OPTIMIZATION OF THE PRODUCTION OF SURFACTANT FROM LOCALLY SOURCED ALOE VERA USING ALKALI FROM CORN COBS FOR ENHANCED OIL RECOVERY

BY

JOHNSON ENWONOABASI USEN

ENG1905011

A PROJECT SUBMITTED TO THE DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF BENIN, BENIN CITY, NIGERIA

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IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF BACHELOR OF ENGNEERING IN CHEMICAL ENGINEERING

FEBRUARY, 2025

CERTIFICATION

This is to certify that this research project was carried out by **JOHNSON ENWONOABASI USEN** with matriculation number **ENG1905011** in the Department of Chemical Engineering, University of Benin, Benin City, Edo State Nigeria.

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DEDICATION

This project work is dedicated to God Almighty for his endless love, wisdom and for bringing me thus far in my academic journey and to my amazing parents for their love and support.

ACKNOWLEDGEMENT

I wish to express my profound gratitude to my project supervisor Engr. Prof. (Mrs.) E. A Oyedoh for her help, teaching and support during the course of the project. This contributed to the success of the project work.

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I also want to sincerely appreciate Engr. Dr. Taiwo A. Oluwaseun and Engr. Ojukwu N. Izuchukwu from the department of Petroleum Engineering for their support and help during the course of the project work. They provided guidance and timely corrections that contributed to the success of the study.

I would like to express my sincere gratitude to my lovely parents, Mr. and Mrs. Johnson for their constant support all through my stay in school. I want to appreciate my wonderful big sisters for their love and financial support. I also want to thank my brothers for their constant encouragement. My family's unwavering support, love and belief in me have been my greatest source of motivation.

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ABSTRACT

This study investigates a plant-based surfactant alternative as a result of the growing need for surfactants that are both economical and ecologically friendly for enhanced oil recovery. Using alkali from corn cobs, this study explores the synthesis of a natural surfactant from Aloe vera for possible use in enhanced oil recovery (EOR). Corn cobs were calcined for eight hours at 450°C to produce the alkali, which was then extracted using distilled water. Aloe vera leaves were macerated with 62.5% ethanol to extract saponins, which were then filtered and the solvent evaporated. To create the surfactant, the isolated saponins were mixed with the alkali solution that had been created under controlled conditions.

Several tests were carried out to assess the surfactant's effectiveness. Tests for emulsification and foam stability were carried out to evaluate the characteristics. The surfactant's functional groups were also compared to those of the synthetic surfactant Tween 80 using Fourier Transform Infrared Spectroscopy (FTIR). Response surface methodology (RSM) was employed using Box-Behnken Design to optimize the experimental variables and produce surfactant.

The research results showed that the aloe vera-derived surfactant proved a viable alternative for conventional synthetic surfactants due to its foaming ability and emulsion formation. The existence of functional groups typical of surfactants was confirmed by the FTIR analysis which was similar to that of tween 80. The surfactant produced had an optimum volume of emulsion of 2.52 ml which was achieved with saponin concentration of 0.0587 g/ml, 0.0186g/ml alkaline concentration at the duration of 53 mins. The RSM model was seen to be quite effective in optimizing surfactant production because of the R^2 of 0.9719. This study demonstrates the viability of using agricultural waste (corn cobs) with locally produced aloe vera to create an affordable and sustainable surfactant, supporting environmentally friendly industrial processes.

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NOMENCLATURE

CMC – Critical Micelle Concentration

CSS- Cyclic Steam Stimulation

EI – Emulsification Index

EOR – Enhanced Oil Recovery

FTIR – Fourier Transform Infrared Spectroscopy

IFT – Interfacial Tension

ISC- In-Situ Combustion

ML- Millilitre

V_e – Volume of emulsion layer (mL)

V_t – Total volume of the liquid mixture (ml)

RSM- Response surface methodology

BBD- Box-Behnken Design

ANOVA- Analysis of variance

C.V- Coefficient of Variation

LS- Local surfactant

CHAPTER ONE

INTRODUCTION

1.1. Background of study

Worldwide demand for oil and gas continues to rise, even with the recent advancements in alternative energy sources like solar energy, wind energy, geothermal energy and hydroelectric energy. By the end of 2030, global energy consumption is predicted to rise by 50% beyond its current levels. There is a high and rising need for oil as a primary energy source since renewable resources are unlikely to be able to meet this growing demand for global energy consumption (Shamsijazeyi et al., 2014). The world's growing industrialization is the primary cause of the high demand for oil. Recovering trapped hydrocarbons and improving the production of oil become the two main problems of petroleum engineers due to demand pressure (Abbas et al., 2020).

Production of oil and gas begins with the extraction of hydrocarbons from reservoir deposits as a result of decreased pressure within the reservoir. After primary and secondary recovery methods are applied, a considerable amount of oil remains in the reservoir as either bypassed or residual oil. As a result, various Enhanced Oil Recovery (EOR) techniques have been developed to extract more oil from the reservoir (Afeez et al. 2022). Exploring new reservoirs and fields involves greater risk and expense compared to employing tertiary recovery techniques to boost oil production. Only 15–30% of the original oil is usually recovered using primary and secondary oil recovery procedures, depending on the reservoir's starting pressure and fluid compressibility (Shamsijazeyi et al., 2014). Given that over half of the original oil remains trapped after primary and secondary methods, interest in Enhanced Oil Recovery (EOR) strategies has grown significantly (Emadi et al., 2019).

Enhanced Oil Recovery (EOR) methods are generally categorized into thermal and non-thermal types (Imuetinyan et al., 2022). Heavy oil, extra-heavy oil and tar sands can be extracted from reservoirs using thermal Enhanced Oil Recovery (EOR). Various thermal injection techniques have been investigated and utilized to enhance the recovery of high-viscosity oils like cyclic steam stimulation, steam flooding, steam-assisted gravity drainage, and in-situ combustion. Thermal EOR works by applying high temperatures to lower oil viscosity, thereby facilitating its mobility toward the production well (Afeez et al. 2022). High costs associated with heat supply, significant carbon dioxide (CO_2) emissions, and expensive post-treatment and maintenance requirements are the reasons for the economic and environmental challenges this method face despite the technical success (Guo et al., 2016). As a result, non-thermal EOR methods are increasingly preferred for Enhanced Oil Recovery.

Chemical EOR, gas EOR and Microbial EOR are the types of Non- Thermal EOR (Gbadamosi et al., 2018). The Chemical Enhanced Oil Recovery technique is considered highly advantageous because of its manageable capital costs, superior efficiency, and practical financial viability. Alkaline, polymers and surfactant are the chemicals that can be used for this EOR technique (Agi et al., 2020). Chemical EOR methods enhance oil recovery by improving the efficiency of water injected into the reservoir to displace the oil. This EOR method gained popularity in the 1980s as rising oil prices and advancements in technology made it possible to understand its mechanisms better. Depending on the specific chemical EOR process, the chemicals injected along with the water slug modify the interactions between fluids and/or between fluids and rock in the reservoir thereby reducing Interfacial Tension (IFT). Additionally, the injected chemicals alter the rock's wettability to enhance oil permeability (Gbadamosi et al., 2019).

Surfactant flooding, a chemical EOR method, has gained significant attention for its ability to enhance pore-scale displacement efficiency in reservoirs. Multiple field trials indicate that the application of surfactants can enhance overall oil recovery efficiency (Imuetinyan, Agi, Gbadamosi, Junin, et al., 2022). Surfactant molecules, also known as surface-active agents, are organic compounds that consist of two functional groups: a hydrophilic head (water soluble) and a hydrophobic tail (oil soluble). When the surfactant is injected into the reservoir, the hydrophilic head of the surfactant molecules is drawn to the water, while the hydrophobic tail is attracted to the crude oil (Dashtaki et al., 2022). The type of surfactants is determined by the charge on the hydrophilic group at the head: anionic surfactants have a negative charge, cationic surfactants have a positive charge, amphoteric surfactants carry both positive and negative charges, and non-ionic surfactants have no charge (Abbas et al., 2020). Surfactants lower the interfacial tension between oil and water phases and modify the wettability of the rock, which helps to decrease capillary pressure.

Due to the negative environmental impacts of industrial surfactants and the high cost of these surfactants, natural surfactants have gained significant attention in the EOR and petroleum industries over the past 10 years (Emadi et al., 2019). Recently, natural surfactants have been derived from plant leaves and plant oil extracts and utilized for Enhanced Oil Recovery (EOR). The phytochemical properties indicate that natural surfactants are surface-active because of the presence of saponins and sapogenins in the leaves. Saponins are high molecular weight glycosides regarded as natural surface-active agents with detergent properties capable of producing stable foam in water (Daghlian Sofla et al., 2016a). Saponins are classified as non-ionic surfactants due to their hydrophilic head and hydrophobic tail structure (Imuetinyan, Agi, Gbadamosi, Junin, et al., 2022). All plant extracts utilized to lower interfacial tension (IFT) contain surfactants like saponins in their composition (Abbas et al., 2020).

In contrast to conventional surfactants, the newly developed surfactants are renewable, non-toxic, and environmentally friendly. Additionally, because they are synthesized and produced from waste and readily available raw materials, these natural surfactants are cost-effective, enhancing the overall efficiency and affordability of the EOR process (Imuetinyan, Agi, Gbadamosi, Junin, et al., 2022).

1.2. Statement of the problem

Enhancing oil recovery from existing reservoirs is a challenge facing the petroleum industry, especially when conventional procedures become less effective and environmental concerns about synthetic surfactants increase. The limitations of synthetic surfactants, which are mostly expensive, hazardous, and sourced from non-renewable resources, have been identified by the need for efficient and ecologically friendly Enhanced Oil Recovery (EOR) techniques. Natural surfactants, which come from renewable resources, offer a viable substitute because of their lower toxicity and less detrimental effects on the environment. Although natural surfactants present an alternative, their application in EOR is underexplored.

The potential of aloe vera as a natural surfactant source that can successfully lower Interfacial Tension (IFT) and increase the efficiency of oil recovery has gained attention. In reservoirs, aloe vera may be used as a natural surfactant that increase oil displacement and lower interfacial tension because of its high saponin concentration and surface-active qualities. Nevertheless, little is known about the production procedures used to extract these surfactants from aloe vera, especially with regard to improving extraction techniques and analysing how well the surfactants work in enhanced oil recovery (EOR) applications.

It will be of great importance to the petroleum industry to determine the economic viability, practicality, and effectiveness of manufacturing surfactants from aloe vera for EOR applications.

In order to meet the need for sustainable and efficient alternatives for conventional surfactants, this study intends to explore the production of natural surfactants from aloe vera with the focus on their effectiveness in EOR.

1.3 Aim and objectives

The aim of this study is to optimize and investigate aloe vera, a plant source, for the extraction of a natural surfactant that is readily available, affordable and environmentally friendly and with acceptable performance in (Enhanced Oil Recovery) EOR.

The following are the objectives of the study

1. Preparation of suitable alkali using corn cob.
2. To synthesize surfactant from a locally sourced material, aloe vera as a natural surfactant for Enhanced Oil Recovery.
3. Conduct a foam test and emulsion test to know the quality of the natural surfactant.
4. Carry out a comparative study of the natural surfactant and a known synthetic surfactant.
5. To optimize the production of surfactant using response surface methodology (RSM).

1.4. Scope of the study

This project is a laboratory scale study carried out at the petroleum engineering and chemical engineering department of the University of Benin, Benin City. The preparation, optimization and evaluation of natural surfactants made from aloe vera for use in enhanced oil recovery

(EOR) applications are the main objectives of this study. The results of this study, which will only include laboratory-scale studies, are meant to guide future field research and the possible scalability of surfactants derived from aloe vera in EOR operations.

1.5 Methodology

Alkali made from corn cobs was used in the study to produce a natural surfactant from aloe vera. The procedure was broken down into several key stages:

Alkali production from maize cobs was accomplished by crushing, drying, and washing the corn cobs. After that, they were calcined for eight hours at 450°C to produce ash. 20g of corn cob ash and 500ml of distilled water were combined to create a solution, which was then heated, agitated, and allowed to soak for 48 hours before being filtered to extract the alkali solution.

After being washed, the leaves of the aloe vera plant were blended into a pulp. Using the maceration procedure, a solvent solution containing 62.5% ethanol was made and combined with the aloe vera pulp. After three days of shaking every day, the mixture was filtered. The isolated saponins were left behind after the solvent evaporated.

75 ml of saponin extract and 25 ml of alkali solution were combined to subject the derived saponin to alkaline hydrolysis. The alkaline surfactant was created by heating the mixture for an hour while stirring it with a magnetic stirrer. Response surface methodology (RSM) was employed to optimize the experimental variables and produce surfactant.

The following characterization procedure of the Surfactant was carried

I. Chemical Characterization: The functional groups in the natural surfactant were examined using Fourier Transform Infrared Spectroscopy (FTIR) and compared with those in the synthetic surfactant Tween 80.

II. Physical Characterization: To assess foam stability over time, experiments for foam generation were conducted by shaking the surfactant in test tubes. Oil, water, and the surfactant were mixed for emulsification experiments, and the emulsion index was calculated.

1.6 Relevance of the study

The goal of this research project is to produce a natural surfactant from aloe vera as an environmentally sustainable and cost-effective alternative to synthetic surfactants used in Enhanced Oil Recovery (EOR).

There is a great demand for effective EOR approaches because primary and secondary recovery methods frequently leave more than half of the original oil in place. Aloe vera-derived natural surfactants, for example, offer potential in lowering interfacial tension and enhancing oil displacement, which can increase oil recovery rates and extend the oil reservoirs' productive lifespan.

The high cost of raw materials and intricate manufacturing procedures make synthetic surfactants used in EOR expensive. EOR could become more financially feasible by using aloe vera, a readily available and renewable resource, to drastically reduce the cost of producing surfactants, particularly for small- to medium-sized oil fields.

Generally, this study is significant since it aims to increase understanding of EOR while encouraging sustainability and financial effectiveness in oil production methods.

