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Chapter

Application of Emulsions and Microemulsions in Enhanced Oil Recovery and Well Stimulation

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Abstract

Hydrocarbons are produced and transported in a form of mixtures containing oil, gas, and water plus organic and inorganic contaminants. The flow presence of these contaminants (emulsifiers) with the continuous agitation from reservoirs up to surface facilities leads to formation of tight emulsions that need to be dealt with carefully to treat and process them adequately. Emulsions, in the other hand, are sometimes intentionally formed for using in enhanced oil recovery (EOR) and well stimulation. In EOR, emulsions are formed and injected into the reservoirs for the objective of improving both the microscopic displacement efficiency and the macroscopic sweep efficiency, which leads to higher recovery factor. In well stimulation emulsified acids are used during matrix acidizing and acid fracturing to retard acid reaction with rocks, to generate deeper penetration inside the reservoir. Microemulsion is a form of emulsion with less droplet size, and hence higher stability, that occasionally used during EOR and hydraulic fracturing to further improve the reservoir recovery and well production rate. This chapter discusses the application of emulsions and microemulsions in petroleum industry. The chapter discusses emulsions, microemulsions, emulsification processes, application of emulsions and microemulsions in enhanced oil recovery and well stimulations, and ended with conclusions.

Keywords: emulsion, microemulsion, enhanced oil recovery (EOR), microemulsion flooding, microscopic displacement, macroscopic displacement, interfacial tension, surfactant injection, phase behavior, physical stability

1. Introduction

According to Khan et al. [1] "An emulsion may be defined as a biphasic system consisting of two immiscible liquids, one of which (the dispersed phase) is finely and uniformly dispersed as globules throughout the second phase (the continuous phase)." In other words, an emulsion is an insoluble mixture composed of two different types of liquid in which one liquid, i.e., dispersed phase, is spreading in the other liquid, which is in a continuous phase. Emulsions are widely used in our daily lives, examples of the most frequently used emulsions are milk, lotion, and creams. Emulsions in different industries can be formed intentionally to meet required applications, but emulsions occurrence in many cases is undesired and may cause

Emulsions as problems	Emulsions as solutions
Oil treatment More retention time (larger required separator), gas bow-by, formation of rag layer will affect level control system, additional cost (chemical/heating).	Enhance oil recovery The injection of emulsions and/or microemulsion into oil reservoirs is believed to enhance oil recovery due to their favorable rheological, and thermodynamical properties.
Oil transportation Equipment upsets, piping corrosion and scaling, affecting design throughput, single phase correlations become inaccurate when dealing with emulsions.	Well stimulation Emulsified acids are frequently applied to retard acids-rock reaction and hence increase penetration. Microemulsions also are used in hydraulic fracturing

Table 1.
Emulsions as problems and solutions in petroleum industry.

serious problems. In petroleum industry, for instance, emulsions can intentionally be formed for application in some upstream operations such as enhanced oil recovery (EOR), hydraulic fracturing, and emulsified acids. Nevertheless, negative impact due undesired emulsion is also encountered downstream operations. If the produced oil/water streams reach surface facilities in form of stabilized emulsions then more time, money, and technical knowhow are needed to separate the produced streams into distinct phases and make them ready to subsequent treatments. When crude oil is extracted from a well, it frequently leaves the wellhead in a form of mixture containing water phase. This will make it difficult to deal with in surface facilities and transportation areas [2]. **Table 1** introduces where emulsions is considered as problems and solutions in petroleum industry.

2. Emulsion

2.1 Type of emulsion

The two most common types of emulsion are oil-in-water (O/W) emulsion and water-in-oil (W/O) emulsion. There are also multiple emulsions in a complex system. Various types of emulsion can exist in the form of W/O, O/W, O/W/O, and W/O/W, however the most familiar ones are the first two [3]. In oil-in-water emulsions tiny nonpolar droplets of oil spread in a polar water phase [4]. As shown in **Figure 1**, the O/W system appears as a heterogeneous emulsion in which oil is dispersed in a form of bubbles of different sizes in the continuous water phase. In contrary, in water-in-oil emulsions oil forms the primary (continuous) phase in which water droplets disperse with different sizes.

W/O emulsions can further be categorized into stable, entrained, meso-stable, and unstable based on visual appearance, elasticity, and viscosity difference [6]. Nevertheless, in practice only stable and meso-stable states can be considered as real emulsions. The four types of water-in-oil emulsions have been clearly described by Fingas and others [6, 7] as follow:

- Stable emulsions are described as reddish brown semi-solid substances having 70–80% water cut. Experimental examinations conducted by [6] indicated that stable emulsions can remain stable for more than 4 weeks and the stability can extend to more than least 1 year. They also pointed out a dramatical viscosity increase to more than 800 folds after 1 week.

- Meso-stable emulsions the meso-stable water in oil emulsions are viscous liquids and similar in color with the stable emulsions (reddish brown).

Unlike the stable emulsions, the initial value of water content in meso-stable emulsions is in the range 60–65% but the water cut declines to less than 30% after 1 week of formation. The viscosity of meso-stable emulsions also increases with time but the increment rate is not as high as that of stable emulsions [7].

- Entrained emulsions: the entrained emulsions have less water cut and less viscosity increment than that of meso-stable emulsions. The water cut at the date of formation is in the range 40–50% and drops to 28% after 1 week [6].
- Unstable emulsions: contains very little amount of water which almost remain constant with time [7] (**Figure 2**).

