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Oil emulsions and the different recent demulsification techniques in the petroleum industry - A review

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Abstract. The emulsions are formed during the production of crude oil, which is often accompanied by water. These emulsions are undesirable and should treat to remove the dispersed water and accompanying inorganic salts .so, many researchers have over the years focused to probe of the appropriate demulsification techniques in the petroleum sector in order to meet production and transportation requirements, and to reduce corrosion and catalyst poisoning and to maximize the overall profitability of the crude oil production. Therefore, this study presents an overview of the emulsions, formation, classification, Stability, and properties. practical demulsification techniques in the petroleum sector, including chemical, microwave irradiation, biological, thermal, membrane, electrical, and ultrasonic techniques for both oilfield and synthetic emulsions. Amongst these techniques, chemical demulsification has been the most widely applied and reported in the literature. Moreover, a more effective demulsification process could be attained by leveraging synergistic effects by combining one or more of these techniques

1. Introduction

Oil production and transportation via pipelines results in the formation of water-oil emulsions due to the presence of shear forces and pressure [1-2]. They are formed as water droplets or brine which are continuously dispersed in crude oil and are referred to as water-in-oil (w/o) emulsions. There are also emulsions which consist of crude oil droplets in brine or water (o/w) although they are rarely encountered [3-4]. When crude oil is extracted from a reservoir, it contains several impurities like sediments and water [5]. It may also contain hydrocarbons like asphaltenes, waxes, resins, solids from crude, and carboxylic acids which serve as natural emulsifiers [6]. There may be an accumulation of some of these components at the water-oil interface, resulting in the formation of a stable film that surrounds the droplets. This film promotes the formation of stable w/o emulsion by hindering the water droplets from coalescence [7].

Several problems may arise from the co-production of water and crude oil. This may include the cost associated with the pumping or transportation of the water by tanker or via the pipeline, corrosion of production facilities (like pipes, pumps, and downstream distillation columns), poisoning of the downstream by industrial catalysts, the need to install the extra equipment for the production of crude oil of export quality, as well as the issues related to improved crude oil viscosity as a result of the presence of small water droplets in the crude oil [8]. From the economic and operational perspectives, there is a need to ensure complete separation of water from crude oil prior to its transportation and subsequent refining [9]. The available crude oil demulsification techniques can be grouped into mechanical, chemical, thermal, and electrical techniques [10]. Chemical demulsification involves the use of chemicals to induce the destabilization of the shielding interfacial films, resulting in an improved



rate of emulsion breakage. As an economical and effective method, chemical additives are widely used in dewatering of crude oils emulsions [11]. Several parameters are involved in oil demulsification and the alteration of each parameter can have a significant influence on the stability of the emulsion. Such parameters include salinity, temperature, conc. of the emulsifier/demulsifier, agitation rate and its duration, pH, oil/water content, size and distribution of droplet [12, 13].

This review is a comprehensive survey of the related literature (previous and current studies) on petroleum emulsions, types, formation, stability, properties and braking of emulsions. The review also covered surfactant, their structure, type, and properties. Demulsifiers, their mechanism, influencing parameters, and water separation techniques from crude oils were also reviewed. The importance of separating water from petroleum was also reviewed from both technical and environmental perspectives.

2. Crude Oil Emulsions

2.1. Definition of Emulsions

An emulsion is defined as a phase that contains two immiscible liquids such as oil and water. In an emulsion system, one of the stages is dispersed in the second as globules; the phase that exists as globules is called the sparse phase, while the continuous phase is the phase that produced the dispersion model wherein the droplets are suspended. The diameter of the emulsion droplets usually falls within 0.5 μm or more [14]. The widespread occurrence of emulsion in our daily lives (such as in food, pulp, cosmetics, and pharmaceutical industry) made them a thing of great practical interest [15]. Although petroleum emulsions may not be well known, they are widespread and of significant importance in the petroleum industry. They are encountered in almost all aspects of the petroleum recovery and production processes, ranging from crude oil drilling, production, transportation, and processing [16]. Being that they are undesirable in the petroleum sector, they are often associated with the high pumping costs, reduced throughput, and corrosion of pipeline and other equipment [17].