CHAPTER TWO

LITERATURE REVIEW

Enhanced oil recovery (EOR) methods are employed to extract additional crude oil from reservoirs beyond what is recoverable by primary and secondary recovery methods In order to improve oil mobilization, chemical EOR techniques—in particular, surfactants—are essential for lowering the interfacial tension (IFT) between water and oil. Furthermore, surfactants have the capacity to alter the wettability of reservoirs, which encourages more effective oil displacement and improves recovery efficiency overall. Bio-based surfactants have received great interest for their environmental benefit and cost-effectiveness. This review is an approach in a better use of Aloe vera as a surfactant's feedstock.

2.1 WHAT ARE SURFACTANTS?

Surfactants are also referred to as surface active agents. They are molecules that absorbs on the water- surface interface and lower the water's surface tension to improve surface cleaning. Surfactants are also referred to as amphiphiles. This is because they have polar heads and no polar tails. The polar heads are also referred to as hydrophilic heads and they are attracted to polar solvents. The non-polar tails are also referred to as hydrophobic tails. Surface tension is lowered as a result of these molecules' structural shapes, which reduces the cohesive forces that hold water molecules together. Apart from lowering surface tension, they can also be used as emulsifiers, foaming agents, corrosion inhibitors and antistatic agents (Nagtode et al., 2023).

Surfactants have the ability to form micelles. Surfactants are great emulsifiers, dispersing and foaming agents because of their surface activating ability. Surfactants assist polar compounds in dissolving within organic solvents. They are key ingredients in soaps and detergents and surfactants are commonly used to get rid of oily substances from different materials. This ability makes them useful in many industrial applications. Surfactants have widespread use in industries like manufacturing, food production, agriculture, cosmetics, and pharmaceuticals (De et al., 2015).

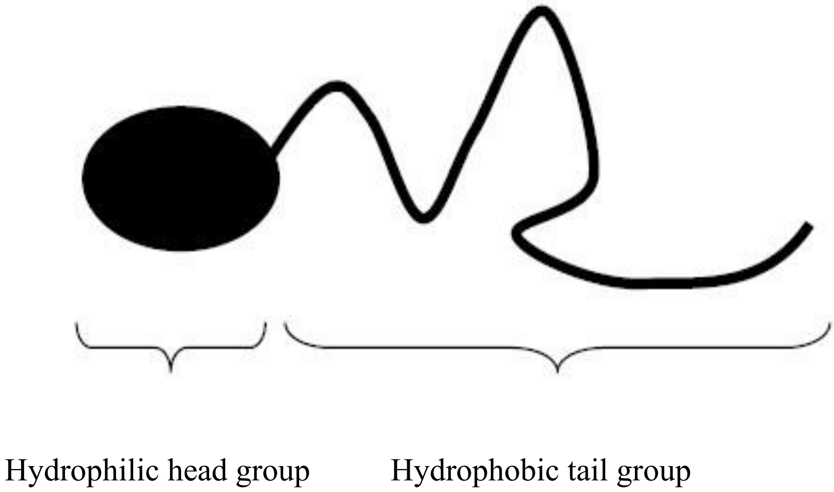

Figure 2. 1: schematic illustration of a surfactant (Saad et al., 2020)

2.2 BACKGROUND ON ENHANCED OIL RECOVERY (EOR)

Enhanced Oil Recovery (EOR), also known as tertiary recovery, is the extraction of crude oil from an oil field that could not be extracted otherwise. EOR is a process of extracting oil from a well that has already gone through primary and secondary stages of oil recovery (John, 2021). Primary production typically recovers less than 20% of the original oil (Bülow, 2012). Secondary recovery techniques, like gas or water injection, serve to maintain reservoir pressure (Baled & Morsi, 1987). EOR techniques are employed when primary and secondary methods have become exhausted (John, 2021). When EOR is used, 30% to 60% or more of a reservoir's oil can be extracted, compared to 20% to 40% using only primary and secondary recovery. EOR functions by altering the chemical composition of the oil to make it easier to extract, rather than relying on the pressure differential between the surface and the underground well (John, 2021). EOR techniques involve injecting materials not normally present in petroleum reservoirs (Baled & Morsi, 1987). These techniques can be complex and expensive, making them viable only when primary and secondary recovery methods are no longer effective or when the price of oil is high enough to justify the investment (John, 2021). Petroleum companies look to EOR to potentially prolong the life of wells in proven or probable oil fields. There are four main EOR techniques: carbon dioxide (CO2) injection, other gas injection, thermal EOR, and chemical EOR. Gases, such as carbon dioxide, are forcefully injected into the well, reducing the oil's viscosity and forcing it to the surface (Bülow, 2012). Steam can be pumped into the well to heat the oil and make it less viscous, or a fire can be lit around the periphery of the oil reservoir to drive the remaining oil closer to the well. Polymers and other chemical structures can also be injected into the reservoir to reduce viscosity and increase pressure(John, 2021).

2.2.1 Types of Enhanced Oil Recovery

Enhanced Oil Recovery (EOR) includes advanced techniques aimed at extracting extra oil from reservoirs that surpass the capabilities of primary and secondary recovery methods. A range of EOR techniques has been created to enhance recovery efficiency and facilitate oil mobility. The main types of EOR are thermal EOR, chemical EOR, and gas injection EOR, each possessing distinct mechanisms and uses (Owen & Floyd, 1981).

2.2.1.1 Thermal EOR:

Thermal Enhanced Oil Recovery (EOR) uses heat to lower the viscosity of oil, which increases its flow and eases extraction. This technique is especially successful when dealing with heavy crude oil and tar sands (Muzzafaruddin, 2019).

Different types of thermal EOR includes

I. **Steam Injection**

Steam injection is the most commonly utilized thermal enhanced oil recovery (EOR) method. It entails introducing steam into the reservoir to raise the temperature of the oil, thereby decreasing its viscosity and enhancing its flow. There are two primary categories:

a. Cyclic Steam Stimulation: Cyclic Steam Stimulation (CSS), commonly referred to as the "huff and puff" technique, involves injecting steam into a well, permitting it to soak for a period, and then utilizing the same well for production.

b. Steam Flooding: This technique entails the ongoing injection of steam through specific injection wells, driving the heated oil towards the production wells *(Green & Willhite, 2018)*.

II. **In-Situ Combustion (ISC):** This technique involves burning a segment of the oil within the reservoir to produce heat, which subsequently lowers the viscosity of the leftover oil. Although ISC is more intricate than steam injection, it can potentially recover as much as 80% of the oil available in the reservoir (Thomas, 2008).

III. **Hot Water Flooding**: Hot water flooding is a method that involves injecting heated water into the reservoir to decrease oil viscosity, serving as an alternative to steam flooding. Although it is not as efficient as steam injection, it demands less energy and can be used in certain reservoir conditions (J. Sheng, 2020).

2.2.1.2 Chemical Enhanced Oil Recovery:

The process of Chemical EOR includes the introduction of chemicals into the reservoir to modify fluid characteristics and enhance oil displacement (Lwisa, 2021).

Different types of chemical EOR includes

I. Polymer Flooding: Polyacrylamide polymers are introduced into the reservoir to enhance the viscosity of the water being injected, thereby boosting the efficiency of sweep. This technique is particularly beneficial in heterogeneous reservoirs where traditional waterflooding is inadequate (Fink, 2012).

II. Surfactant Flooding: Surfactants lower the interfacial tension between oil and water, which helps in mobilizing and recovering trapped oil. Natural biosurfactants, such as those sourced from Aloe vera, are increasingly being recognized for their environmentally friendly characteristics (Muzzafaruddin, 2019).

III. Alkaline Flooding: Alkaline flooding involves the injection of alkaline materials like sodium carbonate to interact with acidic elements found in crude oil, producing natural surfactants that improve recovery rates. This method is frequently used in conjunction with surfactant and polymer flooding to achieve greater efficiency(Khan et al., 2021).

IV. Smart water flooding: This unique method alters wettability and enhances oil recovery by changing the ionic composition and salinity of injected water. Smart water flooding has drawn interest due to its economic and ecological advantages *(Alvarado & Manrique, 2010)*.

2.2.1.3 Gas Injection Enhance Oil Recovery

Gas Injection EOR entails introducing gases into the reservoir to displace oil and increase extraction (J. Sheng, 2020).

Different kinds of Gas Injection Enhance Oil Recovery include

I. CO_2 Injection: Carbon dioxide is fed into the reservoir and dissolves in the crude oil, lowering viscosity and increasing mobility. This approach is frequently employed because of its potential for carbon capture and storage (CCS), which reduces greenhouse gas emissions (Crawford, 1978).

II. Nitrogen and Hydrocarbon Gas Injection: Nitrogen and hydrocarbon gases, such as methane and ethane, can also be employed for miscible and immiscible gas flooding, improving recovery in various reservoir conditions *(Ahmed & Meehan, 2012)*.

III. Foam assisted gas injection: This approach increases gas flooding by adding surfactants to create foam, which improves gas distribution and avoids gas channelling, making the operation more efficient (Sharp, 1975).

2.2.2 Importance of Surfactants in EOR

Chemical EOR (CEOR) enhances oil production by optimizing the effectiveness of water injection into the reservoir (Petkova et al., 2012). Surfactant flooding is an EOR technique that manipulates the phase behaviour inside the reservoir by injecting surfactants and co-surfactants (Bülow, 2012). Surfactants can lower the interfacial tension (IFT) between oil and water, which is important for mobilizing trapped oil (Druetta et al., 2019; Massarweh & Abushaikha, 2020a). Biosurfactants offer economic and environmental benefits in surfactant technologies for the oil industry (Druetta et al., 2019)

Here's a detailed breakdown of their importance:

I. **Improved Oil Recovery:** Surfactants can significantly enhance oil recovery from reservoirs, potentially eliminating the need for additional drilling (Ling et al., 2005). They achieve this by decreasing the interfacial tension between oil and water, which facilitates the movement of oil through porous rock (Bülow, n.d.).

II. **Reduction of Interfacial Tension (IFT):** Surfactants are instrumental in reducing IFT, which allows for better displacement of the oil by injected water (Bülow, n.d.). The hydrophilic head and hydrophobic tail structure of surfactants adsorb onto the oil/water interface, weakening the capillary forces that trap oil within the rock pores (Bülow, n.d.). Surfactant systems can create microemulsions at the interface between crude oil and water, reducing the IFT to ultra-low levels (0.001 mN/m), which consequently mobilizes the residual oil and results in improved oil recovery (Bülow, n.d.).

III. **Wettability Alteration:** Surfactants alter the contact angle of oil on the rock surface, changing it from an "oil-wet" state to a "water-wet" state (Ling et al., 2005)(J. J. Sheng, 2013). This weakens the capillary forces holding the oil in place, further increasing oil recover (Ling et al., 2005).

IV. **Versatility:** Surfactant flooding is effective in situations where polymer and alkali displacement methods are not suitable, such as in low permeability rock or reservoirs with high salinity(Bülow, n.d.).

V. **Environmental Benefits:** Some of the newest and most effective EOR surfactants are derived from plant resources and are readily biodegradable, non-toxic, and non-hazardous.

VI. **EOR Techniques:** In EOR, surfactants are used in micellar-polymer flooding and alkaline-surfactant-polymer flooding to increase the proportion of oil extracted from a reservoir (Bülow, n.d.).

VII. **Surfactant Compositions:** Surfactant compositions useful for oil recovery comprise a propoxylated C12-C20 alcohol sulphate, a C12-C20 internal olefin sulfonate, and an ethoxylated C4-C12 alcohol sulphate (*Surfactants for Enhanced Oil Recovery*, n.d.). Including a minor proportion of the ethoxylated alcohol sulphate reduces or eliminates the need to rely on costly cosolvents for achieving good performance in enhanced oil recovery processes (*Surfactants for Enhanced Oil Recovery*, n.d.).

VIII. **EOR in Carbonate Reservoirs:** There is increasing interest in improving oil recovery in carbonate reservoirs using surfactants, as surfactant EOR has the potential after other EOR methods have been tried (J. J. Sheng, 2013).

2.2.3 Objectives and Scope of the Literature Review

This review analyses different chemical enhanced oil recovery techniques, discussing the chemical products used and how these can be optimized to increase the efficiency of current conventional oilfields (Petkova et al., 2012). It also reviews surfactant characterization and phase behaviour, the role of surfactants in oil recovery, and surfactant adsorption onto reservoir rock (Baled & Morsi, 1987).

2.3 DEFINITION AND CLASSIFICATION OF SURFACTANTS

Surfactants, also known as surface-active agents, are amphiphilic molecules with the unique ability to interact with both water and oil. In enhanced oil recovery (EOR), surfactants are injected into the reservoir to alter the interfacial tension between oil and water, which allows trapped oil to flow more easily through rock pores and reach production wells. Surfactants can be classified based on their charge and chemical structure. The most common types include anionic, cationic, non-ionic, and zwitterionic surfactants, each offering specific advantages in the EOR process.

The classification of surfactants is a fundamental aspect of understanding their diverse applications and behaviours. Surfactants, short for surface-active agents, are amphiphilic molecules characterized by their ability to reduce surface tension between liquids, gases, and solids. This unique property stems from their molecular structure, which consists of a hydrophobic (water-repelling) tail and a hydrophilic (water-attracting) head. The interplay between these opposing regions allows surfactants to accumulate at interfaces, reducing interfacial energy and enabling phenomena such as emulsification, foaming, detergency, and wetting. The classification of surfactants is primarily based on the nature of their hydrophilic head group, as this determines their charge characteristics and influences their interactions with other molecules and surfaces. The most common classification system divides surfactants into four major categories: anionic, cationic, non-ionic, and amphoteric. This classification creates four basic groups of surfactants. Each class exhibits distinct properties and finds use in various applications ranging from household cleaning products to industrial processes and biomedical applications.

