregate, asphaltene began to flocculate and grow in size to become precipitation. Resin, which surround entire asphaltene act as stabilizer which prevent asphaltene from flocculate. This is due to steric repulsion with another resin layer which surround the asphaltene molecule [7].

During production, changes in pressure, temperature and composition will result in precipitation and deposition of asphaltene particles [8]. EOR method that is widely used nowadays: CO_2-Water Alternating Gas (WAG) injection. The method is used to counter pressure drop in reservoir and recover remaining oil. However, this method has flaw. Injecting WAG will result in sudden change in composition of crude oil and deposition of asphaltene will follow [9]. This is because; solubility of crude oil will drop when contacting with CO_2 and thus favor asphaltene precipitation [10].

Precipitation of asphaltene may occur due to pressure and temperature changes during production and transportation. Other than that, CO_2 injection and acid simulation can change the composition of crude oil which can destabilized the asphaltene molecule [11].

The asphaltene colloidal become unstable at low temperature due to interaction energy differences between two molecules, asphaltene and crude oil [12]. Meanwhile, pressure depletion will increase relative volume fraction in crude oils components and the solubility parameter difference will increase between asphaltene and crude oils. The maximum solubility difference is at bubble point pressure. As pressure drop below bubble point pressure, light crude oil will evaporate and asphaltene will become soluble again [8]. Deposition of asphaltene based on the effect of temperature and pressure changes is shown below.

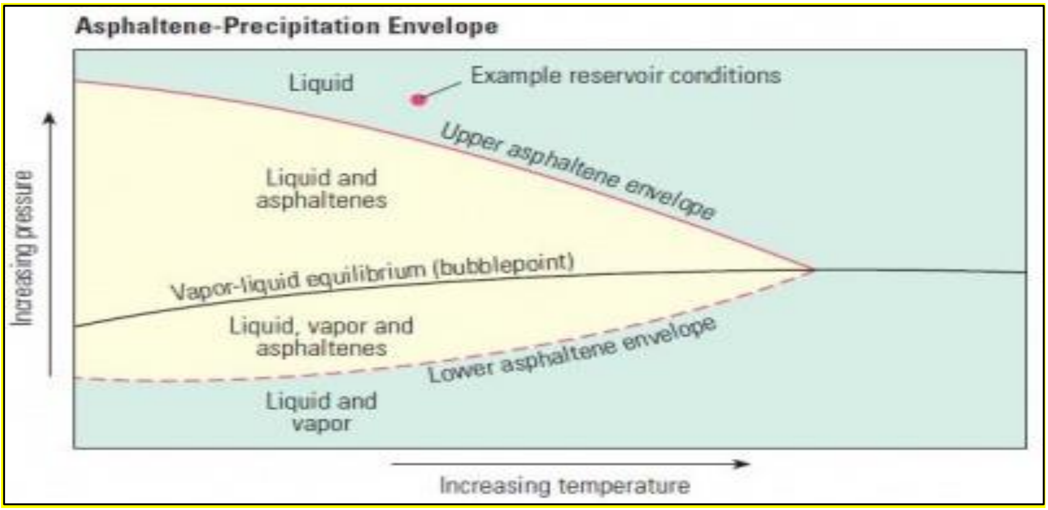

FIGURE 2.4. Asphaltene Deposition Based on the Effect of Temperature and Pressure [13]

Carbon dioxide can reduce the asphaltene solubility and eventually change the composition of crude oil [14]. As the resin weakens, the asphaltene began to aggregate and flocculate. Asphaltene precipitation and deposition during production causes severe damage such as pipeline and tubing clog, wettability changes which reduce the efficiency of WAG performance and equipment damages. Moreover, expensive treatments are required to repair the damage done by asphaltene precipitation [9].

For the experiment, asphaltene can be obtained from crude oil by adding n-heptane into the crude oil. Based on the experiment, n-heptane and heavier n-alkanes are tested and the result indicated that n-heptane is the most preferable solvent [15]. The amounts of precipitations are almost the same for heavier n-alkane but increase sharply as the number of n-alkanes getting smaller.

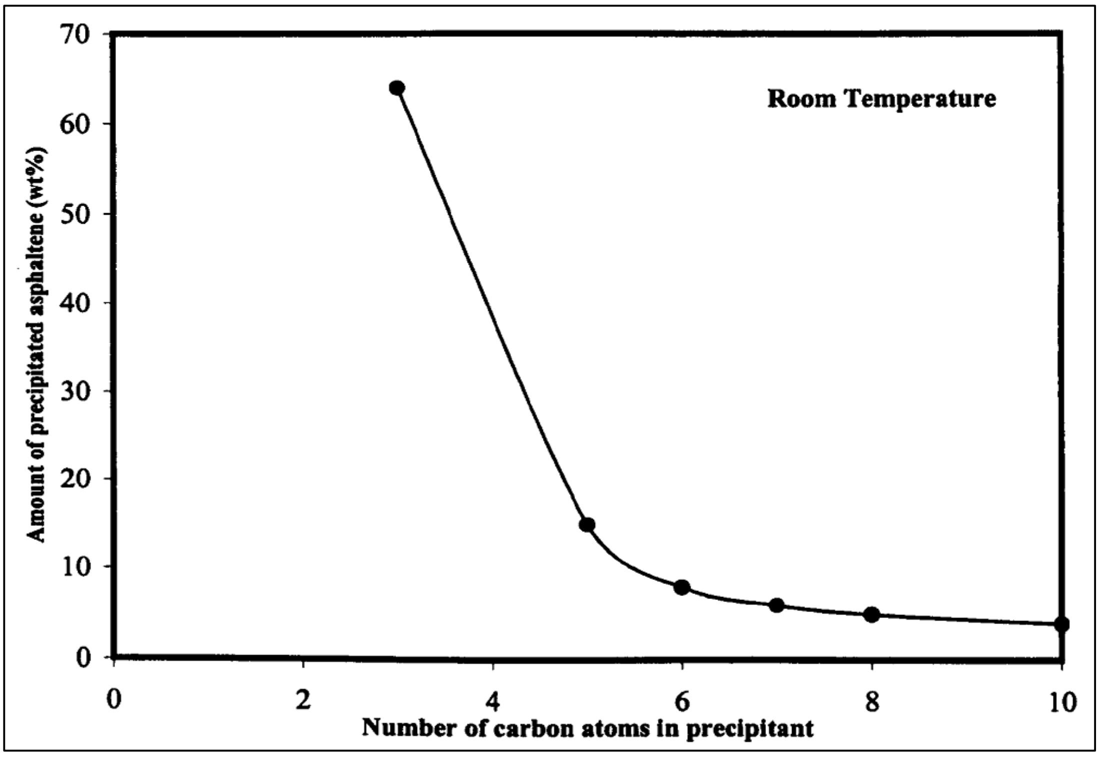

FIGURE 2.5. Effect of Carbon Number on Asphaltene Deposition [6]

Chemical inhibitors such as Xylene and Toluene are effective asphaltene inhibitor. But, government regulations limit the use of these inhibitor in oilfield. This is due to volatile emission, flammability and biodegradability concern make the use of these inhibitor less advantageous [16].

2.2 Environmental friendly inhibitor

Asphaltene precipitation must be removed to ensure the efficiency of oil recovery. Many procedures and methods are available in removing asphaltene such as dispersants and inhibitors addition, water steam and hot fluid removal, cleaning with solvent, ultrasonic and mechanical removal [17].

Commercially available chemical solvents in the market are toluene; benzene and xylene are widely use as asphaltene treatment. Asphaltene are defined as crude oil precipitation that produced when uncontrolled amount of n-heptane present in the crude oil, thus, creating fluid particles that are soluble in benzene and toluene. However, chemical solvents have harmful side effect toward environment and people handling the chemicals [10].

Low solubility of crude oil substances become a major obstacle in searching and developing new inhibitors [17]. Polymers with same functional group as asphaltene stabilizing-agents are selected and tested. Based on the test results, most of the polymers are insoluble in the crude oils [18].

A new environmental friendly asphaltene inhibitor is made to provide alternatives for existing chemical solvents. Vegetable oils are tested and show potential in preventing asphaltene deposition. Chemical nature of vegetable oils made it soluble in crude oil and thus quality of crude oils during production can be sustained. Other than that, vegetable oils are widely available which can reduce the production cost. By using environmental friendly substances, the process of handling and operation become much easier than chemical solvent [18].

Study on cashew nut shell liquid (CNSL) shows element of phenolic compounds with linear alkyl-chain (fifteen carbon atoms) with variable unsaturation degrees and meta-substituted in the aromatic ring [18]. Phenolic are important secondary plant metabolites that affect development, growth and defense mechanisms of plants. [19]

Phenolic compounds consist of aromatic hydrocarbon group bonded to hydroxyl group (-OH). Phenolic compounds are popular because of antioxidant properties [20].

The chemical structures for phenolic compounds are similar to amphiphile, a stabilizing agent for asphaltene precipitation problem [21]. Amphiphile can absorb unstable asphaltene particle which in isolated polar group, occluding and turn it into nonpolar. This will increase the interaction and efficiency of aliphatic solvent. Since a chemical structure is the same, experiments and tests are made whether phenolic compounds can deliver the same result as amphiphile. The tests show a good result as alkyphenol with hydrocarbon tail (medium to long) prevent asphaltene precipitation [22].

Vegetable oils are tested to determine the effectiveness in preventing asphaltene precipitation. Pepper Jamaican essential oil, Jamaican essential oil, Brazil nut oil, coconut essential oil, andiroba oil, grape seed's oil, pinewood essential oil, sweet almond oil, sandalwood essential oil and pepper Jamaican essential oil are tested with Brazilian crude oils [18]. As shown in the figures 2.3, coconut oil shows a good performance as asphaltene inhibition for crude oil A.

