EVALUATE THE USAGE OF ECO-FRIENDLY BIO-OILS AS ASPHALTENE ANTI-

SLUDGE AGENT IN MATRIX ACIDIZING

A Dissertation

by

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ABSTRACT

Asphaltene precipitation, flocculation, and deposition are vital problems that may cause serious damage to reservoirs, wells, and production facilities. Asphaltene precipitation may occur during primary depletion or acidizing jobs, as well as after the injection of rich gas or carbon dioxide. The organic deposition removal is considered a costly workover job with the current oil prices. The solvents that are usually used are toluene and xylene, which are considered carcinogenic and toxic chemicals. The use of dispersion to inhibit the organic deposition is essential and can be expensive, as it is required for the life of the well.

This project was aimed to find an alternative bio-oil dispersant that can be used as an eco-friendly and cost effective option. Coconut oil and andiroba oil were tested against chemical asphaltene dispersants to inhibit asphaltene in Kuwaiti crude oil. The effectiveness of the bio-oils was studied under reservoir temperature at 70°C and several concentration of the dispersants were tested to achieve optimum performance.

Acid induced asphaltene sludge is a well-known problem that can result in loss of the well in some cases, after acidizing an oil well. The majority of the development in the industry has been focused on controlling the iron concentration instead of stabilizing the asphaltene while interacting with the acid. The anti-sludge agent used is DBSA or it's derivate.

A Kuwaiti crude oil was used in this study having an API of 38° and 2% asphaltene content. The crude oil was characterized by a variety of analytical techniques including: total acid and base numbers (TAN, TBN), saturates, aromatics, resins and asphaltene analysis (SARA), density, viscosity and elemental analysis. Indiana limestone and Carbon tan cores were used with average porosity of 16% and permeability ranges (9-30) md. X-ray diffraction (XRD)

and scanning electron microscopy was used to analyze the mineral and clay content in the cores. Sludge tests were used to examine the acid and oil compatibility using a aging cell under 500 psi and 70°C. Coreflooding experiments under reservoir condition were done with the selected two acid systems, 15 wt. % HCl and chelating agent (GLDA). CT scans were done on the cores at dry, wet, oil-saturated and after acidizing and then were used to analyze the porosity profile within the core. The produced fluids were also analyzed by pH values of spent acid solutions.

This study provides a novel idea of using bio-oils as anti-sludge agent in matrix acidizing. The use of coconut oil with GLDA in matrix acidizing considered a 100% green stimulation system with high bio-degradability.

This study concluded that the use of dispersant can help reduce the asphaltene sludge and create better acid propagation through the core. The coconut oil gave a comparable performance to chemical dispersant in limestone acidizing with 15 wt% HCl. Limestone acidizing with GLDA showed the coconut oil outperforming the chemical dispersant by reducing the injected pore volume needed to breakthrough. The results can be employed to design the optimum better acid formulation and create the desired wormhole in limestone formation.

DEDICATION

This work is dedicated to my parents, my husband, my daughters, and my siblings. Without their love and prayers, nothing was possible.

ACKNOWLEDGEMENTS

CONTRIBUTORS AND FUNDING SOURCES

Contributors

This work was supervised by a dissertation committee consisting of Professor Hisham A. Nasr-El-Din, Assistant Professor Hadi Nasrabadi, Assistant Professor Berna Hascakir of the Department of Petroleum Engineering, and Professor Mahmoud El-Halwagi of the Department of Chemical Engineering.

All of the work conducted for the dissertation was completed by the student, under the advisement of Professor Hisham A. Nasr-El-Din of the Department of Petroleum Engineering.

Funding Sources

NOMENCLATURE

°C	degree Celsius
°F	degree Fahrenheit
μm	micrometer
ADT	Asphaltene dispersant test
Andi.	Andiroba oil
ASTM	American society for testing materials
BT	Breakthrough
cc	cubic centimeter
cm	centimeter
CI	corrosion inhibitor
CII	Colloidal instability index
CO_2	Carbon dioxide
Coco.	Coconut oil
cP	centipoise
CT	Computed tomography
DAO	Deasphalted oil
DBSA	Dodecylbenzenesulfunate acid
Disp.	Dispersant
DLS	dynamic light scattering
EDTA	Ethylenediaminetetraacetic acid
Fe	Iron

FTIR	Fourier Transform infrared spectroscopy
g	gram
GLDA	Glumatic acid diacetic acid
HCl	Hydrochloric acid
HF	Hydrofluoric Acid
IPA	Isopropyl alcohol
KCl	Potassium chloride
KOH	Potassium hydroxide
mD	millidarcy
ml	milliliter
nm	nanometer
NTA	Nitrilotriacetic acid
P	Pressure
ppm	part per million
ppt	precipitate
psi	pounds per square inch
PV	Pore volume
rpm	Revolutions per minute
SARA	Saturate, aromatic, resin and asphaltene
T	Temperature
TAN	Total acid number
TBN	Total base number
UV-vis	Ultraviolet visible spectroscopy

XRD X-ray Diffraction

TABLE OF CONTENTS

Page

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

Asphaltenes are highly condensed polyaromatic structures or molecules, consisting primarily of carbon, hydrogen, and a minor proportion of hetero elements such as: sulfur, nitrogen and oxygen. Asphaltenes are soluble in low-molecular weight aromatics and insoluble in low-molecular weight alkanes.

Once asphaltene precipitation occurs, it causes severe permeability and porosity reduction, wettability alteration, changing relative permeability in the reservoir, and in severe cases, plugging the wellbore and surface facilities (Leontaritis and Mansoori 1988).

Asphaltene Precipitation and Deposition Problem

Conventional solvents such as xylene, toluene, and benzene are used as a treatment in the industry for asphaltene deposition during production or processing of crude oil. However, these chemicals faced a lot of opposition from health, safety, and environment organizations due to their high level of toxicity.

Jamaluddin et al. (1996) discussed using deasphalted oil as a non-toxic and bio-degradable solvent for removal of asphaltene deposition in the wellbore. The authors suggested to use deasphalted oil with saturate content less than 35 wt% to keep the asphaltene particles stable and in suspension.

As a preventative chemical method asphaltene dispersants or inhibitors should be used to stabilize the asphaltene (Kelland 2014). Asphaltene contains sheets of aromatic with alkyl chains that have several functional groups (Kokal and Al-Juraid1998). The dispersant/inhibitor must be designed to interact with asphaltene functional groups.

1

Vegetable oils are considered oil-soluble amphiphiles that can adsorb onto asphaltene. The dispersing power of the vegetable oils is based on the fatty acids and amines groups that mainly interact with asphaltene with hydrogen bonding. The fatty acids contain acidic protons, which can form hydrogen bonds with hydroxyl groups in asphaltene or interact with the metal ions destabilizing the asphaltene aggregation process (Kelland 2014).

Asphaltene precipitation prevention by using dispersants can be an expensive option since it is required for the lifecycle of the well. Phenolic compounds extracted from cashew-nut shell was used as asphaltene stabilizer agent, the results showed good performance when compared to nonylphenol, which is considered an efficient peptizing agent for asphaltene (Morira et al. 1999). Junior et al. (2006) conducted experiments to investigate the use of vegetable oils as asphaltene precipitation inhibitors against ionic and non-ionic surfactants. The onset of asphaltene precipitation was determined by n-heptane titration of the crude oil. The results showed that the ionic surfactants give similar results on different types of crude, while non-ionic surfactants require balance between the additive and crude portion. As for vegetables oils, the results showed that the coconut oil performed excellently in one of the crude oils. The recommendations were to use the vegetable oils because they are easier to obtain, cheaper, and environment friendly.

Chang and Fogler (1993) investigated the stability of asphaltene in alkane solvents as precipitant using a series of alkyl benzene-derived amphiphiles. The authors showed that the effectiveness of amphiphiles on asphaltene stabilization is strongly influenced by their chemical structure, polarity of the head group, the length of the alkyl tails, and the existence of extra polar group. They concluded that the effect of an oil-soluble amphiphile on asphaltene depends on the

strength of the polar head groups, the presence and arrangement of side groups, and the length of the alkyl tail.

The selected asphaltene dispersant concentration must be optimized to take into consideration the self-association of asphaltene or inhibitor monomers if the interactions between aggregated asphaltene and inhibitor reduced (Madhi et al. 2017). Asphaltene inhibitors and dispersants interact with asphaltenes through the following mechanisms (Kelland 2014; Afra et al. 2017):

- Acid-base interactions

- π-π interactions between asphaltenes and unsaturated or aromatic groups

- Hydrogen bonding

- Complexing with metal ions

One particular asphaltene dispersant has been widely studied. Dodecyl benzene sulfonic acid (DBSA), can stabilize asphaltene colloids by strong acid–base interactions (Hashmi and Fairoozabadi 2013). Although DBSA is very effective in dissolving asphaltene, it is more expensive than aromatic solvents (Hashmi and Fairoozabadi 2016).

The first part of the present study is to find a cost effective bio-dispersant that will prevent asphaltene precipitation. Also utilize some of the produced oil as asphaltene dissolver by using the deasphalted oil, to the best of the author's knowledge, pairing deasphalted oil with bio-oil never been tested before.

Asphaltene Problem In Acidizing Treatment

Acidizing treatment is a common workover that done overcome near wellbore damage resulted from drilling and production. In oil wells, stimulation treatment can result in reduction

in permeability reduction or total loss of the well due to the formation of induced asphaltene sludge.

Moore et al. (1965) investigated the asphaltene sludge after the problem was noticed in several California wells. The authors suggested to use akyl-phenol or fatty acids as an anti-sludge agent to target the asphaltene colloidal stability. Good results were obtained after field implementation. Further studies were done to understand the cause of the asphaltene sludge after the problem continued even with the use of anti-sludge agent. Jacobs & Throne (1986) concluded that the presence of iron (Fe) contamination is one of the main causes of the sludge. They suggested to use an iron control agent with the anti-sludge in the acid package. They also recommended a pre-flush with aromatic solvent.

The acid concentration and type of acid were studied to monitor their effect on the sludge. The studies showed that acid concentration threshold for hydrochloric acid is 15% and mud acid showed not exceed 12%:3% HCl: HF. (Hochin et al. 1990)

As the awareness of the sludging problem grown in the industry, more suggestion to design the acid treatment and test the acid additives for compatibility and their tendency for sludge. Several acid additives were proved to increase the sludge or emulsion such as some corrosion inhibitors. (Jacobs 89, Suzuki 93 & Hochin et al. 1990, Wong et. Al 1996)

Several studies were later conducted to tackle the asphaltene sludge by reducing the iron presence. Chelating agent, such as NTA, EDTA were used as iron control agent. Nonionic reducing agent (NIRA) also tested as acid additives against dodecyl-benzene-sulphonic acid (DBSA) (Vinson 1996).

Research Objectives

To the best of our knowledge, the effect of vegetable oils and deasphlated oil as a dispersant on Kuwaiti crude has not been discussed in the literature.

Therefore, the objectives of the present study are to:

1. Compare the effectiveness of two chemical dispersants oil against vegetable oils on the inhibition of asphaltene precipitation on Kuwaiti Crude.

2. Investigate the effect of pairing deasphalted oil (DAO) to the dispersants as an asphaltene dissolver.

3. Examine the performance of the dispersants under study while used in acidizing as anti-sludge agent.

4. Develop a bio anti-sludge agent that targets asphaltene stabilization.

5. Evaluate bio-oils against chemical dispersants as anti-sludge agents in matrix acidizing.

6. Compare the performance of HCl against chelating agent glutamic acid diacetic acid (GLDA) in acidizing oil saturated cores.

CHAPTER II

MATERIALS AND EXPERIMENTAL PROCEDURES

Material

- Crude oil was provided from Kuwait Oil Company.

- Two Chemical dispersants were provided from Clarinet used as received.

- Fractionated Coconut Oil and Andiroba Oil.

Oil Characterization

Asphaltene Content

The asphaltene content will be measured according to the IP-143/ASTM 6560 standard method as follows:

1. Heptane is added to the sample at a ratio of 1 g: 30 ml; sample size depends on the fraction of asphaltene in the oil.

2. The sample is heated under reflux for 60 minutes, then allowed to cool down for 90 to 150 minutes in a dark place.

3. The sample is then filtered using filter papers with a pore size of 2-4 μm (Whatman).

4. The filter paper is placed in a soxhlet extraction apparatus and refluxed with heptane for 2-3 hours.

5. Reflux is continued with Toluene instead of heptane until no more residue is noticed on the filter paper.

6. The toluene containing the asphaltene shall be added to an evaporating dish and heated in a water bath.

7. The asphaltene content is calculated by comparing the weight of the residue to the weight of the original sample.

Total Acid and Base Numbers (TAN, TBN)

In order to measure the acidity and basicity of the crude oil with the Auto-Titrator (Metrohm 907 Titrando), the crude oil must be diluted with a solvent; up to 60 ml must be added to a weighted oil sample. The solvent is prepared by mixing the following chemicals in a certain ratio (1 Toluene: 0.95 Isopropyl Alcohol: 0.05 Distilled water).

Total Acid Number (TAN) - ASTM D664

1. In a clean, dry beaker, add 60 ml of the solvent and measure the blank TAN using KOH in IPA as a titrant.

2. Weight an oil sample in a clean, dry beaker. The sample should be between 1-3 g.

3. Add the solvent to the oil sample to reach 60 ml.

4. Run the Auto-titrator to measure the TAN (mg KOH/g oil) with blank subtraction.

Total Base Number (TBN) - ASTM D974

1. In a clean, dry beaker, add 60 ml of the solvent and measure the blank TBN using HCl in IPA as a titrant.

2. Weigh an oil sample in a clean, dry beaker, the sample should be between 1-3 g.

3. Add the solvent to the oil sample to reach 60 ml.

4. Run the Auto-titrator to measure the TBN (mg HCl/g oil) with blank subtraction.

Water Content

The water content is measured using the volumetric Karl Fischer method with the Metrohm Titrando 906 following ASTM E203-16.

1. The sample first needs to be prepared by centrifuging it at 3000 rpm for 1 hour, then sonicating it for 30 minutes to homogenize the sample.

2. HYDRANAL Solver for crude oil is used as a working medium and Composite 5 is used as the titrant. All the chemicals are provided by Metrohm.

3. The sample then should be weighed and injected by syringe into the measuring chamber, and sample size is not to exceed 2 g.

This measurement is based on 4-5 readings.

Saturates, Aromatics, Resins & Asphaltenes (SARA) Analysis

SARA analysis is conducted according to the ASTM D2007-11 standard. All the chemicals used are Reagent 99.99% purity, ordered from Sigma Aldrich.