2.2. Classification of Emulsions

Kokal et al. [18] inferred that oil is produced in a combined form with water and this mixture referred to as oil emulsion or oil field emulsion. A crude oil emulsion is often produced when the oil and water phases are vigorously stirred; nevertheless, once the stirring is stopped, there is an immediate breakdown in the emulsion [19]. There are three wide groups of emulsion - oil-in-water (o/w), water-in-oil (w/o), and multiple emulsions [like water-in-oil-in-water (w/o/w) and oil-in-water-in-oil (o/w/o)]. For instance, o/w/o implies the dispersion of oil droplets in water droplets which are further dispersed in a continuous oil phase, as depicted in figure. 1 [20]. Salomon (2006) suggested that there are other complex structures of emulsion. For instance, the disperse phase in double emulsions consists of another stage which may differ from the continuous phase in composition. Water-in-oil (w/o) emulsions normally contain less than or equal to 50 % of water while o/w emulsions have more than 80 % of water (o/w emulsion can also exist with less than 20 % of water) [21].

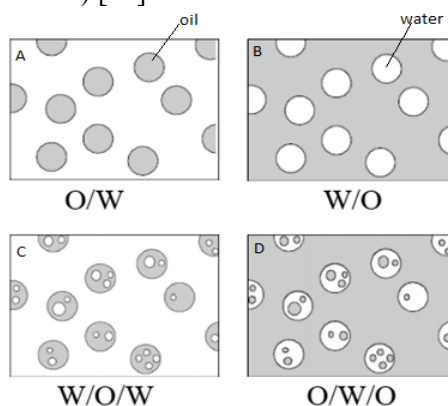


Figure 1. Types of emulsion (a) oil-in-water (b) water-in-oil (c) & (d) multiple emulsion.

2.3. The Formation of Crude Oil Emulsions

The formation of crude oil emulsions is usually observed in all stages of production, starting from the oil reservoirs through transportation. The formation of crude oil emulsion is initiated when there is contact between two immiscible liquids in the presence of an emulsifying agent provided there is adequate blending or an agitator that facilitates the dispersal of one liquid as droplets [22]. Several studies have shown that the formation of crude oil emulsions is strongly dependent on the composition of the crude oil which often consist of natural emulsifying agents such as asphaltenes, acidic compounds (naphthenic acids, fatty acid acids, aromatic acid), and resins [34]. These natural emulsifiers are abundant in heavy and extra heavy crude oils.

Authors have established that the emulsion formation and behavior can vary from one crude oil to another. A study by Delgado-Linares et al. [35] revealed that the natural surfactants in crude oil facilitate the reduction of interfacial tension of oil-water which in turn leads to the formation of the interfacial film. This interfacial film is characterized by mechanical strength and serves an important function in the formation and stability of the emulsion [36]. Hence, the variation in crude oil compositions might influence the significant changes in emulsification behavior. During the emulsification process, each of the natural surfactants plays a unique role. Asphaltene, which consists of a myriad of non-hydrocarbon compounds, helps to improve emulsion stability as a result of its good interfacial activity [37]. Analogous to asphaltene is resin, which consists of a myriad of macromolecular non-hydrocarbon compounds (relatively low molecular weight and polarity) and plays a significant role in the formation of crude oil emulsion [43]. Ashrafizadeh et al. [23-25] suggested that there are many ways of producing oil droplets to form emulsions, such as the utilization of devices like colloid mills, homogenizers (high pressure), dispersing machines, application of high shearing stresses, etc. Alwadani [26] also mentioned the possibility of automatic emulsification via chemical processes or via temperature-mediated nucleation processes in one of the phases. Table 1 shows some of the important parameters used by researchers to prepare emulsions.

Table 1. Some important parameters researchers used by previous researchers to prepare emulsions.

Type of emulsion	Water content (v/v)	Mixing time (min)	Mixing speed (rpm)	Type of emulsifier	Emulsifiers concentration	Ref
W/O	70/30	5-15	1800	Low sulfur waxy residue and Triton X-100.		[3]
O/W	50/50	0.5-1	1000	Ethoxylated nonylphenol family (RENEX) with an ethoxylated amine (Ultramina, 5 EO groups)		[27]
O/W	69, 72, and 66 vol.%	5-15	1000-2000	Triton X-100	0.3-2.5wt.%	[28]
W/O	70/30	30	800	Tallowalkylamine acetates or ARMACT	0.036 m3	[29]
O/W	Oil ratio 50-70% by total volume	5-15	10000-15000	SDDS, Triton X-100, Span 83, Tween 80, and Coco-Amide	0.5-1%	[30]
W/O	4/1	5	10000	n-heptane (analytical grade) and Toluene		[31]
O/W	90/10, 70/30 and 50/50	30 min.	9000			[32]
W/O	70/30	5	1300	Span 80	3%	[33]

