Petroleum Research 7 (2022) 459–472

Contents lists available at ScienceDirect

Petroleum Research

journal homepage: http://www.keaipublishing.com/en/journals/petroleum-research/

Formation, stabilization and chemical demulsification of crude oil-in-water emulsions: A review

Edith Yonguep [a], Kashala Fabrice Kapiamba [b, *], Katende Jonathan Kabamba [a], Mahabubur Chowdhury [a]

[a] Department of Chemical Engineering, Cape Peninsula University of Technology, Symphony Way, PO Box 1906, Bellville, 7535, Cape Town, South Africa
[b] Department of Civil, Architectural and Environmental Engineering, Missouri University of Science and Technology, Rolla, MO, 65401, USA

ARTICLE INFO

Article history:
Received 17 November 2021
Received in revised form
27 January 2022
Accepted 28 January 2022
Available online 7 February 2022

Keywords:
Crude oil
Enhanced oil recovery
Emulsions
Stabilization
Demulsification
Surfactants
Demulsifiers
Coalescence

ABSTRACT

The crude oil recovery process is frequently associated with the formation of stable emulsions due to factors such as turbulent flow in pipelines and the presence of surface-active substances that naturally occur in crude oil. These emulsions are undesirable for the petroleum industry because their destruction/treatment adds to the overall production cost and causes the loss of valuable amounts of crude oil. Therefore, it is essential, for economic and environmental reasons, to optimize the crude oil demulsification process. The effective treatment of crude oil emulsions requires understanding of the process and factors leading to their formation and stabilization. In this sense, suitable treatment methods and possible preventive measures to avoid their formation can be employed. The present study reviews recent oilfield emulsion types and the factors responsible for their formation and stabilization. The different demulsification techniques employed were then extensively examined. Demulsification techniques include mechanical, thermal, electrical, and chemical methods with different demulsification mechanisms affected by many factors such as emulsions type and properties, demulsifiers characteristics, presence of solids stabilized emulsions, etc. The demulsification efficiency depends on the operating parameters of the process, the economics involved, and the environmental impact, which are the main factors considered in selecting a suitable demulsification technique. Future research on the demulsification of crude oil emulsions should focus on real crude oil emulsions studies at a pilot scale level, the effect of aging on crude oil emulsions, the combination of multiple demulsification techniques and their synergistic effects, and the use of natural, ecofriendly demulsifiers.

1. Introduction

Crude oil, also known as petroleum, is a natural product from dead animals and vegetation that accumulated below the Earth's surface thousands of years ago (Umar et al., 2018). Intensive exploration and production of crude oil has remained a prominent activity for over a century due to the increasing demand for energy and fuel derivatives in several sectors of society (Abdulredha et al., 2020). The crude oil is usually extracted by creating a reasonable pressure gradient to propel the oil from the reservoir to the surface. The overall extraction process (on-shore and off-shore) is often achieved in the primary, secondary, and tertiary stages. In the primary stage, the crude oil is recovered by the inherent underground pressure within the reservoirs. This pressure is high enough to force the crude oil from the production reservoir to the surface during drilling. Next, the crude oil is brought to the surface using an artificial lifting mechanism consisting of valves, pumps, and fittings connecting the head of the well to the pipeline network. However, over a long processing time, the underground pressure drops and declines the recovery efficiency. The recovery efficiency at this primary stage varies from 10% to 30% of the initial amount of crude oil in the reservoir (Alagorni et al., 2015). Next, water and gases such as CO_2, CH_4 or N_2 are injected into the reservoir to improve crude oil recovery (Pashakolaie et al., 2015). The expansion of these gases as they dissolve in the crude oil provides additional pressure in the reservoir to maintain the initial pressure; thus, this is known as the secondary stage to improve recovery efficiency. This technique can improve the recovery efficiency to about 50%. Both

* Corresponding author.
E-mail address: kapiamba.kashalafabrice@mst.edu (K.F. Kapiamba).

https://doi.org/10.1016/j.ptlrs.2022.01.007

primary and secondary recovery stages produce, on average, less than one-third of the original oil-in-place. Hence, the tertiary or enhanced oil recovery stage (EOR) is generally employed to recover the remaining oil trapped underground. There are three types of EOR stages: thermal method (injection of heat), miscible gas injection method (injection of solvent), and chemical method (injection of chemicals such as surfactants, alkali, and polymers). The thermal method is usually used for heavy or viscous crude, the heat in the form of hot water or steam is introduced into the reservoir to raise temperature of the oil to reduce its viscosity and subsequently facilitate the crude oil extraction. The miscible gas injection is used for light oil reservoirs, commonly, the used gases include CO_2, N_2, and hydrocarbon gases such as propane and butane. In the chemical method, chemicals such as polymers and surfactants or alkali are used to reduce mobility of the injected fluid and reduce the interfacial tension (IFT) of oil and water (Pashakolaie et al., 2015; Zolfaghari et al., 2016). EOR methods usually improve crude oil production up to 80% more than primary and secondary recovery.

The crude oil share decreases towards the end of reservoir life while the amount of water increases, especially if the reservoir is driven by a natural aquifer. Therefore, fluids generated from EOR are a mixture of crude oil, water, dissolved solids, sand, silt, and other compounds, including organic and inorganic elements and some chemical compounds injected during production (Abdulredha et al., 2020a). This mixture is generally recovered in the form of emulsions known as crude oil emulsions. The common crude oil emulsions encountered in oilfields are water-in-oil emulsions (W/O) which consist of droplets of water dispersed in the crude oil and oil-in-water emulsions (O/W) consisting of oil droplets dispersed in water, other types such as water-in-oil-in-water and oil-in-water-in-oil types may also be found.

The formation of emulsions during the crude oil extraction is almost inevitable and very costly to the petroleum industry. Researchers have reported that the crude oil emulsions are associated with corrosion of pipelines and equipment due to the presence of alkaline clay products, increase in pumping cost due to the high viscosity of the emulsions, poisoning of catalysts. They therefore require longer retention times to separate, which increase the cost of the overall crude oil production (Abdulredha et al., 2020). The emulsions also influence the nature of the oil spilled in the sea and the clean-up process. They must therefore be treated to meet set standards for production and transportation and to reduce corrosion and catalyst poisoning that could occur in further processes. In this paper, the formation of emulsions in crude oil industries is analyzed, and the mechanisms and factors that affect their formation and stabilization are discussed; furthermore, techniques that have been employed to demulsify crude oil chemically are introduced; lastly, some future directions and areas for study are proposed.

2. Formation of crude oil emulsions

Crude oil emulsions form when the crude oil comes into contact with water during the extraction from the reservoir to the surface and during processing (Abdulredha et al., 2020). Although crude oil and water are initially present in separated phases, formation of these emulsions occurs mainly due to turbulent flow in pipelines (Fingas, 1995). The turbulence occurs when the kinetic energy of one liquid (single-phase) becomes higher than the other two liquids (two-phase) at the same liquid flow rate. This turbulence produces enough energy to deform, break and disperse the phases (oil and water) into one another. The process can also be achieved by shaking, mixing with a rotor-stator system, or high-pressure homogenization when a liquid is injected through porous membranes (Schultz et al., 2004). For instance, during drilling, the emulsions form from the movement of the pump bars, pump cylinders, and elevating pipes. Throughout the drilling process, the agitation, mixing, and turbulence energy formed in the wellbores, the surface of the chokes, valves, and pumps, generate sufficiently high shear forces to disperse water as droplets in the oil phase and vice versa, which cause emulsions to form.

Kobayashi et al. (2002) studied the process of emulsion formation using a novel hydrophilic polycarbonate membrane with a mean pore size of 10 μm. The droplet deformation processes was analyzed using a microscope video system. The emulsion was prepared by forcing the dispersed phase into continuous through a peristaltic pump's membrane pores. The average flow velocity of the continuous phase varied from 0.023 to 0.52 m/s. They observed a significant distortion of the shapes of the droplets at high flow velocity which led to the reduction of their size. Furthermore, they observed that as the flow velocity increased, a higher shear force was produced to weaken the interfacial tension force between crude oil and water, reduce the droplets' size, which consequently facilitated the formation of emulsions. Dol et al. (2018) carried out a study on the formation of water-in-oil emulsions using a continuous flow loop. Parameters such as water cuts (0–40%), Reynolds number flow regimes: laminar ($1100 < Re < 1800$) and turbulent ($2400 < Re < 2800$) as well as the pipeline constrictions: gradual contraction ratios of 0.50 and 0.75, and sudden contraction with contraction ratios of 0.50 and 0.75, were investigated, to study their impact on the emulsification process. The results indicated that the shear stress increased with increased water cut from 0 to 10%, and 5–10% for laminar and turbulent flow regimes, and the collision frequency of dispersed water droplets was high when the water droplets per unit volume were high; at a higher flow rate, there is more energy in the flow as a result of that, the emulsions are broken into smaller droplets; additionally in pipelines with sudden contraction higher shear stress was produced as compared to those with gradual contraction and as a result more emulsions were formed.

Besides the turbulence through chokes and valves, natural surface-active agents called surfactants asphaltenes, resins, waxes present in the reservoirs significantly contribute to the formation of emulsions (Dicharry et al., 2006). Surfactants work by attaching themselves to the dispersed droplets and preventing them from coalescing thus promoting emulsions formation. It can be said from the above studies that crude oil emulsions form because of high agitation energy called turbulence, but they are stabilized by the natural compounds of the crude oil.

