



A Comparative Study of Various Agro-waste based Oil and Synthesized Derivatives as Asphaltene Inhibitors

By

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Of the Requirements for the
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School of Mineral Resources Engineering
Technical University of Crete
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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the School of Mineral Resources Engineering

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In partial fulfillment of the requirement for the
Masters of Science (Hons) in Petroleum Engineering

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October 2022

CERTIFICATION OF ORIGINALITY

This is a certification that the work submitted for this project belongs to me, that it was not done by anybody else (apart from those mentioned in the references and acknowledgements), and that I am accountable for it.

MOSES EKENE OBASI

ABSTRACT

In order to avoid the deposition of asphaltenes, this study looked at the use of chemical additives based on the liquid derived from a variety of agricultural goods, such as cashew nut shells, palm kernel nuts, coconut, jojoba, and castor. Since these chemicals have structural similarities with those shown to be effective peptizing agents for asphaltenes, we studied their potentials as stabilizing agents for asphaltenes contained in the crude oil. They were further evaluated for performance against chemical inhibitors including Toluene and Salicylic Acid. Generally, the chemical inhibitors performed well in all concentrations for the whole period of time, however, Toluene performed best even among agro inhibitors. Notwithstanding, oil from palm kernel nut performed best among agro inhibitors. Oil from mustard seed had the least performance which on average increased asphaltene precipitation and further deposition. Results also showed that inhibition capability is strongly determined by concentration of selected inhibitors. For some agro solvent like Jojoba oil, Coconut oil and Castor oil; an increase in concentration prompted increase in the propensity to inhibit asphaltene formation while in others like Mustard seed oil, an increase in inhibition concentration resulted to an increase in precipitation formation. CNSL did not perform as expected according to documented literature because Coconut oil and Palm kernel oil outperformed it towards inhibiting asphaltene precipitation based on volume.

DEDICATION

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

ACKNOWLEDEMENT

I would like to praise God for His blessing I managed to complete this Project. I would like to thank all my professors, for their continuous encouragement, guidance, and support throughout this program. Also I would like to express my sincere gratitude to my friends and colleagues for making my time a great experience most especially to Dimosthenis Telemenis and Renata Kanakaki for all the guide, help, and efforts offered. I would like to express my gratitude to Dr. Obinna Ofoegbu and laboratory technician Dr. Ogoli both from the University of Agriculture Makurdi for their cooperation, guidance, assistance and providing all the information, equipment and support needed to complete my project.

NOMENCLATURE

CNSL	Cashew Nut Shell Liquid
CPKO	Palm Kernel Oil
CCNO	Coconut Oil
CSTO	Castor Oil
JOJO	Jojoba Oil
MDSO	Mustard Seed Oil
SFLO	Sunflower Oil
SYCA	Salicylic Acid
TOLU	Toluene

Contents

CERTIFICATION OF APPROVAL	i
CERTIFICATION OF ORIGINALITY	ii
ABSTRACT.....	iii
DEDICATION	iv
ACKNOWLEDEMENT	v
NOMENCLATURE	vi
LIST OF FIGURES	x
LIST OF TABLES	xi
Chapter 1	1
INTRODUCTION	1
Study Background	1
Problem Statement	2
The Study's Goal	3
The Study's Scope	3
The Importance of the Study	3
Chapter 2.....	4
LITERATURE REVIEW	4
Asphaltenes	4
Asphaltene Properties:.....	5
Asphaltene Stabilization:.....	6
Asphaltene Precipitation	7
Asphaltene Test Methods	8
Implications of Asphaltene Deposition	8
Agro-waste Oil.....	11

Composition of CNSL.....	11
Reactivity of CNSL.....	13
Oil Extraction Method	13
Processing Cashew Nut Shells (CNS).....	14
Chapter 3.....	15
MATERIALS and METHODS.....	15
Raw Materials	15
Chemicals and Reagents.....	15
Experiment.....	15
Methods.....	15
Pretreatment	15
Oil Yield Determination.....	16
Characterization of Green Liquid/Extracts	16
Chemical Analysis.....	16
Asphaltene Processing	17
Stabilization Test	18
Experimental Model.....	19
Activity Log	20
Experimental Model and Detailed Processes	21
Project Timeline	22
Chapter 4.....	23
RESULTS AND DISCUSSION	23
Physiological Properties of Agro Inhibitors.....	24
Physiochemical Properties of Agro Inhibitors	25
Properties of Non-Agro Inhibitors	26

Deposit Level Test for blank	27
Asphaltene Dispersant Test (ADT)	27
Chapter 5	33
CONCLUSION and RECOMMENDATION.....	33
Conclusion	33
Recommendation and Future Work	34
IMAGE GLOSSARY	35
References	37

LIST OF FIGURES

	Page
Figure 1. Asphaltene molecular structures.....	5
Figure 2. Pressure/Temperature dependence of asphaltene stability in crude oil.....	6
Figure 3. Pressure/Composition dependence of asphaltene solubility in crude oil	8
Figure 4. Chemical composition of CNSL	12
Figure 5: Conversion of anacardic acid to cardanol	14
Figure 6: Asphaltene Dispersion test	18
Figure 7a: Experimental Model Overview	19
Figure 7b: Experimental Activity Log.....	20
Figure 8: Deposition Level Test	28
Figure 9: Deposition Level Test	29
Figure 10: Inhibition Efficiency.....	31
Figure 11: Inhibitor Residue Level	32

LIST OF TABLES

	Page
Table 1: Experimental Model and Detailed Processes	21
Table 2: Overall Project Timeline.....	22
Table 3: Properties of Crude oil.....	23
Table 4: Properties of solvent	23
Table 5: Physical properties of agro inhibitors	24
Table 6: Chemical properties of agro inhibitors	26
Table 7: Properties of chemical inhibitors	26
Table 8: Blank test deposit level.....	27
Table 9: Solvent deposit level.....	28

Chapter 1

INTRODUCTION

Study Background

Crude oils are a mixture of many chemical components, and their overall properties vary from well to well. Production equipment may become polluted or covered with materials like coke, asphaltenes, wax, stable emulsions, or inorganic particles from the oil well to the refinery (Otzisk & Kempen, 2009). For oil production companies and refiners, this contamination is a common problem, and on occasion, this causes process units to be shut down for mechanical cleaning, resulting in considerable losses or halting output. There are strong incentives to further reduce these depositions since doing so would increase productivity and reduce operational costs.

Asphaltene is defined as crude oil precipitation that is produced when an uncontrolled amount of n-heptane is present in the crude oil, thus, creating fluid particles that are soluble in benzene and toluene. Asphaltene does not crystallize, making it difficult to determine the individual components and composition because the molecules are extremely complex, containing hundreds of atoms (Basir, 2014). As the molecules aggregate, asphaltene begins to flocculate and grow in size to become precipitation. Resin, which surrounds the entire asphaltene, acts as a stabilizer which prevents the asphaltene from flocculation (Maruska & Rao, 1987; Madhi, Kharrat, & Hamoule, 2018). This is due to steric repulsion with another resin layer that surrounds the asphaltene molecule (Leontaritis & Mansoori, 1988). Asphaltene deposition is influenced by several factors like pressure-temperature reduction (Kaiser, 2020), CO₂/CO₂-Water Alternating Gas (WAG) injection (Choiri, 2010; Basir, 2014), acidizing and stimulation techniques (Jacobs & Thorne, 1986) among others. Plugging of tubing and surface facilities, permeability reduction/impairment (Minssieux, 1997) and wettability alteration are results of asphaltene deposition (Madhi, Kharrat, & Hamoule, 2018)

Maintaining the asphaltic fraction in a stable or well-peptized condition is advantageous for all oil production, treatment, and mobility processes (Moreira, Lucas, & Gonzalez, 1999). There are several techniques and methods for removing asphaltene, including adding dispersants and inhibitors, using steam and hot fluid, cleaning with solvent, and removing asphaltene mechanically

and ultrasonically (Ramos, Haraguchi, Nostrispe, Mohamed, & Mohamed, 2001). Chemical solvents that are readily accessible on the market are frequently used to cure asphaltene. However, the majority of chemical solvents now in use have negative side effects on both the environment and those using them (Basir, 2014).

When used industrially, alkylphenols with a medium-to-long hydrocarbon tail found in many vegetable oils function admirably as stabilizers for asphaltene (Otzisk & Kempen, 2009). According to Gonzalez and Middea (1991), the inclusion of amphiphiles has decreased asphaltene's adsorption on mineral surfaces. Among other things, the chemical composition of cashew nut shell liquid (CNSL), Coconut (CCNO), and crude palm kernel oil (CPKO) among others contains polar phenol groups that can interact with the functional groups of the asphaltene particles quite strongly. Additionally, it was noted that the presence of extra polar groups in the aromatic ring, particularly OH, may enhance the stabilizing capacity (Gonzalez & Middea, 1991; Moreira, Lucas, & Gonzalez, 1999). Furthermore, the side-chain unsaturation enables the addition polymerization of polymers with a range of free phenol groups in a single molecule (Moreira, Lucas, & Gonzalez, 1999). Theoretically, this offers a compelling opportunity to improve the capacity of phenolic compounds to disperse asphaltic fractions.