2.4. The Stability of the Crude Oil Emulsions

Crude oil is made up of several components but mainly composed of carbon, hydrogen, and small

amounts of oxygen, nitrogen, sulfur, and other common metals like nickel, iron, and vanadium in trace amounts. The role of these elements is to encourage hydrogen bond formation and polar interactions between the asphaltene components. This interaction gives rise to the formation of the interfacial film and accounts for its strength and elasticity [34]. Except for microemulsions, all other emulsions are thermodynamically unstable. Meanwhile, emulsion destabilization requires a lot of time, and it may be impossible for a stable emulsion to resolve itself within a defined period without undergoing some chemical or mechanical treatments [35]. After the formation of some emulsions, they can be easily decomposed into oil and water phases; however, some other may persist for prolonged periods. Stability results from the small-sized droplet, the ratio of oil to water, the presence of some factors such as temperature, water pH, salt concentration, surfactants, etc. According to Mat et al. [36], stability refers to the “persistence of an emulsion in the environment” and has been considered an important property of w/o emulsions. The formation of a stable w/o emulsion requires the presence of an emulsifying agent like clay particles, chemicals, asphaltenes, naphthenic acid, waxes, and resins [37] which will help in the rigid layer formation around the dispersed droplets to prevent the occurrence of coalescence.

3. Emulsion Rheology and Shear Viscosity

The flow property of emulsions is their most important property, i.e., their rheology which is generally defined as the study of the flow and deformation of materials that are subjected to the influence of shear stress. The study of the rheological characteristics of emulsions is of great interest for both its scientific understanding and industrial application [38, 39]. The rheology characteristics of any material is an important physical attribute. According to Becker [50], the rheological characteristics of emulsions can be affected by six factors, including the surface phase viscosity, the division of the droplet volume in the continuous part, the indoor stage viscosity, the size and concentration of the dispersed phase, the type of emulsifying agent used and the created interfacial film at the interface, as well as the shear rate. As per Alwadani [40], the rheology behavior of an emulsion, based on its structure, can either be Newtonian or non-Newtonian. Emulsions may generally exhibit Newtonian behavior when the concentration of the disperse is low to medium but may behave as shear-thinning fluids when the dispersed amount is high. The interaction between droplets accounts for the increase in the viscosity as the amount of the dispersed phase increases. For the shear-thinning liquids, emulsions can be described by apparent shear viscosity η , which is similar to that of pure fluids. From Newton's law, $\eta = \tau_{ij} / \dot{\gamma}_{ij}$. η is the proportionality coefficient (or ratio) between shear stress (τ_{ij}) and rate of strain (or shear rate, $\dot{\gamma}_{ij}$). Factors affecting the shear viscosity of an emulsion are the viscosity of the constant phase, the dispersed part content, the viscosity of the dispersed phase, shear rate, temperature and the average size, and size distribution of droplets. The viscosity increases with the dispersed phase content due to interactions among droplets. If the pressure of a given emulsion sample is stable, the major influencing factor on the viscosity becomes the temperature and the dispersed phase concentration [38].

4. Phase Inversion Temperature (PIT)

The phase inversion phenomenon is described as an operation in which the continuous and dispersed phases of an emulsion abruptly exchanges phases from o/w to w/o emulsion or vice versa. Shinoda & Arai [41] devised an approach which depends on the determination of the phase inversion temperature (PIT) of a surfactant-oil-water mixture stirred under heat. In the presence of a surfactant, the dispersed phase is dependent on either the surfactants' relative affinity to the competent phases or on the arrangement of the phase additions that make up the emulsion. For instance, an o/w emulsion will be formed by a surfactant that has a high affinity for water at low temperatures, but when there is a change in the status of the emulsion, there may be phase obverse which implies a situation where the dispersed phase becomes the continuous phase, and vice versa. Similarly, any change in the temperature will cause phase inversion due to the altering of the surfactants' affinity to each phase. As per Friberg, the PIT is the temperature where the preferential solubility of an emulsifier or a surfactant shifts from water to oil or oil to water [42]. Being that this approach considers several variables that influence the PIT, it is a more trusted approach compared to the earlier methods. One thing is that the PIT method is only applicable to nonionic surfactants due to the low sensitivity of ionic surfactants to temperature [43, 44]. Other factors which may be considered to affect phase inversion are the type and concentration of the

emulsifiers, as well as the influence of physical parameters like temperature and mechanical shear. Phase inversion may also be said to depend on the characteristics of the emulsification protocol which portrays the way of making or modifying the emulsion, or the changes in the composition of the emulsion with time or space [45].

