Application of Natural Surfactants for Enhanced Oil Recovery – Critical Review

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Abstract. The huge worldwide energy demand, and the need for more crude oil production, together with the low-efficiency of the conventional abstraction methods are part of the reasons for increasing interest in Enhanced Oil Recovery (EOR) techniques for recovering more oil from existing reservoirs. Utilization of different types of surfactants (synthetic or natural) in order to decrease the water-oil interfacial tension (IFT) is one of the most common methods for EOR. However, polymers and synthetic chemicals have a number of disadvantages such as linking to fossil fuels, high cost and environmental impacts. In this review, the application of natural surfactants produced from the leaves of Olive, Spistan, Prosopis, Mulberry, Zizyphus spina Christi, Soapnut and Chamomilla plants in EOR processes are investigated. The effects of natural surfactants extracted from the leaves of the mentioned plants on reduction of the oil-water interfacial tension (IFT) are studied and compared extensively. Pendant drop and ring methods have been employed by most of researchers to identify the IFT values as a determining parameter in performance of natural surfactant flooding to increase ultimate oil recovery. This comparative study in the application of natural surfactants in EOR will pave the way for future studies and helps further research in EOR schemes.

1. Introduction

The worldwide demand for energy is predicted to increase in the coming decades. The International Energy Agency’s 2007 World Energy outlook states that between now and 2030 energy needs are likely to rise by 55% to around 17.7 billion tons of oil equivalent. With the current suite of alternative energy sources this increasing demand cannot be met; therefore, an important role in the energy consumption will continue to be played by crude oil in the future. It is recognized that current methods of oil recovery (which can be produced by primary and secondary oil recovery methods) is running out and a large amount of the oil remains in the reservoir after using these conventional methods. So it is important to find a way to decrease the amount of residual oil. Hence the performance of Enhanced Oil Recovery has become extremely necessary to guarantee a continuation of crude oil production. EOR is a challenging field which is related to several scientific disciplines and has a lot of patents that make this area even more important [1-4].
Initial pressure energy stored in the reservoir can produce only 5-30% of original oil-in-place (OOIP). This part of oil production is called the primary production period. In order to maintain this pressure of oil in the reservoir, water or special gas can be injected, this is called the secondary production period. This method will usually increase oil production to a total recovery of 40-60% of oil and maintain reservoir pressure during production [5-8].

Enhanced oil recovery methods (sometimes called tertiary oil recovery) follow on from the secondary recovery processes. EOR refers to processes of producing oil by methods that are different from conventional forms of reservoir recovery like gas and water flooding. The purpose of using EOR is to extend the lifetime of reservoir by supporting the use of water flooding or other conventional methods, to take the reservoir life beyond previous economic limits. Figure 1 summarizes the phases of a reservoir development plan. [9-12]

By using the EOR methods, the capillary forces (typically quantified by the Young-Laplace equations) which are the main reason for the large volume of the oil remaining in the reservoirs, can be overcome [13]. Hence, having some information about the rock structure (especially type of material, sizes and distribution of pores) is crucial to determine the amount of relative water and oil saturations [14, 15].

Reservoir conditions such as temperature, pressure, economical factors, chemical factors, brine characterization and pollution levels are the main issues which should be used for selecting the most suitable fluid. Among these parameters the viscosity and the interfacial tension of the injected fluid play an essential role in EOR. As the injected fluid has a lower viscosity than the fluid to be displaced, the flowing of the injected mixture would be greater than the original one across the porous medium. Also high IFT hinders the ability of the injected fluid to displace the oil which causes high amount of the oil to remain in the wells. So as the interfacial tension between water and oil decrease under the influence of the EOR fluid, the amount of residual oil will become less [16-20].