3. Crude oil emulsions characteristics

The composition of crude oil emulsions varies depending on the type of production reservoir, geology of the rock, and oilfield location. In general, crude oil emulsions possesse the characteristics of the rocks it has been in contact with. Crude emulsion comprises a mixture of natural organic and inorganic compounds and chemicals added during EOR processes. The organic compounds are the oil and grease components, including benzene, toluene, ethylbenzene, and xylene (BTEX), which is usually present in the form of tiny droplets (0.5–200 μm), dissolved in water. Inorganic compounds are total dissolved solids (TDS) and total suspended solids (TSS) found in the form of anions such as Cl^-, SO_4^{2-}, CO_3^{2-}, HCO_3^- and cations such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+} and Fe^{2+}. Crude oil contains a percentage of dissolved gasses, liquids and solids, commonly grouped as saturates, aromatics, resins and asphaltenes and referred to as SARA analysis (Fakher et al., 2020). Some naturally occurring radioactive material (NORM) such as Radium ^{226}R and ^{228}R isotopes have also been identified. Heavy metals are mostly Cadmium, Chromium, Copper, Lead, Mercury, Nickel, Silver,

and Zinc at mild concentrations. Table 1 shows physicochemical composition of a typical crude oil emulsion.

4. Stability of crude oil emulsions

From a thermodynamic perspective, emulsions are unstable systems due to the natural tendency of the phases to separate (Ho et al., 2021; Umar et al., 2018). The crude oil emulsions are stable because there exists an interfacial network (usually a thin and rigid film) surrounding the droplets of water, which prevents the droplets from assembling and coalescing (Dicharry et al., 2006). The compounds responsible for the formation and stabilization of the crude oil emulsions are not explicitly known because the nature and the composition of crude oil vary depending on reservoir location and composition of the reservoir's rocks. Moreover, it is believed that colloidal asphalt, which includes all asphalts and similar substances present in crude oil colloidal dispersions with surfactant properties, can stabilize crude oil emulsions. The crude oil emulsions form due to the asphaltenes, and resins compounds found in the crude oil. Additionally, compounds with higher solubility in oil than the water phase are also responsible for the formation of stable emulsions. Organic and inorganic compounds like BTEX TDS, TSS, and chemicals (surfactants) initially present or added to the reservoir may also contribute to the formation and stabilization of the crude oil emulsions. The stability of crude oil emulsion depends on the rheological properties of the emulsion (high viscosity of the interfacial film), the concentration of the asphaltenes and resins compounds as well as the oil concentration (I. Masalova et al., 2018; Irina Masalova et al., 2018). As the viscosity of the interfacial films increases, it reduces the drainage rate of the films during the 'droplets' coalescence by creating a repulsive force, which consequently lowers the rate of the emulsion droplet's breakdown (Kang et al., 2011). The properties of interfacial films depend on several factors, including but not limited to, polar molecules concentration in the heavy oil, crude oil type (asphaltic and paraffinic), aging time, temperature, pH, and composition of the water phase. Solid particles such as sand, particles found in seawater including suspended sediments, dissolved surfactants that accumulate at the water-oil interface, including metallic salts, organic acids, organic bases and organometallics, and other tiny solid particles can also enhance the formation of the interfacial film resulting in further emulsion stabilization. These factors affect the emulsions stabilization process in various ways. For example, the oil's lighter components (alkanes and aromatics) dissolve species with higher molecular-weight (Asphaltenes, resins, and waxes). The crude oil emulsion remains stable for as long as the solvency interaction is maintained in the oil and thermodynamic conditions do not vary.

Various factors influence the formation and stability of crude oil emulsions. These factors which include but not limited to the presence of asphaltenes, resins, surfactants, and brine water, which will be discussed in the following sections.

Table 1
Characteristics of oil field emulsions (Adapted from (Fakhru'l-Razi et al., 2009)).

Parameters	Values, mg/L	Heavy metals	mg/L
Density	1014–1140	Calcium	13–25 800
Conductivity	4200–58 600	Sodium	132–97 000
Surface tension	43–78	Potassium	23–4300
pH	4.3–10	Magnesium	8–6000
TOC	0–1500	Iron	<0.1–100
COD	0–1220	Aluminium	310–410
TSS	1.2–1000	Boron	5–95
Total oil	2–565	Barium	1.3–650
Volatile (BTEX)	0.39–35	Cadmium	<0.005–0.2
Base neutrals	0 – <140	Copper	<0.02–1.5
Total non-volatile (μg/L)	0–275	Chromium	0.02–1.1
Chloride	80–200 000	Lithium	3–50
Bicarbonates	77–3990	Manganese	0.004–175
Sulfate	<2–1650	Lead	0.002–8.8
Ammoniacal Nitrogen	10–300	Strontium	0.02–1000
Sulphite	0–10	Titanium	<0.01–0.7
Total polar	9.7–600	Zinc	0.01–35
Higher acids	<1–63	Arsenic	<0.005–0.3
Phenols	0.009–23	Mercury	<0.005–0.3
Volatile fatty acids	2–4900	Silver	<0.001–0.15

4.1. Asphaltenes

Asphaltenes are the fraction of crude oil that possesses the highest number of aromatic rings, high molecular weights in the range of 500–1500 g/mol, a high atomic ratio of carbon/hydrogen, and a high aromaticity (Tchoukov et al., 2014). Asphaltenes are the most polar molecules, insoluble in aliphatic hydrocarbons (e.g.: n-heptane) and soluble in aromatic hydrocarbons (e.g., toluene). These asphaltenes molecules consist of a mixture of heterogeneous aromatic, naphthenic rings, aliphatic chains, and other heteroatoms such as sulfur, nitrogen, oxygen in the form of carboxylic acids, amides, amine, and alcohols responsible for the stabilization of crude oil emulsions (Saad et al., 2019). Asphaltenes molecules aggregate at the oil-water interface to form a viscoelastic and physical cross-linked network to prevent the dispersed droplets from coalescing. Politova et al. (2017) showed that the stability of emulsions by asphaltenes films is attributed to their specific ability to assemble into 3D networks inside the emulsion and their acidic and basic behaviour. This structure changes the rheology of the film-forming oil to non-Newtonian, which prevents the film drainage at a thickness less than 50–100 nm.

Wong et al. (2018) experimentally demonstrated that asphaltenes do not have well-defined structures, however, they possess hydrophobic moieties, thus, cannot stabilize emulsions the way traditional emulsifiers would, but rather aggregate in a gel-like structure within the oil film to separate the approaching water droplets. As this gel-like structure forms: first, it changes the rheology of the fluid within the film to non-Newtonian with a minimal but not negligible Bingham yield stress which is too small to be measured in a conventional rheometer, but large enough to prevent film drainage. Second, it forms a steric layer to provide steric emulsion stabilization to prevent the coalescence of the droplets. The mechanism of asphaltenes stabilization is shown in Fig. 1. Emulsions stabilized by asphaltenes require different emulsion breaking techniques and possibly different demulsifiers to successfully destabilize them. Ali and Alqam (2000) studied the effect of asphaltenes solvency on stabilizing water-in-crude oil emulsions and showed that the crude oil emulsions stability is governed primarily by the state of solubility of asphaltenes in the crude oil. At or near the point of precipitation, the asphaltenes are more surface-active than those that are sufficiently solvated or molecularly dispersed. Additionally, the solubility state of asphaltenes is determined by the resin-to-asphaltenes ratio and the concentration of the polar functional groups in the resins and asphaltenes.

4.2. Resins

Resins are the compounds of crude oil that contain heteroatoms, including nitrogen, oxygen, or sulfur, as seen in Fig. 2. These compounds are characterized by their higher hydrogen-carbon (H/C) ratio and possess similar structures as asphaltenes but have smaller molecular weights. It is the fractions of crude oil that are insoluble in propane and ethyl acetate but soluble in *n*-pentane and *n*-

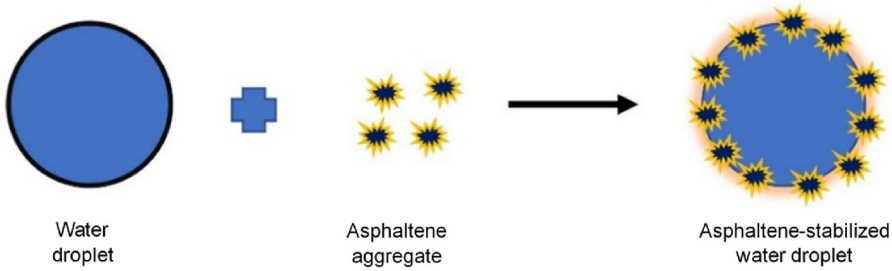

Fig. 1. Mechanism of emulsion stabilization by Asphaltenes compounds; the latter form a thin layer around dispersed water droplet to provide steric emulsion stabilization.

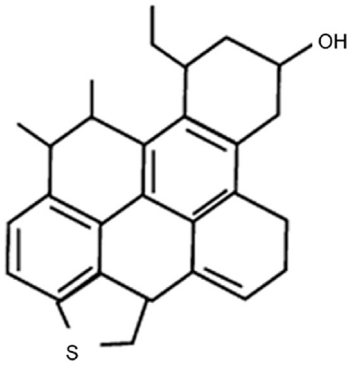

Fig. 2. Structure of a typical resin compound (Fakher et al., 2020).

heptane. Unlike asphaltenes, the resins have a smaller molecular volume with molecules that do not aggregate. A resin exists as a single molecule on the interfacial film, making the formed interface film weak and easily broken under a small shear force. The role of resins in crude oil is to solvate the asphaltenes molecules. Additionally, resins can desorb from the asphaltenes, leading to larger asphaltenes aggregates (Fingas and Fieldhouse, 2009). Resins and asphaltenes both comprise polar functional groups, such as aromatic components and hydrogen donor/acceptors in their molecules, which form a solid intermolecular interaction of π-π bonds; the hydrogen bonding leads to the strong binding of asphaltenes with resins which results in the solvation of asphaltenes in the resins (Fajun et al., 2020).

