

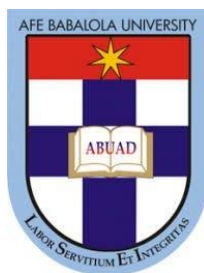
**ENHANCED OIL RECOVERY USING NOVEL BIO-BASED SURFACTANT
SYNTHESIZED FROM ALGAE**

BY

**ELUWA, TOCHUKWU DIVINE
17/ENG07/010**

**PETROLEUM ENGINEERING PROGRAMME
DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING
COLLEGE OF ENGINEERING
AFE BABALOLA UNIVERSITY, ADO-EKITI, EKITI STATE, NIGERIA**

MAY, 2022



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AFE BABALOLA UNIVERSITY, ADO-EKITI, EKITI STATE, NIGERIA**

**IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD
OF BACHELOR OF ENGINEERING (B.ENG.) DEGREE IN PETROLEUM
ENGINEERING**

MAY, 2022

DECLARATION

I, ELUWA Tochukwu Divine (17/ENG07/010), hereby declare that this project work titled “Enhanced Oil Recovery using Novel Bio-based Surfactant Synthesized from Algae”, carried out under the supervision of Engr. A.T. Ogunyemi and submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (B.Eng.) Degree in Petroleum Engineering, is my original work and has not been presented for any degree elsewhere, to the best of my knowledge. All sources of information are specifically acknowledged using references.

.....
ELUWA Tochukwu Divine

.....
Date

CERTIFICATION

This is to certify that this research project titled “Enhanced Oil Recovery using Novel Bio-based Surfactant Synthesized from Algae” was carried out by ELUWA Tochukwu Divine (17/ENG07/010) and submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (B.Eng.) Degree in Petroleum Engineering.

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DEDICATION

This research project is dedicated to God Almighty, my creator for giving me the strength and guidance to complete this project. I am also dedicating it to myself for the constant push and motivation I instilled on myself. My family, parents and siblings, were huge support systems to me and they deserve this too.

ACKNOWLEDGEMENT

This project would not have been possible without God's unending mercy and love on me. Huge special gratitude goes to my supervisors, Engr. Ogunyemi Adebayo and Engr. Dr. Afeez Gbadamosi for the extra help, insightful comments, enthusiasm and guidance concerning this research. I wish to extend my appreciation to Engr. Donatus for his assistance throughout the research period. I am grateful to the department of chemical/petroleum engineering, ABUAD for the consistent support. I would also like to acknowledge the help of my friends who impacted me one way or another and gave me constant emotional supports. Finally, I cannot begin to express my loving gratitude to my parents and siblings for financial, spiritual, mental, psychological support given to me at all times.

I truly recognize and regard the help of everyone who impacted me in a way, I am filled with gratitude.

ABSTRACT

Cost of conventional surfactants coupled with decreasing oil prices and increasing recovery has led to the search and quest for more low-cost yet effective methods and techniques to recover residual and heavy oil in the reservoir. More research has been steered towards environmental-friendly and lowered toxicity fluids to be used in tertiary recovery of oil. Oil extracted from algae has been seen to have a promising yield for biodiesel bio-based surfactant production, hence the need to find its potentials in EOR. The aim of this study was to formulate an algae-based Methyl Ester Sulfonate (MES) and to find its effectiveness in lowering surface tension between rock matrix and oil and application in core flood process. The produced MES was analyzed using Fourier Transform Infrared Spectroscopy it showed that the absorption peaked in the presence of single chained alkane stretch bond (C-H stretching alkane) with wavenumber and transmittance of 2918.39 cm^{-1} and 18.77 % respectively and presence of sulfonate group that indicates the surfactant is a methyl ester sulfonate. The CMC value of the surfactant was seen to be 1.24 and an IFT reduction from 28 to 5.1mN/m with a decrease of 81.8%. In the core flood process, at the end of the surfactant flooding, the novel surfactant was able to displace residual oil from the two cores with efficiencies of 35.9% and 41.8%.

Keywords: Enhanced Oil Recovery, methyl ester sulfonate, surfactant flooding, surface and interfacial tension, core flooding, critical micelle concentration, displacement efficiency, residual oil.

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NOMENCLATURE

AP	Alkali/Polymer
API	American Petroleum Institute
AS	Alkali-Surfactant
ASP	Alkali/Surfactant/Polymer
cEOR	Chemical Enhanced Oil Recovery
CMC	Critical Micelle Concentration
EOR	Enhanced Oil Recover
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
FTIR	Fourier Transform Infrared Spectroscopy
GC/MS	Gas Chromatography/Mass Spectrometer
IFT	Interfacial Tension
mEOR	Microbial Enhanced Oil Recovery
MES	Methyl Ester Sulfonate
MMP	Minimum Miscibility Pressure
O/W	Oil/Water
OOIP	Original Oil In Place
ppm	Parts Per Million
PV	Pore Volume
SAGD	Steam Assisted Gravity Drainage
SFT	Surface Tension
S_{oi}	Initial Oil Saturation
S_{or}	Residual Oil Saturation
SP	Surfactant/Polymer
S_w	Water Saturation
S_{wi}	Initial Water Saturation
W/O	Water/Oil

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of Study

During oil production, reservoir drive mechanisms are being used to push the oil from the reservoir to the surface. These reservoir mechanisms can be classified generally into 3 classes; Primary Recovery, Secondary Recovery and Tertiary Recovery also known as Enhanced Oil Recovery (EOR). The term 'Primary Recovery' refers to the production of hydrocarbons from a reservoir without the use of any mechanism (such as fluid injection) to improve the reservoir's intrinsic energy (Ahmed and McKinney, 2005). There are basically six driving mechanisms that provide the natural energy necessary for oil recovery: rock and liquid expansion drive, depletion drive, gas cap drive, water drive, gravity drainage drive and combination drive. After the depletion of the initial pressure in the reservoir, water or natural gas is injected into that same reserve to provide an external source of reservoir energy in 'Secondary Recovery'. The most typical type of secondary recovery applied in crude oil production is *Waterflooding* (King, 2020). The successive use of primary and secondary recovery in an oil reservoir yields approximately 15-40% of the Original Oil in Place (OOIP).

Enhanced Oil Recovery

This is the practice of extracting oil from a well that has already gone through the primary and secondary stages of oil recovery. EOR techniques can significantly increase the recovery factor from reservoirs by injecting some fluids into the reservoir and sweeping the remaining oil (Tunio *et al.*, 2011). EOR techniques are applied after primary and secondary recovery techniques for light and medium oil reservoirs. They attempt to recover oil beyond what can be collected through secondary methods, or what is left. On the other hand, EOR techniques may be applied immediately after primary recovery for heavy and extra-heavy oil reservoirs. This is because recovery using secondary recovery in high viscosity oil reservoirs is infinitesimal.

Overall, oil recovery is inextricably linked to the price of oil. The global recovery factor from conventional recovery methods is approximately one-third of what was originally present in the reservoir. (Kamil, 2015). Other than using water alone, there are only three basic mechanisms for extracting oil from rock. The methods are classified into those that rely on:

- a) Reducing oil viscosity
- b) Extracting the oil with a solvent
- c) Modifying capillary and viscous forces between the oil, injected fluid, and the rock surface.

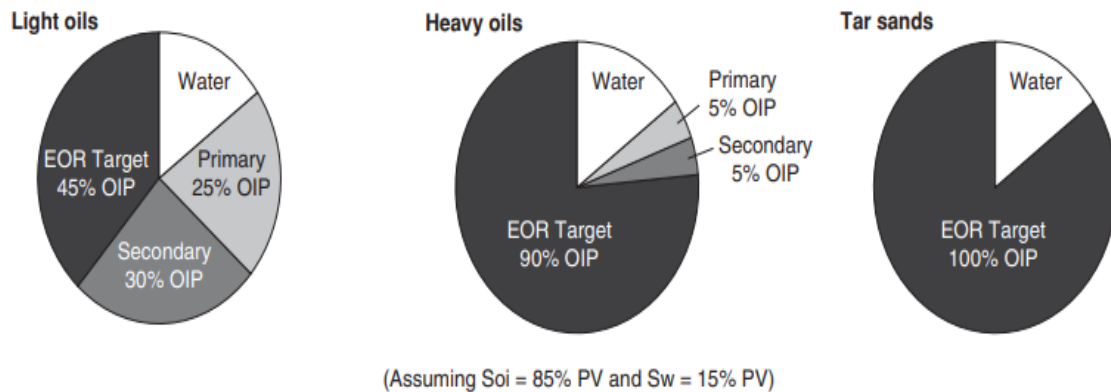


Figure 1.1: Worldwide EOR production rates (Thomas, 2008, bk. Enhanced oil recovery-
An overview)

EOR methods are divided into three categories: thermal methods (heat injection), miscible gas injection methods (injection of a solvent) and chemical methods (injection of chemicals/surfactants). Thermal EOR methods are typically used on heavy, viscous crudes and involve injecting thermal energy or heat into the reservoir to raise the temperature of the oil and reduce its viscosity.(Kamal, Hussein and Sultan, 2017) The most common thermal recovery methods are steam (or hot water) injection and in-situ combustion. Three common methods involving steam injection are cyclic steam stimulation (huff and puff), steam flooding and steam assisted gravity drainage (SAGD). In-situ combustion involves the injection of air into the area where the oil is ignited, which generates heat internally as well as combustion gases that improve recovery.(Kamil, 2015). Miscible flooding methods include carbon dioxide injection, natural gas injection, and nitrogen injection. Miscible gas injection must be carried out at a sufficiently high pressure to ensure miscibility between the injected gas and the in situ oil. When the interfacial tension (IFT) between the aqueous and oleic phases is significantly reduced, miscibility is achieved. Typically, the desired IFT reduction ranges from around 1 dyne/cm to 0.001 dyne/cm or less. Any reduction in IFT can improve displacement efficiency, and a near miscible process can produce much of the incremental oil that a miscible process would. If the reservoir pressure is not kept above the system's minimum miscibility pressure (MMP), the gas flood will be an immiscible gas injection process.(Fanchi, 2018). The primary goal of chemical EOR or chemical flooding is to recover more oil through one or more of the following processes: (1) mobility control

by adding polymers to reduce the mobility of the injected water, and (2) interfacial tension (IFT) reduction by using surfactants and/or alkalis. The well-known traditional chemical EOR methods are polymer flooding, surfactant and alkaline flooding. However, traditional chemical EOR methods have limitations. Polymers, whose primary recovery mechanism is to increase injectant viscosity and thus mobility, experience viscosity loss in the presence of reservoir brines and elevated temperature conditions. Surfactant and alkali lose their efficiency during their flow in porous media due to adsorption phenomena. Following that, various modes of chemical flood injections were developed, studied, and applied to EOR processes. These include the binary mix of alkali–surfactant (AS), surfactant/polymer (SP), alkaline/polymer (AP), and alkaline/surfactant/polymer (ASP) slug.(Gbadamosi, 2019).

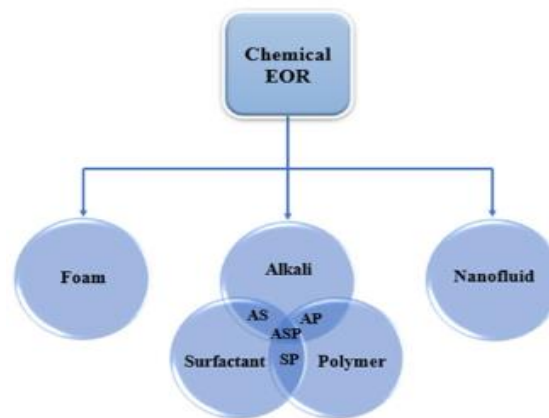


Figure 1.2: Classification of chemical EOR techniques (Gbadamosi, 2019)

Surfactant flooding

Surfactant flooding is one of the most well-known chemical EOR techniques, used primarily in low- and medium-viscosity oilfields. Surfactants are compounds that lower the surface tension (or interfacial tension) between two liquids, between a gas and a liquid, or between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents or dispersants (Salager, 2002). The earliest surfactants known to man are soaps (ECI, 2013). Surfactants are long-chain molecules with a hydrophilic (water-soluble) head group and an oil-soluble tail group. A long-chain hydrocarbon, fluorocarbon, siloxane chain, or short polymer chain can be used as the hydrophobic group. Surfactant classification is mainly based on the nature of the hydrophilic head group. The hydrophilic group in anionic and cationic surfactants is negatively and positively charged, respectively. Because the hydrophilic group is non dissociative, nonionic surfactants do not ionize in aqueous solution. Nonionic surfactants' water solubility is due to hydrogen bonding between the

hydrophilic groups, typically an ethylene oxide chain or a similar group, and water. In amphoteric surfactants, a hydrophilic group is both negatively and positively charged.(Kamil, 2015). Surfactants reduce the interfacial energy between the oleous and aqueous phases, reducing the forces that cause capillary trapping and mobilizing the remaining oil.(Druetta and Picchioni, 2020). Surfactants are interesting because of their hydrophilicity and lipophilicity, which makes them useful in immiscible and multiphase systems.

Table 1.1: Common hydrophilic surfactant groups

Type of surfactant	Hydrophilic group
Cationic	Ammonium quaternary ammonium halides ($r4n+ x-$)
Non-ionic	Polyoxyethylene, polyols, sucrose esters, and polyglycidyl
Anionic	Carboxyl ($rcoo-m+$), sulfonate ($rso3 -m+$), sulfate ($roso3 -m+$), phosphate ($ropo3 -m+$)
Amphoteric	Betaine, sulfobetaine $rn+ (ch3)2ch2ch2so3 -$ imidazole derivatives

When designing surfactants for EOR, the goal is to achieve low interfacial tension at low surfactant concentrations, as well as low adsorption levels on the formation rock.(Kamil, 2015; Druetta and Picchioni, 2020).

Bio-based surfactants

Bio-based surfactant is a surface active agent made from biological organisms that can reduce interfacial tension, allowing oil to be recovered to the surface due to improved mobility. This innovation is eco-friendly and cost effective compared with other EOR techniques. (Kanna, Kumar and Gummadi, 2014). Decreased interfacial tension (IFT) and a shift in reservoir wettability toward strongly water-wets are the key mechanisms of surfactant EOR. They are capable of lowering interfacial tension by lowering capillary pressure and allowing water to bypass entrapped oil. Furthermore, surfactant can also drive the reservoir wettability towards more water-wet and lifting off the attached oil film from the pore wall, thus decreasing residual oil saturation and enhancing oil recovery (Negin, Ali and Xie, 2017) at more environmentally-friendly rate.