Capillary forces are responsible for limitation of oil recovery. To show the effect of these forces a non-dimensional number named capillary number is defined. This crucial number is introduced as the ratio of viscous force to that of capillary as follows:

\[
N_{ca} = \frac{\text{viscous force}}{\text{capillary force}} = \frac{\nu V}{\sigma \cos \theta}
\]

(1)

Where \(V\), \(\mu\), \(\sigma\) and \(\theta\) represent the fluid velocity, viscosity, IFT of system of oil and water and contact angle, respectively [18]. To reduce the volume of oil residue noticeably, the aforementioned ratio should increase four to five orders in magnitude in any EOR process. Reaching this goal calls for either a decline
in the IFT (σ) or manipulating the contact angles of the inter-phase (θ) to reach about 90 which is known as a moderate wettability of the overall reservoir system (including rock and fluid). [21-23]

The main activity in the Enhanced Oil Recovery (EOR) processes is injecting a particular type of a fluid into the reservoir which has different characteristics such as thermal, chemical and microbial [24], [25]. One of the most effective methods for increasing oil recovery production is chemical flooding. Chemical EOR processes are based on injection of polymers, alkalis, acids, surfactants and other chemical compounds [26, 27].

In polymer injection, polymers are dispersed into the injection water to boost oil recovery. Without using these polymers in the injection water, there is no way to achieve efficient oil recovery. This type of chemical can be useful by increasing the viscosity of the aqueous system to achieve a higher capillary number and therefore better upward movement control and more vertical sweep power can be attained. [28, 29].

Alkaline flooding has been studied for enhanced oil heavy recovery since the 1970s and many projects have been carried out. The acidic compounds in heavy oil react with Alkali, so that surface active materials will be formed. These materials become ionized at the oil water interface and thereby reduce the interfacial tension by several orders of magnitude. A positive point of this method is that there is no need for expensive surface equipment, and that can be applied without the restriction to greater well depths and formation thicknesses compared to other methods [30, 31].

Using alkaline-surfactants (AS), alkaline polymer (AP) and alkaline-surfactant-polymer (ASP) are other techniques of chemical EOR. ASP flooding is one of the most important techniques which has attracted a lot of attention and a wide variety of experiments have been carried out in this field. One area of research on this subject was completed by Delshad et al. (1998) who used a device to simulate reservoir properties with a particular process and estimated the extent of oil recovery from the Karamay field, a Chinese onshore oil field. Among the chemical methods examined were alkaline, S-P and A-S-P flooding, the last one led to the lowest amount of remaining oil by exhibiting 24 percent increase of OOIP additional recovery compared with simply using water [22, 32-34].

Surfactant flooding is another kind of chemical EOR which includes using chemical surfactants and natural surfactants or biosurfactants. Biosurfactants are amphiphilic compounds which are generated in living surfaces. The best grounds for them to be produced are excreted extracellular hydrophobic and hydrophilic moieties or microbial cell surfaces. Factors that influence biosurfactant production are the Carbon: Nitrogen Ratio, the nature of the nitrogen source, carbon source, PH, temperature and aeration. These compounds have the ability to accumulate between liquid phases and decrease interfacial and surface tension at the interface and surface respectively with the same mechanisms as chemical surfactants [35-37].

Another type of surfactants include natural surfactant which have a plant source. The classification of natural surfactants which is used in chemical EOR is like the classification of chemical surfactants; i.e. they are non-ionic, cationic, anionic and amphoteric types [3]. Olive, Seidlitzia rosmarinus, Spistan and Prosopis are some examples of innovative nature-based cationic surfactants and Saponin that can be produced from Zizyphus Spina Christi leaves and Glycyrrhiza Glabra are nonionic examples. In this review, natural surfactants which are the extracts from a range of plants are investigated. In the past several years many attempts have been made to understand clearly the effect of these surfactants on the IFT between water and oil. In those studies, first of all surfactants were derived by specific sets of processes from the leaves of different trees mentioned in the references. Ring and pendant drop methods were then used to evaluate the IFT which is the representative of the resistance between the surfactant solution and oil. At the end, the surfactants will be compared according to their ability to reduce the IFT by addition of different concentrations of surfactants.
2. Materials and Methods

2.1. Materials

2.1.1. Olive

Olive tree (or Olea europaea) shown in figure 2-a is a kind of evergreen fruit tree which has silvery green in color and elongated leaves (about 4–10 cm in length and 1–3 cm in width) that are replaced at 2-3 year intervals during the spring. Delgado-Pértől et al. [38] investigated the nutritive value of the olive leaf and showed that it consists of 93.6% dry matter, 91.3% organic matter, 12.9% crude protein, 44.5% neutral detergent fibre, 34.5% acid detergent fibre, 23.3% acid detergent lignin and 5.1% gross energy. The olive tree is native to the Mediterranean and Asia especially the Middle-East and extensively accessible in many regions like north of Iran, east of the Mediterranean Basin, northwest of Iraq and Saudi Arabia. In addition to the benefits for human health, Olive leaves have the property of being able to generate surfactants for EOR [39].