5. Demulsification techniques

Demulsification refers to the breaking down of emulsion into its component incompatible phases (i.e. water and oil). It is an important process in the petroleum sector where emulsions are always encountered as deliberate or natural occurrences. The separation of water from crude oil is an important process in the petroleum refineries as it must be performed prior to oil refining. The current method of breaking w/o emulsion via the use of chemical additives called emulsion breakers but technically, the resistance of w/o emulsions to coalescence, as well as their response to demulsification processes is a function of the physical and chemical properties of the oil from which such emulsions are formed. They also depend on aging and emulsification conditions. This suggests variability in the methods for the optimization of w/o emulsion demulsification from one setting to the other [46]. Various methods of emulsion separation have been suggested by the previous researchers; however, there are two major demulsification approaches in current use – physical and chemical approaches. With the chemical method, a suitable demulsifier is added into the emulsion while the physical technique involves heating, mechanical or electrical methods [47]. The thermochemical method is the commonly used method in the industries; it involves heating with the addition of a demulsifier [48]. Emulsions can also be demulsified using methods like filtration, membrane separation, and pH adjustment [49]. The subsequent sections will focus on the survey of the existing and future methods of demulsification.

5.1. Chemical demulsification

This involves the flocculation and/or alteration of the characteristics of the interfacial films using chemicals to cause coalescence. It is the common method for the treatment of w/o and o/w emulsion where the breaking process is facilitated by the chemical additives [3]. Several factors like the type of oil and its viscosity, the size distribution of the water phase, and the presence of solids can affect the performance of a demulsifier [50]. A study by Ben Mya et al. [51] reported the use of REB09305 OS demulsifier to treat Algerian crude oil; the study focused on the effects of the contact time, temperature, and centrifugation speed on the w/o separation efficiency. The results of the study showed a 100% demulsification ratio to be achieved at the process condition of demulsifier dose 20 ppm, ambient temperature, centrifugation speed 1200 rpm, and contact time of 45 min. Furthermore, Yau et al. [52] evaluated the performance of different demulsifiers (including 37 different types of anionic, cationic and nonionic emulsifiers) on the demulsification of Marpol oil waste. From the results, the best o/w separation performance was achieved by the anionic and nonionic surfactants after 30 h at a temperature of 70°C.

Another study by Liu et al. [53] used magnetic graphene oxide (M-GO) to separate o/w emulsions. The results showed the capability of M-GO to facilitate the separation of the o/w emulsions within a short period. The M-GO was recycled 6–7 times and still achieved 99.98% demulsification efficiency at the optimum concentration. Alginite was used as a demulsifying agent by Hippmann et al. [6] to demulsify Hungarian crude oil shale. During the study, the w/o emulsion used was made up of equal concentrations of crude oil and brine. From the results, the addition of alginite to the emulsion caused phase separation within a few minutes. Li et al. [54] demulsified water-in-aging crude oil (WACO) emulsions using a novel type of tannic acid phenol-amine (TAPA) polyether with numerous branches and aromatic rings. From the results, the laboratory tests showed a demulsification efficiency of 91.7% in 90 min while the offshore test showed 97.9% within 45 min toward w/o emulsions. Hazrati et al. [55] demulsified w/o emulsion samples using different ionic liquids ILs. The results showed the maximum water separation performance of 86–95% and interfacial tension (IFT) of 0.7–6.26 mN/m to be achieved within 24 h.

Table 2. Summary of the recent studies on chemical demulsifiers.

Type of emulsion	Type of demulsification	Emulsifier/demulsifier concentration	Ratio & effect of demulsifier on separation	Year of study	Ref.
W/O	REB09305 OS demulsifier	5-40 ppm	100% demulsification ratio achieved at the process condition of demulsifier dose 20 ppm, ambient temperature, centrifugation speed 1200 rpm, and contact time of 45 min	2017	[51]
W/O	Anionic, cationic and nonionic.		Anionic and nonionic surfactants performed best after 30 h at 70°C.	2017	[52]
O/W	Magnetic graphene oxide	0.04-0.25 wt%,	99.98% demulsification efficiency achieved at an optimal dosage.	2017	[53]
W/O	Alginate	0.5 wt.%	The water removal capacity was >98%.	2018	[6]
WACO	Polyether	50-150 mg/L	laboratory test showed 91.7% demulsification efficiency within 90 min and 97.9% within 45 min on an offshore platform.	2018	[54]
W/O	Ionic liquids	500-3500 ppm	86–95% water separation efficiency achieved within 24 h.	2018	[55]

