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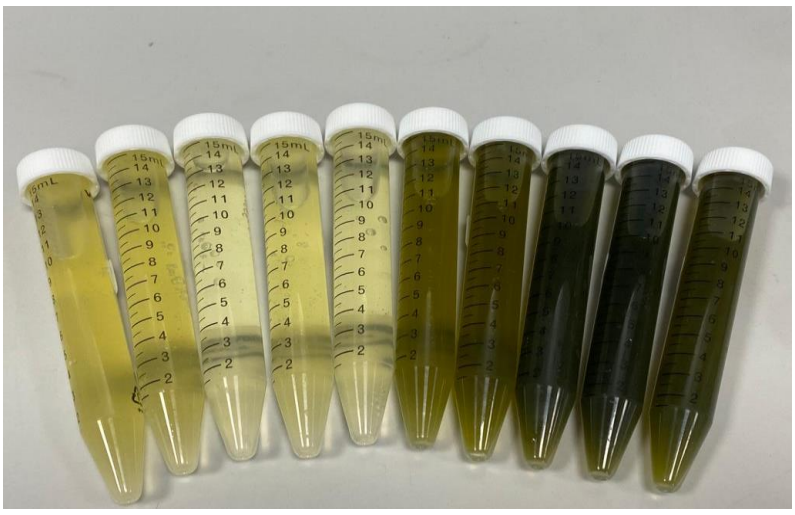
College of Engineering

Department of Chemical and Petroleum Engineering

SELECTION OF NATURAL SURFACTANTS FOR POSSIBLE USE IN IMPROVING OIL RECOVERY OF CARBONATE OIL RESERVOIRS

Hiba Hachem Mohammed Limam



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Hiba Hachem Mohammed Limam

This thesis is submitted in partial fulfillment of the requirements for the degree of Master of Science in Petroleum Engineering

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Cover: Natural surfactant used in lab experiments

(Photo: By Hiba Hachem Mohamed Limam)

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Declaration of Original Work

I, Hiba Hachem Mohammed Limam, the undersigned, a graduate student at the United Arab Emirates University (UAEU), and the author of this thesis entitled "*Selection of Natural Surfactants for Possible Use in Improving Oil Recovery of Carbonate Oil Reservoirs*", hereby, solemnly declare that this is the original research work done by me under the supervision of Prof. Abdulrazag Zekri, in the College of Engineering at UAEU. This work has not previously formed the basis for the award of any academic degree, diploma or a similar title at this or any other university. Any materials borrowed from other sources (whether published or unpublished) and relied upon or included in my thesis have been properly cited and acknowledged in accordance with appropriate academic conventions. I further declare that there is no potential conflict of interest with respect to the research, data collection, authorship, presentation and/or publication of this thesis.

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Date: 29 November 2023

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Abstract

Middle East petroleum industry is currently searching for the most suitable enhanced oil technique to improve the oil recovery from local oil reservoirs. The biggest challenge for the application of enhanced oil recovery (EOR) in the Middle East is the harsh environment (high salinity and temperature). Surfactant (synthetic or natural) is one of the EOR major players considered for application in the Middle East. However, synthetic surfactants have several drawbacks, such as economically unattractive and environmental impacts. This study investigated the possible use of natural surfactant extracted from the leaves of three types of plants, namely Aloe Vera, Tetraena qatarensis, and Soapnut in a harsh carbonate reservoir environment. The efficiency of the extracted surfactants was assessed through various laboratory experiments, Including interfacial tension (IFT) measurement, contact angle measurement, emulsion tests, and core flooding experiments. The present study follows the static and dynamic experimental work of the combination of the selected three natural surfactants at different concentrations with formation brine (232,000 ppm), seawater (50,000 ppm), and low salinity water (5,000 ppm). Interfacial tension and contact angle measurements were measured to assess the effect of water salinity on interfacial activity and system wettability. Core flooding experiments of the optimum systems with the lowest IFT and salinity of (232,000 ppm) at high pressure and temperature (1,100 psia, 90°C) were also performed to evaluate the selected natural surfactant oil recovery under dynamic conditions. Experimental results show that the Soapnut surfactant solution (18%) and Aloe Vera (10%) made with formation brine reduced the IFT from 25 dyne/cm to 0.9 dyne/cm and 0.5 dyne/cm, respectively. The oil recovery factor by formation water, Aloe Vera surfactant-FW, and Soapnut surfactant-FW flooding were 15, 93, and 94.1%, respectively. Results indicate that the Soapnut natural surfactant at a relatively low concentration is capable of working effectively in a harsh environment and was able to remove almost all the oil in place.

Keywords: Natural surfactant, interfacial tension, formation water, core flooding, carbonate reservoir, oil recovery factor.

Title and Abstract (in Arabic)

مجموعة مختارة من المواد الخافضة للتوتر السطحي الطبيعية التي تعزز استخلاص النفط في بيئة قاسية في خزانات الكربونات

الملخص

يعمل القطاع البترولي في منطقة الشرق الأوسط لإيجاد أفضل التقنيات و الحلول لتحسين الإنتاج البترولي من الخزانات البترولية المحلية. يعتبر أكبر تحدي وعائق لعملية استخراج النفط المحسن هو الطبيعية القاسية عالية الملوحة و الحرارة. تعمل المؤثرات السطحية المصنعة و الطبيعية دورا كبيرا في تحسين الإنتاج النفطي في الشرق الأوسط و لكن المؤثرات السطحية المصنعة لها دور سلبي نتيجة لتأثيرها البيئي والاقتصادي. في هذه الدراسة قمنا باستخدام ثلاثة نباتات :صبار الألوفيرا وعشبة القوماميلا بالإضافة لنبتة الهرم القطري لدراسة قابلية عملها كمؤثرات سطحية في الخزانات البترولية الجوفية تحت عوامل بيئة قاسية. تتبع الدراسة الحالية العمل التجريبي الثابت والديناميكي لدمج المواد الخافضة للتوتر السطحي الطبيعية الثلاثة المختارة بتركيزات مختلفة مع تكوين محلول ملحي (232,000 جزء في المليون)، ومياه البحر المصنعة (50,000 جزء في المليون)، ومياه منخفضة الملوحة (5000 جزء في المليون). تم قياس التوتر السطحي وقياسات التلامس لتقييم تأثير ملوحة الماء على نشاط السطح البيني وقابلية بلل النظام. كما تم إجراء تجارب الغمر الأساسية للأنظمة المثلى عند الضغط العالي ودرجة الحرارة فوق 90 درجة مئوية لتقييم استخلاص النفط الطبيعي المختار للتوتر السطحي في ظل ظروف ديناميكية. أظهرت النتائج التجريبية أن محلول الفاعل بالسطح المستخلص من نبتة القوماميلا بتركيز (18%) و أن محلول الفاعل بالسطح المستخلص من صبار الألوفيرا (10%) و المصنوع من محلول ملحي للتكوين قلل من التوتر السطحي من 25 داين/سم إلى 0.9 داين/سم و0.5 داين/سم على التوالي. كان عامل استخلاص النفط باستخدام مياه التكوينات، من مادة الصبار و القوماميلا السطحي، بنتائج 15، 93 و 94.1٪ على التوالي. إنه يشير إلى أن الفاعل بالسطح الطبيعي لقوماميلا بتركيز منخفض نسبيًا قادر على العمل بشكل جيد في بيئة قاسية وقد كان قادرًا على إزالة كل النفط الخام المقدر وجوده في العينات.

مفاهيم البحث الرئيسة: العامل السطحي الطبيعي، التوتر السطحي، مياه التكوين، الفيضانات الأساسية، خزان الكربونات، عامل استخلاص النفط.

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Dedication

To my beloved parents, siblings, and friends.

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List of Abbreviations

AlO	Aloe Vera
AS	Asab oil
Bu	Bu Hassa oil
DL	Dolomite
EOR	Enhanced oil recovery
FW	Formation water
IFT	Interfacial tension
LS	Limestone
LSW/LS	Low salinity water
OIIP	Oil initially in place
OW	Oil wet
RF	Recovery factor
SH	Sahil oil
SP	Soapnut
SW	Synthetic seawater
WW	Water wet

Chapter 1: Introduction

1.1 Overview

Discovery of new oil fields are declining and the oil demand is increasing at an alarming fast rate of around 1.4% per year from the current levels of 99.4 million b/d million barrel of oil per day. The Middle East is the only region in the world that can play a critical role in securing a future supply of oil to balance the growing demand. A significant portion of the future demand can be met by increasing oil recovery using improved and enhanced oil recovery techniques from the current oil reservoirs. Figure 1 presents Global oil demand according to EIA (2023).

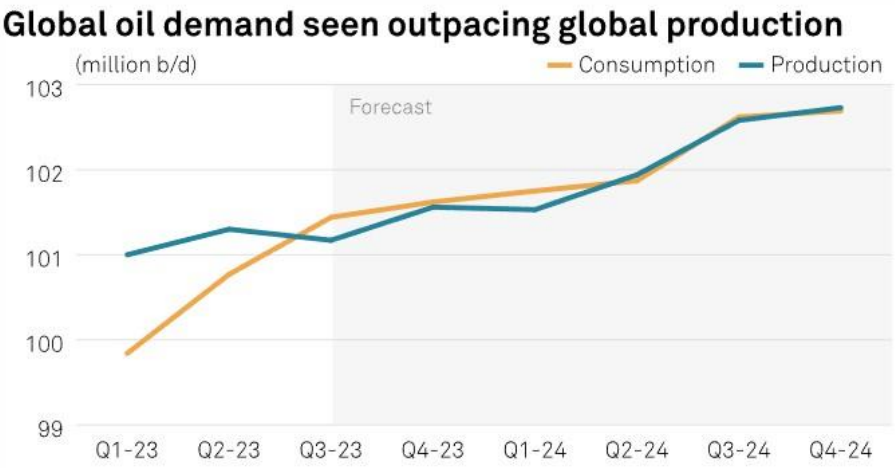


Figure 1: Global Oil Demand, Source U.S EIA

Chemical flooding consists of the following three main branches: surfactant flooding, polymer flooding, and alkaline flooding. All the previously stated processes have, to a certain degree, a toxic effect and are considered unfriendly to the environment. The need for an environmentally friendly chemical oil recovery process is clear, especially as the Gulf/UAE oil industry moves rapidly toward the application of such techniques. Recently, natural-based surfactants have been considered as the solution to the problems of toxicity associated with the application of industrial surfactants, and several researchers have investigated the possible application of these kinds of surfactants.

Surfactants are materials that reduce the interfacial tension between two liquids or between a liquid and a solid. Based on the composition of the polarity of the head group,

there are 4 types of surfactants: nonionic, anionic, cationic, and amphoteric. A natural surfactant has to have both the head and tail groups to come from accurately natural sources. Natural surfactants can be extracted from many kinds of plants. Common sources are coconut or palm, but they can also be obtained from other kinds of fruits and vegetables.

The first natural surfactant reported in the literature to our knowledge is Quillaja Saponaria Molina, which was extracted from a Chilean Soar bark tree (Rigano & Lionetti, 2009). The effect of soapnut surfactant concentration with 1%, 2%, 4%, 8%, and 12% using deionized water at 50°C was investigated by Chhetri et al. (2009). The experimental results showed that the extract has great potential to be used as a surfactant for enhanced oil recovery. Shahri et al. (2012) extracted a natural surfactant from Zyziphus Spina Christi employing a mott cell. They have reported oil recovery about ~16% OOIP (Oil originally in place) for oil-wet cores by using this surfactant. Shahri et al. (2012) investigated the adsorption behavior of this surfactant on carbonate rocks under different conditions. Deymeh et al. (2012) investigated the viability of using a new natural cationic surfactant named Seidlitzia Rosmarinus. The results show that Seidlitzia rosmarinus decreased the interfacial tension values from 32 to 9 mN/m. Results confirm the fair surface activity of Seidlitzia rosmarinus in comparison with other natural and synthetic surfactants. Ahmadi et al. (2014) extracted a natural-based surfactant from the leaves of the mulberry tree. Micro-sized particles of mulberry leaf were used to formulate a micro-fluid. The results demonstrated that a micro-fluid containing only 1 wt.% of micro-sized mulberry leaf particles was able to lower the Oil/water IFT of a system consisting of distilled water and kerosene by 60%.

Khorram Ghahfarokhi et al. (2015) have introduced natural surfactants extracted from three types of plants, named Olive, Spistan, and Prosopis. The results demonstrated that Olive extract was able to lower the IFT between kerosene and distilled water from 36.5 to 14 mN/m, while Spistan and Prosopis extract could reduce the IFT from 36.5 to 20.15 mN/m and 36.5 to 15.11 mN/m, respectively. Mosalman Haghighi and Mohsenatabar Firozjaii. (2020) have investigated the feasibility of the dodecanoyl glucosamine as a new surfactant and combination with smart water for enhanced oil recovery of an oil-wet carbonate rock. They have concluded that making a surfactant

solution using smart water can be more effective compared to a surfactant solution using high salinity brine. Smart water is a type of water used in enhanced oil recovery (EOR) processes. It is formulated to have specific ionic compositions. Nowrouzi et al. (2022) have used the aqueous extract of a powdered leaf of Myrtus communis as an available source of natural surfactant. They concluded that Myrtus communis natural surfactant has a great ability in interfacial tension reduction and an IFT value of 0.861 mN/m is obtained at surfactant CMC of 5000 ppm.

The proposed study will investigate the possible use of three naturally extracted surfactants Aloe Vera, Soapnut, and Tetraena qatarensis see Figure 2 by the local and international oil industry in enhancing the oil recovery of a carbonate reservoir. The effect of salinity, surfactant concentration, and different mixtures of the three surfactants on the displacement efficiency will be presented. An optimum system for the selected oil reservoir will be highlighted.

Tetraena qatatrensis Aloe Vera Soapnut

Figure 2: Plants Used in the Study

1.2 Statement of the Problem

The surge in the global human population, coupled with an escalating demand for energy and the rapid expansion of industries, has led to a significant strain on the world economy. This surge necessitates a substantial boost in oil production. However, many of the largest and most established oil reservoirs are now in the phase of depletion. This presents a pressing challenge. Today, we face the need for innovative and distinctive approaches and solutions to address these evolving demands in the field of energy

production. It's imperative that we look beyond the traditional methods and embrace a forward-thinking perspective to ensure sustainable energy resources for the future. This journey towards more efficient and sustainable oil production methods represents a critical frontier in the global energy landscape. Using surfactants for chemical flooding is a promising technique for improving oil recovery. However, like any method, it does come with limitations. According to Belhaj et al. (2020) one primary concern is the stability of surfactants under reservoir conditions, particularly in environments with high temperatures or salinity levels. Additionally, there can be losses due to the adsorption of surfactants onto the reservoir rock, which can reduce their effectiveness. Moreover, there's the challenge of ensuring the injected fluid effectively displaces and recovers the trapped oil within the porous structure of the rock. These limitations highlight the need for ongoing research and development in the field of chemical flooding using surfactants. And the success of the surfactant flooding process mostly depends on how much the surfactants cost. By understanding and addressing these challenges, we can work towards optimizing this technique for enhancing oil recovery.

1.3 Research Objectives

The purpose of this study is to explore the potential of plant-based surfactants, which have not yet been utilized so much in the industry but are readily available and can be cultivated in our local environment. We aim to assess its effectiveness in enhancing oil recovery in challenging conditions, characterized by high salinity, elevated temperatures, and pressure, particularly using UAE crude oils.

Our investigation will encompass various factors including interfacial tension (IFT), wettability, recovery efficiency, and emulsion properties. The ultimate goal is to contribute to the current trend of adopting environmentally friendly solutions that have a minimal long-term impact on the environment. Furthermore, we aim to discover a cost-effective alternative compared to the well-known high-priced synthetic surfactants.

The goal of this study is to discover the most effective design solution. Since we're not sure which one is best, we're going to explore all possible options through experiments. We'll use various concentrations of surfactants from different plants, and we'll test them

under conditions of low, moderate, and high salinity. We'll look at their interfacial tension (IFT) as an indicator of their effectiveness.

Next, we'll examine if these solutions can withstand high temperatures during the interaction between liquid-liquid and liquid-solid. We'll do this test using different types of carbonates, including limestone and dolomite. We'll also assess emulsion properties to determine if emulsions could potentially play a role. We'll analyze whether they form and how they behave about IFT and surfactant flooding.

Additionally, we'll investigate how wettability alteration by using different types of carbonates, considering two different conditions of permeability: high and low. This will help us understand how different materials affect the way fluids interact with the rock.

1.4 Relevant Literature

1.4.1 Enhanced Oil Recovery

Enhanced oil recovery (EOR) encompasses a set of techniques and technologies aimed at extracting the remaining oil to optimize economic retrieval beyond what primary methods, such as artificial lift that is used to lift oil from the wellbore and Natural flow of the well, can achieve. According to the U.S. Department of Energy, these primary methods typically yield less than 10% recovery. Additionally, secondary methods like water flooding and pressure maintenance using gas or other fluids typically yield between 20-40% recovery.

According to the Office of Fossil Energy within the U.S. Department of Energy, enhanced oil recovery (EOR) holds significant importance as it substantially increases the overall recovery factor, making it financially viable to extract oil from reservoirs that would otherwise be deemed economically unfeasible using conventional methods. This not only prolongs the life of oil fields but also reduces the need for additional drilling, thereby minimizing environmental impacts compared to conventional drilling practices. In contrast to primary and secondary extraction methods, Enhanced Oil Recovery (EOR) has the potential to retrieve between 30% and 60%, or even greater quantities, of oil from a reservoir (Alutbi, 2020).

There are various types of enhanced oil recovery (EOR) methods, including chemical, thermal, and gas injection techniques. Figure 3 illustrates these methods, and in addition to these, there are many more being developed by scientists each year. These emerging techniques open up new avenues to enhance oil recovery in different areas.

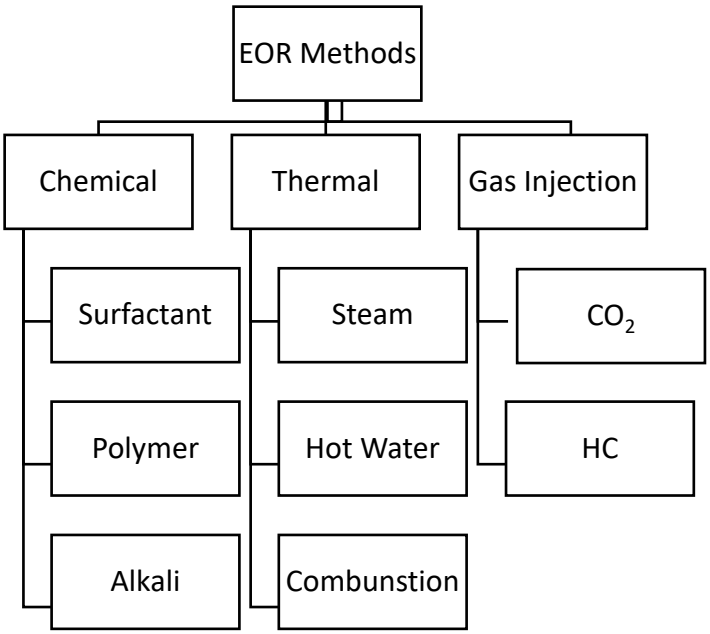


Figure 3: Main EOR Techniques Summary

Carbonate reservoirs, which contain a significant portion of the world's hydrocarbon reserves, typically exhibit low porosity and may have fractures. This combination of features, along with the mixed wet rock properties, commonly leads to lower rates of hydrocarbon recovery. In enhanced oil recovery (EOR) processes, the injected fluids tend to preferentially travel through the fracture network, bypassing the oil present in the rock matrix. This is attributed to the fracture network's high permeability and the relatively limited equivalent porous volume, causing the injected fluids to breakthrough prematurely (Alvarado & Manrique, 2010).