Green Algae (*chlorophyta*)

A group of organisms capable of photosynthesis is referred to as algae. They share some characteristics with plants but lack the majority of plant features such as leaves, stems, roots, a vascular system, and so on. Algae are mostly unicellular organisms that come in a wide range of shapes and sizes. Algae are found in a wide variety of environments. They are either microscopic or macroscopic, and they live in colonies. They may also be multicellular organisms. Green algae are a type of algae that can photosynthesize and belong to the Chlorophyta family. Many microalgae are exceedingly rich in oil, which can be converted to biodiesel using existing technology. More than 50% of their biomass as lipids, sometimes even up to 80%, and oil levels of 20%–50% are quite common.

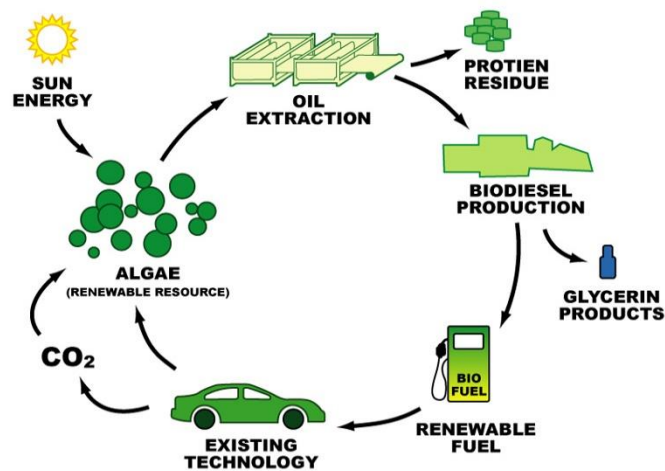


Figure 1.3: Process for conversion of algal oils to biodiesel

1.2 Problem Statement

Oil prices and concerns about future oil supply are driving a renewed emphasis on EOR. Some of these EOR techniques are currently being used to produce significant additional oil. Oil and gas companies are looking for oil in very remote areas; like deep waters, areas where the temperature is below zero and to develop fields in areas like these is very costly, (Tunio *et al.*, 2011) instead we can still produce the remaining amount of oil in the existing fields by applying new technologies to reduce cost, degradation to the ecosystem and increase the recovery factor through introducing the enhanced oil recovery techniques.

1.3 Aim and Objectives

1.3.1 Aim

The aim of this study is to determine the effectiveness of using inexpensive bio-oil extracted from Algae to produce surfactant that can be used in EOR.

1.3.2 Objectives

The objectives of this study are:

- a) To synthesize and characterize the non-edible oil based surfactant from Algae oil
- b) To determine the CMC and lower IFT between crude oil and water.
- c) To evaluate the oil recovery factor of the novel surfactant via oil displacement tests.

1.4 Scope of study

This scope of this study is limited to using only green algae oil to provide an alternative in place of conventional expensive surfactants in chemical flooding. The biodiesel and surfactant produced would be characterized by FT-IR. The IFT and oil displacement tests in core flooding experiment for studying the effectiveness of the non-edible based surfactant for EOR will be carried out room temperature.

1.5 Justification

Most research and reviews suggest that primary drive mechanisms can extract about 20–30 percent of oil, while secondary recovery can reach up to 40 percent. However, current enhanced oil recovery (EOR) systems can recover up to 60–65 percent of oil. (Tunio *et al.*, 2011). Surfactants are commonly used in EOR processes for a variety of purposes, including reducing oil/water interfacial tension, changing wettability, and generating foam. Surfactant flooding has been deemed a promising enhanced oil recovery technique. However, surfactants are also some of the most expensive chemicals used during EOR. The cost of the conventional surfactants used in enhanced oil recovery coupled with decrease in global hydrocarbons prices have led to the search for low cost surfactants that can be used in place of conventional ones. Bio-surfactants injection results in hydrocarbon emulsification, changes of hydrophobic surface properties and washing off of oil film from the rock surface. Bio-surfactants cost averages to 30% of the cost of synthetic surfactants. (Kamal, Hussein and Sultan, 2017). Environmental degradation and diminishing supplies of fossil fuels are also driving the search for alternative energy sources. Hence, this research seeks to extend the frontier of knowledge in surfactant flooding process by proffering a novel, cheap and environmentally benign bio-based surfactant for EOR.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Enhanced Oil Recovery (EOR) Overview

Since the end of World War II, when operators with diminishing reserves realized that considerable amounts of oil remained in their reservoirs after primary and secondary recovery (primarily waterflooding), the development of enhanced-oil-recovery (EOR) techniques has been continuing. As production from major reservoirs plummeted, global oil consumption climbed, and major new reservoir discoveries became less common, research and field activities increased. The oil embargo of 1973 and the subsequent energy "crisis" sparked a surge in interest in EOR procedures. The period of high activity lasted until 1986, when global oil prices collapsed (Latil, 1980). EOR projects have long been known to be heavily driven by economics and crude oil prices. The readiness and desire of investors to manage EOR risk and economic exposure, as well as the availability of more appealing investment options, are all factors that influence the start of EOR projects. One of the screening factors for EOR approaches is reservoir lithology, which can limit the use of some EOR techniques. Figure 2.1 shows statistically that according to a database of 1,507 international EOR projects compiled by various authors, the majority of EOR applications have been in sandstone reservoirs in the last decade (Alvarado and Manrique, 2010).

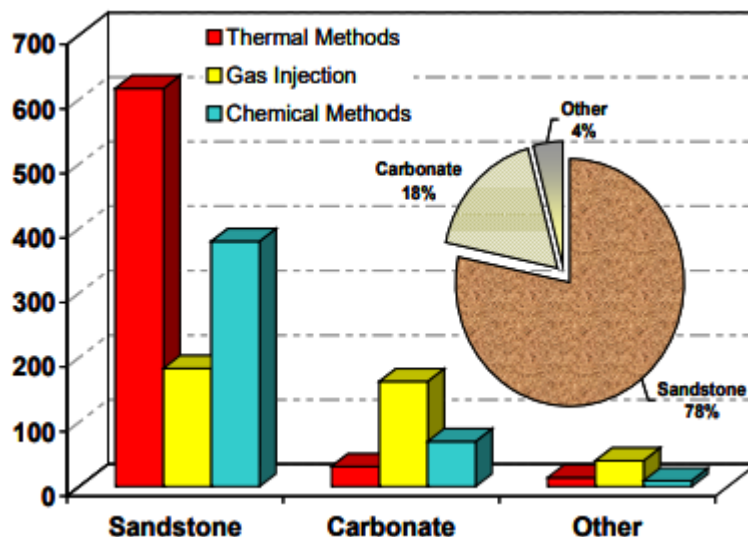


Figure 2.1: EOR methods by lithology (Alvarado and Manrique, 2010)

EOR techniques have been widely used in sandstone formations, and this is well known. Sandstone reservoirs, in general, provide the best prospects for EOR projects because most technologies have been proven at experimental and commercial scale in this lithology. Furthermore, several EOR technologies have been successfully examined at pilot scale in

specific sectors, indicating the technological applicability of different EOR approaches in the same field.

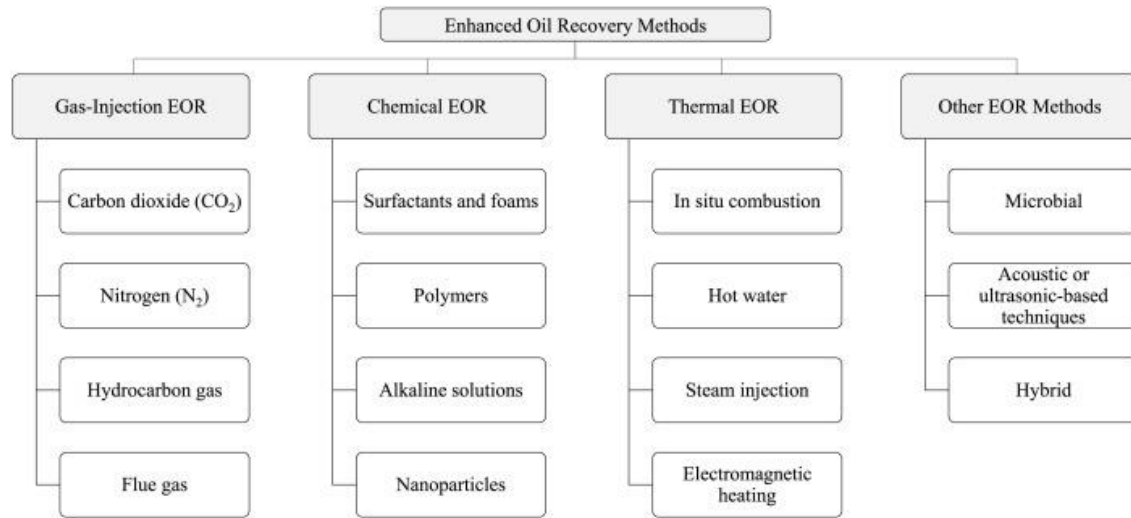


Figure 2.2: Main methods of EOR (Gbadamosi, 2019; Brantson et al., 2020)

2.2 Surfactant Flooding in EOR

Surfactants are organic molecules with two separate parts: a hydrophilic head and a hydrophobic tail. Surfactants are classified into four groups based on the charge on the hydrophilic head.

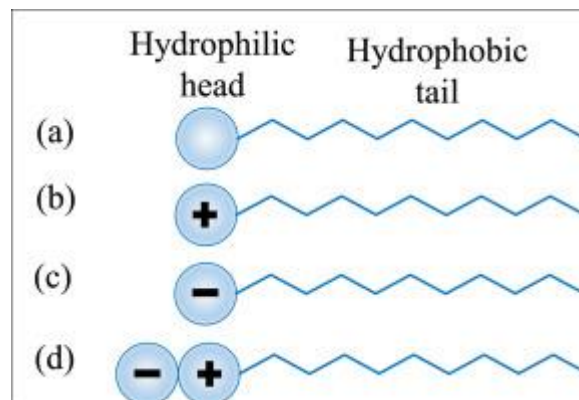


Figure 2.3: Types of surfactants according to the head group charge: (a) non-ionic, (b) cationic, (c) anionic, and (d) zwitterionic surfactants. (Massarweh and Abushaikh, 2020)

Surfactants adsorb on the oil/water interface, lowering the interfacial tension (IFT) and capillary forces that cause the pore trapping phenomenon. When alternative nonchemical procedures fail to increase extraction efficiency, surfactant solutions are injected into an appropriate location, away from the production well, to create very low interfacial tensions that will allow the mobilization of trapped oil in the reservoir. Normally, a mobile zone with

favorable mobility ratios should be maintained, which can be accomplished by including polymers and alkali in the surfactant formulation, thereby describing ASP mixes or solutions. The mobilized oil then forms an oil bank before being transported to the production well for improved recovery (Gurgel *et al.*, 2008). Insoluble residues left by surfactant and/or polymer-based formulations, on the other hand, could destroy petroleum reserves, with clear environmental consequences. As a result, a growing line of research tries to offer novel chemical systems for use in EOR operations, with the goal of reducing or even eliminating this difficulty. Throughout the years, several academic investigations and technological activities have proved the critical necessity of surfactant-based chemical systems.

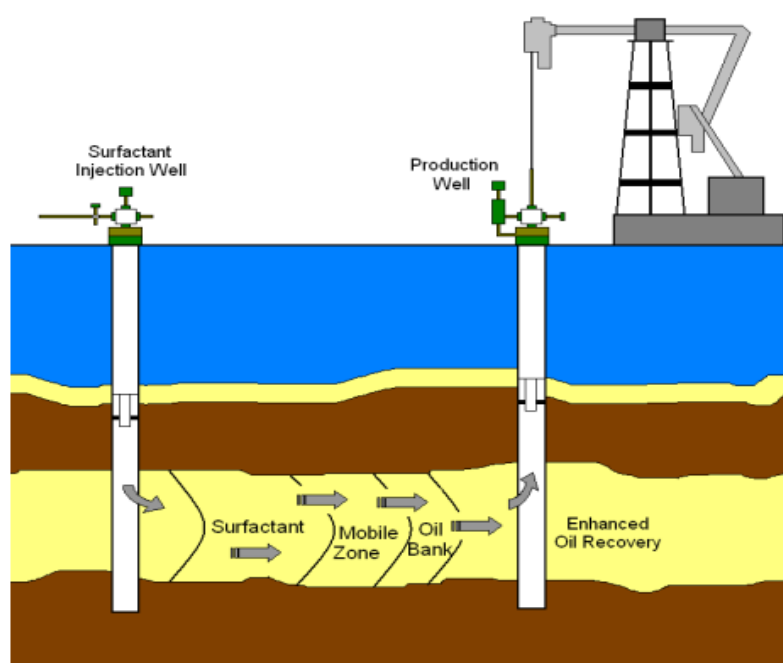


Figure 2.4: Schematic of a surfactant-based flooding process applied to a petroleum field (Gurgel *et al.*, 2008)

The surfactant solution injected will contact the trapped oil left in the pores of the rock and decrease the interfacial tension, thus allowing oil to flow. Descriptions of typical experimental procedures to optimize and implement a suitable chemical method employing surfactants involve the construction of a fluid injection prototype, insulation of the porous medium simulating the original well formations, determination of the CMC of each surfactant tested, and saturation of cores with reservoir fluids (brine and petroleum, depending on the original reservoir) characteristics, Porosity and permeability of the medium, in relation to oil and water, are determined (Karnanda *et al.*, 2012).