5.2. Biological demulsification

The early 1980s witnessed the start of researches on biological demulsification [56] when it was suggested as potential substitutes to chemical demulsifiers in the petroleum sector. Microbial demulsification is based on the concept that the existing hydrocarbons in the emulsion can serve as the source of nutrients to microbes. A study by Wen et al. [57] reported the use of S-XJ-1 as a biological demulsifier. The investigation, with the aid of a Turbiscan stability analyzer, showed a similar performance to chemical demulsification as they S-XJ-1 cells participated in the breakdown of the emulsion, thereby achieving 81.3% demulsification of w/o emulsion within 24 h at the cell conc. of 500 mg/L. Xuwei et al. [58] reported the use of novel biodemulsifier, rhamnolipid to demulsify waste crude oil. The results showed that waste crude oil treatment with the novel rhamnolipid achieved a dewatering efficiency of over 90%. Another study by Roostaie et al. [59] had investigated the use of cellulose-based compounds as demulsifier. The study focused on the performance of different forms of cellulose at different viscosity levels. It also investigated the breakdown of crude oil emulsion using a mixture of ethylcellulose and ethoxylated coco amine. From the results, all the cellulose variants exhibited poor dehydration efficiency when used alone. However, a dehydration efficiency of 96.8% was achieved with the mixture of 500 ppm ethoxylated coco amine and 1000 ppm ethylcellulose 46 (EC46) within 12 h.

Saxena et al. [60] studied the use of a biodegradable anionic as a chemical to enhance the process of oil recovery. The surfactant exhibited good wetting properties by changing the surface of the quartz and carbonate rocks from oil-wet to water-wet. The surfactant slugs were used at different concentrations to perform flooding experiments and an additional 25%–27% oil recovery was reported after the conventional flooding. Jiang et al. [61] studied α -amylase and its effect as a bio demulsifier on the demulsification rate and viscosity of amphiphilic polymer solution. The conc. of α -amylase, salinity, and temperature were altered during the experiments and the results show α -amylase to be a good bio demulsifier as it can improve the rate of de-emulsification of such emulsions. Akbari & Biria [62] investigated *Acinetobacter calcoaceticus* for the production of bio-demulsifiers and the ability of such demulsifiers to breakdown w/o emulsions. From the results, the microbe, at the optimal conditions,

produced an extracellular biodemulsifier which caused a reduction of the surface tension to 38.6 mN/m and facilitated the breakdown of 95% of a surfactant-reinforced emulsion.

Table 3. Summary of the recent studies on bio-demulsifiers.

Type of emulsion	Name of biodemulsifier	Demulsifier concentration	Ratio & effect of demulsifier on separation	Year of study	Ref
W/O	<i>Candida sphaerica</i> UCP 0995		40% demulsification ration achieved.	2015	[63]
W/O	Cellulose-based compounds	100-1500ppm	Ethylcellulose is efficient in breaking the emulsion but its major drawback is the low dehydration rate.	2017	[59]
Enhanced oil recovery process	Alpha sulfonated ethyl ester (α -SEE)		The surfactant exhibited good wetting characteristics	2017	[60]
O/W	α -amylase	0-6000 mg/L	α - amylase exhibited good bio demulsification performance.	2018	[61]
W/O	Biodemulsifier		95% of the emulsion was demulsified.	2018	[62]

5.3. Mechanical demulsification

According to Auflem & Jiang [64, 65], the mechanical demulsification process involves the use of mechanical forces to breakdown the physical barrier/difference in the water and oil phase densities to achieve separation. Among the tools that can be used to achieve mechanical separation during crude oil, demulsification include cyclones, centrifugal separators, gravity settling tanks, etc. The centrifuge has not been as widely used as the other methods for treating emulsions due to its high capital cost and low capacity [66]. A study by Hao et al. [67] focused on the removal of oil from water using centrifugal contactors. The aim of the study is to address the over-standard oil content problem in electric desalting wastewater. The parameters considered during the study include the effects of the rotor speed, the water temperature, the inlet flow rate, the crude oil density, and the oil content. From the results, there were increases in oil removal efficiency as the inlet flow rate was decreasing and increasing oil conc. with decreasing oil density. Under gravity, the emulsions were allowed to sediment under the influence of normal gravitational force. This sedimentation promoted coalescence by bringing the dispersed phase droplets closer. Centrifugation is utilized in some processes to achieve closer contact with droplets in a rapid manner [68].