The following steps should be followed to acquire the asphaltene content measurement:

1. Weigh out 10 g of the oil sample in a beaker. Add 100 ml of Pentane and stir for 30 min to mix.

2. Warm the mixture in a water bath for a few seconds. The temperature should not exceed 50 °C to prevent evaporation of the light components of the oil.

3. Allow the sample to stand for 30 minutes at room temperature and set up the filtering assembly using a 500 ml flask, 125 mm filtering funnel, and 15 cm rapid filter paper (VWR 413 were used).

4. Filter the sample; use 60 ml of pentane to rinse the flask and the stirring rod and pour it through the filter paper.

5. Use 60 ml of pentane in small portions to rinse the funnel sides, filter paper, and contents.

6. Transfer the solution to an anti-creep beaker and heat it on a hot plate at $100 - 105 \, °C$ to evaporate the pentane.

7. Weigh the recovered oil. The difference between the original sample and the recovered oil will be considered the asphaltene content.

8. The sample recovered is considered deasphalted, and can be diluted and charged to the column.

Procedure:

1. Prepare the percolation column that consists of two parts: a lower column containing 200 g of activated silica gel topped with 50 g of attapulgus clay adsorbent, and an upper column containing 100 g of clay adsorbent. The columns should be at a constant level and no air should be allowed in the columns at any time during the experiment.

2. The deasphalted sample should be diluted with 25 ml pentane and mixed well before charging it to the column.

3. 25 ml of pentane should be added to the clay column, then the diluted sample is charged. The beaker should be washed with pentane, with washed fluid added to the column.

4. Keep charging the clay column with pentane and maintain around a 1 in. level of pentane to ensure washing all the saturate. The recovered pentane effluent in the accumulating 500 ml receiver flask should be around 280 ml.

5. Connect the upper column to a new 500 ml receiver flask, while keeping the lower column to be fully drained in the accumulating receiver.

6. Keep washing the clay column (upper) with pentane until 200 ml are collected in the receiver flask to ensure that all saturates and aromatics have been washed out of the clay bed. Discard the pentane collected in this step since aromatics will be calculated by the difference.

7. Charge the clay column with a 50:50 volume mixture of toluene and acetone (150 ml of each is used) to drain out the polar components (resins) into a 500 ml separatory funnel.

8. To drain the water from the collected fraction, stopper the separatory funnel and gently swirl it, then let it settle for 5 minutes.

9. Discard the water, then add 10 g of Anhydrous Calcium Chloride granules to the funnel. Shake it for a few seconds and vent it frequently, then, allow it to settle for 10 minutes.

10. Filter the fraction through filter paper, as used for asphaltene, and collect it in a 500 ml conical flask. Wash the separatory funnel with 15 ml of pentane and add the washed fluid through filter paper.

11. To remove the solvent, add the pentane effluent collected and the fraction to anti-creep beakers and heat on a hot plate at $100 - 105\ °C$ until it evaporates.

From SARA analysis, the Colloidal Stability Index (CII) may be calculated:

If the oil has a CII value below 0.7, it is considered stable, while 0.9 and higher values are considered unstable.

$$CII = \frac{Saturates + Asphaltenes}{Aromatics + Resins}$$

Density

A DMA 4100 density meter is used to measure the density of the oil samples as a function of temperature. The density meter also gives the specific gravity reading at the corresponding temperature.

The steps to measure the density are as follows:

1. Clean the device by 3 pumps of distilled water. Use toluene if oil was used, then followed by water and press the pump to discharge.

2. Pump two syringe volumes of the fluid, check for air bubbles in the injection window, and keep the syringe at the inlet to create pressure.

3. Adjust the temperature as desired and wait for the reading to appear.

4. After completion, set the temperature back to 25 °C, discharge the sample and clean the device as stated in step 1.

Viscosity

The viscosity measurements are done following the standard method IP-71/ASTM D445, using an Ubbelohde type capillary viscometer and an oil bath to adjust the temperature as desired. Different sizes of capillary viscometers are used based on the viscosity range. The following steps should be followed:

1. Charge the viscometer with the oil sample and place it into the holder.

2. Insert the holder in the oil bath. Allow approximately 20 minutes for the sample temperature to rise to the bath temperature.

3. Use the vacuum hand pump to elevate the oil in the capillary tube in order to measure the efflux time.

4. To measure the efflux time, allow the oil sample to flow freely down past the second bulb marking.

5. Calculate the kinematic viscosity of the sample by multiplying the efflux time (in seconds) by the viscometer constant.

6. Repeat steps 3-5 for each temperature.

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra were carried out using a Thermo Nicolet 380 FTIR spectrometer in the absorbance mode with the spectral resolution of 4 cm^{-1} in the wavelength range 400-4,000 cm^{-1}. The functional groups of oil, asphaltene, and dispersant samples were characterized using FTIR spectroscopy.

Asphaltene Dispersant Evaluation Test

This test evaluates the presence of asphaltene and its tendency to precipitate in a crude oil, and enables determination of the efficiency of the dispersant.

1. 10 ml of heptane is to be added to the test tube. The oil is then added after being treated with dispersants at a certain concentration.

2. Treatment is performed with 150, 300, and 500 ppm by volume (on the basis of crude oil)

3. The test is performed on two different temperatures, 25 & 70 °C.

4. The samples are to be monitored after 1 hr., 1 day, and 1 week for precipitation.

5. If no precipitation is observed, a sample is categorized as clear. If asphaltene is observed, but does not settle, a sample is categorized as trace, and if asphaltene accumulates, precipitation is the designated label.

6. After the end of the week, the samples are filtered to measure precipitation against the blank oil sample.

Asphaltene Dispersant Effectiveness Test by IP-143

– The effectiveness of each dispersant is related to the decrease in the amount of asphaltene precipitation.

– The various dispersants at different concentrations (150, 300 & 500) ppm are solved in 10 g of oil. The sample is centrifuged for 15 min. Finally, asphaltene precipitation is measured following the IP-143 standard procedure.

– Precipitation reduction versus concentration plots are drawn for each dispersant.

Dynamic Light scattering (DLS) Measurement

Size evaluation was run by DLS technique using a Malvern Zetasizer. The DLS data were applied in measuring the hydrodynamic radius of particles in the fluid. The samples were prepared following ADT, the measurement were done at room temperature after aging the samples for 7 days. The particle sizes in each prepared solution measured at least three times to yield accurate results. The average size of the asphaltenes particles in toluene at low concentrations ranged from 12 to 22 nm. With the successive addition of heptane, the particle size increased and considered precipitated at sizes greater than 1,000 nm (Mansur et al. 2012). The presence of a dispersant will cause a reduction in the size of the asphaltenes aggregates, inhibiting the formation of particles keeping the size less than 1,000 nm.

UV–vis spectroscopy

The crude oil, and other treated samples at the selected concentrations, were analyzed by UV–vis using a GENESYS 10S instrument, equipped with a Xenon lamp with a measurement range from the UV to the near IR 190–1,100 nm. For the analyses, all samples were diluted in heptane following asphaltene dispersant test. The measurements were conducted under two fixed wavelengths, 640 and 720 nm, and the transmittance reading were recorded (Elochukwo et al. 2006).

CHAPTER III

INVESTIGATE THE EFFECTIVENESS OF ECO-FRIENDLY BIO-OILS AGAINST

COMMERCIAL DISPERSANTS ON THE INHIBITION OF ASPHALTENE

PRECIPITATION IN KUWAITI CRUDE *

Introduction

Asphaltene precipitation and deposition is a well-known problem that can be expensive to control due to the pricy inhibitors used in the industry. The chemical used in asphaltene deposition treatments are considered toxic and cancerogenic. Extensive literature review highlighted that no developments were made to find an environmental friendly and cost effective alternative for these problems.

In this chapter, the effectiveness of two vegetable oils were evaluated against chemical dispersants in inhibiting asphaltene precipitation in Kuwaiti crude oil. The effect of pairing deasphalted oil with the dispersant as asphaltene dissolver was tested. The effect of temperature, pressure, time, and different concentrations of dispersant was studied. Asphaltene dispersant test was conducted using heptane to induce asphaltene precipitation. Dynamic light scattering was used to measure the effect of the dispersants under study on the asphaltene particle size, while UV-vis spectrometer was used to monitor the effect of each dispersant as function of time by measuring the concentration of asphaltene particles in the treated samples.

The results showed that vegetable oils can be used as asphaltene dispersants, coconut oil optimum concentration was 300 ppm at room temperature, while andiroba oil was at 150 ppm. The coconut oil proved to inhibit asphaltene as reservoir temperature when paired with deasphalted oil at 500 ppm.

Results and Discussion

Crude Oil Characterization

Temperature, °C	viscosity, cP	density, g/cc
25	4.178	0.834
30	3.671	0.831
40	3.003	0.824
50	2.443	0.817
60	1.990	0.810
70	1.641	0.803
80	1.392	0.796
90	1.243	0.789

Table 1: Viscosity and density as function of Temperature

Water content %	0.3
TAN, mg KOH/g oil	0.1
TBN, mg HCl/g oil	0.01

Table 2: Water content, Total acid and base numbers

16

sample	Saturate, %
Saturates	48
Aromatic	45
Resin	5
Asphaltene	2
CII	1.00
Asphaltene content % (g/g)	1.4

Table 3: SARA analysis and asphaltene content for the crude oil

Fourier Transform Infrared (FTIR) Spectroscopy

The use of FTIR spectroscopy allows for the identification of functional groups. In addition, the spectra supports estimates on the polarity of the samples (i.e., crude oil, asphaltene, and four dispersants) under study. The functional groups were identified based on the interpretation and instructions mentioned in Bellamy1975, Pavia 2008 & Field 2012. The representations in Fig. 1 through Fig. 6 illustrate the wavelength of the sample (cm^{-1}) by the absorbance rate for the crude oil, asphaltene, and the four selected dispersant samples in the current study

The crude oil spectrum in Fig. 1 displays the profiles of hydrocarbon in the strong peaks around the 2,800, 1,400 to 1,600, and 719 wavelength regions. The peak at 2,800 represents C-H aliphatic stretching, whereas the peaks between 1,400 and 1,600, and 719 represent C=C aromatic bonding. Similar results occur in Fig. 2. The spectrum in Fig. 2 displays the profiles of hydrocarbons in similar peaks at 2,900, 1,400 to 1,600, and 725 wavelength regions. As with Fig.

1, the peak at 2,900 represents C-H aliphatic stretching whereas, the peaks between 1,400 and 1,600, and 719 represent C=C aromatic bonding. In identifying difference between the two spectra ; differences in the ratio of aromatics and alkanes reflect the poly-aromatic structure of asphaltene.

Dispersant A, as mentioned in the safety data sheet, contains Hydrocarbon C10 mainly aromatic, naphthalene, and 1, 2, 4-Trimethyl-benzene. The FTIR spectrum in Fig. 3 illustrates an agreement peak for aromatic bonding between 700 to 900 cm-1 and 1,450 to 1,600 cm^{-1}. In contrast, Dispersant B contains Toluene, propane, solvent naphtha and fatty amine. The spectrum of dispersant B, in Fig. 4, shows the toluene fingerprint at 690 cm^{-1}, C-H aliphatic stretching at 2,800 to 2,900 cm-1, and C=C aromatic bonding at 1,450 cm^{-1}.

The FTIR spectra of the chemical dispersants showed that the mainly functional groups are aromatic rings, the mechanism of stabilizing the asphaltene based on π-π interactions between the polar aromatic head groups and the aggregated asphaltene, while the long alkyl chains on the periphery of the asphaltene aggregate and make the it dispersible in the crude oil. The FTIR spectrum of coconut oil, in Fig. 5, illustrates polar molecules between 1,737 and 1,300 cm^{-1}. These molecules are often associated with C=O and C-O esters. The spectrum for Andiroba oil, shown in Fig. 6, exhibits a phenol peak between 3,100 to 3,600 cm^{-1} and the C-O peak at 1,150 cm^{-1}.