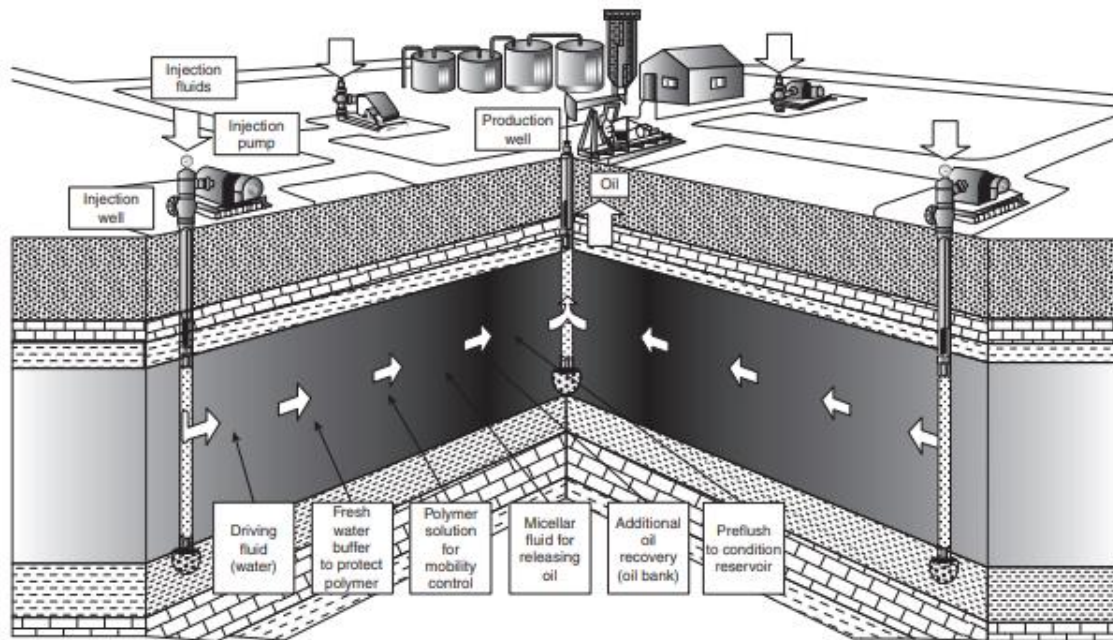


Figure 2.5: Surfactant/polymer process (Latil, 1980)

Figure 2.5 describes the highest potential in term of ultimate oil recovery in cEOR methods. In this method, the major displacing liquid slug in this process is a micellar solution, which is a complicated chemical system. A surfactant is present in this solution (usually a petroleum sulfonate), oil, electrolytes, and water, as well as a co-surfactant (an alcohol). Surfactant slugs are approximately 10 percent PV and are relatively tiny. A mobility buffer, a solution containing polymer at a concentration of a few hundred ppm, follows the surfactant slug. This polymer solution is frequently graded in concentration, becoming more dilute as the polymer concentration increases as the amount of solution injected increases. Typically, the total volume of the polymer solution is around 1 PV.

2.3 Types of surfactants for EOR

2.3.1 Cationic surfactants

Cationic surfactants have a quaternary ammonium structure with a number of long ($>C_{10}$) alkyl chains connected to the nitrogen atom directly or via an ester bond. (Lawrence, 2000). For example, Cetyl Trimethyl Ammonium Bromide (CTAB's) phase behavior was investigated, and it was discovered that this amine-based cationic surfactant is suited for EOR in carbonate reservoirs and performs well when combined with nanosilica particles. Cationic surfactants have been proven to be useful in changing the wettability of carbonate

rock, but combinations of cationic and nonionic surfactants appear to produce even better outcomes. Long-chain alkyltrimethyl ammonium bromide cationic surfactants have been studied for wettability modification (or chloride) (Han *et al.*, 2021).

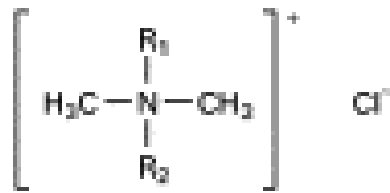


Figure 2.6: Cationic surfactant (Dialkyldimethylammonium chloride)

2.3.2 Anionic surfactants

Petroleum sulfonates have been popular since the beginning of the use of surfactants for EOR, owing to the ease with which they may be made by sulfonating a fraction of the crude in place with either strong sulfuric acid or oleum as the sulfonating reagent. Because of their low tendency to adsorb on the negatively charged rock surface, they have been discovered to be suitable candidates for sandstone reservoirs.

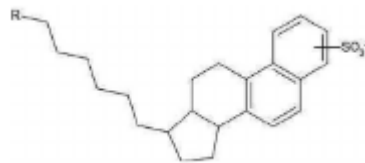


Figure 2.7: Petroleum sulfonate

2.3.3 Zwitterionic surfactant

Because zwitterionic surfactants have both a positive and negative charge, they have a net zero charge and are sometimes classified as nonionic surfactants. The charges, however, do not have to be permanent. If the positive charge is derived from a quaternary ammonium group, it is permanent; but, if it is derived from a protonated amine, it will progressively lose its charge as pH rises.

2.3.4 Nonionic surfactant

A nonionic surfactant is a surfactant that is neutral in nature. One of the most important properties of this chemical compound is its ability to emulsify oils and remove organic soils. This surfactant also has a special property called cloud point, which is the temperature at which it begins to separate from the cleaning solution. Some of the popular examples of

nonionic surfactants include ethoxylated amines, ethoxylated alcohol, and ethoxylated and alkoxyated fatty acids.

2.3.5 Polymeric surfactant

Polymeric surfactants are polymers with surfactant properties [e.g. acrylate copolymers, such as 2-acrylamide-2-methyl-1-propanesulfonic acid and alkyl methacrylamide, alkyl acrylate, poly (alkylamine)-supported phases, poly (ethyleneimine), etc]. When it comes to formulation stability, polymeric surfactants are crucial. They can act as dispersants and emulsifiers, separating particles in emulsions and suspensions and reducing formulation breakdown mechanisms such flocculation and coalescence.

2.3.6 Viscoelastic surfactant

Viscoelastic surfactants have a molecular weight of fewer than a thousand, smaller molecules than guar. They have a lengthy hydrophobic tail and a hydrophilic head group. Injection fluids with low IFT and high viscosity have been created using viscoelastic surfactants. High shear does not permanently destroy viscoelastic surfactants, unlike polymers. Furthermore, unlike polymers, large electrolyte concentrations have no effect on their viscosity-building properties. (Grant and Szasz, 1948)

2.3.7 Magnetic surfactant

Surfactants with magneto-responsive characteristics are known as magnetic surfactants. When compared to traditional surfactants, these surfactants have lower critical micelle concentrations and are more effective at reducing surface tension.(Shehzad *et al.*, 2021)

2.3.8 Fluorosurfactant

Fluorosurfactants, often known as fluorinated surfactants, are multifluorine synthetic organofluorine chemical compounds. They can be fluorocarbon-based or polyfluorinated. As surfactants, they are more effective at lowering the surface tension of water than comparable hydrocarbon surfactants. They have a hydrophilic "head" and a fluorinated "tail." They are more effective than comparable hydrocarbon surfactants at lowering water surface tension.

2.3.9 Natural surfactant

Many different plants can be used to make natural surfactants. Coconut and palm oil are common sources, although they can also come from other fruits and vegetables. Sugars surfactants and amino acids are two of the most common natural-source surfactant polar headgroups. (Holmberg, 2001).

2.3.10 Bio-surfactants

Bio-surfactants are a group of surface active agents which are produced by microorganisms. Bio-surfactants, like chemical surfactants, have hydrophobic and hydrophilic moieties. Bio-surfactants are categorized as glycolipids, lipoproteins, lipopeptides, polymeric, and particulate bio-surfactants based on their hydrophilic and hydrophobic moieties.

2.3.11 Gemini surfactant

Gemini surfactants are dimeric surfactants with two hydrophobic chains and two hydrophilic heads connected by a spacer near the head groups.

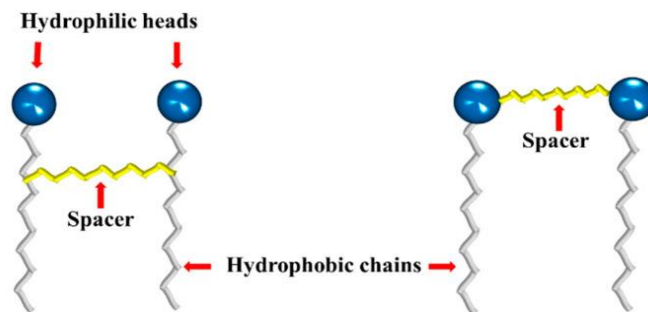


Figure 2.8: Typical structures of Gemini surfactants

2.4 Review of Technical Terminologies in surfactant EOR

2.4.1 Krafft temperature

The critical micelle temperature, also known as the Krafft temperature, is the lowest temperature at which surfactants create micelles. Micelles cannot form below the Krafft temperature. In the micro emulsion phase, the solubilization ratio for oil (water) is defined as the ratio of the solubilized oil (water) volume to the surfactant volume.

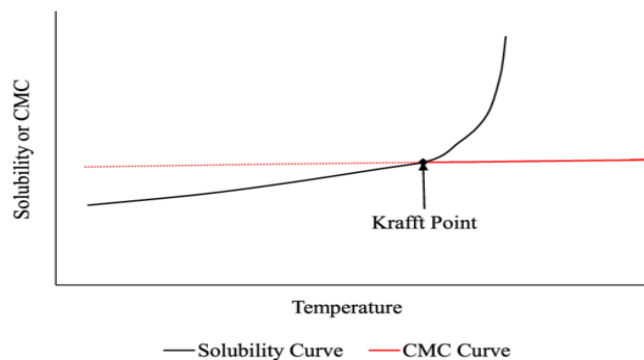


Figure 2.9: Krafft point plot

2.4.2 Critical Micelles Concentration (CMC)

CMC is the surfactant concentration above which micelles develop and all additional surfactants added to the solution create micelles. Below this concentration, micelles do not form. Surfactant ions and counter ions exist in solution as individual ions. Almost all extra surfactant molecules produce micelles over the threshold micelle concentration. (Marzzacco *et al.*, 2005). When CMC is reached, the surface tension remains relatively constant or changes with a lower slope.

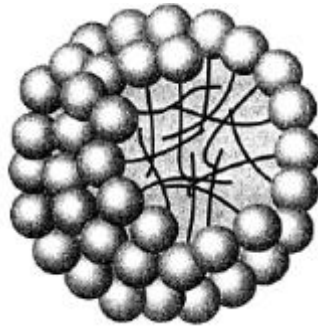


Figure 2.10: Micelle formation

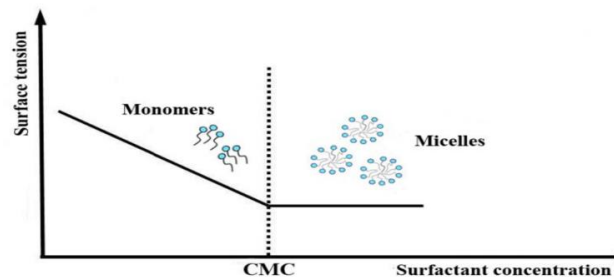


Figure 2.11: Surface tension and surfactant concentration relationship

2.4.3 Cloud point

The temperature at which a surfactant-rich phase separates from an aqueous solution is known as the cloud point. When a nonionic surfactant, for example, becomes insoluble as a result of increased heat, the outcome is a cloudy or hazy dispersion in the solution. Cloud point determination of surfactants is typically performed with a 1% weight dilution of the water-soluble surfactant in water. The surfactant is transparent at the start of the experiment, but the solution becomes turbid once the Cloud Point is reached. Surfactant solutions tend to phase separate above the cloud point (i.e., they separate into two distinguished phases). The first phase is a surfactant-rich phase with a high concentration of surfactants. In comparison to the first phase, the second phase is a bulk aqueous phase with a low surfactant

content. (Massarweh and Abushaikh, 2020). According to (Negin, Ali and Xie, 2017), surfactant phase separation (cloud point) at high temperatures may result in a drop in surfactant concentration, indicating poor efficacy in lowering IFT.

2.5 Critical parameters to be considered in surfactant flooding

2.5.1 Emulsification

Emulsification is one of the mechanisms that can increase oil recovery in the tertiary phase. Emulsions mostly form during alkaline and/or surfactant flooding under the conditions of low/ultra-low IFT and under shear resulting from fluid flow in rock pores. Emulsions are droplet suspensions, greater than $0.1\ \mu\text{m}$, made up of two totally immiscible liquids, one of which is dispersed throughout the other. The inclusion of a surface-active substance or emulsifier in an oil-water emulsion lowers the interfacial tension between trapped oil and the displacing fluid and stabilizes the interface against coalescence after it has formed. The emulsions with micro emulsion drops effectively block the more permeable routes and force the displacing fluid to flow through the unswept regions, resulting in an increase in overall efficiency and displacement efficiency. (Mandal *et al.*, 2010). Because of their favorable rheological and thermodynamic features, injection of emulsions and/or micro emulsions into oil reservoirs is thought to improve oil recovery.

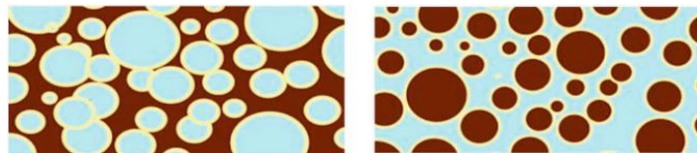


Figure 2.12: Water-oil (W/O) emulsion (left) and oil-water (O/W) emulsion (Mohyaldinn, 2019)

2.5.2 Phase behaviour

Surfactant phase behavior and temperature change are substantially determined by the type of the hydrophilic group. The solubility of ionic surfactants increases slowly at first as the temperature rises, until a point is reached at which the solubility suddenly rises. (Hassan, Verma and Ganguly, 2012). This temperature is also known as the Kraft point or the Kraft temperature. When both the solubility and the CMC curves are plotted as a function of temperature, an intersection point is discovered. The Kraft point, or the temperature at which the solubility equals the CMC, is the temperature at which the intersection occurs. The micelles, monomers, and solid surfactant are all in equilibrium at the Kraft point.

2.5.3 Wettability alteration

Wettability describes the ability of one fluid to stick to a rock surface when another immiscible fluid is present. As a result, the wettability type determines how fluids are distributed throughout the rock pore space and framework:

- Water-wet: the rock/mineral surface is water-coated, with oil and gas occupying the greatest pores in the center.
- Oil-wet: in comparison to the water-wet state, the relative locations of oil and water are inverted; the rock/mineral surface is coated with oil, and the water is in the center of the greatest pores.
- Intermediate wettability describes reservoir rocks in which both oil and water have a tendency to stick to the pore surface.

