Chapter

An Overview of Natural Surfactant Application for Enhanced Oil Recovery

Afeez Gbadamosi, Adeyinka Yusuff, Augustine Agi and Jeffrey Oseh

Abstract

Surfactant flooding is an enhanced oil recovery (EOR) method that recovers residual and capillary trapped oil by improving pore scale displacement efficiency. Due to toxicity and high cost of conventional surfactant, recent trend involves the use of natural surfactant for EOR. Natural surfactants are benign and biodegradable as they are derived from plant leaves and oil extracts. Herein, a synopsis of recent trend in the incorporation of newly devised natural surfactant for EOR was reviewed. Experimental results show that the surfactants exhibited sterling properties desired for EOR such as lower adsorption, interfacial tension (IFT) reduction, stable emulsion, and wettability alteration of sandstone and carbonate rocks. Overall, natural surfactants are suitable replacement for conventional surfactant. Nonetheless, an accurate modeling and pilot scale studies of natural surfactants remain obscure in literature.

Keywords: surfactant, natural surfactant, biosurfactant, enhanced oil recovery, wettability, interfacial tension

1. Introduction

Global demand for oil and gas continues to increase despite the recent development in other sources of energy. The production of oil and gas is in stages. Firstly, hydrocarbons are produced from reservoir deposit due to pressure reduction in the reservoir. Thereafter, waterflooding is performed to push more oil towards the production well. Substantial amount of oil is left in the reservoir as bypassed and/or residual oil after the application of primary and secondary recovery techniques. This is adduced to viscous fingering phenomenon as the injected waterflood creates a path of least resistance to the production well. Hence, several enhanced oil recovery (EOR) methods have been devised to recover additional oil from the reservoir [1]. **Figure 1** depicts the classification of EOR processes.

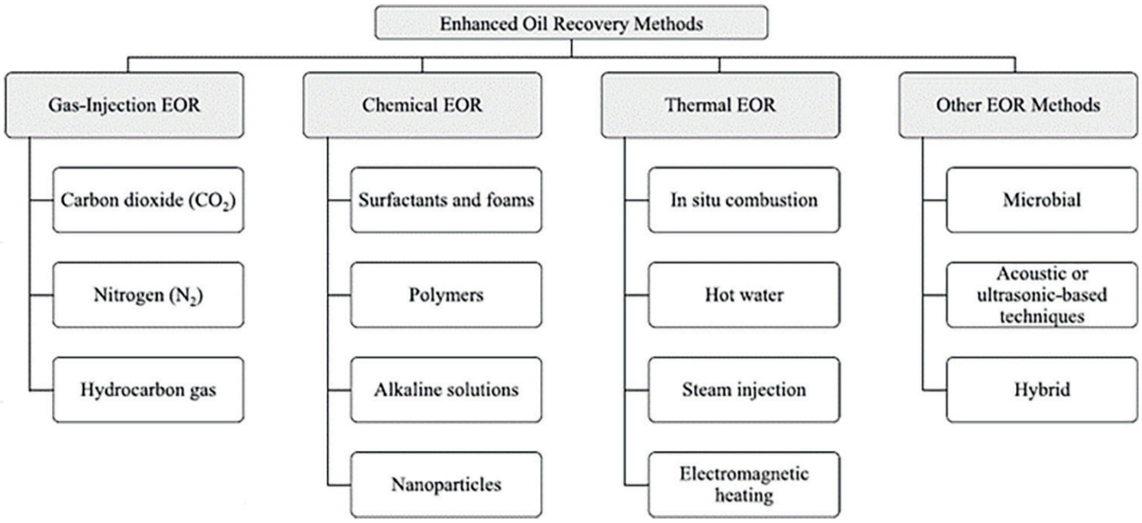

Figure 1.
Enhanced oil recovery process classification [2].

The EOR methods are broadly categorized into thermal and non-thermal EOR methods [3]. Thermal EOR are majorly used for the recovery of heavy oil, extra-heavy oil, and tar sands in the reservoir. Several thermal injections have been explored and exploited to improve recovery of high viscosity oils. These include cyclic steam stimulation, steam flooding, steam-assisted gravity drainage, and *in-situ* combustion. The mechanism of thermal EOR is to use high temperature to reduce the high viscosity and consequently improve the mobility of the oil towards the production well. Despite the success recorded for the field application of thermal EOR techniques during field application, they are deemed unsuitable for reservoir with huge depth and thin pay zones. Besides, they have high energy consumption, and large CO_2 emissions, thereby, increasing the environmental and economic costs of application [4]. Thus, non-thermal EOR methods have recently received prodigious attention.