Abdulredha et al. (2018) suggested that if the resins are mixed with asphaltenes at a ratio of 2:1, the stability of the emulsion can be enhanced twice; this effect may be attributed to the polar components present in the resins as well as in the asphaltenes molecules. Aguiar and Mansur (2015) evaluated the solubility parameter range of the resin with and without the presence of asphaltenes by ultraviolet–visible spectrometry. The results indicated that the resins tested could improve the solubility of the asphaltenes even at a concentration as low as 1.0% w/v. Yang et al. (2007) studied the stability of water-in-oil emulsions using the critical electric field (CEF) technique. The emulsions were prepared in the presence of asphaltenes and resins. It was found that the stability of the emulsions increased and reached its maximum at the asphaltenes to resins mass ratio of 0.5:1. This was explained by the fact that the resin-solvated asphaltenes aggregates could diffuse and adsorb at the emulsion interface more rapidly than pure asphaltenes aggregates. At a elevated concentrations, the resins become the primary adsorbent by penetrating the asphaltenes network and displacing them, thus reducing the stability of the emulsion.

From the above literature it can be noted that the stability of crude oil emulsions results from the interaction between resins and asphaltenes molecules present in the crude oil. Moreover, the degree of emulsion stability depends on the resin-to-asphaltenes ratio present in the crude oil.

4.3. Surfactants

Surfactants are surface-active molecules capable of reducing the interfacial tension (IFT) between two immiscible liquids and allowing them to mix (Katepalli and Bose, 2014). Surfactants are amphiphilic molecules which comprise two dissimilar parts: a polar head, and a non-polar tail. The polar part is hydrophilic, while the non-polar part is hydrophobic. The surfactant's amphiphilic nature dictates the surfactant's position at the emulsion interface and determines the type of emulsion formed (Umar et al., 2018). The amphiphilic nature of the surfactant is quantified in terms of the hydrophilic-lipophilic balance (HLB) number. This dimensionless number (HLB) varies in the range of 0–20. If the HLB of a surfactant is > 10, the surfactant is likely to stabilize water-in-oil emulsions, whereas HLB is < 10, it will stabilize oil-in-water emulsions (Udonne, 2012). Two phenomena take place when the surfactant molecules are in solution, namely desorption and adsorption. The adsorption of surfactants at liquid interfaces results into lower interfacial tension, higher surface elasticity and electric double layer repulsion (ionic surfactants), and possibly increases surface viscosity thus affecting emulsion stability.

Surfactants are used in the petroleum industry to form drilling fluids. For instance, surfactants act as emulsifiers and wetting agents in oil-based drilling fluids whereas in water-based muds, they perform various functions: prevention of wellbore instabilities by acting as shale-swelling inhibitors, prevention of sticking to drill bit by action as detergents, elimination of unwanted foam in water-based fluids by functioning as de-foaming additives, enhancing of properties in fluids for the low-pressure reservoir by functioning as surfactant-polymer complexes. The oil and gas industry requires surfactants for applications such as gas-liquid and liquid-liquid systems, production of oil well and well-head foams, process froth for oil flotation, and emulsion drilling fluids for EOR in situ emulsions. Surfactants are classified based on the charge present in their structure, usage, and solubility in water. For instance, cationic surfactants are positively charged and are suitable for carbonate reservoirs; anionic surfactants are negatively charged and are most widely used for the EOR process; non-ionic surfactants are neutral and used for EOR, and amphoteric surfactants possess both anionic and cationic behaviors (Mateos et al., 2017).

The adsorption of surfactants influences the stability of crude oil emulsion at the interface between liquids. Some surfactants can either stabilize oil-in-water or water-in-oil emulsions or stabilize both types of emulsions. For example, oil-soluble surfactants have more affinity to oil than water and can stabilize the water-in-oil emulsion. In comparison, water-soluble surfactants have more affinity to water and stabilize oil-in-water emulsions. Yarranton et al.

(2007)'s study demonstrated that the stability of the emulsions is associated with the change in the interfacial film properties, crumpling film ratio and interfacial compressibility. The adsorbed interfacial film is compressed during coalescence and becomes more resistant; if the film compression is stronger than the driving force for coalescence, the emulsion will stabilize. Meanwhile predicting the surfactants' for emulsion interfacial film breaking or their effect on the emulsion's stability is not entirely clear. Still, it is suggested that an effective surfactant partially or entirely replaces the asphaltenes at the emulsion interface to weaken the film (increasing the compressibility and decreasing the crumpling ratio), weaker films favor coalescence and destabilize emulsions (Ortiz et al., 2010). Furthermore, Ortiz et al. (2010) investigated the effect of different surfactants on the properties of asphaltenes films and the stability of crude oil emulsions; they observed that indeed surfactants replaced the asphaltenes on the emulsion interface. Their results further showed that the increase of surfactant molecule increases the film compressibility and decreases the crumpling ratio of the asphaltenes films. It was also noticed that the surfactants, which failed to decrease the crumpling ratio and reduced the emulsion interfacial tension, produced stable emulsions. Kang et al. (2011) studied the stability mechanism of synthetic water-in-crude oil emulsions stabilized by surfactants using the Turbiscan lab expert stabilizer. A slow migration of crude oil droplets in the Turbiscan tube as surfactants were gradually added to the emulsions was observed; the final emulsions obtained were more stable as the result of their smaller oil droplet size.

4.4. Brine water

Brine water also known as formation water, is naturally present in the reservoir rock. It contains ions including Na^{+}, Cl^{+}, Ca^{2+}, and Mg^{2+}, often at high concentrations (from 100 to about 300 000 mg/L), depending on the characteristics of the reservoir. The ionic strength of the aqueous phase decreases the interfacial tension (IFT) of the emulsion, hence affects the emulsion stability. The salinity of the water injected during EOR, for example, critically affects the emulsion droplet size distribution, which in consequence affects the emulsion stability and the flow of emulsion through porous media. Alves et al. (2014) conducted laboratory experiments to investigate the effect of NaCl on the interfacial properties of a Brazilian crude oil-brine emulsion. Rheological investigations were done using the pendant drop technique. Measurement of viscoelastic properties were conducted using dynamic tests running for up to 24 h. The effect of the interfacial film aging on the compressibility was also investigated at a constant temperature of 40 °C. It was reported from the experimental studies that increase of the concentration of salt in the brine solutions enhanced the total interfacial elasticity; in this sense a more rigid interfacial film was formed because of the high concentration of salt. A stronger interfacial activity of the surfactants as a result of the presence of salt, leading to increased interfacial elasticity and compressibility was also reported. Maaref and Ayatollahi (2018) experimentally investigated the crude emulsion stability using various salts, including Na_2SO_4, $MgCl_2$, and NaCl, to determine the influence of each ion on emulsion stability, and this stability was analyzed by observing the 'growth of the droplets using microscopic imaging. Their study revealed that the addition of Na_2SO_4 to the emulsions samples caused the interfacial film of the emulsion to become thinner and rigid; a reduction of the droplet size was also observed, and the emulsions produced seemed more stable and stayed stable for a longer period than the ones containing other salts. The study suggested that the high stability could be related to the divalent sulfate ion present in SO_4^{2-}, which creates a higher electrostatic and steric repulsion forces between the two adjacent water droplets than the other salts, causing the emulsion to be more stable. Crude oil emulsions stabilize because of the formation of an interfacial barrier or film between oil and water that prevents the dispersed phase droplets to assemble and coalesce. The amount of salt in the brine water is one of the parameters that influence the strength of this film; studies showed that high salt content as well as the type of salt cause this film to be more rigid thus producing more stable emulsions.

5. Mechanism of demulsification of crude oil

The process of demulsification does not occur spontaneously; several factors are involved. These factors include gravitational forces, surfactants interchange with the emulsion phases. Fig. 3 illustrates the steps involved in chemical demulsification.

5.1. Creaming or sedimentation

Creaming or sedimentation occurs because of droplet's natural tendency to rise or sink through a fluid under the influence of gravity or density difference. The creaming occurs when the dispersed phase has a lower density than the continuous phase; the dispersed phase rise on top of the emulsion. This process depends on the droplets' size (bigger droplets will rise if their density is lower than the continuous phase or remain at the bottom if their density is higher). It is also influenced by the rheology of the continuous phase, the hydro-dynamic and colloidal interaction between droplets, the electrical charge on the droplets, and the nature of the interfacial membrane or film (Jones et al., 1978).

5.2. Flocculation

Flocculation is the process in which the distance between droplets of the dispersed phase decreases due to weakening of the net attraction force (van der Waals) between them, causing the droplets to clump together without any rupture. The flocculation rate often depends on the water cut, the temperature, the oil viscosity, and the density difference between the oil and water.