Problem Statement

Asphaltene deposition has an impact on petroleum industry productivity. Due to the inefficient procedure, physical removal of asphaltene deposition is not a good alternative. Asphaltene problems are frequently solved with chemically based asphaltene inhibitors. However, these substances are poisonous, non-biodegradable, combustible, and have negative side effects on both the environment and the individuals who touch them (Basir, 2014). To offer an alternative to current inhibitors, new biodegradable and environmentally acceptable asphaltene inhibitors with high solubility rates are required.

The Study's Goal

The goals of this study are:

- Take advantage of the chemical compositions and characteristics of phenolic compounds Cashew nut shell liquid (CNSL), Jojoba oil (JOJO), Coconut oil (CCNO), Sun flower oil (SFLO), Mustard seed oil (MDSO), Castor oil (CSTO) and crude palm kernel oil (CPKO) as asphaltene inhibitors on Nigerian crude.
- To characterize the properties of the extracted inhibitor.
- To compare the effectiveness of selected phenolic compounds to commercially available chemical inhibitor, like Toluene (TOLU) and Salicylic Acid (SYCA).

This, however, will be limited to static conditions to limit control variables and ensure result consistency due to limited samples.

The Study's Scope

The goal of this dissertation is to learn more about the conceptual understanding of asphaltene and inhibitors. Theory and information can be found in past research, academic publications, and reference books. The following criteria were used to pick this topic: promoting the use of low-cost renewable resources (agricultural byproducts) in value-added end products; all compounds chosen are amphiphile, phenolic, environmentally friendly, and biodegradable.

The Importance of the Study

This study builds on earlier research and advances knowledge of the interactions between asphaltene and agro-based inhibitors. It will give insight into how asphaltene is deposited, which might aid in improving workflow, output, and cost of manufacturing. As a result, the amount of time equipment has to be shut down for mechanical cleaning will be reduced. Additionally, it will be helpful for all stages of oil production, processing, and transportation.

Chapter 2

LITERATURE REVIEW

Asphaltenes

Asphaltenes are a group of heavier, nonvolatile, dark-colored, and more polar chemicals found in crude oil that are insoluble in *n-heptane*, *n-pentane*, or *n-hexane* (Choiri, 2010). They precipitate when an excess is found in the crude oil. Aromatic solvents such as toluene or benzene, on the other hand, are good solvents for asphaltenes. From an organic chemistry standpoint, they are large molecules with side branches made up of polyromantic and heterocyclic aromatic rings. Asphaltenes originate from the complex molecules found in living plants and animals, which have only been partially broken down by the action of temperature and pressure over geologic time. The majority of the inorganic components of crude oil, such as sulfur, nitrogen, and metals like nickel and vanadium, are carried by asphaltenes. A small quantity of asphaltene, which is suspended by microscopic colloidal particles, is present in all oils (Bai & Bai, 2018).

Structurally, asphaltenes are often desorbed into a compact stack of many thin sheet-like layers. They are represented by folded alkane chains in polynuclear aromatic layers, which come together to form a micelle, a solid structure. Some rings may be nonaromatic, but many are fused and share at least one side (Kaiser, 2020). The condensed polyaromatic rings contain aliphatic and naphthenic side chains as well as sulfur, oxygen, and nitrogen as heteroelements or functional groups. Madhi, Kharrat, & Hamoule, (2018) used asphaltene dispersant tests and core flood to evaluate various inhibitors in static and dynamic conditions, and their results revealed distinguished mechanisms for asphaltene stabilization/dispersion and the influence of additional side group (OH) on the inhibition power of the inhibitor. Mechanisms identified include hydrogen bonding of functional groups (OH, NH, COOH) (Siddiqui, 2003), pep and acid-base interaction caused by heteroatoms (N, O, and S) and organometallic constituents (Ni, V, Fe) in crude oil (Maruska & Rao, 1987).

Additionally, changes in chemical inhibitor concentration, such as increasing it, can result in particle formation and a decrease in asphaltene stabilization (Madhi, Kharrat, & Hamoule, 2018). Polymers with the same functional group as asphaltene stabilizing-agents have been tested in various literature and results show that most of them are insoluble in crude oils and do not act as good inhibitors.

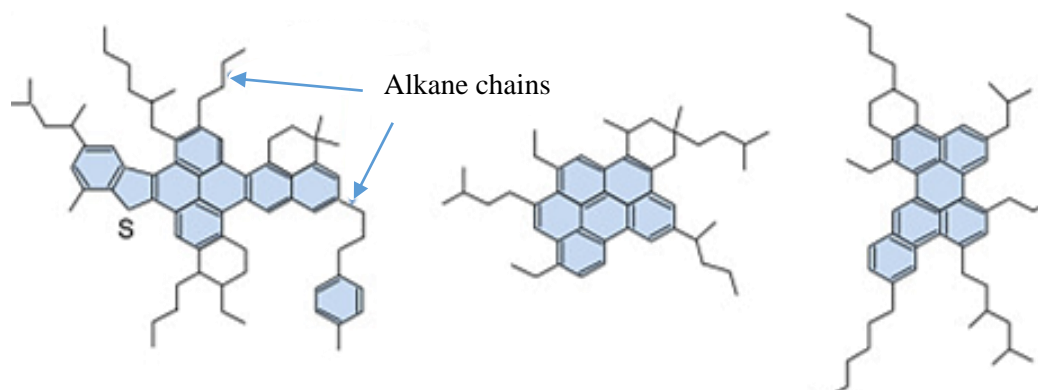


Figure 1. Asphaltene molecular structures (Kaiser, 2020).

Asphaltene Properties:

The industry currently has a limited understanding of asphaltenes, and little is known about their chemical characteristics because they do not crystallize and cannot be studied. Asphaltenes in crude oil or aromatic solvents may, under the right circumstances, be thought of as dissolving as a stable liophobic colloidal dispersion or dispersing as a liophilic (macromolecular) colloid (Moreira, Lucas, & Gonzalez, 1999). Most of the color in crude oil is added by asphaltenes and resins. Asphaltene particles have a strong desire to stick together and to connect with one another. The vast range of size distribution suggests that asphaltenes exist in both dissolved and colloidal and/or micellar forms to varying degrees. Asphaltenes are also susceptible to electrostatic interactions and shearing pressures. Asphaltenes tend to aggregate and may go through phase separation due to their higher polarity, which makes them less hydrophobic than other petroleum fractions (Talbiersky, polaczek, Ramamoorthy, & Shishlov, 2009).

Asphaltene Stabilization:

Stabilizing asphaltene particles can effectively and affordably prevent unwanted asphaltene aggregation or precipitation (Otzisk & Kempen, 2009). The ratio of asphaltene to stabilizing components like aromatics and resins in the crude determines how stable asphaltene is. The main factor affecting asphaltene's stability is pressure (Bai & Bai, 2018). The volume proportion of aliphatic components rises as the well's pressure falls below bubble point. Certain acids, completion fluids, and high temperatures employed in crude oil refining can also destabilize asphaltene. When the oil's aliphatic component reaches a certain level, asphaltenes start to flocculate and precipitate (Bai & Bai, 2018; Kaiser, 2020).

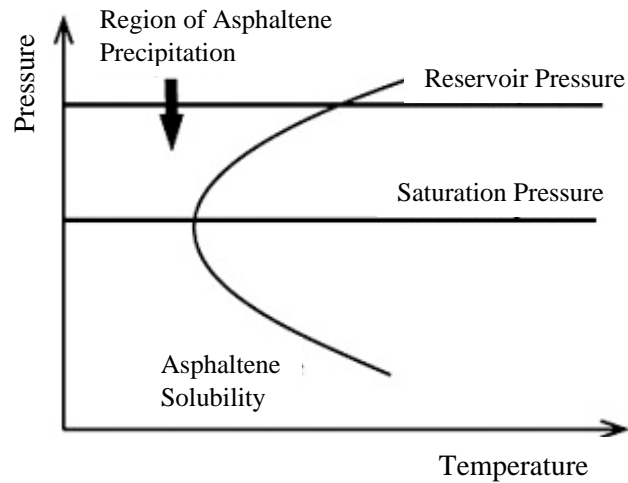


Figure 2. Pressure/Temperature dependence of asphaltene stability in crude oil (Kaiser, 2020)

The above figure depicts how temperature and pressure affect the stability and deposition of asphaltene. Asphaltenes are unstable at low temperatures on the left side of the curve because of a discrepancy in the interaction energies of the two molecules, asphaltene and crude oil (Herve, Jean, Simon, & Sylvain, 2006). In contrast, asphaltenes are stable on the right side of the curve because pressure depletion would increase the relative volume fraction in crude oil components and the solubility parameter difference between asphaltene and crude oil (Bai & Bai, 2018). At bubble point pressure, the solubility difference is greatest. Asphaltene will become soluble once again and tend to redissolve when pressure falls below bubble point pressure and light crude oil evaporates, although the process can be sluggish and inefficient (Basir, 2014; Kaiser, 2020).

