

# Green water flooding of fractured and heterogeneous oil reservoirs at high salinity and high temperature

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## Abstract

Many oil formations contain water having high salinity and/or high concentrations of divalent ions such as calcium or magnesium dissolved therein, and are additionally at high temperatures. Most of the available surfactants used in oil recovery operations are either ineffective in high salinity or high hardness waters, or incapable to stand the higher temperatures encountered in many formations. A powerful natural material that improves enhance oil reservoirs recovery through the reduction of interfacial tension and increases the volumetric sweep efficiency of fractured and /or heterogeneous oil reservoirs is introduced in this paper. The novel green surfactant for EOR is extracted from Sisyphus Spina Christi plant and Aloe Vera plant. The surfactant is 100% natural, safe and environmental friendly. It recovers more than 96% of the oil trapped in any oil reservoir. This recovery is a breakthrough in the field of enhanced oil recovery. It works at high salinity (up to 172000 ppm) and a temperature over than 90° Celsius. It can handle a bivalent ions (14000 ppm for Ca<sup>+2</sup> and 3000 for Mg<sup>+2</sup>) and monovalent ions (57600 for ppm Na<sup>+</sup> and 122000 ppm Cl<sup>-</sup>). The green material is mixed with the formation water and is stable over a wide range of formation temperatures and water salinities and hardness values. Copyright © 2018 VBRI Press.

**Keywords:** Green material, EOR, green flooding, high salinity, high temperature, reservoir, IFT.

## Introduction

Fulfilling worldwide energy demand in the 21st century is the most challenging problem. New kinds of energy sources along with the new technological breakthroughs to maintain enough oil and gas supply are needed to meet the tremendous rise in world's energy demand. Recent dramatic fall in oil prices has accentuated the problem. Now, the challenge is to fill out the increasing gap between energy demand and supply with more cost effective techniques. In addition, environmental consequences must be considered because it has become clear that long-term sustainability cannot be assured without including environmental constraints. In order to meet such a challenge, we need stunning new discoveries that can create a paradigm shift in technology development, making it economically attractive, socially responsible, and environmentally appealing. Recently, Abu Dhabi University has filed a patent application (US – Patent Application No 15/342,664) reporting the invention of Dr. Omar Chaalal that fulfills practically all criteria discussed above. This paper introduces a powerful natural material that relates to improve/ enhance oil

reservoirs recovery through the reduction of interfacial tension and the improving of the volumetric sweep efficiency of fractured and /or heterogeneous oil reservoirs by using the extract of natural plants. The novel green fluid for EOR is extracted from two plants. The first plant is known in Arab region as “Sidr” with the scientific name Sisyphus Spina Christi. The second plant is known as “Sabbar” with the scientific name Aloe Vera. In this paper, a ‘green’ alternative to chemical flooding is proposed in Oil recovery.

Nowadays, methods for improving oil recovery, in particular those concerned with lowering the interstitial oil saturation, have received a great interest in the industry, with particular focus on environmental sustainability [1], [2]. There are many different types of chemical compositions used in the oil recovery process involving the individual or combined injection of surfactants that lower the surface interfacial tension between the injected water and crude oil in the reservoir and/or change the wettability of the reservoir rock surface, allowing the desorption of crude oil. During the past several decades, various methods have been sought in order to efficiently increase the secondary and tertiary

oil recovery process, while improving the economic viability and efficiency of operations. Examples of said method includes, but are not limited to, chemicals, polymer, surfactant and alkaline flooding techniques. Although said methods have showed to be responsible in decreasing the interfacial tension while increasing the sweep efficiency, there is still a need of enhanced oil recovery from the reservoirs, in particular where such oil recovery process should be carried out from high salinity and high temperature of oil reservoirs. Most of the available surfactants used in oil recovery operations are either ineffective at high level of salinity hardness of the water, or incapable to stand the higher temperatures of many processes. Most importantly, the chemicals used are toxic to the environment and hence unsustainable [3].

There are many different types of chemical enhanced oil recovery involving the individual or combined injection of surfactants that lower the surface interfacial tension between the injected water and crude oil in the reservoir and/or change wettability of the reservoir rock surface, allowing 'desorption' of crude oil. During the past several decades, significant and considerable research has been carried out on secondary and tertiary recovery of trapped residual oil remaining within the producing formations underground despite the efficient, current primary production strategies and methods. Methods have been sought of increasing oil recovery, while revamping and improving the economic viability and efficiency of operations. A brief review of the operations used in oil recovery is necessary.