1.4.2 Surfactant

The recent utilization of surfactant injection stands out as the solitary chemical technique employed for well-stimulation and altering wettability in carbonate reservoirs. In instances of fractured reservoirs, there is a natural occurrence of water being drawn from the rock matrix into the fractures through spontaneous imbibition. Consequently, this

process leads to the migration of oil from the matrix towards the network of fractures. This makes surfactants a promising option for enhancing oil recovery in carbonate reservoirs that are typically oil-wetting. This enhancement is achieved by modifying the wettability of the rock (towards mixed/water wet) and encouraging the imbibition process. Notable instances of successful surfactant stimulation can be found in the extensively documented cases of Cottonwood Creek (Alvarado and Manrique, 2010).

Surfactant molecules shown in Figure 4 are categorized into five main classes based on the polarity of their head group. These include (1) non-ionic surfactants, which have no charge on their head group and are therefore more resistant to electrolyte-rich solvents; (2) anionic surfactants, characterized by a negative charge on the head group, commonly utilized in the detergent industry; (3) cationic surfactants, featuring a positive charge on the head group, often used as disinfectants and preservatives; (4) zwitterionic surfactants, which possess both positive and negative charges in their head group; and (5) gemini surfactants, a distinct class with two polar heads and two non-polar tails (Saxena et al., 2022).

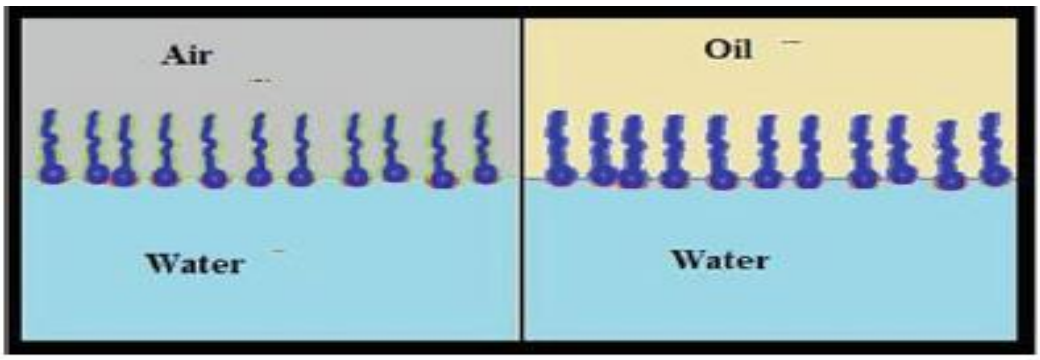


Figure 4: The Arrangement of Surfactant Molecules at the Interface between Air and Water, and Interface between Oil and Water (Saxena et al., 2022)

The main factors contributing to the decline of EOR through chemical flooding are the escalating prices of surfactants and their long-term environmental impacts (Chhetri et al., 2009). Figure 5 illustrates their cost escalation from 1983 to 2023 according to U.S. Federal Reserve Bank.

Figure 5: The Producer Price Index for Chemicals and Allied Products, Specifically, surfactants (Bulk Surface-Active Agents), indicates an increase in prices, as reported by the U.S Federal Reserve

1.4.3 Plant-Based Surfactant

The term 'natural surfactant' lacks a precise definition. It strictly refers to a surfactant directly sourced from nature, obtained through separation methods like extraction, precipitation, or distillation, from either plants or animals. This excludes any involvement of organic synthesis, even in post-processing stages. At present, there are only a few surfactants that meet these criteria. Lecithin, derived from soybean or egg yolk, stands as a prime example of a genuinely natural surfactant. The scarcity of true natural surfactants is not due to their limited availability. Amphiphiles, which are abundant in both the plant and animal realms, are often termed as polar lipids. In biological systems, these surface-active agents serve similar purposes to surfactants in technical applications, addressing issues like solubility, and acting as emulsifiers, dispersants, and surface modifiers, among other functions (Holmberg, 2001).

Plant sources serve as the main source for producing natural surfactants. Foundational elements like wood oils, lignin, its derivatives, rosin, gums, and leaf extracts are employed in the synthesis of these surfactants. In the process of wood digestion, vital for pulp production, a bio-catalyst is utilized to break down diverse fatty acids. This

catalytic process results in the hydrolysis of a significant portion of esters, releasing fatty acids that can be utilized as primary materials (Cao et al., 2021; Saxena et al., 2022).

Saponins, with a longstanding history of use as natural detergents, are among the notable active compounds found in various parts of plants. Plants exhibit an impressive capacity to produce an array of substances that function as natural defenses against microorganisms, insects, and herbivores.

Saponins are characterized by a robust structure comprising a minimum of four hydrocarbon rings, along with one or two groups of sugars, typically totaling fewer than 10 units. They are traditionally classified into triterpenoid and steroid glycosides. Steroidal saponins predominantly consist of 27 carbon atoms, forming the central structures known as spirostan (16β, 22:22α, 26-diepoxy-cholestan) and furostan (16β,22-epoxycholestan) as shown in Figure 6.

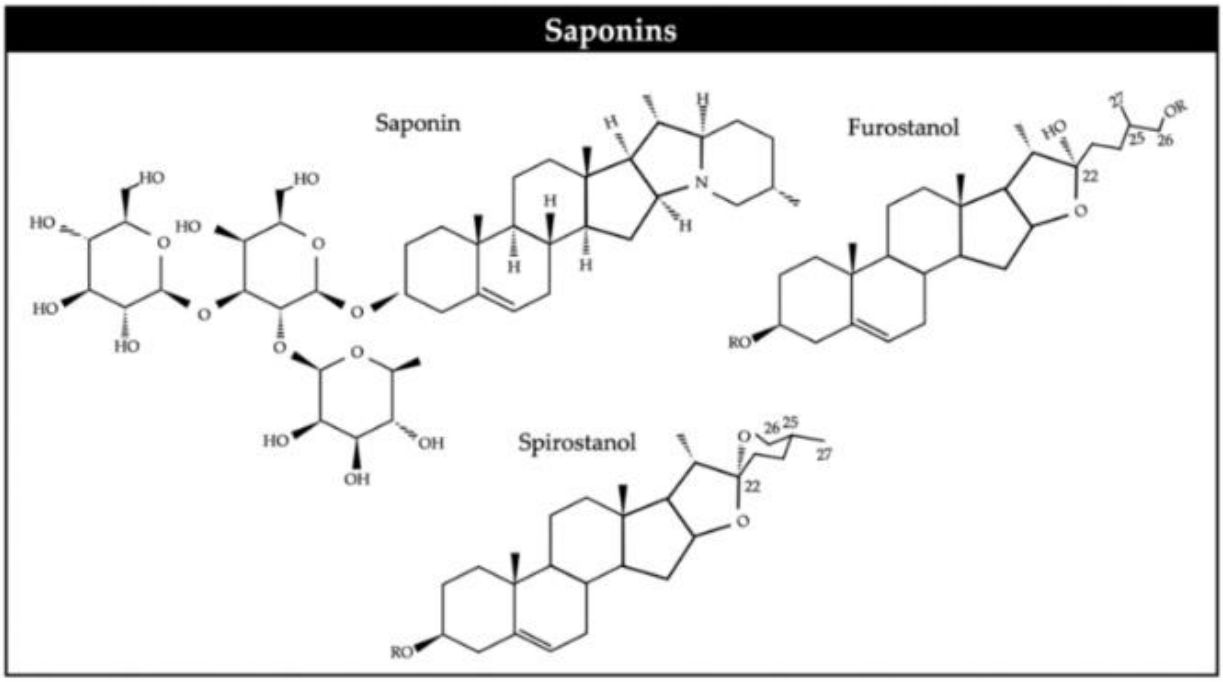


Figure 6: SP Structure (Ku-Vera et al., 2020)

When saponin molecules encounter water, they arrange themselves vertically on the surface, positioning their hydrophobic ends away from the water. This results in a reduction of water's surface tension, leading to the formation of foam.

In aqueous solutions, surfactants form groups called micelles once their concentration reaches a specific level known as the critical micelle concentration (CMC). Below this concentration, molecules remain separate. Micelles consist of a portion that is attracted to fats, which explains the ability of detergents to dissolve grease and oils refer to Figure 7.

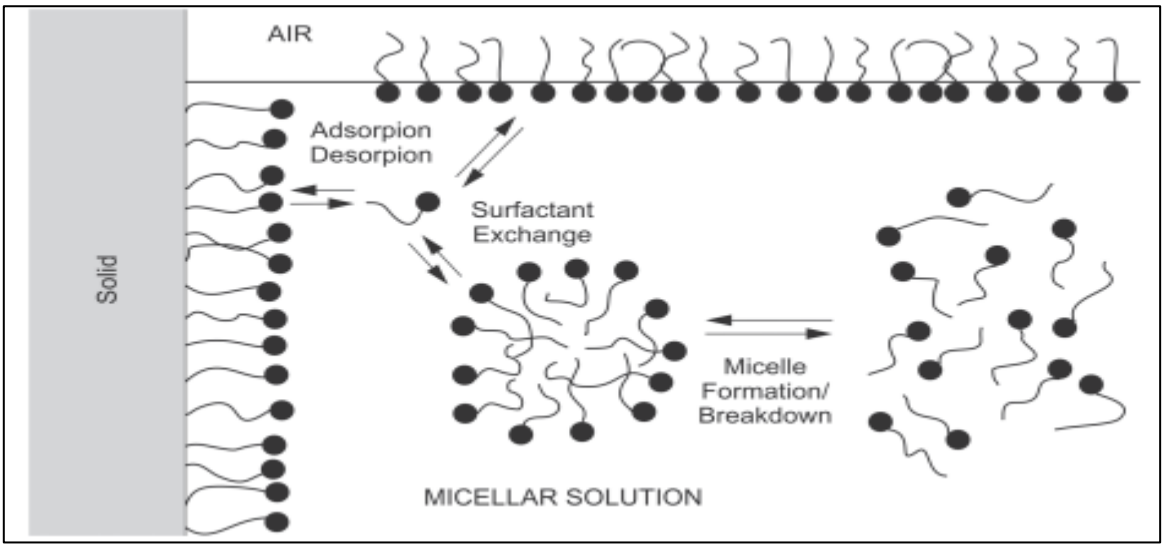


Figure 7: Micelle Formation (Kregiel et al., 2017)

The size and configuration of micelles vary depending on the type of saponin. For instance, saponins from S. officinalis and soya bean generate small micelles composed of only two molecules, whereas Quillaya saponaria saponin groups can contain up to 50 molecules. Ongoing research is exploring the properties and quantity of molecules within these micelles (Kregiel et al., 2017).

According to Eshun and He (2004), another chemical found in Aloe Vera is Polysaccharides, which are complex carbohydrates—large molecules consisting of multiple linked sugar units shown in Figure 8. They exhibit hydrophilic properties, indicating an affinity for water. Due to their amphiphilic nature, some polysaccharides can function as surfactants under specific conditions. This complex carbohydrate has been identified as having surfactant properties in certain instances. Some plants also contain polysaccharides that can serve as surfactants, such as the plant-derived guar gum.

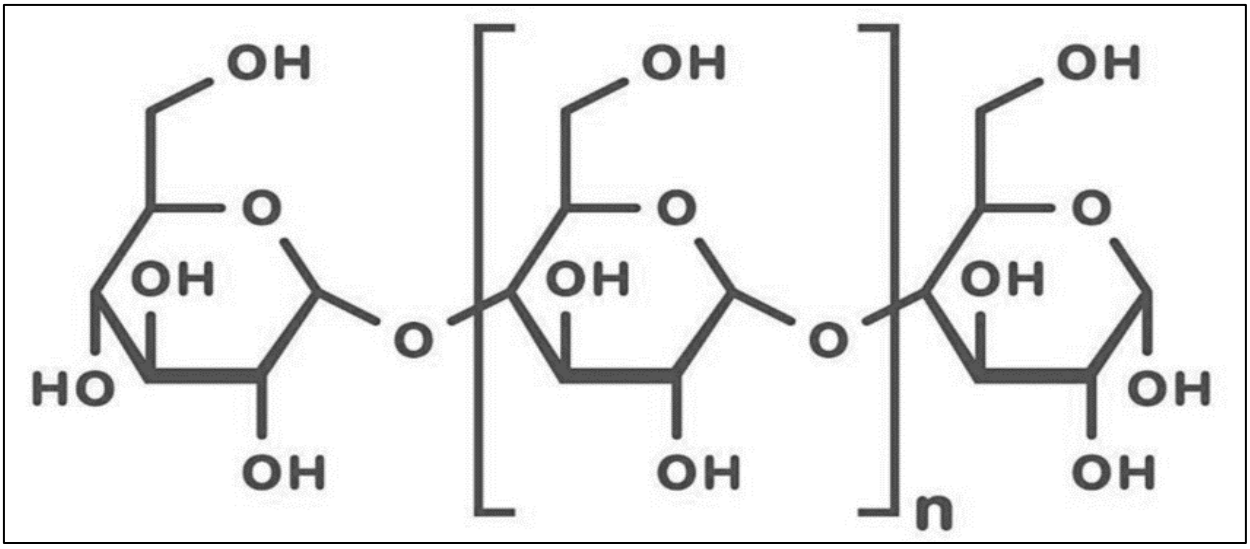


Figure 8: Structure of Polysaccharides (Morganti et al., 2022)

Conventional surfactants, often chemically synthesized from petroleum, are usually non-biodegradable. This characteristic poses a serious threat to the environment and ecosystem as these substances can accumulate in water bodies and potentially enter the food chain, leading to significant environmental risks. With the increasing awareness of environmental conservation, there is a pressing demand to transition from synthetic chemical compounds to those derived from natural sources. Many bio-surfactants set themselves apart from their conventional counterparts by featuring notably shorter alkyl chains. This is in contrast to the 10-12 carbon unit chains commonly found in surfactants widely used in industries.

The advantages of natural surfactants over conventional ones, as outlined by (Meshram et al., 2021; Saxena et al., 2022; Rahman & Gakpe, 2008) can be summarized as follows:

Availability of Raw Materials: Easily available, cost-effective raw materials in ample supply can be used to manufacture natural surfactants and biosurfactants. Hydrocarbons and carbohydrates, as carbon sources, can be effortlessly converted into biosurfactants, and they can be blended with ease.

Physical Factors: Surfactants of both natural and biological origin exhibit activity across a wide range of extreme temperatures, salinity levels, and pH conditions.

Acceptable Production Economics: Utilizing industrial wastes and other by-products of the industry provides a convenient and advantageous source for the easy preparation of natural surfactants, particularly in bulk production.

Specificity: Natural surfactants are intricate organic compounds with distinct functional groups that exhibit specificity in their functions. This specificity holds significant importance in processes like detoxification of pollutants, formulation of cosmetics, and de-emulsification in industrial applications, as well as various uses in the pharmaceutical and food industries.

Environmental Control: Bio-surfactants play a highly effective role in managing scenarios involving oil spills, and industrial emulsions, as well as in processes related to detoxification and biodegradation of industrial waste.

1.4.3.1 Tetraena Qatarensis

The small, partially succulent shrub known as Tetraena qatarensis (also referred to as Zygophyllum q.) is a group of closely related species that is not well understood. In this context, it is considered to encompass Tetraena mandavillei. This particular species is found across a significant portion of the Emirate and is locally quite common. Recently, it has been identified at the foothills of Jebel Hafit. It's important to differentiate this species from Tetraena migahidii, as the latter is often grouped with T. qatarensis despite being a distinctly different taxon (Sakkir & Brown, 2014).

The plant is a small, upright shrub that branches out extensively. It reaches a height of around 75 cm and has smooth to slightly downy leaves (Miller, 1993).

This species thrives in various types of terrain, including sandy-rocky and silt-loamy soils, as well as both dry areas with meager winter rainfall and more moist environments. It demonstrates an impressive tolerance to salinity levels of up to 11.8 dS.m-1. Notably, T. qatarensis exhibits a leaf succulence of approximately 11.4, as defined by its ratio of fresh weight to dry weight (Abulfatih et al., 2002; Khan et al., 2020; Sayed, 1998).

In a study conducted by Khan et al. (2020), one of the tests conducted revealed the existence of saponins and carbohydrates. The procedure for identifying these compounds was as follows:

For carbohydrates, a crude extract was combined with a few drops of α-naphthol solution in alcohol. Then, concentrated H_2SO_4 was introduced into the test tube. The formation of a violet ring at the interface of the two liquids confirmed the presence of carbohydrates.

To test for saponins using the foam test, the residue extract was dissolved in 5 mL of water and then heated. The appearance of froth during the test indicated the presence of saponins. Additionally, the persistence of froth formation in the aqueous extract upon shaking further confirmed the presence of saponins.

Table 1: Phytochemical Analysis of Tetraena Qatarensis (+, low concentration; ++, moderate concentration and +++, high concentration) (Khan et al., 2020)

S. No.	Phytochemicals	Leaves	Woody Stem	Tender Stem	Roots
1	Terpenoids	+++	+++	+	+
2	Steroids	+++	+++	+++	++
3	Tannins	+++	++	+++	+
4	Coumarins	+++	+++	+++	++
5	Saponins	+++	-	-	-
6	Phenol	+	++	+	++
7	Carbohydrate	+++	+++	++	+
8	Proteins	+++	+	++	++
9	Phlobatannins	+++	++	+++	-
10	Flavonoids	++	++	+++	-
11	Alkaloid	+++	+	++	+
12	Anthraquinones	++	++	++	+
13	Triterpenoid	+++	+	++	-
14	Emodin	-	-	-	-
15	Cardiac glycosides	-	-	-	-
16	Anthocyanin	+++	-	+++	+
17	Glycosides	+++	+	+++	-
18	Phytosterols	+	-	-	-

1.4.3.2 Aloe Vera

Aloe, originally hailing from South Africa, has a long history of human use. It thrives in warm, arid climates, not only in South Africa but also in regions across Africa, Asia, and Southern Europe, particularly in Mediterranean areas. Aloe saponaria represents a distinct species within the Aloe genus, which encompasses approximately 400 plant

species. Typically, Aloe plants possess features well-suited for arid environments, displaying modified leaf structures.

The distinctive spiky, tongue-shaped leaves of Aloe, including Aloe saponaria, contain a rich array of compounds such as saponins, aluin, lignin, anthraquinones, vitamins, and minerals. The outer layer of Aloe leaves is shielded by a protective cuticle, while the inner part primarily consists of Aloe gel surrounded by mesophyll tissue. Notably, saponin, a vital compound found in Aloe leaves, is renowned for its biological benefits, including antiviral and antidiabetic properties. This explains the longstanding tradition of various cultures using Aloe for its health-promoting properties (Kwon, 2016). The study has demonstrated the presence of saponin in every part of the Aloe leaf shown in Table 2.

Table 2: Total Saponin Content in 1 Gram each Part Aloe Vera Leaf (Kwon, 2016)

Leaf Part	**Aloe Saponaria (mg / g)**	**Aloe Vera (mg / g)**
Bottom of the Leaf (B)	1.132 +0.026	0.806 ±0.013
Middle of the Leaf (M)	0.876 +0.007	0.579 ±0.003
Tip of the Leaf (H)	1.083 ± 0.020	0.689 ± 0.029
Leaf Skin (S)	1.519 ±0.048	1.212 ± 0.035
Leaf Flesh (I.S)	0.638 ±0.064	0.253 ±0.012

Businesses like Aloetrade America have found innovative applications for Aloe Vera beyond its traditional uses. They utilize Aloe Vera as a polymer in enhanced oil recovery (EOR) flooding, a process that improves oil extraction. This is due to the robust and lengthy polysaccharide chains found in Aloe Vera, particularly cellulose. These polysaccharides enable Aloe Vera to withstand harsh conditions within the oil reservoir.