Asphaltene Precipitation

A potential issue during oil production and transportation is the precipitation of asphaltenes inside the production system. The molecular weight, aromaticity, and polarity of an individual crude are frequently associated with the possibility of asphaltenes precipitating from that crude (Kaiser, 2020). The saturation of asphaltene in crude oil, however, is a critical aspect in deciding if asphaltene would cause any problems. If the asphaltenes are not completely saturated in the crude oil, they will be stable and no precipitation will occur (Guo, Song, Ghalambor, & Lin, 2014). On the other hand, asphaltene precipitation will occur if they are heavily saturated with crude oil.

During oil production, there may be significant temperature and pressure changes between the production pipeline and the oil reservoir. Fluid composition can alter dramatically throughout manufacturing, just as fluid pressure can. When oil pressure drops below the bubble point, for instance, causing gas to separate from the oil, or when enhanced oil recovery (EOR) techniques are used, or even during processing, the composition of fluids might alter (Guo, Song, Ghalambor, & Lin, 2014). Asphaltene saturation in crude oil can change from undersaturated to supersaturated throughout any process if the pressure, temperature, and composition change, which will also result in precipitation.

When the pressure is above the bubble point, asphaltene solubility is relatively constant, but when the pressure decreases and the density of the crude oil rises due to oil expansion, asphaltene solubility also rises, as shown in Figure 3. Asphaltene solubility falls to its lowest point when the pressure approaches the bubble point. Below the bubble point, the solubility of asphaltene increases as the oil density rises and gases begin to emerge from the oil.

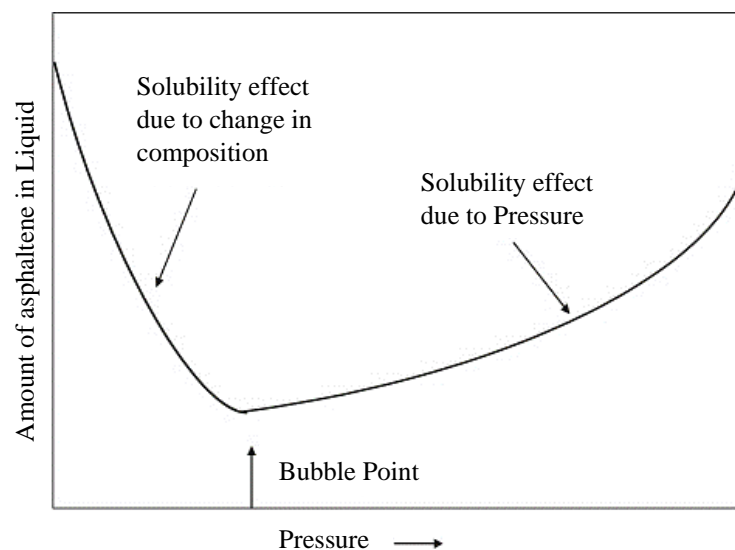


Figure 3. Pressure/Composition dependence of asphaltene solubility in crude oil (Guo, Liu, & Tan, 2017)

Asphaltene Test Methods

A crude oil's asphaltene concentration ought to be known. Numerous analytical methods and tools can be used to analyze asphaltene, including nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared spectroscopy (FTIR), X-ray analysis, mass spectrometry, diffusion methods (Taylor dispersion, Time-resolved Fluorescence Depolarization (TRFD), and Fluorescence Correlation Spectroscopy (FCS), as well as elemental analysis (Otzisk & Kempen, 2009). In the petroleum industry, ASTM D2007-80 is a commonly used standard procedure for separating asphaltenes from crude oils. By mixing n-heptane with the crude oil, asphaltene may be produced for the experiment (Basir, 2014).

Implications of Asphaltene Deposition

Asphaltene precipitation during oil extraction and processing is a serious problem. Asphaltene starts to agglomerate and flocculate as resins weakens. Damages from the precipitation and deposition of asphaltene during manufacture is significant (Basir, 2014). The bulk of these

problems are contamination-related and can block downstream equipment, including valves, strainers, process pumps, chokes, filters, tubing, separators, and other equipment in the refinery. Additionally, vacuum bottom heat exchangers, crude preheat trains, and vacuum distillation units are typically impacted by asphaltene blockage. As a result, chemical or mechanical cleaning is essential; otherwise, throughput must be decreased, which lowers productivity. The financial repercussions are significant and can be quite pricey. The majority of problems are caused downstream by mixing or extreme heat. In the upstream, the wellbore and wellbore formation are mostly at risk, with the wellhead or flowline occasionally being affected as well. Depositions of asphaltene can reduce or terminate production and, in extreme situations, require well redrilling.

Asphaltene Control

Physical removal of deposits, solvent washes using coiled tubing, and treatment with dispersing chemicals are some of the techniques utilized to address issues with asphaltene material (Junior, Ferreira, & Ramos, 2006). In other cases, they are frequently controlled by inhibitors before becoming unstable and flocculating. Controlling remediation following instability is even more difficult (Kaiser, 2020). Chemical treatment (asphaltene inhibitor) is the most common and effective method of management, but much of the underlying chemistry is still unknown (Kaiser, 2020).

Commercial inhibitors that are widely used include Triton X-100, Sodium Dodecyl Sulfate, Cetyl Trimethyl Ammonium Bromide, and Duo Benzene Sulphonic Acid (DBSA). Naphthalene, Benzene, Benzoic Acid, Salicylic Acid, Xylene, and Chlorate are among the chemical inhibitors employed for asphaltene inhibition (Basir, 2014; Madhi, Kharrat, & Hamoule, 2018). Few operators employ these inhibitors, most likely due to the expense and unpredictability of their use (Bai & Bai, 2018). Additionally, due to concerns about these inhibitors' extremely low flash point, significant acute toxicity, volatile emission, flammability, and biodegradability, government laws restrict their usage in oilfields (Basir, 2014). Additionally, according to published studies, amphiphile and phenolic compounds have the power to inhibit asphaltene. Another strategy for reducing contamination, particularly in the downstream sectors, is to use common sense to prevent contamination from occurring. Asphaltenes do not melt at temperatures beyond 300–400 °C; instead, they disintegrate into carbon and volatile parts.

Environmental Friendly Inhibitor

Environmentally safe asphaltene inhibitors are promoted as alternatives to the harmful inhibitor solvents already in use. Vegetable oils have been studied and have the ability to stop the deposition of asphaltene. Vegetable oils are thought of being oil-soluble amphiphiles that are capable of adhering to asphaltene. The alcohols, fatty acids, and amines group in vegetable oils, which mostly interact with asphaltene through hydrogen bonding, are responsible for its dispersing ability. The fatty acids include acidic protons that can interact with metal ions or create hydrogen bonds with the hydroxyl groups in asphaltene, disrupting the process of asphaltene aggregation. Vegetable oils are also commonly accessible and reasonably priced. Utilizing this will, in essence, make handling and operation easier than when using chemical solvents (Basir, 2014).

Aromatic hydrocarbon groups are joined to hydroxyl groups to form phenolic compounds (-OH). Due to their antioxidant effects and comparable chemical structures to amphiphile, a stabilizing agent for the problem of asphaltene precipitation, these compounds are well-liked (Basir, 2014). According to published research, coconut oil outperforms other oils, such as Brazil nut oil and Jamaican essential oil, in terms of inhibiting the production of asphaltene. The effectiveness of CNSL and certain oil derivatives in terms of inhibiting asphaltene has also been promising. These oils' phenolic composition makes it feasible to employ them as asphaltene inhibitors.

Vegetable oils are chosen because:

- It is necessary to create new solvents with a high solubility rate to replace the current ones.
- When compared to organic acids, vegetable oils perform well.
- It is more affordable than commercial dispersants and widely accessible.
- The paraffin deposit in oil wells is removed using a triglyceride derived from vegetable oil.

This is feasible because the 12 to 24 carbon fatty acid ester solvent contained in the vegetable oil improves the surface area of contact and regulates the hydrocarbon's viscosity, hence improving the cleaning action.