### ***Chemical flooding***

Chemical flooding is a broad term for techniques relating the injection of chemicals to decrease interfacial tension and increase sweep efficiency [2]. The three principal groups are polymer, surfactant and alkaline flooding. They can be mixed to attain the best characteristics of each. Reservoir characteristics dictate a particular restriction as carbonates and clays absorb the chemicals. Recoveries up to 40% can be achieved by those techniques. However they are restricted by the high cost of the chemicals. Latest developments include the use of emulsions, foams and microbes.

### ***Polymer flooding***

It is known that water flooding operation does not normally recover residual oil that has been stuck in pore spaces and isolated by water. Polymer flooding is seen as an improved water flooding technique. This method is mentioned as polymer-augmented water flooding. The injection of dilute water-soluble polymers, such as polyacrylamides and polysaccharides, can produce additional oil compared with that obtained by ordinary water flooding by improving the displacement efficiency and increasing the volume of reservoir that is contacted by increasing the viscosity of the water. This reduces the probability of the flood breaking through to the production well while also producing oil at a higher rate.

In most cases, polymer flooding is applied as a slug process and is driven using dilute brine [3]. Loss of polymer to the porous medium, particularly in reservoirs with high clay content, is particularly problematic as can be polymer degradation.

### ***Surfactant flooding***

In the operation of Surfactant Flooding, surface-active agents such as petroleum sulfonates are combined with other compounds like alcohol and salt and mixed in water. The mixture injected to mobilize the crude oil. These surface active materials lower the interfacial tension between oil and water.

The major difficulty in the past has been due to excessive surfactant loss to the porous medium and the presence of clay minerals can be particularly problematic and therefore good understanding of the reservoir conditions is essential [4], [5], [6].

### ***Alkaline flooding***

In alkaline flooding an aqueous solution of an alkaline, such as sodium hydroxide, sodium carbonate or sodium orthosilicate, is injected in a slug form [7], [8]. The alkali reacts with acidic components of the crude oil and generates the surfactant in situ, therefore a sufficiently high organic acid content is necessary. On the other hand, the process is not appropriate for practice in carbonate formations due to abundance of calcium which may react with the alkali to form precipitates that damage the formation.

### ***Micellar flooding***

Micellar flooding refers to a fluid injection process in which a stable solution of oil, water, and one or more surfactants along with electrolytes of salts is injected into the formation and is displaced by a mobility buffer solution [9],[12]. The main components of this method are a micro emulsion slug and a polymer slug. These two slugs are driven using brine. Micro emulsions are surfactant-stabilized, oil-water dispersions with small drop size distribution (10-4 to 10-6 mm) which are miscible with reservoir oil as well as water. The two chemical slugs are designed to promote very low interfacial to increase the mobility of the oil. Recovery factors have ranged between 35-50% of oil in place in field projects [13]. This technique is unsuitable for reservoirs with high salinity, temperature and clay content.

### ***Alkaline-surfactant-polymer (ASP) flooding***

Alkaline-Surfactant-Polymer flooding [14], [15] takes advantage of the individual alkali, surfactant and polymer methods while lowering injection costs and reducing surfactant adsorption. The major mechanisms are interfacial tension reduction and improved reservoir sweep. A recovery factor 25-30% of oil in place can be reached.

### ***Microbial enhanced oil recovery (MEOR)***

Microbial Enhanced Oil Recovery (MEOR) relies on microbes to ferment hydrocarbons and produce a by-product that is useful in the recovery of oil [16], [18]. Nutrients such as sugars, nitrates or phosphates are regularly injected to stimulate the growth of the microbes, which are indigenous to some reservoirs, and aid their performance. The microbes then generate surfactants and carbon dioxide that help to displace the oil in a similar way to other displacement methods. Since growth occurs at exponential rates, the process quickly generates considerable surfactant in a cost effective manner. Studies have shown that several microbially produced bio-surfactants compare favorably with chemically synthesized surfactants.