The vegetable oils are considered oil soluble amphiphiles that can be adsorb onto the asphaltene. The dispersing power of the vegetable oils based on the fatty acids, alcohols, and amines group that mainly interact with asphaltene through hydrogen bonding. The fatty acids contains acidic protons, which can form hydrogen bonds with hydroxyl groups in asphaltene or interact with the metal ions destabilizing the asphaltene aggregation process.
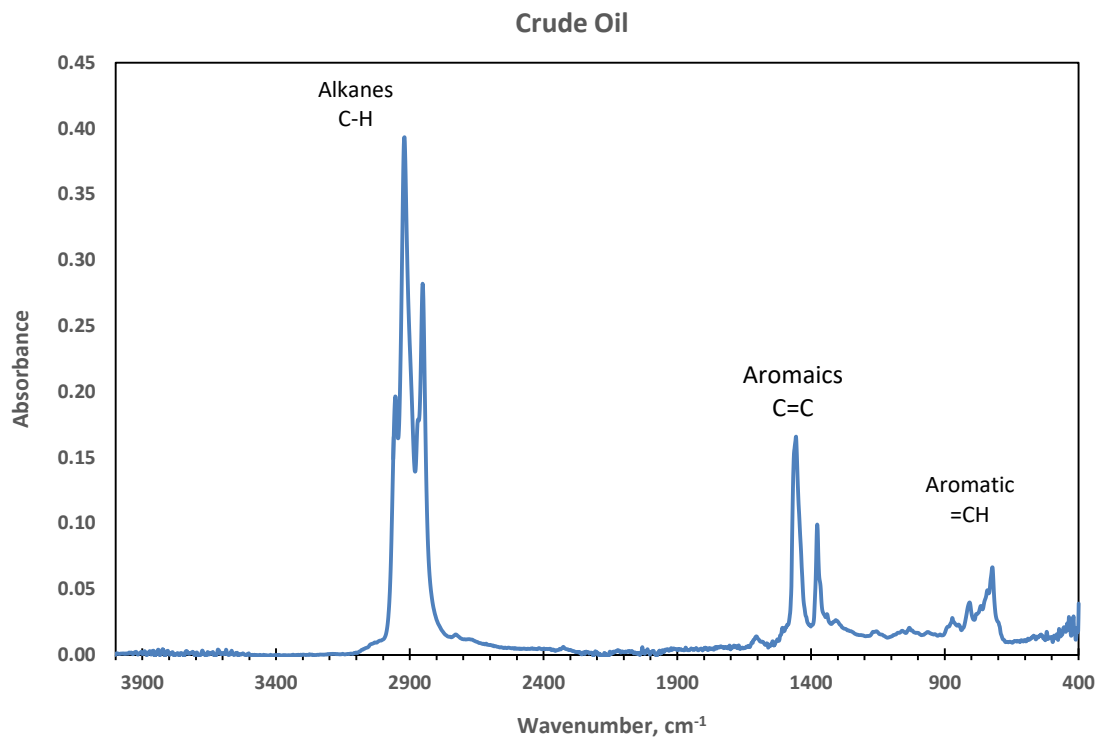
Figure 1: FTIR spectrum of the crude oil
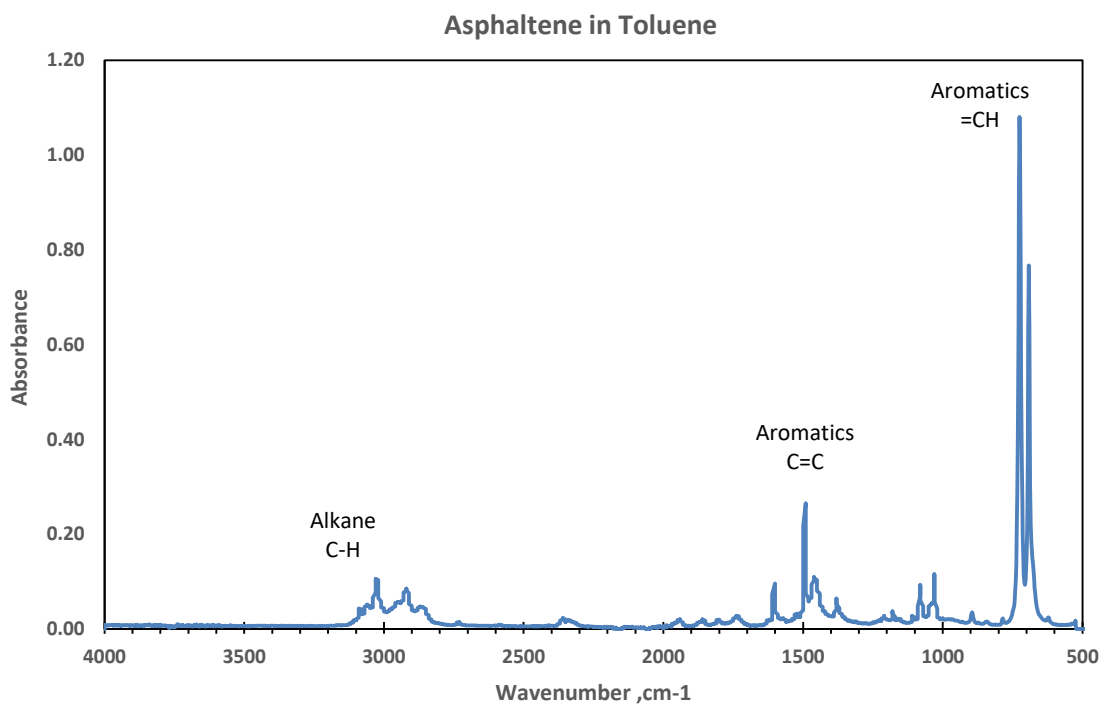
Figure 2 : FTIR spectrum of the asphaltene –toluene solution
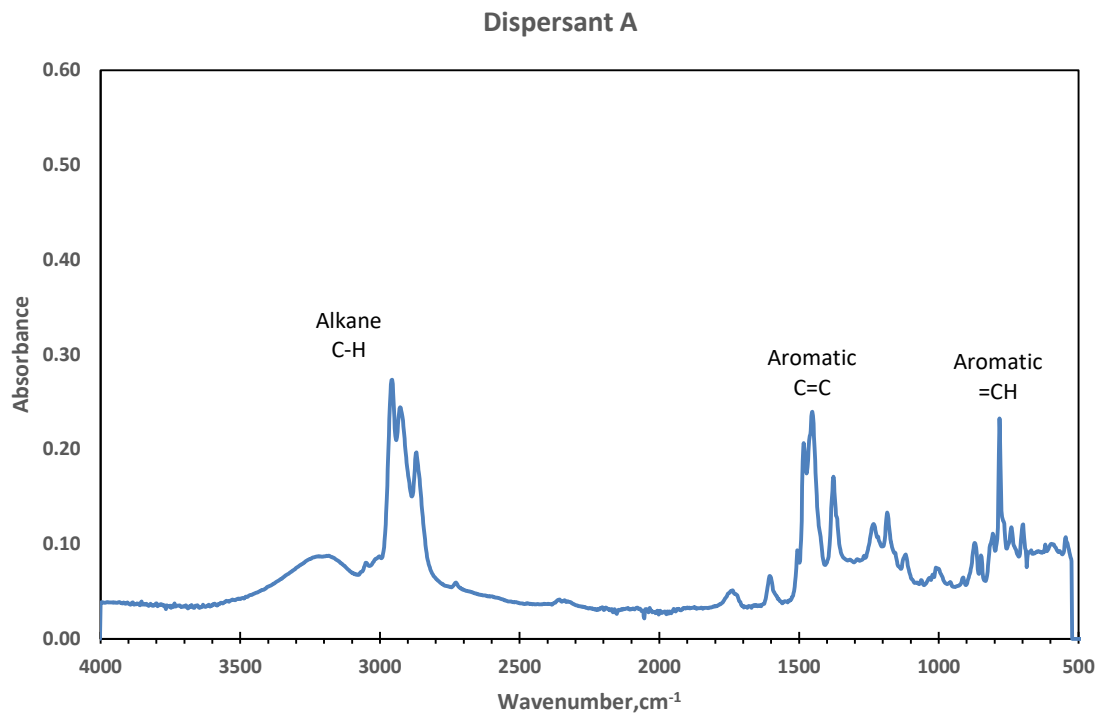
Dispersant A

Figure 3: FTIR spectrum of commercial dispersant A
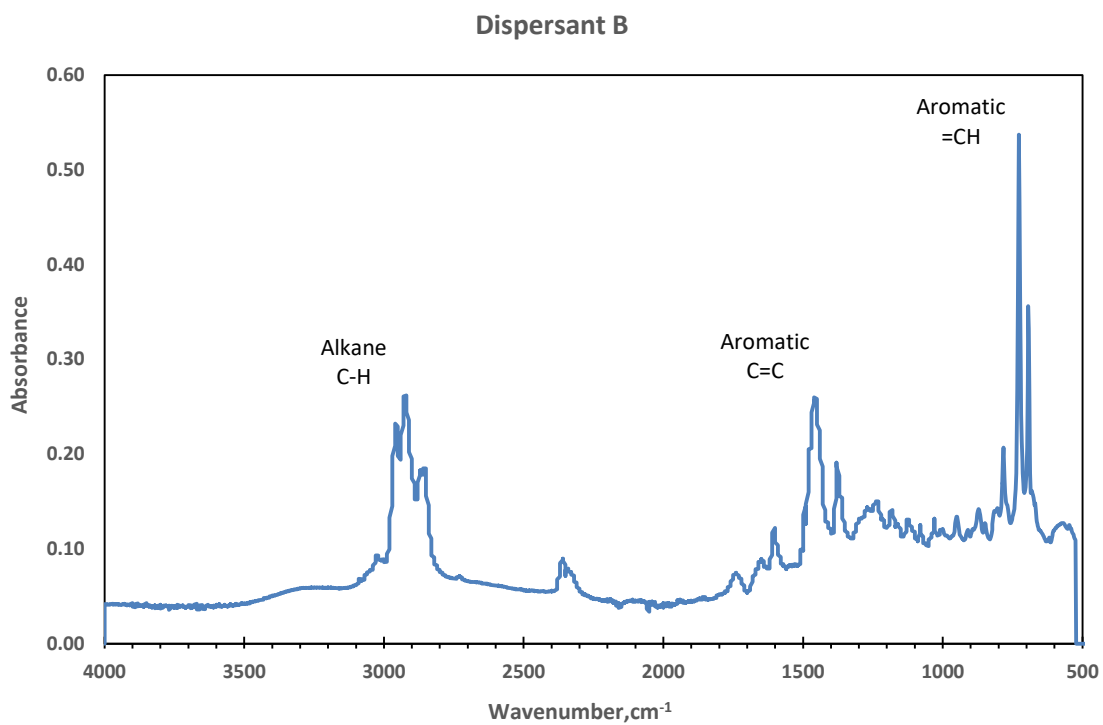
Dispersant B

Figure 4: FTIR spectrum of commercial dispersant B

20

Coconut Oil

Alkanes
C-H

Ester
C=O

Ester
C-O

Absorbance

Wavenumber,cm⁻¹
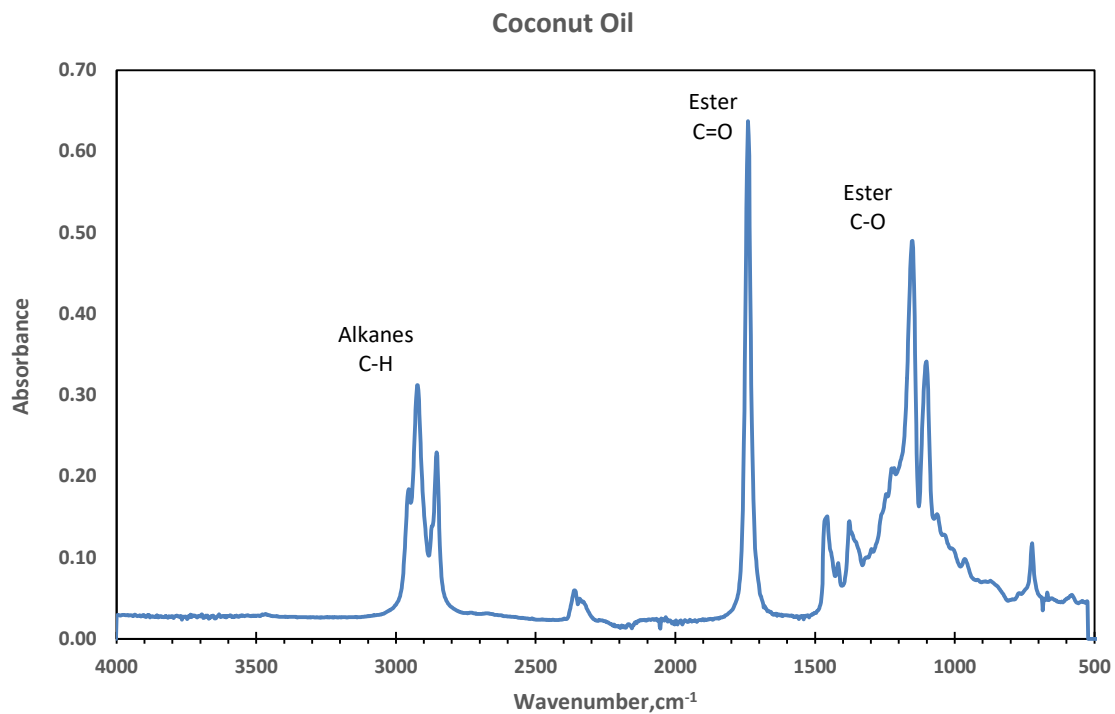
Figure 5: FTIR spectrum of coconut oil

Andiroba Oil

Alcohol/Phenol
O-H

Aramotic
C=C

Alcohol
C-O

Absorbance

Wavenumber,cm⁻¹
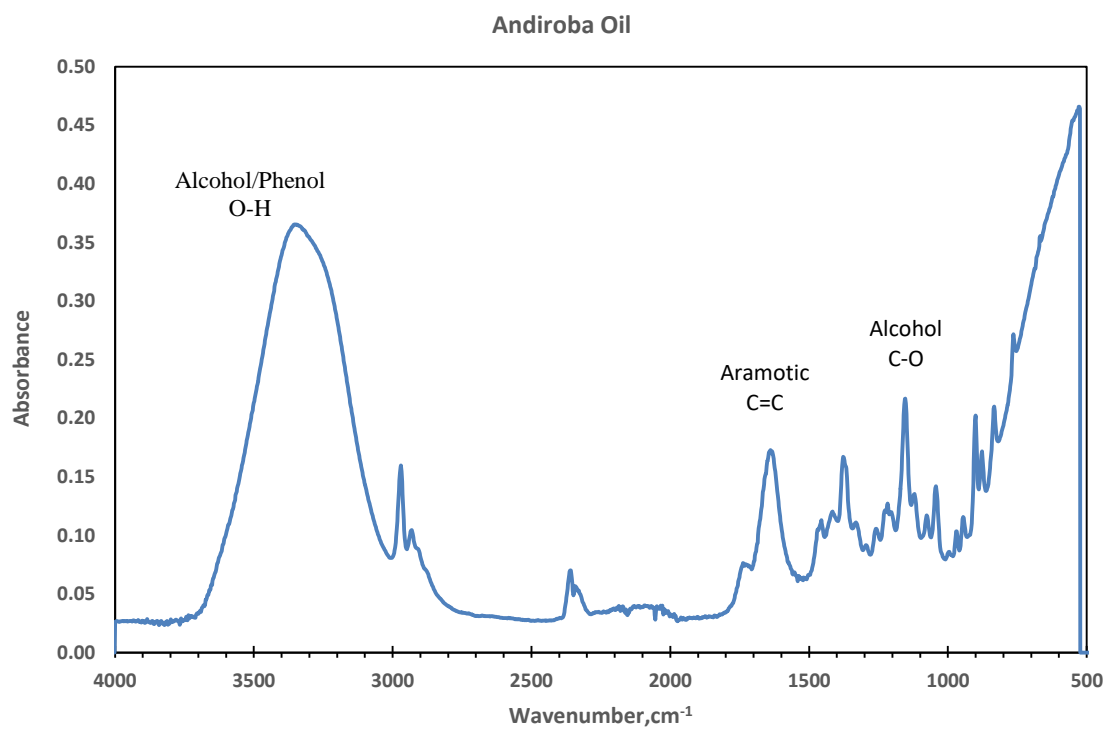
Figure 6: FTIR spectrum of andiroba oil