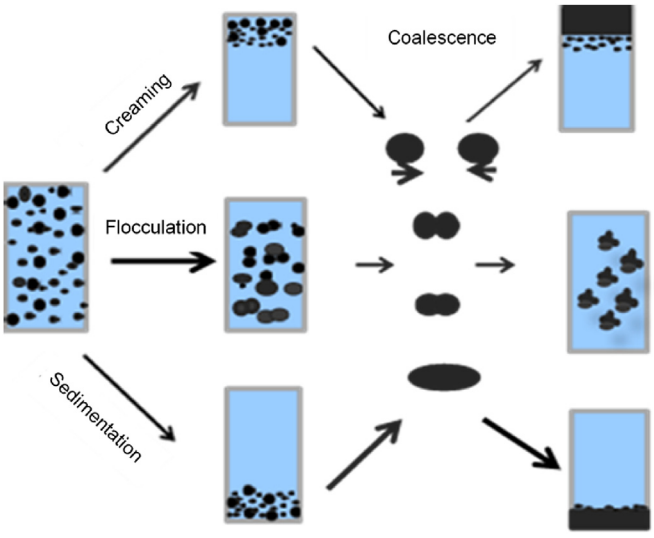

Fig. 3. Illustration of demulsification mechanisms. The dark and grey drops refer to oil and water phases.

5.3. Coalescence

Coalescence occurs when smaller droplets come together to form bigger ones. This process involves eliminating thin interfacial films that separate the dispersed droplets, leading to reduced droplets number and enabling complete de-emulsification. Factors such as high flocculation rate, absence of strong films, high interfacial tension, low viscosity, high water cut and high temperature enhance coalescence.

5.4. Ostwald ripening

Ostwald ripening is the process in which larger droplets grow at the expense of smaller droplets. This effect is produced by the mass transport of the dispersed phase material between the droplets because of the degree of solubility in the continuous phase.

6. Demulsification techniques of crude oil emulsions

In the previous sections, we have described the processes of crude oil emulsions formation and stability. We are now considering the latest developments in the breaking process of crude oil emulsions. Several conventional oilfield emulsions demulsification methods, including mechanical, electrochemical, thermal, and chemical, have been reported. For effective demulsification, the rate of phase separation must be fast. The residual water content in the crude oil must not exceed 0.5%. The wastewater to be discarded should not contain oil amounts larger than 0.05%. Finally, the method of demulsification must be cheap. However, these specifications are subject to companies and types of pipeline used.

6.1. Physical or mechanical demulsification

The mechanical demulsification is a method by which emulsions are separated utilizing mechanical equipment such as two and three-phase centrifugal separators, cyclones, free water knockout drums, and gravity settling tanks (Kato and Kawasaki, 1988). This equipment provides sufficient mechanical force to break down the water and oil interfacial barrier to separate the two phases. This technique's separation efficiency is mostly influenced by the oil's viscosity, the temperature, and the difference between oil and water phase's densities. The rate at which oil is separated depends on the oil concentration in the mixture (Van Schie, 2013). Hao et al. (2013) investigated the effects of rotor speed, inlet flow rate, water temperature, oil content, and the crude oil density on the demulsification efficiency of a centrifugal contractor to treat the overstandard oil content in electric desalting wastewater. The study showed that the demulsification efficiency increased with decreasing inlet flow rate, increasing oil concentration and decreasing oil density. This method is highly efficient as emulsions of oil concentrations ranging from 4000 mg/L to 60000 mg/L are reduced to below 200 mg/L. Additionally, Krebs et al. (2012) studied the demulsification kinetics of a model oil-in-water emulsion using a centrifuge. Their study was aimed at investigating the forces acting on the emulsion droplets in the separator, the growth rate of the separated oil phase and the change in mean droplets diameter measured as a function of the centrifugal speed and time. The result showed that an increase in the centrifugal speed and time promotes the coalescence between the oil droplets. Similarly, Kumar et al. (2021) investigated the coalescence and separation of oil from crude oil emulsions using a packed bed system, the effect of pore size, flow rate, retention time, surface wettability, and the length of a sand-packed bed system were studied. The results showed that the oil separation efficiency improves as the pore diameter approaches the diameter of the 'emulsion's droplets, the oil separation only occurs at low flow rates and high residence time and is attributed to the elasticity of the surfactant present in the emulsions. The wettability of the system is evaluated based on the hydrophobicity and hydrophilicity of the sand-packed bed. It is noticed that the hydrophobic sand pack beds leads to higher oil separation efficiency (47.37%) than the hydrophilic beds (12.95%) due to the strong adsorption of the hydrophobic sand beds to the oil interface. Further experiments were carried out at various bed lengths notably 7.6 cm, 20 cm, and 40 cm. Oil separation efficiency increased from 33.65 to 46.03% when the bed length was increased from 7.6 to 20 cm; further, increase of the bed length (40 cm) did not significantly affect the oil separation efficiency; 47.74% was the maximum efficiency achieved. Similarly, Ma et al. (2014) investigated the effect of the bed porosity (0.850–0.925), bed length (2–20 mm), and the flow velocity (1.0–20 mL/s) of a vertical sleeve separator using a glass microfiber on the oil removal efficiency of oil-in-water emulsions. Their studies showed that the bed porosity determines the pore size of the bed. At high porosity (large pore size of the bed), a decrease in droplets collision frequency was noticed, and binary and interfacial coalescence becomes more difficult. Moreover, it was found that a thicker bed is advantageous to the droplets coalescence, this is attributed to the longer hydraulic retention time that the emulsion could spend through the bed. It is suggested that the longer the bed, the longer the hydraulic residence time, the higher the demulsification efficiency. High fluid velocity (>2 mL/s) on the other end resulted in a shorter hydraulic residence time of the emulsions in the bed, leading to low coalescence and demulsification efficiency. The mechanical demulsification method has not been widely used due to its high capital cost. Additionally, the shearing force created during agitation can further break the phase droplets, leading to further emulsification. Another disadvantage of this technique is that the mechanical equipment is limited in capacity and is difficult to operate; this results in increase of storage cost. The equipment is limited to emulsions with high oil content, generally above 90% (Abed et al., 2019).

6.2. Electrical demulsification

Electrical demulsification is the process in which oil is separated from the emulsion employing electrodes through oxidation-reduction reactions. This process occurs when an electric current is applied, causing an imbalance of electric potential in the emulsion (Ichikawa, 2007; Zhang et al., 2018; Saad et al., 2019). The presence of an electric field during electrical demulsification leads to the polarization of droplets, then the droplets coalesces by collision in a short period of time (Peng et al., 2016). The induced dipoles interaction leads to droplets aligning in chains parallel to the applied field, thus increase their sedimentation velocity and ultimate separation (Zhang et al., 2018). The electric system consists of a transformer and two electrodes which provide high voltage current to the system. The electrodes are placed in opposited direction to each other, providing enough energy to break the interfacial barrier of the emulsion placed between them (A Issaka, 2015). When DC voltage is applied to the system, an electric field is generated within the emulsion, this breaks the interfacial barrier between droplets, and the water molecules are hydrolyzed into hydrogen and oxygen gases molecules. A study conducted by Hjartnes et al. (2020) revealed that the demulsification efficiency in the presence of an electric field depended on the strength of the electric field. El-Ashtoukhy and Fouad (2014) made similar observations from their studies on the demulsification of crude oil emulsion using an electrocoagulation cell. The cell used a rotating aluminium cylinder as anode and a stationary cylindrical screen of aluminium as a cathode. Parameters such as the current density, the NaCl concentration, and pH were also studied. It was found that

increase of the current density led to an increased rate of demulsification; a current density of 11.4 mA/cm^2 allowed complete emulsion phases separation, while a current density of 17.1 mA/cm^2 allowed complete demulsification (100% efficiency) after 6 min only. Acidic media (pH 3–5) retarded the electrocoagulation process, thus retarding the demulsification process. The increase in the concentration of the NaCl leed to an increase in demulsification efficiency. Mousavi et al. (2014) investigated the effect of pulsatile electric fields (PEF) on the formation of the secondary droplets in the presence of a shallow direct current (DC) electric field. They concluded that an increase in the electric field strength decreases the interfacial tension, resulting in the coalescence and separation of the droplets. Additionally, an increase in the PEF leads to the suppression of the secondary droplets in the low-frequency electric domain. Hjartnes et al. (2020) investigated the mechanism of chemical demulsifiers and the synergy between chemical demulsification and electro coalescence by applying pulsed field gradient NMR (Nuclear magnetic resonance). To reduce crude oil viscosity experiments were carried out at 65 °C; the emulsified water content was measured as a function of sample height for 2 h consecutively using the NMR, the droplet size distributions were obtained at the beginning and end of each experiment, with the intent of mapping the coalescence and sedimentation effect of droplets. The results revealed that there is a synergy between demulsifiers and low AC fields, but only in a range where the field effect is not dominant (50–100 V/cm); however, tracking the droplet size evolution was found to be challenging due to rapid change within the emulsions; furthermore, it was observed that sedimentation by electro coalescence dominated the effect of chemical demulsifiers. Hadidi et al. (2019) examined the effect of asphaltenes flocculation on the electro coalescence of water-in-crude oil emulsions in the presence of a DC electric field. In their study, a uniform DC electric field was applied to the emulsion layer using a parallel plate electrode cell; the extent of coalescence was indicated by the current running through the emulsions. It was observed that asphaltenes flocculation negatively affected the rate of electrocoalescence. This was mainly attributed to the increased oil-water interface stabilization and partly due to the reduced conductivity of the oil phase. A study conducted by Hadidi et al. (2019) investigated the behavior of binary droplets collision exposed to an external non-uniform electric field, focusing on the impact of the applied voltage amplitude. It was observed that the applied non-uniform electric field remarkably altered the electro coalescence performance. The magnitude of the force applied on the droplets is dependent on the external electric field; stronger electric fields led to quicker approaches of the droplets. Moreover, by increasing the electric field intensity, the bipolar force between the droplets increases, hence improving coalescence. Mohammadian et al. (2018) investigated the rate of demulsification of water in crude oil emulsions in direct current fields under various conditions by using an electrochemical cell. They found out that the rate of demulsification increased along with the strength of the applied field. It was concluded that the rate of demulsification is governed by the magnitude of the applied electric field as well as the type of electrode.