MEOR has the advantage that microbes do not consume large amounts of energy and that they are independent of the price of crude oil, compared to other processes. However with increasing subsurface depth, temperature appears to be the principal factor limiting microbial life, besides availability of suitable nutrients. They are also susceptible to salinity which limits their use [19], [20].

### ***Foam enhance oil recovery***

Foam is a metastable dispersion of a relatively large volume of gas in a continuous liquid phase that constitutes a relatively small volume of the foam. The gas content in classical foam is quite high (often 60 to 97 vol. %). Bulk foams are formed when gas contacts a liquid containing a surfactant in the presence of mechanical agitation [21].

In oilfield applications, the use of CO<sub>2</sub> foams has been considered a promising technique for CO<sub>2</sub> mobility control [22] and steam flooding mobility control [23]. The use of foams for mobility control in surfactant flooding, specifically at high temperatures (due to polymer degradation), in alkaline-surfactant flooding, surfactant/polymer projects, and in alkaline/surfactant/polymer flooding have been reported [23], [24].

## **Experimental**

### ***Green material solution preparation***

The leaves of both plants were collected from Al-Ain, a town in the district of Abu Dhabi in the United Arab Emirates. The leaves were dried at 40°C and grounded into a fine powder.

Prior to mixing, the two extracts were prepared by dissolving 1g of dried powder of each plant in 100 ml of water that contains variable concentrations of salt varying from zero ppm to 171600 ppm. The two extracts were filtrated and kept in sealed bottles and stocked in a fridge. Furthermore, the two extracts were mixed in different proportion in order to find the best mixture that gives the lowest IFT and highest oil recovery. The IFT at various

salt concentrations was examined for each mixture. The mixture of 80% Sisyphus Spina Christi extract and 20 % of Aloe Vera extract, the green material, was found to be the best combination to get the best IFT and the highest oil recovery. The composition of the green material is presented in **Table 1**.

**Table 1.** Composition of 80%-20% green material mixture.

<b>Compounds</b>	<b>Concentrations (mg/l)</b>
Fructose	563.10
Sucrose	179.50
Maltose	183.61
Total sugars	926.21
Proteins	281
Lipids	6
Saponin	13.6 (mg/gr)

### **Core samples preparation.**

Four core samples were prepared. Cores 1, 2 and 3 were cut from a rock collected from Jabel Hafeed Mountain near Al Ain town. Core 4 was from a real reservoir located in Um Rudhuma oil field. The characteristics of the cores such as length L, diameter D and porosity P are presented in **Table 2**.

## **Results and discussion**

### ***Interfacial tension investigation***

Low interfacial tension (IFT) between crude oil and water is significant for successful enhanced oil recovery by surfactant flooding. Generally, the main requirement of surfactant processes is targeting of ultralow interfacial tensions. For this purpose, the right surfactant should be selected and evaluated at low and economic concentrations. On the other hand, maintaining low IFT during the displacement process is a critical challenge because of dilution and adsorption effects in the reservoir. Today's technology suggests the use of a variety of means such as CO<sub>2</sub> injection, surfactant agent injection, natural gas miscible injection, and steam recovery in the final tertiary or enhanced oil recovery (EOR) phase. In this phase the injection of different materials to improve the flow between oil, gas and rock, and to recover crude oil remaining after the primary and secondary oil recovery phases. Oil that is left behind after water flooding is there because: either it has not been contacted by the injected fluid, or because of the capillary forces that exist between oil, water and the porous rock in the contacted portions that trap and retain it. The interfacial tension was measured at different salt concentrations and different temperatures and the effect of salinity and temperature on the interfacial tension water-oil were reported.

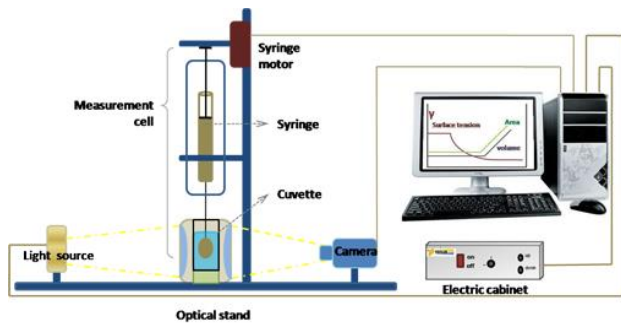


Fig. 1. Schematic drawing of the electronic tensiometer.