21
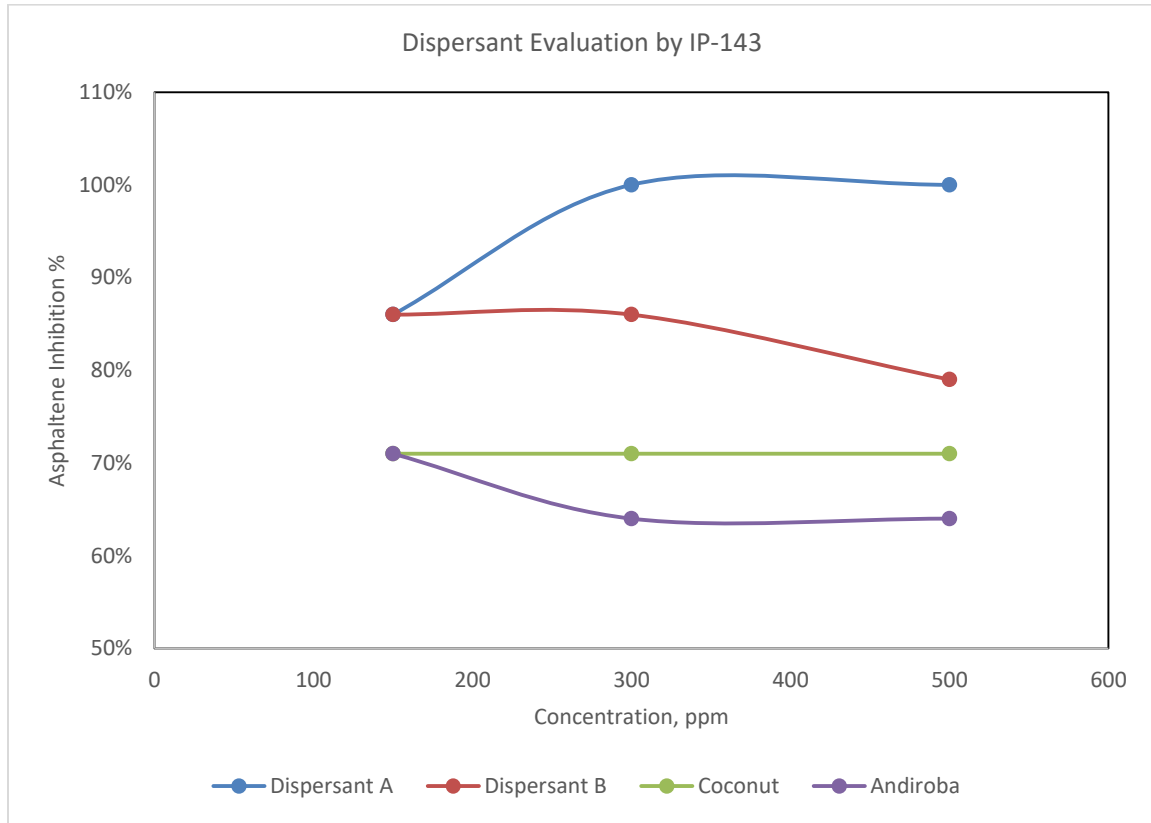
Figure 7: Asphaltene dispersant effectiveness using IP-143

The data in Figure 7 showed the concentration of dispersant versus the percentage of asphaltene inhibition. The reduction of asphaltene content in all the dispersants while added to the oil at several concentration. The commercial dispersants showed better performance compared to the vegetable oils.

Concentration	Dispersant	Asphaltene Content %	Inhibition %
	deasphalted oil	0.4	71%
150 PPM	dispersant A	0.2	86%
	Dispersant B	0.2	86%
	Coconut	0.4	71%
	Andiroba	0.4	71%
300 PPM	dispersant A	0	100%
	Dispersant B	0.2	86%
	Coconut	0.4	71%
	Andiroba	0.5	64%
500 PPM	dispersant A	0	100%
	Dispersant B	0.3	79%
	Coconut	0.4	71%
	Andiroba	0.5	64%

Table 4: Asphaltene dispersant effectiveness by IP_143

Asphaltene Dispersant Test (ADT)

Table 5 illustrates the results of ADT at 25 °C, the chemical dispersants perform well in all concentrations for the whole period of time. The effect of adding the deasphalted oil (DAO) to the dispersants have different results. For dispersant A, the DAO helped help peptize the asphaltene precipitation when the concentration was around 150 ppm, for the other cases it caused asphaltene to precipitate faster and that might be due to asphaltene self-association in the case of not enough polar head groups in the solvent for optimum interactions. For the case of

dispersant B, adding DAO helps keep the asphaltene stabilized in the crude oil for all the concentrations.

For Bio-oils, coconut oil gave promising results inhabiting the asphaltene precipitation when it added to the oil at 300 ppm and 500 ppm when combined with DAO. Andiroba oil best performance was at 150 ppm. The addition of DAO to andiroba oil tend to aggregate the asphaltene precipitation in the oil.

The results of ADT at 70 °C in table 6 showed that the chemical dispersants perform very well with and without the DAO. On the other hand, both of the vegetable oils failed to peptize the asphaltene. that may be due to the increase of the polarity and shortage of head groups to interact with them. The addition of DAO makes no difference except when paired with coconut oil at 500 ppm.

	Basic	Deasphalted oil	dispersant A	dispersant B	Coconut oil	Andiroba oil	DAO+disp. A	DAO+ disp. B	DAO +coconut	DAO+ andiroba
at concentration = 150 ppm										
1 hr.	clear	trace	clear	clear	trace	clear	clear	clear	clear	clear
24 hr.	trace	trace	clear	clear	ppt	clear	clear	clear	clear	ppt
1 week	ppt	ppt	clear	clear	ppt	clear	clear	clear	trace	ppt
at concentration = 300 ppm										
1 hr.	clear	trace	clear	clear	clear	clear	clear	clear	clear	clear
24 hr.	trace	trace	clear	clear	clear	clear	trace	clear	trace	clear
1 week	ppt	ppt	clear	clear	clear	trace	trace	clear	ppt	trace
at concentration = 500 ppm										
1 hr.	clear	trace	clear	clear	clear	clear	trace	clear	clear	trace
24 hr.	trace	trace	clear	clear	trace	ppt	ppt	clear	clear	trace
1 week	ppt	ppt	clear	clear	ppt	ppt	ppt	clear	clear	ppt

Table 5: ADT observation at 25 °C

25

	Basic	Deasphalted oil	dispersant A	dispersant B	Coconut oil	Andiroba oil	DAO+disp. A	DAO+ disp. B	DAO +coconut	DAO+ andiroba
at concentration = 150 ppm										
1 hr.	trace	trace	clear	clear	ppt	ppt	clear	clear	ppt	ppt
24 hr.	ppt	ppt	clear	clear	ppt	ppt	clear	clear	ppt	ppt
1 week	ppt	ppt	clear	clear	ppt	ppt	clear	clear	ppt	ppt
at concentration = 300 ppm										
1 hr.	trace	trace	clear	clear	clear	trace	clear	clear	trace	trace
24 hr.	ppt	ppt	clear	clear	trace	ppt	clear	clear	ppt	ppt
1 week	ppt	ppt	clear	clear	ppt	ppt	clear	clear	ppt	ppt
at concentration = 500 ppm										
1 hr.	trace	trace	clear	clear	trace	trace	clear	clear	clear	clear
24 hr.	ppt	ppt	clear	clear	trace	ppt	clear	clear	clear	trace
1 week	ppt	ppt	clear	clear	ppt	ppt	clear	clear	clear	ppt

Table 6: ADT observation at 70 °C

Dynamic light scattering was used as an indirect method to measure the effect of the dispersants and the addition of DAO. The particle size of the oil added to heptane was 1,037 nm while adding 10% DAO reduce the size slightly to 966 nm. Fig. 8 compares the results of all dispersants at several concentration with and without DAO. The results are in agreement with the asphaltene dispersant test, the chemicals help to control the particle size below 400 nm except for dispersant A at 300 ppm, when pairing it with DAO. As for the vegetable oils, both worked in reducing the particle size slightly and the results confirmed the finding from ADT that the optimum concentration for coconut oil is 300 ppm, while andiroba at 150 ppm. It also proved that pairing the dispersant with DAO helped peptize the asphaltene aggregates since it's enhance the performance of dispersant B at concentration of 150 ppm.
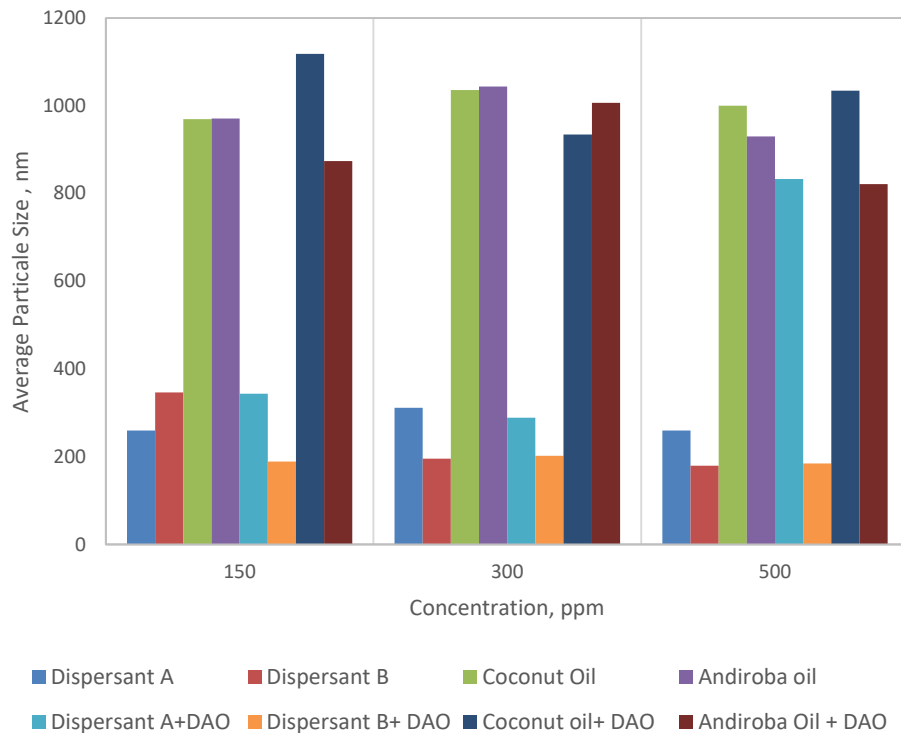
Figure 8: Comparison of asphaltene particle size by dynamic light scattering.

27

Ultraviolet-visible Spectroscopy (UV-vis)

The supernatant of the ADT samples was collected and the transmittance was measured using a UV-Vis spectrometer at two fixed wavelength, 640 and 720 nm. The higher transmittance indicating a greater dispersed asphaltene after dissolution. The results in **Figs**. 9 and 10 compare the transmittance reading after 1 hour and 1 week duration. The results are in agreement with the asphaltene dispersant test discussed previously. The performance of chemical dispersants decline dramatically after 1 week while the vegetable oils, even though didn't disperse 100 % of asphaltene, have sustained performance compared to the chemical dispersants. The addition of DAO to the oil tends to enhance the asphaltene precipitation as seen in ADT and the results in agreement with Jamaluddin et al. 1996 finding to use deasphalted oil with saturated less than 35%. On the other hand, pairing DAO with the vegetables oil enhance the efficiency comparable of the chemical dispersants.
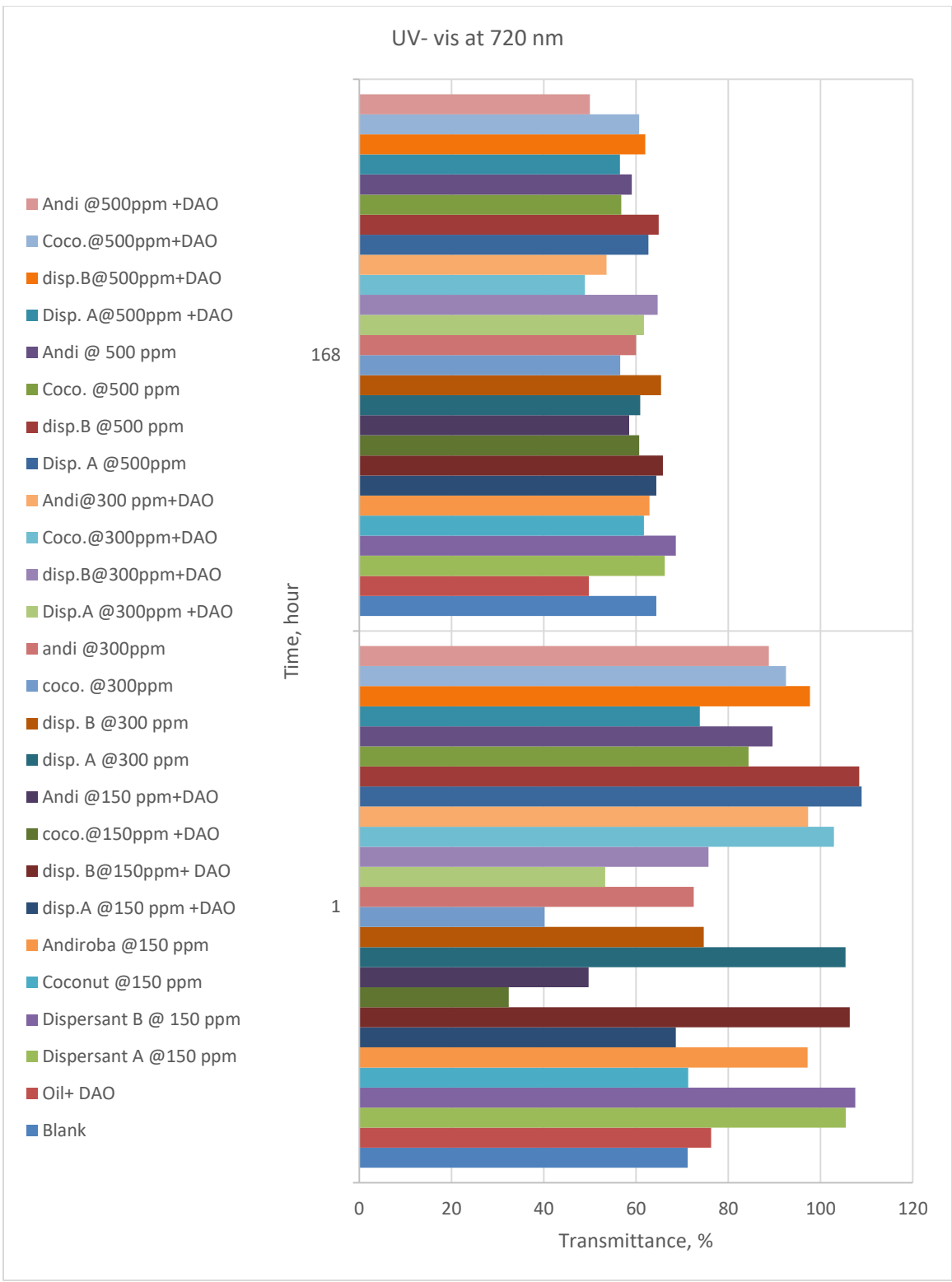
Figure 9 : The transmittance readings for the treated samples at 720 nm
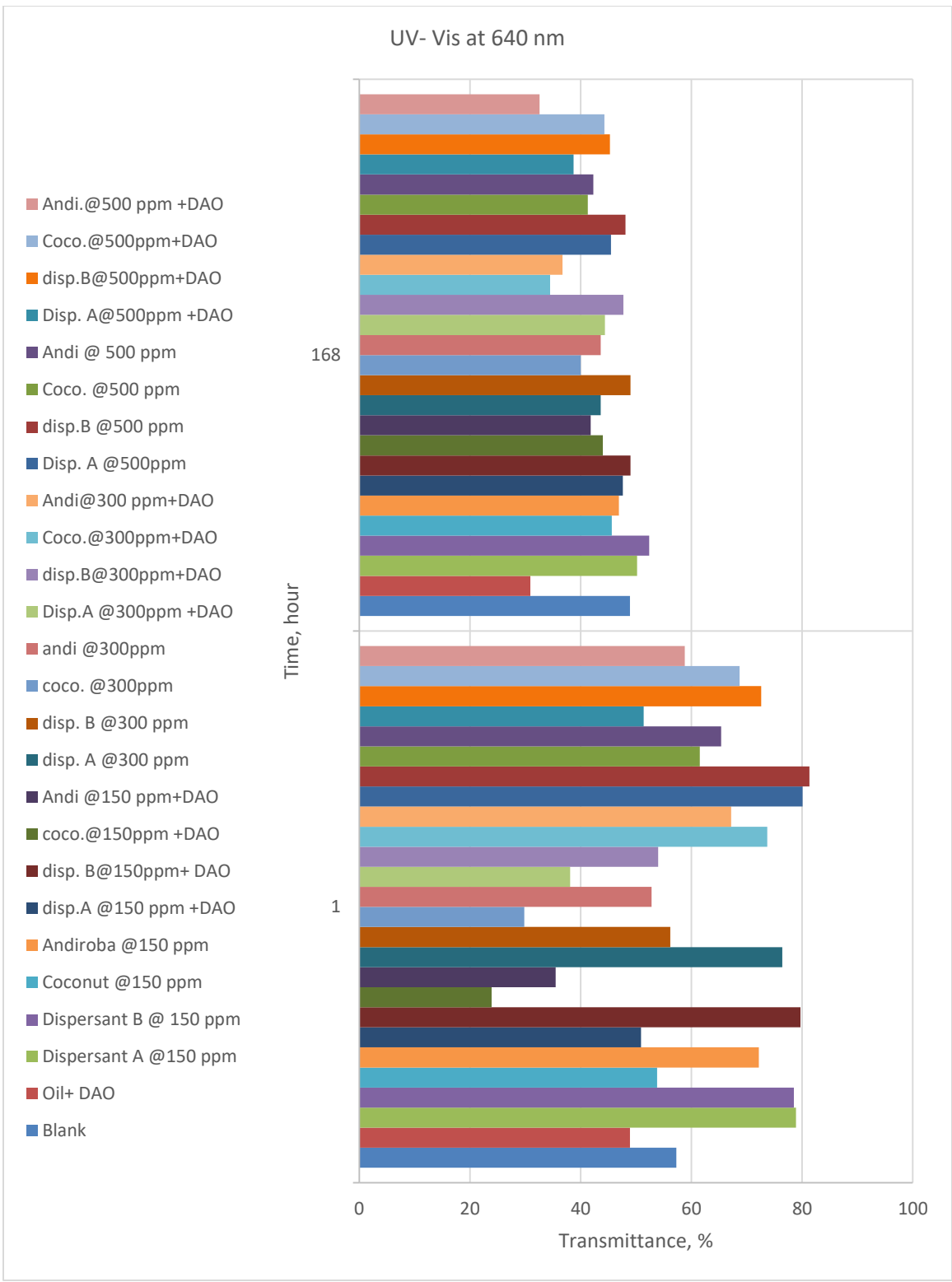
Figure 10: The transmittance readings for the treated samples at 640 nm