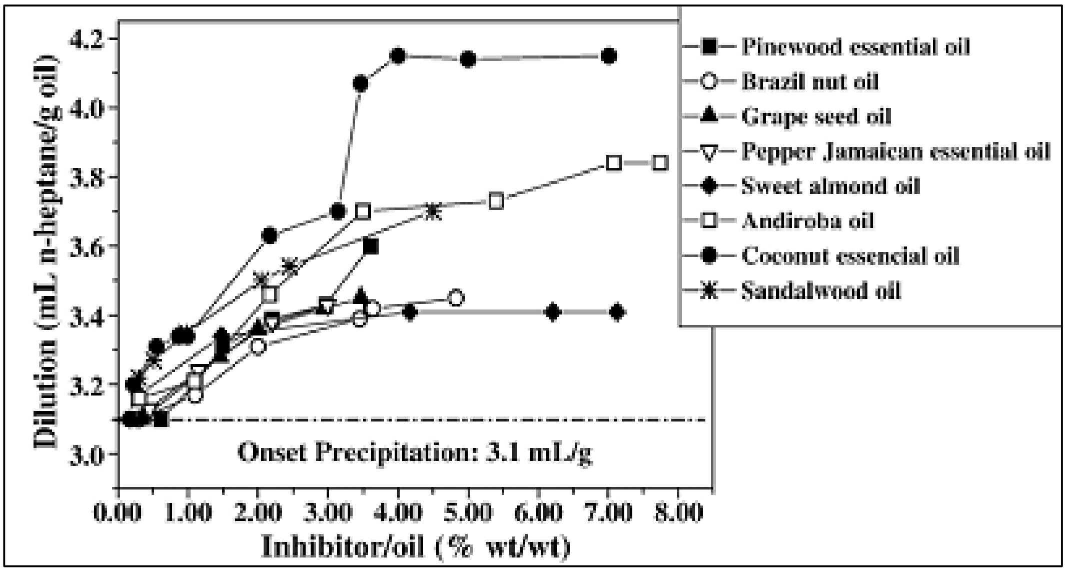

FIGURE 2.6. Performance Assessment of Plant Extracts for Crude Oil A [18]

Vegetable oils are chosen because of three factor:

1. new solvents with high solubility rate need to be made to replace the existing ones
2. vegetable oils show good results when compare with organic acids
3. cheaper than commercial dispersants and readily available everywhere

Triglyceride from vegetable oil is used to remove paraffin deposit in oil well. The fatty acid from ester solvent comprised of 12 to 24 carbons with the preferable length from 16 to 18 carbons. The characteristic of carbons having that length will increase the area of contact and control viscosity of the hydrocarbon. With increasing surface area, more cleaning action can be done. Based on the experiment, paraffin is partially dissolved when it is treated with ester solvent. Vegetable oil that fall within 16 to 18 carbons length is corn oil, cotton seed oil, soybean oil and peanut oil. Commercial lecithin consists of lower alkyl composition such as methyl. The presence of methyl increased the polarity of the lecithin and hence it will attracted to the metal surface of the well [23]. Based on the experiment, polar part of the lecithin will hydrolyzed and break the scale from iron surfaces. Other than that, sodium resinate such as methyl cyclohexanol can promote cleaning job due to its dispersant properties [24]. Other than that, phenolic concentration extracted from lemongrass, cinnamon and green tea leaves are 2100.769 mg/l GAE [25], 186 mg/l GAE [26] and 2100 mg/l GAE [27, 28] respectively.

In a nutshell, deposition of asphaltene will cause a severe effect in oil recovery process because of reduction in the oil flow and well productivity. Environmental friendly approach in preventing asphaltene deposition is recommended as alternative to chemical asphaltene inhibitor. The experiment will focused on plants that have amphiphile and phenolic properties. Polyphenol plants are lemon grass, green tea leaves and cinnamon while amphiphile plants are palm methyl ester, methyl ester oleate, coconut oil and olive oil. Based on the literatures, these plants possessed amphiphile and polyphenol which can be used in the experiment.

CHAPTER 3

RESEARCH METHODOLOGY/PROJECT ACTIVITIES

3.1 Project Activities

The project involves activities such as plant extraction (grinding, soxhlet extraction and rotary evaporation), sample composition identification by using Fourier Transform Infrared Spectroscopy (FTIR), deposit level test, turbidity test and Uv-Vis test. Since palm methyl ester, methyl ester oleate, coconut oil and olive oil are collected from industries, the amphiphile content is guarantee. Thus, plants that need to be extracted are phenolic plants; cinnamon, green tea and lemon grass.

TABLE 3.1. Chemicals, Equipment and Experiment Lists

Chemical	Equipment	Experiment
DBSA	Soxhlet extractor	Deposited level test
Green tea oil	Centrifuge	Turbidity meter test
Lemon grass oil	Centrifuge tube	UV-Vis spectroscopy meter test
Palm methyl ester	UV-spectroscopy meter	FTIR
Methyl ester oleate		
Coconut oil		
Olive oil		
Cinnamon oil		
Crude oil		
n-heptane		

3.1.1. Plant Extraction

The samples (green tea, cinnamon and lemon grass) are cut into smaller pieces and dried in the oven at 60°C for about 12 hours. Then, the samples are ground into smaller powder by using mortar grinder.

FIGURE 3.1. Mortar Grinder for Grinding Plant Samples

After that, the samples are placed into soxhlet thimble for soxhlet extraction process. Ethanol is used as a solvent and placed in the flask, where it undergoes heating process with the aid of thermal blanket. The temperature is set at 78℃ (boiling point of ethanol). In this process, the solvent evaporates, condenses and drip into soxhlet thimble. The extraction process is left for one day. The figure below shows plant extraction for one cycle.

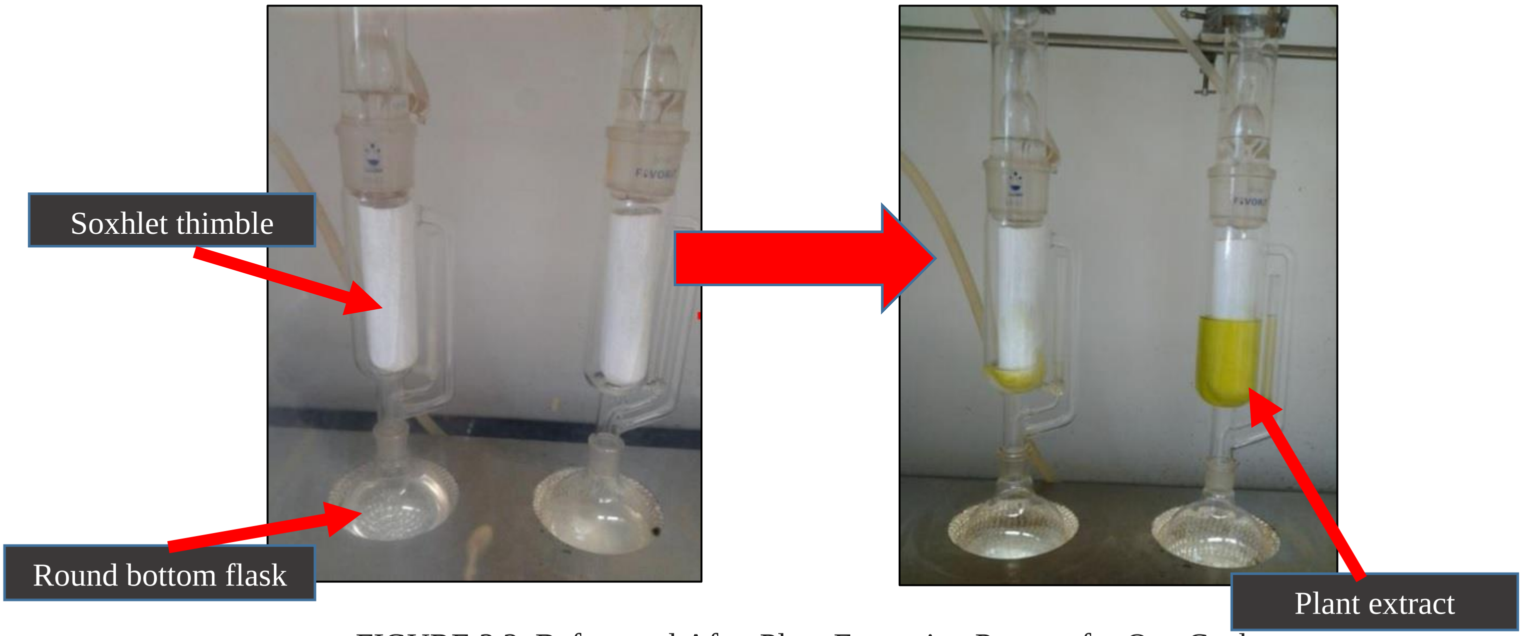

FIGURE 3.2. Before and After Plant Extraction Process for One Cycle

Then, the samples are evaporated by using rotary evaporator to remove ethanol from extracted plants. The temperature is set at 60℃ with 100rpm.

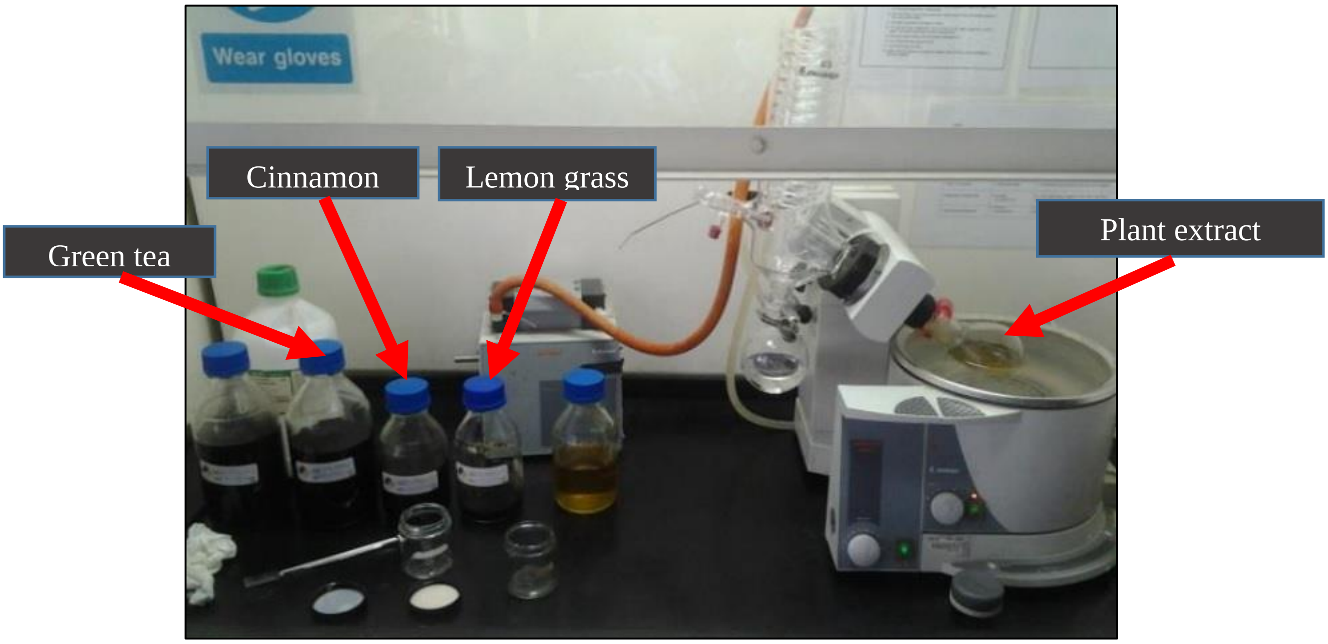

FIGURE 3.3. Separation of Ethanol by Using Rotary Evaporation

3.1.2. Deposit Level Test

Blank test are made by using n-heptane and crude oil. N-heptane is used to promote the deposition of asphaltene. The experiments are performed with similar set of condition and parameter so that accurate result and data can be produced. Separation of liquid from solid (asphaltene from crude oil) is aided by gravity.