5.4. Thermal demulsification

Thermal demulsification involves the use of heat to promote the breakdown of emulsion in an oil field or refinery. In the lab scale, the commonly used method is the conventional hot plate to generate the required temperature. The rigidity of the interface which promotes the coalescence of droplets when they collide may be affected high temperature. Furthermore, a higher temperature can encourage the rate of collision between the droplets and cause a reduction in the stability of the emulsion. One effect of heating is that light compounds that help increase the density of crude oil could be lost, thereby affecting gravity settling [69, 70]. Heat treatment is often used in conjunction with chemicals in most cases to enhance the efficiency of the process since the viscosity of emulsions can be tremendously reduced by temperature [71]. The effectiveness of thermal demulsification has been reported by various researchers; for instance, Tov et al. [72] studied the effect of a thermo-chemical demulsification process on w/o emulsion resolution and reported as follows: the thermo-chemical method is more efficient in breaking down w/o emulsions of paraffinic petroleum compared to asphaltene oil; the application of

heat could facilitate a slow breakdown of the emulsion but the addition of the chemicals will progress the separation process rapidly. Abdurahman et al. [73] compared hot-plate w/o emulsions breakdown with microwave-assisted demulsification and reported the microwave-assisted process to have demonstrated a great separation power compared to the hotplate heating possibly due to the microwave heating pattern where materials are volumetrically heated based on their dielectric characteristics. Binks and Rocher [74] investigated the effect of temperature on the breakdown of wax-stabilized w/o emulsion. For the stability test, the amount of water or oil resolved from the emulsion was tested over a given period. The results showed a temperature-mediated increase in the rate of coalescence because of the fusing, melting, and varnishing of the wax particles at the interface at an elevated temperature, thereby inducing the droplets to come together easily and merge (meaning separation) [74]. Taylor et al. [75] investigated the temperature effect on the breakdown of bitumen emulsions and reported a gradual breakage of the emulsion as the temperature of the system approaches the cloud point. Furthermore, there was a decrease in the bitumen-water interfacial tension as the temperature was increasing; this decreases almost vanished at the cloud point temperature. The effect of temperature on demulsification processes was investigated by Al-Sabagh et al. [76] using TE18P. From the results, the demulsification efficiency of asphaltene crude oil improved by 8.7% asphaltene content as the temperature was increased from 50°C to 70°C.

5.5. Microwave demulsification

The first microwave irradiation-assisted demulsification process was reported by Wolf in 1986 [77]. Microwave heating has been reported to be superior to the traditional heating schemes in the breakdown of emulsions as a result of its less energy consumption and faster separation rate [78]. The microwave heating technique can be applied as a standalone demulsification process in the petroleum sector as it can minimize the use of chemical demulsifiers [79]. For instance, Martínez-Palou et al. [48] comparatively studied the performance of microwave and oil bath heating in terms of the water separation time of o/w emulsion. They also studied the effect of salt content and a chemical demulsifier on the demulsification of o/w emulsion. From the results, a greater degree of water separation was achieved by the microwave heating technique in less time compared to the traditional oil bath heating; increase in the microwave power and salt content also increased the separation of o/w emulsions under the co-influence of chemical demulsifier [48]. Binner et al. [80] studied the use of microwave heating and natural gravity settling techniques to separate w/o emulsions. The result of the study showed microwave heating to improve the coalescence of the water phase droplets in w/o emulsions, while the separation time was reported to reduce significantly compared to the untreated emulsions. da Silva et al. [81] applied microwave technology to the breakage of water-in-heavy crude oil emulsions. The study focused on the effects of the heating mode, pH, temperature, and process time on the acidic species migration from crude oil to water during heavy crude oil demulsification. From the results, the temperature was found to be the most influential variable as it favors the separation of a larger number of acidic species. The use of a microwave to breakdown emulsion was reported by Santos et al. [82]. The study focused on the influence of the modes of microwave application (single and multiple modes) on the efficiency of a synthetic w/o emulsion separation. The results showed the microwave efficiency to be influenced by the heating temperature and water content of the emulsion. Regarding the modes, the single-mode reached highest demulsification efficiency using lesser energy compared to the multimode; however, the reproducibility of the multimode was better than that of the single-mode.