2.1.2. Spistan

Spistan also known as Assyrian Plum, Lasura, Pidar and Cordia Myxa is a tree which has a height of about 13ft. Its leaves are wide, egg-shaped and slightly rough with a surface area of 3 to 6 in²; the young leaves tend to be hairy but older ones are glabrous above and pubescent below (figure 2-b). In the matter of health benefits several medicinal properties can be mentioned such as Laxative, smoothing chest, decreasing blood pressure and reducing phlegm. The ripe fruit is also full of vitamins and regular use is supposed to be helpful in the hair growth. Spistan leaves contain crude protein, crude fiber, carbohydrate, lipid and ash and can be used as a resource for generating antioxidants and surfactants [39].

2.1.3. Prosopis

Prosopis is an evergreen tree which can grow up to 30–50 ft in height (figure 2-c). Dry Prosopis leaves have variety of nutritious, organic and inorganic materials including proteins and lipids and possess the characteristic of being a source of surfactants [39].

2.1.4. Mulberry

Morus Alba tree is another plant whose leaves can be used as a surfactant. This tree is fast-growing when young, but soon become slow-growing and rarely exceeds 33–49 ft in height. Mulberry is the fruit of this plant and appears in deep purple to black in color as shown in figure 2-d. Its leaves are thin, glossy and light green, arranged close to each other and are mostly pointed and jagged on the margins. Cheema et al. [40] analysed the mulberry leaf, and showed that it consists of dry matter 25%, organic matter 90%, crude protein 23%, neutral detergent fibre 26.2%, Acid detergent fibre 16%, hemicelluloses 10.2%, acid detergent lignin 7%, ash 10% and metabolizable energy 10.5 My/kg. The elements available in the mulberry leaf are calcium 3.6%, phosphorus 0.57%, magnesium 0.72%, sodium 0.2%, potassium 1.75% [18, 41].

2.1.5. Zizyphus Spina-Christi

Zizyphus spina Christi is a tree with a medium height having spiny branches and small orange-yellow fruits (figure 2-e). It grows up indry climates, from Africa to India, including Jordan, Iraq, Egypt and the south of Iran. Besides being nutritious, this plant has several different herbal applications (e.g. healing wounds, ulcers and swollen eyes, or treating illnesses like asthma, allergies, bronchitis and depression, or being used as anti-inflammatory, febrifuge and diuretic). Some useful phytochemicals that include flavonoids, tannins, peptides, cyclopeptide alkaloids, terpenoids, sterols and glycosides have been extracted from this plant. Natural surfactants from saponin which is reported by some researchers to be a surfactant and can be used in petroleum engineering applications can be extracted from Zizyphus Spina-Christi leaves. The powdered leaves of Zizyphus Spina-Christi look light brown and show good solubility in water and alcohol [42-44].
2.1.6. Soapnut

Soapnut is a tropical and near-tropical tree which is found in many countries such as Pakistan, India, Bangladesh, Nepal and many other countries in America, Asia and Europe continents. Its leaves are 6
to 16 inches in length with pinnate of 14-30 leaflets. The fruits are white covered by a brown sphere-shaped shell having a diameter of 1–2 cm (figure 2-f). Soapnuts are helpful in medicinal treatment and making soaps. Soapnut fruit shells have been used as traditional medicines, natural laundry detergents for washing fabrics and bathing from ancient times. It is reported that the saponin derived from the soapnut shells has a great potential for treatment of contaminated soils. The potential of a soapnut surfactant extracted from this plant in EOR is investigated in this study.

2.1.7. Chamomilla

During the Mughal period, Chamomilla was presented to India and now it is grown in Maharashtra, Punjab, Uttar Pradesh and Jammu and Kashmir. This plant could also be found in North and South America, Australia, North Africa, Asia, and New Zealand. It is a resistive plant withstanding cold weathers with temperatures ranging from 2-20 °C and can grow in any kind of soil. It often grows near roads, around land fields, and in farmed fields as a weed, owing to the fact that the seeds require open soil to survive. Chamomilla has a straight, soft and branched stem with a short height of 15-60 cm (6–23.5 in). Its flower has two parts, a head and florets. The head is like a yellow hemisphere and the florets are white rays lying beneath the head (figure 2-g). The flowers bloom in summer, and have a strong, aromatic odor [41, 45-46].