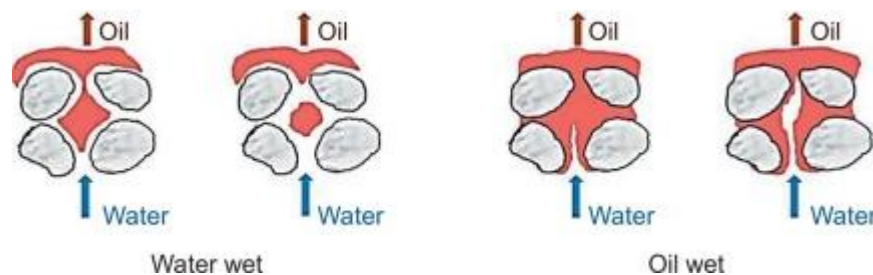


Figure 2.13: Wettability types (Fjær et al., 2021)

Several approaches have been used to alter the wettability of rocks to make them more water-wet. Surfactant injection, Nano fluid injection, low salinity waterflooding, and thermal recovery techniques are some of these methods. The rock is either water-wet or oil-wet, therefore wettability is viewed as a binary switch. Wettability has an impact on productivity and oil recovery during primary recovery. The profile of initial water saturation, S_{wi} , and production characteristics in a formation are influenced by the formation's original wettability and altered wettability during and after hydrocarbon migration. Prior to oil migration, most reservoirs are water-wet and have a long transition zone where saturation changes gradually from primarily oil with irreducible water at the top to water at the bottom. This distribution is gotten by buoyancy-based pressure which is the pressure differential between the oil and water phases, called the capillary pressure. (Abdallah, Jill S. Buckley and Carnegie, 2007).

2.5.4 Interfacial tension reduction

The attraction force between the molecules present at the interface of two fluids is referred to as interfacial tension. The interfacial tension between hydrocarbons and water molecules causes an increase in the capillary force that plays an essential role in the trapping of hydrocarbons in porous medium. Therefore, surfactant injection can be used to lessen the interfacial tension. (Massarweh and Abushaikh, 2020). The capillary force increases as the interfacial tension between hydrocarbons and water molecules increases, which is important for hydrocarbon trapping in porous media. As a result, surfactant injection is utilized to lower interfacial tension. The presence of a surfactant in water reduces surface tension in the absence of oil because the surfactant molecules replace part of the water molecules at the water surface. The attraction forces between water and surfactant molecules are weaker than those between water molecules themselves. Surfactants' potential to lower interfacial tension between crude oil and brine is highly dependent on the type and concentration of ions in the brine.

2.5.5 Surfactant adsorption

Surfactant retention in porous media happens in three mechanisms throughout the flooding process: precipitation, adsorption, and phase trapping. Surfactant precipitation and phase entrapment can be avoided by using a temperature and salinity-tolerant surfactant. Surfactant adsorption onto reservoir rock, on the other hand, can only be reduced. The adsorption process lowers the surfactant content in the injected solution, reducing its ability to minimize the oil–water IFT. As a result, this adsorption affects the efficiency of surfactant-based EOR in mobilizing stored oil. Surfactant adsorption, on the other hand, can be beneficial in wettability change in reservoirs that are intermediate to oil-wet. Surfactant molecules are adsorbed at the spots where crude oil was desorbed during the flooding process. Further interactions between crude oil and the rock's surface are thus prevented. As a result, the wettability of the rock is changed to water wet. Surfactant adsorption, on the other hand, diminishes their concentration in the aqueous phase, lowering the effectiveness of surfactant-EOR processes. (Massarweh and Abushaikh, 2020).

2.6 Field Application of Surfactant Flooding

In comparison to laboratory investigations, the number of studies reporting on surfactant EOR performance in the field is quite restricted. Studies have shown that most of these surfactants were applied in sandstone formations with a limited application in carbonates. In contrast to laboratory investigations, field studies reveal that surfactants are mostly

employed in the presence of other additives. Alkalis (such as NaOH and Na₂CO₃) and polymers make up the majority of these additives (e.g., HPAM and AP-P7). Alkalis are commonly used to raise the pH and hence reduce surfactant adsorption on reservoir rock. They also contribute to additional IFT reduction by producing surfactants in situ. Polymers, on the other hand, are used to provide even more mobility control.

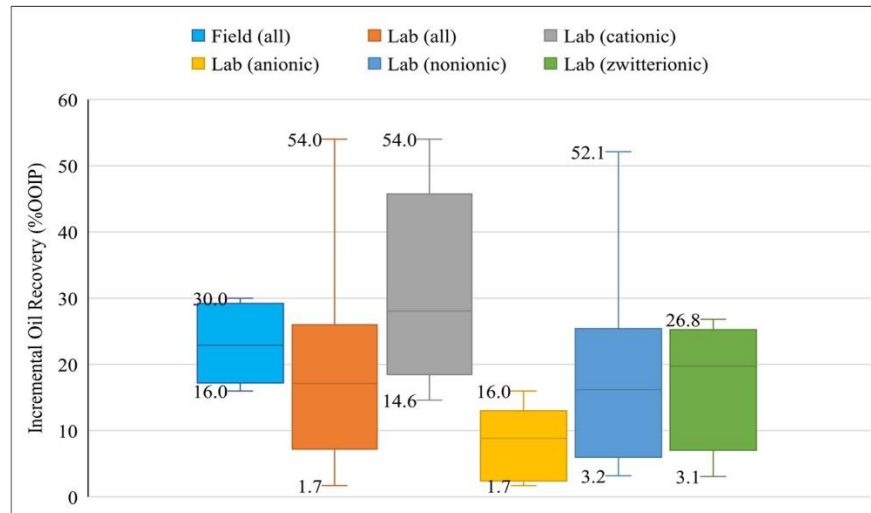


Figure 2.14: Incremental oil recovery obtained by employing surfactants at field and laboratory scales. (Massarweh and Abushaikh, 2020)

Figure 2.14 shows surfactants, which included additives such as alkalis and polymers, could provide incremental oil recovery of 16–30% of OOIP in the field. On the other hand, incremental oil recovery at the laboratory scale ranged from 1.7 percent to 54.0 percent of OOIP, with the majority of results falling between 7.2 percent and 26.0 percent.

2.7 Empirical Literature Review

A very noticeable amount of work have been done on using non-edible plant/organism based oil in production of biodiesel and bio-surfactants and its application in core flooding experiments. These works all have a common aim of finding greener, low-cost yet efficient techniques and methods to be used in biodiesel production and surfactant flooding as conventional surfactants are expensive and not environmental friendly.

According to (Patel, Nagar and Shah, 2013), they were able to identify various non-edible seeds potentials in the production and application of biodiesel done by different researchers. In their research, it was stated that there are many ways and procedures to convert seed oil into diesel like fuel but transesterification is the one of the best process for production of biodiesel and the fuel properties were compared with standard established by USA –

American Society for Testing and Materials (ASTM D6751) and German Institute for Standardization – Deutsches Institut für Normung (DIN EN 14214). Some of the seeds they worked on were *Jatropha curcas* L., non-edible seed from which oil (JO) was extracted and its methyl ester (JOME-biodiesel) was produced from and it had given a yield of 97%. The esterification was performed using acid catalyst (5% H₂SO₄) and methanol (20% of oil), while transesterification reaction was carried out for 2 hours keeping molar ratio of methanol to oil at 6:1 and sodium hydroxide concentration of 0.7 weight percentage of oil and it was observed that the calorific value of JOME is 37.2 MJ/kg, which is low compared to diesel fuel of 42 MJ/kg. Using Jojoba seed, acid – catalyzed pretreatment of jojoba oil was carried out as higher acid value and base catalyst lead to soap formations and transesterification of pretreated oil was done by adding freshly cut sodium metal into methyl alcohol, after which this mixture was heated at 65°C for 4 hour with stirring at reflux. The experiment showed the properties of jojoba oil and its methyl ester which had the potential as an alternative nonfood feedstock for biodiesel production.

(Farooq, Amin and Abdullah, 2013) reviewed the transesterification process of different species of algae for biodiesel production. Transesterification of algal oil was performed by using sodium methoxide as a catalyst. Yield of biodiesel from extracted oil was calculated for *C. vulgaris* (95%), *R. hieroglyphicum* (91%) and mixed algae culture (92%). Biodiesel produced by transesterification of algal oil was analyzed for various parameters and results showed that quality of biodiesel obtained from all species was comparable to ASTM D-6751~02 standards. It was also observed that there was no significant difference in the properties of biodiesel produced from *C. vulgaris*, *R. hieroglyphicum* and mixed algae culture and properties of biodiesel were in accordance with standards limits so it can be blended with fossil fuels or can be used individually.

A pea protein isolate was hydrolyzed by a double enzyme treatment method in order to obtain short peptide sequences used as raw materials to produce lipo-peptides-based surfactants according to (Rondel *et al.*, 2011). The influence of the process variables was studied to optimize the proteolytic degradation to high degrees of hydrolysis. The average peptide chain lengths were obtained at 3–5 amino acid units after a hydrolysis of 30 min with the mixture of enzymes. Then, N-acylation in water, in presence of acid chloride (C₁₂ and C₁₆), carried out with a conversion rate of amine functions of 90%, allowed to obtain anionic surfactant mixtures (lipopeptides and sodium fatty acids). These two steps were performed in water, in continuous and did not generate any waste. This process was

therefore in line with green chemistry principles. The surface activities (critical micelle concentration (CMC), foaming and emulsifying properties) of these mixtures were also studied. These formulations obtained from natural renewable resources and the reactions done under environmental respect, could replace petrochemical based surfactants for some applications.

Algal species, *Spirogyra* was used to produce biodiesel applying the alkaline and acid transesterification process. A single homogenous catalyst (KOH) and heterogeneous mixture of catalysts (KOH+NaOH+H₂SO₄) were treated to obtain a high quality biodiesel fuel that complied with the specifications of the American Standard Testing and Material, ASTM D 6751 and European Norm, EN 14214 standards in the research done by (Hossain, 2015). The highest biodiesel yield of 96.9% was achieved dealing 1:3 volumetric oil-to-methanol proportions by 1.5% mixture of catalysts (NaOH+KOH+H₂SO₄) at 40°C reaction temperature and a stirring speed of 320 rpm. The analysis showed that biodiesel yield from *Spirogyra* sp., was greater when a mixture of catalysts was used compared to when a single catalyst was employed.

(Paper, Hertadi and Gozan, 2019) worked on 'Processing of Ozonized Biodiesel Waste to Produce Bio-surfactant Using *Pseudomonas aeruginosa*'. *Pseudomonas aeruginosa* was used in the present study to bio-transform the pretreatment biodiesel waste into bio-surfactant. The biodiesel was pretreated by ozonation with different times. This study was conducted to determine the optimum time in the ozonation process to increase the activity of bio-surfactants. From the results, the optimum of ozonation time is 30 minutes. Ozonation can breakdown biodiesel waste compounds without change olefin compounds and long-chain paraffins because ozone attacks cycloalkanes and aromatic compounds. The lowest value of the surface tension (SFT) is 22.86 mN/m with a decrease of 27.71% and for the interfacial tension (IFT) is 0.12 mN/m with a decrease of 99.09%. The result of interfacial tension from the activity of bio-surfactants are close to the bio-surfactant criteria for the petroleum recovery.

(Torres Ortega, 2012) described the sulfonation/sulfation process technology for anionic surfactant manufacture. He explained how FAME were the main feedstock for detergent formulating in the future due to their applicability in detergent formulations, their high stability to pH and temperature hydrolysis. The sulfonation reactions can be carried out in different configurations, either liquid-liquid contact, or gas-liquid contact reactors, and a

diversity of sulfonating reagents can be applied for the sulfonation process, such as: Sulfuric acid, SO_3 from stabilized liquid SO_3 , SO_3 from sulfur burning and subsequent conversion of the SO_2 formed, SO_3 from boiling concentrated oleum and chlorosulfonic acid.

A novel anionic surfactant was synthesized from Jatropha oil by (Pal *et al.*, 2019). The aggregation and adsorption behavior of Jatropha oil-derived anionic surfactant were studied to investigate its favorability for use in micro emulsion systems. The interfacial tension values between micro emulsion and alkane systems were found to be much lower than that of surfactant and alkane systems. It was found that the injected micro emulsion formulations can achieve about 30% oil recovery close over conventional secondary water-flooding.

An investigation was done on the prospect of using hot water injection followed by injection of a chemical surfactant and/or a bio-surfactant produced by a *Bacillus subtilis* strain to improve oil recovery from a Middle East heavy oil field (Hamoud and Abdulkadir, 2016). Core flood experiments were carried out to recover heavy oil, as initially flooded by hot water (as the secondary mode) followed by either chemical surfactant or bio-surfactant individually and as a mixture. It was observed that the bio-surfactant injection recovered more oil compared to chemical surfactant only injection, which was around 1.4 % - 18.5 % over the residual oil saturation (S_{or}), whereas the mixture of the bio-surfactant and the chemical surfactant at different ratios gave the highest recovery of 27 % - 34 % over S_{or} . Furthermore, it was discovered that combining the bio-surfactant with the chemical surfactant improved the performance of the bio-surfactant.

A binary or ternary surfactant mixture for use in enhanced oil recovery within a reservoir having total dissolved solids greater than approximately 150,000 parts per million (i.e., extreme brine conditions) includes at least two of a propoxylated/ethoxylated alcohol sulfate, an ethoxylated alcohol Sulfate, and a monoalkyl or dialkyl diphenyl oxide disulfonate in the prospective study by (Hsu *et al.*, 2015). The developed surfactant blends exhibit exceptional solution stability, excellent oil recovery capability, and good compatibility. These systems also do not require the addition of alcohol or solvent to maintain solution stability and good coalescence rates, which improves their compatibility with polymers added to improve the mobility ratio. Thus, these new surfactant blends could be great candidates for EOR applications under extreme brine conditions. The formulation is also effective at concentrations below 1% by weight, possibly as low as 0.1%.

CHAPTER THREE

3.0 RESEARCH METHODOLOGY AND MATERIALS

This chapter aims to show the apparatuses, procedures and methods of producing the synthetic surfactant, analysis and core flooding experiment.