The non-thermal EOR methods are gas EOR, microbial EOR and chemical EOR [5, 6]. Gas EOR methods involves the injection of miscible, immiscible, or inert gases into the reservoir to improve recovery factor. In addition to improving recovery factor, the use of gas injection also aids sequestration of gas in subsurface geologic formations. The mechanism of gas flooding includes the mass transfer of components between the oil and injected gas, swelling and viscosity reduction. The application of gas flooding is limited for high viscosity oils because of gravity override. Microbial EOR entails the use of microorganisms and their metabolites to mobilize capillary trapped oil. This method of EOR is cost-effective as it utilizes cheap raw materials from corn syrups, molasses, and agricultural by-products. Unfortunately, the raw materials for microbial EOR require huge facilities for their cultivation and have limited application due to high sensitivity and logistic problems especially on offshore platform [7].

Chemical EOR methods are adjudged to have a high efficiency, thus, they have witnessed numerous field applications [8]. The method basically involves tuning the efficiency of the injected waterflood to alter the rock-fluid and/or fluid-fluid properties of the reservoir. Hence, a high pore displacement and/or sweep efficiency is achieved, and consequently a higher recovery factor. The chemicals injected for EOR include alkaline, surfactant, polymer and more recently nanoparticles [9, 10]. Sometimes, a binary combination of the chemicals may be used to explore the synergic mechanism of the chemicals for a higher oil recovery. Several binary combinations used comprises of alkaline-surfactant flood, alkaline-polymer flooding, surfactant-polymer flooding, and alkaline-surfactant-polymer flooding [11–14]. The mechanism of alkaline and surfactant lowers the interfacial tension (IFT) between the oleic and aqueous phase and alter the wettability of the porous media, thereby, improving the pore scale displacement efficiency. On the other hand, the polymers thicken the viscosity of the injectant and, thus, reduce the mobility ratio and enhance the sweep efficiency [9, 10, 12, 15].

Surfactant flooding involves the use of surfactant molecules also referred to as surface active agents which are amphiphilic molecules with a hydrophilic (polar) head and hydrophobic (non-polar) tail [16, 17]. The hydrophobic tail, which is mostly oil soluble, is characterized by a long chain of alkyl groups which may be branched. The hydrophilic head which are mostly water soluble consists of moieties and are classified according to their ionic charge. Surfactant aid microscopic displacement efficiency by reducing IFT of the fluid-fluid interface. By reducing the IFT, the capillary forces of the trapped oil are minimized, and the oil saturation decreases [18]. Consequently, the dimensionless capillary number increases, and the recovery factor increases. Additionally, wettability alteration at the rock-fluid interface, foam generation and emulsification at the oil-interface are other mechanisms through which surfactant aid oil recovery. Surfactants alter wettability of the porous media via coating and/or cleaning mechanism. Besides, the emulsion generated ensure conformance control by creating a stable front while foam generated diverts subsequently injected water to thief zones in the reservoir to aid additional oil recovery [19].

Surfactants are classified based on the hydrophilic head group. The conventional surfactants based on ionic charge are the cationic surfactant, anionic surfactant, zwitterionic (amphoteric) surfactant, and non-ionic surfactant [20]. For cationic and anionic surfactants, the hydrophilic head groups are positively and negatively charged, respectively. Non-ionic surfactants have no charge and, hence, do not ionize in solution but are soluble in water due to the presence of hydrogen bonding between the hydrophilic groups [18]. Zwitterionic surfactant consists of hydrophilic head with positive and negative charges. Recently, the design and use of new surfactant such as Gemini surfactant, viscoelastic surfactant and polymeric surfactant have been exploited for EOR. Gemini surfactant is a surfactant composed of two single-chain surfactants linked by a spacer. The properties of the Gemini surfactants are dictated by the type and length of the spacer [21]. On the other hand, viscoelastic and polymeric surfactants are surfactants that form a supramolecular structure in solution and characterized by a high viscosity with additional ability to decrease interfacial tension which are both beneficial for EOR [22]. Nonetheless, the major issues associated with the use of conventional surfactants are high costs and environmental concerns. With recent issues associated with global warming and persistent regulation to lower environmental impacts on climate change, the industry is dissipating more energy and drive towards surfactant chemicals with less toxicity.