2.3.1 Types of surfactants

2.3.1.1 Anionic Surfactants

Anionic surfactants are characterized by a negatively charged hydrophilic head group(Tiwari et al., 2018). They are dissolved in water with generating the negatively charged surface active group, whose aqueous solution is neutral or alkaline (Yuan et al., 2014). This negative charge typically arises from functional groups such as sulphate, sulfonate, phosphate, or carboxylates (Yuan et al., 2014). These surfactants are widely used due to their excellent detergency, foaming, and emulsifying properties (Yuan et al., 2014). The negative charge of the head group allows anionic surfactants to effectively interact with positively charged or neutral surfaces, making them particularly effective in removing oily and particulate soils from surfaces. Anionic surfactants are commonly found in laundry detergents, dishwashing liquids, shampoos, and hand soaps (Yuan et al., 2014). They are the earliest development, the biggest production and the largest species in various types of surfactants (Yuan et al., 2014). They can be widely used as detergents, foaming agents, emulsifiers, antistatic agents, dispersants and stabilizers in the family and chemical aspects of life (Yuan et al., 2014). Prominent alkyl sulphates include sodium lauryl sulphate (sodium dodecyl sulphate, SLS, or SDS), and the related alkyl-ether sulphates sodium laureth sulphate (sodium lauryl ether sulphate or SLES), and sodium myreth sulphate.

One of the most widely used anionic surfactants is sodium lauryl sulphate (SLS), which is commonly found in personal care products such as shampoos and shower gels. SLS is effective at removing grease and dirt but can also be irritating to the skin due to its ability to disrupt the skin's lipid barrier.

2.3.1.2 Cationic Surfactants

Cationic surfactants are characterized by a positively charged hydrophilic head group(Tiwari et al., 2018). Cationic surfactants are dissolved in water with generating the surface activity positive ions (Yuan et al., 2014). They have good surface activity in an acidic medium and are likely to precipitate and lose activity in alkaline medium (Yuan et al., 2014). The positive charge is typically associated with a quaternary ammonium ion (Phil et al., 2000). Cationic surfactants are less commonly used than anionic surfactants due to their generally lower detergency and higher cost. However, they possess unique properties that make them useful in specific applications.

Cationic surfactants are often used as fabric softeners and antistatic agents. The positive charge of the head group allows them to bind to negatively charged fabrics, reducing static electricity and imparting a soft feel. They are also used as disinfectants and sanitizers due to their ability to disrupt the cell membranes of bacteria and viruses. Cationic surfactants are classified into open-chain cationic surfactants, heterocyclic group cationic surfactants and bonded.

Examples of cationic surfactants include cetyltrimethylammonium chloride (CTAC) and benzalkonium chloride (BAC). Cationic surfactants are typically not compatible with anionic surfactants because they can form insoluble complexes that reduce the effectiveness of both surfactants.

2.3.1.3 Non-ionic Surfactants

Non-ionic surfactants are characterized by a hydrophilic head group that does not carry a charge (Tiwari et al., 2018). Instead, their hydrophilic character is derived from the presence of polar groups, such as polyethylene glycol (PEG) chains or polyol groups (© EOSCA EOSCA European Oilfield Speciality Chemicals Association Bioaccumulation Potential of Surfactants: A Review, n.d.). Non-ionic surfactants are generally milder and less irritating than ionic surfactants, making them suitable for use in products for sensitive skin or delicate surfaces.

Non-ionic surfactants are widely used in detergents, emulsifiers, and wetting agents. They are effective at removing oily soils and are often used in combination with anionic surfactants to improve detergency. Non-ionic surfactants are also used in cosmetics, pharmaceuticals, and food products due to their low toxicity and good compatibility with other ingredients. They derive their polarity from having an oxygen–rich portion of the molecule at one end and a large organic molecule at the other end.

Examples of non-ionic surfactants include alcohol ethoxylates, alkyl polyglucosides (APGs) and sorbitan esters (Phil et al., 2000).

2.3.1.4 Amphoteric Surfactants

Amphoteric surfactants, also known as zwitterionic surfactants, possess both a positive and a negative charge in their hydrophilic head group (Tiwari et al., 2018)(Yuan et al., 2014). Special features or new type surfactant is as special surfactant(Yuan et al., 2014). The charge can vary depending on the pH of the solution (Phil et al., 2000). Those surfactants that change their charge with pH (Phil et al., 2000). They can be anionic, non-ionic, or cationic depending on pH (Phil et al., 2000).Amphoteric surfactants are mild and gentle on the skin and are often used in personal care products such as shampoos, shower gels, and baby products. They have good foaming and cleaning properties and are compatible with both anionic and cationic surfactants.

Examples of amphoteric surfactants include betaines and sultaines. These surfactants are often used in combination with other surfactants to improve foaming and reduce irritation.

2.3.2 Mechanism of Surfactant Action in EOR

The main role of the surfactant used for EOR is to reduce the interfacial tension between the oil present in the reservoir and the injected water(Han et al., 2022). By lowering this tension, surfactants facilitate the detachment of oil droplets from the rock surface, enabling their mobilization towards production wells. Surfactants can also alter the wettability of reservoir rocks, converting them from oil-wet to water-wet, which improves the displacement of oil by water, leading to higher recovery rates. Correctly designed surfactant systems together with the crude oil can create microemulsions at the interface between crude oil and water, thus reducing the interfacial tension (IFT) to ultra-low (0.001 mN/m), which consequently will mobilize the residual oil and result in improved oil recovery (Bülow, n.d.).

2.3.3 Advantages of Surfactant-Based EOR

Surfactant-based EOR techniques have demonstrated the potential to recover a substantial amount of additional oil from reservoirs, leading to significantly higher ultimate recovery factors. Compared to other EOR methods, surfactant-based techniques can be cost-effective, especially in reservoirs with high permeability and good well infrastructure. Surfactant EOR can often be implemented with minimal modifications to existing oilfield infrastructure, making it an attractive option for brownfield developments.

The main benefits of using surfactant-based EOR, which are backed by current research findings, are listed below.

2.3.3.1. Reduction of Interfacial Tension

The potential of surfactant-based EOR to considerably lower interfacial tension (IFT) between water and oil is one of its main benefits. By facilitating the mobilization of trapped oil droplets, this decrease in IFT improves oil recovery. For example, compared to conventional surfactants like sodium dodecyl sulphate (SDS), sodium cocoyl alaninate (SCA), an amino acid-based surfactant, showed a 91% reduction in IFT (Tackie-Otoo & Ayoub Mohammed, 2020). Likewise, ultra-low IFT values which are essential for efficient oil displacement have been proven by bio-based surfactants (Saxena et al., 2019).

2.3.3.2. Change in Wettability

Oil recovery can benefit from surfactants' ability to change the wettability of reservoir rocks, changing oil-wet surfaces into water-wet ones. The oil's displacement efficiency is improved by this change in wettability. Studies have demonstrated that surfactants such as SCA can change the oil-wet surface of carbonate and quartz to a water-wet surface, increasing recovery rates (Tackie-Otoo & Ayoub Mohammed, 2020). Recovery has also been further improved by surfactant-nanoparticle combinations that have been successful in changing wettability (Almahfood & Bai, 2018).

2.3.3.3. Environmental Benefits

There are major environmental benefits to the production of eco-friendly surfactants, such as those derived from amino acids. Because these surfactants are biodegradable and non-toxic, they lessen the environmental effect of EOR activities (Madani et al., 2019). Sustainable EOR techniques are further aided by the use of bio-based surfactants, which are made from natural sources such as soap-nut oil (Saxena et al., 2019).

2.3.3.4. Improved Performance and Stability

Gemini surfactants offer improved stability and performance in EOR applications because of their unique molecular structure. Their capacity to reduce IFT and change wettability is facilitated by their stable micellar structures and lower critical micelle concentrations (Pal et al., 2021). Because of these characteristics, gemini surfactants are an affordable choice that offers petroleum corporations substantial returns.

2.3.3.5. Adaptability and Versatility

EOR based on surfactants is adaptable to different reservoir conditions. Operators can maximize recovery processes by choosing the right surfactants based on reservoir parameters including temperature, salinity, and rock type (Massarweh & Abushaikha, 2020b) (Negin et al., 2017a). For instance, it has been demonstrated that using zwitterionic-anionic surfactant blends can increase oil recovery and obtain ultralow IFT without the requirement for alkali, which can result in scaling and other problems (Kurnia et al., 2020).

2.3.3.6. Synergistic Effects with Nanoparticle

Synergistic effects have been demonstrated when surfactants and nanoparticles are used to improve EOR performance. Nanoparticles coated with surfactants have the ability to alter the characteristics of the oil-water interface, improving wettability and lowering IFT (Almahfood & Bai, 2018). This collaboration solves some of the problems associated with conventional EOR methods and enables more effective oil recovery.

2.3.4 Comparison of Natural vs Synthetic Surfactants in Oil Recovery

Table 2. 1 Comparison of Natural and Synthetic Surfactants

Aspect	Natural Surfactants	Synthetic Surfactants
Environmental Impact	Natural surfactants are safe for the environment and are	Synthetic surfactants are often non-biodegradable and harmful, creating

	biodegradable(Abdurrahman et al., 2023)(Atta et al., 2021).	environmental concerns (Abdurrahman et al., 2023)(Tackie-Otoo et al., 2020).
Cost	Natural availability and reduced manufacturing costs result in generally lower prices. (Daghlian Sofla et al., 2016b).	Increased expenses for environmental management and production (Daghlian Sofla et al., 2016b).
Effectiveness in EOR	Similar to synthetic surfactants in its ability to alter wettability and reduce IFT (Daghlian Sofla et al., 2016b) (Torres et al., 2011).	Proven effectiveness in EOR, however there may be negative environmental effects (Daghlian Sofla et al., 2016b)(Torres et al., 2011).
Performance in Harsh Conditions	Some natural surfactants function well in environments with high salinity and temperatures (Zhuniskenov et al., 2024) .	Although synthetic surfactants are made to endure severe conditions, they might require further chemical treatment (Zhuniskenov et al., 2024).
Applications	utilized in a variety of EOR operations, including harsh environments and offshore settings (Zhuniskenov et al., 2024).	Extensively utilized in EOR, although environmental impact is subjected to harm more and more(Zhuniskenov et al., 2024).
Research and Development	Continuous investigation on improving extraction and synthesis techniques for	Research into minimizing environmental impact is still ongoing, despite established methods

	improved yields (Zhuniskenov et al., 2024) (Atta et al., 2021).	(Zhuniskenov et al., 2024) (Atta et al., 2021).

2.3.5 Properties of an ideal surfactant for enhanced oil recovery (EOR)

Surfactants play an important role in chemical Enhanced Oil Recovery (EOR) because they reduce interfacial tension and improve trapped oil mobilization. An excellent surfactant for EOR should have certain key features that assure efficiency, cost-effectiveness, and environmental sustainability. The following are the essential characteristics:

i. Low interfacial tension (IFT)

The fundamental role of a surfactant in EOR is to dramatically reduce interfacial tension between oil and water. Reduced IFT improves residual oil displacement, resulting in higher overall recovery rates (Chatterjee & Muralidhar, 1995b). (Nandwani et al., 2017) found that efficient oil displacement requires ultra-low IFT values ($<10^{-3}$ mN/m).

ii. High thermal and chemical stability

Surfactants must be thermally stable due of the high temperatures and pressures that are frequently seen in reservoirs. The surfactant must not degrade when exposed to reservoir brine, alkaline conditions, or severe chemical environments (AlRadhwan et al., 2023). Stability in high salinity conditions enhances surfactant performance in reservoirs (JL, 2023).

iii. Compatibility with reservoir fluids and rocks

An excellent surfactant should not react adversely with reservoir minerals or formation water. It must be efficient under varying salinity and hardness conditions, ensuring broad applicability throughout reservoirs (Sagi, 2015). Some surfactants are better suited to sandstone reservoirs, whereas others prefer carbonate deposits (Negin et al., 2017).

iv. Low adsorption on rock surfaces.

High adsorption on reservoir rocks can cause significant surfactant loss, lowering efficiency. Surfactants should be tailored to reduce retention in porous media, increasing cost-effectiveness (Liu et al., 2012). Nanoparticle-stabilized surfactants can help minimize adsorption losses (Liu et al., 2021).

v. Environmental friendliness

To reduce the influence on the environment, the surfactant should be biodegradable and nontoxic. It should follow environmental rules for chemical discharge and management (Majidaie et al., 2011). Surfactants generated from plant-based oils offer an environmentally acceptable alternative to synthetic chemicals (Saxena et al., 2017).

vi. Cost-Effectiveness

The surfactant's manufacturing and application should be economically viable for widespread use. It should be made from easily accessible and inexpensive raw resources (M. K. Sharma & Shah, 1989). Using inexpensive surfactants, such as anionic and non-ionic combinations, can improve oil recovery while lowering costs (Oby et al., 2020) **.**

vii. Foaming and Emulsification Properties

Surfactants with good foaming properties can enhance mobility control and ensure effective oil displacement. Emulsification qualities contribute to the formation of stable oil-in-water emulsions, which facilitate oil flow (Saw et al., 2023).(Saw et al., 2023) Foam-stabilized surfactants increase recovery efficiency in gas-assisted EOR systems (Memon et al., 2017).

viii. Compatible with Other EOR Agents.

The surfactant should be effective when combined with polymers, alkaline solutions, and other chemical additives utilized in EOR. When coupled with other recovery agents, it must remain stable and perform without precipitation or separation (M. Sharma, 1991). Combining surfactants with alkaline and polymer floods can improve oil recovery by controlling mobility (Mandal & Khan, 2007).

2.4 ALOE VERA

Aloe vera has been used for centuries as a medicinal plant and has many benefits for the skin, making it a popular ingredient in skincare products. *Aloe barbadensis*, or aloe vera, is rich in nutrients and antioxidants. Aloe vera is suitable for all skin types, especially dry, damaged, broken, sensitive, and irritated skin, offering anti-inflammatory, antimicrobial, antioxidant, humectant, soothing, and anti-itch qualities.