The electrical demulsification has been commonly applied for more than a century as it seems to be more sustainable than other demulsification methods. Different industries have widely adopting the technique as a suitable process for the demulsification of crude oil emulsions. Electrical demulsification offers advantages such as low sludge production, simple equipment requirement, and little to no use of chemical agents. Although the electrical demulsification has been successfully applied to different industrial processes, such as paint manufacturing and oilfield-produced water, more investigations need to be conducted to improve and optimize the efficiency of the process.

6.3. Thermal or conventional microwave demulsification

The thermal demulsification encompasses microwave demulsification and conventional thermal heating. The thermal demulsification refers to using a microwave device to break and separate water from oil in crude oil emulsions. Heating crude oil emulsions at high temperature enhances the breaking of the interfacial film between the phases by reducing the film's rigidity, hence increasing the settling rate and coalescence frequency of the phases (El-Ashtoukhy and Fouad, 2014; Hjartnes et al., 2020). The higher the thermal energy, the higher the collision rate between the dispersed droplets, and hence, the separation of phases is enhanced. The mechanism of microwave demulsification is often considered as a combination of thermal and non-thermal effects. The thermal effect is due to the formation of the high-frequency electromagnetic field under microwave irradiation. The capacity of water molecules to absorb in the microwaves is higher than that of oil molecules; this is due to expansion of water droplets as they absorb more energy resulting into thinner and weaker film interface. The non-thermal effect is attributed to the likelihood of emulsified droplets to collide and coalesce due to lower Zeta potential of the oil-water interface films under a high-frequency electromagnetic field (Xu et al., 2020). Many works have been developed regarding microwave irradiation for demulsification purposes because of its advantages, such as high efficiency, low energy consumption, and being environment friendly (Chan and Chen, 2007; Mohammed and Mohammed, 2013; Santos et al., 2017; Sun et al., 2018; Xu et al., 2020). The evaluation of the effect of a set of operations parameters namely: microwave irradiation powers (700, 800, and 900 W), water content (20–80%, 30–70%, 50–50%), and salt content (10000, 20000 and 30000 ppm) on the demulsification efficiency using microwave irradiation has been reported by Mohammed and Mohammed (2013). The highest demulsification efficiency (85%) was achieved at 900 W, 50% water content, and 160 s irradiation time. It was reported that at high water content there was improved emulsion breaking due to increased heating effect caused by higher electrical conductivity and energy dissipation per unit volume. Furthermore, it was observed that higher microwave power leading to increased wavelength and penetration depth favored the demulsification process. Similarly, Kusumastuti et al. (2020) applied the microwave irradiation method to break used emulsions, and investigated the demulsification efficiency in terms of irradiation time and settling time. It was observed that the demulsification efficiency increased when the irradiation time and the settling time were prolonged. Increment of the demulsification rate by the increase of microwave irradiation time is affected by dielectric heating properties that are able to separate water-in-oil emulsions. The highest demulsification efficiency of 82.45% was achieved by applying irradiation time of 15 s and settling time of 15 min.

The microwave demulsification is often combined with thermal demulsification to improve the efficiency of the process. The demulsification efficiencies of microwave irradiation and conventional heating have been reported (Abdurahman et al., 2017; Sun et al., 2018). It was found that the microwave irradiation was more efficient compared to the other methods, it achieved 100% demulsification efficiency, whereas the conventional heating achieved 96% demulsification efficiency. The maximum demulsification efficiency was obtained after a 3 min irradiation time, microwave power of 360 W, and demulsifier concentration of 2.5 vol %. Nour et al. (2012) conducted a comparative study on effectiveness of the microwave irradiation and conventional heating on the demulsification of water-in-crude oil emulsion encountered in refineries. It was found that the microwave irradiation efficiently enhanced the demulsification as compared to

conventional heating. They deduced that the electromagnetic heat wave generated by the microwave significantly reduced the viscosity of the emulsion as compared to conventional heating, leading to rapid droplets coalescence. It was also reported that the demulsification efficiency is affected by the microwave power and the demulsification time. As the microwave power and time increased, the demulsification efficiency increased as well. Another study on microwave irradiation was conducted by Lv et al. (2020). Their work focused on some microwave parameters, including heating temperature and time, microwave power, and centrifuge speed on the droplet size distribution and total demulsification efficiency of oily sludge. The results showed that microwave irradiation strongly depends on the microwave heating temperature and power. It was suggested that the demulsification temperature of the oily sludge is kept below 77 °C; excessive heating could cause other oil components such as olefins and aromatics to begin to precipitate and also increase the energy consumption. The demulsification efficiency of oily sludge first increased with increasing microwave power and temperature up to a maximum of 67.4% at 700 W and 55 °C in 25 min and centrifuge speed of 6000 rpm; it then decreased when the temperature and power were raised to 75 °C and 900 W respectively. Extreme temperature may affect the non-thermal effects of the microwave, making the agglomerated droplets to break into smaller droplets caused by the violent oscillation movement of the high-frequency electromagnetic field produced under excessively high microwave power, and consequently, reduce the total demulsification efficiency.

Kovaleva et al. (2021) presented a comparative study on the efficiency of electromagnetic treatment of oil-in-water emulsions using radio frequency and microwave irradiation. Their studies focused on the influence of the dielectric properties and emulsions water content on radio-frequency and microwave irradiation efficiency. The results showed that the radio-frequency demulsification demonstrated higher efficiency for samples with low water content, whereas the microwave exhibits higher efficiency with a sample containing high water content. It was concluded that the radio-frequency electromagnetic treatment does not strongly depend on the water content in the emulsions, but on the electromagnetic field frequency that falls into the polarization region of the polar oil components (asphaltenes and resins). In contrast, the microwave electromagnetic field acts only on water molecules; high temperatures due to heating facilitates the drainage of the interfacial film and the step of coalescence between the water droplets.

Ferreira et al. (2013) assessed the influence of emulsion aging on the efficiency of demulsification of water-in-oil emulsion utilizing conventional heating and microwave radiation. In their study, the emulsion temperature and the demulsifier dosage were kept at 60 °C and 40 ppm, respectively. The results showed that aging negatively affects the demulsification efficiency for both techniques, this was attributed to the fact that the interfacial film characteristics of emulsion are more likely to change with time, thus affecting the demulsification process. However, this effect is minimized with microwave radiation because the heating rate is higher than the conventional heating.

Thermal demulsification uses heat to separate water or oil from the crude emulsions, however excess heat affects the quality of the crude oil obtained, water molecules easily absorb in the microwave as compared to oil molecules which makes this method not to be favorable for all types of emulsions.

6.4. Chemical demulsification

Chemical demulsification consists in adding chemicals called

Table 2
Summary of recent studies on chemical demulsification.

Emulsion type	Demulsifier types	Demulsifier concentration	Demulsification Efficiency	References
Oilfield emulsion	Synthesized carbonized cotton coated with SiO_2 (CC@SiO_2)	400 mg/L	90.38% after 120 min at 65 °C	Yuan et al. (2021)
(W/O)	Natural locus leaf treated via simple hydrothermal process	1000 ppm	88.18% after 90 min and 70 °C	Ye et al. (2021)
O/W and W/O	ethylene oxide-propylene oxide (EO-PO) block copolymers	1, 2, and 5 ppm	Demulsification increased as the dosage of the demulsifier increased	Niu et al. (2019)
W/O from alkaline-surfactant-polymer (ASP) flooding	Novel polyether-polyquaternium (PPA) copolymer	110 mg/L	80.6%	Sun et al. (2020)
W/O containing light, medium, or heavy crude oils	Alginite, a naturally occurring and abundant oil-shale rock	0.0025 wt%	Less than 1.0% of water remained after demulsification at 60 °C for all emulsion types	Salih et al. (2021)
O/W from alkali surfactant polymer flooding	a silica-supported polyether polysiloxane quaternary ammonium (PPQA@SiO_2)	300 mg/L	92% in 50 min	Zhai et al. (2020)
Crude oil emulsion	2-Amino-5-Dodecyl Benzene Sulfonic Acid (ADBSA) surfactant	In the range of 0.065 −0.109 wt%	95–98% at a temperature of 60 °C	Zargar et al. (2018)
Synthetic W/O using seawater (SW) and deionized water (DW)	Ionic liquids (IL) containing Chloride, Decanoate, and Dicyanamide ions	1000 ppm, 700 ppm	99% efficiency was achieved using IL with Chloride ions from DW emulsion with 1000 ppm. and 99% efficiency was achieved with Decanoate and Dicyanamide ions with 1000 ppm and 700 ppm, respectively	Adewunmi and Kamal (2019)
water-in asphaltenes solution emulsion	novel aliphatic alcohol nonionic polyether (MJTJU-2)	400 ppm of MJTJU-2	>97% efficiency was achieved after 15 min at 60 °C	Ma et al. (2019)
W/O	SiO_2 nanoparticles (NP) and graphene oxide (GO-SiO_2) nanocomposite	–	Complete (100%) demulsification was achieved after 110 min with SiO_2 and 90 min with GO-SiO_2	Javadian and Sadrpoor (2019)
Polymer surfactant flooding (PS) produced water emulsion	Cationic branched quaternary ammonium chloride and a non-ionic copolymer of propylene oxide and ethylene oxide	350–500 mg/L	The cationic demulsifiers, in general, exhibited better performance than the non-ionic under ambient temperature (14 -20 °C)	Chen et al. (2018)