1. Blank test is made by using n-heptane and crude oil
2. 1 ml of crude oil is added to each centrifuge tubes
3. 10 ml of n heptane is added to each centrifuge tubes
4. The centrifuge tube is shaken sideway with the bottom of the tube held slightly upward for 2 minutes to agitate the asphaltene and ensure the liquid is mixed properly.
5. Then, it is left for 24 hours in order to let the asphaltene agglomerate
6. The deposit level is evaluated, and noted

Commercial asphaltene inhibitor (DBSA) and green solvent are compared by conducting deposit level test. The procedures are the same as blank test with some additional step such as addition and mixing of inhibitor into heptane.

1. 1 ml of crude oil is added to each centrifuge tubes
2. 10 ml of Heptane is added into centrifuge tubes.
3. Different concentration of solvents are added to each of the centrifuge tubes.
4. The centrifuge tube is shaken sideway with the bottom of the tube held slightly upward for 2 minutes to ensure the liquid is mixed properly.
5. Then, it is left for 24 hours in order to let the asphaltene agglomerate.
6. The deposit level is evaluated, and noted

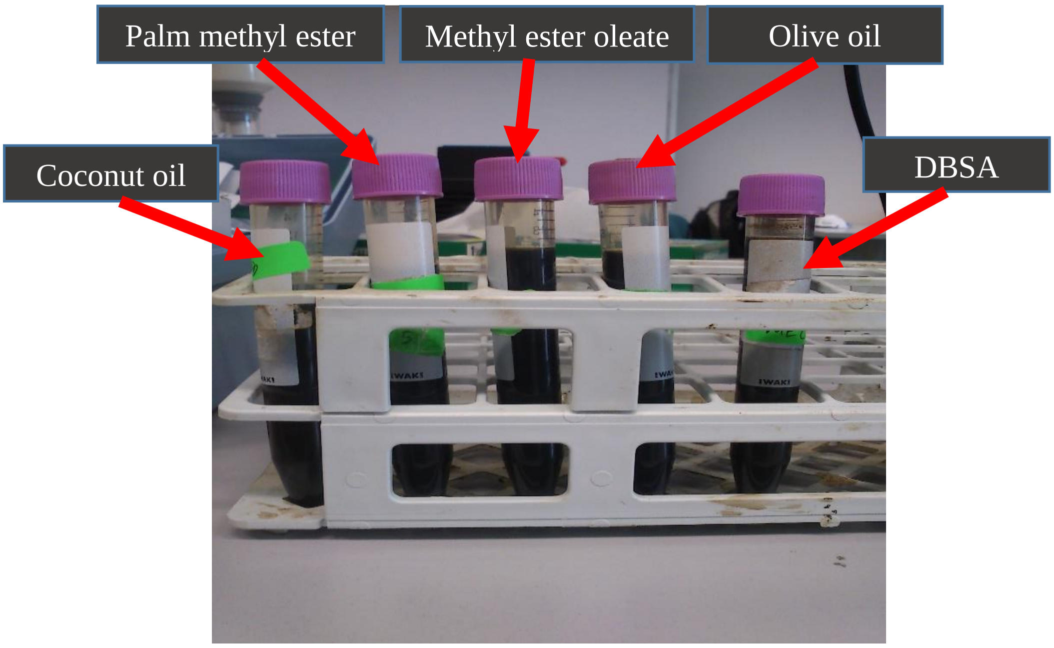

FIGURE 3.4. Deposit Level Test

3.1.3. Sample Composition Identification

Sample composition identification is made by using Fourier transform infrared spectroscopy (FTIR) assisted by technician in Block P.

3.1.4. Turbidity and UV-Vis spectroscopy meter test

The effectiveness of asphaltene inhibitor can be measure by turbidity and UV-Vis spectroscopy meter. In ultraviolet (UV) region, atoms and molecules have the ability to absorb or emit electromagnetic radiation although sometimes very short wavelengths. A high absorbance measurement indicates an effective dispersant, where the asphaltene in solution absorb the incoming light.

1. 4 ml of crude oil from the centrifuge tube is transferred to the cuvette with a cap covering the sample.
2. Then, the sample is placed into the UV-Vis spectrophotometer with different parameter set.
    i. 600nm
    ii. 660nm
    iii. 740nm

3. The absorption (or emission) results can be plotted graphically by a spectrum. An absorption spectrum plots absorbance versus wavelength.