Agro-waste Oil

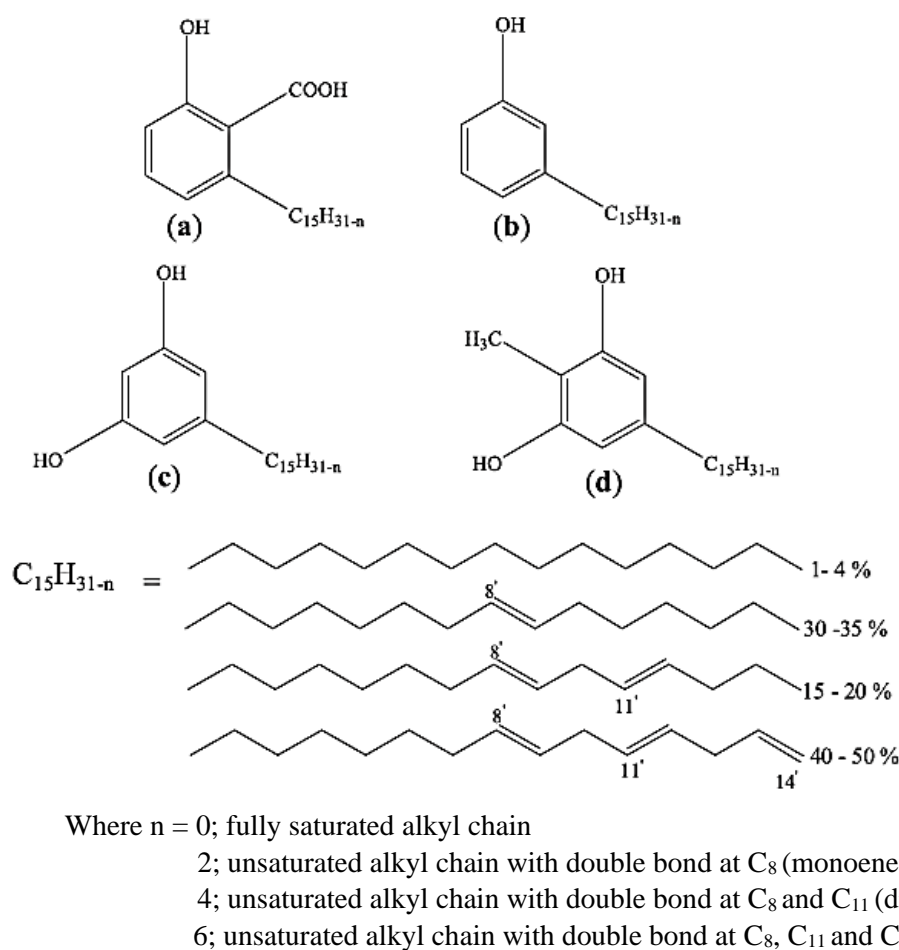
The cashew nut shell (CNS), an agricultural waste, includes certain naturally occurring phenolic compounds or liquid (CNSL), with long linear alkyl chains comprising 15 carbons and substituted aromatic rings at the meta position. These substances are valuable as versatile and prized raw ingredients for the creation of polymers (Bhunja, Basak, Chaki, & Nando, 2000; Talbiersky, polaczek, Ramamoorthy, & Shishlov, 2009; Ike, Ibezim-Ezeani, & Akaranta, 2021). The amount of nutshell oil present in a raw cashew nut is thought to be around 30%. (Akinhanmi, Atasie, & Akintokun, 2008; Nasrollahzadeh, Sajadi, Sajjadi, Issaabadi, & Atarod, 2019). Because of their many reactivity sites, which make them appealing for several chemical reactions, decarboxylated CNSL molecules are challenging to synthesize. Some of the reaction sites included in this variant are the ortho and para positions at the aromatic nucleus, the phenolic hydroxy group, and the double bonds in the side chain (Talbiersky, polaczek, Ramamoorthy, & Shishlov, 2009).

The dark brown color, odor, percentage yield, choke, specific gravity, boiling point, refractive index, density, moisture content, viscosity, and chemical characteristics like free fatty acids, acid value, ester value, percentage brix, saponification value, pH, ash content, and FTIR spectra have all been reported by authors (Moreira, Lucas, & Gonzalez, 1999; Idah, Simeon, & Mohammed, 2014; Kyei, Akaranta, Darko, & Chukwu, 2019; Ike, Ibezim-Ezeani, & Akaranta, 2021). The majority of physical and chemical characteristics were similar across publications.

Composition of CNSL

Cashew nut shells (CNS) can contain up to 30% cashew nut shell liquid (CNSL), despite the fact that the composition of a specific CNSL is dependent on the method used to extract the material from the cashew nut shell (Moreira, Lucas, & Gonzalez, 1999; Nasrollahzadeh, Sajadi, Sajjadi, Issaabadi, & Atarod, 2019; Ike, Ibezim-Ezeani, & Akaranta, 2021). A thorough analysis of the individual components of CNSL reveals that its main constituents are anacardic acid (which accounts for 70% of the raw material), cardanol (18%), cardol (5%), and 2-methylcardol (7%) in that order (Moreira, Lucas, & Gonzalez, 1999; Talbiersky, polaczek, Ramamoorthy, & Shishlov, 2009; Ike, Ibezim-Ezeani, & Akaranta, 2021).

The chemical structures of these phenolic compounds are very similar to those of the amphiphiles investigated as asphaltene-stabilizing agents (Moreira, Lucas, & Gonzalez, 1999; Junior, Ferreira, & Ramos, 2006). Additionally, side-chain unsaturation makes it possible to produce polymers by addition polymerization that contain a variety of free phenol groups in a single molecule, which in theory seems like a promising way to increase how effectively phenolic compounds disperse asphaltic dispersions (Moreira, Lucas, & Gonzalez, 1999; Ike, Ibezim-Ezeani, & Akaranta, 2021). When heated or in the presence of radicals and certain ionic initiators, this polymerization takes place (acids, metal salts, oxides) (Moreira, Lucas, & Gonzalez, 1999; Taiwo, 2015).



(a) anacardic acid, (b) cardanol, (c) cardol and (d) 2-methylcardol

Figure 4. Chemical composition of CNSL (Ike, Ibezim-Ezeani, & Akaranta, 2021).

Reactivity of CNSL

CNSL may be regarded as a multifunctional and prized raw material for the manufacturing of polymers (Akinhanmi, Atasié, & Akintokun, 2008). Due to the lengthy C15 alkyl side chain substituted at the meta position with regard to the phenolic hydroxy group, it is challenging to manufacture using conventional chemical methods (Talbiersky, polaczek, Ramamoorthy, & Shishlov, 2009). CNSL has multiple functional groups that can be used for various chemical reactions, including esterification, epoxidation, ethoxylation, alkylation, etc. These groups include; carboxylic acid groups that can be used for decarboxylation and esterification; a meta C15 alkyl side chain that can be used for the metathesis reaction, phenylation, epoxidation, hydrosilylation, and hydrogenation among others; and an aromatic ring that serves as a site for hydrogenation, nitration, sulfonation, halogenation (Bhunia, Basak, Chaki, & Nando, 2000; Talbiersky, polaczek, Ramamoorthy, & Shishlov, 2009; Gandhi, Patel, & Dholakiya, 2012; Ike, Ibezim-Ezeani, & Akaranta, 2021). CNSL can be polymerized using condensation polymerization (Odin, 1991). CNSL exhibits a high propensity for structural change, bringing about desired change, or achieving certain high-value features. Chemical alteration of the hydroxyl group, aromatic ring, carboxylic group, or side chain can result in this structural change.

Oil Extraction Method

According to several studies, several ways have been used to extract oil, such as CNSL, CPKO, and CCNO. However, the extraction efficacy varies depending on the method of extraction used. In essence, three basic extraction techniques, including thermal, mechanical, and solvent extraction, have been created for the extraction of oils. However, additional techniques have also been documented, including pyrolysis (Taiwo, 2015), the use of supercritical carbon dioxide, supercritical water, and ultrasonication, among others (Talbiersky, polaczek, Ramamoorthy, & Shishlov, 2009).

Processing Cashew Nut Shells (CNS)

Heat treatment without distillation can be done by hot extraction at 150–190 °C (Yuliana, Tran-Thi, & Ju, 2012). The heating process decarboxylates the anacardic acid, starting a prepolymerization process which converts the anacardic acid to cardanol or 2-pentadeca-diethyl phenol (figure 4). At even elevated temperatures, this process further results in complete polymerization, which accounts for 20–25% of the polymeric substances in the oil (Ike, Ibezim-Ezeani, & Akaranta, 2021). This process also makes all the allergens inactive (Idah, Simeon, & Mohammed, 2014). Depending on the process used, the decarboxylated CNSL has a typical cardanol content of over 60% and 0% anacardic acid (Moreira, Lucas, & Gonzalez, 1999).

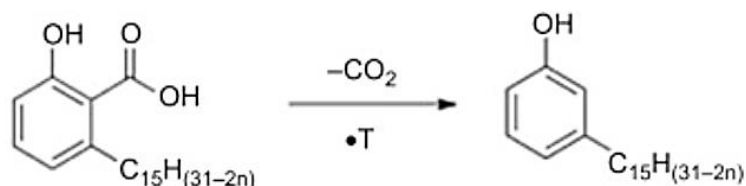


Figure 5: Conversion of anacardic acid to cardanol (Ike, Ibezim-Ezeani, & Akaranta, 2021)

Chapter 3

MATERIALS and METHODS

Raw Materials

The cashew nuts were purchased from Nnsuka, Nigeria while other oils were purchased from a chemical vendor. The crude oil was bought from Rivers, Nigeria and utilized exactly as it is.

Chemicals and Reagents

Acetone, diatomaceous earth, buffer tablets, distilled water, ethyl alcohol, phenolphthalein indicator solution, potassium hydroxide solution (KOH), hydrochloric acid, toluene, and *n*-heptane. All chemicals will be of analytical grade and will be used as received.

Equipment

Oven, centrifuge, centrifuge tube, test tubes, beakers, spatula, pH meter, among others.

Experiment

Deposit level and clarity test.