In petroleum industry, both W/O and O/W emulsions can be recognized in different locations starting from the reservoir and up to refinery and terminal stations. W/O emulsion is frequently recognized at down-hole and downstream to the choke because at these points the flow stream is mainly hydrocarbon (oil and gas) with lesser volume fraction of water. Due to the continuous turbulence and agitation of the stream while it flows through tubing and passing through wellhead and choke, the water phase breaks down into small droplets and scatters

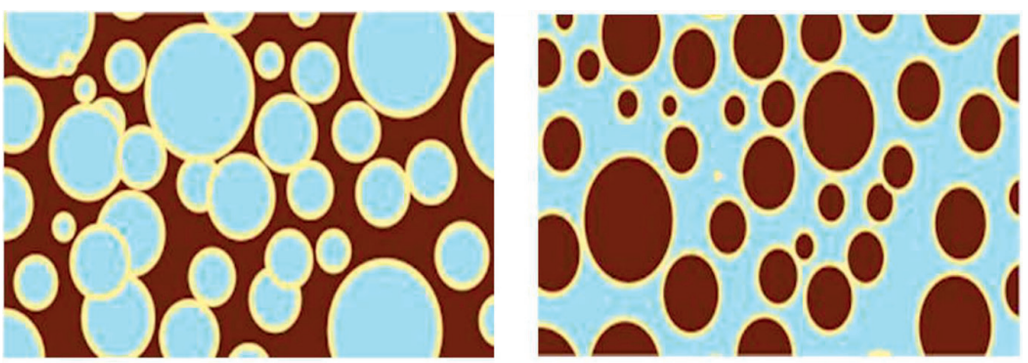


Figure 1.
Water-oil (W/O) emulsion (left) and oil-water (O/W) emulsion (right) [5].



Figure 2.
A photograph of stable emulsion (A) and unstable emulsion (B) [6].

inside the primary oil phase. The presence of impurities in the oil phases, which act as emulsifiers, will increase the possibility of forming W/O emulsion with stability proportional to the degree of turbulence and the concentration of the emulsifiers. O/W emulsion, from the other hand, is more frequently recognized at water outlets downstream to two phase separators and at the inlet of three phase separators and free water knock out (FWKO) facilities. This type of emulsions should be treated properly before it reaches the first pump station for long distance transportation. The main problem arise from flowing of this type of emulsions in pipelines is the corrosion of internal wall of the pipeline due to presence of water. However, presence of emulsions inside pipeline may also be useful as it facilitates smooth transportation of high viscous crude. Because of that heavy and waxy crude oils may intentionally emulsified with water to form (O/W) emulsion.

2.2 Characteristic of emulsion

The main characteristic upon which emulsions are valued is the emulsion stability. Emulsion stability is directly related to the degree of the emulsion tightness and the force of bond between the primary phase and the dispersed phase. High stability is sometimes desired for some applications and processes, whereas it causes problems in others. The applications where high stable emulsions are needed in petroleum industry include enhanced oil recovery (EOR), well stimulation, and heavy/waxy crude transportation. The applications where high stable emulsions are problematic are downstream operations. Highly stable emulsion causes a lot of problems in separation and treatment processes where longer time and more cost are needed to ensure efficient separation and high sale value for the treated hydrocarbons. Emulsion stability is affected by the characteristics of the two immiscible phases (the continuous and dispersed phases), the degree of the agitation to which the mixture is subjected, and the concentration and type of emulsifiers. Thermal stability can be measured in lab using different techniques or can be quantified using the stability indexed as discussed before. The simplest and more accessible measurement technique is the bottle test. A small amount of the emulsion is placed in a scaled bottle and the separated amount of the dispersed phase is noticed over time (**Figure 3**).

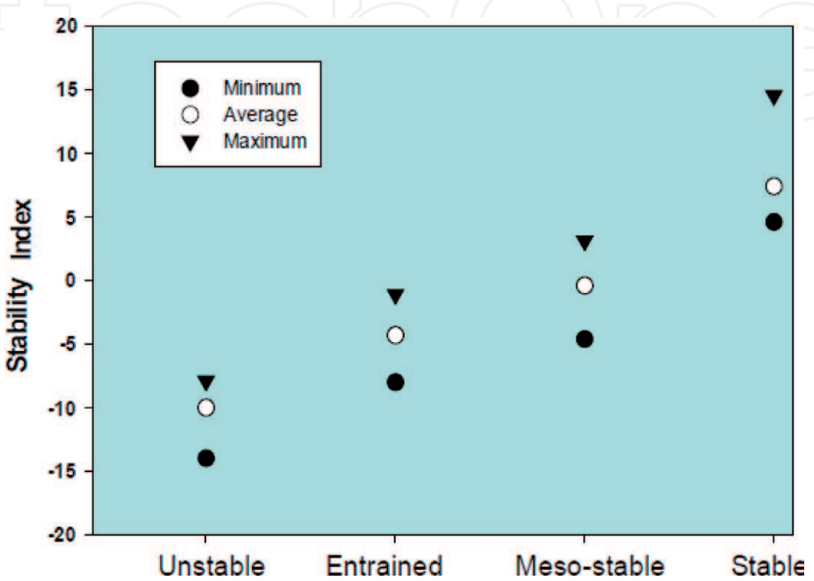


Figure 3.
Water-oil W/O emulsion identification based on stability index [6].

2.2.1 Effect of rheology on emulsion stability

The effect of different flow properties on emulsion has been studied by many researchers [8–10]. The rheology of an emulsion involves the study of the flow of the emulsion itself. Therefore, it concerns with the viscosity of the emulsion. Some of the rheological properties are temperature, dispersed phase volume fraction, the inclusion of surfactant in emulsion and the chemical constituent that exists in each section. All of these properties affect the viscosity of emulsion which is usually measured. It was also revealed that the viscosity becomes substantially lesser as the volume fraction of water was lowered. Even more so, the viscosity is also firmly influenced by temperature [11]. The temperature when it is intensifying at a certain degree it will cause a cracking between the bond with solid components as it will not allow the components which contain in crude oil to have the opportunity to combine and agglomerated. Eventually, less viscous emulsion in obtained. Additionally, other factors that affect the rheology are the shear rate. Greater shear rates result in lower viscosity as there will be less flow ability interruption in the emulsion [2]. Although shear rate is considered to affect the rheology, Keleşoğlu et al. [12] proclaimed that shear rate does not apply to an emulsion with a volume fraction that is less dispersed. Out of all the factors states, temperature is one of the significant parameter that can highly affect the viscosity of emulsion.

- Emulsions are encountered at different steps of petroleum engineering related activities, starting from the moment the hydrocarbons are contained inside the reservoirs and up to separation and treatment of oil and gas.