On the other hand, a study conducted by Eshun and He (2004) supported the presence of polysaccharides shown in Figure 9. Aloe Vera gel is characterized by its high viscosity and contains a blend of long-chain sugar molecules, known as polysaccharides. These polysaccharides are responsible for the gel's thick, gel-like texture and can be likened to polymers due to their similar properties. This makes Aloe Vera gel an interesting candidate for applications in various industries, including Enhanced oil recovery.

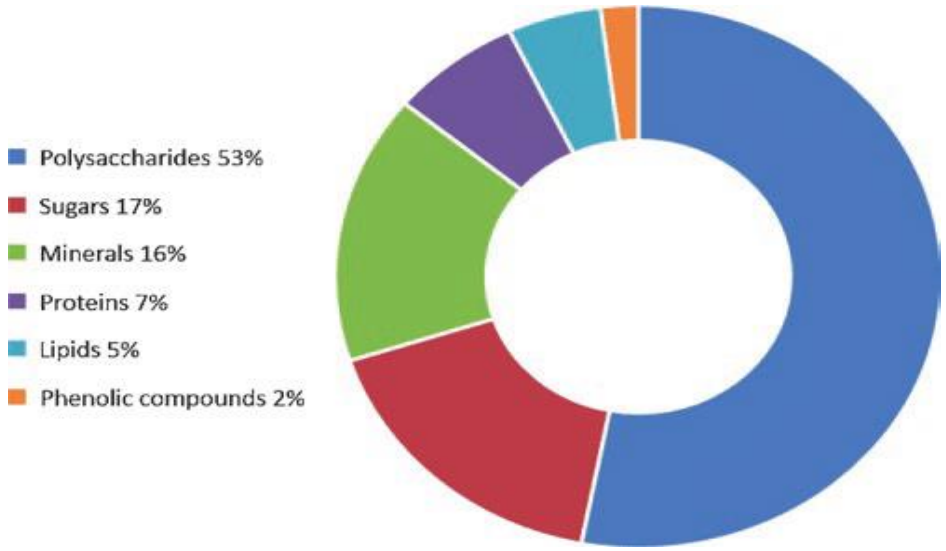


Figure 9: Chemical Composition of Aloe Vera Gel (Malik et al. 2020)

1.4.3.3 Sapindus Mukorossi

Sapindus Mukorossi, commonly known as a soapnut. The soapnut tree, native to tropical and near-tropical regions, can be found in numerous countries including Pakistan, India, Bangladesh, and Nepal, as well as various countries across America, Asia, and Europe. Encased in a brown, spherical shell, the fruits are white and have a diameter of 1-2 centimeters. Soapnut hold medicinal value and are utilized in soap-making. These fruit shells have a longstanding history of use in traditional medicine and as natural laundry detergents for both fabric washing and bathing. Research suggests that saponin extracted from soapnut shells shows significant promise in remediating contaminated soil (Bachari et al., 2019).

In 2009, Dalhousie University conducted a study wherein they followed a similar procedure to ours for sample preparation. Soapnut fruit pericarp shell samples were obtained from Nepal and selected randomly from the stock. These pericarps were then subjected to drying in an oven at 50ºC for a period of 36 hours. Subsequently, the dried shells were finely powdered and combined with deionized water. The mixture underwent continuous stirring, followed by 24 hours of settling, after which the undissolved matter was filtered out. The resulting filtrate was employed for the experiments.

Furthermore, their study illustrated that the increase in interfacial tension (IFT) did not show a direct proportionality to the surfactant concentration. In other words, the IFT initially experienced a sudden decrease, followed by a slight increase, and ultimately decreased once more with higher surfactant concentrations. Concentrations were measured based on weight per unit volume (grams of powder per 100 ml of deionized water). For preliminary assessments, solutions with concentrations of 0.5%, 1%, 2%, 4%, 8%, and 12% were utilized.

In their conclusion, the researchers found that the extract displayed significant potential as a surfactant for enhanced oil recovery schemes. They also highlighted that, in comparison to synthetic surfactants, this natural alternative proves to be a more cost-effective and environmentally friendly option for use in EOR schemes (Chhetri et al., 2009). Furthermore, the study illustrated that the rise in interfacial tension (IFT) did not follow a direct proportionality to the surfactant concentration. To clarify, the IFT initially experienced a sudden decrease, followed by a slight increase, and ultimately decreased again with higher surfactant concentrations (Bachari et al., 2019).

As far as our knowledge extends, limited experiments have been conducted in evaluating the possible use Aloe Vera, Tetraena qatarensis, and Saopnuts in enhanced oil recovery.

Chapter 2: Methods

2.1 Research Design

The following flow chart Figure 10 summarizes the research design used in this study, which outlines the ordered progression of steps from initial core preparation to the comprehensive collection of results encompassing parameters such as interfacial tension (IFT), recovery factor (RF), and wettability, among others. It should be highlighted that the major body of the research will include a complete explanation of the particular methods and methodological approaches, providing a thorough understanding of the experimental framework.

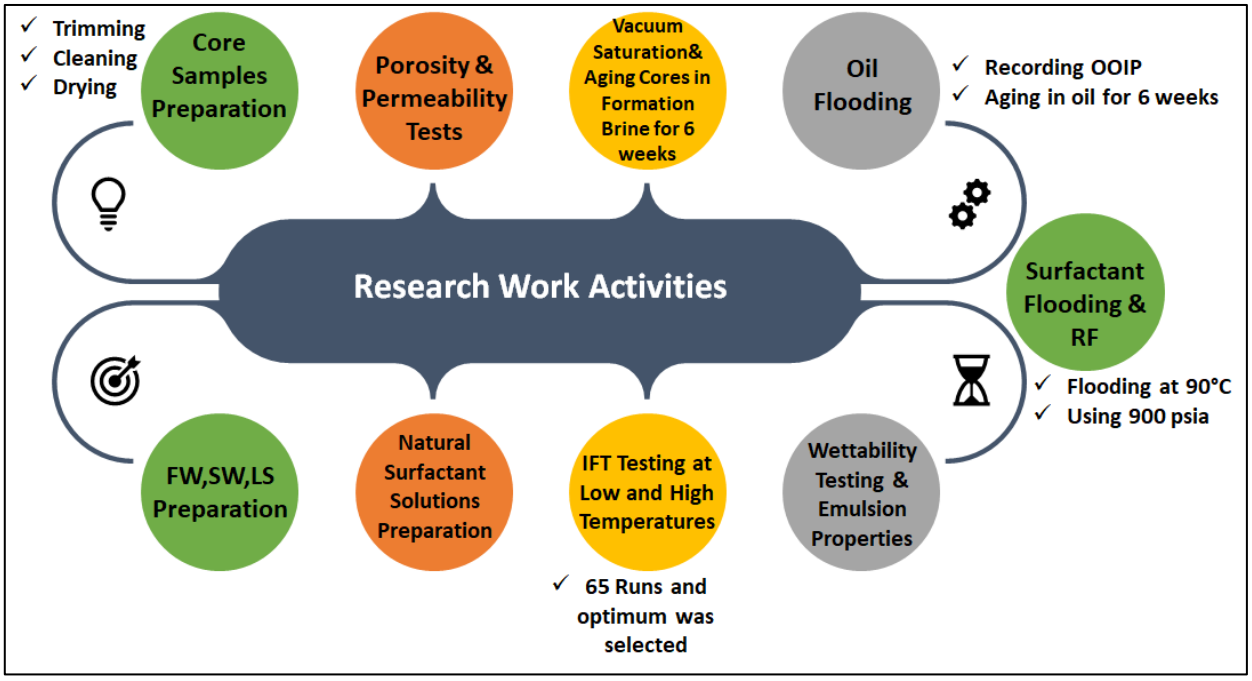


Figure 10: Experimental Workflow

2.2 Data Collection

2.2.1 Core Sample Preparation

In total, 16 core samples purchased from the supplier were used in this study. Samples come from two types of rock ZE-1 group from limestone rock, which has mainly carbonate calcite minerals, and the ZE-2 group from dolomite rock source, which has mostly calcium magnesium carbonates. The X-ray fluorescence (XRF), and X-ray diffraction (XRD) for rock samples are presented in Appendix A.

The Core Samples were cleaned using a Soxhlet extractor for 48 hours. Toluene and methanol, both chemicals were used during the process to clean the samples from any remaining hydrocarbons or salts. Subsequently, the specimen underwent desiccation within a conventional drying oven overnight at 60ºC. Following this, the mass of each sample in its dry state was measured and recorded, and precise measurements of their dimensions were conducted employing a Vernier caliper Figure 11.

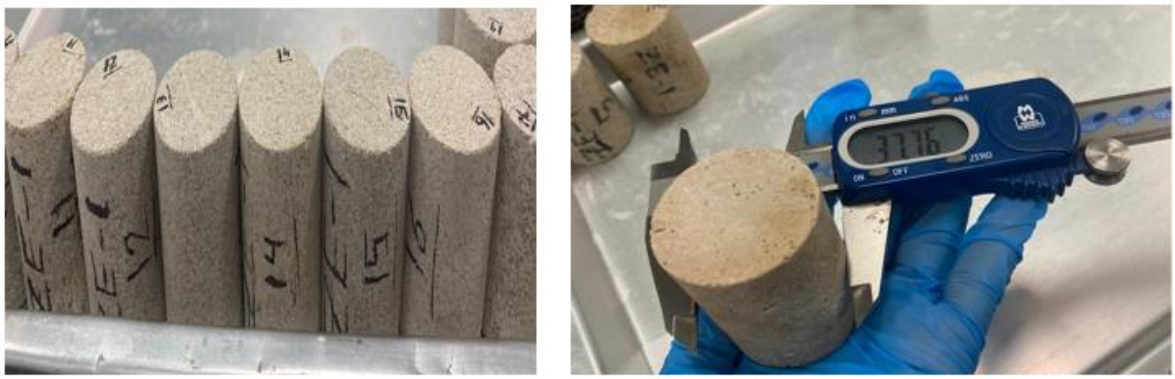


Figure 11: Core Samples Measurements

2.2.2 Porosity Measurement

Fluid-rock interactions are heavily influenced by porosity. A rock's porosity is a measure of its fluid storage capacity (pore volume). Porosity is defined quantitatively as the ratio of pore volume to bulk volume). Induced porosity is characterized by fracture formation, as seen in shales and limestone, as well as slugs or solution cavities, which are typical in limestone. Because it indicates the interconnected pore space that holds the recoverable hydrocarbon fluids, effective porosity is the value used in all reservoir engineering calculations (Ahmed, 2018).

The porosity measurements were done using the Vinci PoroPerm Instrument shown in Figure 12. In the initial step, we input the weight, diameter, and length of the rock sample into the software. Subsequently, the rock sample is placed in a cell with an initially unknown pore volume, which requires measurement. This cell is linked to another cell with a known volume. Nitrogen gas is then pumped into the system, and pressure readings are obtained from sensors after the system stabilizes. Utilizing the ideal gas law, the software can compute both the pore volume and grain density.

Figure 12: Picture of Vinci Equipment Used for Core Properties

2.2.3 Permeability Measurement

Permeability is a characteristic of porous media that determines the formation's capacity and ability to transport fluids. The rock permeability, k, is a critical rock characteristic because it regulates the directional movement and flow rate of reservoir fluids in the formation (Ahmed, 2018). Permeability was tested using the Vinci PoroPerm Instrument, which uses nitrogen gas during the operation due to the tiny and light nature of nitrogen molecules so they can easily flow through porous media without much resistance, making them good for measurements of permeability. Also, nitrogen gas does not react chemically with minerals within the core rock. After placing the core sample into the device, it measures the absolute permeability while accounting for gas slippage. To calculate the liquid permeability, the Klinkenberg correction factor is applied shown in the following Equation:

$$K_L = \frac{K_g}{1 + \frac{b}{P_m}} \quad (1)$$

Where:

K_L: Liquid Permeability.

K_g: Gas Permeability.

b: Klinkenberg Correction Factor.

The summary of 16 core sample findings includes liquid permeability and porosity values and related characteristics for two types of rock: limestone denoted as (ZE1) and dolomite (ZE2), which is listed in Table 3.

Table 3: Limestone and Dolomite sample Petrophysical Properties

Sample No.	**Sample Name**	**Diameter (mm)**	**Length (mm)**	**Bulk Vol (cc) L*A**	**Weight (g)**	**Grain Vol. (cc)**	**Grain Density (g/cc)**	**K (mD)**	**Pore Vol (cc)**	**Porosity (%)**
1	ZE2-1	3.803	5.084	57.76	138.59	49.343	2.81	5.7	8.42	14.6
2	ZE1-2	3.827	5.100	58.65	129.15	48.952	2.64	6.5	9.70	16.5
3	ZE2-3	3.780	5.091	57.13	146.6	52.211	2.81	1.5	4.92	8.6
4	ZE1-5	3.819	5.067	58.04	132.23	49.444	2.67	18.7	8.60	14.8
5	ZE1-6	3.847	5.084	59.08	126.68	47.478	2.67	11.5	11.60	19.6
6	ZE1-7	3.775	5.090	56.97	122.49	46.004	2.66	135.6	10.97	19.2
7	ZE1-8	3.827	5.089	58.54	126.01	46.93	2.69	60.3	11.61	19.8
8	ZE1-9	3.747	5.069	55.9	131.51	49.638	2.65	13.1	6.26	11.2
9	ZE1-10	3.825	5.090	58.49	132.24	49.659	2.66	16.5	8.83	15.1
10	ZE1-18	3.783	5.102	57.36	127.48	47.488	2.68	19.3	9.87	17.2
11	ZE2-18	3.765	5.077	56.52	139.83	50.633	2.76	2.9	5.89	10.4
12	ZE2-17	3.771	5.077	56.69	138.58	49.18	2.818	12.362	7.52	13.26
13	ZE2-6	3.766	5.088	56.67	139.57	50.17	2.782	2.569	6.50	11.46
14	ZE2-8	3.768	5.09	56.76	143.12	51.97	2.754	0.936	4.79	8.44
15	ZE2-12	3.777	5.083	56.95	142.52	51.26	2.780	2.392	5.69	9.99
16	ZE2-16	3.765	5.08	56.56	143.62	51.75	2.775	0.0424	4.81	8.50

2.2.4 Core Sample Brine Saturation

To achieve core brine saturation, a combination of vacuum and pressure technique was used. Initially, the core samples were placed within a sealed cell as shown in Figure 13, ensuring a tight closure. Subsequently, the instrument was connected to a vacuum stream for a duration of 12 hours, effectively eliminating any remaining air from the pores within the rock samples. Finally, pressure (1500 psia) was applied to force brine into smaller pores and fully saturate the sample. This procedure is both simple and effective.

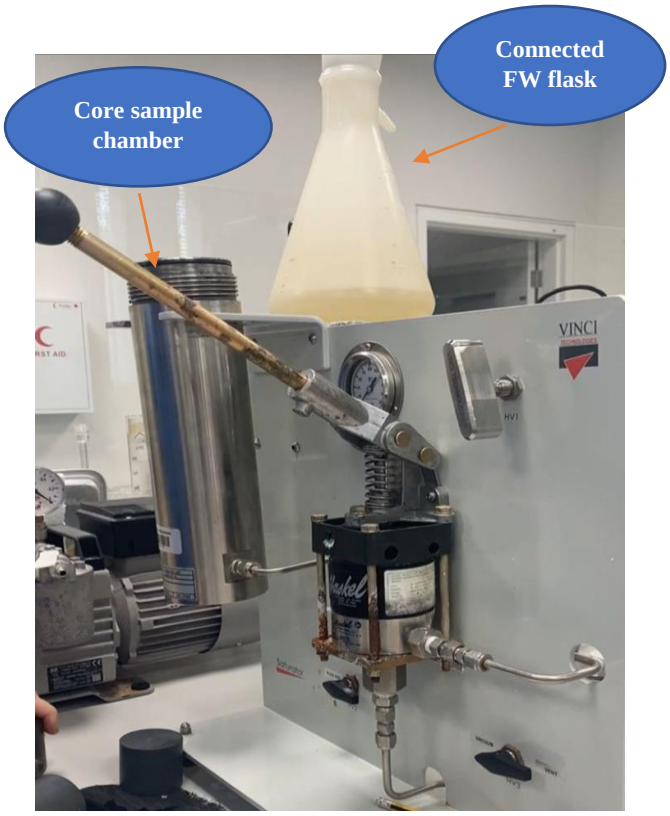


Figure 13: Core Saturation Apparatus

2.2.5 Brine Preparation

Three main types of solutions were prepared in the first stage of the research by combining salts and deionized water and then filtered using a 0.45 mm filter. The mixing process of chemicals is in the following order: (1) $CaCl_2$, (2) $MgCl_2$, (3) Na_2SO_4, (4) $NaHCO_3$, (5) KCl, (6) NaCl. The purpose of this order is to make it possible to manage the saturation level of the solution more accurately by first adding salts with lesser solubility and then adding NaCl. The brine preparation setup is shown in Figure 14.

The first type of brine (Synthetic Sea water) was prepared by using different quantities of NaCl, $CaCl_2.2H_2O$, $MgCl_2.6H_2O$, $NaHCO_3$, Na_2SO_4, and KCl the detailed Table 4 listed below. The Total dissolved salts (TDS) of the Synthetic Sea water was around 50,000 ppm.

The Formation brine is composed of NaCl, $CaCl_2.2H_2O$, $MgCl_2.6H_2O$, and Na_2SO_4 with Total dissolved salts (TDS) of 232,000 ppm. The third solution with low salinity denoted as LSW brine was prepared by diluting Seawater to end up with total dissolved salts (TDS) equal to 5000 ppm using the following dilution formula:

$$C_1V_1 = C_2V_2 \quad (2)$$

This formula is commonly used in laboratories to dilute stock solutions to prepare solutions of specific concentrations.

Where:

C_1: Initial concentration of the solute (before dilution), typically measured in units like moles per liter (mol/L) or grams per liter (g/L) depending on the context.

V_1: Initial volume of the concentrated solution (before dilution), typically measured in liters (L) or milliliters (mL).

C_2: Final desired concentration of the solute (after dilution), also usually measured in units like moles per liter (mol/L) or grams per liter (g/L).

V_2: Final desired volume of the diluted solution, usually measured in liters (L) or milliliters (mL).

All solutions were synthesized using the compositions given by Abu Dhabi Oil Company (ADNOC).

Figure 14: Brine Preparation Set up

Table 4: Chemical Composition of FW, SW, and LSW

Chemicals	**Formation Water (g/L)**	**Sea Water (g/L)**	**Low Salinity Water (g/L)**
NaCl	157.08	29.80	2.895
$CaCl_2.2H_2O$	60.28	1.86	0.18
$MgCl_2.6H_2O$	14.23	13.53	1.314
Na_2SO_4	0.39	5	0.486
$NaHCO_3$	0.17	0.23	0.022
KCl	0	0.92	0.089
TDS (g/L)	232.15	51.34	4.986
Total (ppm)	232,000	51,398	4,986

2.2.6 Crude Oil

In this study, two main types of oil were used: Sahil oil and Asab oil. These oils obtained from two oilfields within the UAE and are all categorized as light oils, falling within an API range of (36-40). The selection of these oils was purposeful. In the case of IFT measurements, which constituted a primary focus of the study, three oils were utilized to gain a comprehensive understanding of surfactant interactions across varying hydrocarbons.

However, for wettability measurements, flooding experiments, and the aging process, Asab oil was used, determined by its availability within the laboratory. Prior to any experiments, all oils were filtered using a 5mm filter paper. Additionally, their

densities were accurately measured. Table 5 presents Asab's and Sahil's physical oil properties.

Table 5: Crude Oil Physical Properties

Property	Unit	ASAB	SAHIL
Gravity at 20°C	API	39.48	37.71
Density at 20°C	g/cc	0.8276	0.835
Viscosity at 20°C & 14.7 psi	mPa.s-cp	2.927	3.05
Viscosity at 123°C (255°F) & 3100 psi (P_{res})	mPa.s-cp	1.8593	2.01

2.2.7 Oil Flooding

After saturating the samples with formation water, we initiated an oil flooding experiment shown in Figure 15 using Asab oil until no more water was extracted from the plug, achieving an irreducible water saturation. Throughout this phase, we maintained an overburden pressure of 1500 psi to ensure the fluid entered the core plug consistently, with a constant injection pressure of 950 psi.