5.6. Electrical demulsification

Electrical demulsification involves the deformation of droplets and generation of an attraction force between drops (thus leading to coalescence) by applying an electric field. The application of the electric field makes it easier for small water droplets to quickly fuse into larger ones. The droplets deform in the electric field as they migrate to each other. Coalescence occurs more quickly as the droplets are elongated and deformed [83]. Electrical demulsification is considered a better option to chemical and thermal demulsification; however, the way to adapt this method to the different emulsion properties is yet to be understood properly [84]. So, in this review, some of the previous studies that used the electrical method as a demulsifier for emulsions will be reviewed. Mousavi et al. [85] studied the effect of pulsatile

electric fields (PEF) on the formation of the secondary droplets. From the results, the production of secondary droplets proceeded at a low-frequency PEF; the study also approved that increases in the PEF frequency will suppress the DC electric field. Another study by Zhang et al. [86] focused on the effect of surfactants on the breakdown of water droplets suspended in a dielectric oil (immiscible) under an electric field. The experiments proceeded on a single drop in a microscopic cell under the influence of an externally applied electric field. Different concentrations of Tween 20 and SDS were also investigated as surfactants. From the results, the extent of deformation of the big drops was faster under the influence of electric field compared to the smaller drops.

Wang et al. [87] investigated two charged droplets for electro-coalescence behaviors under different fields (constant and pulsed direct current) using molecular simulations. The outcome of the simulations showed the exertion of an attractive force on the two droplets upon the application of the constant DC electric field. This electric field was reported to accelerate the approach velocity between the two droplets. However, the approach velocities of the two droplets under the pulsed DC electric field accelerated within the pulse duration but was almost stable during the pulse interval. Qiao et al. [88] investigated the demulsification of steam-assisted gravity drainage (SAGD) by applying the demulsifier FC20 under an electric field. The results indicated the process of the water content separation from the emulsion to be reduced by 1.0% upon the addition of 30% diesel oil and 300 mg/L FC20. This percentage reduction occurred under an electric field of 750 V/cm for 20 min and 4 h settling time at 90°C. Li et al. [89] investigated the effects of power voltage, duty ratio, electric frequency, operating time and operating temperature on the use of the DTS-4C airtight oil dehydration apparatus to dehydrate ultra-heavy oil. From the results, the best performance was achieved at the following condition: 5.5 kV voltage magnitude; 0.5 duty ratio 0.5; 120°C operating temperature, 4.0 kHz electric frequency; and 3 h operating time. This condition achieved a dehydration efficiency of 97.81% and post-electric dehydration water content of 0.37 wt%; these are acceptable results for oil refineries.

5.7. Ultrasonic demulsification

Much attention has been given to ultrasonic demulsification processes in the last couple of years due to its associated simplicity and efficiency [90]. Several studies have been reported on the use of the ultrasonic method as a demulsifier of emulsions. For instance, Check and Mowla [91] investigated the effect of irradiation input power, irradiation time, injected water volume, and temperature on the efficiency of salt and water removal from crude oil via ultrasonic irradiation. The results showed an input power of 57.7 W, the temperature of 100°C, and irradiation time of 6.2 min as the optimal condition for the ultrasonic irradiation of the crude oil. The desalting/dehydration efficiencies under these optimum conditions were recorded as 84% and 99.8%, respectively. Antes et al. [92] studied the possibility of crude oil demulsification via an indirect application of low-frequency ultrasound without any chemical demulsifier. Under the reported experimental condition, a demulsification efficiency of about 65% was achieved on an emulsion with a water content of 50% and DSD of 10 μm . The study reported higher demulsification efficiency at an ultrasound temperature of 45°C and power of 160 W within 15 min. Xie et al. [93] reported the use of a pulsed ultrasonic irradiation technique to develop a method for oil phase separation from waste refinery oil emulsion. The results of the experiments using the method showed the developed method to be better in coalescing the water droplets, thereby dehydrating the waste refinery oil. An 8% decrease in the waste oil water content was achieved which complied with the refinery requirements on the acceptable water content of waste oil.