Methods

Pretreatment

The cashew nuts went through sorting, a complete distilled water washing, and sun drying. Finally, the nuts were fried at 150°C for the oil extraction. The oil was cooled, extracted and stored for one week, to allow complete decarboxylation of the anacardic acid. The resultant mixture was labelled as cardanol.(Idah, Simeon, & Mohammed, 2014).

Oil Yield Determination

At the conclusion of the extraction, the percentage yield of the cashew nut shell liquid was calculated by determining the mass that was removed and expressing that quantity as a percentage of the mass of the sampled cashew nut shell. The following equation was used to compute the percentage yield mathematically (Kyei, Akaranta, Darko, & Chukwu, 2019).

$$\% \text{ Yield} = \frac{\text{mass of extracted oil/liquid}}{\text{mass of cashew nut shell (solid)}} * 100 \quad \dots\dots\dots (1)$$

$$\text{Cashew:} = \frac{390 \text{ g}}{1000 \text{ g}} * 100 = 39\%$$

Characterization of Green Liquid/Extracts

Chemical Analysis

All determinations were made in accordance with the Association of Official Analytical Chemists' (AOAC) standard procedures (AOAC, 2005). pH, acid value, free fatty acid, saponification value, ester value, % glycerin, and ash content are among the chemical characteristics that can be checked (Kyei, Akaranta, Darko, & Chukwu, 2019).

Potential hydrogen (pH) determination: A pH meter was used to determine the sample's pH. The pH meter was calibrated using buffer solution with pH value of 7.0 with BDH buffer tablets.

Acid value and free fatty acid determination: The AOAC standard formula was used to determine the acid value. A hot ethanol solution was used to measure the acid value, and a phenolphthalein indicator was used to neutralize it with potassium hydroxide (0.1 N). Oil was combined with the neutralized ethanol solution (20 ml) (2g). Potassium hydroxide (0.1 N) was titrated into the resultant solution until the colorless solution turned pink. Three titre measurements was taken, with the average titre value being recorded. The Equations below will be used to compute the acid value (AV) and free fatty acid percentage (%FFA).

$$AV = \frac{\text{mL of KOH} * 5.61}{\text{mass of sample}} \quad \dots\dots\dots (2)$$

$$\% \text{ Free fatty acid (FFA)} = AV * 0.53 \dots\dots\dots (3)$$

Saponification value: can be obtained using the technique published by AOAC International (AOAC, 2005). A 250 mL Erlenmeyer flask was filled with 2g of the sample once it has been filtered to remove any contaminants. The flask was then pipetted with 25 mL of a 0.5 N alcoholic potassium hydroxide solution. After an hour of heating in a boiling water bath with a reflux condenser attached, saponification should be complete. After this, it will be confirmed whether the solution is clear. Three drops of phenolphthalein indicator will be added after 10 minutes of cooling, and extra potassium hydroxide will be titrated with 0.5 N hydrochloric acid. Additionally, a blank determination was made by repeating the process but excluding the sample. While the amount of acid used for the blank was recorded as mL of HCl required by the blank, the amount of acid that was utilized was recorded as mL of HCl required by the sample. The equation below can be used to get the saponification value (SV).

$$SV = \frac{56.1 (B-S)*N \text{ of HCl}}{\text{gram of sample}} \dots\dots\dots (4)$$

Where: SV = saponification value
 B = volume of HCl required by blank
 S = volume of HCl required by sample
 N = normality of standard HCl

Determination of ester value: This can be calculated from the saponification and acid values using the equation below.

$$\text{Ester Value (EV)} = \text{Saponification Value (SV)} - \text{Acid Value (AV)} \dots\dots\dots (5)$$

Asphaltene Processing

The asphaltene fraction was precipitated from crude oil by the addition of toluene followed by n-heptane. This mixture was placed in a warm bath for 30 minutes at 40°C to promote the deposition of asphaltene. Next, the mixture was centrifuged at 1500rpm for 10 minutes (Moreira, Lucas, & Gonzalez, 1999). Finally, a photo was taken and using AI, the deposition levels were recorded.

Stabilization Test

The stabilizing effects of agro inhibitors were investigated using two alternative approaches:

(a) Peptization test: To begin, a blank test is made using crude oil and n-heptane. Each centrifuge tube is filled with 1 mL of crude oil, followed by 1ml of toluene and lastly, 10 mL of n-heptane. After shaking the centrifuge tubes for 2 minutes to stir up the asphaltene stability, they will be placed in a water bath set at 40 degrees Celsius for 30 minutes to allow the asphaltenes to precipitate. After 10 minutes of 1500 rpm centrifugation, a clear brown supernatant phase without asphaltene was observed on top of the deposited asphaltene. The level of deposits will be assessed and reported as DBlank.

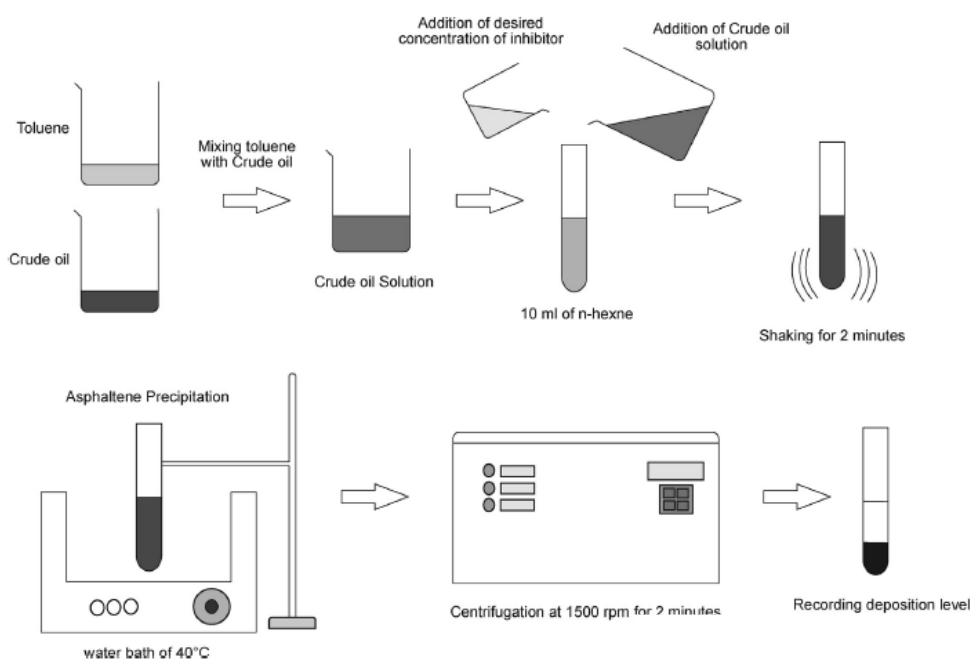


Figure 6: Asphaltene Dispersion test (Madhi, Kharrat, & Hamoule, 2018)

(b) Precipitation test: Using this test, comparisons are made between the various inhibitors. The above procedure (1 ml of crude oil is added to each centrifuge tube, 10 ml of heptane is added into centrifuge tubes, and different concentrations of solvents are added to each of the centrifuge tubes) was repeated again and noted as DTreatment. Different dosages (0.5ml, 1.0ml and 1.5ml) of inhibitors (CNSL, jojoba, castor, sunflower, palm kernel, and coconut oil) will be added to n-

heptane. The following equation was used to compute the quantity of asphaltene reduction detected and the effectiveness of inhibitors in each concentration:

$$\% E = \left(\frac{D_{blank} - D_{treatment}}{D_{blank}} \right) * 100$$

The amount of asphaltenes dispersed was subsequently measured using the procedure described above.

Experimental Model

In summary, the steps that was implord for the project are as follows:



Figure 7a: Experimental Model Overview

Activity Log

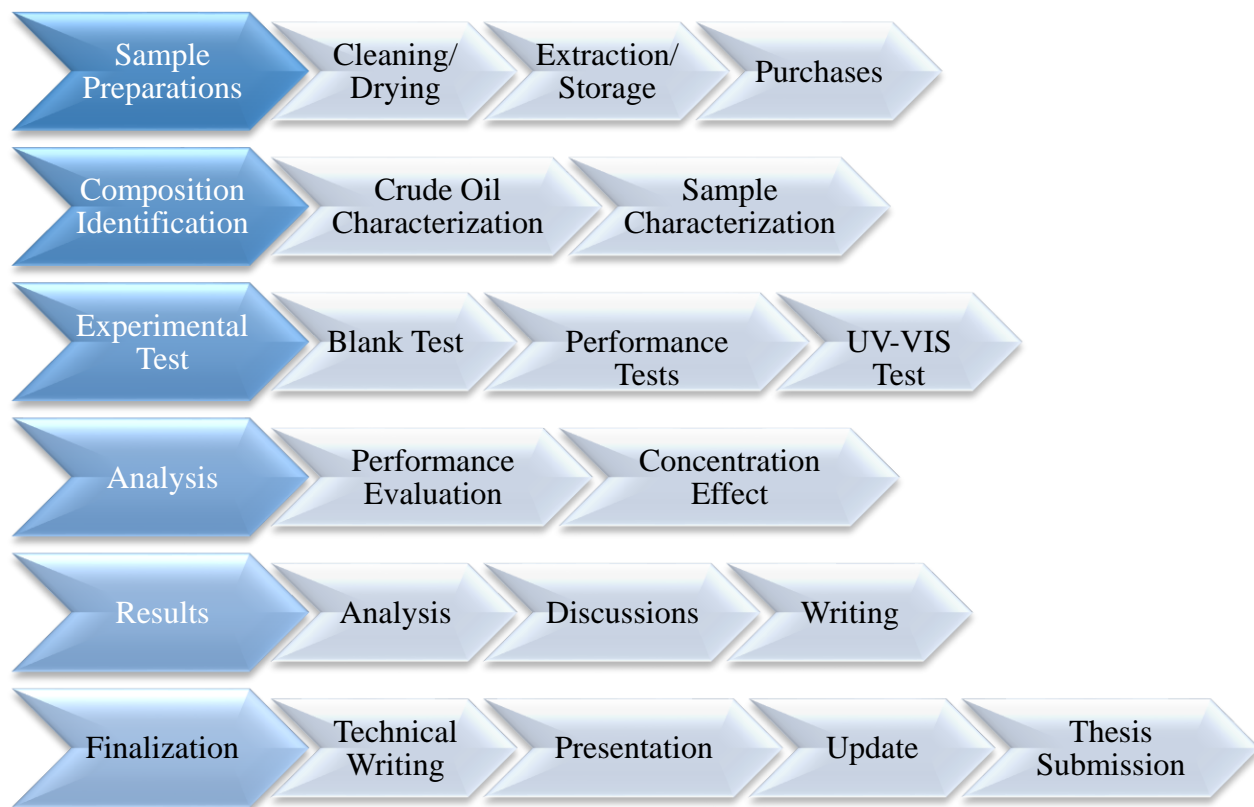


Figure 7b: Experimental Activity Log

Experimental Model and Detailed Processes

Process/Experiment	Method	Equipment
Processing	Cleaning/Drying → Manual	Water & Sun
	Extracting → Lab.	Oven
	Purification → Lab.	Rotary Evaporator
		Reagent
Composition Identification	Various Test → Lab.	Chemical Reagents
	Derivations/Formulas	Test Tubes, pH Meter,
	Computer → Lab.	FTIR machine; Density Meter
Deposition Level	1) Vary Dosage of Oil Vs Constant Volume Heptane Vs Deposit Level at Different Time	Centrifuge Centrifuge tube
	2) Vary Dosage Of Inhibitors Vs Constant Volume Oil Vs Deposit Level at Different Time	

Table 1: Experimental Model and Detailed Processes

Project Timeline

NO	Detail/Work	1	2	3	4	5	6	7	8	9	10	11	12
1	Selection of Topic												
2	Preliminary Research Work												
3	Submission of Extended Proposal												
4	Project Work Continues												
5	Submission of Final Draft												
6	Viva												

Table 2: Overall Project Timeline

Chapter 4

RESULTS AND DISCUSSION

The screening and identification of potential asphaltene inhibitors from vegetable oil, component characterization of procured inhibitors, and performance comparison of green inhibitors with chemical inhibitors (Salicylic Acid, and Toluene) are all goals of the project, and they are all addressed in this results and discussion section. The amphiphile and phenolic compounds found in six plants, including cashew nut shell oil, sunflower oil, castor oil, palm kernel oil, coconut oil, mustard seed oil, and jojoba oil, have been employed as inhibitors.

Crude Oil:

Density ρ (gr/cm^3): $\frac{Final\ mass - Initial\ mass}{Mass\ of\ water}$ NB: all measurement done with 10ml of liquid.

(other results are found in the table of physicochemical properties of agro inhibitors)

$^{\circ}API$:

$$\left(\frac{141.5}{SG}\right) - 131.5 \quad \text{where } SG = \frac{0.84\ (gr/cm^3)}{1\ (gr/cm^3)} = 0.84 \quad \therefore \left(\frac{141.5}{0.84}\right) - 131.5$$

$$= 168.45 - 131.5 = 36.95$$

$^{\circ}API$	ρ (gr/cm^3)	μ (cp) @ 28°C
36.95	0.84	4

Table 3: Properties of Crude oil

Based on API gravity, the crude oil is an intermediate conventional oil.

Materials	MW ($gr/mole$)	ρ (gr/cm^3)	BP $^{\circ}C$
n-hexane	86.18	0.66	69
Toluene	92.14	0.88	110.6

Table 4: Properties of solvent

The solvent properties were obtained as inscribed on the containers of the chemicals. It is observable that no alteration was made to their properties for this study as all procedures were within operation limits.

Physiological Properties of Agro Inhibitors

The pH values of the samples utilized for this experiments were measured using a pH meter. The pH analysis inferred close similarities to that of crude oil, as suppose, to permit miscibility without prompt for change in the chemical state and exposure to corrosion. The boiling point of the samples utilized for this experiments were measured using a thermometer. In general, lower boiling point means decreased particulate emissions, less visible flame, and higher flame temperatures. The boiling point of each sample indicates differences with JOJO having the highest at 380°C, meaning that it has the strongest attractive forces, highest viscosity and surface tension.

		Color	Relative Density (gcm ⁻³)	pH	BP (°C)
CNSL	Result	Dark Brown	0.96	8.9	227
	Literature			7.8	230 ±3%
CCNO	Result	Clear	0.91	9.9	165
	Literature			7-8	177
CPKO	Result	Light Yellow	0.91	9.08	215
	Literature			6.49	220
MDSO	Result	Gold	0.92	8.20	240
	Literature			3.5-6	250
SFLO	Result	Clear	0.91	9.53	115
	Literature			7.38	107
CSTO	Result	Clear	0.70	9.86	197
	Literature			6-8.1	200
JOJO	Result	Light Yellow	0.70	9.99	380
	Literature			8	398

Table 5: Physical properties of agro inhibitors

The Results of pH shows discrepancies between literature and experimental results with an average differential of about 21 %. CNSL showed the least differential of about 12% above literature result while CPKO gave the largest differential with about 28% difference. However, the experimental boiling point of almost all inhibitors were relatively close to the literature results. CNSL also showed the closest match with a -1.3% differential while SFLO had the highest differential (7%). Holistically, differences between the experimental results and literature values can be attributed to several factors including, oil extraction methods, differences in sourcing of materials and conditions surrounding the experiment including relative temperature among others.

Physiochemical Properties of Agro Inhibitors

In simple terms, the acid value is the volume of KOH required to neutralize the free fatty acids present in fat while the free fatty acid accelerates the rate of (OH) decomposition. They are a relative measure of oxidation of unsaturated fat normally formed during decomposition of triglycerides. The higher these values, the higher the chances of oxidation, which means the higher the chances of corrosion and formation of CO₂. According to results, CPKO and MDSO had the highest acid value. Although CNSL shows the highest acid value, this however can be attributed to experimental error as the original color of CNSL was black, as such required excess KOH before a visible pink color change was observed.

Saponification occurs when alkaline mix with cooking oil at high temperatures. In this process, the fatty acid creates a soapy foam layer which holds in vapors and steam exposing the crude oil to further coagulations. Higher saponification value is preferred because the higher this value, the lower the average length of fatty acids. As expected, the saponification value of CNSL was off mark as a result of error from the Acid value. Ester value is used to determine the conversion rate of vegetable oil into consumable fossil. Generally, the higher the ester value, the better the conversion rate. CCNO and CPKO gave the highest saponification and ester value readings indicating the best choice oil for crude oil mixing. JOJO on the other hand had the least readings meaning that it has the highest chance of prompting asphaltene precipitation. Table 7 below contains detailed result of this analysis.

		AV (mg KOH/g)	FFA (mg KOH/g)	SV (mg KOH/g)	EV (mg KOH/g)
CNSL	Result	11.22	5.95	-146	-134.78
	Literature	14.1	6.01	138	
CCNO	Result	2.81	1.49	239.37	242.18
	Literature	0.37		242-263	
CPKO	Result	5.6	2.97	233.41	239.01
	Literature	2.7		240-257	
MDSO	Result	5.6	2.97	176.63	182.23
	Literature	1.5		170-178	
SFLO	Result	4.5	2.37	190.26	194.76
	Literature	0.26	68.5	186-194	
CSTO	Result	2.8	1.48	191.05	193.85
	Literature	0.91-1.14	0.22-0.99	179-187	
JOJO	Result	6.17	3.27	95.52	101.69
	Literature	0.56		92-95	

Table 6: Chemical properties of agro inhibitors

Properties of Non-Agro Inhibitors

The solvent properties were obtained as inscribed on the containers of the chemicals.

Inhibitors	MW (gr/mole)	ρ (gr/cm ³)	BP °C	S (gr/L)
Toluene	92.14	0.88	110.6	Soluble in toluene
Salicylic Acid	138.121	1.443	200	Soluble in toluene

Table 7: Properties of chemical inhibitors

Deposit Level Test for blank

After mixing the crude oil concentrate with n-hexane, the initial deposition level was recorded to be 6.4 ml. This levels did not change even after warm heating in the water bath. Finally, this level was confirmed after the centrifuge process was complete and it did not change as seen in table 9 and figure 8.