The succulent plant aloe vera, which is a member of the Xanthorrhoeaceae family, is widely used in both traditional and modern medicine and other applications due to its varied chemical makeup. The chemical profile of the plant is complex, with a range of bioactive substances found in the gel, rind, and flowers, among other parts of the plant.

Acemannan is the most prominent of the several polysaccharides found in aloe vera gel. Many of the plant's advantageous qualities are linked to acemannan, a storage polysaccharide that is high in acetylated mannose (Minjares-Fuentes et al., 2018) (Femenia et al., 1999). Along with glycoproteins, enzymes, amino acids, vitamins, and minerals, the gel also contains additional carbohydrates like glucose and mannose (Rodríguez et al., 2010). These substances are present in the gel, which helps with its beneficial applications as an anti-inflammatory and wound-healing agent.

Important bioactive chemicals can also be found in aloe vera rind. It is abundant in phenolic compounds with antioxidant qualities, such as anthrones and chromones (Añibarro-Ortega et al., 2019). Compounds such as aloin A, aloin B, aloesin, and aloe-emodin are part of the rind's phenolic composition and have been identified by advanced analytical methods like HPLC-DAD/MS (Solaberrieta et al., 2022) (Quispe et al., 2018). The rind is an important source of bioactive chemicals because these compounds support the plant's antioxidant and antibacterial properties.

Although little researched, aloe vera flowers also contain bioactive substances. They are abundant in apigenin glycoside derivatives, which have been demonstrated to be efficient in inhibiting tyrosinase activity and against specific bacterial strains (Añibarro-Ortega et al., 2019). This demonstrates how aloe vera flowers can be used to create antibacterial and skin-lightening treatments.

Many factors, such as the plant's growing environment, including soil, climate, and cultivation techniques, affect the chemical composition of aloe vera. The concentration and effectiveness of the bioactive substances found in the plant can be impacted by these factors (Baruah et al., 2016) (Rodríguez et al., 2010). For example, postharvest treatments and environmental factors might affect the amount of polysaccharides, especially acemannan (Minjares-Fuentes et al., 2018).

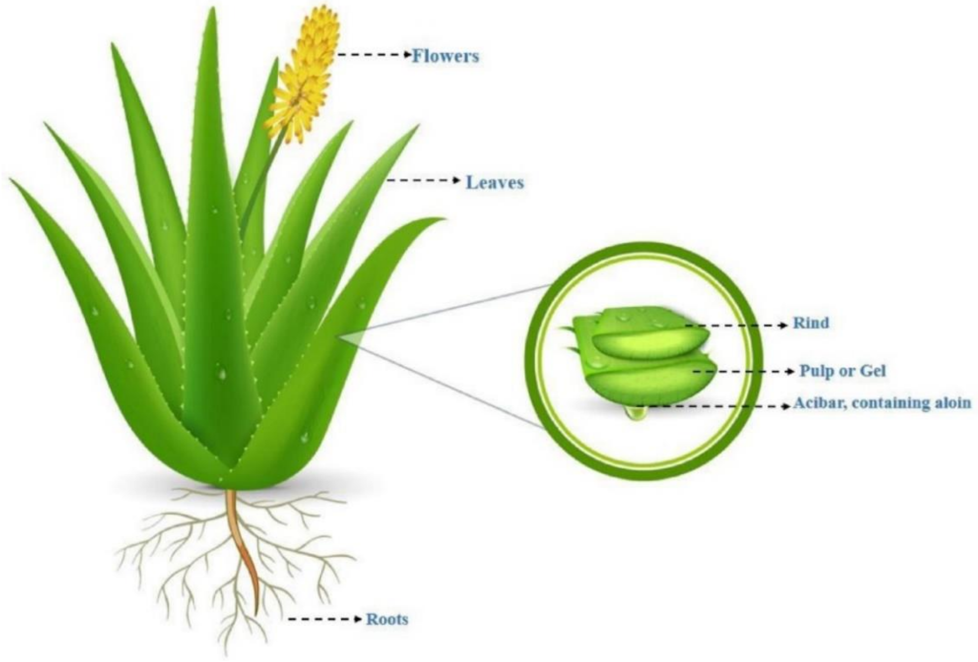

Figure 2.2 Aloe vera plant and cross section of Aloe vera leaf (Martínez-Burgos et al., 2022).

2.4.1 Chemical Composition of aloe vera

Aloe vera contains a variety of components that contribute to its beneficial properties. Key components include:

I. **Vitamins** Vitamin B complex, folic acid, vitamin C, and carotene (a precursor of vitamin A).
II. **Minerals** Aloe vera also contains minerals like zinc, which helps to promote healthy skin.
III. **Polysaccharides** These give aloe vera hydrating, emollient, and anti-inflammatory benefits and create a protective barrier on the skin (Hamman, 2008). They also help in binding moisture into the skin (Surjushe et al., 2008).
IV. **Anthraquinones** These offer antimicrobial and antioxidant characteristics.
V. **Flavones** These offer further protection from free-radical damage.

VI. **Phytosterols** These are anti-inflammatory, calm and soothe itchy skin, and protect the skin from trans-epidermal water loss.
VII. **Glycosides** These promote healthy cell regeneration and offer antihistaminic (anti-allergen) properties.
VIII. **Amino Acids** These soften hardened skin cells (Surjushe et al., 2008).
IX. Enzymes
X. Saponins
XI. Sugars (starch)
XII. Salicylic acid

Aloe vera leaf juice is composed mainly of water, along with polysaccharides, anthraquinones, amino acids, glycosides, minerals, flavones, phytosterols, and salicylic acid. Aloe vera contains approximately 110 potentially active constituents from six different classes: chromone and its glycoside derivatives; anthraquinone and its glycoside derivatives; flavonoids; phenylpropanoids and coumarins; phenylpyrone and phenol derivatives; and phytosterols (Kahramanoğlu et al., 2019).

2.4.2 Aloe Vera as a Source of Natural Surfactants

Aloe vera exhibits cleaning qualities without the use of sulphated surfactants. Aloe vera contains saponins, which possess detergent and surfactant properties (Hamman, 2008). These components contribute to aloe's ability to cleanse and purify and make it a potential ingredient in personal care compositions (*Personal Care Composition Comprising Aloe Vera*, n.d.).

2.4.3 Extraction and Modification for Surfactant Production

Aloe vera extract is a more concentrated form of aloe vera made by extracting the active ingredients from the plant using solvents or other methods. Further concentration can be achieved by removing water from pure aloe vera juice. The resulting concentrate can be incorporated into various formulations, with typical usage levels ranging from 1-10% due to its concentrated nature.

2.5 ROLE OF ALKALI IN SURFACTANT PRODUCTION

The addition of alkali in alkaline-surfactant-polymer (ASP) flooding enhances oil recovery. The synergistic effect between alkali, surfactant, and polymer can respectively promote emulsification performance, reduce interfacial tension, and improve bulk phase viscosity, thus effectively improving flooding efficiency (G. Li et al., 2024).

2.5.1 Importance of Alkalinity in Surfactant Synthesis

Alkali is often added to increase efficiency as it helps to reduce surfactant adsorption to the rock. Alkali can react with organic acids in crude oil to form surfactants in situ (G. Li et al., 2024). The synergies between alkali and surfactants produce ultra-low interfacial tension (G. Li et al., 2024). The active substances generated by the alkali synergize with the surfactant molecules to form a more compact interfacial film(G. Li et al., 2024). Alkalinity plays several crucial roles:

I. **Reduction of Surfactant Adsorption:** Alkali helps in reducing the adsorption of surfactants onto the rock surface, which increases the efficiency of the surfactant.

II. **In-situ Surfactant Formation:** Alkali can react with organic acids present in crude oil to produce surfactants directly within the reservoir (G. Li et al., 2024).

III. **Interfacial Tension Reduction:** The combination of alkali and surfactants can achieve ultra-low interfacial tension between oil and water, which is essential for mobilizing trapped oil (G. Li et al., 2024).

IV. **Emulsification Promotion:** Alkali can also promote the emulsification of crude oil, which aids in the displacement of oil (G. Li et al., 2024).

V. **Wettability Alteration:** Alkali can change the wettability of rocks (G. Li et al., 2024).

VI. **Regulation of pH and Salinity:** It helps in regulating pH and salinity (G. Li et al., 2024).

2.5.2 Conventional Alkalis Used in Surfactant Production

In the production of surfactants, conventional alkalis play a crucial role in enhancing the performance of surfactant systems, particularly in applications such as enhanced oil recovery (EOR). Here, we explore some of the conventional alkalis commonly used in surfactant production.

I. Sodium Hydroxide (NaOH)

Alkali for ASP is Sodium Hydroxide (NaOH). Caustic soda, another name for sodium hydroxide, is one of the most common alkalis used in the manufacturing of surfactants. When combined with surfactants, it is well known for its ability to efficiently lower interfacial tension (IFT), which enhances the surfactant systems' emulsification and wettability alteration capabilities (S. Kumar & Mandal, 2016). By changing the wettability of reservoir rocks and lowering the IFT between oil and water2, NaOH is frequently employed in alkali-surfactant-polymer (ASP) flooding procedures to improve oil recovery (Wang et al., 2019).

II. Sodium Carbonate (Na_2CO_3)

Alkali for ASP is Sodium Carbonate (Na_2CO_3). ASP flooding has shifted from a strong alkaline type to a weak alkaline type (Na_2CO_3)(G. Li et al., 2024). Another popular alkali utilized in the synthesis of surfactants is sodium carbonate, sometimes known as soda ash. It is highly sought after for its capacity to reduce surfactant adsorption on reservoir rocks, which is essential for preserving the surfactant's effectiveness throughout EOR procedures (Rezaei et al., 2020). Anionic surfactants and sodium carbonate are frequently used to produce ultra-low IFT values, which are necessary for effective oil displacement (Lv et al., 2011).

III. Ammonium Hydroxide (NH_4OH)

In oil recovery applications, ammonium hydroxide is employed as an alkali in surfactant systems to improve surfactant effectiveness. Like other alkalis like NaOH and Na_2CO_3, it aids in lowering the IFT and changing the wettability of reservoir rocks *(S. Kumar & Mandal, 2016)*. In some reservoir situations when other alkalis might not work as well, ammonium hydroxide can be useful.

IV.Sodium Metaborate (SMB)

Another alkali employed in the synthesis of surfactants, especially in EOR applications, is sodium metaborate. It is known for its ability to increase the surfactant system's efficiency by decreasing the adsorption of surfactants on reservoir rocks *(S. Kumar & Mandal, 2016)*. To enhance the effectiveness of the flooding operation, SMB is frequently combined with additional alkalis and surfactants.

V.Diethanolamine (DEA)

In surfactant systems, diethanolamine is employed as an alkali to enhance the surfactant's emulsification and wettability alteration properties. It works very well to lower the IFT between water and oil, which is essential for improved oil recovery *(S. Kumar & Mandal, 2016)*. To get the required results in EOR applications, DEA is frequently combined with other surfactants and alkalis.

VI.Monoethanolamine (MEA)

In surfactant systems, monoethanolamine, an organic alkali, has demonstrated advantageous interfacial characteristics. In EOR procedures, it is employed to improve trapped oil displacement and emulsification. MEA is very good at decreasing the IFT and increasing the viscosity of surfactant-polymer slugs, both of which are beneficial for increasing oil recovery sweep efficiency (Pal et al., 2018).

2.5.3 Potential Alkali Reactions:

Potential Alkali reactions in formation are:

$2NaOH+Ca^{+2}\rightarrow 2Na^{+}+Ca\ (OH)_2$

$2NaOH+Mg^{+2}\rightarrow 2Na^{+}+Mg\ (OH)_2$

$Na_2CO_3+Ca^{+2}\rightarrow 2Na^{+}+CaCO_3$

2.6 CORN COB ASH AS A SUSTAINABLE ALKALI SOURCE

Corn cob ash (CCA) is obtained by burning corn cob waste (Singh et al., 2018). After burning about 1000g of dry corn, 150g of corn cob ash is generated(Kumari et al., 2018). The chemical composition of CCA is dependent on factors such as the type of corn, crop timings, climate, and geographical conditions(Kumari et al., 2018).

2.6.1 Composition and Properties of Corn Cob Ash

CCA contains a combined content of about 70% of $SiO2$ and CaO (Singh et al., 2018).The chemical composition of CCA includes (Kumari et al., 2018):

I. Silica ($SiO2$)
II. Alumina ($Al2O3$)
III. Lime (CaO)
IV. Iron Oxide ($Fe2O3$)
V. Magnesia (MgO)
VI. Sodium Oxide ($Na2O$)
VII. Potassium Oxide ($K2O$)
VIII. Sulphate ($SO3$)

The silicon content in CCA is significant (Șerbănoiu et al., 2022). CCA consists of irregular particles with micropores, which are due to the burning of organic components (Kumari et al., 2018).

2.7 CHEMICAL INTERACTIONS BETWEEN ALOE VERA EXTRACT AND ALKALI

Aloe vera contains saponins, which have detergent and surfactant properties (Chauhan et al., 2022). The addition of alkali in alkaline-surfactant-polymer (ASP) flooding enhances oil recovery (Chauhan et al., 2022). Alkali can react with organic acids in crude oil to form surfactants in situ (Chauhan et al., 2022). The synergies between alkali and surfactants produce ultra-low interfacial tension, and the active substances generated by the alkali synergize with the surfactant molecules to form a more compact interfacial film (Chauhan et al., 2022).

2.7.1 Effects on Interfacial Tension, Wettability, and Emulsification

Aloe vera surfactants reduce interfacial tension (IFT) between the oil and water solution to enable greater mobility. Surfactants have a hydrophilic head and hydrophobic tail that work together to adsorb onto the oil/water interface, which reduces IFT and weakens the capillary forces trapping the oil within rock pores. A separate interaction known as wettability alteration can occur simultaneously and further improve oil recovery. Wettability alteration alters the contact angle of oil on the rock surface from an “oil-wet” state.