During this process, we observed that the flow was impeded and showed high signs of restriction. This could be attributed, as per existing literature (Lake, 1989), to factors such as the viscosity of the oil, permeability of the porous medium, capillary forces, heterogeneity in the porous media, potential issues related to fingering and bypassing, immiscible displacement, pressure gradients, and constraints related to the experimental setup.

Figure 15: Oil Flooding Experiment

2.2.8 Aging

Aging is an important process done to alter the wettability of rock samples by putting porous media in a fluid for a certain time and it is widely used in reservoir engineering studies. This will help with chemical reaction, and ion exchange adsorption between rock and fluid leading to a change in wettability (Hirasaki & Zhang, 2004). The samples were subject to an aging process in two distinct environments. Firstly, to achieve complete oil wetting, the samples were immersed in Asab oil for a duration of six weeks followed by oil flooding. For water-wet conditions, the process involved initial saturation using vacuum pressure, followed by an additional six-week aging period in brine. This sequential approach was employed to establish and maintain the desired wetting characteristics for each set of samples shown in Figure 16.

Figure 16: Core Plugs Aged in Oil and Brine

2.2.9 Natural Surfactant Preparation

In this study, a total of 58 natural surfactant solutions were prepared. The selection of the plant was based on its availability in the region and its promising saponin content. The preparation of the solutions was conducted in two stages.

First Stage:

The primary objective was to assess the surfactant behavior and its impact on interfacial tension (IFT) using three main brines: Formation water, Sea water, and low

salinity water. These brines were tested with varying concentrations of the selected plant shown in Tables 6 and 7.

Second Stage:

In the second stage, we selected the additional solutions of the surfactant that exhibited the lowest interfacial tension (IFT) from the results of the first stage. We then created more solutions with higher concentrations of this chosen surfactant shown in Tables 8 and 9. This was done to obtain a comprehensive understanding of the surfactant's behavior in IFT.

Given the novelty of using these specific plants in this region for surfactant purposes, there is limited existing literature to serve as a guide for enhanced oil recovery (EOR).

Table 6: Aloe Vera Natural Surfactant Concentration

Natural Surfactant: Aloe Vera	
Type of Brine:	**Concentration of Surfactant in (wt. %)**
Formation Water	FW 2
	FW 4
	FW 6
	FW 8
	FW 10
Sea Water	SW 2
	SW 4
	SW 6
	SW 8
	SW 10
Low Salinity Water	LS 2
	LS 4
	LS 6
	LS 8
	LS 10

Table 7: Tetraena Qatarensis Natural Surfactant Concentration

Natural Surfactant: Tetraena Qatarensis	
Type of Brine :	**Concentration of Surfactant in (wt. %)**
Formation Water	FW 2
	FW 4
	FW 6
	FW 8
	FW 10
Sea Water	SW 2
	SW 4
	SW 6
	SW 8
	SW 10
Low Salinity Water	LS 2
	LS 4
	LS 6
	LS 8
	LS 10

For the first plant, Aloe Vera, the process began with obtaining fresh Aloe Vera leaves. They were cleaned, and the edges of each leaf were trimmed. The leaves were then

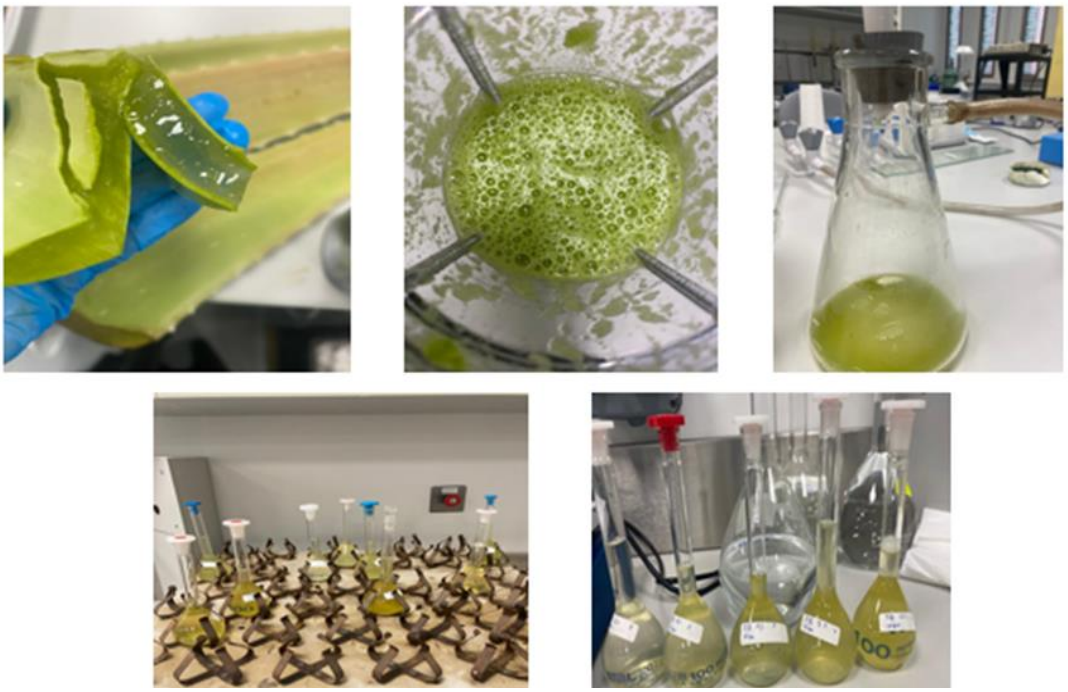


Figure 17: Surfactant Aloe Vera Solution Preparation

cut into small pieces and blended until they reached a homogeneous consistency. Subsequently, the mixture was filtered through a strainer and followed by vacuum filtration illustrated in Figure 17. At the end, the solutions were diluted using Formation water, Sea water, and low salinity water for the desired concentrations and mixed for 5 hours shown in the detailed Table 8 and Table 9.

The Tetraena qatarensis solution design followed the two stages mentioned earlier. The preparation for Tetraena qatarensis started by picking the small leaves and following the same procedure as with Aloe Vera, as illustrated in Figure 18.

On the other hand, the soapnut used in this study was in powder form. The grams for each concentration were accurately measured and calculated. Subsequently, they were diluted using the three main brines. The mixture then underwent vacuum filtration and was mixed at a medium speed for a duration of nine hours shown in Figure 19 and Table 10 summaries of the concertation used.

Figure 18: Natural Surfactant Tetraena Qatarensis Solution Preparation

Table 8: Aloe Vera Natural Surfactant Concentration

Natural Surfactant: Aloe Vera	
Type of Brine :	**Concentration of surfactant in (wt. %) :**
Formation Water	FW 2
	FW 4
	FW 6
	FW 8
	FW 10
	FW 15
	FW 20
	FW 30
	FW 40
	FW 50

Table 9: Tetraena Qatarensis Natural Surfactant Concentration

Natural Surfactant: Tetraena Qatarensis	
Type of Brine :	**Concentration of surfactant in (wt. %) :**
Low Salinity Water	LS 2
	LS 4
	LS 6
	LS 8
	LS 10
	LS 15
	LS 20
	LS 30
	LS 40
	LS 50

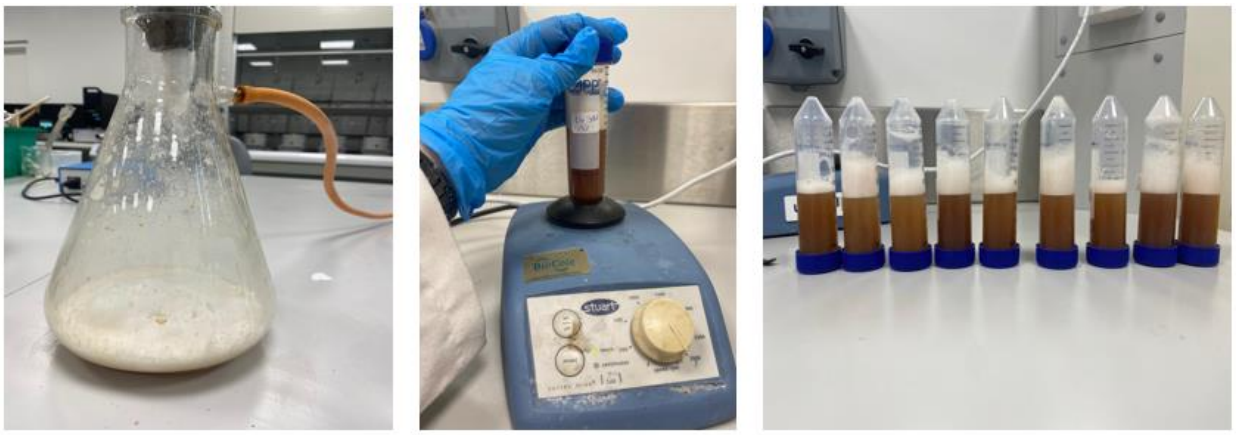


Figure 19: Natural Surfactant Soapnut Solution Preparation

Table 10: Soapnut Natural Surfactant Concentration

Natural Surfactant: Soapnut	
Type of Brine :	**Concentration of Surfactant in (wt. %) :**
Formation water	FW 8
	FW 12
	FW 15
	FW 18
	FW 20
	FW 25
Sea water	SW 8
	SW 12
	SW 15
	SW 20
	SW 25
Low Salinity water	LS 8
	LS 12
	LS 15
	LS 20
	LS 25

2.2.10 Viscosity and Density Measurements

The viscosity measurements for formation water, synthetic seawater, low salinity water, and all surfactant solutions with different concertation and formula were measured shown in Tables 11, 12, and 13 using an Anton Paar Stabinger viscometer in Figure 20, and for crude oils and some other fluids, density was measured using the Pycnometer. Viscosity and density play an important role in both influencing IFT and contact angle between fluid and solid surfaces. this, in turn, affects the behavior of fluid in porous media (Anderson & Thomas, 2009).

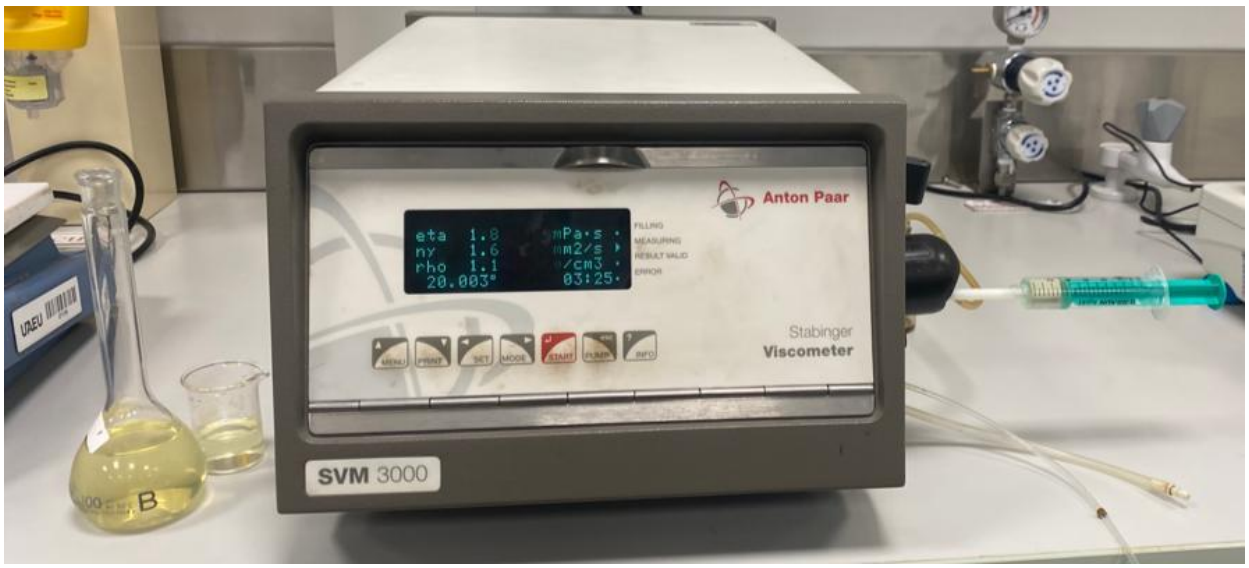


Figure 20: Anton Paar Stabinger Viscometer Device Used for Viscosity and Density Measurements

The results exhibit fluctuations in density and viscosity. This may be attributed to the machine's tendency to generate more errors at higher concentrations. Additionally, there may be a tendency for particles or molecules to aggregate or cluster at higher concentrations, potentially influencing the observed properties.

Table 11: Density and Viscosity Measurements of Aloe Vera Natural Surfactant

Natural Surfactants Aloe Vera				
Brine Type	**Concentration (wt. %)**	**Density (gm/cm^3)**	**Viscosity (mm^2/S)**	**Viscosity (mPa.S)**
	FW 0	1.1245	1.0413	1.1708
	FW 2	1.1018	1.6898	1.8617
	FW 4	1.0996	1.5571	1.7122
	FW 6	1.0984	1.6976	1.8657
	FW 8	1.096	1.7454	1.9127
	FW 10	1.0955	1.82	1.8255
	FW 15	1.1184	1.2847	1.4397
	FW 20	1.1133	1.3182	1.4685
	FW 30	1.1071	1.433	1.5786
	FW 40	1.0877	1.5973	1.7318
FW	FW 50	1.0775	1.728	1.8667
	SW 0	1.0258	1.932	1.1318
	SW 2	1.0051	1.1686	1.1746
	SW 4	1.0293	1.2243	1.2601
	SW 6	1.0245	1.2705	1.3039
	SW 8	1.026	1.3311	1.3655
SW	SW 10	1.0283	1.3702	1.4054
	LS 0	1.0003	1.0343	1.0323
	LS 2	1.0011	1.1484	1.1497
	LS 4	1.0013	1.2204	1.222
	LS 6	1.0016	1.2577	1.2597
	LS 8	1.0017	1.3414	1.3437
LS	LS 10	1.0018	1.3804	1.3828

Table 12: Density and Viscosity Measurements of Soapnut Natural Surfactant

Natural Surfactants Soapnut				
Brine Type	**Concentration (wt. %)**	**Density (gm/cm^3)**	**Viscosity (mm^2/S)**	**Viscosity (mPa.S)**
FW	FW 0	1.1245	1.0413	1.1708
	FW 8	1.1323	1.1643	1.3183
	FW 12	1.1332	1.1802	1.3367
	FW 15	1.1345	1.2334	1.4045
	FW 18	1.1370	1.3855	1.5820
	FW 20	1.1371	1.2568	1.5266
	FW 25	1.1375	1.3043	1.5000
SW	SW 0	1.0258	1.932	1.1318
	SW 8	1.033	1.224	1.2705
	SW 12	1.035	1.3006	1.3554
	SW 15	1.0353	1.3922	1.4451
	SW 18	1.0322	1.2501	1.2912
	SW 20	1.0365	1.3039	1.3576
	SW 25	1.0393	1.337	1.3884
LS	LS 0	1.0003	1.0343	1.0323
	LS 8	1.0068	1.1296	1.1389
	LS 12	1.00712	1.2899	1.2833
	LS 15	1.0087	1.2015	1.2104
	LS 18	1.004	1.2015	1.2083
	LS 20	1.0043	1.3709	1.389
	LS 25	1.0087	1.3212	1.3327

Table 13: Density and Viscosity Measurements of Tetraena Qatarensis Natural Surfactant

Natural Surfactants Tetraena Qatarensis				
Brine Type	**Concentration (wt. %)**	**Density (gm/cm^3)**	**Viscosity (mm^2/S)**	**Viscosity (mPa.S)**
FW	FW 0	1.1245	1.0413	1.1708
	FW 2	1.1011	1.4854	1.6355
	FW 4	1.1016	1.3712	1.5105
	FW 6	1.101	1.3059	1.4377
	FW 8	1.1009	1.3042	1.4358
	FW 10	1.1181	1.419	1.587
SW	SW 0	1.0258	1.932	1.1318
	SW 2	1.0281	1.0981	1.1302
	SW 4	1.0298	1.144	1.1771
	SW 6	1.0315	1.1626	1.201
	SW 8	1.0308	1.1537	1.1885
	SW 10	1.0331	1.1501	1.84
LS	LS 0	1.0003	1.0343	1.0323
	LS 2	1.0014	1.6041	1.6064
	LS 4	1.0033	1.0987	1.024
	LS 6	1.0046	1.0684	1.0731
	LS 8	1.0066	1.0927	1.0988
	LS 10	1.009	1.202	1.2126
	LS 15	1.187	1.1241	1.1419
	LS 20	1.0168	1.1444	1.1348
	LS 30	1.0224	1.1764	1.2029
	LS 40	1.0292	1.2788	1.2958
	LS 50	1.0357	1.2303	1.2731

2.2.11 IFT Measurement

Numerous techniques have been devised to assess boundary tension, although many of them exhibit relatively low precision. Dorsey, (1926) provided a comprehensive list of seventeen methods for measuring boundary tension, with only a select few finding applications in the petroleum industry. These methods are categorized into static and dynamic approaches.

(i) Static Methods

1. Directly measuring the curvature of the liquid surface.
2. Employing flat drops and bubbles on surfaces.
3. Applying the capillary rise method.
4. Utilizing adhesion plates and rings.
5. Determining drop weights and volumes.
6. Employing the method of gas bubble pressure.

(ii) Dynamic Methods

1. Implementing the method of oscillating jets.
2. Applying the method of vibrating drops.
3. Measuring ripple wave phenomena.

For detailed procedures regarding boundary tension determination, Healy and Reed. (1974) have provided extensive documentation in the literature.

In this study, the spinning drop method was used. It's when a fluid drop is placed in a liquid of higher density contained in a rotating horizontal tube it becomes elongated along the axis of rotation until the formation forces due to the centrifugal field are balanced by the interfacial tension. Vonnegut. (1942) used this principle to measure the interfacial tension. He developed an approximate theory in which the bubble is considered to be a cylinder with rounded ends. The theory is strictly valid for high speeds of rotation, but Silberberg (1952) improved the Vonnegut method by calculating correction factors for

low speeds. Cayias et al. (1975) developed a method based on measuring both the length and width of the drop. The volume of the drop can be readily calculated from its dimensions.

The theory, as formulated by Cayias et al. (1975), centers around the measurement of both the length and width of the drop. This method offers the advantage of not requiring a direct volume measurement, although it can be easily calculated. The derivation is contingent on five key assumptions:

1. The drop's axis aligns with the horizontal axis of rotation.
2. The angular velocity of rotation (ω) is significant enough to render the buoyancy effect due to gravity negligible.
3. The surface tension remains independent of curvature.
4. The drop's surface conforms to a surface of revolution.
5. Thermal energy can be disregarded.

To facilitate the calculations, rectangular Cartesian coordinates are selected, with the origin situated at the left-hand end of the bubble (refer to Figure 21). The semi-axes of the drop are xo and yo. The boundary tension of the spinning drop is as follows:

$$\sigma \approx \Delta\rho\omega^2/4C \qquad (3)$$

Where:

σ :Boundary Tension, mN/m.

$\Delta\rho$: the Density Difference, gm/cc.

ω : Speed of rotation, rad/sec.

c : Constant which is a Function of the Shape of the Drop.