- The emulsions are normally considered as problematic when thinking about it from the oil processing and treatment point of view. In this case, an undesirably formed emulsion leads to slowing down oil/gas/water separation and process and, by such, increasing the cost of processing and treatment. In such a case, the emulsion need to be destabilized and broken by heating and/or using chemical demulsifiers,

- Emulsions, from the other hand, may intentionally be formed and stabilized for application in enhanced oil recovery and well stimulations.

- Emulsion stability is affected by (1) the characteristics of the two immiscible phases (the continuous and dispersed phases), (2) the degree of the agitation to which the mixture is subjected, and (3) the concentration and type of emulsifiers.

- Microemulsions are generally composed of hydrocarbons, surfactants/co-surfactants and brine.

- Macro/microemulsions based enhanced oil recovery improve both the microscopic displacement efficiency and the macroscopic sweep efficiency, thus leads to higher recovery factor.

- In enhanced oil recovery, the microemulsion flooding displays the unique properties of microemulsion systems, such as high viscosity and the ability to induce low interfacial tension, increasing oil extraction efficiency.

- In well stimulation emulsified acids are used during matrix acidizing and acid fracturing to retard acid reaction with rocks, to generate deeper penetration inside the reservoir.

3. Emulsification

Emulsion is usually formed by the action of mechanical mixing with the existence of a surfactant molecule. The mechanical mixing action can generate a turbulence effect and break down the two immiscible phases, while surfactant is contributing in building an adhesion force on the surface between the droplets of the two phases (see **Figure 4**). This process of the formation of an emulsion is called emulsification. There are two types of emulsification, spontaneous emulsification and self-emulsification. The spontaneous emulsification is the emulsification process where there is no involvement of external heat or physical action or energy that can affect the emulsification of the two immiscible liquids. In the spontaneous emulsification, the two phases usually take a significant amount of time to completely become an emulsion. In the self-emulsification, the complete emulsification occurs when appropriate surfactants are used [14]. Emulsification can be observed in many activities and processes ranging from simple events people frequently do in daily life to more complicated and sophisticated processes performed in industry. Producing mayonnaise is an example of the emulsification processes where egg yolks and oil are mixed and emulsified by stirring action to form a thick emulsion in which the egg yolk acts as a continuous phase while the oil is the dispersed phase. Similarly, mixing water in oil can generate a water-in-oil or oil-in-water emulsion, depending on which phase is predominate. In this case, however, an emulsified material such as asphaltenes is needed to stabilize the emulsion. Fingas and Fieldhouse [6] mentioned that asphaltenes are the main factor that cause (W/O) emulsion stabilization as it has the ability to build a rigid cross-linked and elastic films. Besides asphaltenes, resins can also act as stabilizing agents. As outlined by Fingas [7], although resins normally assist the asphaltenes by acting as a solvent that can stabilize as the asphaltenes migrates. This shows that asphaltenes and resins can be considered as the main emulsifiers that exist naturally in crude oils. In addition, to asphaltenes and resins, other organic and inorganic stabilizers frequently found in crude oils include waxes and clays [15]. Crude oil does not always appear as a stable emulsion as there is certain phenomenon that continuously destabilizes it. Examples of such phenomenon are flocculation, creaming, and coalescence. Flocculation is the process of the combination of small emulsion droplets each other due to excess surfactants in the continuous phase. When the emulsion is shaken, however, these particles can disperse again in the medium.

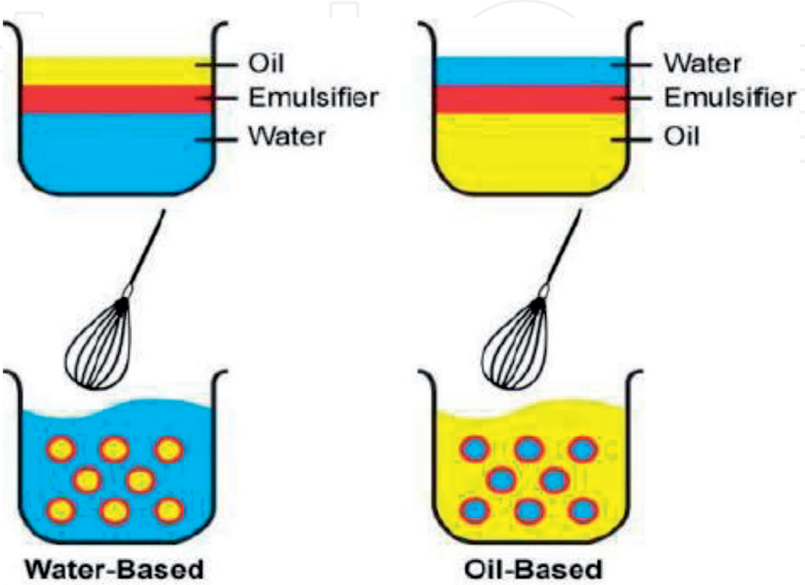


Figure 4.
Main basic types of microemulsions; the three basic types of microemulsions are direct (oil dispersed in water, o/w), reversed (water dispersed in oil, w/o) and bi-continuous [13].

4. Microemulsions

4.1 Type and structure of microemulsion

Microemulsion structure has a key role in the different physicochemical properties of the applied fields. The specific structures of the microemulsions have been extensively studied by many scientist researchers [16–22]. The three basic types of microemulsions are direct (oil dispersed in water, o/w), reversed (water dispersed in oil, w/o) and bi-continuous. Like multiple emulsion, sometimes multiple microemulsion is also possible. In this type, another layer is formed outside the o/w or w/o microemulsions. The schematic diagram of the basic three types of microemulsions is revealed in **Figure 5**. Microemulsion structure depends on salinity, water content, co-surfactant concentration and surfactant concentration. At higher water content, the microemulsion would be a water-external system, with oil solubilized in the cores of the micelles. Although the mixtures remain single phase and thermodynamically stable, the microemulsion structure changes through a series of intermediate states [23]. The structures of these intermediate states are not well known. However, the solutions are thermodynamically stable and isotropic. Salinity also can reverse the structure of the microemulsion. As salinity increases, the direct microemulsion changes to reverse microemulsions. At low salinity, the system remains in water-external phase, but with increasing salinity the system separates into an oil-external microemulsion.