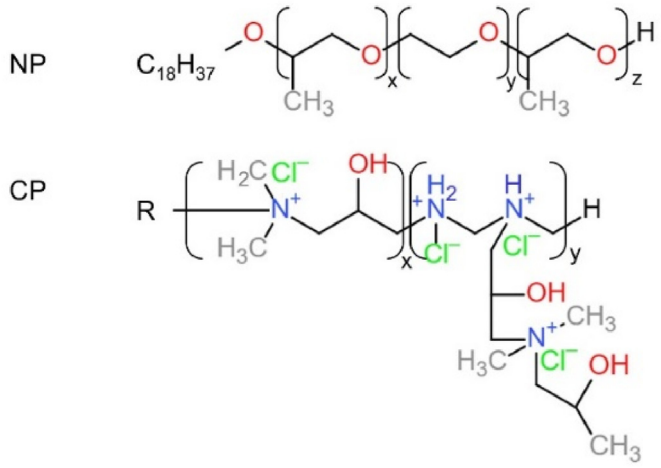

Fig. 4. Basic structure of typical demulsifiers: NP and CP are nonionic and cationic groups, respectively. R is the alkyl group whereas x, y and z are independent for different demulsifier; adapted from (Chen et al., 2018).

demulsifiers to accelerate the coalescence of the dispersed phase of the emulsion (Abed et al., 2019; Hassanshahi et al., 2020; Wang et al., 2021). In addition, these chemicals are designed to neutralize the effect of surfactants that stabilized the emulsion, and displace them from the interfacial film surrounding the emulsion droplets to enhance destabilization. Effective chemical demulsification requires careful selection of demulsifiers for a given emulsion (emulsion characteristics vary from reservoir to reservoir), an appropriate amount of demulsifiers, proper mixing, and sufficient retention time to allow the phases to separate. Table 2 is a summary of recent notable studies on the chemical demulsification of crude oil emulsions.

7. Chemical demulsifiers and demulsifiers selection

Demulsifiers are surface-active compounds that destabilize or break emulsions' stability. Demulsifiers are surfactants polymers including ethylene and propylene oxide, alkyl phenol-formaldehyde resins, ethoxylated or propoxylated phenol-formaldehyde resins, ethoxylated phenol, nonylphenols, alcohol and amines, polyhydric alcohols, and sulphonic acid salts containing high molecular weight compared to natural surfactants (Zhai et al., 2020). They are classified according to the structure of their hydrophilic group and their application. Fig. 4 shows the structure of a demulsifier.

The selection of the right demulsifier is crucial for emulsion breaking as emulsions differ in types (W/O, O/W, or multiple emulsions) and properties, such as composition, salinity, and stability depending on the reservoirs. Generally, demulsifiers are specific for a given emulsion and can be entirely ineffective for other types of emulsions, they are therefore commonly selected demulsifiers based on the type of emulsion to be broken (Oil-in-Water or Water-in-Oil) (Zhai et al., 2020). Because the polarity of the functional group, also known as the HLB, is different for each demulsifier, the hydrophobic (non-polar groups or water-fearing) demulsifiers are suitable for water-in-oil emulsions, in contrast, the hydrophilic (polar group or water-loving) is suitable for Oil-in-Water emulsions. Table 3 presents an extensive list of demulsifier types and their functions. The charge of the demulsifier functional group can either be positive (cationic), negative (anionic), and neutral (non-anionic). A study on the effect of different HLB numbers of demulsifiers on the demulsification of the water-in-oil emulsion was carried out, and revealed that amine demulsifier groups with HLB below 9 exhibited the highest efficiency in breaking emulsions compared to polyhydric, alcohol, and natural group with HLB above 9 (Ichikawa, 2007). Amine demulsifier groups are more effective in demulsifying oil-in-water emulsions than polyhydric, alcohol, and natural groups because of the hydrophobicity and hydrophilicity characteristic of their functional groups and their high molecular weight (Balsamo et al., 2017).

Demulsifiers are also selected based on their equal partitioning capacity between the oil and water phases (partially soluble in oil and water). Balsamo et al. (2017) reported that the greater the molecular weight and hydrophobicity of the demulsifier, the faster the coalescence of the water droplets, thus, the higher the demulsification efficiency of water-in-oil emulsions.

8. Factors affecting emulsion chemical demulsification

To obtain the desired demulsification efficiency, some factors that affect the emulsion chemical demulsification have to be

Table 3
Demulsifier types and functions.

Name	Charge	Type	Function	References
Diallyl dimethyl ammonium chloride polymer	cationic	O/W	Flocculants	Fink (2015); Nasiri et al. (2017)
Poly(sodium acrylate)	Anionic	–	Scale inhibitor and reverse emulsion breakers	Nasiri et al. (2017)
Oxalkylated poly(alkylene) poly(amine)s	Cationic	O/W	Flocculants	Nasiri et al. (2017)
PAM (polyacrylamide)	Cationic	–	Drag reducing agents	Wang et al. (2015)
acryloxyethyltrimethylammonium chloride) copolymer	Cationic	O/W	–	Javadian and Sadrpoor, (2019); Ma et al. (2019)
Polyamines	Cationic	–	Emulsion breakers and corrosion inhibitors	Nasiri et al. (2017)
Polyoxyethylene and polypropylene copolymer	Non-ionic	–	Coagulants	Fink (2015)
Cethyltrimetilammonium bromide	Cationic	O/W or W/O	Reverse emulsion breakers	Nasiri et al. (2017)
AM/MAPTAC (acrylamide/methacrylamidopropyltrimethylammonium chloride) copolymer	Cationic	–	Dewatering agents	Nasiri et al. (2017)
Oxalkylated poly(alkylene)poly(amine)s	Cationic	W/O	–	Fink (2015)
Phenol-formaldehyde resins	–	W/O and O/W	–	Wang et al. (2015)

optimized. The demulsification process is governed by Stake's law (Zaman et al., 2019). The demulsifiers act directly on the film separating oil and water phases, so as to disrupt the interfacial tension between the droplets, and hence increase thermal velocity and speed up the coalescence. The process of demulsification is affected by the temperature, phase volume ratio, residence time, demulsifier dosage, crude oil properties, and aging of emulsions (Yonguep and Chowdhury, 2021).

8.1. Temperature

Heat energy plays an essential role in the demulsification process of crude oil emulsion as it directly reduces the viscosity and the ehances the flow of emulsions. Temperature affects the physical properties of oil-water interfacial films by increasing the droplets' thermal energy, which leads to an increased frequency of drop collisions and coalescence. Heat weakens the interfacial film between the oil and the water droplets, lowers the oil viscosity, and increases the mobility and settling rate of the water droplets, thus, reducing the interfacial viscosity, and resulting in a faster film drainage rate and enhancing droplets coalescence. Oliveira et al. (2007) studied the effect of temperature on the demulsification efficiency of water-in-oil emulsions via microwave demulsification. Experiments were conducted at 80, 95, and 130 °C, respectively, the water content was varied from 0 to 45%. They observed a proportional relationship between the demulsification efficiency and the temperature. The demulsification efficiency increased with increasing temperatures. The experiments conducted at high temperature yielded the highest reduction in the final water fraction (45–2.6%); the maximum demulsification efficiency of 94% was achieved when the temperature was raised to 130 °C. A similar observation was reported by Balsamo et al. (2017), in their study where the demulsification procedure was performed in batch mode at 30, 45, and 60 °C; [Omim][PF6] and Aliquat® 336 ionic liquids (IL) were used as demulsifiers at different concentrations 2.5×10^{-3}, 1.2×10^{-2}, and 2.9×10^{-2} mol/L respectively. The model emulsion was a mixture of n-heptene/toluene and water (70:30 toluene-in-water emulsions). The results showed that faster droplet collisions occured for emulsions treated with Aliquat® 336 as compared to those with [Omim][PF6], this was due to the latter's higher molecular weight and higher hydrophobic character of its cation. The highest demulsification efficiency of 93% was obtained when the temperature is 30 °C with Aliquat® 336 after 1500 min. Hajivand and Vaziri (2015) studied the demulsification of water-in-crude oil emulsion using bottle test and gravity separation. Their experiments were carried out at various temperatures ranging from 10 to 80 °C, the pH was kept constant at 5.5, and testing time was 72 h, with 10 ppm demulsifier concentration. Similar results to Balsamo et al. (2017) and Oliveira et al. (2007) were observed. The demulsification efficiency increased from 15 to 59% with an increase in temperature from 10 to 50 °C. Further increasing the temperature to 70 °C and above had an insignificant effect on the separation efficiency. From these results, it can be concluded that the temperature only affects the demulsification efficiency up to a certain extent, no significant water separation occurs at temperatures above 70 °C. Further increasing the temperature at this stage will only add to the operating costs. Ye et al. (2021) assessed the influence of temperature on the demulsification of a water-in-oil emulsion stabilized by asphaltenes. In their study, the experiments were conducted a 50 and 70 °C. It was observed that the demulsification efficiency increased from 36.21 to 88.17% as the temperature rose from 50 to 70 °C. These results were attributed to the fact that heat alters the viscosity and weakens the strength of the interfacial film of emulsions stabilized by asphaltenes.