More recently, natural surfactants have received prodigious attention due to their lower toxicity, biodegradable, and environmentally benign, and good efficiency at improving recovery efficiency. Herein, natural surfactant is defined as surfactant synthesized from plants and oil. Natural surfactants possess the property of reducing the surface and interfacial tension in similitude to synthetic surfactants. Additionally, the novel surfactant has shown exemplary characteristics of foaming, emulsification, dispersion and wetting which are desirable for EOR. Herein, a synopsis of the application of natural surfactant and biosurfactant application for EOR was elucidated.

2. Natural surfactant

Natural surfactants are surfactants synthesized from leaves of plants and oils and they have shown sterling properties for use in EOR. Natural surfactants are either extracted directly or they are synthesized from plants and animal fats. Several methods have been reported for the synthesis of this biodegradable surfactants such as spray drying, freeze drying, Soxhlet extraction process, supercritical CO_2 extraction, ultrasonic extraction, microwave extraction, hydrolysis, and esterification process [23]. Moreover, several parts of plants such as leaves, roots, seeds, oils, and flowers have been courted for natural surfactants depending on their constituent components. *Jatropha curcas*, almond seed, *Vernonia amygdalina*, *Ziziphus spina-christi*, palm tree, vitagnus plant, and soapnut plant are several plants that have been exploited for natural surfactants [24–28]. Additionally, oils of plants and animals such as palm oil, coconut oil, rapeseed oil, sesame oil, waste cooking oil, linseed oil, and waste chicken fats have been converted into natural surfactants via esterification process [29–32]. Amino acid is another source of natural surfactant and can be derived from both plants and animals [23]. In similitude to conventional surfactants, the synthesized and/or extracted surfactants can be categorized into non-ionic, anionic, cationic, and zwitterionic surfactants. Other categories of synthesized polymeric, Gemini and viscoelastic surfactants [33, 34].

3. Application of natural surfactant for EOR

3.1 Interfacial Tension (IFT)

Interfacial tension is the adhesive tensional force that exists between the molecules of oil and water in porous media that ensures they remain trapped in the pores of the reservoir rock system. To improve recovery factor, the capillary force holding the oil in place must be minimized. This is achieved by lowering the IFT which in turn cause an increase of the capillary number and resultantly cause the residual oil to flow towards the oil bank and later to the production well. When the surfactant is injected into the reservoir rock system, due to their amphiphilic nature, the hydrophilic head of the surfactant aligns with the water and/or brine while the hydrophobic tail attaches with the oleic phase. The IFT of oil-water interface is measured in the laboratory via pendant drop or spinning drop method. Natural surfactant has demonstrated suitability for use in reducing IFT of oil-water interface. An important property of natural surfactant which makes it highly applicable for IFT reduction is its good solubility.

Several studies have demonstrated the viability of natural surfactant for lowering the IFT of crude oil-water interface. Yekeen et al. [26] investigated the IFT and foaming property of natural surfactant extracted from *Sapindus mukorossi*. At high temperature and pressure (80 °C and 8 MPa), the natural surfactant reduced the IFT of the oil-water interface from 23.24 mN/m to 1.59 mN/m. Moreover, the foam stabilized by the saponin-based natural surfactant was stable and perform comparatively well to conventional sodium dodecyl sulfate SDS-stabilized foam. Bahraminejad et al. [35] examined the IFT and foaming characteristic of surfactant extracted from *Gundelia tournefortii* plant. The surfactant lowered the IFT from 28 mN/m to 3 mN/m and generated stable foams. Imuetinyan et al. [36] evaluated the performance of natural surfactant extracted from *Vernonia Amygdalina* at oil-water interface. The natural surfactant lowered the IFT at oil-brine interface from 18 mN/m to 0.97 mN/m in the presence of NaCl brine. Additionally, the emulsion stabilized by the natural surfactant remained stable for longer periods. This implies that the use of the natural surfactant as injectant will ensure good conformance control in the reservoir.