For drops that take the shape of a long narrow circular cylinder with rounded ends Figure 21, the Equation reduces to the Vonnegut Equation:

$$\sigma \approx \frac{\Delta\rho\omega^2 Y^3}{4} \qquad (4)$$

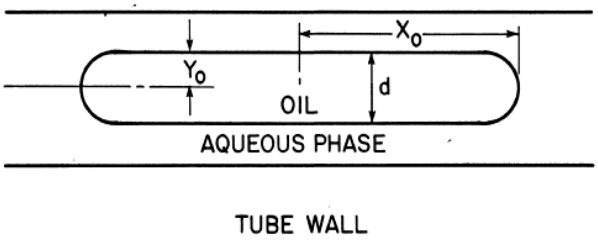


Figure 21: Oil Drop in a Spinning Drop Interfacial Tensiometer

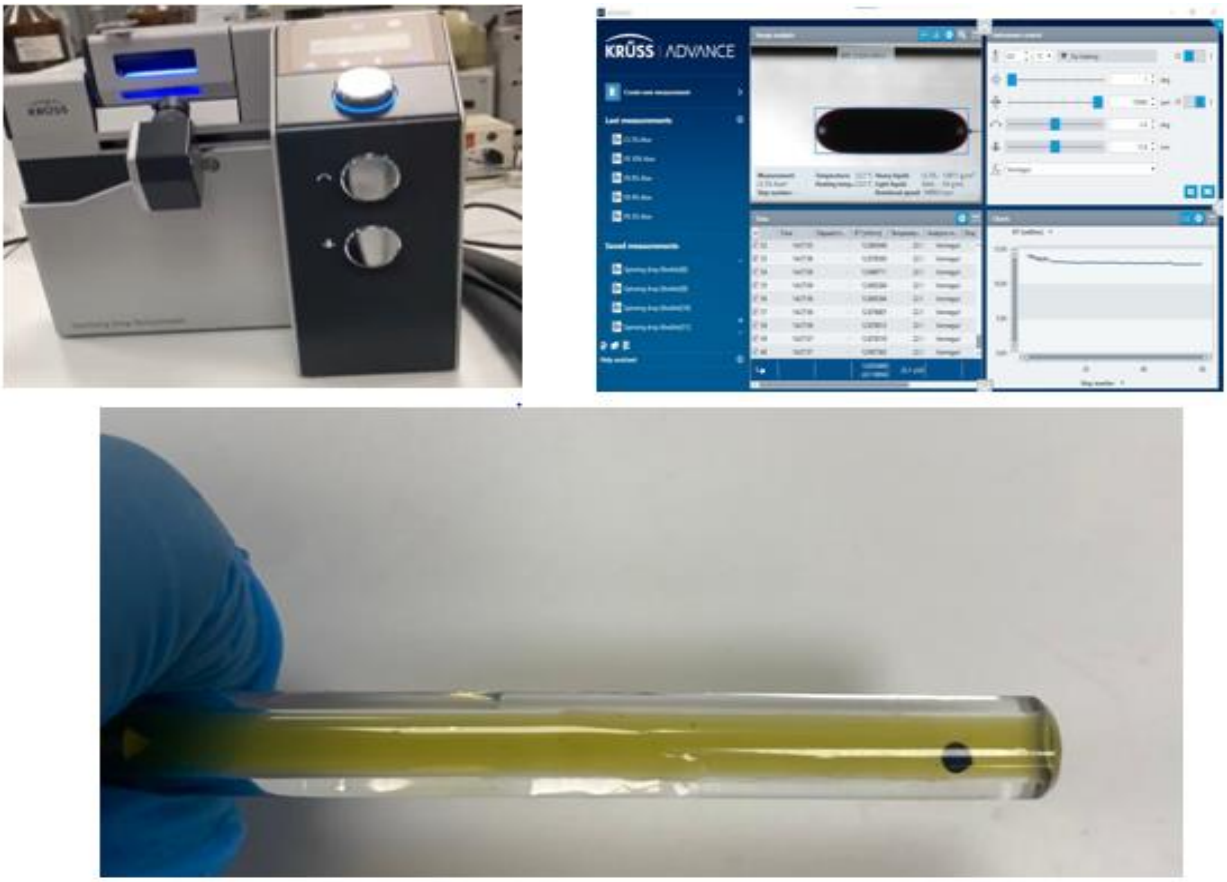


Figure 22: IFT Measurements Process

The interfacial tension (IFT) measurements were performed using the KRUSS spinning drop tensiometer device, employing the previously explained Vonnegut model. The process commenced with the loading of the testing tube with the surfactant solution. Subsequently, an oil droplet, sized at 1mm, was introduced. The device initiated the spinning motion of the sample, which was securely positioned within the instrument, reaching high speeds. This rotation continued until the droplet conformed to the Vonnegut model. Throughout this phase, the dynamic IFT values were continuously recorded, providing the mean IFT along with its standard deviation (STD). Additionally, the entire

process was visualized through the device's camera system. The process of the IFT test unfolds in three distinct stages shown in Figures 23 and 24.

IFT Measurements with Various Surfactant Solutions: Surfactant solutions derived from selected plants were prepared and diluted in three different brines: Formation Water (FW), Sea Water (SW), and Low Salinity Water (LSW). Sahil oil was employed in the tests. This stage sought to identify the most favorable IFT results, pinpointing the optimal surfactant type and concentration.

Follow-up IFT Measurements at Elevated Temperatures: Following the selection of the best surfactant solutions in the first stage, additional IFT measurements were conducted under higher temperature conditions.

Extended IFT Measurements with Alternative Oils and Temperatures: The superior solutions identified in the prior stages were subjected to further IFT measurements, now utilizing two additional types of oil: Abu Hassa and Asab oil. This assessment encompassed both room temperature and elevated temperature settings.

IFT in stage one was measured at room temperature and 1 atm pressure using Sahil oil.

Note: 'FW', 'SW', and 'LS' preceding each concentration indicate the respective waters used for diluting the surfactants.

The initial concentration of SP was determined based on literature that tended to perform better at higher concertation; however, this was done using a different brine.

Obtaining IFT readings posed a slight challenge at higher concentrations of Soapnut and Tetraena qatarensis due to the darker coloration with the oil droplet. Nevertheless, the device was still able to detect it.

Additional concentration was introduced in FW for Aloe Vera, and in LS for Tetraena qatarensis, as shown in Figure 23. This adjustment was made as they exhibited the lowest IFT at a certain point. Further investigation and complete IFT charts were deemed necessary.

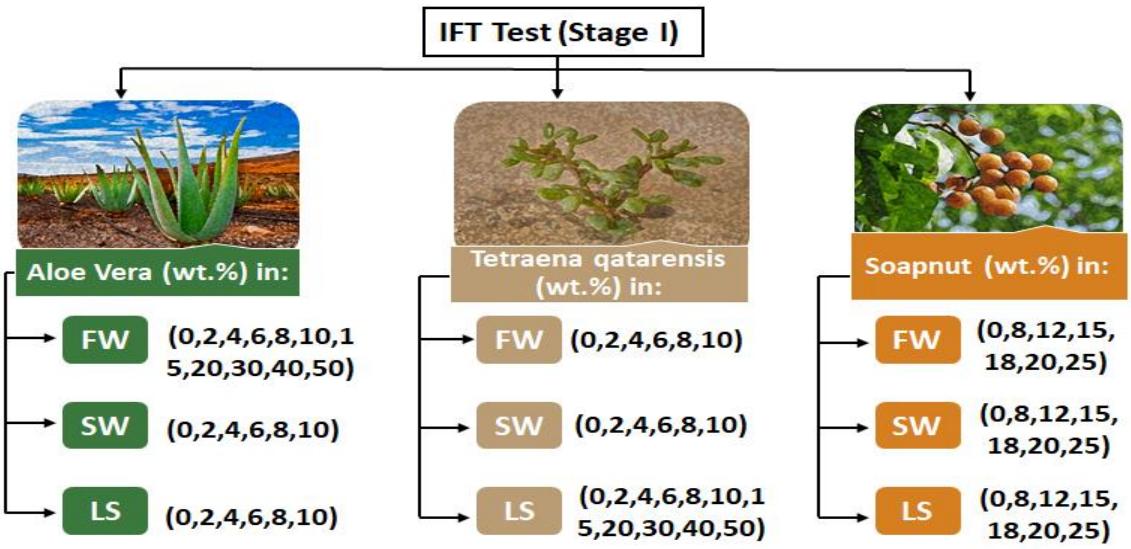


Figure 23: IFT Test Stage 1

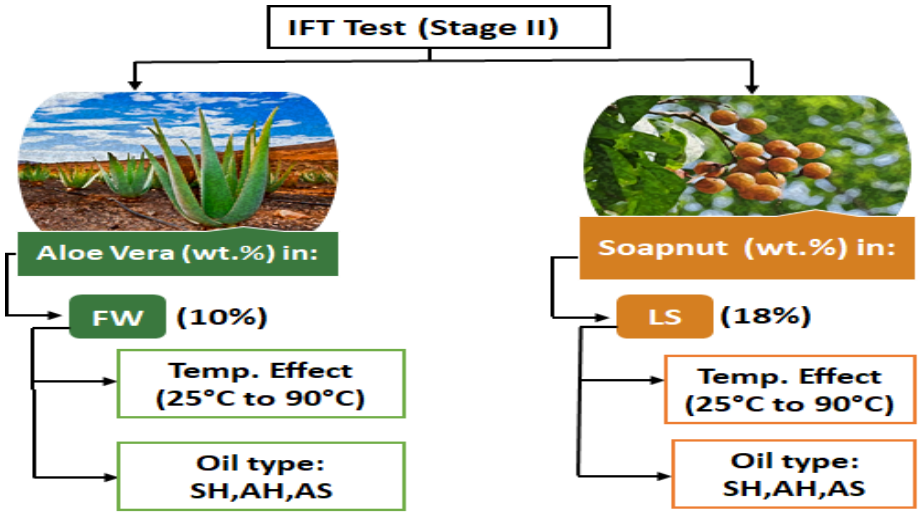


Figure 24: IFT Test Stage 2

2.2.12 Wettability Test Based on Contact Angle Measurements

Sessile drop analysis was used to determine wettability using contact angle measurements. The measurement of contact angle has become a crucial indicator of wettability. A decrease in contact angle signifies an increase in the liquid's wetting properties. Complete wetting would be characterized by a contact angle of zero, while complete non-wetting would result in a contact angle of 180°. In much of the existing literature, intermediate wettability is often defined with contact angles ranging from 60° to 90°, which typically repel the liquid in Figure 25.

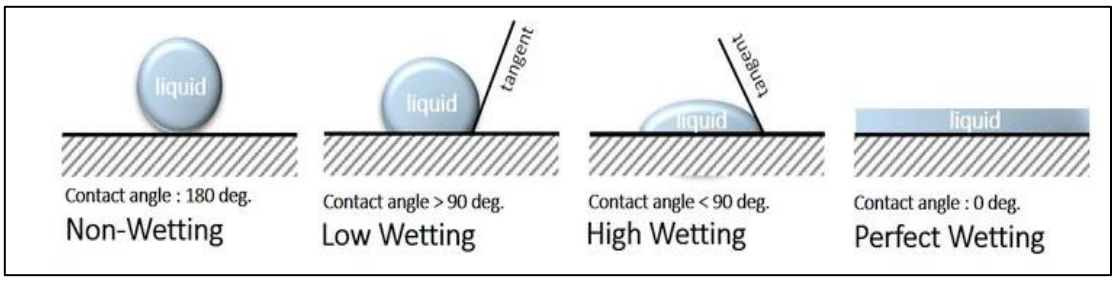


Figure 25: Contact Angles Criteria (Gatenby, n.d.)

Understanding the wettability of reservoir rocks towards fluids holds significant importance. It directly influences how fluids are distributed within porous media. Due to the attractive forces involved, the wetting phase tends to occupy the smaller pores of the rock, while the non-wetting phase occupies the more open channels (Ahmed, 2018).

The procedure involved injecting an oil droplet through a needle into the surfactant solution in Figure 26. This droplet then settled at the base of the polished core samples that were aged in brine. We allowed it to stabilize before capturing an image and subsequently measuring the contact angle using image analysis software, ensuring precise results.

(a) (b) (c)

Figure 26: Oil droplet During Wettability Analysis. a) Formation water, (b) Aloe Vera 10% Solution, and (c) 18% Soapnut Solution

The contact angle was assessed multiple times, and from these measurements, we calculated the mean value. Additionally, we determined the standard deviation to account for any variations.

We selected two types of rocks with properties closely resembling the one used in surfactant flooding. Prior to testing, these rocks were immersed in formation brine. This approach mirrored the conditions encountered during surfactant flooding. To assess the influence on wettability, we utilized solutions containing Aloe Vera at a concentration of 10% and Soapnut at a concentration of 18%. These specific solutions were chosen due to their favorable outcomes in interfacial tension measurements.

2.2.13 High-Pressure Temperature Surfactant Flooding

In this phase, we selected the surfactant with the most effective concentration, which yielded the lowest interfacial tension (IFT) results. This step was crucial for gaining deeper insights into their interaction with the rock. The surfactant solution was introduced at a temperature of 90°C under substantial confining pressure of 1000 psi for the sample with higher permeability, and 2000 psi for the sample with lower permeability. Notably, it was observed that the pressure continued to rise with the increasing temperature of the system. To maintain the desired temperature, a hot bath was employed shown in Figure 27. Additionally, the outlet pressure was regulated to prevent any boiling of the liquid. The collected liquid was then directed into tubes for further analysis. Subsequently, the recovery factor was computed using the following formula:

$$R.F\ \% = \frac{V_{Recoverd}}{V_{Intial}} \times 100 \quad (5)$$

Where:

$V_{Recoverd}$: Oil Recovered.

V_{Intial}: Oil Initially In Place.

In this study, core samples were selected for surfactant flooding experiments based on specific criteria. Two categories of core samples were chosen: high-permeability limestone and low-permeability dolomite stone. These categories were selected due to the limited availability of core samples. The same categories were also employed for wettability analysis to facilitate meaningful comparisons. The experiment was continually monitored, and data on parameters such as pressure, flow rates, saturation levels, and produced oil and water volume were collected.

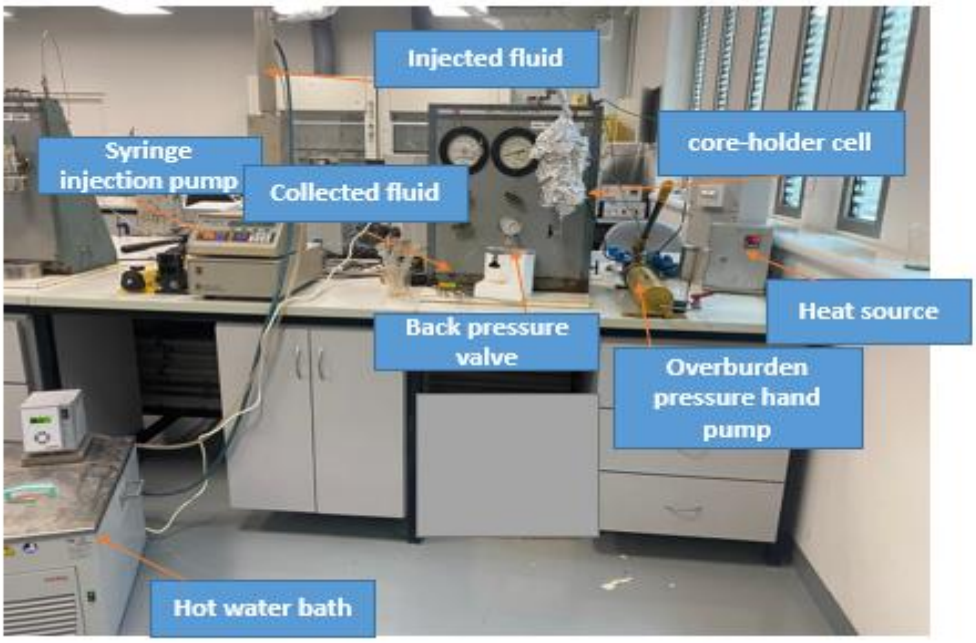


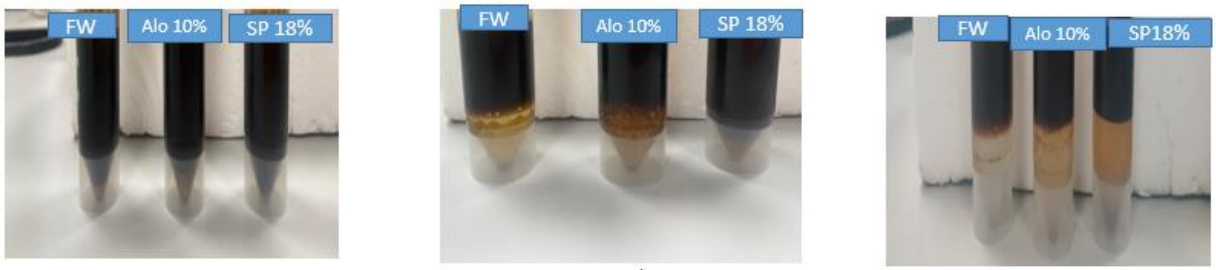
Figure 27: High-Pressure Temperature Surfactant Flooding Set Up

2.2.14 Emulsion Properties

Numerous laboratory studies and pilot applications have demonstrated that achieving a more stable emulsion in produced fluids can lead to improved oil recovery efficiency (Wang et al., 2016). It is widely recognized that enhancing emulsification is a key strategy for enhancing enhanced oil recovery (EOR) in oil displacement systems (Shi et al., 2017).

Two methods were employed to examine emulsification at room temperature and 1 atm pressure. The first method involved combining oil and surfactant in a 1:1 volume ratio of each surfactant type at CMC (SP 18% and AlO 10%). This mixture was mixed for 30 minutes at 1000 RPM. In this phase, the mixture was examined after a two-hour duration, allowing sufficient time for the system to stabilize and for complete separation to occur. Subsequently, photographs were taken, and a visual assessment was conducted to capture any distinctive features or characteristics.

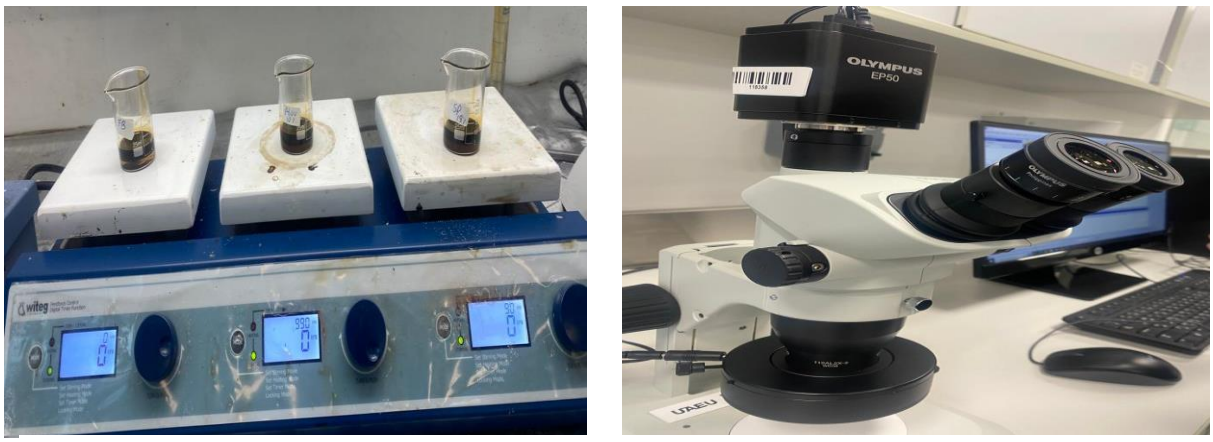
The results indicated a higher rate of water separation compared to oil separation, and the emulsion's internal phase was visible in Figure 28.b.



(a) (b) (c)

Figure 28: Emulsion Photos where (a) Freshly Prepared Emulation, (b) After 30 min, (c) After 2 hours

The second method entailed mixing oil and surfactant (SP 18% and AlO 10%) in a 1:1 volume ratio in a small beaker. This mixture was mixed at 1000 RPM for 30 minutes as shown in Figure 29.a. Subsequently, a drop of the emulsion was placed on a glass slide and examined under a light microscope in Figure 29.b. This allowed for the analysis of drop size and pattern size distribution using *ImageJ* software.