**Effect of salinity on the interfacial tension**

The Abu Hassa oil provided by the United Arab Emirates Company ADCO was used in the experiment. Synthetic brine waters of different concentrations were prepared. The interfacial tensions of different mixtures were measured by a tracker, an automated drop tensiometer, which can measure variations in surface tension or interfacial tension over time. The instrument can also measure contact angle of a liquid against a solid. The instrument is supplied by the French company Teclis France. A schematic drawing of the fully computerized system is shown in Fig. 1.

The results are displayed in Fig. 2, Fig. 3 and Fig. 4.

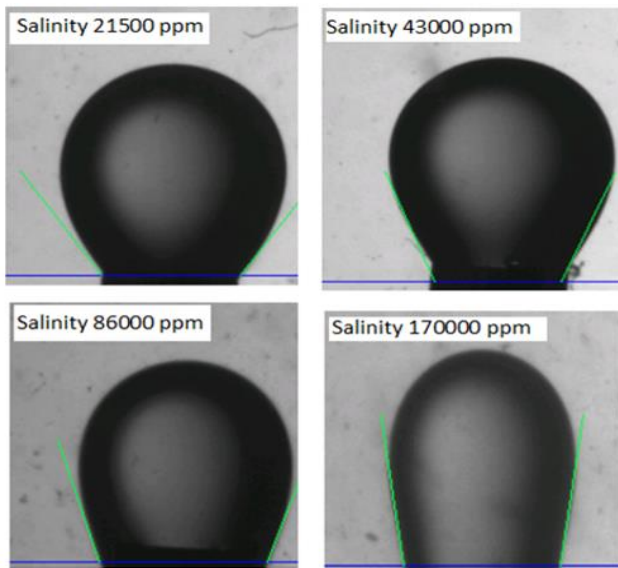


Fig. 2. The effect of salinity on Abu Hassa oil-Um Rudhuma water IFT.

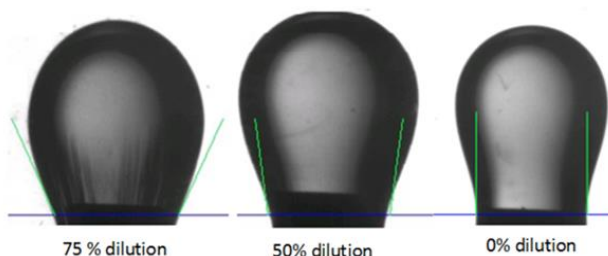


Fig. 3. The effect of dilution on the IFT between Abu Hassa oil and Um Rudhuma water

**Effect of temperature on the Interfacial Tension**

In this section, the interfacial tension between Abu Hassa oil and green water mixture 80%-20% is investigated at different temperatures. The results are displayed in Fig.3.

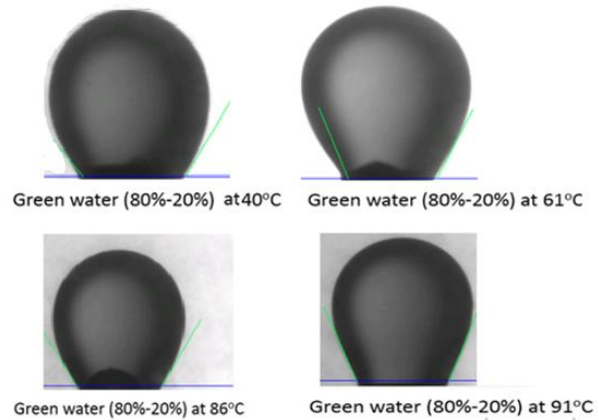


Fig. 4. The effect of temperature on IFT between Abu Hassa oil and green water.