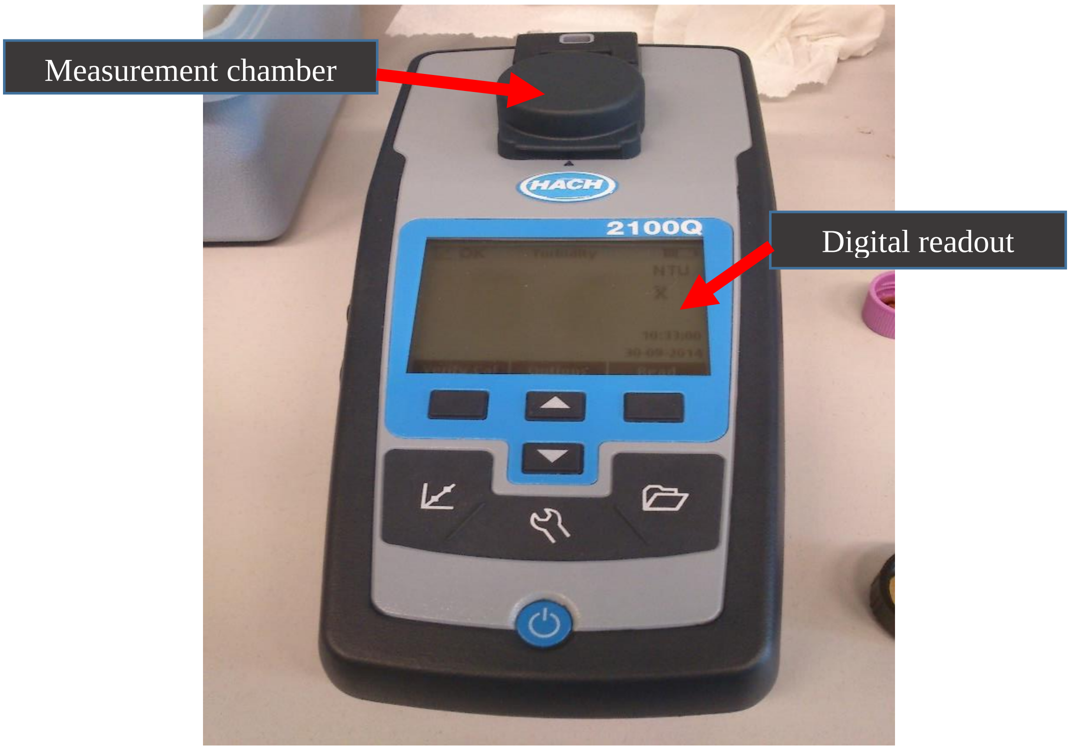

FIGURE 3.5. Turbidity Meter Test

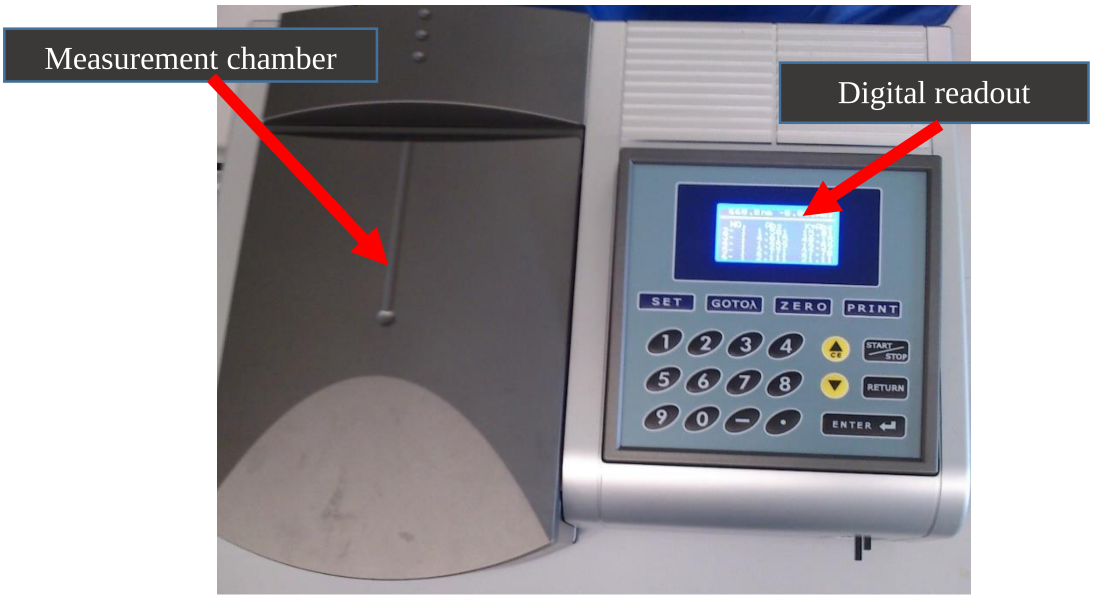

FIGURE 3.6. UV-Vis spectroscopy meter

3.2 Key milestone

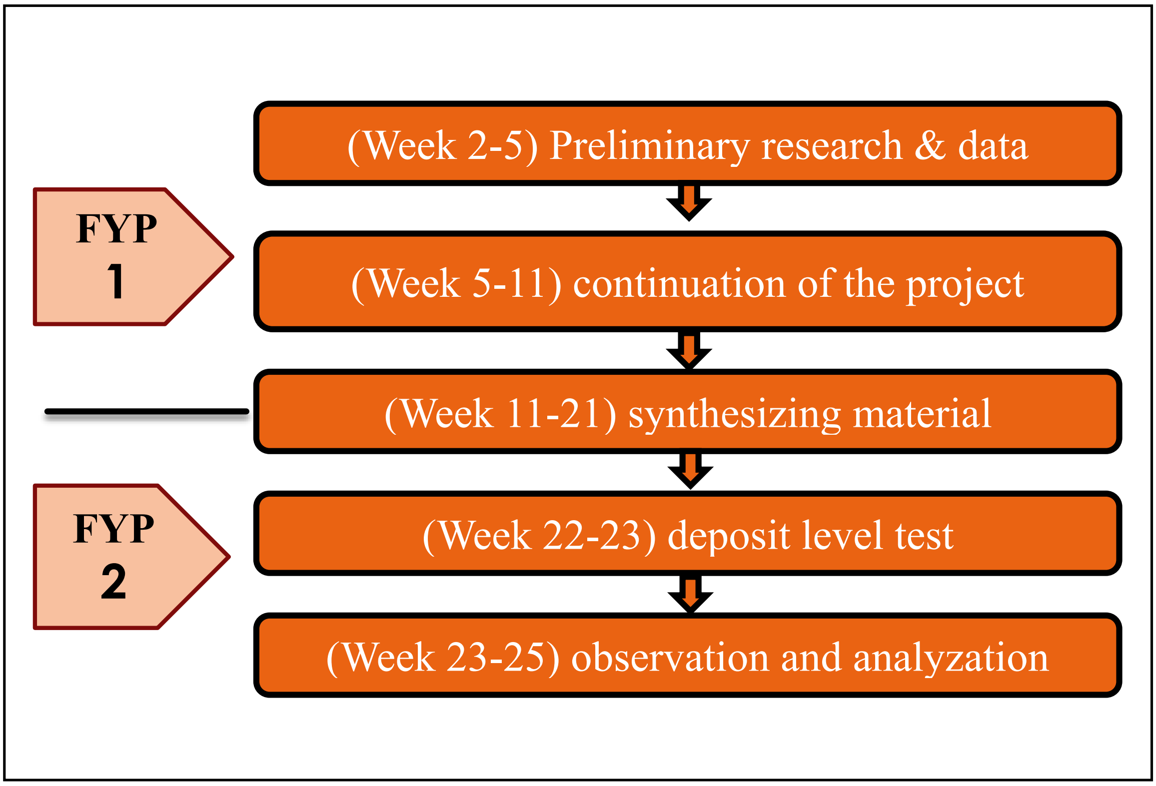

FIGURE 3.7. Key Milestone

3.3 Project timeline

TABLE 3.2. Timelines for FYP1

No	Detail/Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of Topic														
2	Preliminary Research Work														
3	Submission of Extended Proposal														
4	Proposal Defense														
5	Project Work Continues														
6	Submission of Interim Report														
7	Submission of Interim Report														

TABLE 3.3. Timelines for FYP2

No	Detail/Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	Sample Purchasing and Preparation																
2	Submission of Progress Report																
3	Experimental Work																
4	Pre-SEDEX																
5	Submission of Final Draft/Technical Paper																
6	Viva																
7	Submission of Hardbound																

100% complete

plan

1.4 Methodology

In summary, the steps required for the project are as follows:

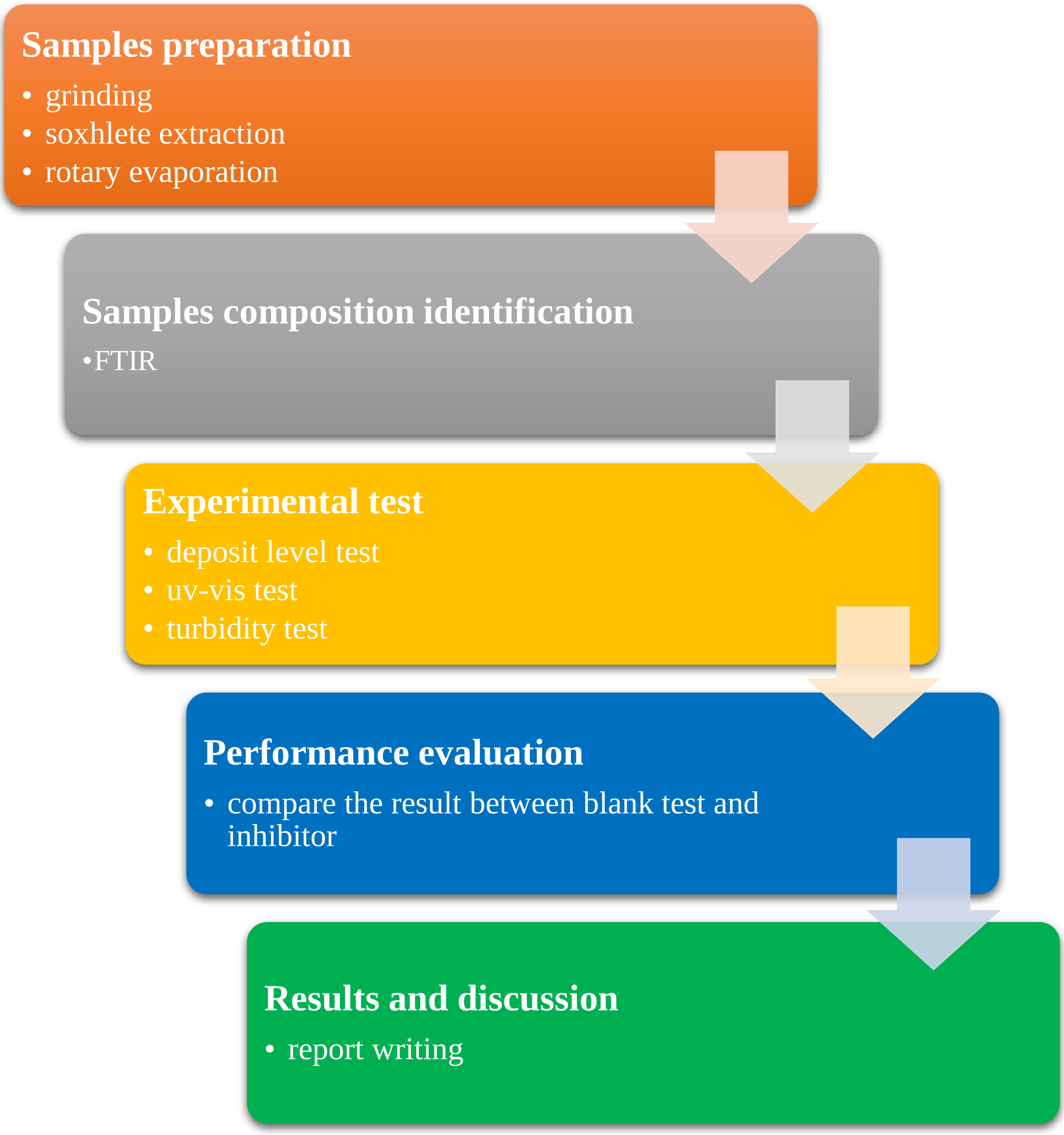

FIGURE 3.8. Execution Process

CHAPTER 4

RESULTS AND DISCUSSION

The results and discussion section are made to tally with the objectives of the project; screening and identification of potential asphaltene inhibitor from green resources, component characterization of extracted inhibitor and comparison between green solvents with commercial inhibitor in term of performance. Seven plants have been found that have inhibition properties (amphiphile and phenolic compound); palm methyl ester, methyl ester oleate, olive oil, coconut oil, green tea, lemon grass and cinnamon.

4.1 Functional Group Identification by Using FTIR

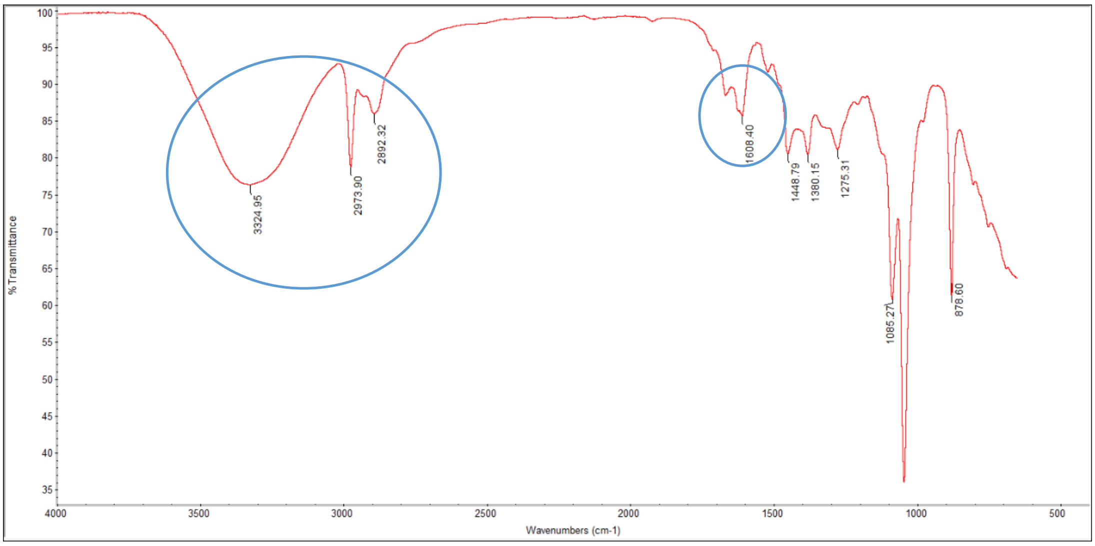

FIGURE 4.1. Cinnamon FTIR

Functional group of plant sample can be determined by comparing IR correlation chart with wave numbers from FTIR Spectrophotometer. Based on the figure above, FTIR spectrum of cinnamon oil shows frequency from 3500 cm^{-1} – 3200 cm^{-1} which indicated the presence of O-H, H-bonded for phenol and alcohol. Frequency from

3000 cm^{-1} – 2850 cm^{-1} indicated the presence of alkane (C-H stretch). Absorption band between 1700 cm^{-1} – 1500 cm^{-1} indicated the presence of aromatic ring.