0 min	Dep. Lvl. (ml)	6.4
	comment	Color segregation (brown and black)
30 mins.	Dep. Lvl. (ml)	6.4
	comment	No color change
Centrifuge	Dep. Lvl. (ml)	6.4
	comment	Deposit level constant

Table 8: Blank test deposit level



Figure 8: Blank Deposit Level

Asphaltene Dispersant Test (ADT)

Table 10 illustrates the results of ADT at 28°C. Generally, the chemical dispersants performed well in all concentrations for the whole period of time. Ten (10) ml of heptane was 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 30 minutes to allow the oil to react with n-heptane and promote asphaltene deposition. Readings were taken digitally and analyzed after the centrifuge process was completed.

0.5 ML										
		CCNO	CNSL	CPKO	MDSO	JOJO	SFLO	CSTO	TOLU	SYCA
0 min	Dep. Lvl. (ml)	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4
Centrifuge	Dep. Lvl. (ml)	4.6	7.0	2.9	4.4	3.8	1.8	4.9	5.6	5.3
1 ML										
		CCNO	CNSL	CPKO	MDSO	JOJO	SFLO	CSTO	TOLU	SYCA
0 min	Dep. Lvl. (ml)	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4
Centrifuge	Dep. Lvl. (ml)	4.6	6.1	0	8.2	3.4	3.8	4.7	0	0.4
1.5 ML										
		CCNO	CNSL	CPKO	MDSO	JOJO	SFLO	CSTO	TOLU	SYCA
0 min	Dep. Lvl. (ml)	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4	6.4
Centrifuge	Dep. Lvl. (ml)	0	3.0	5.4	6.9	2.6	4.2	4.3	2.6	2.6

Table 9: Solvent deposit level

The vegetable oil was tested with three different inhibition volumes; 0.5 ml, 1 ml and 1.5 ml, which were fixed throughout the experiments. Based on the test of 0.5 ml, SFLO performed best with a deposit reduction of 4.6 ml, followed by CPKO (3.5 ml), JOJO (2.6 ml), MDSO (2 ml), CCNO (1.8 ml), CSTO (1.5 ml), SYCA (1.1 ml) and TOLU 0.8 ml. However, CNSL increased the deposition level by 0.6 ml as a result of further precipitation. Image of the deposit level is contained in the image glossary.

Increasing the inhibition concentration to 1 ml, TOLU and CPKO performed best as no visible deposit level was recorded, meaning that this concentration and conditions were perfect to stop asphaltene precipitation. SYCA also performed very well towards inhibition the precipitation of asphaltene with a deposit reduction of 6 ml. However, at this concentration, other vegetable inhibitors performed below average spearheaded with JOJO (3 ml), SFLO (2.6 ml), CCNO (1.8 ml), CSTO (1.7 ml). MDSO on the other hand resulted to further precipitation and deposition resulting to a deposit increase by 1.8 ml.

Finally, increasing the inhibition concentration to 1.5 ml, CCNO outperformed other inhibitors by over 50% efficiency because there was no deposit found after the centrifuge process was completed. The next best inhibitor at this concentration is JOJO, TOLU and SYCA (3.8 ml),

followed by CNSL (3.4 ml), SFLO (2.2 ml), CSTO (2.1 ml), CPKO (1 ml). MDSO on the other hand increased the deposition level by 0.5 ml.

Overall, the asphaltene deposit rests near the bottom of the tube due to the law of gravity, and in favorable lighting, the deposit level is plainly visible through the supernatant. Although the deposit level was difficult to interpret in some cases when the oil created a very dark supernatant, such as in the case of CNSL, unless the supernatant is poured off. However, this was avoided since the deposit may also be mixed with liquid above, poured off and gave erroneous reading.

Putting it all together, for all concentration on inhibitors, TOLU performed best with an average deposition reduction of 3.7 ml followed by SYCA and CPKO (3.6 ml), CCNO (3.3 ml), SFLO (3.1 ml). CSTO and CNSL did not perform as expected with an average deposit reduction level of 1.8 ml and 1 ml respectively. However, for all instances, MDSO had the least performance which on average increased the deposit level by 0.1 ml indicating the propensity to increase asphaltene precipitation. This might be due to asphaltene self-association in the case of not enough polar head groups in the solvent for optimum interactions.

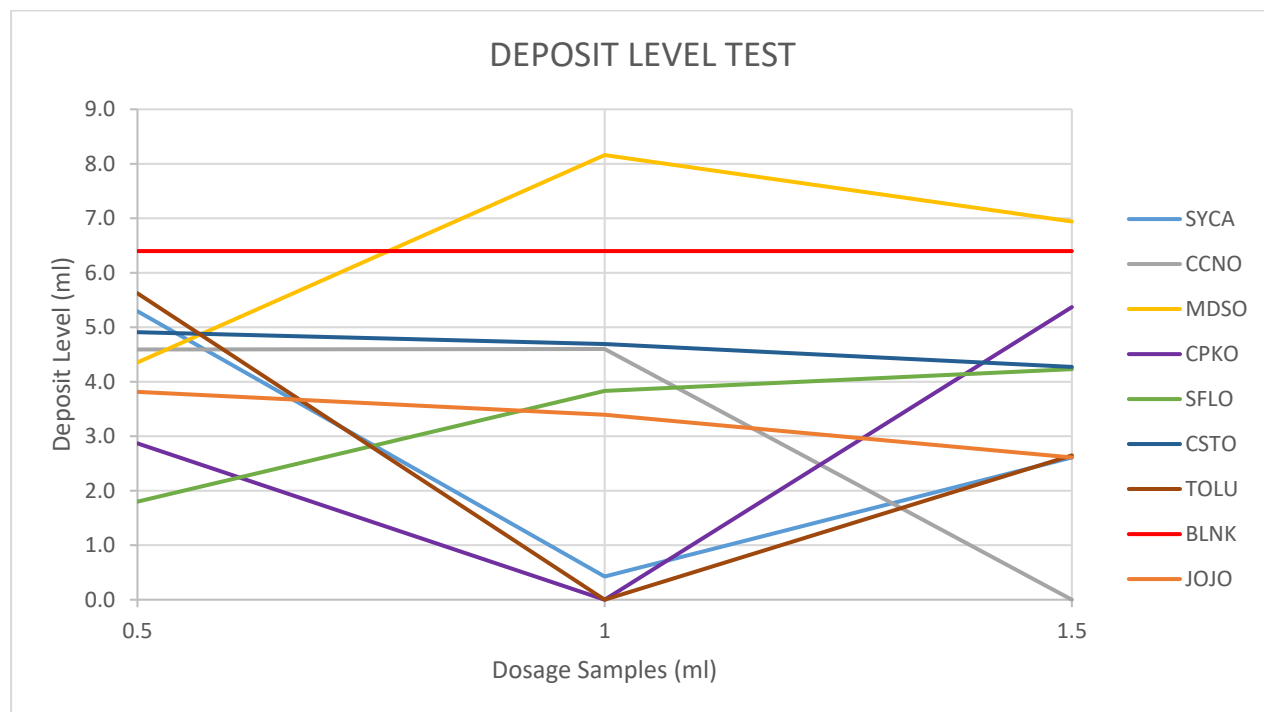


Figure 9: Deposition Level Test

Figure 9 is a graph that shows the performance for all inhibitor at their various concentrations. Based on the graph, for all instance, all inhibitor reduced asphaltene content except in the case of MDSO at concentration of 1 ml and 1.5 ml. CPKO matched with the performance of TOLU and outperformed SYCA at 1 ml with little or no deposit, indicating asphaltene inhibition. Although at higher concentrations, the inhibition efficiency decreased. JOJO and CSTO displays a linear relationship with regards to increasing concentrations. This means that for all instance, increasing the concentration will boost asphaltene inhibition efficiency. However, the reverse is the case for SFLO where increasing the inhibition dosage decreases asphaltene inhibition efficiency there by increasing the propensity for precipitation formation. CCNO showed a different response with increasing inhibition concentration. With increasing concentrations comes better inhibition performance. Thus CCNO can be regarded as an effective inhibitor in preventing asphaltene however, under controlled concentration situations CPKO is a better inhibitor.

Putting it all together, figure 10 below shows the inhibition efficiency racked according to performance based on concentration levels. From the results, MDSO at 1ml, and 1.5 ml, CNSL 0.5 ml, CSTO 1.5 ml and CSTO 1 ml rather agitated asphaltene coagulation and increased deposition level in decreasing order. CPKO 1 ml performed the best results and in decreasing order followed by CCNO 1.5 ml, SFLO 0.5 ml, JOJO 1.5 ml, CPKO 0.5 ml, and CNSL 1.5 ml. The other vegetable oil had below 50% inhibition efficiency including JOJO 0.5 ml, and 1 ml, SFLO 1 ml and 1.5 ml, MDSO 0.5 ml, and CCNO 1 ml and 1.5 ml. CPKO 1 ml, CSTO 0.5 ml CNSL 1 ml, SYCA 0.5 ml and TOLU 0.5 ml had the least effect towards minimizing asphaltene precipitation.