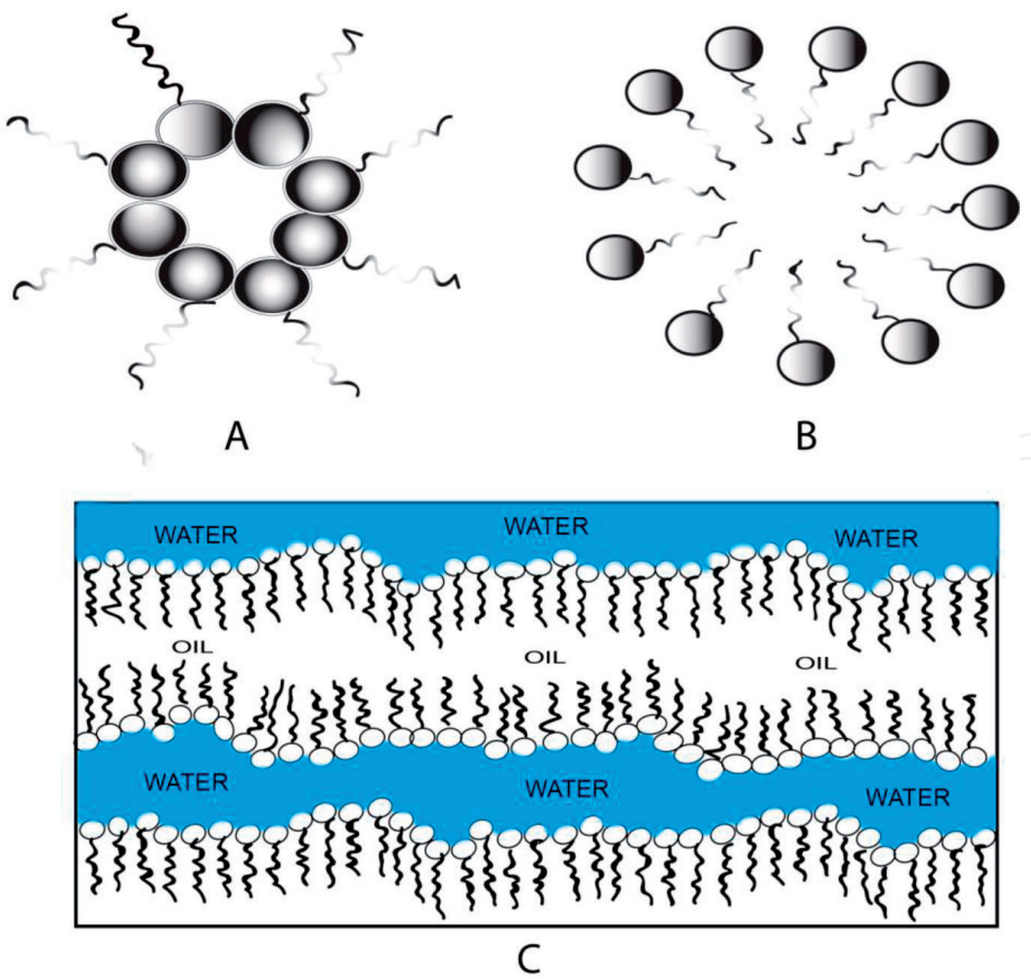


Figure 5.
Main basic types of microemulsions; the three basic types of microemulsions are (A) reversed (water dispersed in oil, w/o), (B) direct (oil dispersed in water, o/w), and (C) bi-continuous [16].

The term "microemulsions" has been introduced for the first time by Schulman et al. [24]. The term was used to describe what is called transparent solutions in a model four component system consisting of water, hydrocarbon, surfactant, and co-surfactant. Microemulsions can be experimentally investigated and described using different characterization apparatus such as low-angle X-ray diffraction [25] and viscosity measurements [26]. Microemulsions [27–29] can also be identified and described using phase mapping which is a tetrahedron shape showing the components of the microemulsions (i.e., water, hydrocarbon, ionic surfactant, and co-surfactant) in the four corners of the tetrahedron, as shown in **Figure 6**.

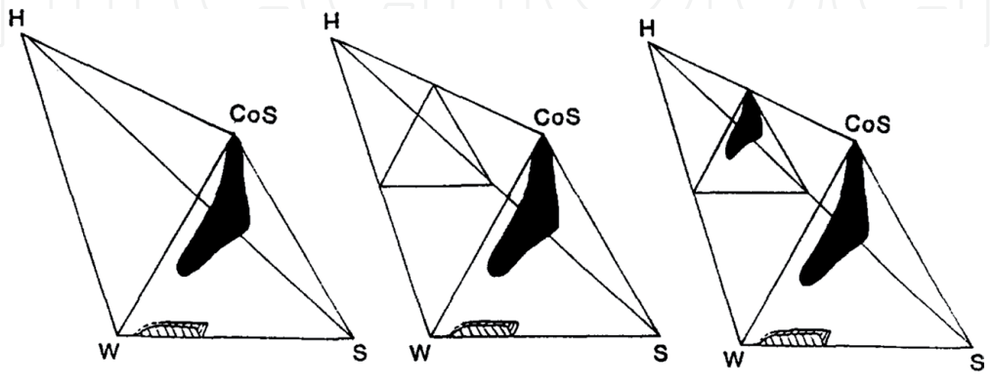


Figure 6.
The four component of microemulsion system water (W), hydrocarbon (H), ionic surfactant (S) and co-surfactant (CoS) [30].