Moreover, the heat strengthens the Brownian motion within the emulsions, thus causing rapid movement of demulsifier molecules at the emulsion interface and promoting the demulsification process. Al-Sabagh et al. (2015) investigated the effect of temperature on the demulsification efficiency of aromatic amines demulsifiers using bottle test or gravitational separation. Their results showed that an increase in temperature from 50 to 70 °C enhanced the demulsification efficiency. The findings suggested that the improvement of the demulsification efficiency could be due to two reasons: first, the increase in temperature increased the rate of coalescence by offering adequate energy for the bombardment of two droplets occurring prior to coalescence. Second the increase in temperature leads to the reduction of the continuous phase viscosity which facilitates the kinetic motion of the dispersed water droplets, hence, causing increased bombardment resulting in film relaxation, film rupture and coalescence. Additionally, higher temperatures may increase the solubility of emulsifiers, from interface, into oil phase, resulting in weaker films and greater degrees of water droplet coalescence and separation.

8.2. Water and oil content

The phase volume ratio is one of the main parameters that affect the efficiency of demulsification. Emulsions with high water content are more readily separated than those with lower water content. High water content in crude oil emulsions promotes demulsification efficiency while decreasing the demulsifier dose and the time needed for the phases to separate, provided that water content falls within volumetric fractions ranges of 30–70%. Generally, the emulsions are likely to separate faster when the volume of the dispersed phase is increased as the distance between the droplets is reduced. Ahed et al. (1999) reported that decreasing the oil content from 90 to 60 vol % in a surfactant-stabilized oil-in-water emulsion without a demulsifier resulted in reduced water separation. A better separation could be observed when the oil content was reduced to 50%. Higher oil contents (60% and above) in an oil-in-water emulsion has the potential of shifting the system to water-in-oil emulsions, which happens to be more viscous, dense, more stable, and more difficult to demulsify. The demulsification of crude oil emulsions containing 30, 50, and 70% water was also investigated to assess the effect of water content on the demulsification efficiency. The synthetic water-in-oil emulsion was prepared by homogenizing the mixture of crude oil and water at 200 rpm at room temperature, the emulsion was kept for 48 h to ensure complete stabilization (no phase separation). Results revealed that the demulsification efficiency increases with increasing water content from 30 to 70%, this was due to the internal pressure of water which is lower than the external pressure of the oil at low water content. Additionally, the rigidity of water-in-oil films decreased with increasing water content, causing rapid rupture of the emulsion interface. This increased the coalescence of water droplets which promoted the demulsification process. The effect of water content on the demulsification efficiency of demulsifiers used to treat water-in-oil emulsion was investigated by Al-Sabagh et al. (2011). Their experiments were conducted at various water to oil ratios: 30, 50, and 70% with the demulsifier concentration kept constant at 300 ppm. The results showed that the demulsification efficiency increased with increasing of water content; it required less time (33 min) for water to separate from emulsions with 70% water content than 50 and 30%. It was concluded that the repulsion of the water-oil interface depends on the pressure of both the internal (water) and external (oil) phases; at a low water content, the internal pressure of a water droplet is lower than the external pressure of an oil droplet leading to an increase in the mechanical stability of the emulsion which retards the demulsification process.

8.3. Retention or settling time

Retention time in the context of demulsification is the duration the emulsions stay in a non-agitated state to allow it to separate into individual phases. Higher retention times enhance the demulsifier diffusion through the oil-water interface and gravity settling, thus, improving the demulsification efficiency. Although increased retention time positively affects the demulsification efficiency, it comes at the expense of high separator equipment costs. Therefore, there is a need to optimize retention time to avoid waste of time and money. Kokal and Al Ghamdi (2006) observed an almost complete oil separation in 5–10 min by mixing two different types of demulsifiers.

It was suggested on the one hand that retention time may lead to an increase in the demulsification efficiency of crude oil-in-water emulsion when increased from 10 to 30 min. On the other hand, it should be noted that high retention times might also have a negative effect on the demulsification efficiency as they may lead to re-emulsification, which would reduce the efficiency of demulsification. Rajak et al. (2016) investigated the effect of settling time on the demulsification efficiency of crude oil-in-water using various types of demulsifiers. Their experimental conditions were as follows pH: 10.5, temperature: 25 °C, and demulsifier dosage: 60 mg/L. The results showed that the demulsification efficiency first increased with increasing settling time then remained constant after 60 min for all types of demulsifiers. Since the dynamic equilibrium of molecular motion at the emulsion interface was reached after 60 min, further increase in the settling time could not have any further effect on the demulsification efficiency.

Yi et al. (2017) studied the impact of settling time on crude oil demulsification by combining ultrasound and chemical demulsification methods. The experiment was carried out under constant temperature (40 °C), constant chemical demulsifier concentration (250 mg/L), and constant ultrasonic power (150 W). The settling time was varied from 10 to 25min in 5min intervals. The results showed that the combined use of ultrasound and chemical demulsifier achieved the highest demulsification efficiency. It was also observed that the dehydration rate increased with the increasing temperatures and ultrasonic power. Increasing the ultrasonic treatment time had an insignificant effect on the demulsification efficiency. It was concluded that the combination of ultrasound and chemical demulsifier is not only effective in heavy crude oil demulsification-dehydration but also possibly reduces demulsification time.

8.4. Demulsifier concentration

The separation rate of emulsions is greatly influenced by the amount of demulsifier used, the degree of stability of the emulsions, and the type of emulsions. In experimental setups, the demulsifiers are usually applied using a trial-and-error approach. The operator injects a given quantity of chemicals, observes the effect on the efficiency then adjusts the quantity injected accordingly (Al-Otaibi et al., 2003). The best demulsifiers are those that rapidly displace preformed rigid films and leave a mobile film in their place (Rajak et al., 2016).

Zolfaghari et al. (2016) mention that the emulsions formed during the EOR process require higher demulsifier concentration than those formed from first and secondary recovery processes. Usually, hundreds of ppm or even more are used in extreme conditions. However, overdosing demulsifiers can result in the re-stabilization of the emulsions. The hydrophilicity or lipophilicity and molecular weight of demulsifiers are the determining factors for optimum amount of demulsifier to achieve best demulsification efficiency. Javadian and Sadrpoor (2019) and investigated the influence of different demulsifiers concentration on the their ability to separate both water and oil from a Malaysian oil field emulsions. Acrylic acid and Methyl trioctyl ammonium chloride (TOMAC) were the demulsifiers selected for the study. The concentrations used in these tests were 10 ppm, 20 ppm, and 100 ppm; the temperature was kept constant at 70 °C, the total duration of the experiment was 180 h. The water seperation efficiencies found were 17.4, 12.0 and 23.0% for acrylic acid concentrations of 10, 20 and 100 ppm respectively. When TOMAC was used, the water separation efficiencies were found to be 94.0, 44.0, and 6.2% using 100, 10 and 20 ppm TOMAC respectively. Higher TOMAC concentrations were found to have higher water separation efficiencies than acrylic acid; this is attributed to the fact that TOMAC being an oil-soluble demulsifier promotes quicker aggregation and coalescence of the oil droplets, thus favoring the water separation. Rajak et al. (2016) investigated the effect of demulsifier dosage on the oil separation efficiency of an oil-in-water emulsion collected from Digboi area, India. The experiment is conducted at 25 °C and pH of 10.5 and demulsifier (*n*-Octylamine) dosage ranging from 10 to 100 mg/L. The result showed that an increase in demulsifier dosage leads to an increased demulsification efficiency due to the ability of the demulsifier to neutralize the emulsion stabilizers (emulsifiers). At demulsifier concentrations of 70 mg/L and above, only a minimal increase in demulsification efficiency is observed; this indicates that the point at which complete neutralization of the stabilizers have has been reached. The study also showed that high doses of demulsifier increases the number of demulsifier molecules per unit area on the interface layer, causing the droplets to coalesce with one another, thus enhancing the demulsification. Some optimum experimental conditions for chemical demulsification are listed in Table 4.

8.5. Crude oil emulsion properties

The characteristics of crude oil emulsions variy from field to field (Gazali et al., 2017), hence chemical demulsifiers behave differently depending on the type emulsions encountered. One of the most important properties of crude emulsions is the rheology. Viscosity plays a key role in the stability and demulsification of crude oil emulsion. Pajouhandeh et al. (2016) mentioned that the viscosity of emulsions is affected by their average droplet size and size distribution; in general emulsions with small droplet size distribution tend to be more viscous and more stable than those with bigger droplets, due to friction increment between droplets. It will normally takes longer for the smaller droplets to coalesce than

Table 4
Summary of some optimum conditions for the demulsification oil crude oil emulsions.

Emulsion type	Demulsifier concentration	Water content (%)	Temperature (°C)	Time (h)	Efficiency (%)	reference
ASP emulsion	100 mg/L	50	45	4	96	Huang et al. (2019)
W/O	100 mg/L	–	70	75	80	Hajivand and Vaziri (2015)
W/O	1039.22 ppm	10	78.49	–	100	Biniaz et al. (2016)
O/W	15 ml/L	–	35	24	92.25	Cai et al. (2019)
W/O	500 ppm	20	25	2	100	Hazrati et al. (2018)

for bigger ones, this decreases the rate of separation (Souza et al., 2015).