Conclusions

1. The colloidal instability index (CII) was measured for the crude oil and found to be greater than 0.7 indicating definite asphaltenes instability.

2. Vegetable oils have special structures and functional groups (ester and alcohol) that interact with asphaltene and prevent precipitation.

3. Pairing the DAO with commercial dispersants is a cost effective option as it may lower the chemical concentration needed to peptize asphaltenes.

4. Combining DAO with 500 ppm coconut oil at reservoir temperature can help disperse any asphaltene aggregate.

5. Using vegetable oils as inhibitors is economically acceptable, as well as being environmentally friendly.

6. DLS measurements showed the reduction of asphaltene particle size with vegetable oils and the addition of DAO.

7. UV-vis readings illustrated that the performance of vegetable oils after a week are comparable to the chemical dispersants.

CHAPTER IV

COREFLOOD EXPERIMENTS

This chapter discussed the experimental setups, equipment, and procedures needed to achieve the objectives from the second part of the study regarding asphaltene problems in matrix acidizing.

Materials

Indiana limestones and Carbon tan cores were used in all the experiments. The permeability of the oil-saturated cores varied from 9 to 38 mD. All the cores are 6" length and 1.5" in diameter. The properties are listed in table 7.

Experiment #	Lithology Type	Porosity ,%	Initial Permeability, mD
1	Indiana limestone	16.12%	11.30
2	Indiana limestone	16.30%	11.26
3	Indiana limestone	16.25%	13.26
4	Carbon Tan sandstone	16.66%	30.00
5	Carbon Tan sandstone	16.85%	32.33
6	Carbon Tan sandstone	15.77%	27.00
7	Indiana limestone	14.75%	13.00
8	Indiana limestone	16.00%	11.30
9	Indiana limestone	15.90%	9.40
10	Carbon Tan sandstone	16.15%	28.50
11	Carbon Tan sandstone	16.55%	30.27
12	Carbon Tan sandstone	16.26%	29.67

Table 7: The Core properties

Experimental Studies

Fluid Properties

The density of Deionized water and 5 wt% KCl brine prepared was found to be 1 and 1.0315 g/cc, while the viscosity equals 1 and 1.077 cP, respectively at room temperature and pressure.

Fluid Preparation

The acid solution was prepared using deionized water obtained from a water purification system that has sensitivity of 18.2 MΩ. cm at room temperature. The concentration of the hydrochloric acid used for this experiment was 36.46 wt%. This acid was diluted to 15 wt% using deionized water.

The corrosion inhibitor used is (CI-27) added to the acid/GLDA solution to prevent corrosion of the accumulators and lines. The acid/GLDA system was prepared by mixing deionized water, corrosion inhibitor, and hydrochloric acid or GLDA for 30 minutes with magnetic stirrer.

Core Preparations

The cores were dried in the oven for overnight to remove any moisture. Carbon tan sandstone cores were dried at temperature 120°F, while Indiana limestone cores were dried at 200°F the weight were measured.

Core Saturation

Indiana lime stone cores were saturated with deionized water for 3 hours using a vacuum pump. Then at least 4 pore volumes of deionized water were pumped to measure the initial permeability of the cores and fully stature them with water. The same procedure followed for carbon tan cores using 5 wt% KCl brine. The cores were kept immersed in the saturation fluid

until the next step. The cores were then saturated with the crude oil by pumping at least 5 pore volume s of oil through the cores at extreme flow rates over a period of 32 hours. This ensured complete saturation of the core. The weight of the cores was measured after each saturation step to estimate the porosity and effective permeability.

Sludge Test

The crude oil and acid system was tested for sludge tendency. The testing involves mixing 50:50 ratios of acid system: crude oil. The mixture agitated for 15 minutes then placed in aging cell under 500 psi pressure and placed at the oven at 70°C for an hour. The mixture then observed, if there is two separate phase indicates that there is no sludge, and if not, the sample is then filtered and the slug is weighed.

Corrosion Inhibitor Compatibility Test

The compatibility of corrosion inhibitor with the dispersant and acid was determined to ensure that all the additives are miscible. Several corrosion inhibitor was mixed with the acid and the dispersants. The samples were monitored frequently for 24 hours for any precipitation.

Computer Tomography Scan (CT scan)

The cores were subjected to CT scan after each step in order to determine the CT number of the core. CT number served the primary source of identifying the extent of dolomitization, presence of anhydrites, and can be used to detect wormholes propagation. Porosity of the core after treatment can be determined from the CT number (Izeg and Demiral 2005).
A CT number of about 2350 and 2250 indicates the presence of pure dolomite and pure limestone, respectively. The cores were scanned and imaging software named ImageJ was used to analyze and stack the images. The software designed to compile the images of cores taken

over different cuts along the length of the core and to visualize the wormholes after the treatment.

PH measurements

The pH values of the effluents samples collected during the coreflood experiments were measured using a pH meter. The analysis of the pH will help to recognize the time of breakthrough when the pH reach near zero, while higher pH numbers represent that the acid is spent.

Coreflood Setup

The coreflood setup used to stimulate the matrix acidizing process has been described in Figure.11. The experimental setup consists of three accumulators, syringe pump, core holder, backpressure regulator, hydraulic pump, differential pressure transducer, and a data acquisition system. A heating system is used to heat the core in the core holder
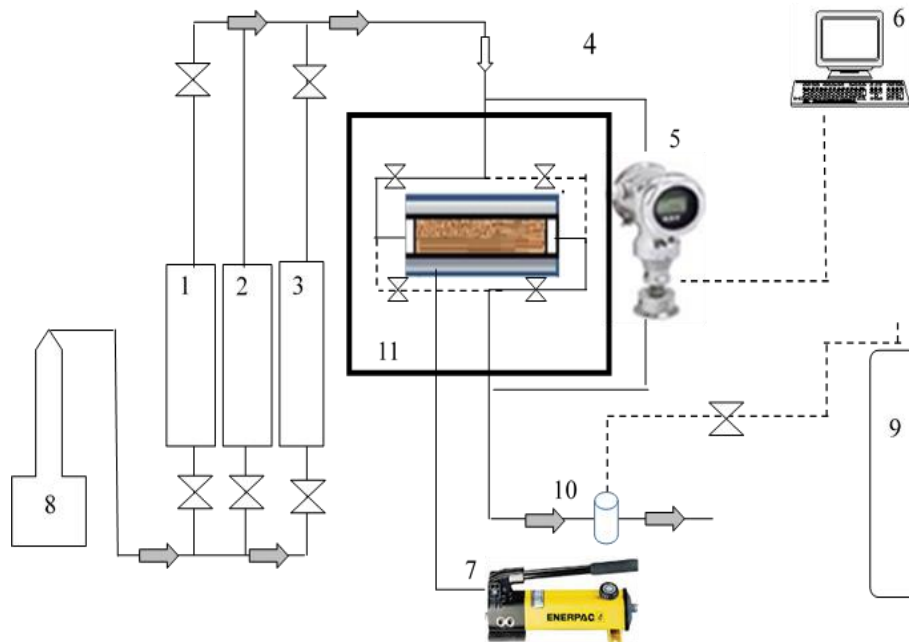

Figure 11: Coreflood experiment setup: 1-3 Accumulators 4-core holder 5-pressure transducer 6-computer LabView 7-handpump 8-syringe pump 9-nitrogen cylinder 10-backpressure regulator 11-oven

Accumulators

Three accumulators were used: one to store the oil, the second to store the brine or deionized water and the third used to store the acid. The accumulator consist of a Teflon piston which splits the unit into two compartments, one side filled with hydraulic oil and the other compartment filled with the designated fluid. When the experimental setup is complete, the syringe pump removes hydraulic oil from the reservoir and pushes it up into the oil compartment. The hydraulic oil in turn moves the piston up, which pushes the brine/acid/deionized water/oil out of the accumulator and into the connected lines to the core holder. The lines and acid accumulator were made of Hastelloy C-276.

Core Holder

The core holder is a metallic cylinder where the core held under a confining pressure called the overburden pressure. Generally, an overburden of 1700 psi was maintained throughout all the experiments. The confining pressure is required to be at least 400 psi greater than the core inlet pressure. The core holder is made of hastelloy C-276, which contains tungsten in addition to the regulator Nickel-Chromium-Molybdenum alloy for improved corrosion resistance. The core holder is capable of withstanding pressures up to 3000 psi and temperature as high as 300 F. a rubber sleeve within the core holder prevents direct contact between the core and the metallic-alloy cylinder.

Syringe Pump

A Teledyne ISCO D500 precision syringe pump, with a capacity of 1000 ml and a maximum allowable working pressure of 2,000 psi, was used to inject the fluids into the core. The pump is used to set a constant flowrate ranging from 0.1 ml/min to 400 ml/min.

Back Pressure Regulator

The downstream pressure at the end of the core holder is regulated using a back pressure regulator. The pressure is maintained at about 1,200 psi throughout the acidizing experiment in order to keep the CO2 produced from the dissolution of carbonates in solution, without affecting the system hydrodynamics (Lund et. Al 1973; Fredd and Fogler, 1998c). The back pressure setup helps simulate the actual reservoir conditions, wherein under static condition the pressure inside the core equals reservoir pressure.

Hydraulic pump

The confine pressure within the core holder is provided using a hydraulic pump which can supply pressure up to 5,000 psi. The hydraulic pump is a product of Enerpac Co., model P-39 with a usable oil capacity of 770 cc.

Data Acquisition System

The data acquisition system consists of a pressure transducer, which monitors the pressure drop across the core. It relays the pressure drop to a signal processing board, which in turn delivers the processed signal to a computer operating LabVIEW®, recording the pressure drop at regular intervals. Foxboro model IDP10 I/A series differential pressure transmitters record the pressure drop across the cores.

CHAPTER V

EVALUATE THE BIO-OILS AGAINST CHEMICAL DISPERSANTS AS ANTI-SLUDGE AGENT IN MATRIX ACIDIZING

Introduction

Acidizing treatment is a common practice to overcome the near wellbore damage. Unfortunately, in some of the oil wells, it can end up with more permeability reduction, or in severe cases, total loss of the well due to the formation of acid induced asphaltene sludge. The extensive literature review showed that although the asphaltene sludge problem is well recognized in the industry, all of the recent developments were aimed to tackle this problem by controlling the iron (Fe). The most used anti-sludge agent is DBSA, developed years ago and considered one of the costly chemicals in the industry.

The aim in this chapter is to test the vegetable oils (coconut oil and Andiroba oil) as anti-sludge agent in matrix acidizing against the chemical asphaltene dispersants. The performance of these dispersants and bio-oils were studied in two different lithology with multiple acid systems. Comparison between the performance in acidizing oil bearing cores using inorganic acid such as hydrochloric acid and chelating agent (GLDA) were studied.

The results showed excellent performance of coconut oil as anti-sludge agent in limestone acidizing. The coconut oil have a comparable performance to the chemical dispersants when used with 15 wt% HCl. It's enhances the acid propagations and reduced the injected pore volume to breakthrough. In the case of stimulating the cores with chelating agent (20 wt% GLDA), the coconut oil exceed the expectations with the minimum pore volume needed to breakthrough compared to the GLDA alone or with the chemical dispersant B.