2.7.2 Corn Cob Ash as an Alkali Source

Corn cob ash (CCA) contains a combined content of about 70% of $SiO2$ and CaO (Chauhan et al., 2022). The chemical composition of CCA includes Silica ($SiO2$), Alumina ($Al2O3$), Lime (CaO), Iron Oxide ($Fe2O3$), Magnesia (MgO), Sodium Oxide ($Na2O$), Potassium Oxide ($K2O$), and Sulphate ($SO3$) (Chauhan et al., 2022). CCA is produced by burning the corn cob pieces in a furnace at around 700°C for up to 5 hours (Chauhan et al., 2022).

2.8 Response Surface Methodology (RSM) in Optimization of Surfactant Production

A statistical method for simulating and examining the relationship between several independent variables and response variables in an optimization process is called Response Surface Methodology (RSM). It is frequently used in biotechnological and industrial operations to maximize results, lower expenses, and increase efficiency. RSM creates empirical models which predict the best responses from controlled experimental data by combining statistical and mathematical tools (Montgomery & St, 2022).

A key component of RSM is the design of experiments (DOE), which allows researchers to methodically assess several variables at once. Box-Behnken design (BBD), central composite design (CCD), and factorial designs are a few often utilized designs. These designs aid in assessing the importance of each component, as well as the interactions and quadratic effects between them, which eventually improves process control and optimization (Box & Wilson, 1951).

2.8.1 Advantages of RSM in Process Optimization

I. **Fewer Experimental Runs**: Traditional optimization methods involve significant trial-and-error testing, which consumes time and resources. RSM reduces the total number of experimental runs required, conserving both time and resources.

II. **In-depth Insight into Variable Interactions:** It facilitates a thorough analysis of the interactions between various factors. This leads to a better understanding of the synergistic and antagonistic connections between factors or variables.

III. **Enhanced Prediction Accuracy**: By utilizing second-order polynomial models, RSM offers precise estimations of optimal conditions (Montgomery & St, 2022).

IV. **Cost and Time Efficiency:** RSM saves industries money on raw materials, labour, and operational costs by reducing the number of runs required.

2.8.2 Common RSM Designs

Box-Behnken Design (BBD)

i. This method is efficient for quadratic response surfaces.

ii. It requires fewer experimental runs than full factorial designs.

iii. Additionally, it avoids extreme values, making it safer for optimization.

Central Composite Design (CCD)

- **i.** Offers enhanced flexibility and accuracy in predicting optimal conditions.
- **ii.** Incorporates factorial, axial, and center points to estimate curvature.

(Mouafi et al., 2016a) applied CCD to enhance the production of biosurfactants from Acinetobacter sp., resulting in a biosurfactant yield of 5.12 g/L under optimal conditions of 2.8% soybean oil, 1.2% ammonium sulphate, and a pH of 6.8.

2.8.3 Key Process Parameters Affecting Surfactant Yield

i. Saponin Concentration

- a) Saponins from Aloe vera perform as natural surfactants, affecting emulsification and reducing surface tension.
- b) Higher saponin concentrations can improve surfactant efficiency, but they may also cause precipitation or undesirable interactions.

ii. Alkali Concentration

- a) Alkali derived from corn cobs has a significant impact on saponin surface activity.
- b) Proper alkali content ensures the emulsion's stability and increases biosurfactant yield.

(Mouafi et al., 2016b) optimized the alkali concentration to 1.5%, yielding an 85% emulsification index.

Reaction Time and Temperature

- a) Surfactant production is influenced by enzymatic and chemical mechanisms that vary with time and temperature.

b) Short reaction durations may result in inadequate surfactant production, whereas prolonged exposure can destroy saponins.

2.9 RESEARCH GAP

Plant-based alternatives are becoming more and more popular as a result of the rising need for biodegradable and ecologically friendly surfactants. Aloe vera has been recognized as a possible source of biosurfactants due to its extensive phytochemical content. Furthermore, using alkali made from agricultural waste—like corn cobs—offers a sustainable and environmentally beneficial method of producing surfactants. Though a lot of study has been done on microbial and synthetic surfactants, little has been established about how to produce surfactants generated from aloe vera utilizing alkali from corn cobs for enhanced oil recovery. Research on biosurfactants has mostly examined microbial sources such as sophorolipids and rhamnolipids (Negin et al., 2017b), with little investigation into plant-based substitutes.

Although bioactive substances like saponins and glycosides, which have surfactant-like qualities, are found in aloe vera, little has been established about how to systematically extract and purify these substances using alkali made from corn cobs. Instead of investigating bio-based alternatives like alkali obtained from corn cob ash, the majority of studies concentrate on traditional alkali sources (such as sodium hydroxide and potassium hydroxide (Sahare et al., 2012).

Surfactants produced from Aloe vera need to meet specified physicochemical qualities, such as surface tension reduction, emulsification efficiency, and stability under reservoir conditions for Enhanced Oil Recovery (EOR) applications. Few research have evaluated the efficacy of aloe vera surfactants to reduce interfacial tension (Chatterjee & Muralidhar, 1995b)(Chatterjee & Muralidhar, 1995b). In comparison to conventional synthetic and microbial surfactants, very few research examine the foaming capacity, wettability alteration, and emulsification efficiency of aloe vera surfactants.

Comparative research on surfactants obtained from Aloe vera is limited, despite the extensive study of biosurfactants originating from microorganisms (Navaei & Esmaeilnezhad, 2020). Research on using waste biomass, like maize cobs, to produce surfactants is still in its development; the majority of studies concentrate on producing bioethanol (Saliu & Sani, 2012).

Therefore, the goal of this study is to address the following research problems and overcome the seemingly insurmountable obstacles associated with the synthesis of natural surfactants for more effective oil recovery:

I. What are the environmental effects of using alkali made from corn cobs as a sustainable substitute for artificial alkali?

II. Can commercial surfactant manufacturing be supported by sustainable techniques of production corn cobs and growing aloe vera?

III. What are the characteristics of aloe vera surfactants, such as their foaming capability and emulsification efficiency?

IV. How can the different variables that affect the production of surfactant be optimized using RSM?

In light of the aforementioned issues, the research's purpose and goals were established, and a different strategy for producing natural surfactants—one that is affordable, effective, and sustainable.

CHAPTER THREE

MATERIALS AND METHODS

This chapter of the project report puts forward the materials and methods used in the experiment.

3.1 MATERIALS

3.1.1 Raw Materials Used

Table 3. 1: The raw materials used for this study

S/N	RAW MATERIALS	SOURCE	USE
1	Aloe vera leaves	Purchased from the local market.	Extraction of saponins.
2	Corn cob	Purchased from the local market.	Used as a local source of alkali.

3.1.2 Reagents Used

Table 3. 2 The reagents used for this study

S/N	REAGENTS	FUNCTIONS
1	Ethanol	Acts as a solvent to efficiently extract saponins from the aloe vera gel and leaves.

2	Distilled water	Used for the various surfactant tests and other purposes during the course of the experiment
3	Crude oil sample	Characterization of the local surfactant.
4.	Tween 80	Synthetic surfactant used for the comparative study.

3.1.3 Apparatus Used

Table 3. 3 The apparatus used for this study

S/N	APPARATUS	FUNCTION
1	Laboratory furnace	Used for the calcination of the corn cob to ash.
2	Measuring cylinder	Used to accurately measure the volume of the ethanol and distilled water.
3	Beakers, glass vessels, round bottom flasks and test tubes	Used to measure, mix and hold liquids at various stages of the experiment.
4	Heating mantle	Used to uniformly heat the ash solution.

5	Magnetic stirrer	Used to ensure uniform mixing of the surfactant solution.
6	Funnel	Used to separate the solid residues from the liquid extract after the maceration process.
7	Conical Flask	Used to mix the ethanol and aloe vera extract solution uniformly to aid the maceration process.
8	Filter paper	Used to separate solids from liquids through filtration.
9	Crucible	Used to hold the corn cob piece during the calcination process.
10	pH meter	To determine the pH of the ash solution.
11	Weighing balance	Used to measure the mass of the oil samples, surfactant and corn cob ash during the experiment.

12	Volumetric Flask	Used to prepare the diluted ethanol.
13	Orbital Shaker	Used to agitate the aloe vera and ethanol solution to aid the maceration process
14	Blender	Used to blend the aloe vera leaves and gel to form a pulp.
15	Capillary Tube	Used to calculate the surface tension.
16	Syringe	Used to accurately measure small volume of oil sample, distilled water and surfactant produced during characterization.
17	Metre Rule	Used to measure the height of the liquid in the capillary tube.

3.2 METHODS

The workflow is as follows:

1. Preparation of alkali using locally sourced corn cobs.

2. Extraction of saponins from aloe vera leaves and gel.
3. Alkaline Surfactant production
4. Design of experiment and RSM modelling
5. Characterization of the surfactant produced.

3.2.1 Preparation of alkali using locally sourced corn cobs.

a. **Processing of corn cob:** The corn cobs were washed to remove sand and dirt. Then, they were dried in the sun to remove excess moisture. After they were properly dried, they were crushed into smaller pieces.

Plate 3. 1 crushed corn cobs

b. **Corn cob ash production:** The crushed corn cobs were placed in different crucibles and calcined in a laboratory furnace at 450°C for 8 hours and then allowed to cool (Sidi et al., 2016).

c. **Alkali Production:** A solution was created by mixing 20g of the corn cob ash with 500ml of distilled water. The solution was agitated using a magnetic stirrer. It was then heated using a heating mantle and allowed to cool and soak for 48 hours. Then, the soaked ash was then filtered from the solution using a filter paper and a funnel to get the liquid which is the alkali. The pH of the liquid was determined using pH meter to know if it was alkaline.

Plate 3. 2 :20g of ash mixed with 500 ml of distilled water

3.2.2 Extraction of saponins from aloe vera leaves and gel.

a. **Preparation of the aloe vera leaves:** The aloe vera leaves were properly washed to remove the yellow sap. The leaves with the gel were cut into smaller pieces. Then, a blender was used to break it down into a fine pulp.

b. **Preparation of the solvent:** The solvent was absolute ethanol and it was diluted to a concentration of 62.5%v/v by mixing 500ml of absolute ethanol with 300ml of distilled water in a volumetric flask.

c. **Extracting the saponins:** 700ml of the diluted ethanol solvent was mixed with the 355.928g of the aloe vera pulp in order to get the saponin using maceration process (Dashtaki et al., 2020). The mixture was shared in different conical flasks and the maceration process was done for three days. The orbital shaker was used to shake the mixture for two hours daily. A filter paper and funnel were used to separate the solid from the liquid. The liquid was transferred to a beaker and the solvent was completely removed by evaporation process using a magnetic stirrer that also provided heat. The resulting liquid was the saponin.

Plate 3. 3 filtration of the blended aloe vera and ethanol mixture

3.2.3 Alkaline Surfactant production.

75ml of the saponin was mixed with 25ml of the ash solution. The mixture was agitated in a magnetic stirrer for one hour that also supplied heat. The resulting solution was the alkaline surfactant.

3.2.4 Design of experiment and RSM modelling

As shown in Table 3.4, a Box-Behnken design (BBD) with three variables was used in the surfactant production process. The process variables for the experimental design are saponin concentration, alkali concentration and reaction time as shown in table 3.5. The volume of middle microemulsion phase was taken as response to the experiment. The surfactant concentration was varied from 0.02g/ml to 0.06g/ml, alkali concentration was varied from 0.005g/ml to 0.02g/ml and reaction time was varied from 20 minutes to 60 minutes. The values of input factor were selected as per BBD experimental design as shown in table 3.5. Preliminary testing and existing literature were used to determine the range of these input values (A. Kumar et al., 2019). A quadratic regression model was fitted to the data received from the 17 experimental runs generated by the BBD. Several regression analyses were utilized to calculate the model terms, and analysis of variance (ANOVA) was employed to determine the model terms' effectiveness. The response data were analysed statistically using ANOVA and the developed quadratic model was used to optimize the process.

Table 3. 4: Range of input factors for Box-Behnken design.

Variable	Coded and actual levels		
	-1	0	1
Saponin Concentration (g/ml)	0.0200	0.0400	0.0600
Alkali Concentration (g/ml)	0.0050	0.0125	0.0200
Reaction time (minutes)	20	40	60

The experimental design as shown in table 3.5 and related statistical analysis were conducted using Design Expert software version 13.0 (Stat-Ease Inc., Minneapolis, USA).

Table 3. 5: Design of experiments.

Runs	**Factors**			**Response-Volume of emulsion (ml)**
	Saponin concentration (g/ml)	**Alkali concentration (g/ml)**	**Reaction time (minutes)**	
1	0.06	0.0125	60	
2	0.04	0.02	60	
3	0.04	0.0125	40	
4	0.04	0.0125	40	
5	0.06	0.0125	20	
6	0.02	0.005	40	

7	0.06	0.005	40	
8	0.04	0.005	20	
9	0.04	0.005	60	
10	0.04	0.0125	40	
11	0.04	0.02	20	
12	0.04	0.0125	40	
13	0.06	0.02	40	
14	0.02	0.0125	60	
15	0.04	0.0125	40	
16	0.02	0.0125	20	
17	0.02	0.02	40	

3.2.5 Characterization of the surfactant produced.

3.2.5.1 Chemical Characterization

a. Fourier Transform Infrared Spectroscopy (FTIR): This analysis was done to get information about the different functional groups in the tween 80 commercial surfactant and the alkaline surfactant produced.

3.2.4.1 Physical Characterization

a. Foam Formation Test: 2 ml of distilled water and 2 ml of saponin extract were accurately measured with a syringe into a test tube. Simultaneously, 2ml of distilled water and 2ml of the alkaline surfactant were accurately measured into another test tube.