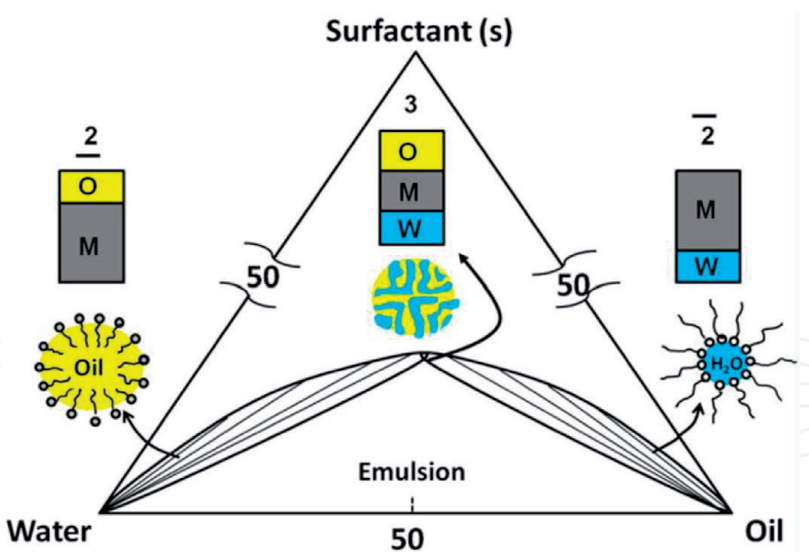


Figure 7.
Typical water-surfactant-oil microemulsions as depicted by the ternary phase diagram [31, 32].

Similar to emulsion classifications, microemulsions are classified into three types as follow:

- Oil-in-water (O/W) microemulsion: in this type, i.e., the water phase predominates the oil phase, the oil volume fraction is smaller than the water volume fraction.

- Water-in-oil (W/O) microemulsion: in contrary to the O/W microemulsions, in this type the oil phase volume fraction predominates the water phase.

- Bi-continuous microemulsion: also referred to as "sponge-like" microemulsions. In this type the volume fractions of oil and water re almost similar and both can be considered as continuous, while the surfactant molecules is forming rapidly fluctuating interfaces [27, 28].

The phase diagram for a typical there-component surfactant-water-oil is shown in **Figure 7** [31, 32].

5. Demulsification

Demulsification play an important key in separating water and salts from crude oil which is vital during industrial procedure [33]. Since crude oil consists of impurities and if it is not removed, thus it will cause fouling and major corrosion to the equipment in the industry. As a matter of fact, this process can only be executed when demulsifiers are utilized. This chemical component is capable to inflict the coalescence of water droplets by forming film drainage and elevate the surface activity as the gradient is inversed. Thus, it means that demulsifier can undeniably change the interface physical characteristics. When demulsifiers are added to a dilute emulsion of low concentration, a specific process call adsorption takes place and it will adsorb the emulsion particles and situate it on the surface in forms of droplets. Furthermore, the demulsifier contain organic particles and it will locate and adsorb the dispersed phase in such a way that the non-polar part will be in the crude oil while the polar part will maintain in water [34]. Demulsifiers are also known as a non-ionic that consists of two separate parts of hydrophobic and hydrophilic. The hydrophobic group contains oxypropylenes, alkyls or alkyl phenols whereas the hydrophilic group contains amine groups, carboxyl, hydroxyl or oxyethylene. There are also several methods in separating the emulsions which involves separation in terms of chemical, electrical and mechanical [34]. Usually, it is observed in the industry, the use of chemical method is the most common. The coalescence of (W/O) emulsion is maximized and the protective film breaks with the use of chemical demulsifier [35]. As a result, researchers are looking for a way to accelerate the demulsification process effectively. Several methods were applied, for example, the use of microwave energy, adding Janus magnetic microparticle in demulsifier and others. Based on the research conducted by Martínez-Palou et al. [3]. It was found that the rate of separation of (W/O) emulsion were highly efficient when microwave power was applied compared to the use of chemical non-ionic surfactants and also the solubility of surfactants in water decreases with the aid of a saline solution like seawater. Conversely, the application of the Janus magnetic submicronic particles or P(MMAAA-DVB)/Fe_3O_4 was very promising as it exhibits a high rate of coalescence whereby the water droplets are settled magnetically through the attraction of an outer magnetic field and it is also recyclable, hence lowering the cost in the petroleum industry [36]. To enhance the demulsification efficiency, the factors that can affect it are the molecular weight, hydrophile lipophile balance (HLB), concentration, water content, temperature and asphaltene content. Concerning the molecular weight, the lower the molecular weight of the demulsifier, the higher the rate of partitioning the emulsion as an elevation in the molecular weight causes a difficulty for the demulsifier to spread in the highly thick or viscous crude oil. Beside, a rise in the amount of HLB, concentration and water content shows an increasing rate in the efficiency of this process. However, the asphaltenes which acts as stabilizing agents can prevent the demulsification of crude oil because when the content becomes higher, it will result a dense film that protects the emulsion. To summarize, the complete separation of (O/W) emulsion can be attain based on two prime factors which is the temperature and the quantity of asphaltenes [32, 37].

6. Applications of emulsion/microemulsion in oil industry

6.1 Background

It is to be expected that the future energy demand will be met by a global energy mix that is undergoing a transition from the current dominance of fossil fuels to a more balanced distribution of energy sources. After conventional waterflood processes, the part of the oil in the reservoir remains as a discontinuous phase in the form of oil globules trapped by capillary forces and is likely to be around 30% of the original oil in place (OOIP) [38], whereas another 40% is bypassed by the water. However, technically it is possible to improve this recovery efficiency by applying enhanced oil recovery (EOR) processes. Traditionally, oil recovery operations comprise three stages: primary, secondary, and tertiary. These stages describe the production from a reservoir in chronological manner. During primary recovery, which starts right from the earliest stages of production, the energy for displacing the oil to the production wells results from the use of natural energy present in the reservoir [39]. Continual withdrawal of the fluids from the reservoir, results in a decrease of the supporting energy. Consequently, it reaches a stage whereby further removal of fluids approaches the limits of a profitable operation. Here, it requires an intervention for increasing the reservoir energy and thus fostering production. This implies the initiation of the second stage, which entails the application of secondary recovery methods. The secondary recovery method results in the augmentation of the natural energy of the reservoir. One of the most popular secondary recovery methods is waterflooding. The estimations showed that the unproduced residual oil reserves from primary and secondary oil production methods are about two to three trillion barrels worldwide [40]. Given the tremendous amount of the unrecovered oil, the introduction of new intervention techniques is crucial. This entails the application of methods for tertiary recovery or enhanced oil recovery (EOR). Typically, the methods consist of injection of (nonreservoir) gases [40, 41], liquid chemicals and/or the use of thermal energy. This work focuses on the use of emulsions and/or microemulsions as effective method to improve oil recovery in the field. Previous experiences clearly indicate that emulsion and/or microemulsion-based EOR methods are an ideal, as well as a feasible alternative that can effectively recover this enormous resource base [42, 43].