Results and Discussions

This section contains the results of the experimental studies discussed in the previous chapter.

X-ray Diffractions (XRD)

X-ray diffraction was conducted for mineralogy examination in figures 12 and 13. Carbon tan cores were analyzed to have 93.12% quartz, 1.05% dolomite and the remaining 5.83% represents a mixture of clays. Indiana limestone cores identified as more than 99 wt % calcite, less than 1 wt% quartz, and clean from clays.
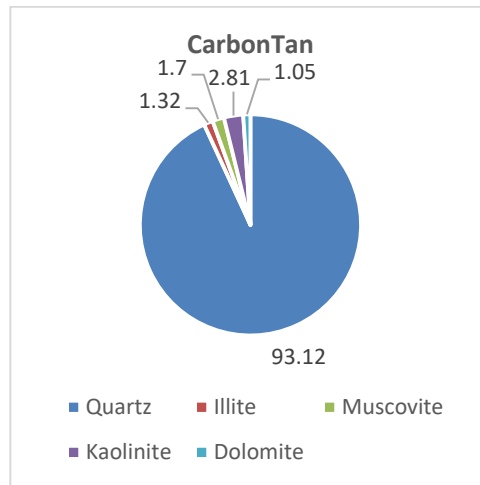

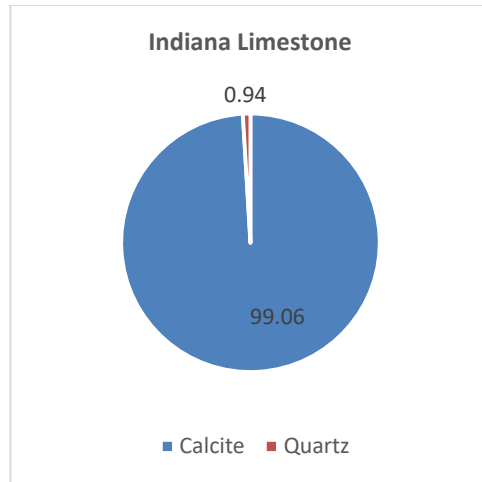**Figure 12: XRD for Carbon Tan Sandstone cores**

Figure 13: XRD for Indiana limestone cores

Sludge Test

The sludge test was conducted to test the tendency of the oil to form sludge under different concentration of HCl and iron.

The first set of the sludge test was conducted to select the optimum acid concentration to use in the experiments. The common three acid concentration used in the field were tested 15 wt%, 20 wt.% and 28 wt.% HCl, the results furnished in table 8. As the acid concentration increase the sludge wt.% increase, the decision was made to choose the lowest concentration for further analysis.

HCl concentration	Sludge wt. %
15 wt% HCL	13
20 wt% HCL	19
28 wt% HCL	29.75

Table 8: Sludge test for different concentration of HCl

The second set of sludge test was conducted to measure the effect of the presence of iron on the formation of the sludge. The results listed in table 9 showed that as the iron concentration increases the sludge increased. That's due to the interaction between the ferric cation with the un-stabilized negative charged asphaltene particles.

Iron Concentration+15 wt% HCl +CI	Sludge wt. %
1000 ppm	7.625
2000 ppm	11.5
3000 ppm	16.75

Table 9: Sludge test for 15 wt% HCl and corrosion inhibitor with different concentration of Iron

The effect of each dispersants was tested at its optimum concentration in the third set of sludge tests. The results in table 10 showed that dispersant B prevents the sludge completely. The sample showed complete phase separation between the acid system and the oil while in dispersant A, 3 wt% sludge was recovered after filtering the sample. In the case of the vegetable oils, coconut oil reduce the sludge caused of 15 wt.% HCl to almost 45%, while andiroba oil failed to prevent the sludge. From these results the decision was made to select the best performance dispersant fromed each category, dispersant B as chemical dispersant and coconut oil as bio-oil dispersant.

15% HCl+ Dispersant+ CI	Sludge wt. %
Disp. A (300 ppm)	3
Disp. B (300 ppm)	0
Coconut oil (300 ppm)	7.875
Andiroba (150 ppm)	18.75

Table 10: Sludge test for 15 wt% HCl and corrosion inhibitor with different dispersants

The last set of sludge test was conducted to test the second stimulation system that contains 20 wt.% GLDA and 1 vol.% corrosion inhibitor, with the selected dispersants. The

results represented in table 11 showed that there is no sludge at all form in the three cases. That agrees with the literature as the chelating agent should be a choice in acidizing oil wells with acid induced asphaltene sludge problems.

20 wt% GLDA +Dispersant+ CI	Sludge wt. %
20% GLDA	0
20% GLDA+ Dispersant B (300 ppm)	0
20% GLDA+ Coconut oil (300 ppm)	0

Table 11 Sludge test for 20 wt% GLDA and corrosion inhibitor with different dispersants

Cores Characterization

In all experiments, an overburden pressure at least 300 psi higher than the inlet pressure was kept to prevent the fluid from bypassing the core. The temperature of all the experiments kept at 70° C to represent the reservoir temperature. The flow rate was chosen to be as low as 0.5 cc/min to ensure maximum interaction between oil and stimulation fluid. From the results of the sludge test, the experiments scheme was designed to test the two different lithology using six different stimulation systems in a total of 12 coreflood experiments. Table 12 contains details about the core properties and stimulation fluid corresponded to it.

Experiment #	Lithology Type	Porosity ,%	Initial Permeability, md	Stimulation fluid	flow rate, cc/min
1	Indiana limestone	16.12%	11.30	15 wt% HCl	0.5
2	Indiana limestone	16.30%	11.26	15wt% HCl +disp. B	0.5
3	Indiana limestone	16.25%	13.26	15wt% HCL +coconut	0.5
4	Carbon Tan	16.66%	30.00	15% HCL	0.5
5	Carbon Tan	16.85%	32.33	15wt% HCl +disp. B	0.5
6	Carbon Tan	15.77%	27.00	15wt% HCL +coconut	0.5
7	Indiana limestone	14.75%	13.00	20 wt. % GLDA	0.5
8	Indiana limestone	16.00%	11.30	20%GLDA+disp.B	0.5
9	Indiana limestone	15.90%	9.40	20% GLDA+ coco	0.5
10	Carbon Tan	16.15%	28.50	20 wt. % GLDA	0.5
11	Carbon Tan	16.55%	30.27	20% GLDA+ disp.B	0.5
12	Carbon Tan	16.26%	29.67	20%GLDA+ coco	0.5

Table 12: Experiments Scheme

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Case I: Indiana Limestone Acidizing with 15 wt% HCl

In case I , the base experiment was acidizing with 15 wt% HCl and 1 vol.% corrosion inhibitor without adding any dispersants. The second was using the same system and adding dispersant B at 300 ppm, while the third experiment used coconut oil at 300 ppm as anti-sludge agent. In all the three experiments, oil was injected first until stabilization pressure was reached, followed by acid. Deionized water was used to flush the acid after the breakthrough was reached.
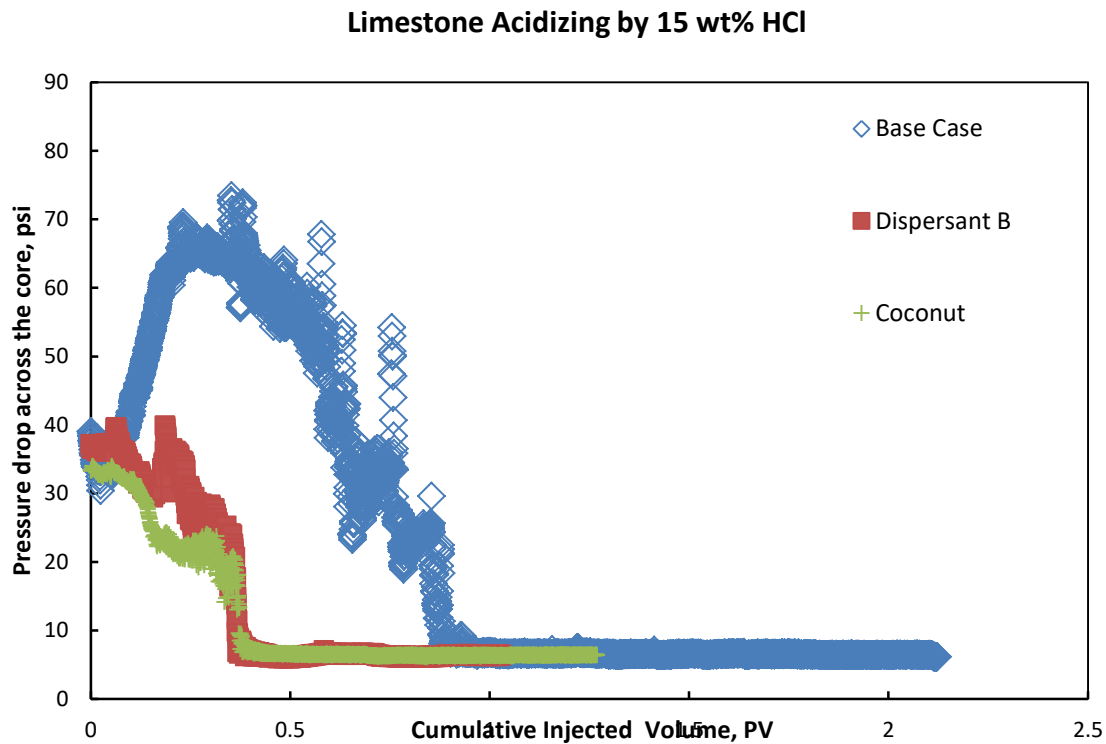

Figure 14: Pressure drop across the core vs. cumulative injected PV for limestone acidizing with 15 wt% HCl
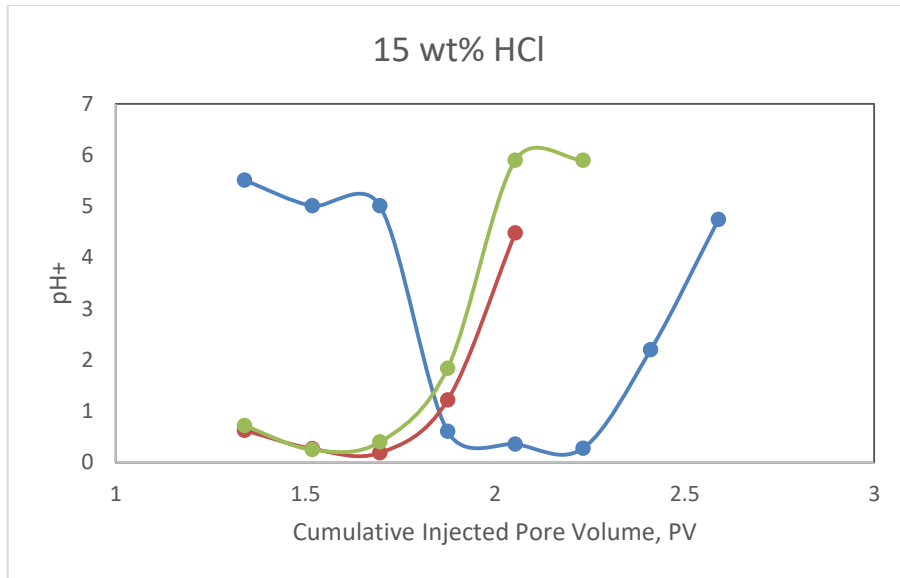
Figure 15: pH+ vs. cumulative injected PV for limestone acidizing with 15 wt% HCl

Figure 14 represents the cumulative injected pore volume (PV) versus pressure drop in psi. The base case was noticed to have distinguish behavior than the two cases with the dispersants, in the base case, an increase in pressure noticed after the acid injected and that indicate that the acid reacted with the oil to form insoluble sludge. The sludge made acid penetration harder reflected in almost double acid quantity of pore volume needed in the base case to breakthrough compared to the cases with coconut oil and dispersant B. The performance of the acid systems containing dispersants B and coconut oil was almost identical. Both systems reached breakthrough after injecting 0.37 PV while 0.9 PV is needed in the base case. The pressure drop didn't show steep increase in the cases with the dispersants, that indicates that both the coconut oil and dispersant B stabilize the asphaltene which make the propagation of the acid smoother within the core. Figure 15 represents the pH of the collected effluent samples versus the cumulative injected pore volume. The results in agreement with pressure drop analysis,

showed the breakthrough in the experiments with added dispersants occurred at the same time while in the base case double the pore volume was required.

Figure 16: Wormhole profile: 15 wt% HCl

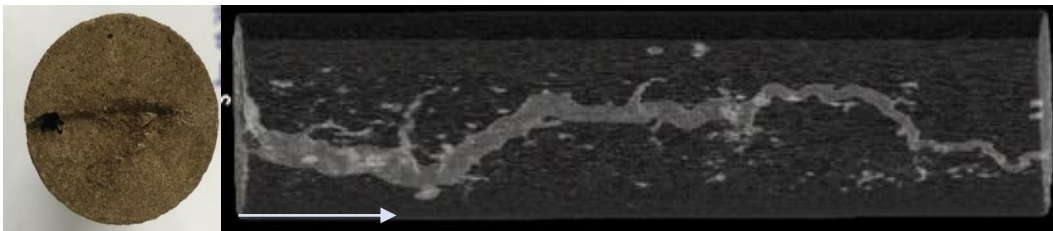**Figure 17: Wormhole profile: 15 wt% HCl + dispersant B**

Figure 18: Wormhole profile: 15 wt% HCl + coconut oil

Figure 16 reflects the results in the pressure drop analysis for the base experiment. The high increase in pressure drop caused by more reaction in the inlet section of the core resulted in conical shape wormhole with wide top and narrow end. Some face dissolution was noticed on the inlet.

In figures 17 and 18, the propagation of the acid were smooth resulted in a long uniform wormhole. The addition of dispersant B and coconut oil gave desirable results in acidizing the Indiana limestone cores.