The different mixtures were shaken in the test tubes to generate foam. The presence of stable foam indicates the presence of saponins (Aluola et al., 2021). The volume of the foam was observed and recorded at 0 mins, 5 mins, 10 mins and 20 mins respectively.

b. **Emulsification Test:** The mixture was done in a volume ratio of 1:1 (Zhang et al., 2022). 2 ml of oil sample and 2m of distilled water were accurately measured with a syringe into a test tube. The process was repeated into two other test tubes. 2 ml of just the saponin extract was added to one of the test tubes, 2 ml of the alkaline surfactant was also added to one of the test tubes and nothing was added to the last test tube. The volume and stability of the emulsion was observed and the emulsion index was calculated using the formula below.

$$\mathbf{EI\%=\frac{Ve}{Vt}\times 100} \tag{3.1}$$

Where:

I. EI% = Emulsification Index (percentage)
II. V_e = Volume of the emulsified layer (ml)
III. V_t = Total volume of the liquid mixture (ml)

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1Alkali from Corn Cob Ash

The chemical analysis of corn cob reported by (Adesanya & Raheem, 2009) indicated the presence of significant amounts of potassium oxide (K_2O), sodium oxide (Na_2O), and calcium oxide (CaO), which contributes to its alkalinity. These compounds effectively react with water to form bases. The pH of the corn cob ash solution prepared in the lab was 8.2 when measured with a pH meter and this indicated alkalinity.

4.2 Foam formation and stability

Foam created through mechanical means is not thermodynamically stable and will collapse as it sits. The speed at which this collapse happens determines the foam's stability (Chen et al., 2010).

4.2.1 The change of the foam height in a test tube versus the time is shown in Table 4.1 to determine the foam stability.

Table 4. 1 Foam height of various solutions at the initial stage and after 5mins

Solution (50%)	Foam Height (cm)		
	0 min	5 min	R5
Saponin extract only	0.84	0.74	88.1%
Alkaline Surfactant	0.79	0.74	93.7%

R5 is the ratio of the height of the foam at 5 min to that at 0 min. Foam with R5 values higher than 50% can be regarded as metastable (Chen et al., 2010).

The R5 value of 50% saponins extract only solution was 88.1% and that of the alkaline surfactant was 93.7%, representing the good foam stability of the saponins from the aloe vera. This is close to the R5 value reported by Chen (Chen et al., 2010) as 96.3%. Although, the R5 value of the alkaline surfactant is higher than that of just the saponin extract. This indicates that the addition of the alkaline made from the corn cob ash increased the foam stability of the surfactant.

4.2.2 The foam's stability was determined by measuring how its volume changed as time passed after the foam was generated .

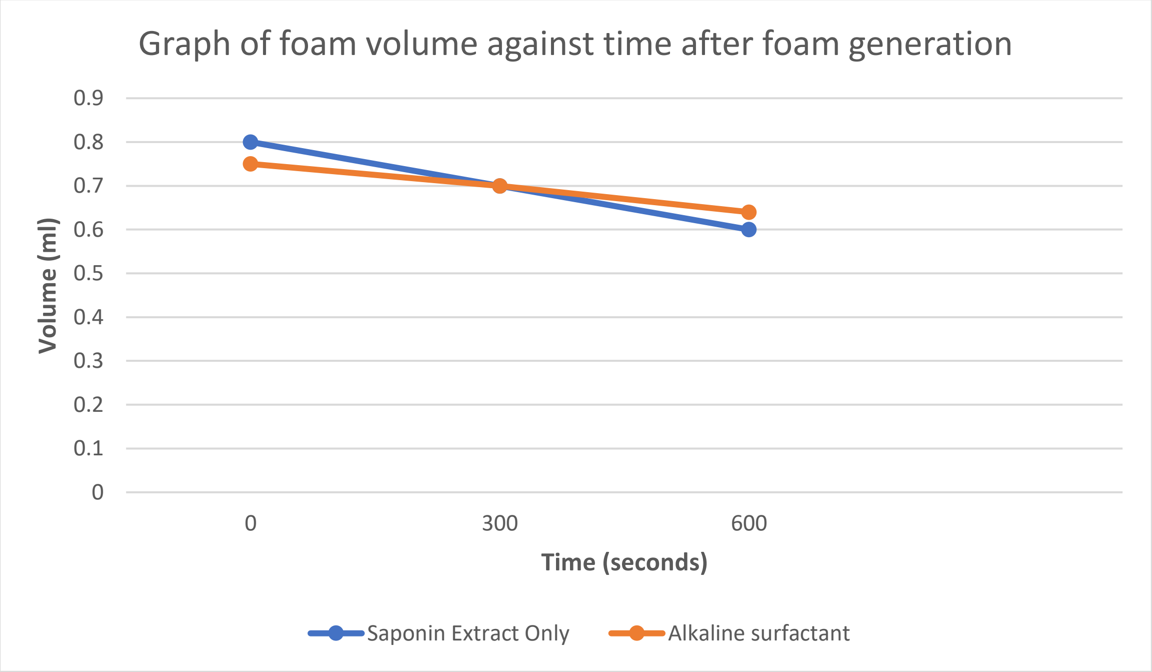

Figure 4. 1:Graph of volume of foam against time

The graph shows how foam volume changes over time for two different substances:

1. Saponin Extract Only (blue line)
2. Alkaline Surfactant (orange line)

Both substances initially generate foam, and their volumes are measured over time. At that t=0 seconds, the saponin extract only starts with a slightly higher foam volume and the alkaline surfactant starts at a slightly lower foam volume. Both foam volumes decrease over time, indicating foam collapse. At 300 seconds, the foam volumes are nearly the same. At 600 seconds, the volumes decrease further, with the alkaline surfactant maintaining slightly more foam than the saponin extract. Both substances form foam, but the alkaline surfactant retains foam slightly better than saponin extract alone.

4.3 FTIR Spectra Analysis

Among various characterization techniques, Fourier transform infrared (FTIR) spectroscopy is a particularly valuable tool for determining the functional groups (Mohamed et al., 2017). The FTIR is a plot of Transmittance (%) against wavenumber (cm^{-1}) and the signals are generated when the sample absorbs light energy and can be broad or sharp depending on the polarity of the bonds.

4.3.1 FTIR Spectra of the locally made alkaline surfactant

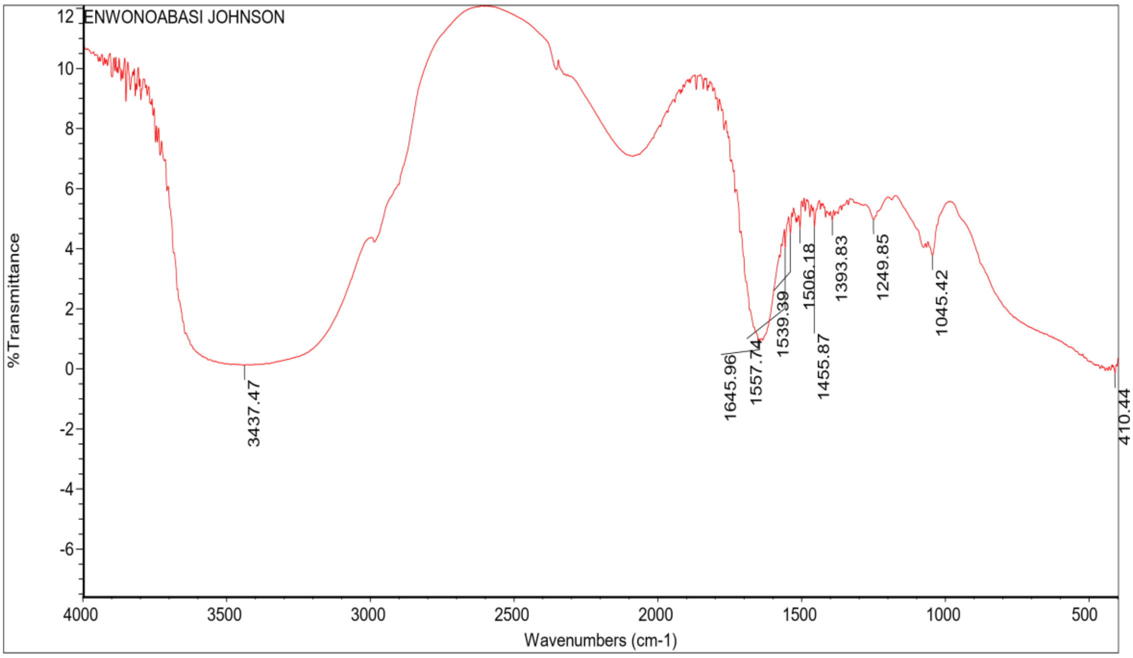

Figure 4. 2: FTIR Results for locally produced alkaline surfactant

Table 4. 2 Peak number, their corresponding wavenumber (cm^{-1}), intensity and functional group for locally produced Alkaline solution

Peak Number	wavenumber (cm^{-1})	Intensity	Functional Group
1	3437.47	0.114	O-H
2	1645.96	0.936	C=O
3	1557.74	4.025	N-O
4	1539.39	4.475	N-H
5	1506.18	4.652	C=C
6	1455.87	4.717	C-H
7	1393.83	4.930	O-H
8	1249.85	4.962	SO_2
9	1045.42	3.783	C-O
10	410.44	-0.148	Si-O

4.3.2 FTIR Spectra of tween 80

Figure 4.1 gives the FTIR result of the alkaline surfactant produced from aloe vera with the alkali gotten from corn cob ash. It can be seen that the broadband frequency of 3437.47 cm^{-1} depicts the presence of O-H (Hydroxyl) in aloe vera (polysaccharides, alcohols) and water content. This is essential for hydrophilicity in surfactants. Strong absorption at 1645.96 cm^{-1} indicates C=O stretching, suggesting ketones or carboxyl groups. This indicates saponified fatty acids or ester hydrolysis, key for surface activity. Peak at 1506.18 cm^{-1} indicates aromatic compounds, possibly substituted benzene derivatives. This may be possible due to lignin or phenolic components from corn cob ash, thereby contributing to emulsification. C-O peak at 1045.42 cm^{-1} suggest ethers, esters, or alcohols. The low wavenumber peak (410 cm^{-1}) may indicate the presence of metal-oxygen bonds, suggesting an inorganic component. This confirms the presence of silicates and metal oxides from the corn cob ash, which help enhance surfactant stability in high-salinity reservoirs. C-O Stretch matches biosurfactants Like Saponins and confirms the presence of saponins in the produced alkaline surfactant. These functional groups are similar to the one reported by (Almutairi & Ali, 2015) which include OH, C=O, C-H, C-O and C=C when detecting the presence of saponin in soapnut.

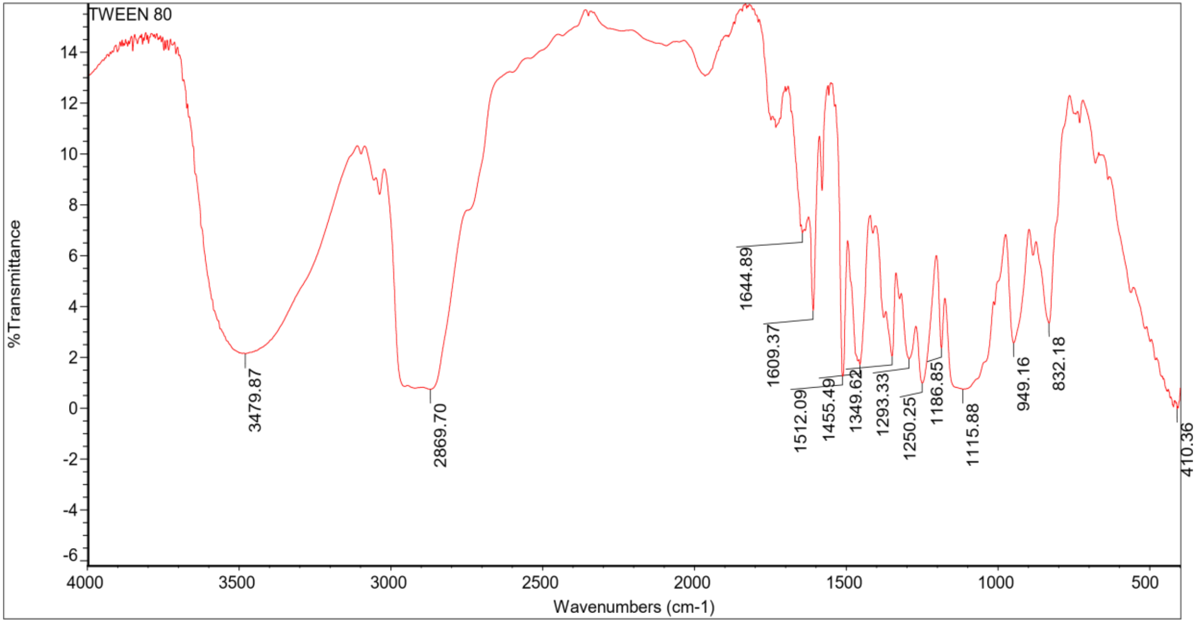

Figure 4. 3 FTIR result for commercial tween 80

Table 4. 3: Peak number, their corresponding wavenumber (cm^{-1}), intensity and functional group for commercial tween 80

Peak Number	wavenumber (cm^{-1})	Intensity	Functional Group
1	3479.87	2.137	O-H
2	2869.70	0.734	C-H
3	1644.89	6.889	C=O
4	1609.37	3.837	C=C
5	1512.09	1.252	N-O
6	1455.49	1.700	C-H
7	1349.62	2.044	O-H
8	1293.33	1.942	C-O
9	1250.25	0.983	C-O
10	1186.85	2.359	C-O
11	1115.88	0.738	C-O
12	949.16	2.562	C-H
13	832.18	3.346	C=C
14	410.36	-0.0415	Si-O

Figure 4.2 gives the FTIR result for the commercially used tween 80 synthetic surfactant. The broad O-H stretching band at 3479.87 cm^{-1} and the multiple C-O stretching bands (1186.85 cm^{-1}, 1115.88 cm^{-1}) confirm the presence of polyoxyethylene ($-OCH_2CH_2-$) groups, which contribute to Tween 80's high solubility in water. The presence of strong C-H stretching (2869.70 cm^{-1}) and bending (1455.49 cm^{-1}) vibrations supports the long alkyl chains, specifically from the oleate moiety. The 1609.37 cm^{-1} (C=C stretching) and 949.16 cm^{-1} (C-H out-of-plane bending) peaks indicate some degree of unsaturation, likely due to the oleic acid moiety. The presence of peak 1455.9 confirms the presence of CH_2 and CH_3 groups in the hydrocarbon chains. The FTIR spectrum of Tween 80 confirms the presence of key functional groups, including hydroxyl (-OH), ester (-C=O), ether (-C-O-), and alkane ($-CH_2$, CH_3) groups.