The measurements of the interfacial tensions between Abu Hassa Oil and Sisypus Spina Christi green material show that the interfacial tension decreases from 10.85 mN/m to 9.10 mN/m when the salinity increase from 43000 ppm to 172000 ppm. Furthermore, it was noticed that the interfacial tensions between Abu Hassa Oil and Aloe Vera green material are low and exhibit a decrease. When the salinity increases from 43000 ppm to 172000 ppm the surface tension decrease from 4.46 mN/m to 3.11 mN/m. The shapes of the droplets of oil in contact with the green water show clearly the effect of the salinity of the interfacial tension. At low salinity the droplet is spherical. In contrast, when the salinity is high the shape of the droplet is elongated and drawn out. The same phenomenon was seen when Um Rudhuma brine water was used. In Fig. 3, the dilution of Um Rudhuma water provokes the opposite phenomenon. At zero dilution the angle is 90 degrees and it increases at higher values when the dilution increase. The shape of the droplets is spherical at high dilution and elongated at zero dilution.

In Fig. 4, the shapes of the droplets of oil in contact with the green water show the effect of the temperature on the interfacial tension. At low temperature the droplet is spherical. In contrast, when the temperature increases the shape of the droplet is elongated. In Fig. 5, the same phenomenon was seen when Um Rudhuma brine water was used. At high temperature, 90 °C, the shape of the oil droplet shows an elongation and the angle is a right angle.

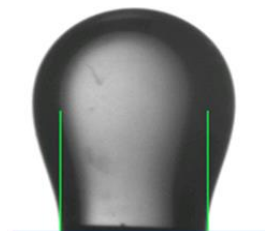


Fig. 5. Interfacial tension between Abu Hass oil and Um Rudhuma water at 90 °C.

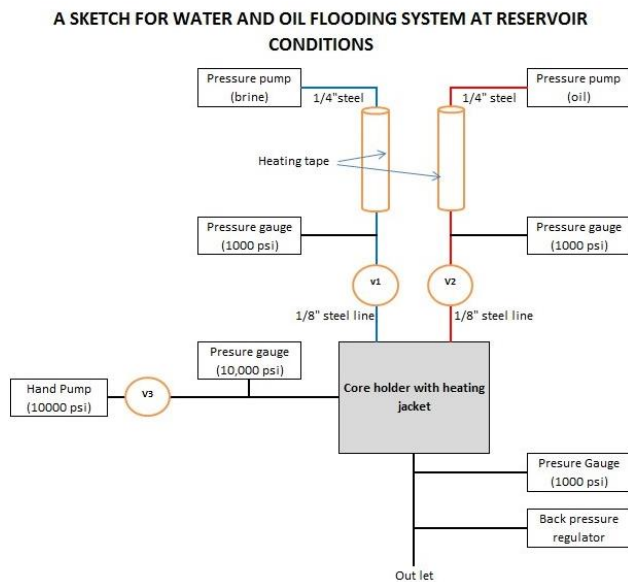


Fig. 6. Experimental setup for core flooding.

**Core flooding experiments**

4 cores were prepared to perform the flooding in order to conduct 4 experiments. Abu Hassa oil and Um Rudhuma brine, supplied by the oil company ADCO, were used in the experiment. Flood system is made by Core Lab instruments-USA. The cores were placed in the core holder as show in Fig. 6.

**Experiment 1**

Core 1 was flooded with saline water containing 86000 ppm total dissolved salts at reservoir temperature of 90°C till saturation. The core being saturated with water, the volume of water inside the core was estimated to 18.019 ml. After flooding with oil, the volume of water out was 11.90 ml. The remaining oil in the core was 18.019 ml - 11.90 ml = 6.119 ml. This is equivalent to an initial water saturation 66% or a residual oil at saturation of 33.96%. When the core is flooding with a green water of the same salinity the volume of the oil that comes out was estimated to 9.20 ml. Therefore the volume of oil in place (the oil remaining in the core after flooding with green water) is 11.90ml – 9.20ml = 2.70ml which is equivalent to a 22.69 % residual oil at saturation or 77.31 % oil recovery.

**Experiment 2**

Core 2 being saturated with water is flooded with oil till an initial water saturation of 44.76% is reached. This was equivalent to 6.20 ml of oil in the core. In the secondary flooding, the core is then flooded with Um Rudhuma water alone till 50% of the oil is out. This is equivalent 3.10 ml of oil in the core. In the tertiary flooding, the core was flooded with Um Rudhuma green water containing 830000 ppm of total dissolved salts. The flooding was at reservoir temperature 90 oC. The oil coming out after flooding with green water was

1.10 ml. The volume of water in place is 3.10ml - 1.10ml = 2 ml. The percent of residual oil was 32.26%. This is equivalent to 68% recovery.