2.1.8. Glycyrrhiza Glabra

Glycyrrhiza Glarba has taken its name from Glykys, meaning "sweet" and Rhiza, meaning "root". It is also known as sweet root. Glycyrrhiza glarba is a 4-5 feet shrub growing on lands with moderate temperature and the areas where the height is less than 1200 m above the sea level and is classified as a member of Fabaceae or pea family. Figure 2-h shows a picture of this plant which has pinnate leaves with 4 to 8 pairs of green elliptic leaflets 2-3 long. It is native to Eurasia, northern Africa and western Asia (including Iran) and is also found in America where it grows as a weed beside the roads. Glycyrrhiza glarba is also cultivated as a crop plant, especially in Russia, Spain and the Middle East [48].

2.2. Methods

2.2.1. IFT Measurement by pendant drop

The device used in this method is pendant drop tension meter which consists of four main parts, namely an experimental chamber, a video capturing system, an illuminating system and a data acquisition system (figure 3-a). This method is based on the drop shape analysis. For this purpose, a ratio of maximum diameter to the horizontal diameter is defined. In fact, the maximum diameter, de, is determined by the device and then it is used to measure horizontal diameter, ds, as shown in figure 3-b. The aforementioned ratio, S, is the ratio of these diameters which is crucial to determine interfacial tension by the following relations:

$$\sigma = \frac{\Delta \rho g b^2}{\beta}$$  \hspace{1cm} (2)

$$S = \frac{d_s}{d_e}$$  \hspace{1cm} (3)

$$\beta = 0.12836 - 0.7577S + 1.7713s^2 - 0.5426s^3$$  \hspace{1cm} (4)

$$b = \frac{d_e}{2(0.9987 + 0.1971\beta - 0.0734\beta^2 + 0.34708\beta^3)}$$  \hspace{1cm} (5)

where $\Delta \rho$ is the density difference between the drop and the material by which the drop is surrounded and $\beta$ and $b$ are calculated from equations (4) and (5) respectively [52-56].
As is clear from the formula, a measurement of density is required before the IFT determination. Density Meter Apparatus (DMA) is implemented to measure the densities of solutions with different surfactant concentrations [50, 51].

Figure 3. a) Pendant drop tension meter  

b) Drop scheme

2.2.2. Ring method

In this method, a ring is pulled off the interface separating water and oil phases by a wire (which has a radius of 1/30 or 1/60 of that of the ring), and the force needed to carry this out is measured (figure 4).

This force is directly related to the IFT value between oil and water by the following equation:

\[
\sigma = \frac{F}{P \cos \theta}
\]

where \( P \) is the three-phase contact line perimeter being twice the circumference of the ring in this method (\( P=4\pi R \)) and \( \theta \) is the contact angle between the interface and the liquid meniscus. Due to the additional liquid lifted while the ring is being pulled out, a correction factor, \( f \), is defined to adjust the calculations. The values of \( f \) are given for contact angle of zero and different \( R/r \) ratios in literature [8]. This correction factor could also be determined by the following relation which applies where \( 0.045 \leq \Delta \rho g R^3/F \leq 7.5 \).

\[
f = 0.725 + \left( \frac{9.075 \times 10^{-4} F}{\pi \Delta \rho g R^3} - \frac{1.679 r}{R} + 0.04534 \right)^{1/2}
\]
As the force is measured by a microbalance and \( f \) is determined by the above relation, the corrected equation is used to calculate the IFT.

\[
\sigma = \frac{F}{p \cos \theta} \times f
\]  

Nowadays, the correction factor and interfacial tension are determined consecutively by modern devices which consider these relation and equations in determination of IFT [57, 58, 60].