3.1 Equipment and Materials

3.1.1 Equipment

1. Weighing balance
2. Beakers
3. Spatula
4. Conical flasks
5. Soxhlet apparatus
6. Pycnometer
7. Magnetic heating stirrer
8. Retort stand
9. Thermometer
10. pH meter
11. Thimble
12. Separating funnel
13. Gas Chromatography Mass Spectrometer (GCMS)
14. Core samples
15. Core flooding apparatus



Figure 3.1: Soxhlet apparatus held by the retort stand and a beaker with spatula

3.1.2 Materials

1. Fresh green algae
2. n-hexane
3. Potassium hydroxide pellets
4. Sodium hydroxide pellets
5. Ethanol
6. Sodium chloride
7. Diethyl ether
8. Conc. Hydrochloric acid
9. Distilled water
10. Phenolphthalein indicator
11. Pyridine
12. Sodium bicarbonate
13. Chlorosulfonic acid
14. Sodium chloride
15. Crude oil
16. Sodium dodecyl sulfate (SDS)

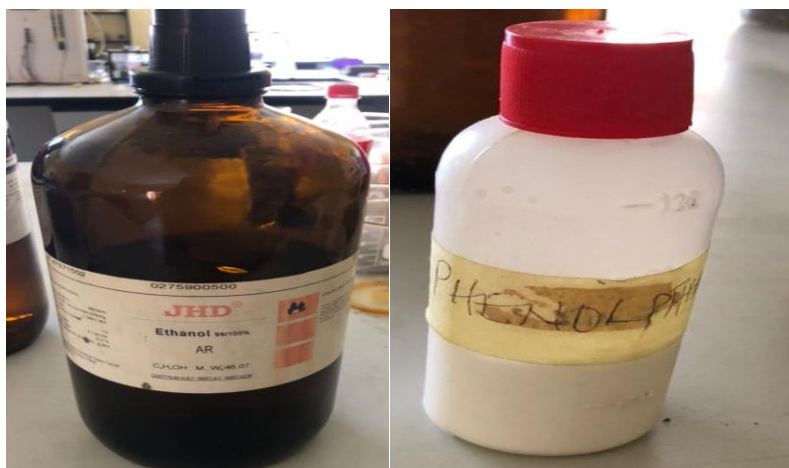


Figure 3.2: Ethanol and phenolphthalein indicator

3.2 Research Approach

This research involves the extraction of oil from the algae, conversion to bio-diesel, further conversion to surfactant and core flood process.

3.2.1 Algae oil extraction process

The fresh green algae was gotten from ABUAD farm in Ado-Ekiti, Ekiti state, Nigeria. These steps were taken accordingly.

1. The algae was washed with water and kept under the sun for about 24 hours to dry till crushable shown in figure 3.3.
2. The total weight of the crushed algae was measured using the weighing balance.
3. Some of the crushed algae were put in a thimble which was inserted into the extraction chamber of the Soxhlet apparatus.
4. A round bottom flask filled with 350ml of n-hexane (which was used as a solvent) and a condenser was properly fixed to the apparatus.
5. Cool water flowing constantly through the condenser was used to condense the evaporating solvent back into the Soxhlet apparatus at a temperature of 700°C. This set up is shown in figure 3.1.
6. The magnetic heating stirrer was set to 400°C and the extraction started.
7. When the n-hexane began boiling, the vapor was passed through the condenser, which condensed it to liquid and then dropped into the sample until the thimble was filled.
8. As the liquid dropped into the sample, it extracted the oil and when the thimble was filled up the oil extracted together with the n-hexane was emptied into a round bottom flask.



Figure 3.3: Sun drying and crushing of sundried algae

9. After about 2 hours of each run, the mixture of n-hexane and the extracted oil was separated by gently heating the mixture to evaporate the n-hexane.

10. The total weight of the extracted oil was taken and the oil yield was calculated using equation (3.1)

$$\% \text{ oil yield} = \frac{\text{weight of oil extracted (in grams)}}{\text{weight of algae used (in grams)}} \times 100 \quad (3.1)$$

3.2.2 Characterization of the Algae oil

This involves the various processes that were used to attain the physiochemical properties of the oil. These tests were density, specific gravity, viscosity, cloud point, pour point, free fatty acid and saponification tests.

Density Test

1. The weight of empty pycnometer with stopper was taken.
2. The empty pycnometer was filled with distilled water and the weight was taken. The volume of water that is filling the pycnometer at the stopper is:

$$\text{volume of water} = \frac{a}{b} \quad (3.2)$$

Where a = mass of water which is experimentally determined weight of water, (weight of pycnometer filled with distilled water – weight of empty pycnometer) in grams and b = density of water in g/cm³

3. The procedure was repeated for the oil of unknown density and its weight m was determined (measured weight – weight of empty pycnometer).
4. The density was calculated with the volume of water from equation (3.2)

$$\text{density of oil} = \frac{\text{mass of oil}}{\text{volume of reference fluid (water)}} \quad (3.3)$$

5. The specific gravity was also calculated.

Viscosity Test

Viscosity describes a fluid's internal resistance to flow and may be thought of as a measure of fluid friction. All real fluids (except super fluids) have some resistance to stress and therefore are viscous, but a fluid which has no resistance to shear stress is known as an ideal fluid or inviscid fluid. The study of flowing matter is known as rheology, which includes viscosity and related concepts (Kiselev, Vorozhtsov and Fomin, 2017). These were the steps:

1. The Brookfield rheometer was turned on and a spindle with spindle factor of 0.01 was attached to it due to the amount of oil used.



Figure 3.4: Brookfield Rheometer

2. An RPM of 200 was selected and the rheometer was auto-zeroed.
3. The oil was poured in a 50ml beaker and was heated to about 50°C. It was attached to the rheometer and the spindle was put into it.
4. The rotation started and the dynamic viscosity was taken when the temperature of the oil was at 40°C

Cloud point Test

Cloud point is the temperature below which wax in liquids tends to form a cloudy appearance. It is the highest temperature at which the oil begins to solidify. To determine the cloud point of the algae oil, the following steps were taken:

1. The algae oil was poured into a test tube and covered with a foil paper
2. A thermometer was inserted in it and it was placed in the freezer where at intervals of 5 minutes, it was checked to see if wax had formed
3. When it became cloudy it was taken out and the temperature was quickly read. This temperature was taken as the cloud point.

Pour point Test

This is the temperature below which the liquid loses its flow characteristics. After the cloud point was taken, it was returned to the freezer and was checked every 5 minutes. When the test tube was tilted for 5 seconds and the oil could not flow again, the temperature was immediately read and recorded.

pH Test

pH shows how acidic or basic an aqueous solution is. A pH of less than 7 indicates that an aqueous solution is acidic, whereas a pH of greater than 7 indicates that it is basic. A pH of 7 is regarded as neutral. The oil was placed in a beaker and the pH probe was placed in it until the pH meter displayed “ready” with a value.

Acid Value Test

1. 34g of 0.05mol of potassium hydroxide (KOH) was measured in dissolved in 20ml of water.
2. The mixture was brought up to 1000ml with ethanol to make alcoholic KOH.
3. 50ml of ethanol and 50 ml of diethyl ether was measured and mixed together. 25ml of this mixture was mixed with 2g of the algae oil.
4. After it had been mixed, 2 drops of phenolphthalein indicator was dropped in it.
5. This mixture was then titrated against the alcoholic KOH until a pink color appeared while shaking continuously.
6. This was done 3 times to get an average titre value.
7. A blank experiment was done which did not include the oil in the mixture.
8. The acid value was calculated using equation (3.4)

$$\text{Acid value} = \frac{0.1N \times Mw \times (B - V)}{\text{Weight of oil used}} \quad (3.4)$$

Where N is the Normality of the base, Mw is the molecular weight of KOH, B is blank titre value and V is average titre value

Free Fatty Acid (%FFA) Test

The %FFA was gotten using equation (3.5)

$$\%FFA = \frac{\text{Acid value}}{2} \quad (3.5)$$

Saponification Test

Saponification is the hydrolysis of esters. Oils and fats are the fatty acid esters of the trihydroxy alcohol, glycerol. The saponification value of an oil is defined as the number of milligrams of potassium hydroxide required to neutralize the fatty acids resulting from the complete hydrolysis of 1 g of the sample (Kim and Siang, 2022). The process was as follows;

1. 0.5mol of Hydrochloric acid was prepared using 50ml of conc. Hydrochloric acid and 1000ml of water
2. 0.5KOH was also prepared by dissolving 28.05g of KOH pellets in 1000ml of water
3. Ethanol ether was prepared by mixing ethanol with diethyl ether.
4. 4ml of the ethanol ether was mixed with 25ml of the KOH solution. In this mixture, 1g of oil was mixed with it.
5. This final mixture was mixed on a magnetic heating stirrer for about 30 minutes. When it was done, it was allowed to cool then 3 drops of phenolphthalein indicator was placed in it. The mixture turned pink in color
6. This was then titrated against the 0.5mol of HCl, shaking continuously, until the pink color vanished.
7. This was done 3 times to get an average titre value.
8. A blank experiment was done which did not include the oil in the mixture.
9. The saponification value was then calculated using equation (3.6)

$$\text{Saponification value} = \frac{Mw \times M \times [Vb - Va]}{W} \quad (3.6)$$

Where M is the molarity of acid, Vb is volume of blank titre, Va is actual average titre volume and W is weight of oil used.

3.2.3 Fatty Acid Methyl Ester (FAME) biodiesel production

Fatty acid methyl esters have physical qualities that are closer to those of fossil diesel fuels than pure vegetable oils, but their properties vary depending on the type of oil. A mixture of different fatty acid methyl esters is commonly referred to as biodiesel, which is a renewable alternative fuel. FAME has physical properties similar to those of conventional diesel. It is also non-toxic and biodegradable (European Biofuels Technology Platform, 2011). FAME is produced from oils by transesterification. In the transesterification process, a glyceride reacts with an alcohol in the presence of a catalyst, forming a mixture of fatty acids esters and an alcohol. Using triglycerides results in the production of glycerol.

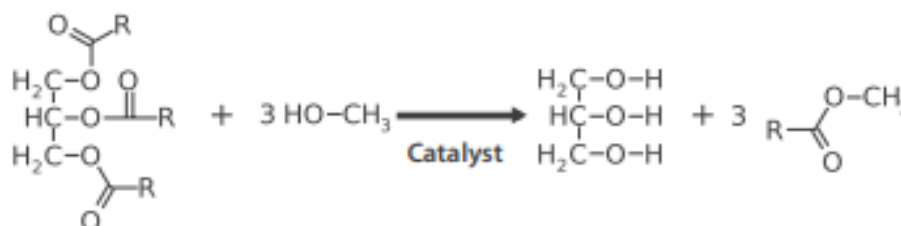


Figure 3.5: FAME reaction with products

3.2.3.1 Alkaline-catalyzed transesterification process

Alkali catalyzed transesterification reaction is the most adopted methods for production of biodiesel because it is simple to extract the respective esters. This process is only applicable for oils that have low free fatty acid level (<4) and acid catalyst transesterification process is applicable only for high free fatty acid level (>4) oils. This experiment was conducted to produce methyl esters from the extracted algae oil. The following steps were used in conducting this experiment:

1. 2g of NaOH pellets were dissolved in 180ml of methanol and mixed with 45g of the extracted algae oil. This made it a methanol-oil ratio of 4:1. The NaOH was used as the catalyst in this reaction.
2. After it was mixed, the reaction was heated and stirred on the magnetic heating stirrer for 2 hours at a temperature of 170°C .
3. The heated mixture was allowed to cool before separating the glycerol from the methyl ester produced on a separating funnel.
4. The methyl ester was heated to remove the remaining methanol that may have dissolved in it.
5. Another methanol-oil ratio of 6:1 was used to produce more methyl ester.

3.2.3.2 FAME analysis with Gas Chromatography/Mass Spectrometer (GC/MS) and Fourier Transform Infrared Spectroscopy (FTIR)

The biodiesel produced was characterized like also to get its physiochemical properties. An analysis was done using the GC/MS to know the percentage of methyl esters present in the biodiesel obtained from the Algae oil. It was carried out in the Analysis Laboratory of the Chemical/Petroleum department in Afe Babalola University, Ado-Ekiti. The FTIR analysis showed the biodiesel content in the reaction and was done in Redeemer's University.

3.2.4 Sulfonation process

The term "sulfonation" refers to an electrophilic chemical reaction in which a sulfonic group SO_3H is integrated into a molecule that can give electrons. If the electron donor molecule is a carbon, the product of this chemical reaction is known as sulfonic acid. Sulfuric anhydride interacts readily with electronic densities that are delocalized, such as those found in aromatic groups or alkenes in general. Derivate polysulfones, for example, are produced through these processes. The sulfating process, on the other hand, requires the addition of SO_3H molecules to an oxygen atom in an organic molecule to generate C-O-S bonds and

the sulfate group (Torres Ortega, 2012). The steps taken to produce the anionic methyl ester sulfonate were:

1. 6.23g of chlorosulfonic acid was measured and mixed with 15ml of pyridine.
2. 50ml of the methyl ester biodiesel formed was mixed with the mixture in a reflux condenser with a magnetic stirrer. This mixture went on for about 30 minutes.
3. Sodium bicarbonate solution was prepared by dissolving 33g of sodium bicarbonate in 500ml of distilled water and kept in the freezer to be cold.
4. After chilling, the NaHCO_3 solution was poured in the earlier and kept back in the freezer to cool more.
5. After cooling, it was poured into a separating funnel to separate the surfactant mixture and foam formed shown in figure 3.6.



Figure 3.6: MES surfactant separation

3.2.4.1 Surface and Interfacial Tension (IFT) measurement

Surface tension measurement of the cell free broth was determined by K6 Tensiometer using plate method. 10ml of surfactant sample was placed in the glass container. Measurements were carried out by automatic controller which smoothly pulls down the plate such that it gets into contact with the liquid placed. The force acting on the rectangular plate with known length were measured and converted into surface tension digitally. For interfacial tension measurement equal amount of oil is added to the sample and similar procedure is followed.

3.2.4.2 Analysis with Fourier Transform Infrared spectroscopy (FR-IR)

The produced surfactant was characterized by FTIR to show the chemical bonds functional groups present in the surfactant.

3.3 Core Flooding Procedure

The core flooding tests aimed to reveal the capability of the MES surfactant to recover residual oil in sandstone reservoir rocks after brine flooding. The surfactant was injected as tertiary fluid. At the beginning of the test, the core was inserted in the sleeve and then mounted in the core-holder. Low pressure (~250 psi) CO₂ gas was passed through the sample for 1 h. Because of its high diffusivity, CO₂ can displace and replace any air trapped in the pores. The remaining CO₂ after evacuation would readily be dissolved in the saturating dead brine and evacuated from the core sample during the later in-situ saturation process. After flushing the sample by CO₂, all the flow-lines and the sample inside the core-holder were evacuated using a vacuum pump for 6 h. The temperature was set to the reservoir temperature on the system.

Crude oil and 2 sandstone core samples were gotten from an oil reservoir in a Niger Delta field in Nigeria. The cores were of different length and it was labelled core 1 and core 2. The physical parameters of the core samples are shown in table 3.1 below.