The experimental FTIR can be compare to existing journal in order to determine the presence of phenol in cinnamon essential oil. Based on experiment, same absorption band can be seen in both FTIR result. O-H stretch, H-bonded indicated the presence of alcohol and phenol while second blue circle indicated aromatic ring. This shows that the experimental FTIR is reliable and can be used for turbidity test.

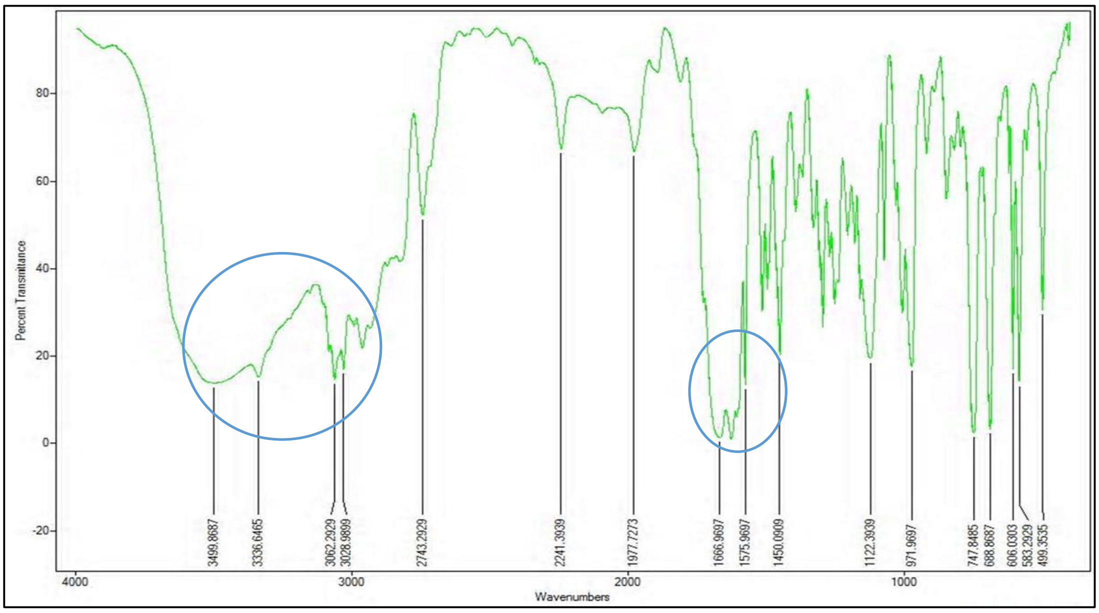

FIGURE 4.2. Cinnamon FTIR from Journal [29]

Based on the figure below, FTIR spectrum of green tea oil shows frequency from 3500 cm^{-1} – 3200 cm^{-1} which indicated the presence of O-H, H-bonded for phenol and alcohol. Frequency from 3000 cm^{-1} – 2850 cm^{-1} indicated the presence of alkane (C-H stretch). Absorption band between 1700 cm^{-1} – 1500 cm^{-1} indicated the presence of aromatic ring.

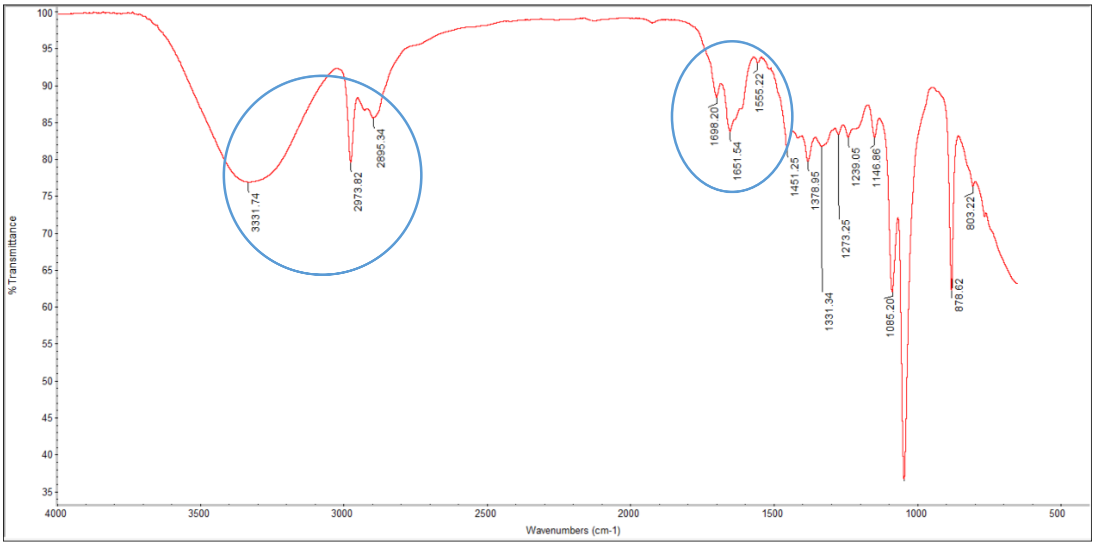

FIGURE 4.3. Green Tea FTIR

The experimental FTIR is then compared to existing journal in order to determine the presence of phenol in green tea oil. Based on existing journal, same absorption band can be seen in both FTIR result. O-H stretch, H-bonded indicated the presence of alcohol and phenol while aromatic ring can be located at second blue circle. This shows that the experimental FTIR is reliable and can be used for turbidity test.

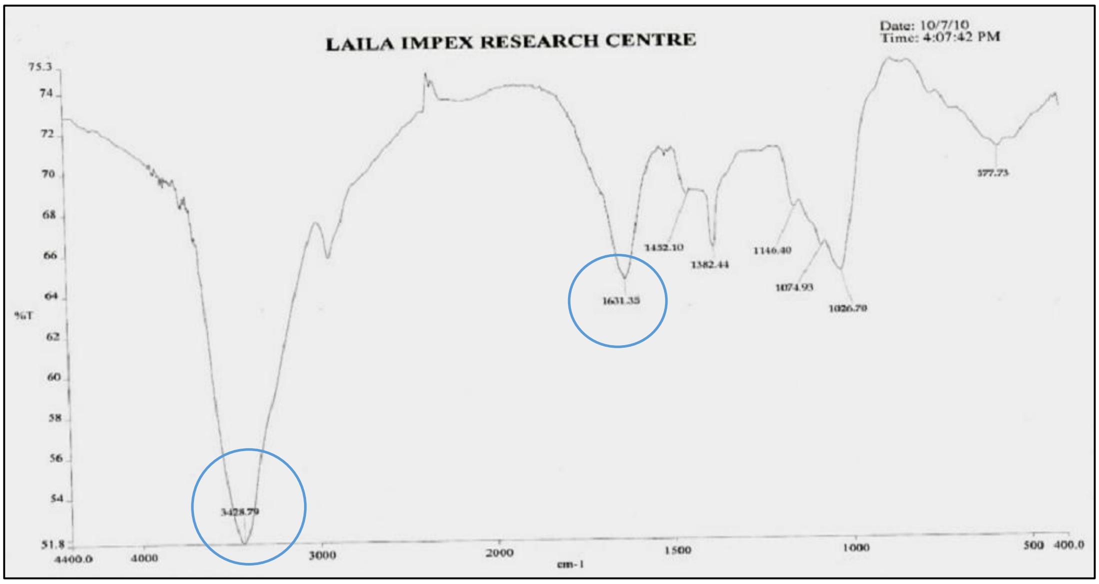

FIGURE 4.4. Green Tea FTIR from Journal [27]

Based on the figure below, FTIR spectrum of lemon grass oil shows frequency from 3500 cm^{-1} – 3200 cm^{-1} which indicated the presence of O-H, H-bonded for phenol and alcohol. Frequency from 3000 cm^{-1} – 2850 cm^{-1} indicated the presence of alkane (C-H stretch). Absorption band between 1700 cm^{-1} – 1500 cm^{-1} indicated the presence of aromatic ring.

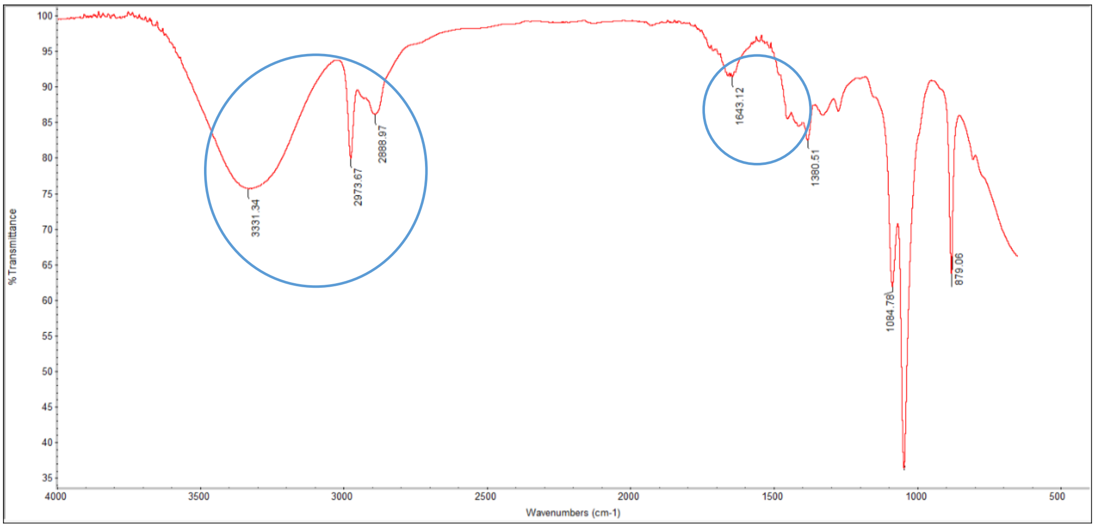

FIGURE 4.5. Lemon Grass FTIR

The experimental FTIR is then compared to existing journal in order to determine the presence of phenol in lemon grass oil. Based on existing journal, same absorption band can be seen in both FTIR result. O-H stretch, H-bonded indicated the presence of alcohol and phenol while aromatic ring can be located at second blue circle. This shows that the experimental FTIR is reliable and can be used for turbidity test.