3. Results and Discussions

Chhetri et al. (2009) investigated a saponin extracted from soapnut as surfactant for EOR applications. In this study, the saponin was extracted in two different ways by employing cold and hot water and both showed similar results. Du Nouy ring method was used (for IFT measurement) before and after employing the surfactant and it was observed that the interfacial tension between water and oil decreased from 19 dyne/cm to 2.5 dyne/cm as the surfactant concentration changed from 0 to 12 (w/w %). It was also demonstrated that the increase in IFT was not directly proportional to the concentration of the surfactant; i.e. the IFT first decreased suddenly, then increased slightly and finally, again decreased by increasing the surfactant concentration (although this reduction was very smooth). The error bars were plotted and it was observed that the optimum standard deviation was about 5.8% [61].

Ahmadi et al. (2012) extracted a natural surfactant from Glycyrrhiza Glabra, and introduced its application for EOR projects. The Glycyrrhiza Glabra was extracted by using spray-drying method and the interfacial tension (IFT) between Glycyrrhiza Glabra solution and oil was measured by implementation of pendant drop apparatus for different surfactant concentrations. They showed that adding this surfactant causes reduction in IFT from 33 to 9 and compared their achieved results with the common surfactants and observed that the IFT reduces by about 69% when Glycyrrhiza Glabra is used, compared to 41% and 52% for alkyl sulfates and alkyl polyglycosides surfactants, respectively. With respect to these findings, Glycyrrhiza Glabra is recognized useful for EOR processes especially in carbonate rocks. Availability and low cost are two main advantages of this kind of surfactant. Another investigation has been done on the adsorption of Glycyrrhiza Glabra onto crushed carbonates in this study. The details of kinetic behaviour of the surfactant and equilibrium were discussed and adsorption parameters for the Langmuir, Freundlich, linear, and Temkin isotherms were determined [62].

Deymeh et al. (2012) presented a futuristic natural cationic surfactant as an enhanced oil recovery agent. This surfactant was extracted from a plant named Seidlitzia Rosmarinus that can be found in desert regions of the Middle East, and western and Central Asia. IFT measurements by pendant drop method showed that as the concentration of Seidlitzia rosamarinus increases, a small change in the interfacial tension occurs below the Critical Micelle Concentration (CMC) of 8 wt%. However, the IFT values were observed to decrease significantly from 32 to 9 mN/m above CMC which was more effective compared to commercial surfactants. Availability and biodegradability of this natural surfactant makes it environmentally and economically feasible for EOR process [63].

Shahri et al. (2012) extracted a natural saponin surfactant, from Zyziphus Spina Christi and determined the performance of this plant based surfactant in oil recovery. Saponin was extracted from leaves of Z. Spina Christi by utilizing a spray-drying technique and the IFT between surfactant solution and oil was measured by the pendant drop method. They observed that the addition of saponin as a natural and biodegradable nonionic surfactant to brine water (with 1 g/L NaCl) can reduce the IFT from 48 to 9 dyne/cm. In comparison with other cationic and anionic surfactants used in chemical EOR, this plant-base surfactant showed extraordinary performance which can be further improved by addition of alcohol and salt to decrease IFT to values lower than 9 dyne/cm [64].

Ahmadi et al. (2013) explored the use of a surfactant taken from the leaves of mulberry tree for EOR and determined its influence on IFT reduction. Experimental results showed that the water-kerosene (i.e. used as oil phase) IFT was decreased from 43.9 to 17.9 dyne/cm by addition of this plant-based surface active agent [18]. The Leaves of this deciduous and highly branched tree can be used to produce
surfactants having the advantages of ease of production, being innocuous to the environment and most essentially, cost effective.

Arabloo et al. (2014) also investigated the applicability of a saponin extracted from Glycyrrhiza Glabra leaves. This surfactant reduced crude oil–water IFT from 31.6 mN/m to an ultra-low value of 6.5 mN/m at CMC which was similar to chemical surfactants. The results determined that saponin is a potentially appropriate additive for surfactant EOR practices in sand stone reservoirs [48].

Khorram Ghahfarokhi et al. (2014) explored the influence exerted on interfacial tension of water–oil system by application of cationic surfactants extracted from the leaves of Olive, Spistan and Prosopis. Among the surfactants studied, Olive extract showed the best result by decreasing the IFT from 36.5 to 14 mN/m in a solution of 3.85 Wt% of surfactant. To compare the impact of the surfactants on IFT, the solutions of the same concentrations were prepared for other surfactants; Spistan and Prosopis extracts lowered the IFT from the same value to 20.15 and 15.11 mN/m, respectively [39].