Table 3.1: Cores with their physical parameters

	Core 1	Core 2
Weight (grams)	103.23	105.65
Length (cm)	5.5	6
Diameter (cm)	3.7	3.7



Figure 3.7: Crude oil sample

3.3.1 Contact angle measurements

Image J software was used to measure the contact angles on the core samples. A plug-in called ‘contact angle plug-in’ was installed together with the image j software. The software was used in getting contact angle using the following steps:

1. The software was launched on the desktop as shown below.

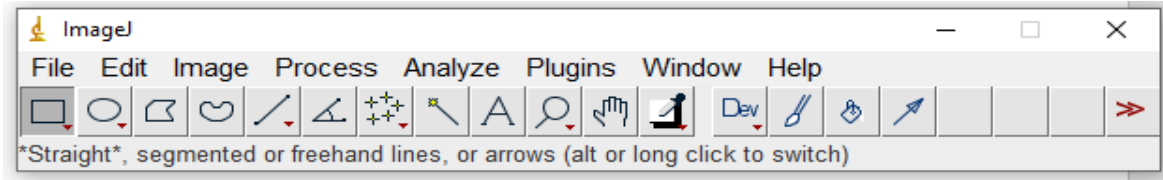


Figure 3.8: ImageJ user interface

2. The image to be used was dragged into this interface, the image popped up and “Plugins” was selected. This turned the image black and white (8-bits).
3. The two base horizontal points and 3 drop profile were selected. The point-list tab was selected and “manual points procedure” was also selected which gave results.

3.3.2 Core samples properties

Bulk volume (V_B)

The bulk volume was calculated using equation 3.7

$$V_B = \pi r^2 L \quad (3.7)$$

Pore volume (V_P)

$V_P = (\text{wet weight} - \text{dry weight}) / \text{density of water}$

Porosity (ϕ)

$$\phi = \frac{V_P}{V_B} \times 100 \quad (3.8)$$

Permeability (K)

Using Darcy equation,

$$Q = \frac{KA\Delta p}{\mu L} \quad (3.9)$$

Therefore, permeability (K) gives

$$K = \frac{Q\mu L}{A\Delta P} \quad (3.10)$$

Where Q = calculated flowrate, μ =viscosity, L =length of core, A = area of the core and ΔP =pressure drop in core flood experiment.

3.3.2 Brine flooding

The core samples are first saturated or injected with brine. This is to create a replica of the situation that occurs in the reservoir and to fill up pore spaces. The steps involved in this process were:

1. Brine was prepared by dissolving 16g of NaCl in 500ml of distilled water.
2. It was poured in a jar and the 2 core samples were put in it and left for 3days.
3. After 3 days, the core samples were taken out and their new weights were measured.

For the brine flooding process, 13g of NaCl was mixed in 1000ml of water to prepare brine. The core samples were set up one after the other in the core flooding apparatus to undergo brine flooding.



Figure 3.9: Saturation of core samples with brine

The time taken to recover various milliliters (2, 4, 6, 8, 10ml) of brine during the process was gotten and recorded and used to calculate the flow rate. After this, the flooding continued for 1hour and 30minutes to know the quantity of brine that can be recovered. This was done for the 2 core samples.

3.3.3 Oil flooding

The crude oil shown in figure 3.7 was characterized to get its physiochemical properties. These tests were density test, viscosity test, cloud point test and pour point test. The

procedures are the same with the ones used during the algae oil characterization except this time, crude oil was used.

After brine flooding, the core samples were immersed in the crude oil and left to saturate for about 48hours. The same process done in for brine flooding was done for oil flooding also to calculate flowrate. The volume of oil and water recovered was measured.

3.3.4 MES surfactant flooding

The surfactant synthesized from algae was used in the flooding experiment to determine the volume of residual oil and surfactant that can be recovered after surfactant flooding.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

4.1 Results

This includes the values gotten from the algae oil extraction, biodiesel production and their characterization. The results of the analysis of MES produced, characterization of the crude oil and the core flood experiments also presented here.

4.1.1 Results from physiochemical properties characterization

4.1.1.1 Extracted Algae oil

Using equation 3.1, % oil yield = 92.26%

Table 4.1: Algae oil properties

S/N	Physiochemical properties	Values
1	Density (g/cm ³)	0.8603
2	Kinematic Viscosity at 40°C (cSt)	0.005
3	Cloud point (°C)	-9
4	Pour point (°C)	-12
5	pH	9.1
6	Acid value (mgKOH/g)	4.57
7	Free fatty acid (%)	2.29
8	Saponification value (mgKOH/g)	116.875

4.1.1.2 FAME production and physiochemical characterization

In this process, the need for acid-catalyzed esterification was not useful because the FFA gotten and calculated from the extracted algae oil was 2.29% as seen in table 4.1 which is less than 4%. This gave rise to using only the alkaline-catalyzed transesterification process here. The Alkaline-catalyzed transesterification process involved a reaction of NaOH (used as alkaline catalyst) with methanol and the extracted algae oil. This mixture was one using methanol-oil ratio of 4:1 and 6:1. These two ratios produced the FAME with glycerol as a by-product but the ratio of 6:1 was seen to have produced better yield. Overall volume of FAME produced was 332.90g. The FAME was characterized to get its physiochemical properties and is shown in table 4.2.

Table 4.2: Biodiesel properties

S/N	Physiochemical properties	Values
1	Density (g/cm ³)	0.8464
2	Kinematic Viscosity at 40°C (cSt)	0.0052
3	Cloud point (°C)	10
4	Pour point (°C)	-5
5	pH	10.19
6	Acid value (mgKOH/g)	0.48
7	Free fatty acid (%)	0.24
8	Saponification value (mgKOH/g)	173.07

4.1.1.3 Crude oil characterization

Table 4.3: Crude oil properties

S/N	Physiochemical properties	Values
1	Density (g/cm ³)	0.8851
2	Specific gravity	0.8851
3	API gravity (°API)	28.37
4	Kinematic Viscosity at 40°C (cSt)	0.36
6	Cloud point (°C)	-5
7	Pour point (°C)	-18

From the characterization, it can be deduced that the crude oil is a medium crude oil (according to API, between 22.3 and 31.1°API) because the API gravity gave 28.37°API.

4.1.2 FAME analysis with GC/MS and FTIR

This analysis showed the various methyl esters present in the biodiesel produced with their percentage composition and also the functional groups present.

For GC/MS

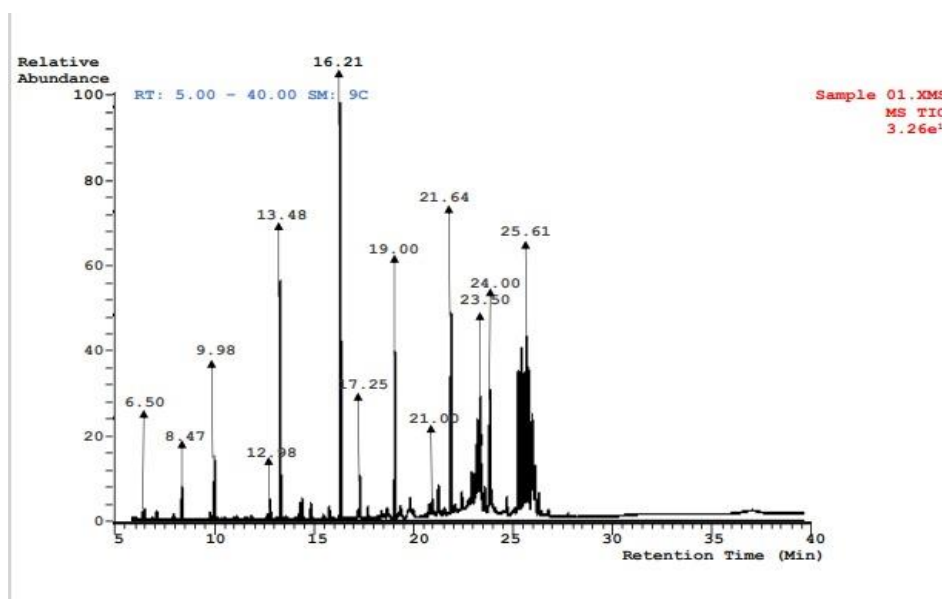


Figure 4.1: Biodiesel GC/MS Chromatogram

Table 4.4: GCMS results

S/N	Compound detected	Composition (%wt)
1	Pentanoic acid methyl ester	0.06
2	Nonanoic acid methyl ester	0.53
3	Methyl tetradecanoate	1.98
4	Pentadecanoic acid, methyl ester	0.31
5	8,11-Octadecadienoic acid, methyl ester	13.80
6	9-Octadecenoic acid, methyl ester	32.84
7	Heptadecanoic acid, methyl ester	0.92
8	Hexadecanoic acid methyl ester	13.93
9	Methyl stearate	0.61
10	11-Octadecenoic acid, methyl ester	13.01
11	9-Octadecenoic acid, methyl ester	14.38
12	9,12,15-Octadecatrienoic acid, methyl ester, (Z,Z,Z)-	7.32
13	Docosanoic acid, methyl ester	6.54

For FTIR

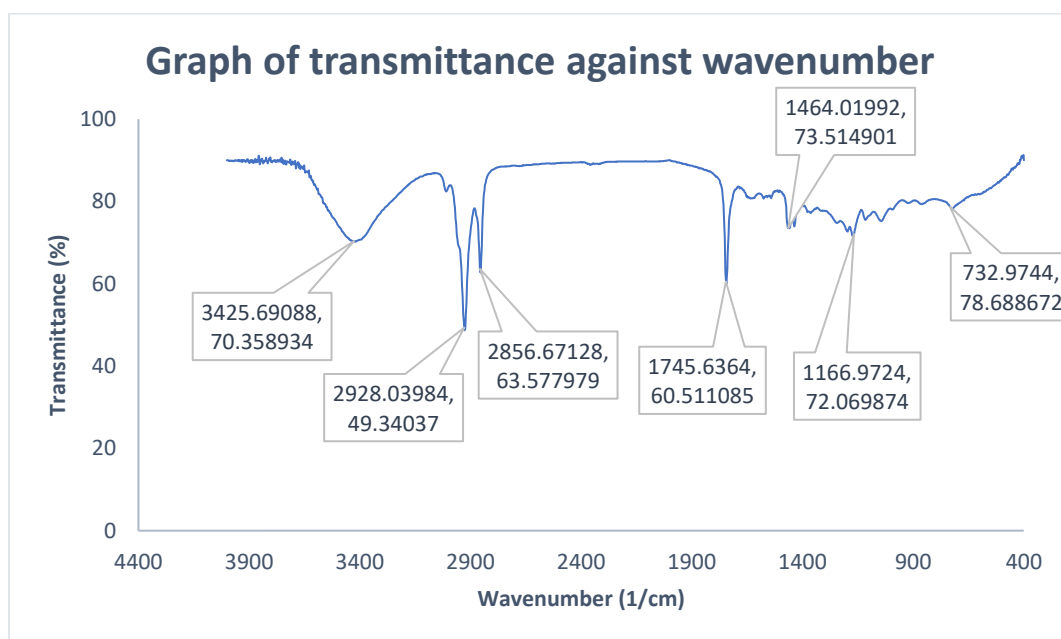


Figure 4.2: FTIR spectrum for biodiesel

From the figure above, it shows that the highest FTIR absorption peaks has the presence of aliphatic single chain alkane bond.

Table 4.5: Attribution of the main biodiesel peaks

Wavenumber (1/cm)	Transmittance (%)	Functional group
> 3300	70.36	OH group (hydroxyl)
2800-3000	49.34	CH (alkane) group
1745	60.51	C=O group (carboxylic bond)
1456	73.51	CH ₂ group
1166	72.17	C-O group
732	78.69	Ring aromatics

4.1.3 MES surfactant analysis

4.1.3.1 Surface and interfacial tension measurement

Table 4.6: Surface tension measurement results

S/N	Concentration (%)	Surface Tension
1	0.00	60.00
2	0.50	45.00
3	1.00	43.00
4	1.50	43.00
5	2.00	44.00
6	2.50	45.00
7	3.00	45.00

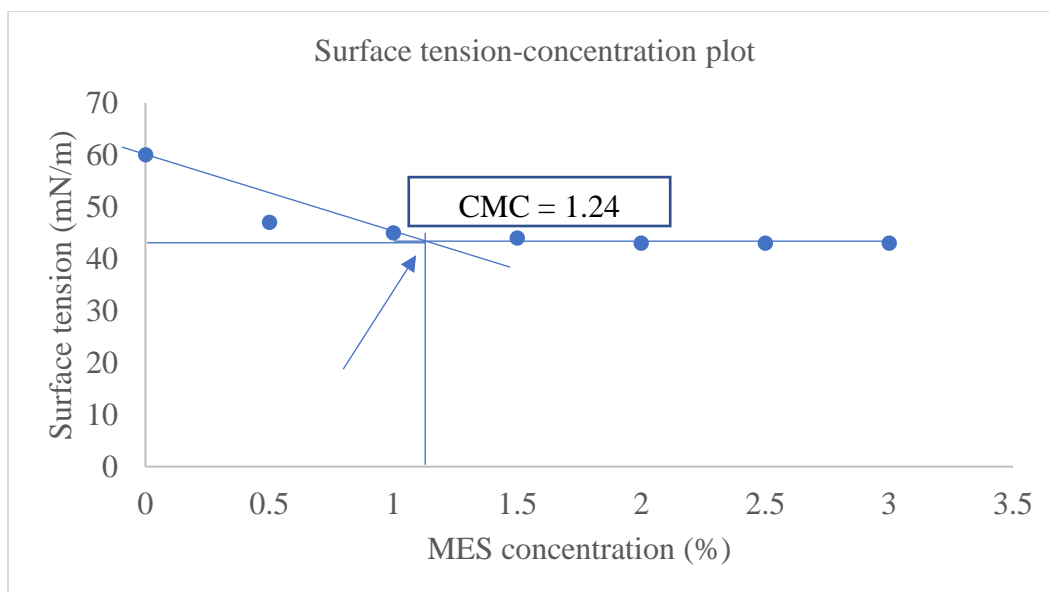


Figure 4.3: CMC determination from surface tension-concentration plot

Table 4.7: IFT-concentration results

Surfactant Concentration	IFT(mN/m)
0.0	28.0
0.50	4.00
1.00	5.10
1.50	5.10
2.00	5.10
2.50	5.20