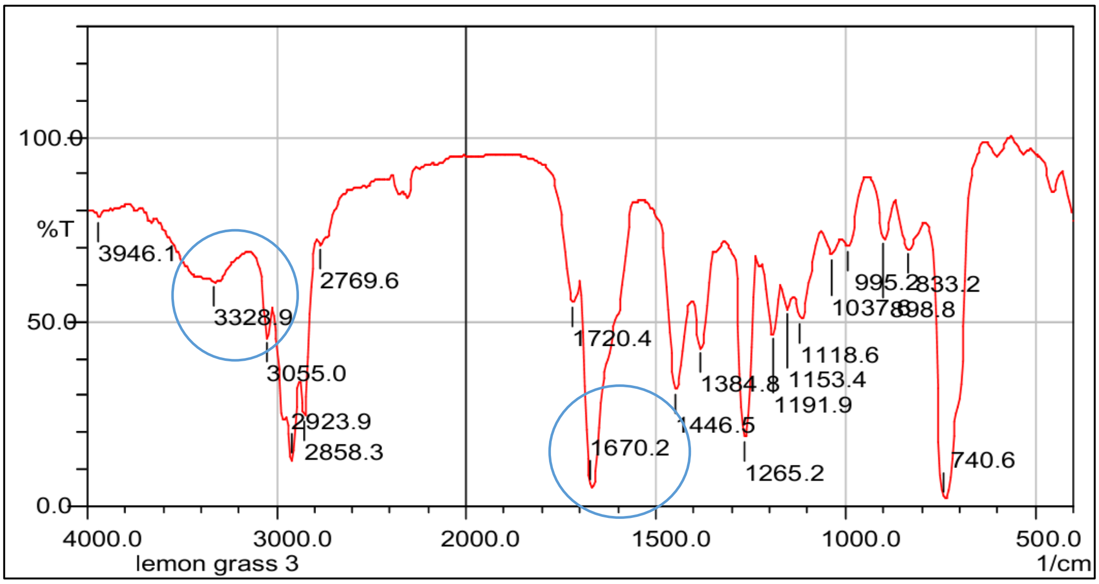

FIGURE 4.6. Lemon Grass FTIR from Journal [30]

1.2 Deposit Level Test

TABLE 4.1. Blank Test

No	Products	Dosage of Oil (ml)	Dosage of N-Heptane (ml)	Deposit Level (ml) with Time (min)			Comments
				0 min	*480 min*	*1440 min*	
1	Dubai oil	0.5	10	0	0.5	1.5	dark supernatant
		1	10	0	0.9	2	
		1.5	10	0	-	-	very dark supernatant
2	Miri oil	0.5	10	0	-	-	deposit level too low
		1	10	0	-	-	
		1.5	10	0	-	-	
3	Kikeh oil	0.5	10	0	-	-	deposit level too low
		1	10	0	-	-	
		1.5	10	0	-	-	
4	Castilla oil	0.5	10	0	-	-	very dark supernatant
		1	10	0	-	-	
		1.5	10	0	-	-	

Table 4.1 shows deposit level of different concentration of crude oils: Dubai (United Arab Emirates), Miri (Malaysia), Kikeh (Malaysia) and Castilla (Colombia). Ten (10) ml of heptane is used since the centrifuge tube can only be filled up to 15 ml of liquid. Other than that, time allocated for blank test is set to 480 and 1440 minutes to allow the oil to react with n-heptane and promote asphaltene deposition.

Dubai oil is tested with three different volumes; 0.5 ml, 1 ml and 1.5 ml. Based on the test, 0.5 ml produced 1.5 ml of asphaltene deposition after one day. The asphaltene deposit rest at the bottom of the tube due to gravity effect and the deposit level can clearly be seen through the supernatant under a good light condition. Meanwhile 1 1.5 ml of oil produced a very dark supernatant. The deposit level is hard to read unless the supernatant is poured off. However, it should be avoided since the deposit may also be poured off, mixed with liquid above and gave inaccurate reading.

Miri and Kikeh oil are tested with the same volumes of n-heptane. Both oils produced small amount of asphaltene which can be seen through the supernatant but cannot be read by the scale.

Castilla oil produced a very dark supernatant for three different volumes of n-heptane and the deposit level is difficult to read even under a good lighting condition. Based on the blank test, Dubai with 1 ml of volume is the most preferable oil for further testing with green and commercial inhibitor.

TABLE 4.2. Deposit Level Test for Commercial Inhibitor

No	**Product**	**Dosage of inhibitor (ml)**	**Dosage Of Oil (ml)**	**Deposit Level (ml) with Time (min)**			**Comment**
				0 min	***480 min***	***1440 min***	
1	DBSA	0.5	0.5	0	0.1	0.5	dark supernatant
		1	0.5	0	-	0.4	
		1.5	0.5	0	-	0.4	
		2	0.5	0	-	0.4	

Table 4.2 shows the deposit level test for commercial inhibitor, Duo Benzene Sulphonic Acid (DBSA). Different volumes of DBSA are used to determine the deposit level of asphaltene; 0.5 ml, 1 ml, 1.5 ml and 2 ml. These volumes are fixed

throughout the experiments. The deposit level test is left for one whole day to allow the oil and n-heptane to react with DBSA. Based on the table, 0.5 ml of DBSA managed to reduce the deposit level from 1.5 ml to 0.5 ml, 1 ml of DBSA reduce the deposit level to 0.4 ml and 2 ml of DBSA reduce the deposit level to 0.3 ml. The deposit level continues to decrease as the volume of DBSA increases. This shows that DBSA is an effective inhibitor in preventing asphaltene deposition.

TABLE 4.3. Deposit Level Test for Green Solvents

<table>
<tr><th rowspan="2">No</th><th rowspan="2">Products</th><th rowspan="2">Dosage of Plant Samples (ml)</th><th rowspan="2">Dosage of Oil (ml)</th><th colspan="3">Deposit Level (ml) With Time (min)</th><th rowspan="2">Comments</th></tr>
<tr><th>0 min</th><th>480 min</th><th>1440 min</th></tr>
<tr><td rowspan="4">1</td><td rowspan="4">coconut oil</td><td>0.5</td><td>0.5</td><td>0</td><td>0.3</td><td>1.0</td><td rowspan="4">dark supernatant</td></tr>
<tr><td>1</td><td>0.5</td><td>0</td><td>0.1</td><td>0.7</td></tr>
<tr><td>1.5</td><td>0.5</td><td>0</td><td>-</td><td>0.5</td></tr>
<tr><td>2</td><td>0.5</td><td>0</td><td>-</td><td>0.4</td></tr>
<tr><td rowspan="4">2</td><td rowspan="4">palm methyl ester</td><td>0.5</td><td>0.5</td><td>0</td><td>0.5</td><td>1.5</td><td rowspan="4">dark supernatant</td></tr>
<tr><td>1</td><td>0.5</td><td>0</td><td>0.4</td><td>1.1</td></tr>
<tr><td>1.5</td><td>0.5</td><td>0</td><td>0.1</td><td>0.9</td></tr>
<tr><td>2</td><td>0.5</td><td>0</td><td>0.1</td><td>0.7</td></tr>
<tr><td rowspan="4">3</td><td rowspan="4">methyl ester oleate</td><td>0.5</td><td>0.5</td><td>0</td><td>0.5</td><td>1.2</td><td rowspan="4">dark supernatant</td></tr>
<tr><td>1</td><td>0.5</td><td>0</td><td>0.2</td><td>0.8</td></tr>
<tr><td>1.5</td><td>0.5</td><td>0</td><td>-</td><td>0.6</td></tr>
<tr><td>2</td><td>0.5</td><td>0</td><td>-</td><td>0.5</td></tr>
<tr><td rowspan="4">4</td><td rowspan="4">olive oil</td><td>0.5</td><td>0.5</td><td>0</td><td>0.5</td><td>1.4</td><td rowspan="4">dark supernatant</td></tr>
<tr><td>1</td><td>0.5</td><td>0</td><td>0.4</td><td>1.0</td></tr>
<tr><td>1.5</td><td>0.5</td><td>0</td><td>-</td><td>0.8</td></tr>
<tr><td>2</td><td>0.5</td><td>0</td><td>-</td><td>0.6</td></tr>
<tr><td rowspan="4">5</td><td rowspan="4">lemon grass</td><td>0.5</td><td>0.5</td><td>0</td><td>-</td><td>1.7</td><td rowspan="12">very dark supernatant, difficult to read the deposit level</td></tr>
<tr><td>1</td><td>0.5</td><td>0</td><td>-</td><td>1.5</td></tr>
<tr><td>1.5</td><td>0.5</td><td>0</td><td>-</td><td>1.3</td></tr>
<tr><td>2</td><td>0.5</td><td>0</td><td>-</td><td>1.3</td></tr>
<tr><td rowspan="4">6</td><td rowspan="4">green tea</td><td>0.5</td><td>0.5</td><td>0</td><td>-</td><td>2</td></tr>
<tr><td>1</td><td>0.5</td><td>0</td><td>-</td><td>1.7</td></tr>
<tr><td>1.5</td><td>0.5</td><td>0</td><td>-</td><td>1.5</td></tr>
<tr><td>2</td><td>0.5</td><td>0</td><td>-</td><td>1.5</td></tr>
<tr><td rowspan="4">7</td><td rowspan="4">cinnamon</td><td>0.5</td><td>0.5</td><td>0</td><td>-</td><td>1.7</td></tr>
<tr><td>1</td><td>0.5</td><td>0</td><td>-</td><td>1.4</td></tr>
<tr><td>1.5</td><td>0.5</td><td>0</td><td>-</td><td>1.3</td></tr>
<tr><td>2</td><td>0.5</td><td>0</td><td>-</td><td>1</td></tr>
</table>