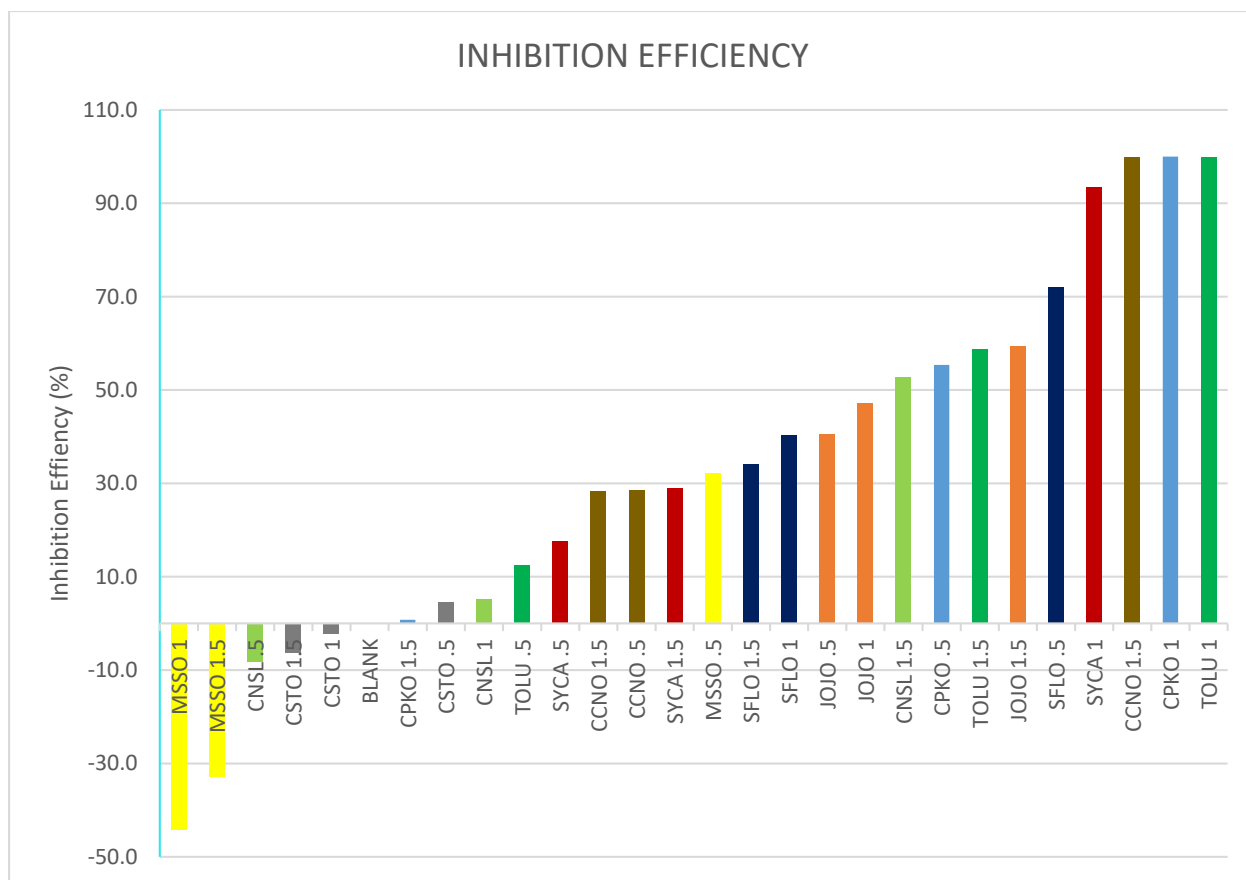


Figure 10: Inhibition Efficiency

Residue

It is vital to note that partial mixing was observed in some of the mixtures. Figure 11 below shows the residue volume of the immiscible fluids. CSTO for all concentration added had some deposit which increased with increased inhibition concentration. MDSO for several concentrations displayed similar characteristics. SYCA and CPKO only had immiscible deposit at high concentrations (1.5 ml), however, the residue level was minimum in CPKO.

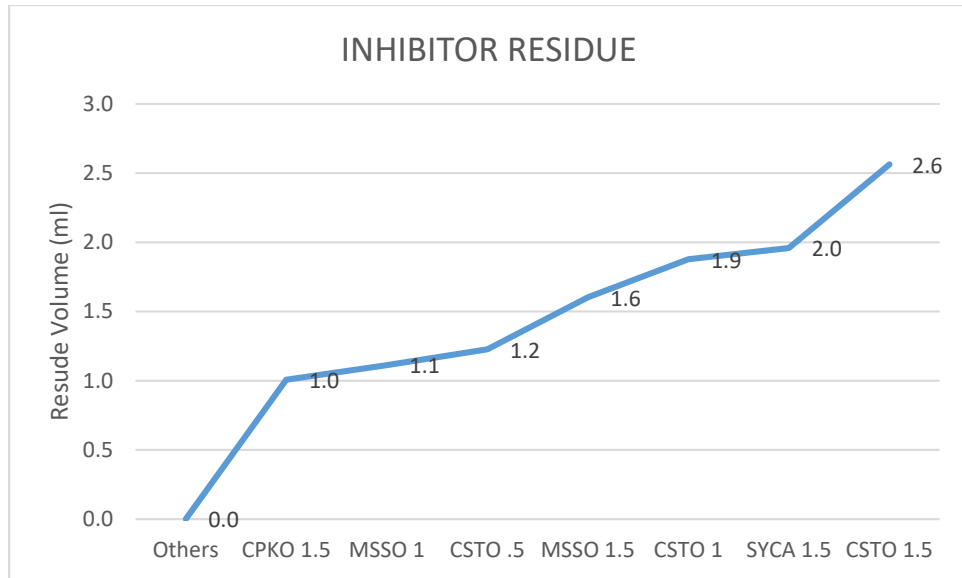


Figure 11: Inhibitor Residue Level

Chapter 5

CONCLUSION and RECOMMENDATION

Conclusion

For oil production and refining, asphaltene contamination is a common problem and maintaining the asphaltic fraction in a stable or well-peptized condition is advantageous for all oil production, treatment, and mobility processes since doing so would increase productivity and reduce operational costs. To offer an alternative to current inhibitors, this study builds on earlier research and advances knowledge of the interactions between asphaltene and agro-based inhibitors which are biodegradable and environmentally friendly. In addition, vegetable oils have special structures and functional groups (ester and alcohol) that interact with asphaltene and prevent precipitation. The components are amphiphile and phenolic compound, a stabilizing agent for asphaltene molecule. Vegetable oils, are organic compound extracted from including cashew nut shell oil (CNSL), sunflower oil (SFLO), castor oil (CSTO), palm kernel oil (CPKO), coconut oil (CCNO), mustard seed oil (MDSO), and jojoba oil (JOJO), have components to be used as inhibitor.












From characterization, the crude oil used was an intermediate conventional oil and the vegetable oil tested with three different inhibition volumes which were fixed throughout the experiments. Generally, the chemical dispersants performed well in all concentrations for the whole period of time. However, based on the test of 0.5 ml, SFLO performed best followed by CPKO and JOJO. Increasing the inhibition concentration to 1 ml, TOLU and CPKO performed best as no visible deposit level was recorded, meaning that this concentration and conditions were perfect to stop asphaltene precipitation. SYCA also performed very well towards inhibition the precipitation of asphaltene. MDSO on the other hand resulted to further precipitation and deposition. Increasing the inhibition concentration to 1.5 ml, CCNO outperformed other inhibitors followed by JOJO, TOLU and SYCA. Based on the experiments, for all concentration of inhibitors, TOLU performed best with an average deposition reduction of 3.7 ml followed by SYCA and CPKO (3.6 ml), while MDSO and CSTO had the least performance which on average increased asphaltene precipitation and deposition.

Recommendation and Future Work

Testing with various crude oils will result in varying levels of deposit for next work. It would be advantageous to test the green solvent with several types of crude oil because asphaltene content varies for each crude oil produced globally. In addition, dynamic testing is advised since it may provide a different amount of asphaltene than static testing and can speed up the process of depositing asphaltene. Crude oil's composition might change as a result of temperature. As a result, using an inhibitor in a water bath may yield different results than when the temperature is ambient or even at operating conditions. Also, engineering and optimizing the inhibitor composition for efficient result is a probable option. This might include mixing agro inhibitors with commercial ones at varying proportions to reduce their toxicity levels. Finally, correction and experimentation should be done under high pressure to mimic real case scenario.

IMAGE GLOSSARY

	0.5 ML	1 ML	1.5 ML	BLANK		0.5 ML	1 ML	1.5 ML
CCNO					CSTO			
CNSL					JOJO			
CPKO					MDSO			

	0.5 ML	1 ML	1.5 ML	BLANK		0.5 ML	1 ML	1.5 ML
SYCA					SFLO			
TOLU								

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