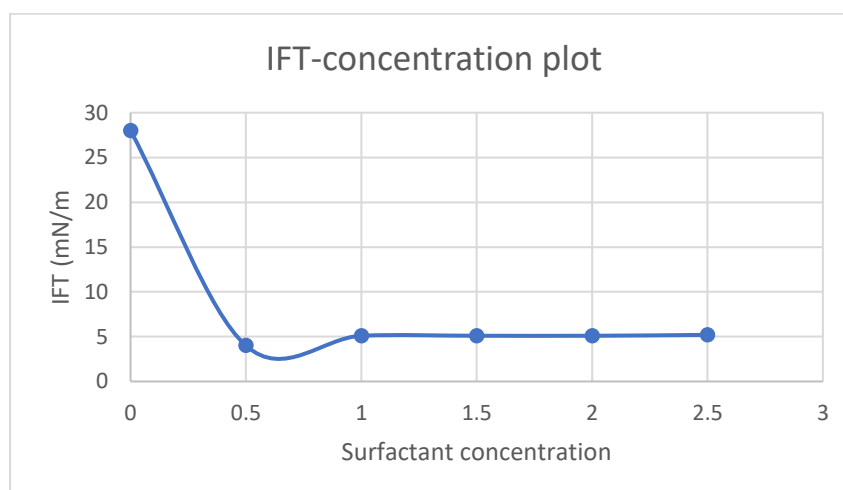


Figure 4.4: IFT-concentration plot

4.1.3.2 FTIR analysis

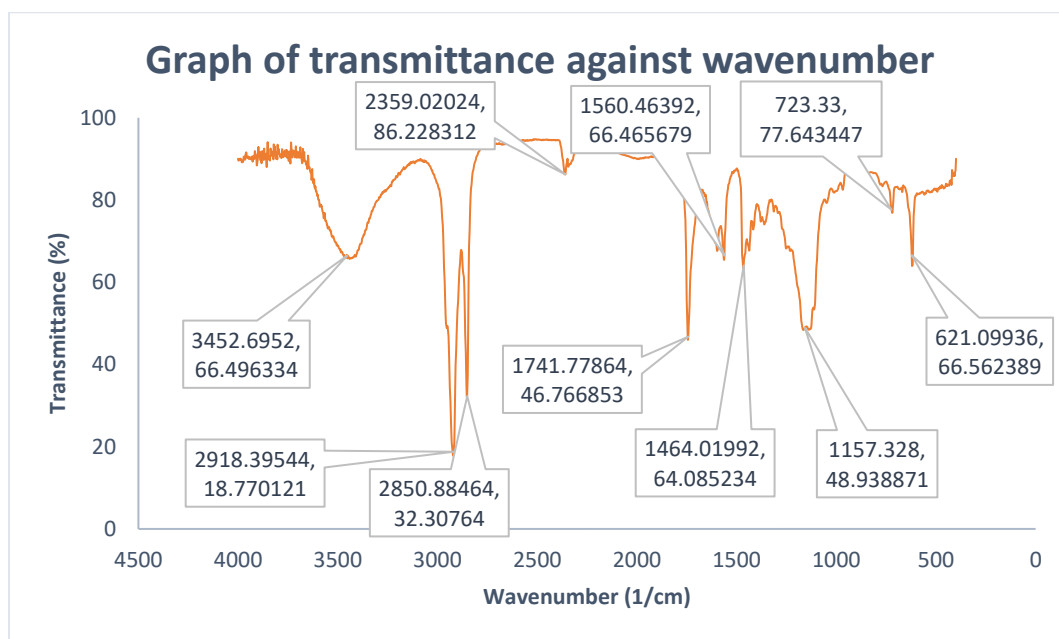


Figure 4.5: FTIR spectrum for surfactant

This graph also shows that the highest FTIR absorption peaks has the presence of single chain alkane bond. There is also presence of sulfonate group that indicates the surfactant is a methyl ester sulfonate.

Table 4.8: Attribution of the main surfactant peaks

Wavenumber (1/cm)	Transmittance (%)	Functional group
> 3300	66.49	OH group (hydroxyl)
2850-3000	18.77	CH (alkane) group
1741	46.76	C=O group (carbonyl bond)
1560	73.51	CH ₂ group
1464	72.17	-NH ₂ group
1157	48.93	S = O stretching vibration group
<750	77.64	Ring aromatics

4.1.4 Core flooding results

4.1.4.1 Contact angle

These are the results of contact angle measurement from the contact angle plugin on ImageJ

Table 4.9: Contact angle results from ImageJ

<u>Core sample 1</u>		<u>Core sample 2</u>	
File name	Core sample 1	File name	Core sample 2
Angle	179.663	Angle	-179.145
Length	170.003	Length	134.019
Theta C	106.1	Theta C	106.6
Uncertainty	0.6	Uncertainty	0.9
Theta Left	119.4	Theta Left	100.4
Theta Right	117.8	Theta Right	126.3
Theta E	118.6	Theta E	113.4
Radius	88.42	Radius	69.92
Circle StDev	0.72991242	Circle StDev	0.833471
Ellipse StDev	3.13621589	Ellipse StDev	0.004455
e	0	e	0.65
Points:	104	Points:	103
Volume	203396.2	Volume	1014827

$$\text{Contact angle} = 180 - \text{theta } E \quad (4.1)$$

For core 1, contact angle = $180 - 118.6 = 61.4^\circ$

For core 2, contact angle = $180 - 113.4 = 66.6^\circ$



Figure 4.6: Contact angle for core sample 1 and core sample 2

4.1.4.2 Core sample properties

Core sample 1

- Bulk volume

$$\begin{aligned}\text{Using equation 3.7, } V_B &= \pi \times (3.7/2)^2 \times 5.5 \\ &= 59.14 \text{ cm}^3\end{aligned}$$

- Pore volume

$$\begin{aligned}V_P &= (126.42 \text{ g} - 103.23 \text{ g}) / 1 \text{ g/cm}^3 \\ &= 23.19 \text{ cm}^3\end{aligned}$$

- Porosity

$$\begin{aligned}\phi &= (23.19/59.14) \times 100 \\ &= 39.21\%\end{aligned}$$

- Permeability

From equation 3.10 with initial flowrates calculated, $\Delta p = 20 \text{ psi}$, $\text{Area} = 10.75 \text{ cm}^2$, $L = 5.5 \text{ cm}$ and $\mu = 1.01 \text{ cp}$

$$K = \frac{0.037 \times 1.01 \times 5.5}{10.75 \times 20}$$

$$\begin{aligned}K &= 9.56 \times 10^{-4} \text{ mD} \\ &= 0.0956\%\end{aligned}$$

Core sample 2

$$\begin{aligned}V_B &= \pi \times (3.7/2)^2 \times 6 \\ &= 64.51 \text{ cm}^3\end{aligned}$$

- Pore volume

$$\begin{aligned}V_P &= (132.39 \text{ g} - 105.65 \text{ g}) / 1 \text{ g/cm}^3 \\ &= 26.74 \text{ cm}^3\end{aligned}$$

- Porosity

$$\phi = (26.74/64.51) \times 100$$

$$= 41.45\%$$

- Permeability

From equation 3.10 with initial flowrates calculated, $\Delta p = 20\text{psi}$, Area = 10.75cm^2 , $L=6\text{cm}$ and $\mu = 1.01\text{cp}$

$$K = \frac{0.037 \times 1.01 \times 6}{10.75 \times 20}$$

$$K = 1.04 \times 10^{-3} \text{ mD}$$

$$= 0.104\%$$

Table 4.10: Core sample properties

Core Samples	Dry weight (g)	Wet weight (g)	Bulk volume (cm ³)	Pore volume (cm ³)	Porosity (%)
Core 1	103.23	126.42	59.14	23.19	39.21
Core 2	105.65	132.39	64.51	26.74	41.45

4.1.4.3 Brine flooding

Weight of core 1 after brine saturation after 72hours = 126.42g

P1 is the air pressure, while P2 is open to flow and it is considered to be at standard condition as 1 atm (14.7psi)

$$P1 = 83.3, 67.3, 60.7, 71.8$$

Table 4.11: Brine flood results for core 1

S/N	Brine recovered (ml)	Time taken (seconds)	Flowrate (ml/s)
1	2	51	0.039
2	4	180	0.022
3	6	351	0.017
4	8	1177	0.007
5	10	1661	0.006

After 1hour 30 minutes, 200ml of brine was recovered and the initial flowrate calculated.

Flowrate (q) = volume/time

$$= 200/5400$$

$$= 0.037\text{ml/s}$$

Mean of flowrates = $(0.039+0.022+0.017+0.007+0.006)/5$

$$= 0.0182\text{ml/s}$$

Weight of core 1 after brine flooding = 132.60g

Table 4.12: Brine flood results for core 2

S/N	Brine recovered (ml)	Time taken (seconds)	Flowrate (ml/s)
1	2	52	0.038
2	4	137	0.029
3	6	214	0.028
4	8	420	0.019
5	10	802	0.012

After 1hour 30 minutes, 200ml of brine was also recovered and the initial flowrate calculated.

Flowrate (q) = volume/time

$$= 200/5400$$

$$= 0.037\text{ml/s}$$

Mean of flowrates = $(0.038+0.029+0.028+0.019+0.012)/5$

$$= 0.0252\text{ml/s}$$

Weight of core 2 after brine flooding = 141.99g

Absolute permeability measurement when each of all the cores was flushed with 2PV of Brine:

Core 1

P2: 14.7psi

P1: 82.0, 82.0, 77.5, 72.8, 72.0

Core 2

P2: 14.7psi

P1: 82.7, 81.3, 76.9, 72.6 72.4

Table 4.13: Flowrate/pressure results

Core samples	2ml	4ml	6ml	8ml	10ml
Flowrates (ml/s)					
Core 1	0.039	0.022	0.017	0.007	0.006
Core 2	0.038	0.029	0.028	0.019	0.012
Pressure differential (Δp)					
Core 1	67.8	66	62.8	58.1	57.3
Core 2	68	66.6	62.2	57.9	57.7

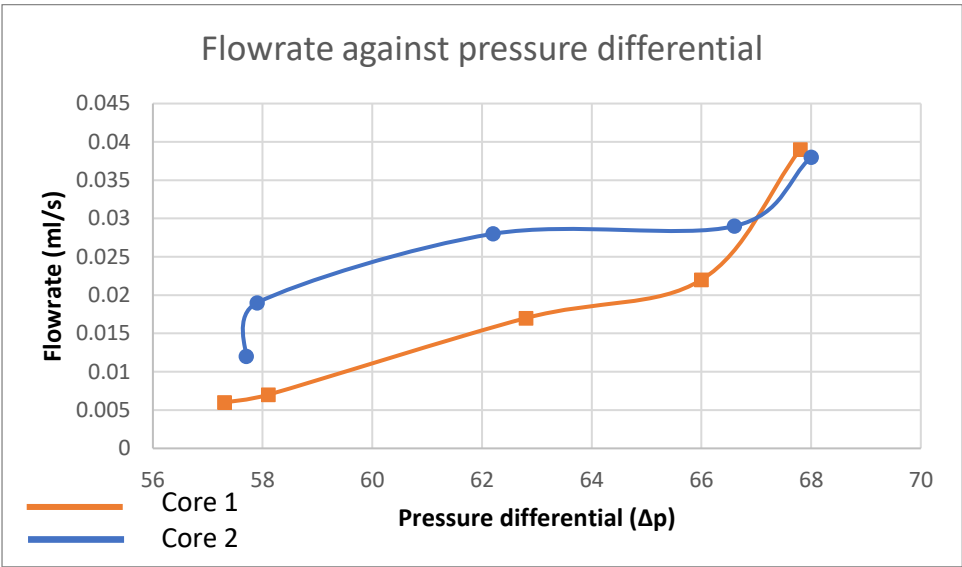


Figure 4.7: Flowrate against pressure differential for core 1 and 2

4.1.4.4 Oil flooding

Table 4.14: Oil flood results for core 1

S/N	Oil recovered (ml)	Time taken (seconds)	Flowrate (ml/s)
1	2	49	0.041
2	4	206	0.019
3	6	447	0.013
4	8	1440	0.006
5	10	2032	0.005

Weight of core 1 after oil flooding = 134.60g

$$S_{oi} = \frac{V_w}{V_p} \times 100$$

Where V_w = Volume of water recovered from oil flood

$$S_{oi} = (17/23.19) \times 100$$

$$= 73.3\%$$

$$S_{wi} = 100 - S_{oi}$$

$$= 100 - 73.3 = 26.7\%$$

Table 4.15: Oil flood results for core 2

S/N	Oil recovered (ml)	Time taken (seconds)	Flowrate (ml/s)
1	2	43	0.047
2	4	197	0.020
3	6	401	0.015
4	8	1295	0.006
5	10	1792	0.005

Weight of core 2 after brine flooding = 149.91g

$$\text{Initial oil saturation, } S_{oi} = \frac{V_w}{V_p} \times 100$$

Where V_w = Volume of water recovered from oil flood

$$S_{oi} = (21.9/26.74) \times 100$$

$$= 81.9\%$$

Initial water saturation, $S_{wi} = 100 - S_{oi}$

$$= 100 - 81.9 = 18.1\%$$

Table 4.16: Drainage data for core 1 and 2

Core samples	Volume of crude oil injected (PV)	Volume of water recovered (ml)	Soi (%)	Swi (%)
Core 1	15	17	73.3	26.7
Core 2	18	21.9	81.9	18.1

4.1.4.5 MES surfactant flooding

P1 for core 1 and 2 are 77.2, 76.9 psi

P2: 14.7psi

Permeability of core samples for surfactant flood

Core 1

$$\mu = 0.98$$

$$K = (2 \times 0.98 \times 5.5) / (10.75 \times 62.5)$$

$$= 0.016 \text{mD}$$

Core 2

$$K = (2 \times 0.98 \times 6) / (10.75 \times 62.2)$$

$$= 0.018 \text{mD}$$

Table 4.17: Absolute permeability results

S/N	Cores for Surfactant flood	Flow q (cm ³ /s)	P ₁ – P ₂	Absolute Permeability (mD) K = QμL/AΔP
1	Core 1	2.00	62.5	0.016
2	Core 2	2.00	62.2	0.018



Figure 4.8: Start of MES surfactant flooding

Table 4.18: MES surfactant flood results for core 1

S/N	Oil recovered from surfactant flood (ml)	Time taken (seconds)	Flowrate (ml/s)
1	2	29	0.069
2	4	66	0.061
3	6	277	0.022
4	8	562	0.014
5	10	890	0.011

After flooding for 1 hour 30minutes, 5ml of crude oil was recovered and 88ml of brine recovered.