4.3.3 Comparing the FTIR result of commercially tween 80 surfactant and the alkaline surfactant produced

FTIR analysis carried out revealed that Tween 80 and the aloe vera-based alkali surfactant possess similar functional groups, implying that they are likely to exhibit comparable surfactant properties. Both spectra exhibit characteristic peaks associated with surfactant structures, including O-H, C-H, C=O, and C-O stretching vibrations. The presence of these peaks confirms functional groups that contribute to their surface activity and high presence of saponins. Both surfactants likely retain amphiphilic properties, because they both have key functional groups like OH, C=O, C-O, and C-H which are essential for their effectiveness in Enhanced Oil Recovery (EOR).

4.4 Emulsification Stability

The creation of an emulsion through the use of surfactants can lead to a reduction in interfacial tension (IFT). It enhances the compatibility with encapsulated oil, reduces the movement of water, and alters the pore structure and microscopic channels, which can enhance oil recovery ,(Imuetinyan et al., 2022).

The emulsion index is a measure of the stability of an emulsion, indicating the percentage of the dispersed phase (usually oil) that remains suspended in the continuous phase (usually water) after a specified period. A higher emulsion index signifies better stability.

To determine the emulsification index, a standard procedure was followed, where equal volumes of oil and surfactant solution were vigorously mixed and allowed to stand for a specified period. After agitation of the alkaline surfactant in a test tube, emulsion was formed and it was observed to be stable over time.

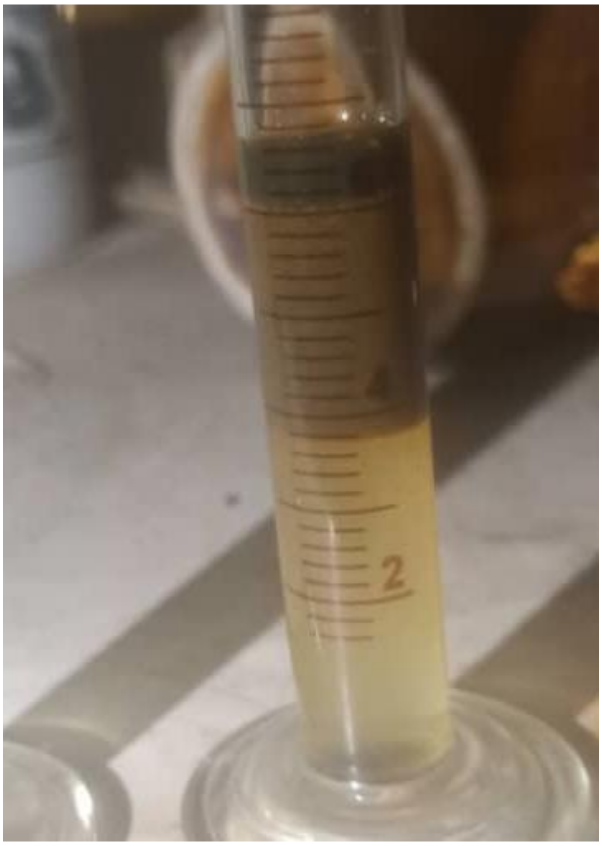

Plate 4. 1: Emulsion formation

According to the picture, the test tube seems to have three separate layers. This is labelled as follows:

I. **Top Layer: Oil Phase (Dark, Nearly Black Layer)**

This is the layer of pure oil that stays on top because it is less dense than water. It is made up of extra, unemulsified oil.

II. **Emulsified Phase (Emulsion Layer) - Middle Layer (Brownish Layer):** This is the real emulsion that was created when water, oil, and surfactant were combined. It is made up of scattered droplets stabilized by the surfactants, which is water-in-oil. Its volume serves as a gauge for emulsification efficiency. The volume of the emulsified layer in plate 4.1 is **2.2 ml**

III. Water Phase, Bottom Layer (Clear or Yellowish Layer): The remaining water that wasn't emulsified is this. Water settles at the bottom of the test tube because it is the densest component in the test tube.

The emulsion index for the alkaline surfactant was calculated and the result was 35.5% using the formula in equation 3.2. This moderate emulsification is as a result of the low concentration of 0.5 wt % of the alkaline surfactant in the test tube.

Further observations of the emulsion formed in plate 4.1 showed that the surfactant maintained its emulsifying capacity. This suggests that the surfactant system has a prolonged effectiveness, making it a viable candidate for field applications in enhanced oil recovery. In this case, an emulsion index of 35.5% moderate emulsification. The results of this study indicate that the locally produced surfactant is capable of generating stable emulsions, which is a critical factor in its application for enhanced oil recovery. The emulsification index of 35.5% suggests that the surfactant provides sufficient surface activity to facilitate oil mobilization while maintaining a stable emulsion system.

4.5 RSM Modelling of Surfactant Production

Response surface methodology was applied using a Box-Behnken Design with three key parameters: saponin concentration, alkali concentration and reaction time. Equation 4.1 representing the actual factors is the volume of emulsion formed.

Table 4. 4: Models with their significance, lack of fit, R-square, and adjusted R-square values

Source	Sequential p-value	Lack of Fit p-value	R^2	Adjusted R^2	Predicted R^2	
Linear	0.0009	0.0594	0.7053	0.6373	0.4109	
2FI	0.4186	0.0516	0.7751	0.6402	-0.0403	
Quadratic	0.0015	0.7969	0.9719	0.9358	0.8731	Suggested
Cubic	0.7969		0.9777	0.9107		Aliased

Based on factors including p-values, lack of fit test, and R-square, the quadratic model was chosen from a range of possibilities, including linear, 2F1, quadratic, and cubic models. A P-value ($P = 0.0015$) indicates the quadratic model's relevance, however a lack of fit ($P > 0.05$) increases the model's dependability. This is similar to be the p-value of 0.0167 reported (A. Kumar et al., 2019) by which suggested that the modelled equation can be used for the prediction of microemulsion volume. The quadratic model's R^2 value was 0.9719, which is close to 1.0, as shown in Table 4.4. This implies that the expected second-order polynomial model adequately captures the system's behaviour. Furthermore, the model's high relevance is further supported by the high modified R^2 value of 0.9358.

4.5.1 Empirical model of volume of emulsion formed by the surfactant

The quadratic equation for predicting the optimum volume of emulsion formed was obtained according to the Box-Behnken Design and surfactant input process variables. The relationship between the response and the independent variables was defined by the use of multiple regression analysis. The empirical relationship between the volume of emulsion formed and the independent variables in the coded unit is presented based on the experimental results in equation 4.1 The final equation representing the actual factors is the volume of emulsion formed.

$$\textbf{Volume of emulsion formed} = +1.78 + 0.1625A + 0.2250B + 0.4375C + 0.0000AB + 0.2250AC - 0.0500BC + 0.0975A^2 + 0.1225B^2 - 0.3525C^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4.1)$$

Based on equation 4.1, the three factors all have positive effects on the volume of emulsion formed by the surfactant. Synergistic interactions between saponin concentration and reaction time (AC) had a positive effect on the volume of emulsion formed by the surfactant while alkali concentration and reaction time (BC) had a negative effect. Among the quadratic terms, C^2 had a negative effect while B^2 and A^2 had positive effects on the volume of emulsion formed by the surfactant.

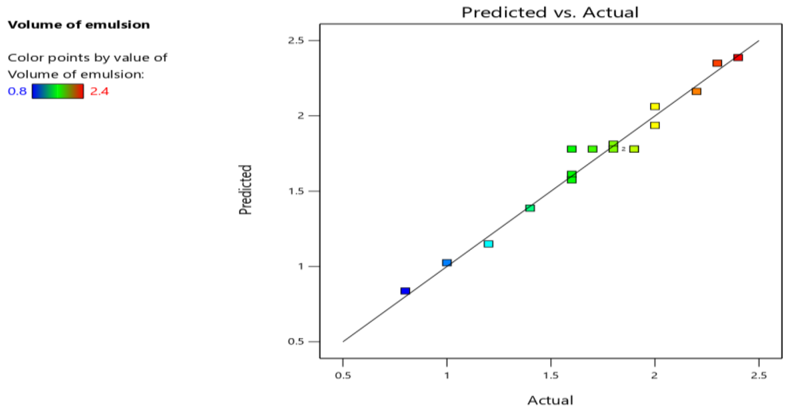

Figure 4. 4: Predicted yield versus actual biodiesel yield.

The utilization of actual versus predicted data (Fig. 4.4) serves as a valuable approach to evaluating the importance of the proposed model. The empirical model aligns well with the observed values within the operational variable range, portraying an agreement with the anticipated responses.

The fit statistics of **table 4.5** gives the values of the other parameters for describing the regression models of **equation 4.1**

Table 4. 5: Fit statistics for RSM model representing volume of emulsion formed

Parameter	value
R^2	0.9719
Adjusted R^2	0.9358
Predicted R^2	0.8731
Mean	1.72
Standard deviation	0.1105
C.V. %	6.43
Adequate Precision	18.2861

A number of goodness-of-fit criteria were used to determine whether the model was appropriate for predicting the volume of emulsion that would form. The following parameters were used: predicted R^2, adjusted R^2, R^2, acceptable accuracy, coefficient of variation, and standard deviation. Table 4.5 displays the results; a high R^2 value close to 1 is preferred. The coefficient of regression (R^2 value) is a statistical measure representing the proportion of the variance for a dependent variable explained by an independent variable or variables. As shown in Table 4.5, the volume of emulsion model has a noteworthy R^2 value of 0.9719, which indicates a significant correlation between experimental results and model predictions. In particular, an R^2 of 0.9719 indicates that the model selection accounts for 97.19% of the variability. Furthermore, a satisfactory fit between the models is indicated by the adjusted R^2 value of 0.9358. The predicted R^2 of 0.8731 is in rational agreement with the adjusted R^2 of 0.9358. There is little difference between the mean observation (1.72) and the standard deviation (0.1105), indicating that the model fits the data. The reliability of experimental runs is further supported by the coefficient of variation, or C.V., expressed as a percentage of the mean. The coefficient of variation (C.V) of 6.43% of the volume of emulsion formed by the surfactant is acceptable because the CV expresses standard deviation as a percentage of the mean and the small value of CV gives a good reproducibility. The model equation 4.1 can be used to navigate the design as analysed above.

4.5.2 Analysis of variance

The linear and quadratic effects of independent variables as well as their interactions with the response variable were evaluated using a thorough Analysis of Variance (ANOVA) (Table 4.6). The ANOVA indicates that the equation and actual relationship between the response and significant variables represented by the equation is accurate. Low p-values show that variables A, B, and C had a substantial impact on the response.

Table 4. 6: Analysis of variance for response surface quadratic model

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	2.96	9	0.3288	26.92	0.0001	significant
A-Saponin concentration	0.2113	1	0.2113	17.30	0.0042	
B-Alkali Concentration	0.4050	1	0.4050	33.16	0.0007	
C-Reaction Time	1.53	1	1.53	125.37	< 0.0001	
AB	0.0000	1	0.0000	0.0000	1.0000	
AC	0.2025	1	0.2025	16.58	0.0047	
BC	0.0100	1	0.0100	0.8187	0.3956	
A^2	0.0400	1	0.0400	3.28	0.1132	
B^2	0.0632	1	0.0632	5.17	0.0571	
C^2	0.5232	1	0.5232	42.83	0.0003	
Residual	0.0855	7	0.0122			
Lack of Fit	0.0175	3	0.0058	0.3431	0.7969	not significant
Pure Error	0.0680	4	0.0170			
Cor Total	3.04	16				

The ANOVA results for the surfactant production process (table 4.6) revealed that the F-value for the model was 26.92 with very low p-value of 0.0001, implying that there was only a 0.01 percent chance of such a large “Model F-value” due to noise and that the regression equation could explain majority of variation in the percentage formation of emulsion and that the model was significant. The P-values of the lack of fit were insignificant with value of 0.7969 which is desirable in order for the model to be fit.

Table 4. 7: Sequential Model Sum of Squares

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Mean vs Total	50.16	1	50.16			
Linear vs Mean	2.15	3	0.7158	10.37	0.0009	
2FI vs Linear	0.2125	3	0.0708	1.03	0.4186	
Quadratic vs 2FI	0.5992	3	0.1997	16.35	0.0015	Suggested
Cubic vs Quadratic	0.0175	3	0.0058	0.3431	0.7969	Aliased
Residual	0.0680	4	0.0170			
Total	53.20	17	3.13			

The RSM program generated a number of models that suit the response, including linear, cubic polynomial, quadratic, and two-factor interaction (2FI) models, in addition to recommending the best model, as shown in Table 4.7.

Table 4. 8: Final Equation in Terms of Actual Factors

Volume of emulsion	=
+0.258611	
-33.87500	Saponin concentration
-11.11111	Alkali Concentration
+0.074042	Reaction Time
-2.71285E-12	Saponin concentration * Alkali Concentration
+0.562500	Saponin concentration * Reaction Time
-0.333333	Alkali Concentration * Reaction Time
+243.75000	Saponin concentration^2
+2177.77778	Alkali Concentration^2
-0.000881	Reaction Time^2

Table 4. 9: Final Equation in Terms of Coded Factors

Volume of emulsion	=
+1.78	
+0.1625	A
+0.2250	B

+0.4375	C
+0.0000	AB
+0.2250	AC
-0.0500	BC
+0.0975	A^2
+0.1225	B^2
-0.3525	C^2

Table 4.8 and 4.9 presents the final regression model in terms of their actual factors and coded

4.5.3 Effects of the interaction of the surfactant production variables on the volume of emulsion formed.

Synergistic effects of the surfactant production variables on the volume of emulsion formed by the locally produced surfactant as shown figures 4.5,4.6 and 4.7.