Khajehesamedini et al. [94] worked on the reduction of the utilization of chemical demulsifiers in crude oil processing by using low-frequency ultrasonic waves as an alternative method. The study focused on the effects of the process parameters (ultrasonic field intensity, initial water content, and irradiation time) on the separation efficiency. From the results, it was concluded that chemical emulsifiers must be involved in demulsification processes, but the rate of its utilization can be reduced by 50% when working on a w/o emulsion by ensuring the use of a suitable ultrasonic waves intensity and irradiation time. Wang et al. [95] reported the use of ultrasonic irradiation to demulsify super-heavy crude oil using static experiments at high temperatures. The experiment investigated the influence of both ultrasonic

(frequency, power, time, and sound intensity) and external factors (temperature, water ratio, and sedimentation time) on the demulsification process. The results showed an increase in the rate of dehydration as the ultrasonic sound intensity increases but up to a certain level. The increase in sedimentation time was also reported to increase the dehydration rate at a given level. It was suggested that higher temperatures improved the ultrasonic dehydration and demulsification processes, while the effect of water ratio on the dehydration rate was reported as heavy and complex.

5.8. Membrane demulsification

Membrane separation has been considered as a treatment method for oily wastewater since 1973. The major advantages of this process include the homogeneity in the quality of the permeate irrespective of influent differences, non-involvement of any chemical, efficiency in the separation of small droplets, high separation efficiency, cost-effectiveness, and compact setting. However, its application is restricted by the high capital costs required for large volumes of effluent, polymeric membranes degradation, and fouling during operation, fairly low permeate flux, as well as sensitivity to chlorinated and polar solutions [96]. Several studies have been dedicated to the use of membranes as demulsifiers. For instance, Zhang et al. [97] focused on the feasibility of treating different emulsion wastewaters using an integrated ultrafiltration process (UF) that consists of a combined chemical and vibratory shear breakage of emulsions in an anaerobic/aerobic biofilm reactor. It was observed from the results that better oil removal was achieved with calcium chloride compared to the other inorganic salts. It was also suggested that chemical pre-treatment prior to demulsification could improve membrane filtration and oil removal in wastewater demulsification via a vibratory shear-enhanced technique.

Lin et al. [98] reported the removal of 4-methoxyphenyl (4-MP) from wastewater using a w/o/w Pickering emulsion liquid membrane. The study reported that the demulsification of the water content of oil can be achieved via magnetic force or centrifugation without significantly affecting the chemistry of the oil phase. From the results, the extraction efficiency of >86% was achieved when functionalized Fe₃O₄ nanoparticle was used as the emulsifier. Skale et al. [99] worked on the feasibility of using ultrafiltration to separate w/o Pickering emulsions. The study reported an unexpected flux behavior of the Pickering emulsions, while the permeability was increasing with higher pressure levels. Pressures between 1 and 4 bars recorded fluxes ranging from 3 to 40 L/ (m² h). It was also reported that the emulsions can be concentrated to about 80% water phase fraction. A study by Othman et al. [33] reported the use of palm oil-based organic phase as diluents in an emulsion liquid membrane process (ELM) for the treatment of artificial wastewater that contains 300 × 10⁻⁶ of phenol. From the results, the palm oil-based ELM showed efficient phenol removal from the wastewater at an optimum condition that consists of 500 rpm agitation rate, 3% span 80 conc., external phase pH of 8, the contact time of 5 min, NaOH conc. of 0.1 mol/L as stripping agent, and treat ratio of 1:10. This condition achieved an extraction performance of about 83%, representing 11 folds' enhancement.

6. Conclusions

Water mix with petroleum oil inside the well or during the process of oil pumping from the reservoir. It also be encountered during desalting processes in the form of different forms of emulsion, such as w/o, o/w, w/o/w, and o/w/o. Such emulsions are sources of economic and operational concerns to the industry; hence, several solutions have been proposed for addressing these concerns. Finding the solution to emulsions demands detailed knowledge and serious studies on both the possible consequence of its formation and the factors that facilitate its formation; factors that contribute to its stabilization must also be considered. Several studies have been performed from both the Industrial and academic perspectives on the role of several factors in the formation of stable petroleum emulsions. This paper strived to overview emulsions, their formation, kinds, constancy, and properties. Also reviewed are effective demulsification parameters and methods, including chemical, biological, thermal, microwave irradiation, electrical, ultrasonic, and membrane methods which are used for both oilfield and synthetic emulsions. Amongst these techniques, chemical demulsification has been the most widely applied and reported in the literature. It is worth noting that the efficiency of each of these techniques is dependent on the operating parameters and their interplay. Moreover, a more effective demulsification process

could be attained by leveraging synergistic effects by combining one or more of these techniques, as discussed in this review.

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