Case II: Indiana Limestone Acidizing with 20 wt% GLDA

In case II, the base experiment was acidizing with 20 wt% GLDA and 1 vol.% corrosion inhibitor without adding any dispersants. The second was using the same system and add dispersant B at 300 ppm, while the third experiment used coconut oil at 300 ppm as anti-sludge agent. In all the three experiments, oil was injected first until the pressure stabilized followed by maximum four pore volume of the stimulation fluid. Deionized water was used to flush the acid after the breakthrough was reached or the full four pore volume injected.
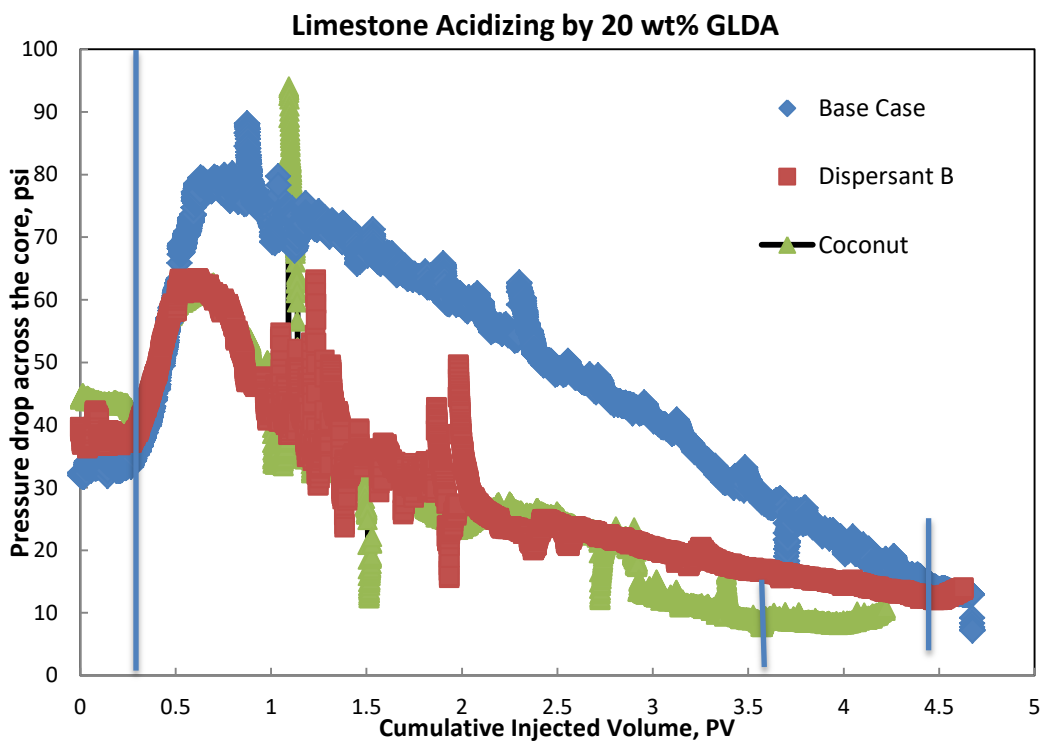

Figure 19: Pressure drop across the core vs. cumulative injected PV for limestone acidizing with 20 wt% GLDA
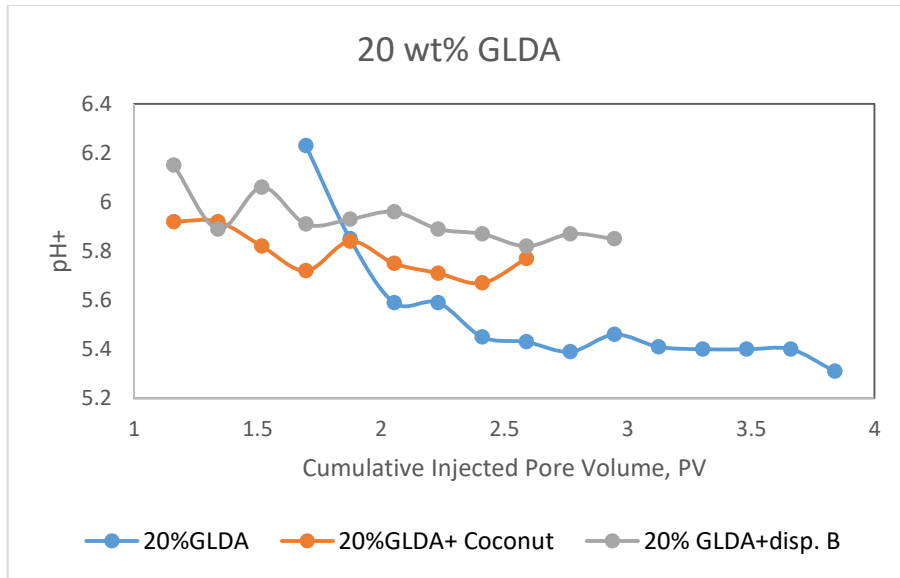
Figure 20: pH+ vs. cumulative injected PV for limestone acidizing with 20 wt% GLDA

The pressure drop results in figure 19 showed similar trend as case I. The base case has a higher increase in pressure drop that reflect more resistance for the stimulation fluid to penetrate the rock. Even though all the results from the sludge test with GLDA showed that no sludge formation. For the base case no breakthrough was noticed after injecting a total of 4 PV.

For the experiments with dispersant B and the coconut oil, although both have similar pressure drop behavior, earlier breakthrough occurred at 3.6 PV in the case with coconut as anti-sludge agent. In Dispersant B experiment, the breakthrough occurred after 4.4 PV was injected.

The pH measurement of the effluent samples in figure 20 is in agreement with the pressure drop analysis. The performance of dispersant B and coconut are similar to the first case, although coconut oil outperformed the chemical dispersant B with less PV needed to breakthrough. It should be noted that the best performance system that contain GLDA and coconut is considered 100% bio degradable and eco-friendly system.
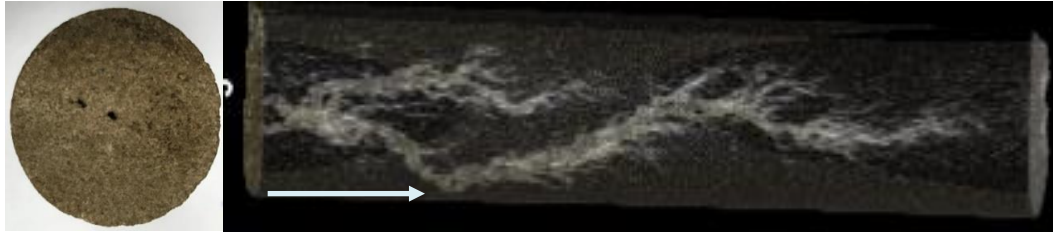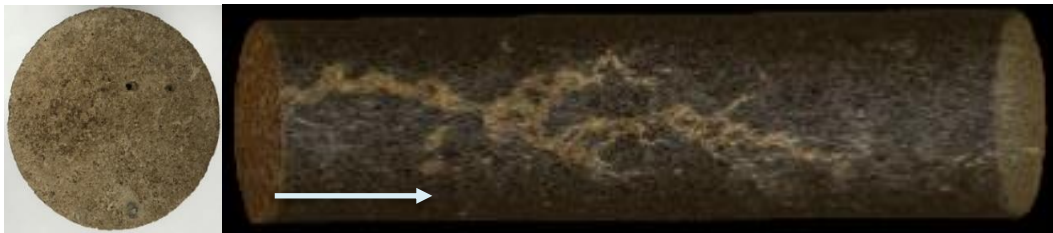
Figure 21: Wormhole profile: 20 wt% GLDA

Figure 22: Wormhole Profile: 20wt% GLDA + dispersant B

Figure 23: Wormhole Profile: 20wt% GLDA + coconut oil

The wormhole profiles in figures 21-22 illustrate the pressure drop behavior during the stimulation treatment. The narrow wormholes in all cases indicates the reaction power of the weak GLDA, since the GLDA have PH around 3.6 it needed more PV to penetrate the core. In figure 21, the excessive branching in the wormhole reflects the high-pressure drop noticed in the base case with 20 wt% GLDA. Dispersant B wormhole profile in figure 22 show less branching in the wormhole with very narrow end. The best performance in case II was the coconut, Figure

23 showed a wormhole with uniform width across the core, with very little branching and that's very favorable performance in matrix acidizing.

Case III: Carbon Tan Sandstone Acidizing with 15 wt% HCl

In case III, the base experiment was acidizing with 15 wt% HCl and 1 vol.% corrosion inhibitor without adding any dispersants. The second was using the same system and add dispersant b at 300 ppm, while the third experiment used coconut oil at 300 ppm as anti-sludge agent. In all the three experiments, oil was injected first until stabilization pressure was reached followed by one pore volume of acid. One pore volume with 5 wt% KCl brine was used to flush the acid.
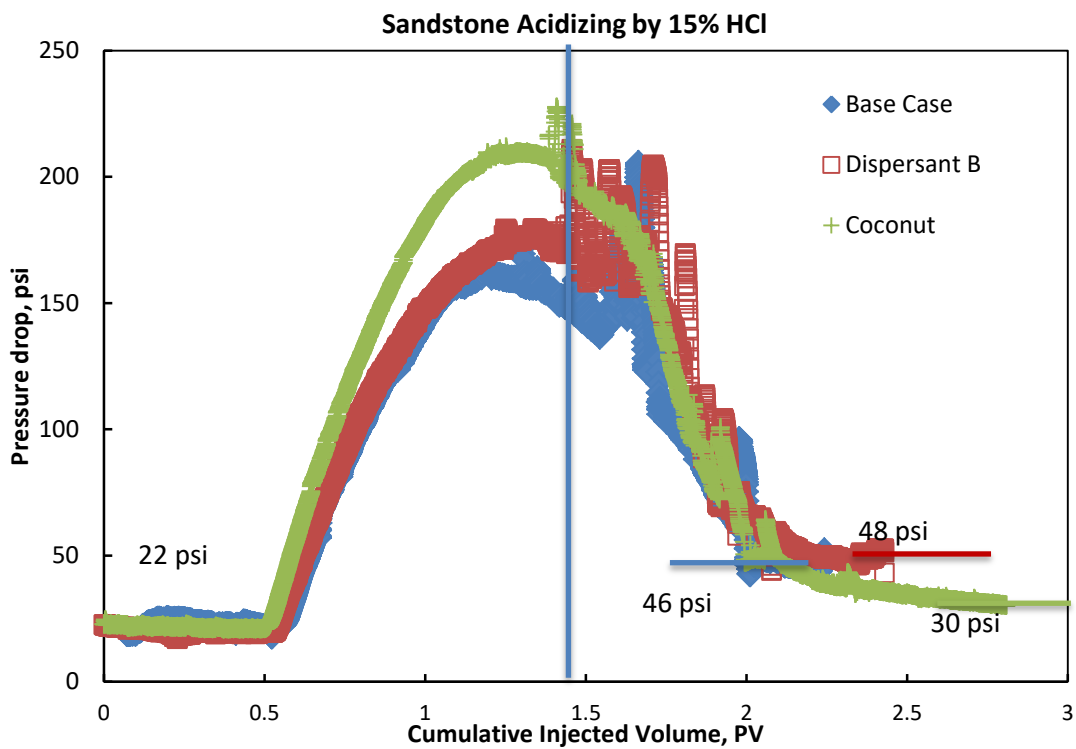

Figure 24: Pressure drop vs. cumulative injected PV for Carbon tan sandstone acidizing with 15 wt% HCl

The pressure drop profiles illustrated in Figure 24 show the increase in pressure drop as the acid injection started, then it declined after the brine post flush. All three cores have stabilization pressure at 22 psi, while there is a slight increase at the final pressure drop, indicating that the acid treatment creates damage within the core. The coconut oil was the least damaged case that reflected with the lowest pressure drop at the end of the treatment.
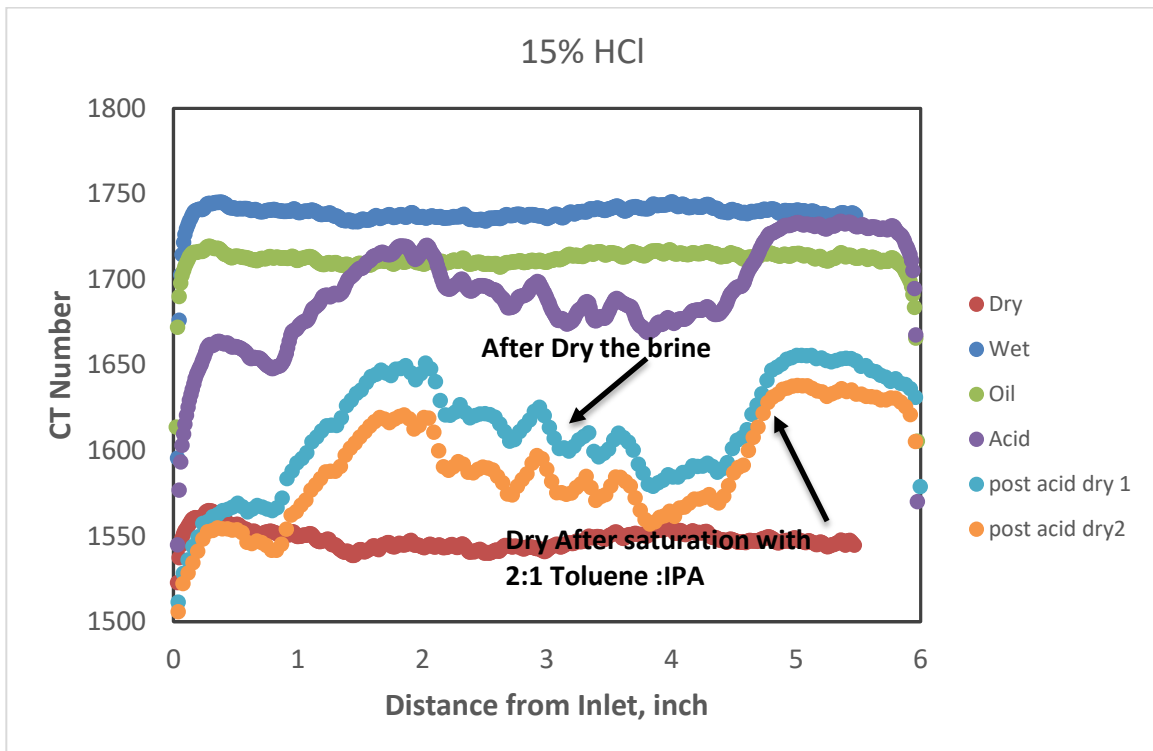

Figure 25: CT number vs. distance from the core inlet, in for Carbon tan sandstone acidizing with 15 wt% HCl

Since the sandstone is harder to analyze compared to carbonate lithology, the CT scan profile was plotted to illustrate the acid performance across the core. Figure 25 represents the base case, acidizing with 15 wt% HCl. The figure represents the CT number versus the distance from the inlet. The lower CT number indicates enhancement in the porosity, while the higher indicate damage.

51

The CT profile for the acid showed enhancement in the porosity in the first two third section of the core where the acid penetrate, and damage in the last section. Sandstone acidizing with HCl can cause problems related with clays and fine migration, as well as acid induced sludge. In an effort to separate the sludge related damage from lithology problem, the core was first dried to evaporate the brine and CT scanned. The first dry post acid gave identical behavior as the acid but with lower CT number due to the brine elimination. The core then saturated with 2:1 Toluene :IPA to dissolve any sludge form within the core, the core then dried and CT scanned again. The profile in the second dry was identical to the acid and first post acid dry. This indicates that the damage was not related to sludge, but more to the fact that the HCl aggressively attacked the clay, which represent around 6% of the core.