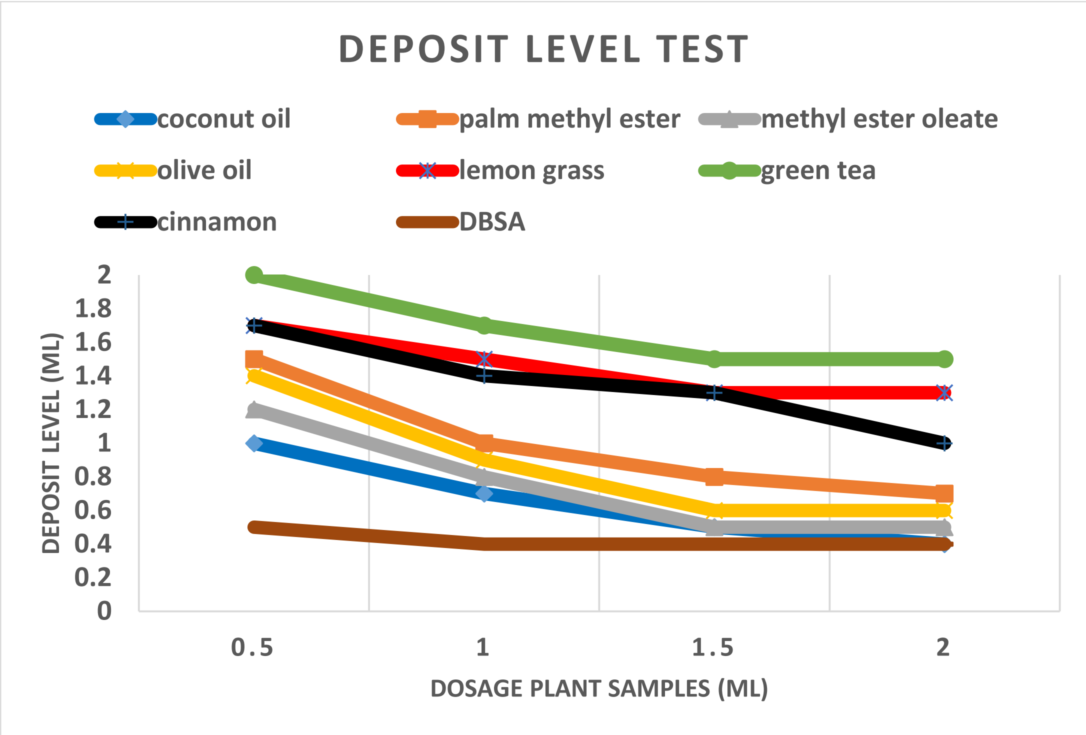

FIGURE 4.7. Deposit Level Test for Various Inhibitors

Table 4.3 and figure 4.7 shows the deposit level test for green inhibitor; coconut oil, palm methyl ester, methyl ester oleate, olive oil, lemon grass, green tea and cinnamon. Different volumes of green inhibitors are used to determine the deposit level of asphaltene; 0.5 ml, 1 ml, 1.5 ml and 2 ml. These volumes are fixed throughout the experiments. The deposit level tests are left for one whole day to allow the oil and n-heptane to react with green inhibitors.

Coconut oil managed to reduce the asphaltene deposit level. Mixture of coconut oil, Dubai oil and n-heptane produced dark supernatant but the deposit level still can be seen under a good lighting condition. Based on the table, 0.5 ml of coconut oil is able to reduce the deposit level to 1 ml when compared to the blank test. By increasing the volume of coconut oil to 1 ml, the deposit level reduced to 0.7 ml. The experiments show that the deposit levels continue to decrease as the volume of coconut oil increases. Thus, coconut oil is an effective inhibitor in preventing asphaltene.

Palm methyl ester managed to reduce the asphaltene deposit level. Mixture of palm methyl ester, Dubai oil and n-heptane produced dark supernatant but the deposit level still can be seen under a good lighting condition. Based on the table, 0.5 ml of palm methyl ester is not able to reduce the deposit level when compared to the blank test. However, when 1 ml of palm methyl ester is tested, it able to reduce the deposit level to 1.1 ml. The experiments show that the deposit levels continue to decrease as the volume of palm methyl ester increases. Thus, palm methyl ester is an effective inhibitor in preventing asphaltene.

Methyl ester oleate managed to reduce the asphaltene deposit level. Mixture of methyl ester oleate, Dubai oil and n-heptane produced dark supernatant but the deposit level still can be seen under a good lighting condition. Based on the table, 0.5 ml of methyl ester oleate is able to reduce the deposit level to 1.2 ml when compared to the blank test. By increasing the volume of methyl ester oleate to 1 ml, the deposit level reduced to 0.8 ml. The experiments show that the deposit levels continue to decrease as the volume of methyl ester oleate increases. Thus, methyl ester oleate is an effective inhibitor in preventing asphaltene.

Olive oil managed to reduce the asphaltene deposit level. Mixture of olive oil, Dubai oil and n-heptane produced dark supernatant but the deposit level still can be seen under a good lighting condition. Based on the table, 0.5 ml of olive oil is able to reduce the deposit level to 1.4 ml when compared to the blank test. By increasing the volume of olive oil to 1 ml, the deposit level reduced to 1 ml. The experiments show that the deposit level continue to decrease as the volume of olive oil increases. Thus, olive oil is an effective inhibitor in preventing asphaltene.

Lemon grass essential oil managed to reduce the asphaltene deposit level. Mixture of Lemon grass essential oil, Dubai oil and n-heptane produced dark supernatant but the deposit level still can be seen under a good lighting condition. Based on the table, 0.5 ml of olive oil is able to reduce the deposit level to 1.7 ml when compared to the blank test. By increasing the volume of lemon grass essential oil to 1 ml, the deposit level reduced to 1.5 ml. The experiments show that the deposit level continue to decrease as the volume of lemon grass essential oil increases. Thus, lemon grass essential oil is an effective inhibitor in preventing asphaltene.

Green tea essential oil managed to reduce the asphaltene deposit level in high dosage. Mixture of green tea essential oil, Dubai oil and n-heptane produced dark supernatant but the deposit level still can be seen under a good lighting condition. Based on the table, 0.5 ml of green tea essential oil does not able to reduce the deposit level of asphaltene. By increasing the volume of green tea essential oil to 1 ml, the deposit level reduced to 1.7 ml. The experiments show that the deposit level continue to decrease as the volume of green tea essential oil increases. Thus, green tea essential oil is an effective inhibitor in preventing asphaltene.

Cinnamon essential oil managed to reduce the asphaltene deposit level. Mixture of cinnamon essential oil, Dubai oil and n-heptane produced dark supernatant but the deposit level still can be seen under a good lighting condition. Based on the table, 0.5 ml of cinnamon essential oil is able to reduce the deposit level to 1.7 ml when compared to the blank test. By increasing the volume of cinnamon essential oil to 1 ml, the deposit level reduced to 1.4 ml. The experiments show that the deposit level continue to decrease as the volume of cinnamon essential oil increases. Thus, cinnamon essential oil is an effective inhibitor in preventing asphaltene.

From the experiments, coconut oil produced the best result followed by methyl ester oleate, palm methyl ester, olive oil green tea, lemon grass and cinnamon. The green inhibitors managed to reduce the deposit level compare to blank test and can match the result produced by DBSA if higher dosage inhibitors are used.

1.3 Turbidity Meter Test

TABLE 4.4. Turbidity Meter Test for Various Inhibitors

No	Plant Samples	Turbidity Test
1	blank	24.6
2	coconut oil	104
3	palm methyl ester	87
4	methyl ester oleate	100
5	olive oil	54

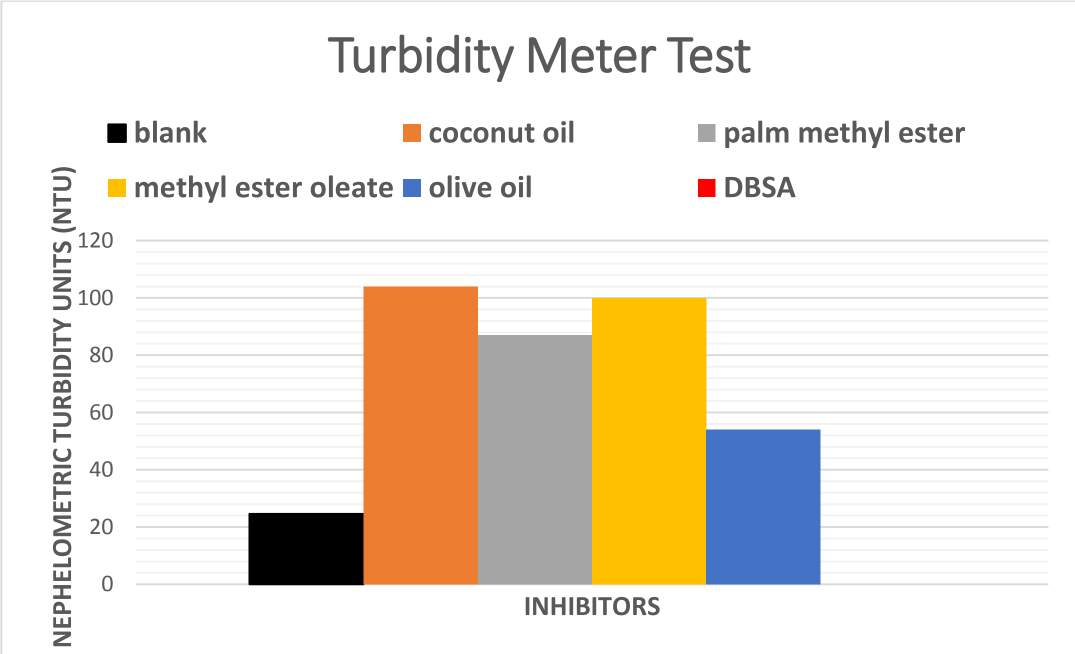

FIGURE 4.8. Turbidity Meter Test for Various Inhibitors

Turbidity meter test is a test on solution clarity with and without inhibitor. High turbidity reading indicate the effectiveness of inhibitor in preventing asphaltene deposition by suspending asphaltene molecule in solution. The dosage of inhibitor is fixed at 2 ml for this test. Based on the figure above, the turbidity reading of blank test is 24.6. Introduction of inhibitor increased the turbidity reading. Coconut oil shows the highest turbidity reading (104) followed by methyl ester oleate (100), palm methyl ester (87) and olive oil (54). Turbidity reading for DBSA exceeds the maximum reading of turbidity meter and thus no reading value for DBSA.