(a) (b)

Figure 29: Emulsion photos: (a) Sample Mixing Prior to Microscope Observation, (b) Light Microscope Used for Emulsion Observation

Chapter 3: Results and Discussions

3.1 Interfacial Tension Test Results

Natural surfactant stability is a critical parameter for the application of a successful enhanced oil recovery process. High reservoir brine salinity is one of the major players that affects the surfactant stability. Therefore, identifying optimum salinity along with the most useful surfactant concentration is required. The three employed natural surfactants were prepared using formation brine (232,000 ppm), seawater (≈50,000 ppm), and low salinity water (≈5000 ppm). The surfactant concentrations varied from 0% to 50% for Aloe Vera and Tetreana, And from 0% to 25% for Soapnut as displayed in details in Figure 23. Figure 30 displays the results of IFT measurements for various Aloe Vera extracted surfactant concentrations in different brines. The presented data indicates that the optimum natural surfactant concentration is around 10 wt.% for all brines employed in this work. Formation brine i.e. high salinity environment is the optimum among the tested brines. This is a pleasant result as a high salinity environment is a more suitable condition for the interfacial activity of the Aloe Vera natural surfactant. IFT value of 0.5 mN/m was achieved at the optimum salinity of 232,000 ppm and 10% Aloe Vera. This result indicated a 98% improvement in the interfacial activity as compared to the IFT of formation brine. Razzaghi-Koolaee et al. (2022) measured IFT between oil and Acanthophyllum plant APRE solution and FW (133,300 ppm). They have reported a minimum value equal to 1.06 mN/m at a concentration of 12000 ppm.

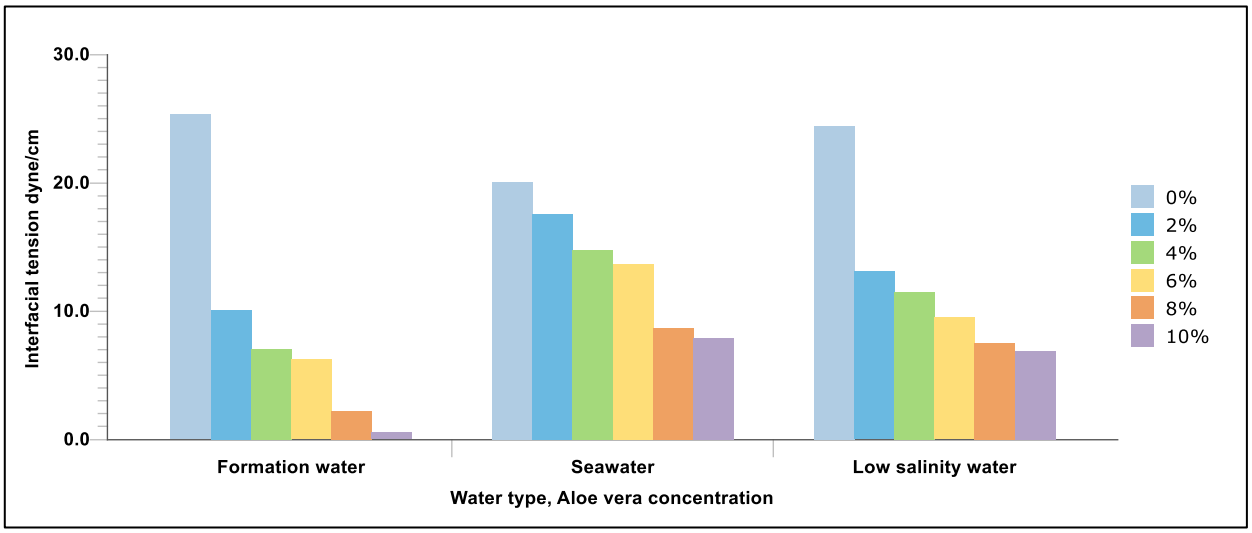


Figure 30: Interfacial Tensions between Aloe Vera Surfactant and SH Crude Oil

Nowrouzi et al. (2022) reported that a natural surfactant extracted from the Myrtus communis plant can reduce IFT to 0.861 mN/m at surfactant critical micelle concentration (CMC) of 5000 ppm with formation brine of 74000 ppm. All employed brines exhibited similar behavior with respect to interfacial activity i.e. decreasing IFT with increasing the surfactant concentration for the used range. Based on the above results it concluded that surfactant extracted from Aloe Vera plants can reduce the interfacial tension between oil and formation brine at 10% concentration. The results also indicated that we did not reach critical surfactant micellar concentration as the IFT reduction trend did not reach a minimum with surfactant concentration. Results also indicated that at high salinity (232,000 ppm) natural surfactant still did not move from the water phase to the oil phase and it concluded that a significant increase of the micro-emulsion phase which is responsible for the reduction of IFT is prevailing at high salinity.

As shown in Figure 31, presented the IFT results for the natural surfactant extracted from the Tetreana plant. Seawater and formation water produced similar IFT reduction at 10% surfactant concentration while low salinity water showed slightly more favorable interfacial activity. The IFT between oil and different brines prepared with 10% Tetreana surfactant is equal to 9.5, 9.2, and 7.5 mN/m for FW, SW, and LSW respectively. Aloe Vera has shown a 94% reduction in IFT with FW as compared to Tetreana for 10% surfactant concentration.

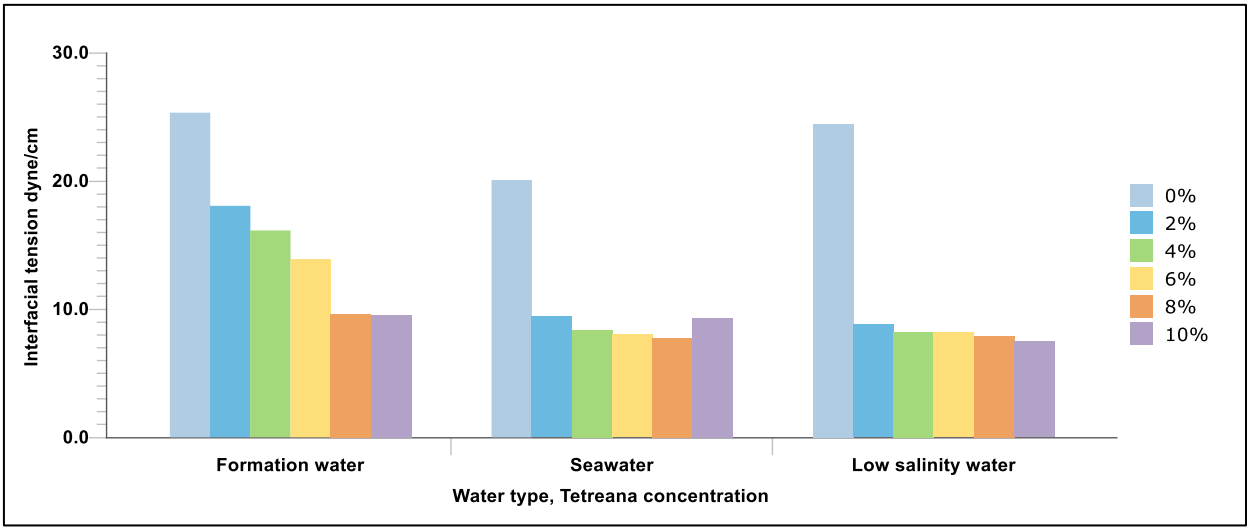


Figure 31: Interfacial Tensions between Tetreana Surfactant and SH Crude Oil

Formation brine, seawater, and low salinity water were used to prepare different solutions with natural surfactant extracted from the Soapnut plant. The concentration of the surfactant in different brines solution varied from 0% to 25% as presented in detail in Figure 22. Interfacial tensions between different Soapnut solutions and Sahil oil were measured by employing a spinning drop system. Figure 32 shows the effects of Soapnut concentrate on the IFT between surfactant solution and Sahil oil for different brines. IFT results indicated that the critical micelle concentration CMC of the Soapnut solutions is directly proportional to the brine salinity i.e. increasing brine salinity increases the CMC concentration. The CMC for FW, SW, and LSW are 18%, 15%, and 12%, and the corresponding IFT are 0.9 mN/m, 1.8 mN/m, and 3.1 mN/m respectively. In terms of interfacial activity, Soapnut exhibited a higher performance at high salinity (FW). Higher salinity required higher surfactant concentration to reach the optimum size of the micro-emulsion zone required for achieving the lowest IFT of the studied system. The natural surfactant employed in this project showed excellent stability at high salinity i.e. no precipitation of surfactant as is normally the case for other chemical surfactants.

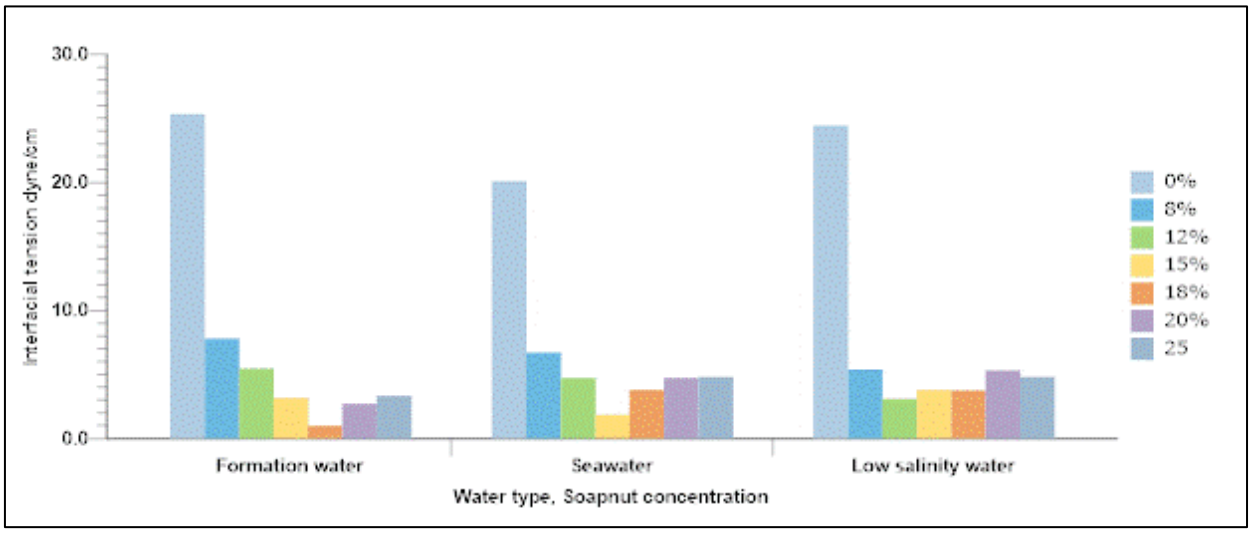


Figure 32: Interfacial Tensions between Soapnut Surfactant and SH Crude Oil

To precisely determine the CMC for both Aloe Vera and Tetreana natural surfactants employing formation brine (232,000) ppm for Aloe Vera and LW (5000) ppm for Tetreana, the concentration of surfactants increased beyond 10 wt.% up to 50 wt.% as presented in Figure 33. Both surfactants displayed a CMC of 10 wt.% with a significant reduction of interfacial tension as compared to formation brine.

The optimum IFT reduction of 98% and 70% resulted in a concentration of 10% of the mentioned natural surfactants respectively. On the other hand, the optimum surfactant concentration CMC, i.e. performance in terms of surface activity obtained using Soapnut surfactant in FW is slightly higher than Aloe Vera and Tetreana surfactants. Overall, interfacial tension measurements of the three natural surfactants employed in this result indicated that both surfactant concentration and brine salinity (high, medium, and low) have a major impact on interfacial activity. Surfactant concentration and salinity tend to balance between the salt-out effect and salt-in effect (solubility of polar compounds increases in salt in the case and decreases in the aqueous phase in the salt-out case) respectively. The balance between the two phenomena takes place at a high brine salinity of 232,000 ppm and reasonable surfactant concentrations of 10% for Aloe Vera and Tetreana and 18% for Soapnut.

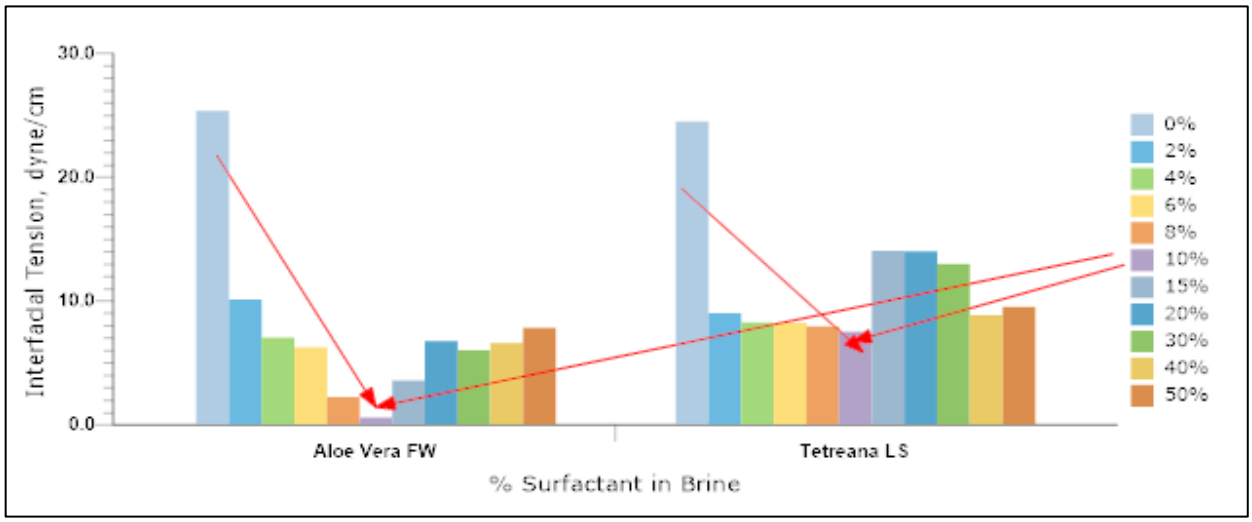


Figure 33: Interfacial Tensions of Aloe Vera _ FW and Tetreana _LSW Surfactants in and SH Crude Oil

To study the impact of different oils on the interfacial activities of the employed surfactants, the IFT between the best two surfactants Soapnut and Aloe Vera, and two additional crude oils (AS and BH) obtained from local reservoirs measured at the optimum surfactant concentrations. Figure 34 presents the results of IFT measurements between the three crudes and the two selected surfactants. IFT results indicated that both Soapnut and Aloe Vera can be used to reduce the IFT significantly for different UAE crudes.

SA crude oil showed slightly higher interfacial activity in the case of Soapnut surfactant and a significant reduction in IFT for Aloe Vera as shown in Figure 35.

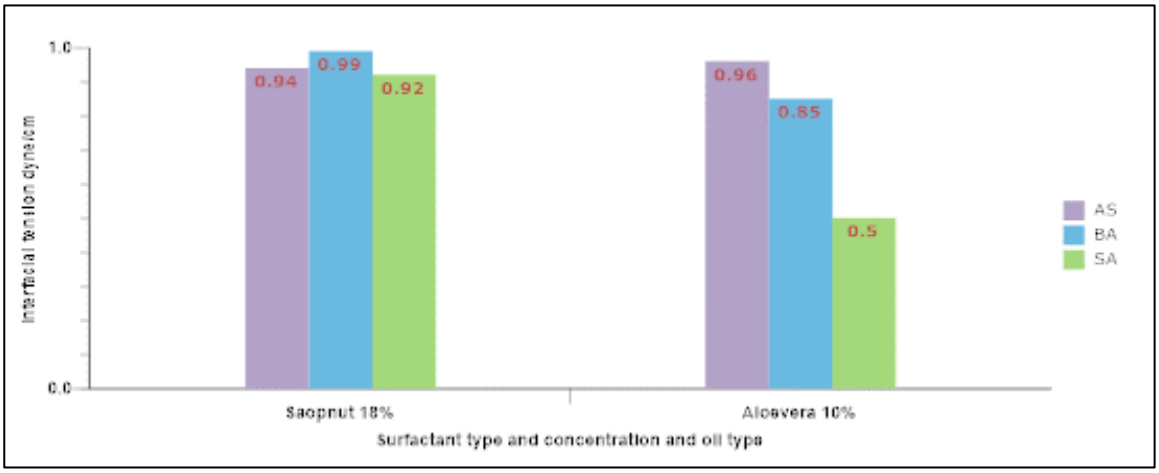


Figure 34: IFT of Soapnut 18% and Aloe Vera 10% in FW and Different Crude Oils

All of the IFT measurements were performed at room temperature employing a spinning drop tensiometer. The effect of temperature on the IFT between two crude oils and CMC of Soapnut and Aloe Vera was evaluated. Figures 35 and 36 show the interfacial tension of the two natural surfactants at different temperatures. As presented in both figures the IFT decreases with increasing temperature and in the case of Soapnut

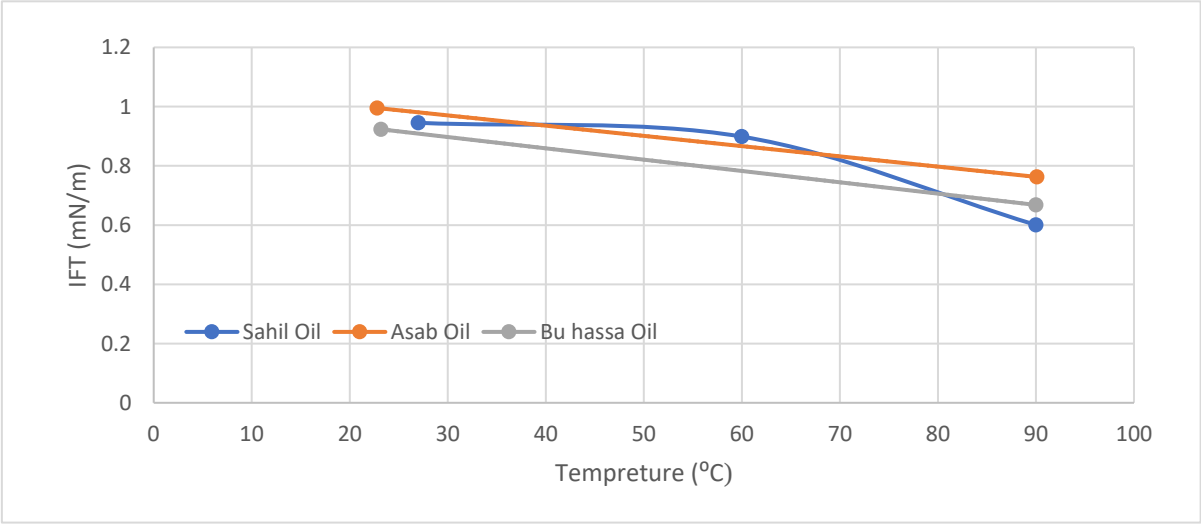


Figure 35: IFT versus Temperature for CMC Soapnut Surfactant and different Crude Oils

surfactant, the rate of IFT reduction with temperature did not change significantly for different crude oils.