Additionally, natural surfactant has demonstrated good stability and sterling properties at high salinity and high temperature conditions. Zhang et al. [37] synthesized a natural zwitterionic surfactant from castor oil and evaluated the salt tolerance and thermal stability and foaming performance. At 33,000 mg/l salinity and 50 $°C$, the synthesized surfactant maintained strong interfacial activity, which demonstrates good use for EOR. Zhang et al. [32] studied the performance evaluation of novel bio-based surfactant from waste cooking oil. The synthesized bio-based zwitterionic surfactant reduced oil-water IFT to 0.0016 mN/m at low dosage of 0.1 g/l. Kumar et al. [38] noted that bio-based polymeric surfactant synthesized from Jatropha oil was stable in 2.5 wt.% brine concentration and reduced the IFT of the oil-water interface from 22.4 mN/m to 0.33 mN/m. Hence, the application of bio-based natural surfactant shows good potential for EOR due to their stability and sterling interfacial properties at harsh condition typical of reservoir condition.

3.2 Wettability

Wettability is a pore scale displacement property and usually defined as the tendency of a fluid to spread on or adhere to a surface in the presence of other immiscible fluid. In similitude to conventional surfactant, natural surfactant has shown good property for altering the wettability of porous media from oil-wetting condition to water-wetting condition. Water-wetting condition is desired for better recovery efficiency (see **Figure 2**). Using contact angle measurement, Deng et al. [39] defined water-wetting condition as contact angle of $0°–70°$, intermediate wetting condition as $70°–110°$, and oil-wetting condition as contact angle $110°–180°$. By modifying the wettability of the rock substrate to water-wetting condition, the capillary adhesive force that strongly attaches the oil to the rock diminishes, thus, allowing oil to flow. The interaction of the surfactant and the rock may cause alteration of the wettability condition depending on the type of surfactant injected and the porous media.

Numerous studies have indicated the ability of natural surfactant to cause wettability alteration of porous media. Imuetinyan et al. [25] observed that the natural surfactant extracted from *Vernonia Amygdalina* altered the wettability of sandstone surface from $118.5°$ to $45.7°$. Similarly, Singh et al. [40] evaluated the wettability of surfactant extracted from Fenugreek seeds. The surfactant reduced the IFT of oil-water interface to $44°$. Zhang et al. [37] reported wettability alteration from $92.04–38.79°$ using natural surfactant synthesized from castor oil. Moreover, natural surfactant synthesized from soybean oil reduced the wettability of rock substrate by 52.08% to $44.1°$ [41].

Figure 2.
Wettability alteration of reservoir rock system [9].

Chen et al. [34] synthesized a thermally stable and salt tolerant natural surfactant from waste cooking oil and evaluated it wettability alteration potential. The biobased surfactant altered the wettability of simulated formation water containing 0.5 g/l of the surfactant from 96.17°–30.7°. The contact angle decreased further to a meager 27.8° on further increment of the surfactant concentration to 3.0 g/l.

Furthermore, Kumar et al. [24] synthesized natural surfactant from Jatropha oil and evaluated the wettability on oil-wet quartz surface. The synthesized surfactant altered the wettability of the quartz surface to water-wetting condition. Despite the ability of natural surfactant to alter wettability to water-wetting condition, many of the natural surfactant do not alter the wettability to strongly water-wetting condition (contact angle <30°). Hence, future research should focus on modifying the structure of the natural surfactant to improve it interaction and efficiency with reservoir rock system. Moreover, wettability studies of natural surfactant on porous media focused more on their behavior on quartz surface and sandstone. More studies of natural surfactant behavior on carbonate (calcite, dolomite, and limestone) surface are required.

3.3 Adsorption

Adsorption is an important property that demonstrates the economic viability of the chemical flooding process [42]. Low retention of chemicals is desired to ensure an economic and cost-effective recovery process. Due to their amphiphilic nature, the injection of surfactant into porous media is followed by the interaction of the surfactant with the rock via electrostatic, van der Waals, ion exchange and association, polarization of the π electrons, and hydrophobic interaction depending on the type of surfactant. The adsorption of natural surfactants has been studied on sandstone and carbonate reservoir rocks and showed minimal adsorption desired for chemical EOR process [43]. Yusuf et al. [44] studied the adsorption behavior of natural surfactant from soapnut fruit on carbonate rocks by batch adsorption experiments using surface tension techniques. They reported lower retention of the natural surfactant compared to ionic surfactants (cationic CTAB and anionic SDS). This was attributed to the weaker hydrogen bonding of the non-ionic surfactant.