1.4 Uv-Vis Spectroscopy Test

TABLE 4.5. Uv-Vis Spectroscopy Test for Various Inhibitors

No	Plant Samples	Uv Vis Test		
		600 nm	*660 nm*	*740 nm*
1	blank	2.071	1.501	0.834
2	coconut oil	3.429	2.771	1.707
3	palm methyl ester	3.037	1.959	1.164
4	methyl ester oleate	3.103	2.111	1.292
5	olive oil	2.431	1.721	1.002
6	DBSA	4.011	3.015	2.002

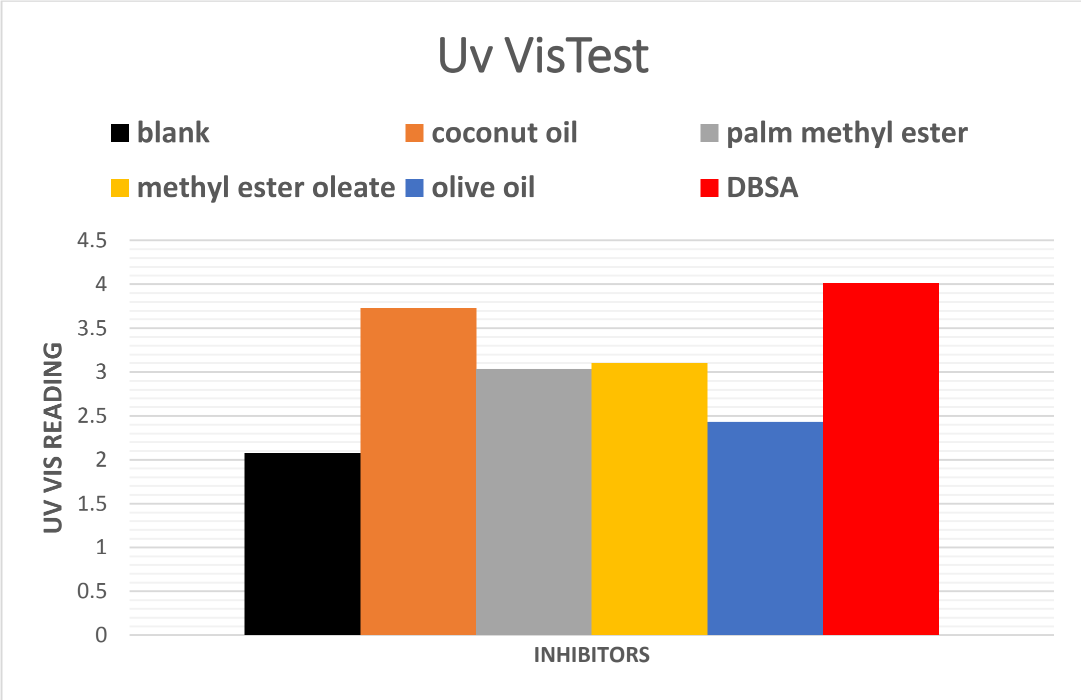

FIGURE 4.9. Uv-Vis Spectroscopy Test for 600nm wavelength

Uv-Vis spectroscopy test is a test on solution clarity with and without inhibitor. High turbidity reading indicate the effectiveness of inhibitor in preventing asphaltene deposition by suspending asphaltene molecule in solution. Uv-Vis spectroscopy test is the same as turbidity test but Uv-Vis has higher accuracy than turbidity meter. The dosage of inhibitor is fixed at 2 ml for this test but wavelength of Uv-vis is different for each test to compare the reading for data accuracy. Based on the figure above, the Uv-Vis reading for 600nm wavelength of blank test is 2.071. Introduction of inhibitor increased the Uv-Vis reading. DBSA shows the highest turbidity reading (4.011) followed by coconut oil (3.429), methyl ester oleate (3.103), palm methyl ester (3.037) and olive oil (2.431).

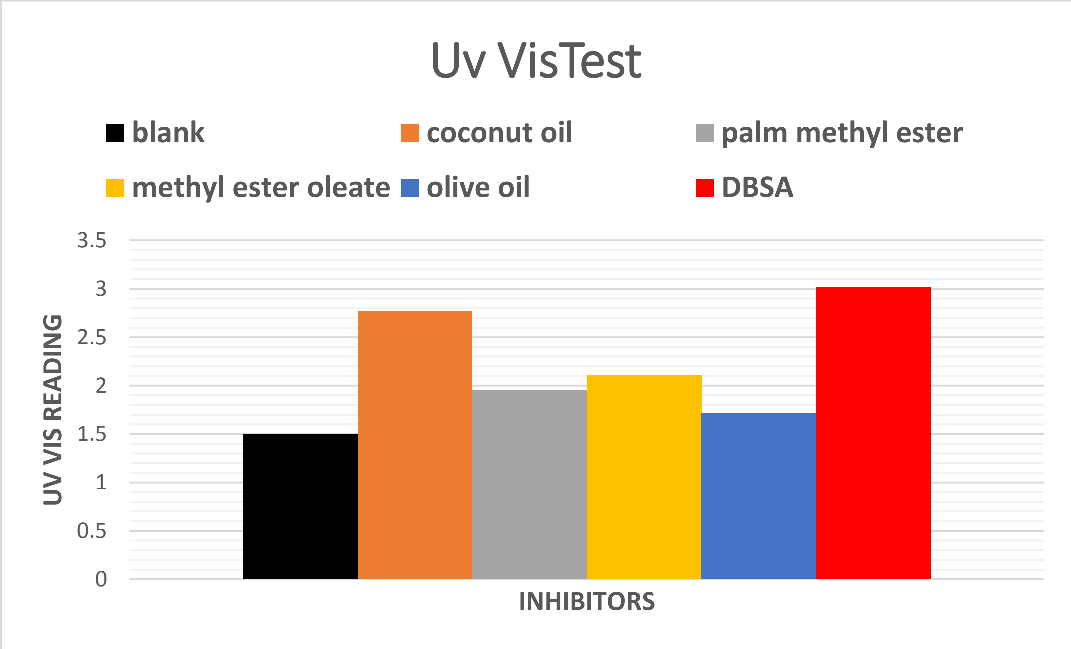

FIGURE 4.10. Uv-Vis Spectroscopy Test for 660nm wavelength

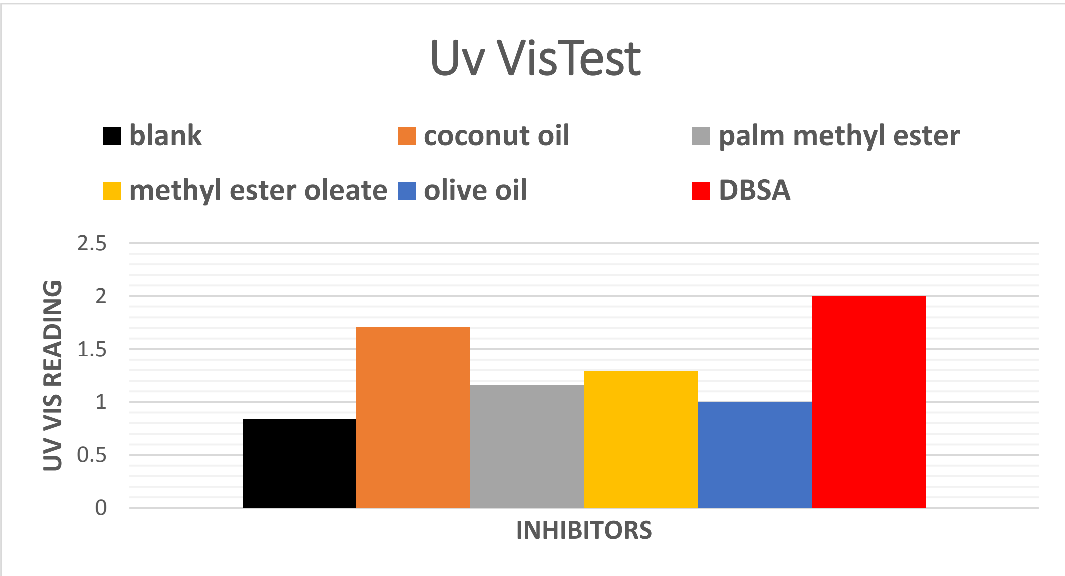

FIGURE 4.11. Uv-Vis Spectroscopy Test for 740nm wavelength

Uv-Vis spectroscopy test is repeated with different wavelength to ensure the reading is accurate. Based on the figure 23 and 24, Uv-Vis with 660nm and 740nm wavelength show similar pattern as 600nm wavelength. DBSA gives the highest turbidity reading followed by coconut oil, methyl ester oleate, palm methyl ester and olive oil. This shows that the Uv-Vis reading is accurate and reliable.

Other than that, Uv-Vis reading is compared to turbidity reading to ensure both data produced similar pattern. Based on the observation, both data produced similar pattern with coconut oil is the highest among green inhibitors followed by methyl oleate, palm methyl ester and olive oil. Thus, both data is reliable and accurate.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Vegetable oils, an organic compound extracted from coconut, olive, palm, lemon grass, cinnamon, green tea have components to be used as inhibitor. The components are amphiphile and phenolic compound, a stabilizing agent for asphaltene molecule.

Based on the experiments, coconut oil shows the best result in reducing asphaltene deposit level when compare with other green inhibitors. All sample of plant extracts showed almost comparable performance against DBSA.

5.2 Future Work Recommendation

For future work, testing with different crude oil will produce different deposition level. Since the composition of asphaltene is different for each crude oil around the world, it would be beneficial to test the green solvent with different type of crude oil.

Other than that, dynamic testing can reduce time taken for asphaltene to deposit and may produce different volume of asphaltene from static test.

The effect of temperature can alter the composition of crude oil. Thus, placing inhibitor in water bath may produce different result than at atmospheric temperature. Different part of plant has different composition. Stalk, leaves, seed, fruit and bark may produce different composition when extracted. It is recommended to try all part of the plant in order to produce solvent that can compete with commercial inhibitor.

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