6.2 Applications in enhanced oil recovery (EOR)

In oil and gas industry, the approach to emulsion and/or microemulsion preparation has associated with the application of energy to a mixture of oil, water, and emulsifier. The emulsifier (i.e., surfactants or amphiphilic proteins) acts to stabilize the interfacial layer between the continuous and dispersed phase which has been generated through the addition of energy to the system. The injection of emulsions and/or microemulsion into oil reservoirs has been acknowledge as a potential tool for oil recovery due to the possibility of rheological, and thermodynamical properties of emulsions [44]. As reviewed by Muggeridge et al. [45] main objective of oil recovery is to improve both the microscopic displacement efficiency and the macroscopic sweep efficiency of the reservoir. The former regards the removal of oil at the pore level, while the latter is targeted at removing oil at the larger scale of the medium by avoiding oil trapping, a feature related to reservoir geological conformation and surface chemistry.

6.2.1 Macro- and microemulsion flooding

The use of microemulsions is of high interest in many aspects of crude oil exploitation, especially in enhanced oil recovery (EOR). Macro- and microemulsion flooding is an efficient EOR recovery method due to its high extraction efficiency by reducing the oil-water interfacial tension [42]. A macroemulsion is a thermodynamics unstable heterogeneous mixture of oil and water with either oil droplet in water (an oil/water emulsion) or water droplets in oil (a water/oil emulsion). The droplets are stabilized by surfactants that absorb at the oil-water inter-phase, which makes that the interfaces are charged preventing the droplets to collide. On other hand, microemulsions are transparent homogeneous mixtures of hydrocarbons and water with large amounts of surfactants [24]. The microemulsions have recently been introduced in enhanced oil recovery processes in which chemicals, especially surfactants, are used to recover the oil from natural oil reservoirs. Since the discovery of microemulsions, they have attained increasing significance both in basic research studies and in the oil fields. In spite of intensive research on microemulsions, the theory behind understanding mechanisms (i.e., predictive power) for microemulsions is still lacking [43, 46, 47]. In addition, many difficulties are encountered in creating a suitable microemulsion film with temperature gradients required large, many ionic surfactants precipitating when contacted with brine, and most non-ionic surfactants unsuitable. Other issues include adsorption of microemulsion components on rocks, and varying salinities and temperatures of the oil reservoirs. Over the past three decades, however, there has been sufficiently great progress made on the recovery of residual oil in particular chemical based enhanced oil recovery with microemulsions. Babadagli [48] has written a review about improvement of mature oil fields. According to his analysis, the most common chemical-based enhanced oil recovery method is the surfactant solution injection due to its relatively lower cost when compared to micellar or microemulsion injection. The way by which the injected chemical, in chemical based enhanced oil recovery (EOR), is a significant parameter for optimization of the EOR-method. Continuous injection of a chemical solution leads to increase operation costs and/or reduce the amount of treated material. Taking into account, injection of chemical solution considering the porous volume number (PV) is required in any efficient enhanced oil recovery (EOR) process. Thomas and co-workers (in: [48]) injected porous volumes (PV) of microemulsion in sandstone rock containing 35% of residual oil, noticing a linear relationship between the values of injected pore volume (PV) and the oil recovery. The Results of the study of Thomas and co-workers showed a 45% residual oil recovery when injecting around 10 pore volume (PV) of microemulsion. Santanna et al. [42] studied the application of different types of microemulsion for chemical based enhanced oil recovery (EOR), including different types of surfactants [42, 49, 50].

6.2.2 Surfactant microemulsion flooding

Microemulsions are generally composed of hydrocarbons, surfactants/co-surfactants and brine. Surfactants are considered to be the principal constituents of microemulsions and are adsorbed at the interface rather than in the bulk phase. Surfactants are classified into four groups based on the charge of the head group such as anionic, cationic, non-ionic and zwitterionic. Anionic surfactants such as sodium dodecylsulfate (SDS) are negatively charged in nature, but a small cation sodium ion occupies the counterpart. Anionic surfactants are most widely used in oil recovery process. Their adsorption phenomena in sandstone and carbonate are different. Their adsorption in sandstone is relatively lower than that of carbonate [49–51].

6.2.3 Mechanism of surfactant microemulsion flooding

In microemulsion flooding, the reservoir is flooded with water containing a small percentage of surfactant and other additives such as hydrocarbon, medium-chain alcohol and brine. The surfactant plays a key role in forming the exact type of microemulsion that reduces the interfacial tension of the target oil [29, 52]. This is critical to both mobilize oil and enable it to escape from the reservoir rock. In general, whenever a waterflood has been successful, microemulsion injection will be applicable, while in many cases where water injection has failed due to its poor mobility relationships, microemulsion flooding can still be successful mainly because the required mobility control.