Shadizadeh et al. (2015) introduced a natural surface-active agent extracted from Matricaria chamomilla for chemical EOR. To study the feasibility of using this plant, the pendant drop technique was utilized to measure the IFT between natural surfactant solution and Kerosene as the oil phase medium. At the CMC level (about 5.5% by weight), there was a significant reduction in interfacial tension values, and consequently a chemical flooding process using this surfactant showed a better oil recovery. The results of this research showed that Matricaria chamomilla decreased the water-oil IFT values from 30.63 to 12.57 mN/m.

The summary of reviewed studies on application of natural surfactants are summarized in Table 1.

Table 1. literature review over natural surfactants that used for EOR

| Surfactant            | Aqueous phase | Oil phase | Surfactant Concentration (Wt %) | IFT Decrease (mN/m) | Author            | Year | Reference |
|-----------------------|---------------|-----------|---------------------------------|---------------------|-------------------|------|-----------|
| Soapnut               | Distilled water | Crude oil | 0 to 12                         | 19 to 2.5           | Chhetri et al.    | 2009 | [61]      |
| Glycyrrhiza Glabra    | Distilled water | Kerosene  | 0 to 8                          | 33 to 9             | Ahmadi et al.     | 2012 | [62]      |
| Seidlizita Rosmarinus | Distilled water | Kerosene  | 0 to 10                         | 32 to 9             | Deymeh et al.     | 2012 | [63]      |
| Zizyphus Spinachristi | Distilled water | Kerosene  | 0 to 10                         | 48 to 9             | Pordel Shahri et al. | 2012 | [64]      |
| Mulberry leaf-derived | Brine          | Kerosene  | 0 to 1.00                       | 44 to 17.9          | Ahmadi et al.     | 2013 | [18]      |
| Glycyrrhiza glabra    | Distilled water | Crude oil | 1-10                            | 36 to 9             | Arabloo et al.    | 2014 | [48]      |
| Prospis leaf-derived  | Distilled water | Kerosene  | 0 to 3.85                        | 36.5 to 15          | 2014              | [39] |
| Spistan leaf-derived  | Distilled water | Kerosene  | 0 to 3.85                        | 36.5 to 20          | Khorram Ghahfarokhi et.al | 2014 | [39]      |
| Olive leaf-derived    | Distilled water | Kerosene  | 0 to 3.85                        | 36.5 to 14          | 2014              | [39] |
| Matricaria chamomilla | Distilled water | Kerosene  | 0 to 13                          | 30.6 to 12.67       | Shadizadeh et.al  | 2015 | [41]      |
Effect of natural and chemical surfactant concentrations on oil-water IFT reduction is presented in figures 5 and 6. As far as the reduction of IFT is concerned, Brii 72 and Step+ampho show the greatest reduction among chemical surfactants from 47.75 and 40.93 to 5.92 and 3.8, respectively. Among the natural surfactants, Glycyrrhiza Glarba and Sedila Rosmarinos have resulted in a considerable decrease in IFT from 36.5 and 32 to 7.9 and 8.9, respectively [41].

![Figure 5. Comparison of IFT reduction vs. surfactant concentration for natural surfactants](image1)

![Figure 6. Comparison of IFT reduction for chemical vs. natural surfactants recently used for EOR](image2)

It is obvious that the IFT reduction caused by natural surfactants is very close to the chemical ones. However, the advantages of natural surfactants to be more environmentally friendly, lower in cost and available makes them superior compared to the commonly used chemical surfactants.
4. Conclusions

Surfactants flooding is one of the most common EOR processes which improves oil recovery by decreasing residual oil saturation via reduction of water-oil interfacial tension. In this work, an extensive review on application of natural surfactants for enhanced oil recovery is presented. These surfactants have the advantages of lower cost, availability, biodegradability and being environmental friendly. Experimental results of IFT measurement by pendent drop method for different chemical and natural surfactants are collected and compared; it is observed that the reduction in IFT for natural surfactants is similar to that of the commercially available polymers and chemical surfactants. It is conclude that the natural surfactants recommend a new prospect for chemical EOR and can be used on a large scale due to their ability to significantly reduce the IFT and increase ultimate oil recovery.

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