**Experiment 3**

Core 3 was flooded with saline water containing 163053.34 ppm of total dissolved salts at reservoir temperature 90 °C. At saturation, the water in the core was estimated to 16.584 ml. The core being saturated with water is then flooded with oil till the volume of water out reached 10.20ml. The volume of water inside the core is 16.584 ml – 10.20 ml = 6.38 ml. This represents an initial water saturation of 38.50%. The secondary flooding was with water containing 163053.34 ppm total dissolved salts. The volume of oil out was estimated to 8.60 ml. Therefore, the volume of oil in place 10.20ml -8.60ml = 1.60 ml. This represents approximately a percent of residual oil of 15.69 %. The tertiary flooding was performed with green water of salinity 163053.34 ppm. The flooding was at reservoir temperature 90 oC. The oil coming out after flooding with green water was 0.6 ml. This represents a volume of water in place of 1 ml. The percent of residual oil was estimated to 9.80 %. This is equivalent 90.20 % of oil recovery.

**Experiment 4**

Core 4 was used in this experiment. The core was flooded with a real water injection from Um Rudhuma Oil filed. The salinity of this water is very high (170000 ppm). The flooding was at reservoir temperature 90°C. At saturation, the volume of water in the core was evaluated to 9.359ml. After flooding with oil, the volume of water out was 6.40 ml. The volume of water remaining inside the core is 9.359ml – 6.40ml = 2.96 ml. This is equivalent to an initial water saturation of 31.62%. In the secondary flooding with water containing 170000 ppm total dissolved salts the volume of oil out the core was estimated to 4.23 ml. This is equivalent to a volume of oil in place of 6.40ml- 4.23ml = 2.17 ml or a percent of residual oil of 33.91 %. The tertiary flooding was conducted with green water of salinity 170000 ppm at reservoir temperature 90°C. The oil coming out after flooding with green water was 2.17ml. The volume of water in place is 2.17ml - 1.95ml = 0.22 ml. This represents a percent of residual oil of 3.44% which is equivalent to an oil recovery of 96.54%.

A summary of the experimental results is presented in Table 2.

Table 2. Oil recovery for different cores.

Cores Id	L cm	D cm	P %	Salinity ppm	Oil recovery %
1	8.22	3.85	18.90	86000	77.31
2	7.16	3.85	13.48	86000	68.00
3	7.81	3.85	19.80	163054	90.20
4	5.22	3.85	15.68	170000	96.54

In addition, the pH measurements were performed for the two extracts and the mixture when added to Um Rudhuma injecting water. The pH was, 6.22, 6.22, 6.8, 4.60 and 6.0 for Um Rudhuma water before injection, Um Rudhuma after injection, Sisypus Spina Christi green water, Aloe Vera green water and 80%- 20% mixture respectively. The highest oil recovery was reached when Core 4 was used with Um Rudhuma water mixture.

## Conclusion

These natural extracts proved to be very effective in formations containing water with a salinity range of 70,000 to 180,000 ppm with temperature going up to 90°C. The high recovery cannot be explained through interfacial tension (IFT) reduction alone, even though IFT was reduced 10 fold for a concentration of 1 % wt of injection fluid. Similarly, polymeric action cannot explain the sweep efficiency as the viscosity of the injected fluid was only slightly higher than water. It is the same for any impact on wettability that in itself wouldn't be able to increase tertiary recovery to that extent. It is explained that there are natural components, such as lipid, fructose, Sucrose, Maltose, plant protein, etc. that have a synergistic role to play in order to increase the efficiency of the recovery process. It turns out that the overall impact of the injecting fluid is positive effect on IFT, total volumetric efficiency, wettability, and others that are not readily observable with synthetic materials, but are available for natural products. It is expected that the newly invented process will be particularly useful in presence of fractures and or complex reservoir heterogeneities that usually impede displacement efficiency. A future research proposal is under preparation in order to understand the mechanisms involved with the recovery process.

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## Author's contributions

OC, EL; Performed the experiments: OC, E; Data analysis: OC; Wrote the paper: OC. Authors have no competing financial interests.

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