6.2.4 Interfacial tension reduction

In enhanced oil recovery, the microemulsion flooding displays the unique properties of microemulsion systems, such as high viscosity and the ability to induce low interfacial tension, increasing oil extraction efficiency. [42] According to Austad and Strand [53, 54], very low interfacial tensions may be reached with microemulsion systems. As stated by Gurgel et al. [55] microemulsions are potential candidates in enhanced oil recovery, especially because of its ultra-low interfacial tension values, attained between the contacting oil and water microphases that form them. Under such circumstances, microemulsions flow more easily through the porous medium, which enhance oil extraction performance rates. Babadagli [48] has written a review about improvement of mature oil fields. According to his review, the most common chemical injection technique, as an enhanced oil recovery method, is the surfactant solution injection due to its relatively lower cost when compared to microemulsion injection. The way by which the fluid is injected, when the chemical method is applied, is an important parameter for optimization of the technique. Continuous injection of a chemical solution may increase operation costs and reduce the amount of treated material. In view of this, injection of chemical solution considering the porous volume number (PV) is required in any efficient recovery process. Thomas et al. (in: [48]) injected porous volumes of microemulsion in sandstone plugs containing 35% of residual oil, observing a linear relationship between the values of injected PV and the oil recovery. Results typically showed a 45% residual oil recovery when injecting 10 PV of microemulsion. Santanna and co-workers [42] studied the application of different types of microemulsion for enhanced oil recovery, one was prepared with a commercial surfactant (MCS), and another contained a surfactant synthesized in laboratory (MLS). The experiments consisted of the injection of fluids into cylindrical plug samples. During the microemulsion flooding, samples were collected as a function of time and the mass of oil recovered by the microemulsion was determined. The chemicals used to prepare the microemulsion systems were commercial anionic surfactant (soap-sodium salt) obtained from fatty acids; anionic surfactant (soap–sodium salt) synthesized in laboratory, extract from fatty acids (100 wt.% of vegetable oil containing 12 carbon atoms); isoamyl alcohol; pine oil; and distilled water. From the results obtained, one could conclude that the use of microemulsion prepared with the commercial MCS allowed for recovery indexes as high as 87.5%, whilst the use of the MLS microemulsion permitted recovery indexes as high as 78.7%. This was because the difference in microemulsion viscosities, corroborated by the fact that the MCS-based microemulsion (32 cP viscosity) could recover more oil than the MLS-based microemulsion (27 cP viscosity).

6.3 Emulsion and microemulsion applications in well stimulation

Matrix acidizing is a well stimulation technique used to eliminate formation damage and/or increase permeability in sandstone and carbonate reservoir. This eventually leads to the improvement of the reservoir inflow performance, which will turn in enhancing wells productivity [56]. Matrix acidizing is performed by injecting acid solution with a prescribed concentration into the formation from surface. The typical acid used for carbonate reservoirs is hydrochloric acid with concentration of 15%, whereas for sandstone reservoirs a mixture of hydrofluoric/hydrochloric acid solution with a concentration 3% HF/12% HCl is used. The efficiency of matrix acidizing process is highly dependent on the distance the acid can penetrate inside the reservoir, which is inversely proportional to the rate of reaction between the acid and the rock. Fast acid reaction yields less penetration distance inside the formation, and hence, the acidizing operation will get less efficient. Therefore, different methods are implemented to retard the acid-rock reaction. One way to do so is by emulsifying the acid solution with a hydrocarbon oil (diesel oil or xylene) with the assistance of an emulsifying agent. This process results in producing an emulsifying acid fluid that more favorable than the ordinary acids because the hydrocarbon oil phase provides a diffusion barrier causing the slow release of acid and deeper penetration [57]. The emulsified acid is considered efficient if it can slow down the reaction rate (i.e., retard the acid) and generate a successful stimulation operation (expressed as increase in the rock permeability). Both effects can be assessed experimentally using core samples from the target rock. The acid retarding effect can be investigated by comparing the solubility of the rock in the blank acid with that in the emulsified acid. Assessment of emulsified acid retarding efficiency (acid solubility test): the acid solubility test is conducted to measure the amount of rock soluble by using the emulsified acid. Mohsin and his co-workers [56] conducted acid solubility test for an Indiana Limestone core sample in hydrochloric acid oil emulsified acid at ambient and 70°C. Approximately 1 g powder of the rock placed in a volume of 150 cc of the emulsified acid for a period of 60 min without stirring at the desired temperature. Hydrochloric acid solution with 15% concentration has been used to formulate three types of emulsified acids each with different type of oil phase (diesel oil, palm oil, and *Jatropha* oil). The solubility value, expressed in percentage, was calculated for each emulsified acid using the following formula:

$$SA\,\% = W1 - W2/(W1 \times 100) \quad (1)$$

The solubility values at temperature of 70°C are shown in **Table 2**.

6.3.1 Assessment of stimulation efficiency

The stimulation efficiency is investigated experimentally using core flooding lab. A core sample from the stimulated rock is placed inside the core holder of the

Emulsion type	Initial weight (W1), g	Final weight (W2), g	Average solubility (70°C)
Jatropha oil-based	1	0.050033	94.99
Diesel oil-based	1	0.0285	97.15
Palm oil-based	1	0.02076	97.924

Table 2.
Emulsified acids with continuous phase of three types of oil [56].

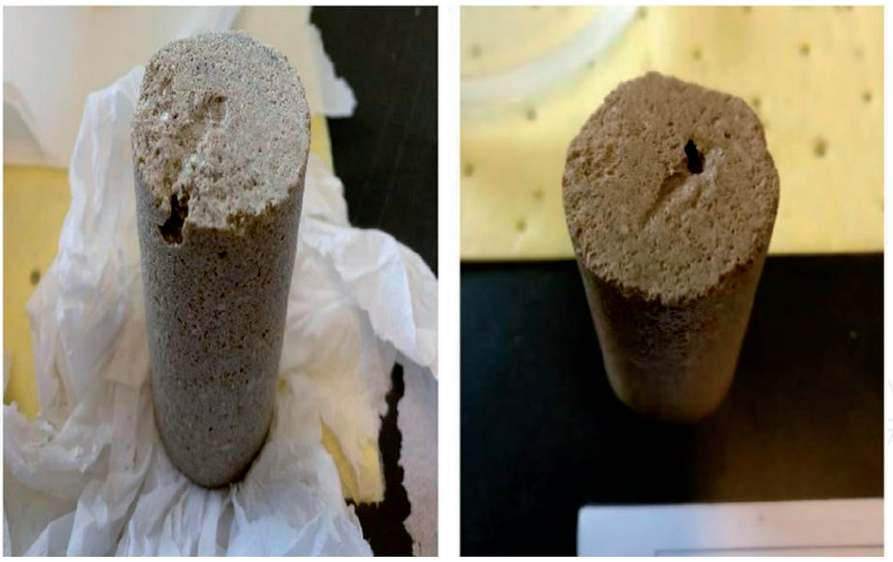


Figure 8.
The cores used for investigating the diesel-based and Jatropha-based emulsified acids [56].