Additionally, Kesarwani et al. [45] examined the adsorption property of novel biodegradable surfactant synthesized from Karanj oil on sandstone. The anionic surfactant had 15% lower retention compared to conventional anionic surfactant (SDS). Abbas et al. [46] performed a comparative study of saponin-based natural surfactants from Fenugreek, Sugar beet leaves and chickenpeas on quartz sand surface using UV-Vis spectrophotometer. They reported lower adsorption of the natural surfactant in high salinity conditions and adduced this phenomenon to the compact configuration of the surfactant and the compression of the electrical double layer. Ahmadi et al. [47] investigated the utilization of natural surfactant extracted from *Ziziphus spina-christi* (ZSC). Adsorption studies of the surfactant on carbonate rock samples via batch tests. The surfactant showed no sign of precipitation, but the presence of salt cations increases the adsorption of the surfactant due to electrostatic attraction force between the positive charge of the carbonate rock surface and the negative charge of the hydroxyl group on the surfactant.

3.4 Oil displacement

The major aim of deploying surfactant as a chemical injectant is to boost oil recovery. Oil displacement test is used in the laboratory to estimate recovery factor of injectant. Several studies have been carried out to ascertain the oil recovery potential

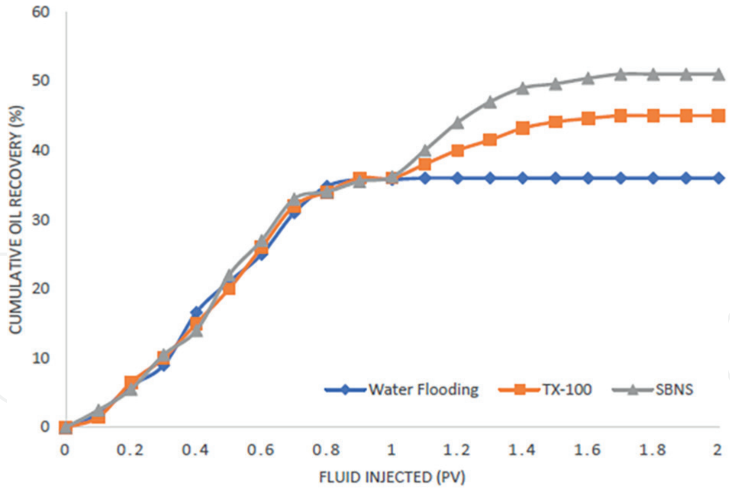

Figure 3.
Cumulative oil recovery of surfactant flooding [36].

of natural surfactant when used as injectants in sandstone and carbonate rocks. Saxena et al. [48] evaluated the oil recovery potential of surfactant synthesized from palm oil. The injection of 0.5 pore volume (PV) of surfactant in sandpack caused an improved recovery factor of 25–27% over conventional waterflooding. Nowrouzi et al. [49] evaluated natural surfactant synthesized from *Myrtus communis*. The surfactant yielded 14.3% incremental oil recovery when injected in carbonate core plugs. Alsabagh et al. [30] investigated oil displacement properties of green surfactant synthesized from waste cooking oils. 0.4 wt.% of the surfactant generated from palm kernel oil yielded 24.3% incremental oil recovery, respectively. Imuetinyan et al. [36] recorded 15% incremental oil recovery from core flooding procedure of saponin-based natural surfactant performed at high-pressure high-temperature condition. The SBNS performed better than conventional Triton X-100 under the same condition as depicted in **Figure 3**. Ahmadi et al. [50] explored the use of surfactant derived from *Glycyrrhiza glabra* for EOR. 8 wt.% of the newly extracted surfactant yielded 36% incremental oil recovery. Nafisifar et al. [29] applied surfactant synthesized from linseeds in sandstone cores. The natural surfactant injected after water flooding process yielded a 7.9% incremental oil recovery. Notwithstanding the numerous research of the application of natural surfactant for oil recovery, some aspects still need to be clarified in subsequent research. Notably, the concentration required for some natural surfactants are extremely high which may make the EOR process uneconomical.

4. Conclusion

This paper reviews the previous studies on natural surfactant application for EOR. The natural surfactants are benign and biodegradable and offer an alternative for existing conventional surfactants. Experimental studies show that natural surfactant can lower the IFT at the oil water interface. Moreover, the application of natural surfactant alters wettability of oil-wet cores to water-wetting condition. Adsorption studies of natural surfactant show that natural surfactant exhibit moderate retention behavior in reservoir cores and compares well to existing conventional surfactants. Moreover, oil displacement studies confirm that the application of natural surfactant can improve the recovery factor. Future studies on natural surfactant should focus on modeling their flow and transport behavior in porous media and scaling up natural surfactant application for field studies.

Conflict of interest

The authors declare no conflict of interest.

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