$$\text{Oil recovery} = (5/17) \times 100 = 29.41\%$$

$$S_{or} = S_{oi} - \text{oil recovery}$$

$$= 81.9 - 29.41 = 52.49\%$$

Displacement efficiency

At the end of the surfactant flooding, the displacement efficiency can be calculated as follows:

$$ED = \frac{S_{oi} - S_{or}}{S_{oi}} \times 100 \quad (4.2)$$

$$ED = ((81.9-52.49)/81.9) \times 100$$

$$= 35.9\%$$

Table 4.19: MES surfactant flood results for core 2

S/N	Oil recovered (ml)	Time taken (seconds)	Flowrate (ml/s)
1	2	21	0.095
2	4	54	0.074
3	6	235	0.026
4	8	551	0.015
5	10	846	0.012

After flooding for 1 hour 30 minutes, 7.5ml of crude oil was recovered and 89ml of brine recovered.

$$\text{Oil recovery} = (7.5/21.9) \times 100 = 34.25\%$$

$$S_{or} = 81.9-34.24 = 47.65\%$$

Displacement efficiency

$$ED = ((81.9-47.65)/81.9) \times 100$$

$$= 41.8\%$$

Table 4.20: Flowrate/pressure differential results from surfactant flood

Core samples	2ml	4ml	6ml	8ml	10ml
Flowrates (ml/s)					
Core 1	0.069	0.061	0.022	0.014	0.011
Core 2	0.095	0.074	0.026	0.015	0.012
Pressure differential (Δp)					
Core 1	67.8	66	62.8	58.1	57.3
Core 2	68	66.6	62.2	57.9	57.7

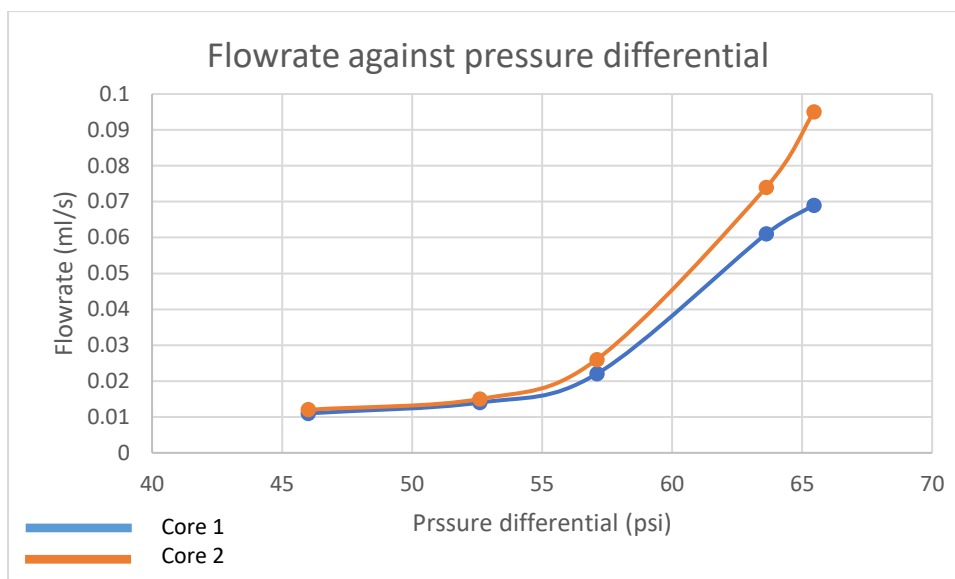


Figure 4.9: Flowrate against pressure differential for core 1 and 2 (surfactant flood)

4.2 Discussion

High oil yield was obtained from the algae oil and this was a good indicator that it was good enough to be converted into biodiesel by transesterification process. This biodiesel formed was then converted to an anionic surfactant. Analysis were performed on both the biodiesel and MES surfactant produced. FTIR analysis showed that the absorption peaked in the presence of single chained alkane stretch bond (C-H stretching alkane) in both the biodiesel sample and the surfactant sample. The presence of alkane in the surfactant lowers surface and interfacial tension in water wet systems and show good foam-ability. The IFT plot showed that the surfactant is able to reduce the interfacial tension between water and crude oil from about 28mN/m to 5.1mN/m with a decrease of 81.8%. For the core flooding process, the core samples gotten were calculated and seen to be water- wet cores. After the process of brine flooding, oil flooding and surfactant flooding, the displacement efficiency by the produced surfactant on the two cores with different properties after a time period of 1 hour and 30 minutes were 35.9% and 41.8% respectively.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Though a lot of research have been done on finding how best to recover heavy and residual oil in the reservoir, this research work was done to examine the efficiency and use of a surfactant prepared for algae oil in EOR processes. From the results, it has been made evident that algae oil being used as a substrate for anionic surfactant production to be used in surfactant flood can be used and profitable because of the displacement efficiencies gotten. Linear core experiment is a good way of examining the efficiency of prepared fluids for enhanced oil recovery. Moreover, the sulfonated biodiesel prepared was also able to lower the IFT between oil and water to a convincing level of 5.1mN/m which is a good indicator of surfactant activities.

5.2 Recommendation

For prospective increment of displacement efficiencies using algae oil MES surfactant, the following recommendations are proposed:

- Core experiments should be run with longer time so as to potentially increase oil recovery.
- Crude oil with high densities and low API gravity (heavy crude) should be used because it properly depicts the grade of residual oil in the reservoir after primary and secondary recovery have been exhausted.
- Various analyses and tests, comparing with standards should be done on the surfactant before application.

5.3 Contribution to Knowledge

To deduce how a novel surfactant synthesized from algae oil lowers crude oil-water IFT, surface tension between reservoir rock and crude oil and to estimate and evaluate the recovery factor of EOR (surfactant flooding) process.

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APPENDIX

FOR ALGAE OIL:

Using equation 3.1 to calculate % oil yield,

$$\% \text{ oil yield} = \frac{92.82g}{100.61g} \times 100 = 92.26\%$$

- Density

Weight of empty pycnometer = 19.02g

Weight of pycnometer filled with distilled water = 44.22g

Weight of pycnometer with oil = 40.70g

Weight of oil = 40.70 - 19.02 = 21.68g

a = 44.22g – 19.02g = 25.20g

b = density of water in g/cm³ = 1g/cm³

$$\text{volume of water} = \frac{25.20g}{1g/cm^3} \quad (3.11)$$

Volume of water = 25.20cm³

$$\text{density of oil} = \frac{\text{mass of oil}}{\text{volume of reference fluid (water)}} \quad (3.12)$$

$\rho = 21.68/25.20$

$= 0.8603g/cm^3$

- Viscosity

Dynamic viscosity (DV) = 0.43cp

Kinematic viscosity = ((DV) x spindle factor)/density

$$= (0.43 \times 0.01)/0.8603 = 0.005cSt$$

- Acid value

$$\text{Acid value} = \frac{0.1N \times M_w \times (B - V)}{\text{Weight of oil used}} \quad (3.13)$$

Average titre = 1.67ml, blank titre = 3.3ml

$$= 0.1 \times 56.1 \times (3.3 - 1.67) / 2$$

$$= 4.57 \text{ mgKOH/g}$$

- %FFA

$$\% \text{FFA} = \text{Acid value} / 2$$

$$= 4.57 / 2$$

$$= 2.29\%$$

- Saponification value

Average titre = 15.83 ml, blank titre = 20 ml

$$\text{Saponification value} = \frac{M_w \times M \times [V_b - V_a]}{W} \quad (3.14)$$

$$= 56.1 \times 0.5 \times (20 - 15.83) / 1$$

$$= 116.875 \text{ mgKOH/g}$$

FOR BIODIESEL:

- Density

Weight of empty pycnometer = 19.05 g

Weight of pycnometer filled with distilled water = 44.37 g

Weight of pycnometer with biodiesel = 40.48 g

Weight of biodiesel = 40.48 - 19.05 = 21.43 g

$$a = 44.37 \text{ g} - 19.05 \text{ g} = 25.32 \text{ g}$$

$$b = \text{density of water in g/cm}^3 = 1 \text{ g/cm}^3$$

$$\text{volume of water} = \frac{25.32 \text{ g}}{1 \text{ g/cm}^3} \quad (3.15)$$

$$\text{Volume of water} = 25.32 \text{ cm}^3$$

$$\text{density of biodiesel} = \frac{\text{mass of biodiesel}}{\text{volume of reference fluid (water)}} \quad (3.16)$$

$$\rho = 21.43 / 25.32 = 0.8464 \text{ g/cm}^3$$

- Viscosity

Dynamic viscosity (DV) = 0.44cp

Kinematic viscosity = ((DV) x spindle factor)/density

$$= (0.44 \times 0.01) / 0.8464 = 0.0052 \text{cSt}$$

- Acid value

$$\text{Acid value} = \frac{0.1N \times Mw \times (B - V)}{\text{Weight of biodiesel used}} \quad (3.17)$$

Average titre = 3.13ml, blank titre = 3.3ml

$$= 0.1 \times 56.1 \times (3.3 - 13) / 2$$

$$= 0.48 \text{mgKOH/g}$$

- %FFA

%FFA = Acid value/2

$$= 0.48 / 2$$

$$= 0.24\%$$

- Saponification value

Average titre = 13.83ml, blank titre = 20ml

$$\text{Saponification value} = \frac{Mw \times M \times [Vb - Va]}{W} \quad (3.18)$$

$$= 56.1 \times 0.5 \times (20 - 13.83) / 1$$

$$= 173.07 \text{mgKOH/g}$$

FOR CRUDE OIL

- Density

Weight of empty pycnometer = 19.45g

Weight of pycnometer filled with distilled water = 44.87g

Weight of pycnometer with crude oil = 42g

Weight of crude oil = 42 - 19.45 = 22.5g

$$a = 44.87 \text{g} - 19.45 \text{g} = 25.42 \text{g}$$

b = density of water in g/cm³ = 1g/cm³

$$volume\ of\ water = \frac{25.42g}{1g/cm^3} \quad (3.19)$$

Volume of water = 25.42cm³

$$density\ of\ crude\ oil = \frac{mass\ of\ crude\ oil}{volume\ of\ reference\ fluid\ (water)} \quad (3.20)$$

$$\rho = 22.5/25.42 = 0.8851g/cm^3$$

- Specific gravity

$$Y = \frac{density\ of\ crude\ oil}{density\ of\ reference\ fluid\ (water)}$$

$$Y = 0.8851g/cm^3/1g/cm^3$$

$$= 0.8851$$

- API gravity

$$API = \frac{141.5}{Y} - 131.5$$

$$API = (141.5/0.8851) - 131.5$$

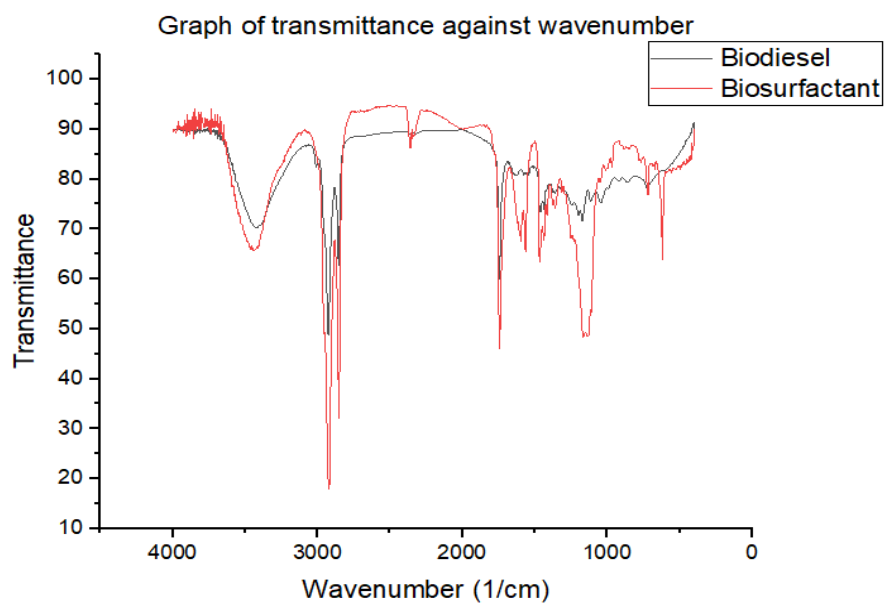
$$= 28.37^\circ API$$

- Viscosity

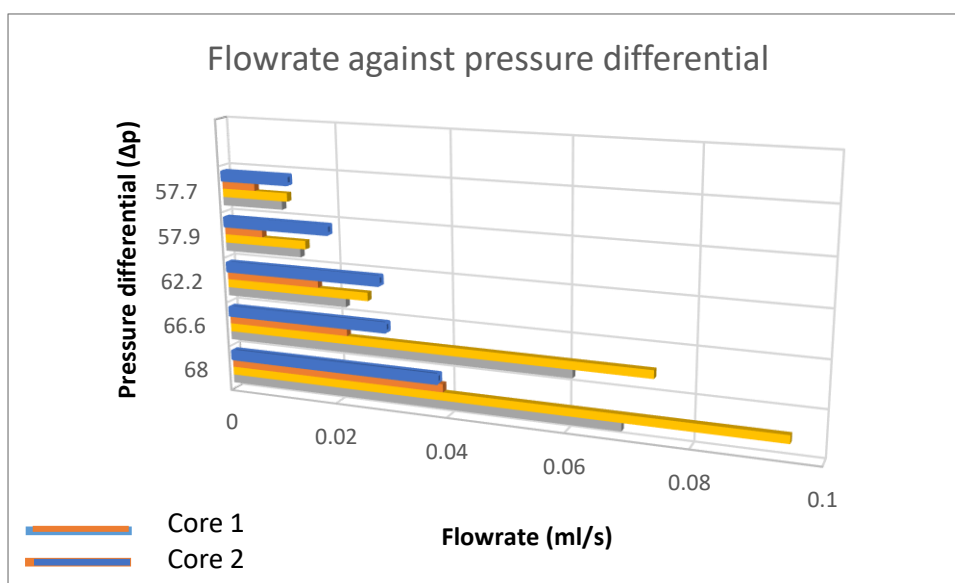
Dynamic viscosity (DV) = 3.20cp

Kinematic viscosity = ((DV) x spindle factor)/density

$$= (3.20 \times 0.1)/0.8851 = 0.36cSt$$



Appendix A.1: Comparing GCMS plots of biodiesel and surfactant



Appendix A.2: Comparing flowrate/pressure plots