4.5.3.1 Effect of Reaction Time and alkali concentration

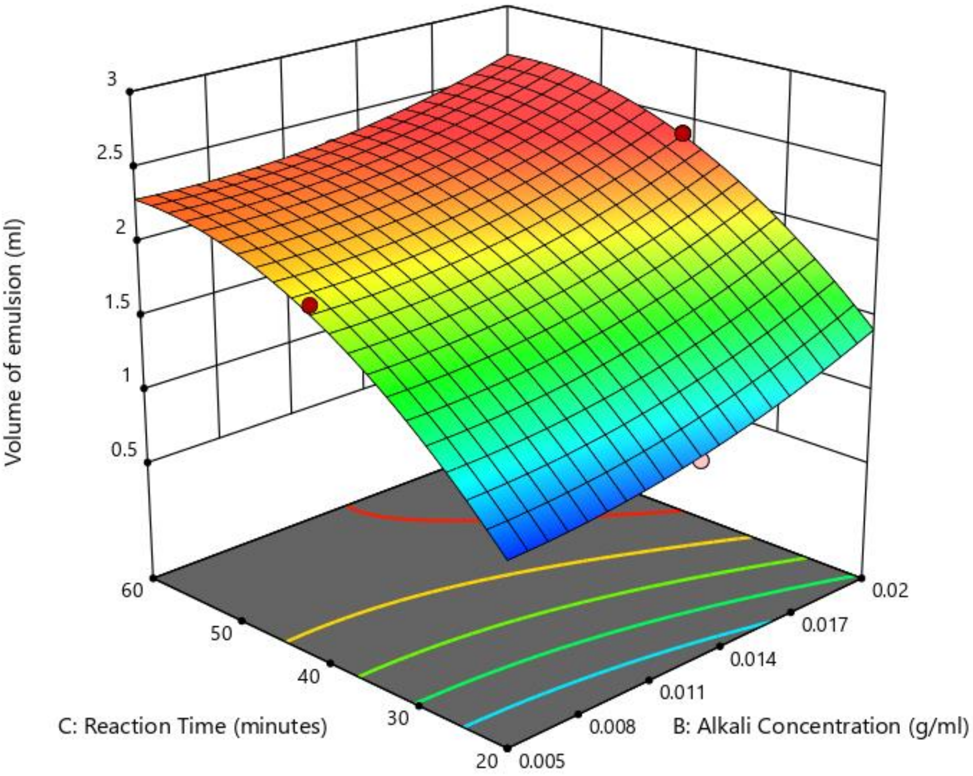

Figure 4. 5: 3D surface plots showing effects of Reaction Time and alkali concentration on the volume of emulsion formed.

The impact of Reaction Time and alkali concentration on the volume of emulsion formed is shown in Figure 4.5. At high reaction time, the volume of emulsion formed is high which indicates better yield of surfactant. The findings show that emulsification is improved and a larger volume of emulsion is produced by increasing both reaction time and alkali concentration. The colour gradient indicates a stronger effect at higher levels, with moderate-to-high alkali concentrations and extended reaction durations showing the highest emulsion volume. However, emulsification is not greatly enhanced by merely lengthening the reaction time at very low alkali concentrations. The trend's validity is confirmed by the experimental data points' tight alignment with the model. Achieving the maximum emulsion yield requires optimizing both the alkali content and the reaction duration.

4.5.3.2 Effect of reaction time and saponin concentration.

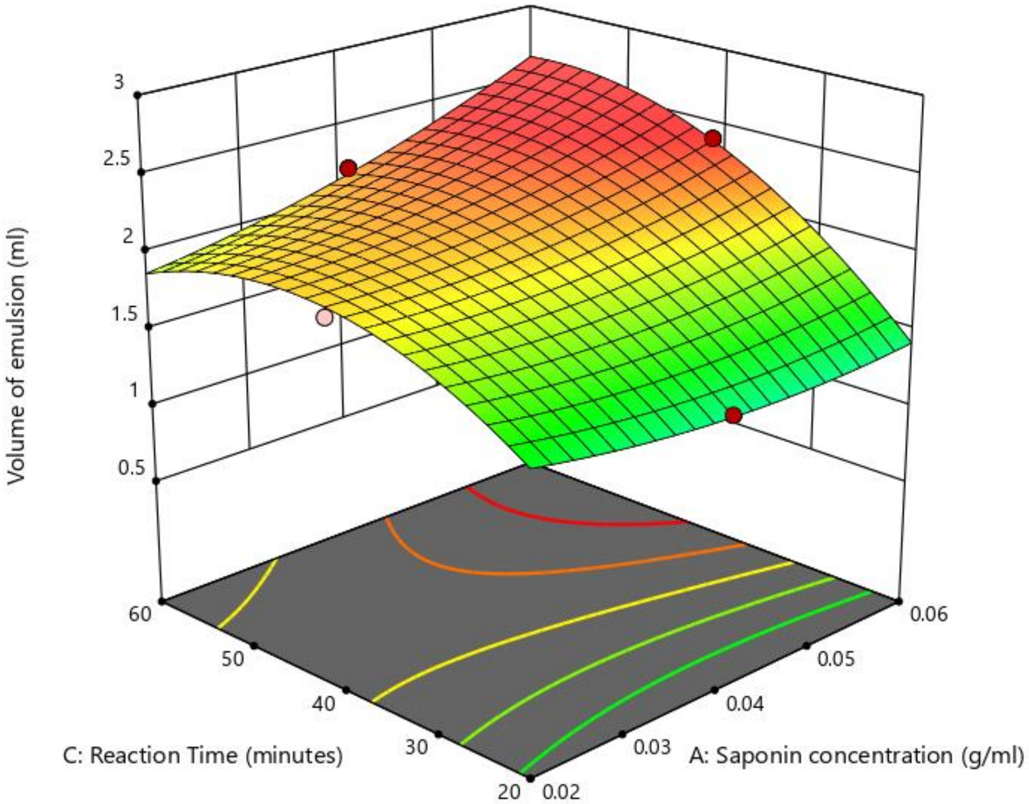

Figure 4. 6: 3D surface plots showing effects of Reaction Time and saponin concentration on the volume of emulsion formed

The relationship between volume of emulsion and reaction time, as well as saponin concentration, is illustrated in Figure 4.6. Higher saponin concentration led to a steady increase in volume of emulsion formed. The 3D surface plot demonstrates that emulsion volume is considerably influenced by both saponin concentration and reaction time. Greater emulsification results from increased surfactant activity at higher saponin concentrations. The emulsion volume decreases with shorter reaction durations, suggesting that the emulsification process needs enough time to stabilize the mixture. But after a while, the effect seems to plateau, indicating that longer reaction times might not offer any more advantages for emulsification. Additionally, the plot shows a synergistic effect, meaning that when both parameters are adjusted, the highest emulsion volumes occur. The accuracy of the model is confirmed by the alignment of experimental data points with the surface. For the best stabilization, emulsion volume maximization requires both appropriate saponin concentration and adequate reaction time.

4.5.3.3 Effect of alkali concentration and saponin concentration on the volume of emulsion formed.

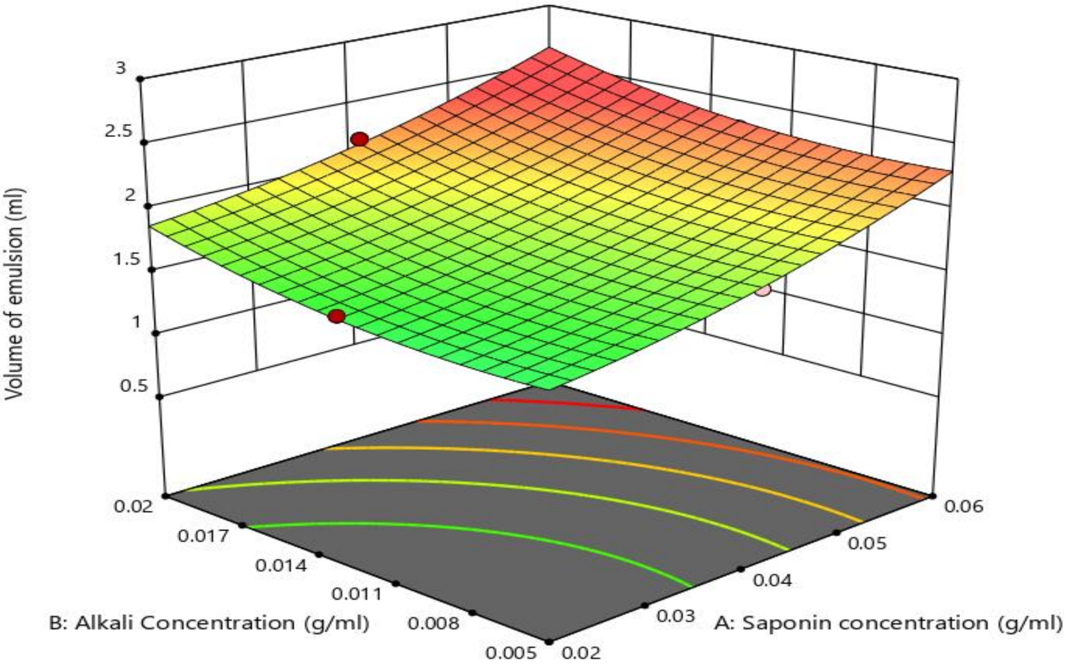

Figure 4. 7: 3D surface plots showing effects of alkali concentration and saponin concentration on the volume of emulsion formed.

Figure 4.7 shows the effect of alkali concentration and saponin concentration on the volume of emulsion formed. The combined effects of alkali and saponin concentrations on emulsion volume are depicted in the 3D surface plot in figure 4.7. Both components play vital roles in stabilizing the emulsion, as seen by the increased emulsification that occurs at higher concentrations of each. Alkali alters pH, increasing saponin activity, whereas saponins function as surfactants, lowering interfacial tension. The plot also demonstrates a synergistic impact, with the largest emulsion volumes occurring at elevated values of both components. The accuracy of the model is confirmed by the good alignment of experimental data points with the projected surface. Considering figure 4.7, optimum emulsion formation requires optimizing both saponin and alkali concentrations. This synergy reflects the results reported by (Z. Li et al., 2018), who found that higher concentrations of natural surfactants, such as quillaja saponins, resulted in improved emulsion stability.

4.5.4 Optimization

Numerical optimization technique using desirability functions was employed to optimize the volume of emulsion produced by the locally produced surfactant. The variable settings with maximum desirability are considered the optimal parameter conditions. The maximum desirability of 1.00 for volume of emulsion produced by the surfactant means that it is possible to reach the maximum volume of emulsion target.

The RSM model yielded an emulsion volume of 2.52ml with a saponin concentration of 0.0587g/ml, an alkali concentration of 0.0186g/ml, and a reaction duration of 53 minutes. The actual volume of emulsion formed was 2.4ml. The closeness of this value to the value gotten from the model indicates the accuracy of the model. The range of values for saponin concentration, alkali concentration and reaction time was 0.02g/ml to 0.06g/ml, 0.005g/ml to 0.02g/ml and 20mins to 60mins respectively.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

This study effectively evaluated the potential of aloe vera as a natural surfactant for enhanced oil recovery (EOR) using alkali made from corn cobs. In line with the growing need for ecologically suitable alternatives for synthetic surfactants, the study showed a sustainable and economical method of surfactant synthesis.

A base was created by preparing alkali from corn cobs, which made it easier to synthesize surfactant produced from aloe vera. The surfactant's surface-active qualities were subsequently confirmed by several types of tests, such as foam stability and emulsion formation test. The result from the emulsification test revealed that the surfactant had an emulsifying index of 35.5% which is a moderate emulsification due to the low concentration of 0.5 wt% of the alkaline surfactant used for the emulsification test. The critical micelle concentration of the surfactant was found to be 2 wt %.

This study effectively evaluated the potential of aloe vera as a natural surfactant for enhanced oil recovery (EOR) using alkali made from corn cobs. In line with the growing need for ecologically suitable alternatives for synthetic surfactants, the study showed a sustainable and economical method of surfactant synthesis.

The results of the Aloe vera-based surfactant were further shown by a FTIR comparison study between it and a conventional synthetic surfactant, tween 80 and similar functional groups were identified. RSM optimized several emulsion variables that affect emulsion formulation in order to produce the maximum emulsion volume using BBD. The quadratic model developed by RSM was evaluated using ANOVA, and the p-value of 0.0015 indicated that the modelled equation can be utilized to predict emulsion volume. The model was further evaluated to determine the impact of specific parameters. The estimated volume was 2.52 ml based on an optimum saponin concentration of 0.0587g/ml, an alkali concentration of 0.0186g/ml, and a reaction time of 53 minutes. The emulsion created had good miscibility with the crude oil, indicating a positive influence on crude oil recovery. In conclusion, this study offers insightful information about the production of bio-based surfactants, which will help create more environmentally friendly and sustainable EOR solutions while encouraging the use of renewable and locally accessible agricultural resources.

5.2 RECOMMENDATION

1. Further studies should optimize the extraction and purification process of Aloe vera surfactant using another design model.
2. Further research is needed to compare the effectiveness of Aloe vera surfactants to other synthetic and biosurfactants.
3. Long-term stability and biodegradability of Aloe vera surfactants should be tested in different environmental circumstances to ensure their sustainability
4. Pilot-scale field applications are needed to assess the efficiency of Aloe vera surfactants in real-world Enhanced Oil Recovery (EOR) scenarios.

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APPENDICES

CALCULATION OF PARAMETER

$$\mathbf{EI\%=\frac{Ve}{Vt}\times100}$$

Where:

V_e = Volume of the emulsified layer (ml) = 2.2 ml

V_t = Total volume of the liquid mixture (ml)=6.2 ml

$EI\%=\frac{2.2}{6.2}\times100$

EI = 35.5%