The CT profiles for the experiments with dispersant B and coconut oil exhibited similar behavior. The remaining figures can be found in the Appendix.

Case IV: Carbon Tan Sandstone Acidizing with 20 wt% GLDA

In case IV, the base experiment was stimulate with 20 wt% HCl and 1 vol.% corrosion inhibitor without adding any dispersants. The second was using the same system and adding dispersant b at 300 ppm while the third experiment used coconut oil at 300 ppm as anti-sludge agent. In all the three experiments, oil was injected first until stabilization pressure was reached, followed by one pore volume of acid. One pore volume with 5 wt% KCl brine was used to flush the stimulation fluid.
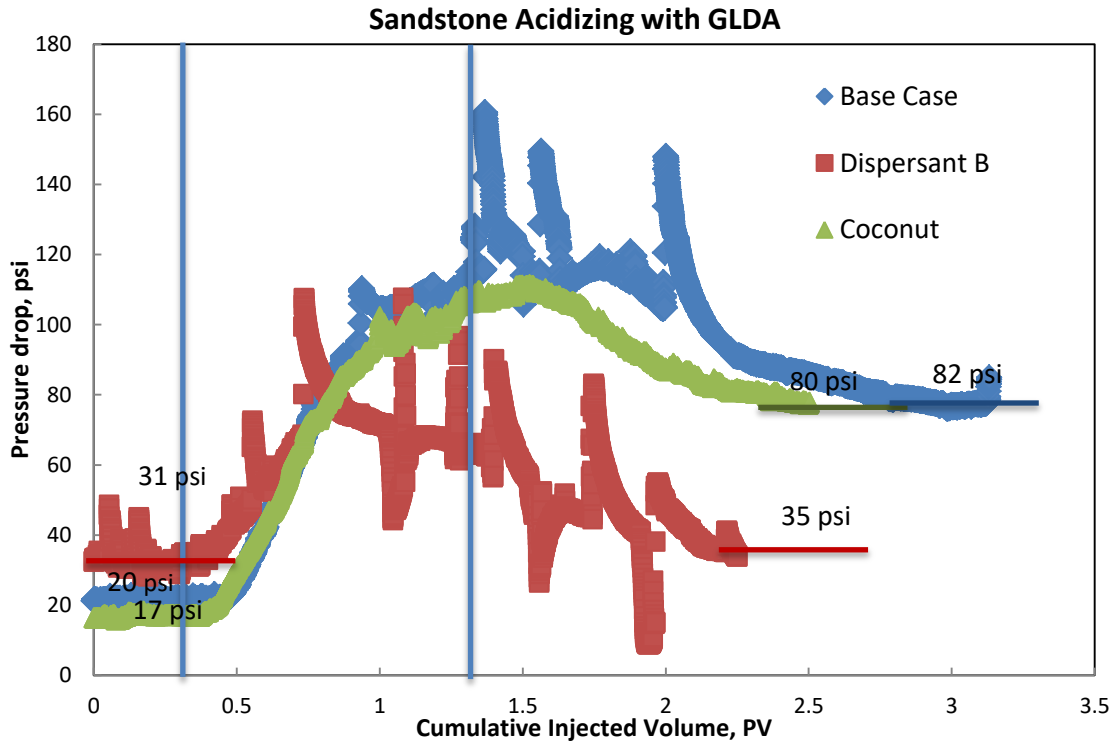
Figure 26: Pressure drop vs. cumulative injected PV for Carbon tan sandstone acidizing with 20 wt% GLDA

In Figure 26, the pressure drop analysis indicates the same as the previous case. The treatment failed to enhance the porosity of the sandstone cores. The least damage was noticed in the experiments with dispersant B. The interaction between GLDA and clays in sandstone is very interesting research that showed to reflect the damage resulted after the treatments.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The first part of the study examined the use of the bio-oil as asphaltene dispersants under the reservoir temperature, the following conclusions were withdrawn:

- The colloidal instability index (CII) was measured for the crude oil and found to be greater than 0.7, indicating definite asphaltenes instability.

- Vegetable oils have special structures and functional groups (ester and alcohol) that interact with asphaltene and prevent precipitation.

- Pairing the DAO with commercial dispersants is a cost effective option as it may lower the chemical concentration needed to peptize asphaltenes.

- Combining DAO with 500 ppm coconut oil at reservoir temperature can help disperse any asphaltene aggregate.

- Using vegetable oils as inhibitors is economically acceptable, as well as being environmentally friendly.

- DLS measurements showed the reduction of asphaltene particle size with vegetable oils and the addition of DAO.

- UV-vis readings illustrated that the performance of vegetable oils after a week are comparable to the chemical dispersants.

The second part of the study was aimed to employ the tested bio-oil in matrix acidizing as Anti-sludge agent. The following conclusions were observed:

- Sludge test results showed that the oil has a tendency to sludge with higher concentrations of HCl and iron.

- The chemical Dispersant B completely prevents the sludging of the oil, while the coconut oil reduces it by 50% when added to 15 wt% HCl.

- GLDA didn't create any sludge when tested with the oil.

- For carbonate rocks, using the coconut oil and Dispersant B as an anti-sludge agent improves the wormhole propagation when added to 15wt% HCl.

- Coconut oil has a comparable performance to Dispersant B with 15 wt% HCl in limestone (PVBT = 0.4) while without dispersants was 0.9.

- Adding coconut oil to GLDA reduces the injected pore volume to breakthrough to 3.6 while Dispersant B was 4.4.

- The chemical dispersant, when added to GLDA, creates the least damage.

- The coconut oil outperformed the chemical dispersants when added to HCl.

- The sludge effect analysis is very complicated in sandstone acidizing due to clays and fines migration.
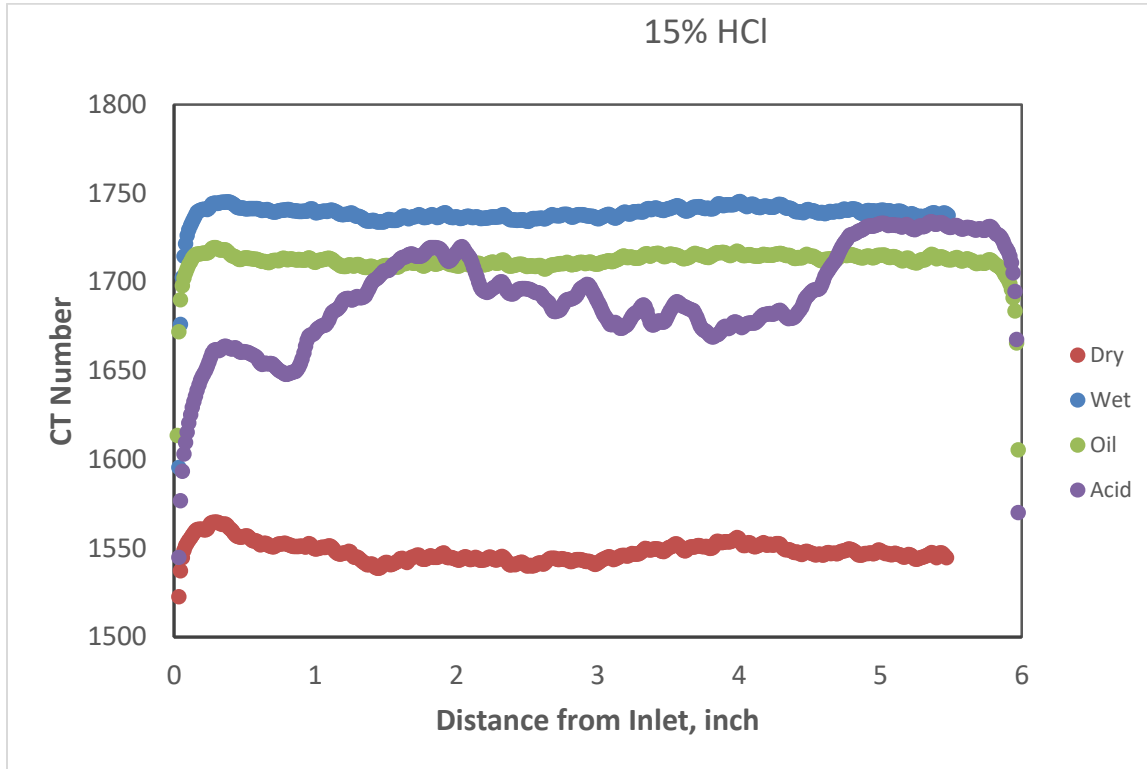
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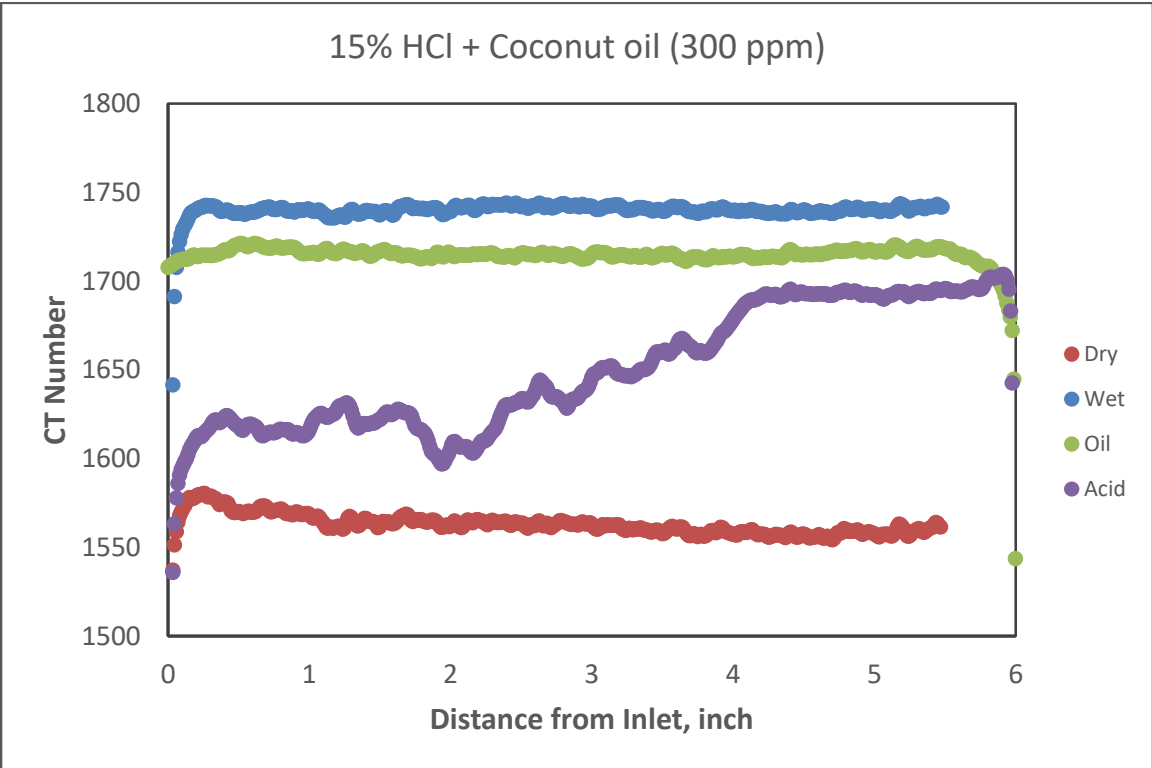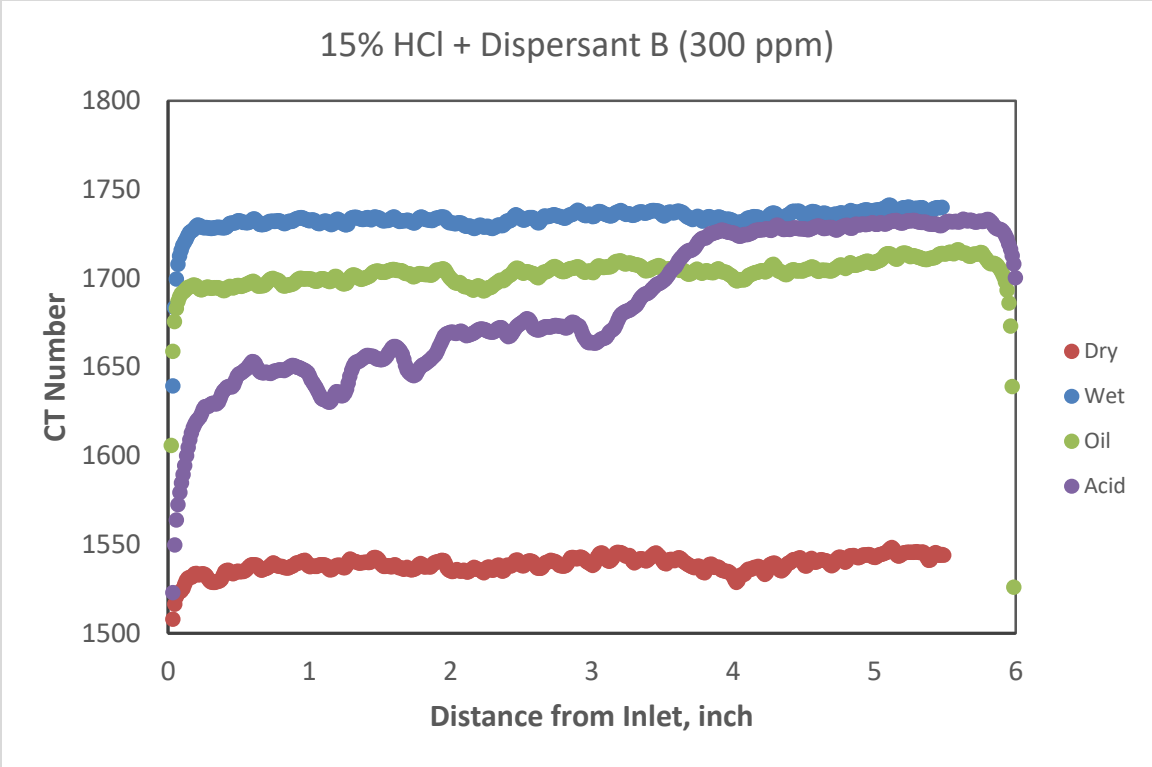
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APPENDIX

Case III: Carbon Tan Sandstone Acidizing with 15 wt% HCl

15% HCl + Dispersant B (300 ppm)

15% HCl + Coconut oil (300 ppm)

Case IV: Carbon Tan Sandstone Acidizing with 20 wt% GLDA

20% GLDA + Coconut oil (300 ppm)