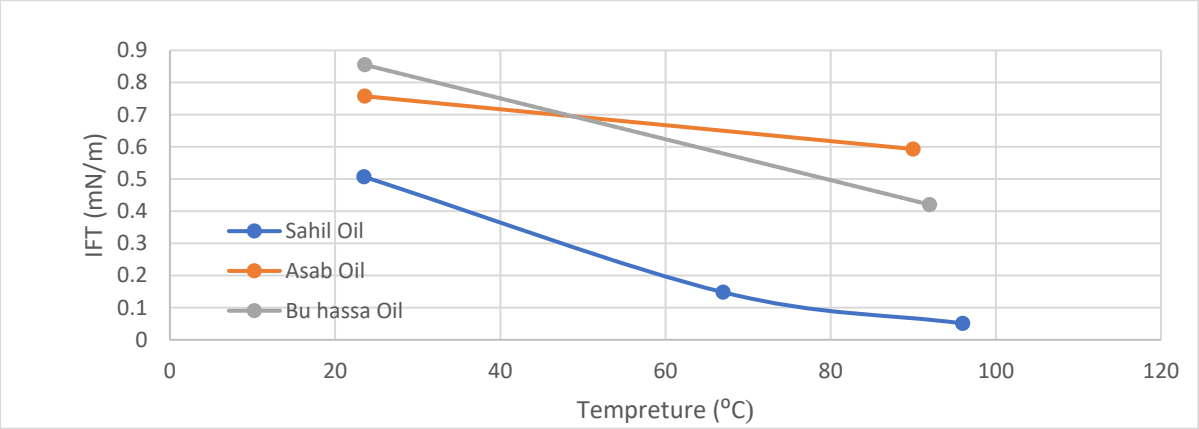


Figure 36: IFT versus Temperature for CMC Aloe Vera Surfactant and different Crude Oils

The percent reduction of IFT with temperature varied from 21.7% to 50.8% as presented in Figure 37. Temperature has a greater impact on the IFT of BH crude oil and CMC Aloe Vera surfactant as presented in Figure 36.

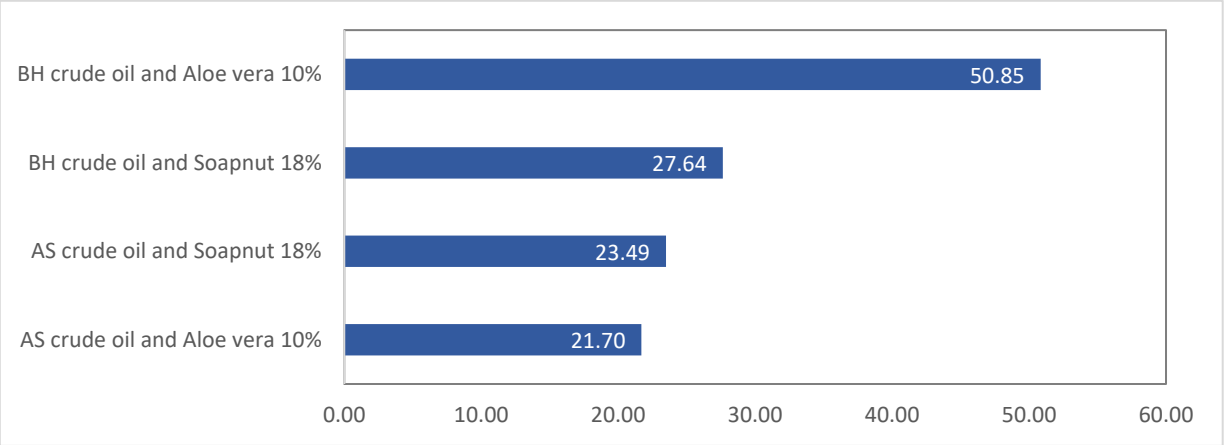


Figure 37: Percent Reduction with Temperature of the IFT between CMC Aloe Vera and Soapnut Surfactant and Different Crude Oils

3.2 Contact Angle Measurements

Wettability is a critical parameter that plays a major role in controlling the fractional flow behavior of oil and aqueous solutions, as it dictates the distribution of fluids in porous media. The measured contact angles, employing relatively high-permeability limestone

and low-permeability dolomite rocks between formation brine, Aloe Vera in FW at 10%, Soapnut in FW at 18%, and SA crude, are presented in Table 14.

Table 14: Contact Angle for Different Surfactants and SA Oil, Limestone and Dolomite Rocks

Samples ID	Rock Type	K (mD)	Solution Type	Contact Angle Replicate (1)	Contact Angle Replicate (2)	Mean	Std	Decrease (%)
ZE1-6	limestone	11.5	Formation Brine	85.406º	90.380º	87.5º	3.533	-
	limestone	11.5	Aloe Vera 10%	62.499º	54.671º	58.585º	5.53	33
	limestone	11.5	Soapnut 18%	47.115º	50.747º	48.931º	2.56	44.1
ZE2-8	Dolomite	0.936	Formation Brine	70.614º	80.680º	75.647º	7.117	-
	Dolomite	0.936	Aloe Vera 10%	31.504º	42.173º	36.8385º	7.544	51.3
	Dolomite	0.936	Soapnut 18%	47.603º	54.067º	50.835º	4.57	32.8

The base contact angles measured for crude oil/formation brine systems were 90° and 80.68° for limestone and dolomite, respectively. These results indicate rock wettability. According to the literature, complete wettability prevails at a zero-contact angle, contact angles between zero and 90° are termed intermediate wettability, and complete non-wetting is evidenced by a contact angle of 180° (Tarek, 2006).

Crude oil, with higher total acid number (TAN) and lower total base number (TBN) values, showed a tendency to change the wettability of rock surfaces towards oil wetness and vice versa (Shabib-Asl et al., 2015). It's important to note that TAN and TBN represent the number of components with negative and positive charges in crude oil, respectively (Cuiec, 1975; Shabib-Asl et al., 2015). The negative components of crude oil tend to be absorbed by the positive charges on the surface of limestone and dolomite rocks. Therefore, the amount of negative charges in the oil phase plays a critical role in system wettability.

For limestone rocks, as presented in Table 14, there is a 33.4% reduction in contact angle value for Aloe Vera at 10% concentration in formation brine and a 44.8% reduction for Soapnut at 18% concentration in formation brine. Both optimum surfactants in terms

of interfacial tension (IFT) shifted the system wettability from intermediate to water-wet, creating a favorable condition. The high salinity environment had no impact on both surfactants in producing favorable wettability conditions, contributing to higher displacement efficiency of natural surfactant flooding.

Soapnut at its critical micelle concentration (CMC) showed a higher reduction in contact angle compared to Aloe Vera at CMC concentration, indicating that Soapnut surfactant shifts the system wettability towards water wetness more effectively than Aloe Vera. In the dolomite environment, there is a 51.3% reduction in contact angle value for Aloe Vera at 10% concentration in formation brine and a 32% reduction for Soapnut at 18% concentration in formation brine. Therefore, Aloe Vera, in terms of wettability reduction, performed better than Soapnut in a limestone environment.

3.3 Emulsion Tests

The emulsification capability of formation brine and Aloe Vera and Soapnut solutions prepared at CMC were investigated using a conventional beaker test. Oil and surfactant, at their CMC, were mixed in a 1:1 volume ratio and agitated for 30 minutes at 1000 RPM. After allowing two hours for stabilization and separation, a drop of the emulsion was examined under a light microscope to analyze droplet size and distribution a high salinity system the surfactant tends to move in a large number of micelles toward the oil phase and extract oil droplets forming an emulsion phase between the aqueous phase and the oil phase. In this process, the smaller oil droplets can easily move through the narrow channels of the porous media and are normally more stable than larger ones. Figure 38 displays oil emulsion in the formation of brine, Soapnut, and Aloe Vera at CMC. Based on observations, here are some conclusions that can be drawn about emulsions formed with natural surfactants.

In drop size distribution:

Formation water: Produces a less stable emulsion with a wide range of droplet sizes and uneven distribution.

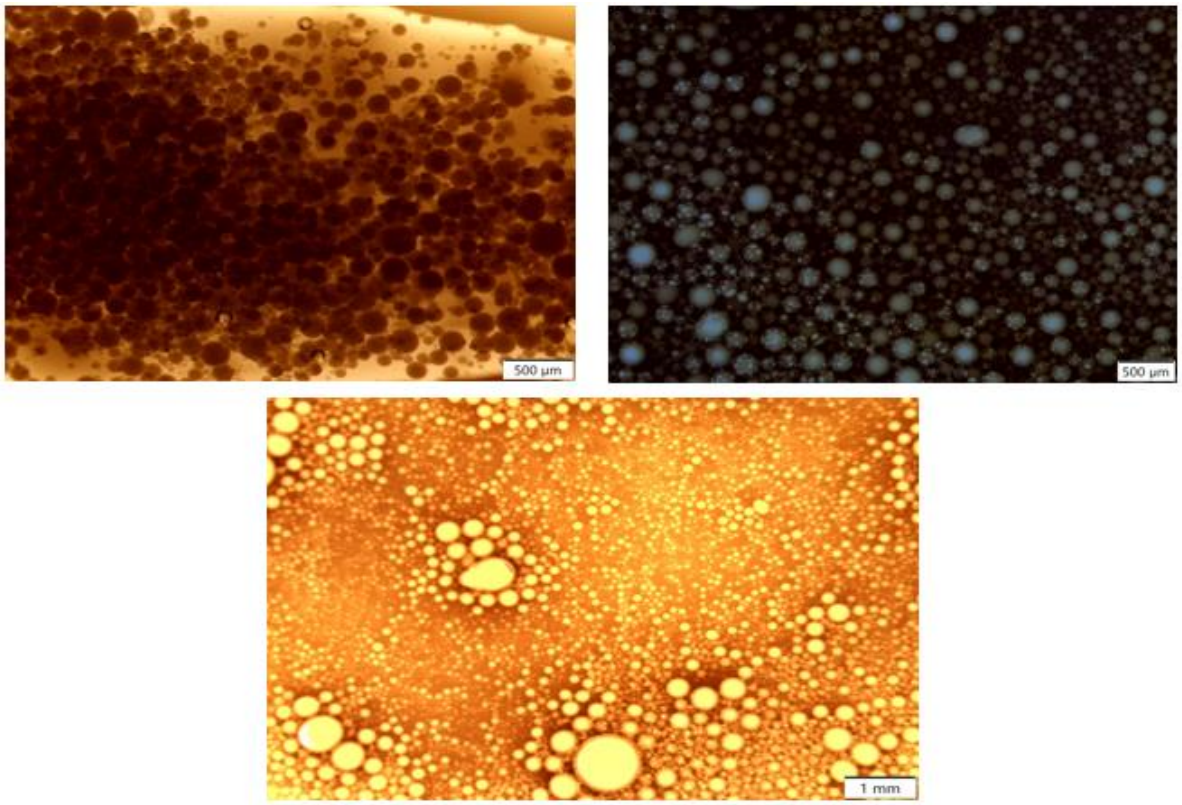


Figure 38: Oil Emulsion in Surfactant Solutions at CMC. From Left to Right (CMC Soapnut and Oil), (CMC Aloe Vera and Oil), and (Formation Brine and Oil)

Aloe Vera 10%: Forms a more stable emulsion with uniform droplet sizes, but some tiny droplets attach to larger ones.

Soapnut 18%: Creates a stable emulsion with uniform droplet sizes, but there is a tendency for droplets to aggregate and overlap.

It's important to note that these conclusions are drawn from the observations provided. For a complete understanding of how these emulsions behave, their stability, and their suitability for specific uses, further analysis or experiments may be necessary.

Drop size:

In FW (Formation water): Droplet diameter ≈ 0.347 mm.

In CMC Aloe Vera: Droplet diameter ≈ 0.0525 mm (or 52.5 µm).

In CMC Soapnut: Droplet diameter ≈ 0.0687 mm (or 68.7 µm).

Depending on the intended application (e.g., EOR), the emulsion with Aloe Vera at 10% concentration might be the most promising due to its smaller droplet size. These conclusions are based solely on the provided droplet diameters. Other factors like the stability of the emulsion over time, phase behavior, and compatibility with the reservoir conditions would also be important for a comprehensive assessment of the emulsions for EOR purposes. Additionally, the specific characteristics of the crude oil and the emulsification process should also be considered in the consideration. Figures 39, 40, and 41 shows the droplet size distribution for formation brine, CMC Soapnut surfactant, and CMC Aloe Vera surfactant respectively.

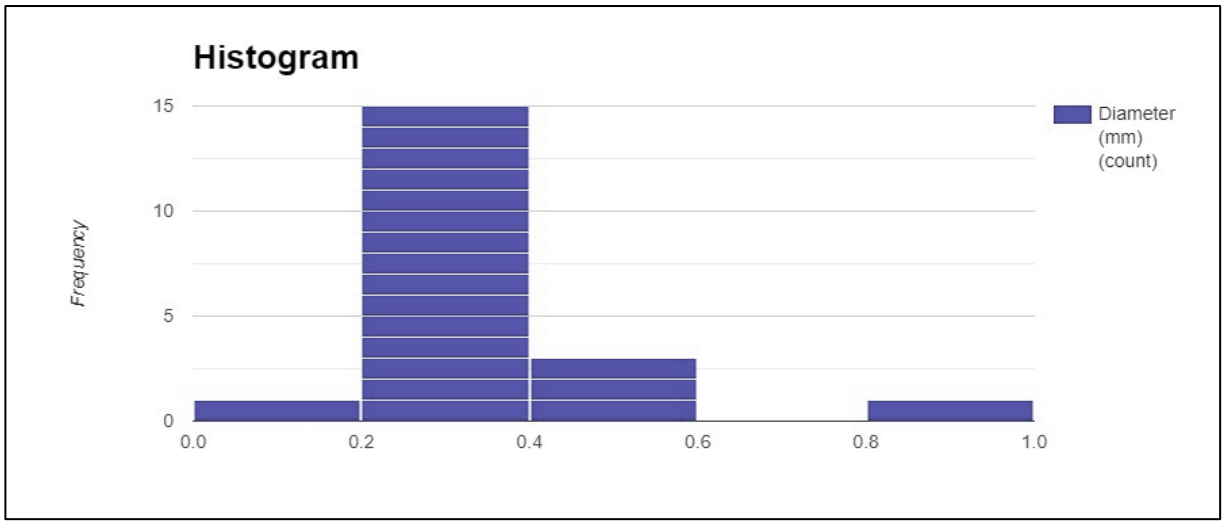


Figure 39: Formation Water Droplet Size Distribution

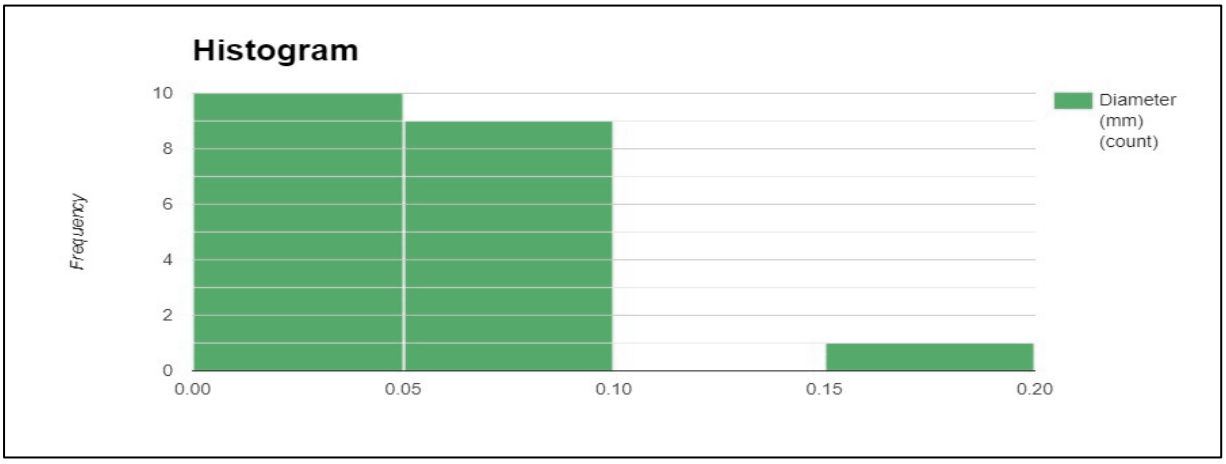


Figure 40: CMC Soapnut Droplet Size Distribution

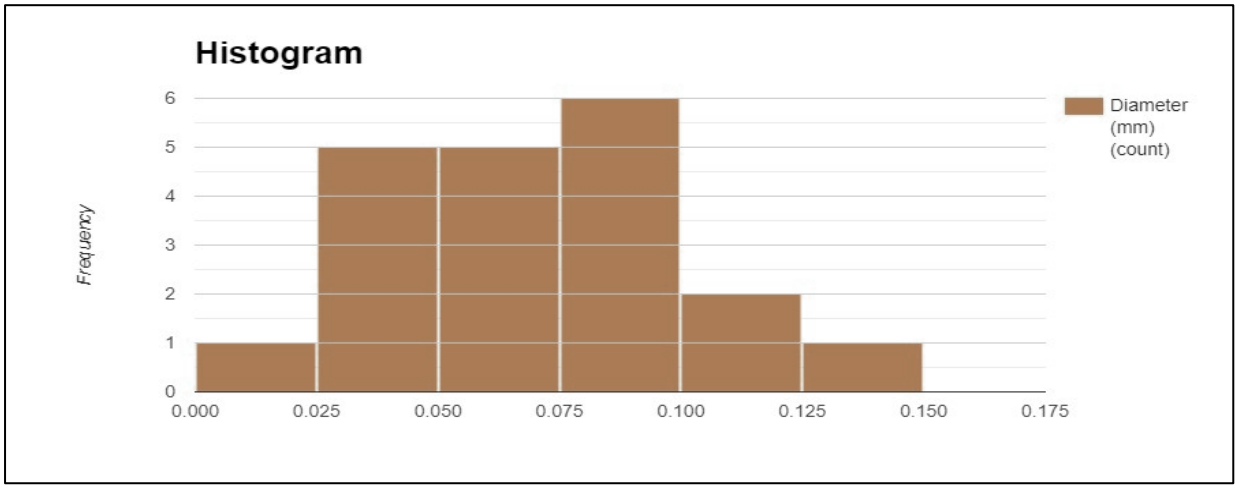


Figure 41: CMC Aloe Vera Droplet Size Distribution

3.3 Core Flooding Test Results

Five flooding runs were conducted in a secondary mode under different wettability and lithology environments to evaluate the performance of formation brine, as well as CMC solutions containing Aloe Vera and Soapnut. The results of the seawater and low salinity water flooding experiments were reported by Zekri et al. (2020).

To assess the possibility of wettability alteration from contact angle measurements, the criteria of wettability classification mentioned earlier were employed in this part. Cores were prepared for specific wettability conditions by aging them in oil and water for six weeks to create oil-wet and water-wet systems, respectively. Contact angle measurements were performed to assess the wettability of the aged system and for wettability estimation.

The core plug properties, wettability conditions, and oil recovery are presented in Table 15. In Figure 42, a comparison of the oil recovery factors for formation brine (FW), low salinity water (LSW), seawater (SW), and CMC surfactant solutions, taking into consideration the system's initial wettability.

Based on Figure 42, during each turn, the injected fluids were introduced until they reached a zero fractional flow of oil (primary recovery). Formation brine flooding resulted in the lowest oil recovery compared to natural surfactant flooding, seawater flooding, and

low salinity flooding due to the high interfacial tension (IFT) between formation brine and crude oil.