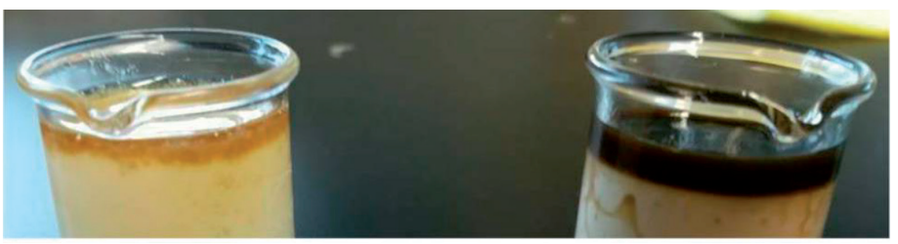


Figure 9.
Filtrate from Jatropha oil-based emulsion (on left side) and filtrate from diesel oil-based emulsion (on right side) [56].

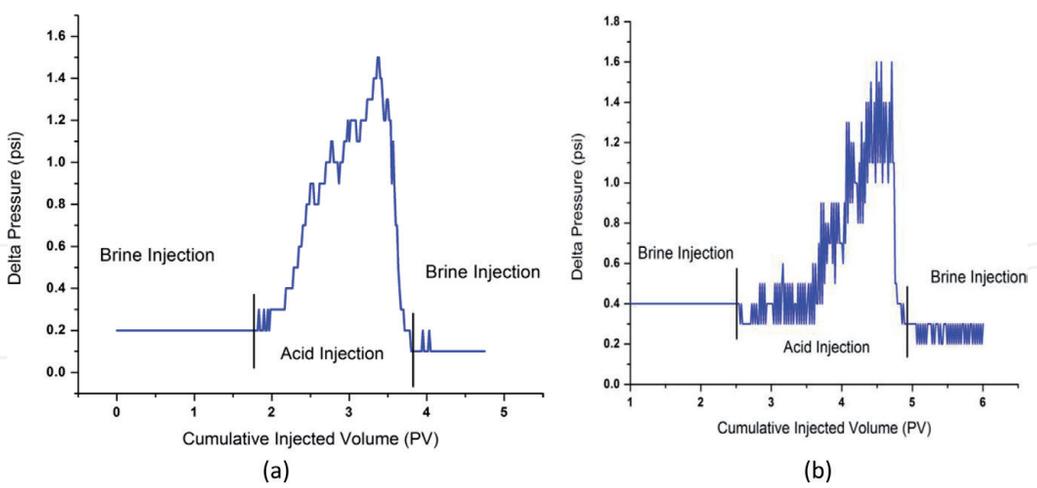


Figure 10.
Pressure drop profiles by the end of the acidizing using (a) diesel based emulsified acid, and (b) Jatropha based emulsified acid [56].

core flooding lab and the reservoir condition can be simulated by setting the pressure and temperature of the core flooding lab at values similar to the real conditions of the reservoir. The core flooding equipment FES 350 has been used by Mohsin and his co-workers [56] to investigate the stimulation efficiency of the diesel-based and *Jatropha*-based emulsified fluids described in **Table 2** at a temperature of 7°C, a back pressure of 700 psi, confining pressure of 1300 psi, and injection rate of 0.5 cc/min. Two carbonate cores, shown in **Figure 8**, were immersed first with

brine to determine permeability of the core by recording the differential pressure points using Darcy's law, as the fluid moves across the core. The 15 wt% HCl emulsified acid was then injected until pressure drop was observed indicating the breakthrough. The cores were then flushed with brine to remove stimulation fluid and was cleaned, dried and was measured for weight, porosity and permeability. **Figure 9** shows filtrate from *Jatropha* oil-based emulsion (on left side) and filtrate from diesel oil-based emulsion (on right side).

Figure 10 shows pressure drop profiles of the cores shown in **Figure 8** by the end of the acidizing with the *Jatropha* oil-based (a) and the diesel oil-based (b) emulsified acids. Both the two pressure profiles figures indicate reaching the end of the core by the acidizing medium while creating the conduit and both cores achieved almost similar pressure drop. However, diesel laced acid achieved slightly higher pressure drop (1.6 psi), whereas *Jatropha* oil-based emulsified acid achieved one peak pressure drop at 1.5 psi. This stipulates higher consumption of the diesel-based acid and possibility of increase residue production due to acid reactivity.

7. Conclusions

- An emulsion may be defined as a biphasic system consisting of two immiscible liquids, one of which (the dispersed phase) is finely and uniformly dispersed as globules throughout the second phase (the continuous phase).

- The main characteristic upon which emulsions are valued is the emulsion stability.

- Emulsion stability is directly related to the degree of the emulsion tightness and the force of bond between the primary phase and the dispersed phase.

- Emulsion stability is affected by (1) the characteristics of the two immiscible phases (the continuous and dispersed phases), (2) the degree of the agitation to which the mixture is subjected, and (3) the concentration and type of emulsifiers.

- Microemulsions are generally composed of hydrocarbons, surfactants/co-surfactants and brine.

- It is to be expected that the future energy demand will be met by a global energy mix that is undergoing a transition from the current dominance of fossil fuels to a more balanced distribution of energy sources.

- Macro/microemulsions based enhanced oil recovery improve both the microscopic displacement efficiency and the macroscopic sweep efficiency, thus leads to higher recovery factor.

- In enhanced oil recovery, the microemulsion flooding displays the unique properties of microemulsion systems, such as high viscosity and the ability to induce low interfacial tension, increasing oil extraction efficiency.

- In well stimulation emulsified acids are used during matrix acidizing and acid fracturing to retard acid reaction with rocks, to generate deeper penetration inside the reservoir.

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