Table 15: Core Plugs Properties, Wettability, and Oil Recovery

Plug ID	Lithology	L (cm)	Porosity (%)	Permeability (mD)	Wettability	Flood. Sys.	Rec. (%OOIP)
ZE1-18	LS	5.102	17.2	19.3	OW	FW	15.4
ZE1-10	LS	5.09	15.1	16.5	OW	Aloe. 10%	93
ZE1-2	LS	5.1	16.5	6.5	OW	Soap. 18%	94.1
ZE2-18	DL	5.07	10.4	2.9	WW	Soap. 18%	76.9
ZE2-6	DL	5.08	11.4	2.6	WW	Aloe. 10%	90.9
UM5	LS	5.1	18	13.9	OW	SW	40
UM8	LS	5.1	19	15.8	OW	LSW	58

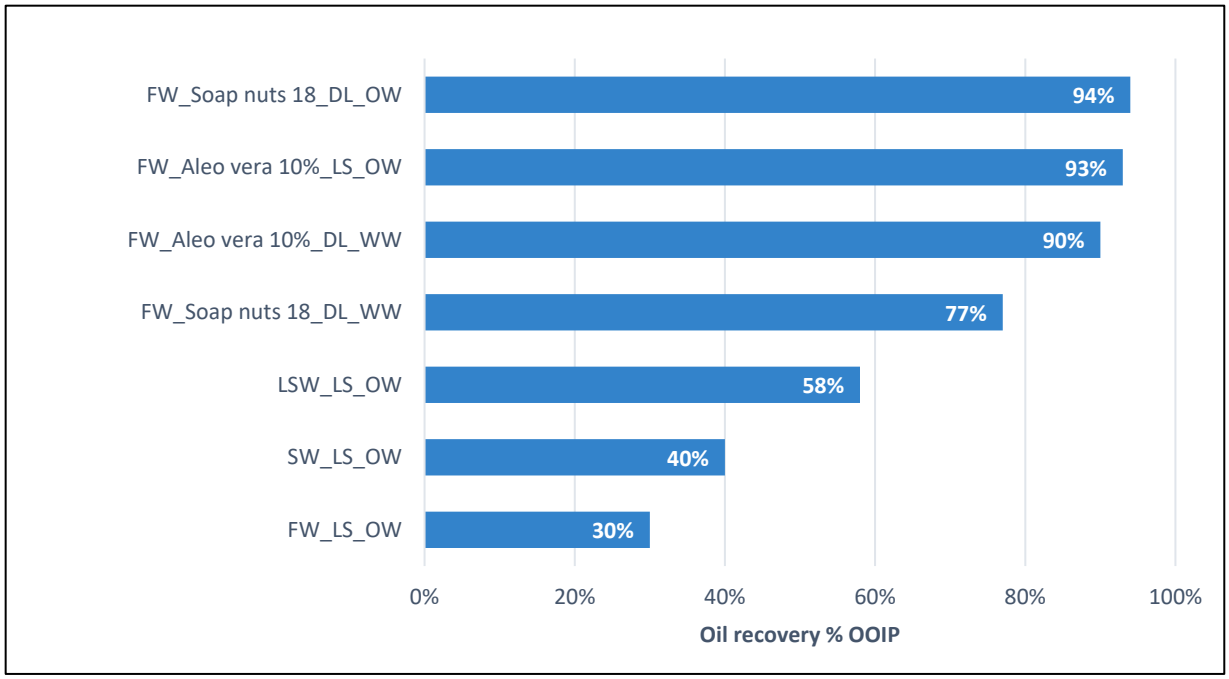


Figure 42: Oil Recovery for Different Brines and CMC Surfactant Solutions

The oil recovery results demonstrated that flooding with natural surfactants prepared with high salinity water (FW) at critical micelle concentration (CMC) is highly effective in improving the oil recovery of oil-wet and water-wet carbonate oil reservoirs. Both natural surfactants exhibited excellent displacement efficiency of oil in an oil-wet environment, and lithology had no significant impact on this system. Soapnut and Aloe

Vera surfactants flooding showed similar performance in the oil-wet system, recovering 94% and 93% of the oil in place, respectively. These results can be attributed to the alteration of wettability from oil-wet to water-wet system and the reduction of IFT between the injected surfactant and crude oil, as supported by the data collected in the IFT and contact angle measurements phases of the study.

In a study conducted by Chaalal et al. (2018) using Bu Hassa oil at high salinity with natural surfactants, remarkably high oil recovery rates of up to 96.54% were achieved. It was observed that the elevated recovery couldn't be solely accounted for by the reduction in interfacial tension (IFT). The researchers found that various natural components, including lipid, fructose, sucrose, maltose, and plant protein, among others, collaborated synergistically to enhance the efficiency of the recovery process. The positive impact of the injected fluid extended to factors such as IFT, total volumetric efficiency, wettability, and other parameters that are not easily discernible with synthetic materials but are present in natural products. The newly developed process is anticipated to be particularly advantageous in situations involving fractures or complex reservoir heterogeneities, which typically pose challenges to displacement efficiency.

Chapter 4: Conclusion

4.1 Managerial Implications

In this study, three plants were tested (Aloe Vera, Soapnut, and Tetraena qatarensis) Aloe Vera and Soapnut plants were selected based on IFT measurements screening process as sources of green, natural surfactants for enhanced oil recovery (EOR) applications. The efficiency of the extracted surfactants was assessed through various laboratory experiments, including interfacial tension (IFT) measurement, contact angle measurement, emulsion stability tests, and core flooding experiments. Experimental results revealed that solutions of the Soapnut surfactant (18%) and Aloe Vera (10%) prepared with formation brine reduced the IFT from 25 dyne/cm to 0.9 dyne/cm and 0.5 dyne/cm, respectively. The oil recovery factors of the formation water, Aloe Vera surfactant-FW, and Soapnut surfactant-FW flooding were 15%, 93%, and 94.1%, respectively. This indicates that Soapnut and Aloe Vera natural surfactants at relatively low concentrations exhibit remarkable effectiveness in harsh environments, and demonstrate the capability to recover nearly all the in-place oil.

4.2 Research Implications

Physico-chemical characterization of the natural surfactant extracted from both Aloe Vera and Soapnut showed that the extracted surfactant has great potential to be used for enhancing oil recovery in limestone and dolomite formations.

The optimum salinity of the tested surfactants at surfactant CMC is 232,000 ppm based on the contact angle and IFT measurement results.

IFT measurement resulting formation of brine as water phase showed that the CMC values of the Aloe Vera and Soapnut surfactants are 10% and 18%, which is near to the chemical surfactants employed for EOR by the oil industry.

The IFT measurement results showed that the Aloe Vera, Soapnuts, and Tetreana surfactants are very compatible with formation brine (high salinity water) in reducing the IFT.

At the CMC, the IFT values of 0.5 mN/m, 0.94 mN/m, and 7.5 mN/m for Aloe Vera (AlO), Soapnut (SP), and Tetraena qatarensis surfactants respectively.

The contact angle measurements results showed that both natural surfactant (ALO and SP) in limestone and dolomite environment reduces the contact angle which implies shifting the system wettability to more water wetness. The highest reduction of contact angle of 51% was obtained for Aloe Vera at CMC in a dolomite environment.

Emulsion test results revealed that Aloe Vera (10%) Surfactant forms a more stable emulsion with uniform droplet sizes, but some tiny droplets attach to larger ones. It also indicated that Soapnut (18%) creates a stable emulsion with uniform droplet sizes, but there is a tendency for droplets to aggregate and overlap. In terms of drop size, the emulsion with Aloe Vera at 10% concentration might be the most promising due to its smaller droplet size.

Both Natural surfactants at CMC (ALO and SP) showed an excellent displacement efficiency of oil in an oil-wet environment and lithology has no significant impact on this system. Soapnut and Aloe Vera surfactants flooding showed similar performance in the oil-wet system as recovered 94% and 93% of the oil in place, respectively.

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Appendices

Appendix A: X-ray fluorescence (XRF) and X-ray diffraction (XRD) analysis

ZE-1 Limestone core sample X-ray diffraction (XRD) result.

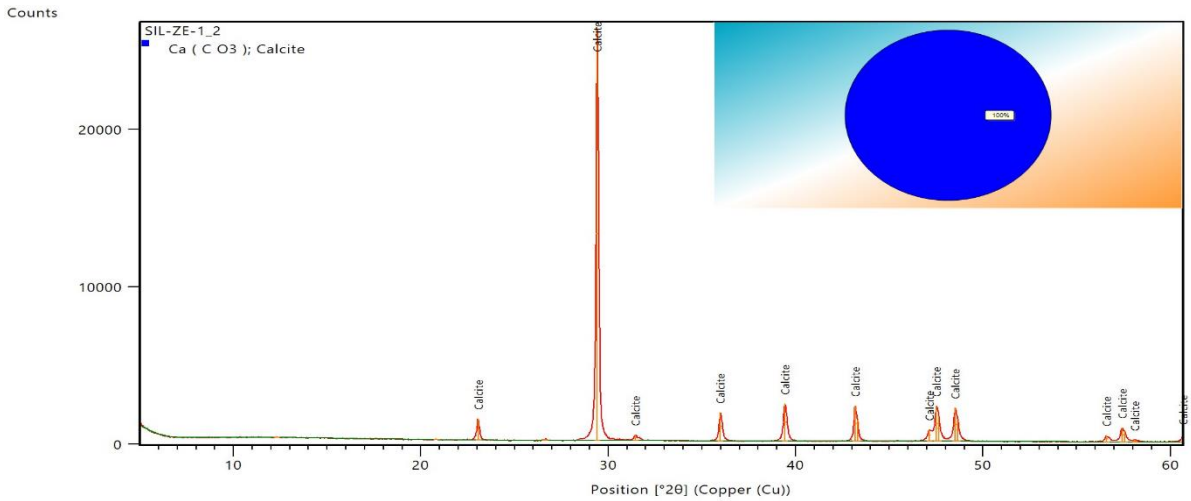

Figure A.1: XRD for ZE1 Sample

ZE-2 Dolomite core sample X-ray diffraction (XRD) result

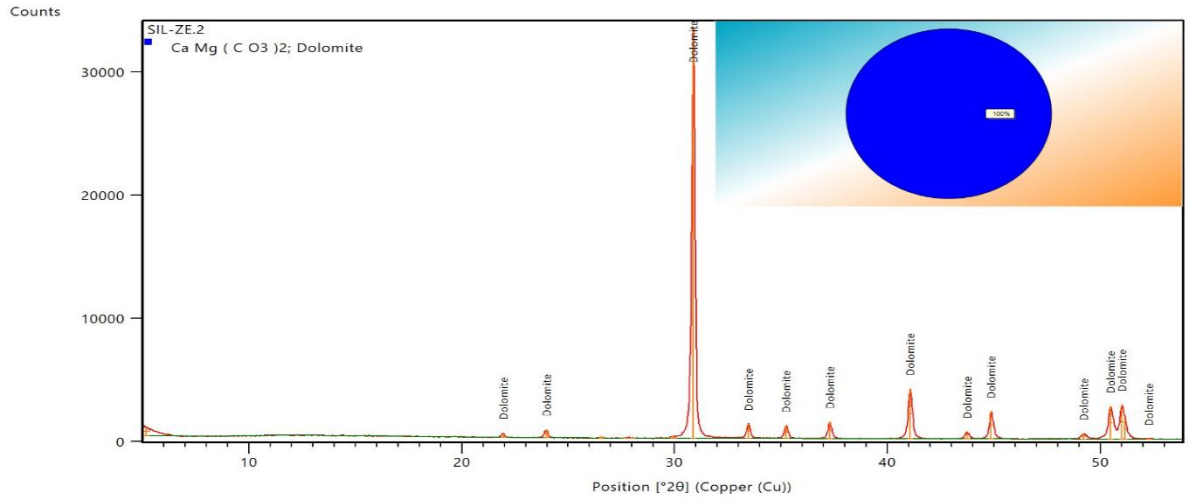

Figure A.2: XRD for ZE2 Sample

Dolomite and limestone Core samples X-ray Diffraction (XRD) Results.

Table A.1: XRF Results for ZE-1 and ZE-2 Samples

Compound	**ZE - 1 ROCK**	**ZE - 2 ROCK**
MgO %	0.996	21.058
Al2O3 %	0.09	0.097
SiO2 %	0.754	0.533
P205 %	0	0.094
SO3 %	0	0.206
CI %	14.557	4.295
Cao %	82.849	72.561
Sc %	0	0.048
V %	0.001	0.003
Cr %	0.002	0.005
Mn %	0.008	0.037
Fe203 %	0.279	0.398
Sr %	0.047	0.02
Pd %	0	0.002

Appendix B: For the Emulsion stability test

1. Formation Water (FW) Emulsion

Initially, the FW emulsion mixed well, indicating effective emulsification of formation water with the oil.

After 30 minutes, the emulsion began to separate, with the water phase becoming more prominent. This suggests that the emulsion was not stable over time, leading to phase separation.

After 2 hours, complete separation occurred, and the water phase became distinct and clear. This indicates that the emulsion was not stable and eventually broke down completely.

2. Soapnut 18% Emulsion

Initially, the Soapnut 18% emulsion formed an intermediate layer between the oil and water phases, indicating some degree of emulsification.

After 30 minutes, the emulsion showed continued separation, but some oil remained mixed in the water phase. This suggests that the emulsion was less stable compared to the Aloe Vera 10% emulsion.

After 2 hours, separation continued, and some darker oil droplets were still present in the water phase, indicating incomplete phase separation.

3. Aloe Vera 10% Emulsion

Initially, the Aloe Vera 10% emulsion also formed an intermediate layer, indicating some emulsification.

After 30 minutes, the emulsion showed a similar intermediate layer, but it appeared to be more stable compared to the Soapnut 18% emulsion. Some oil was still present in the water phase but to a lesser extent.

After 2 hours, separation continued, but there was less oil present in the water phase compared to the Soapnut 18% emulsion.

In summary (i) The Formation Water (FW) emulsion was the least stable, with complete separation observed after 2 hours. (ii) The Soapnut 18% emulsion showed intermediate stability, with some oil remaining in the water phase even after 2 hours. (iii) The Aloe Vera 10% emulsion exhibited better stability compared to the Soapnut 18% emulsion, with some oil present in the water phase after 2 hours.

These observations suggest that the Aloe Vera 10% emulsion may be more effective at stabilizing the emulsion compared to the Soapnut 18% emulsion, while the Formation Water (FW) emulsion demonstrated the least stability. Further experiments and analysis may be needed to fully understand the emulsions' behavior and stability over a longer period.

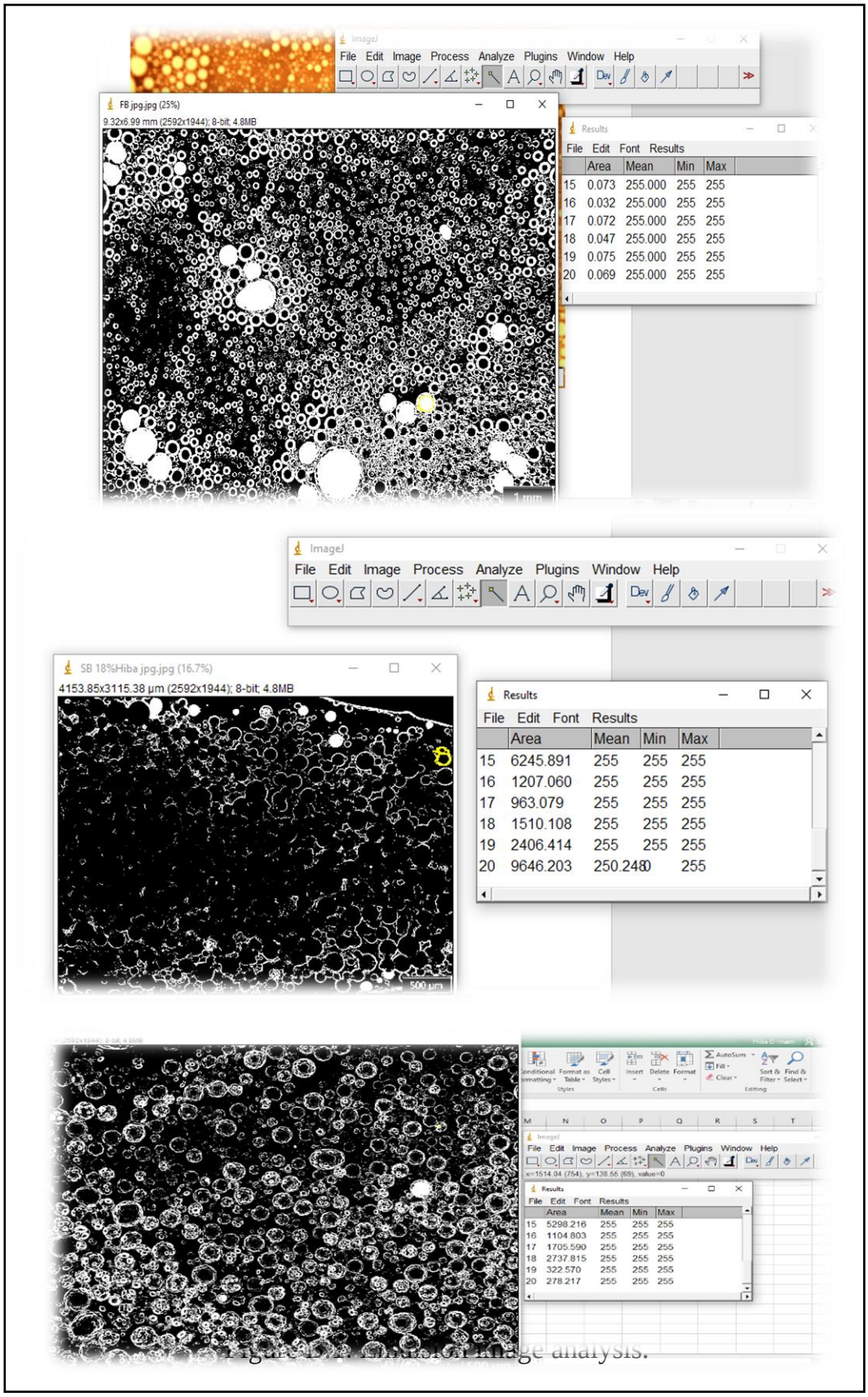

Figure B.1: Emulsion image analysis.

Figure B.1: Emulsion Image Analysis

Appendix C: Dolomite and Limestone Core Samples Data

Table C.1:Dolomite and Limestone Core Samples Data

Sample Name	Dia (mm)	Length (mm)	Bulk Vol (cc) L*A	Weight (g)	Grain Vol. (cc)	Grain Density (g/cc)	K (mD)
ZE2-1	3.803	5.084	57.76	138.59	49.343	2.81	5.7
ZE1-2	3.827	5.100	58.65	129.15	48.952	2.64	6.5
ZE2-3	3.780	5.091	57.13	146.6	52.211	2.81	1.5
ZE1-10	3.825	5.090	58.49	132.24	49.659	2.66	16.5
ZE1-18	3.783	5.102	57.36	127.48	47.488	2.68	19.3
ZE2-18	3.765	5.077	56.52	139.83	50.633	2.76	2.9
ZE2-17	3.771	5.077	56.69	138.58	49.18	2.818	12.362
ZE2-6	3.766	5.088	56.67	139.57	50.17	2.782	2.569
ZE2-12	3.777	5.083	56.95	142.52	51.26	2.780	2.392

Table C.1:Dolomite and Limestone Core Samples Data (Continued)

Sample Name	Pore vol (cc)	Porosity (%)	Saturated sample weight (g)	OOIP (cc)	Si
ZE2-1	8.42	14.6	146.17	4.5	0.53
ZE1-2	9.70	16.5	138.15	5.1	0.53
ZE2-3	4.92	8.6	149.1	1.5	0.30
ZE1-10	8.83	15.1	139.17	4.3	0.49
ZE1-18	9.87	17.2	134.87	2.6	0.26
ZE2-18	5.89	10.4	143.585	2.6	0.44
ZE2-17	7.52	13.26	143.21	2.1	0.28
ZE2-6	6.50	11.46	143.73	1.1	0.17
ZE2-12	5.69	9.99	146.43	1.8	0.32

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The research explores the potential of natural surfactants from Aloe Vera, Tetraena qatarensis, and Soapnut leaves. Through comprehensive laboratory experiments, including interfacial tension measurement, contact angle measurement, emulsion tests, and core flooding experiments, the study assesses the efficiency of these natural surfactants in different salinity waters. Notably, Soapnut surfactant at 18% concentration, along with Aloe Vera at 10%, demonstrates a significant reduction in interfacial tension and achieves notable oil recovery, showcasing its effectiveness in challenging reservoir conditions.

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