In addition, non-Newtonian behaviour, such as shear-thinning, appears to be more pronounced for fine droplets than for coarse emulsions (Johnsen and Rønningen, 2003). Juntarasakul & Maneeintr (2018) explained from experiments that the dispersed phase droplet sizes become smaller when high shear rate is applied, making the emulsions to become more stable due to the increase interfacial tension and area of oil and water caused by the shear. This fact could be attributed to the high shear which facilitates the breaking up of the water droplets into smaller droplets thus influencing the demulsification process. Salam et al. (2013) studied the demulsification of three different heavy oil fields from Niger Delta, Nigeria, gasoline was added as a diluent at different concentrations (2–10 Lm) to lower the viscosity of the emulsions. It was observed that the viscosity proportionally decreased with the increase of the volume of gasoline, leading to the increase of water separated from the emulsions.

8.6. Crude oil emulsion aging

Emulsions properties tend to change after being exposed for a long time, this is probably because oil contains many types of absorbable materials whose effects can only be seen after some time, or when the emulsion is subjected to change in the environmental condition. Additionally time allows the natural surfactants to aggregate at the interface of the emulsion droplets, causing in the formation of a thicker and stronger film which can become difficult to break. A study was done by Maia Filho et al. (2012) on two types of emulsions (fresh or non-aged emulsion and emulsion aged for 60 days), to assess the aging effect on the efficiency of demulsification. 100 ppm of demulsifier was added on both emulsions and the phase separation was monitored for 30 min at 40°C. It was observed a progressive increase in phase separation for the fresh emulsion leading to 90% demulsification efficiency, whereas no phase separation could be noticed on the aged emulsions even when the demulsifier dose was increased 40 times than the one used for the fresh emulsions. And they concluded that the emulsions become more stable with time. Another work by Pajouhandeh et al. (2016) corroborated the study of Maia Filho et al. (2012), who also did not observe any sign of phase separation on the emulsions that were stored for a long time, instead they noticed that the droplets size of these emulsions became smaller. The decrease of the size of emulsion's droplets could be the result of the age of the emulsions. Crude oil emulsions undergo some changes in their properties (e.g., droplet size distribution, viscosity, interfacial films etc.) after being untreated for a prolonged time, these changes often time may cause detrimental effect on demulsifiers and consequently reduce the demulsification efficiency. Very little research has been done on the aging effect on the demulsification of crude oil, therefore, could be used as a subject for further investigation.

9. Conclusions, future challenges and development direction

The formation of crude oil emulsions is almost unavoidable during crude oil production and processing. These emulsions are problematic from an economic and environmental point of view. A thorough understanding of the properties and behavior of crude oil emulsions is essential to successfully treat them. This study systematically reviews theories around the formation, stabilization, and destabilization of emulsions from oilfields. We also report various demulsification methods used to address the crude oil emulsions challenge.

The formation of emulsions occurs at different stages of the crude oil recovery process with the most stable formed during the EOR. Turbulence or agitation during the transportation of the crude from underground wells is the primary cause of emulsions formation. Crude oil emulsions are further stabilized by asphaltenes, resins wax, clay and other solids present in crude oil. The compounds in crude oil form rigid films at the water and oil droplets phases to prevent them from aggregating and coalescing. Other factors include the droplet size distribution, pH, water salinity, and the composition of the crude oil. Emulsions can be demulsified by mechanical, thermal, electrical, and chemical methods. Various demulsification mechanisms have been observed from different studies; they are influenced by many factors including emulsions type and properties, demulsifiers characteristics, presence of solids stabilized emulsions, etc. The selection of the most suitable method is based on the efficiency of the process, economics involved and the environmental impact. The demulsification efficiency of crude oil emulsion depends on the operating parameters (and their interplay) associated with the technique used. Developments in the field of crude oil demulsification should consider pilot scale studies of real crude oil emulsions, the synergistic effects of multiple demulsification techniques, the effect of aging on crude oil emulsions and the use of readily biodegradable demulsifiers.

To the best of our knowledge, most studies on demulsification have been conducted at laboratory scale with simulated petroleum emulsions. Future studies on the subject should involve pilot scale studies with real crude oil emulsions. Studies can also be conducted on the synergistic effects of combining different demulsification techniques. This review has revealed the scarcity of published research on aging effect on the demulsification of crude oil emulsions. Future investigations should consider this aspect which affects crude oil emulsions. Lastly, currently used chemical demulsifiers are of low biodegradability and toxic nature and may present a threat to the environment. Hence, their replacement by natural and green ones is worth investigating.

Declaration of competing interest

The authors have no conflict of interest to declare.

References

A Issaka, S., 2015. Review on the fundamental aspects of petroleum oil emulsions and techniques of demulsification. J. Petrol Environ. Biotechnol. 6.
Abdulredha, M.M., Siti Aslina, H., Luqman, C.A., 2018. Overview on petroleum emulsions, formation, influence and demulsification treatment techniques. Arab. J. Chem. 13 (1), 3403–3428.
Abdulredha, M.M., Hussain, S.A., Abdullah, L.C., 2020a. Optimization of the demulsification of water in oil emulsion via non-ionic surfactant by the response surface methods. J. Petrol. Sci. Eng. 184, 106463.
Abdulredha, M.M., Siti Aslina, H., Luqman, C.A., 2020b. Overview on petroleum emulsions, formation, influence and demulsification treatment techniques. Arab. J. Chem. 13, 3403–3428.
Abdurahman, N.H., Yunus, R.M., Azhari, N.H., Said, N., Hassan, Z., 2017. The potential of microwave heating in separating water-in-oil (w/o) emulsions. Energy Proc. 138, 1023–1028.
Abed, S.M., Abdurahman, N.H., Yunus, R.M., Abdulbari, H.A., Akbari, S., 2019. Oil emulsions and the different recent demulsification techniques in the petroleum industry – a review. IOP Conf. Ser. Mater. Sci. Eng. 702 (1), 012060.
Adewunmi, A.A., Kamal, M.S., 2019. Demulsification of water-in-oil emulsions using ionic liquids: effects of counterion and water type. J. Mol. Liq. 279, 411–419.
Aguiar, J.I.S., Mansur, C.R.E., 2015. Study of the interaction between asphaltenes and resins by microcalorimetry and ultraviolet-visible spectroscopy. Fuel 140, 462–469.
Ahmed, N.S., Nassar, A.M., Zaki, N.N., Gharieb, H.K., 1999. Stability and rheology of heavy crude oil-in-water emulsion stabilized by an anionic- nonionic surfactant mixture. Petrol. Sci. Technol. 17, 553–576.
Al-Otaibi, M., Elkamel, A., Al-Sahhaf, T., Ahmed, A.S., 2003. Experimental investigation of crude oil desalting and dehydration. Chem. Eng. Commun. 190, 65–82.
Al-Sabagh, A.M., Kandile, N.G., El-Ghazawy, R.A., Noor El-Din, M.R., 2011. Synthesis and evaluation of some new demulsifiers based on bisphenols for treating water-in-crude oil emulsions. Egypt. J. Pet. 20, 67–77.
Al-Sabagh, A.M., Nasser, N.M., Khamis, E.A., Abd-El-Raouf, M., 2015. Resolution of

water in crude oil emulsion by some novel aromatic amine polyesters. Egypt. J. Pet. 24, 363–374.
Alagorni, A.H., Yaacob, Z. Bin, Nour, A.H., 2015. An Overview of Oil Production Stages: Enhanced Oil Recovery Techniques and Nitrogen Injection. International Journal of Environmental Science and Development 6 (9), 693–701.
Ali, M.F., Alqam, M.H., 2000. Role of Asphaltenes , Resins and Other Solids in the Stabilization ofWater in Oil Emulsions and its Effects on Oil Production in Saudi Oil Fields. Fuel, 79(11), 1309–1316.
Alves, D.R., Carneiro, J.S.A., Oliveira, I.F., Façanha, F., Santos, A.F., Dariva, C., Franceschi, E., Fortuny, M., 2014. Influence of the salinity on the interfacial properties of a Brazilian crude oil–brine systems. Fuel 118, 21–26.
Balsamo, M., Erto, A., Lancia, A., 2017. Chemical demulsification of model water-in-oil emulsions with low water content by means of ionic liquids. Braz. J. Chem. Eng. 34, 273–282.
Biniaz, P., Farsi, M., Rahimpour, M.R., 2016. Demulsification ofWater in Oil Emulsion Using Ionic Liquids : Statistical Modeling and Optimization. Fuel, 184, 325–327.
Cai, Q., Zhu, Z., Chen, B., Zhang, B., 2019. Oil-in-water emulsion breaking marine bacteria for demulsifying oily wastewater. Water Res. 149, 292–301.
Chan, C.C., Chen, Y.C., 2007. Demulsification of W/O Emulsions by Microwave Radiation. Separation Science and Technology, 37(15), 3407–3420.
Chen, D., Li, F., Gao, Y., Yang, M., 2018. Pilot performance of chemical demulsifier on the demulsification of produced water from polymer/surfactant flooding in the Xinjiang Oilfield. Switzerland Water 10.
Dicharry, C., Arla, D., Sinquin, A., Graciaa, A., Bouriat, P., 2006. Stability of water/crude oil emulsions based on interfacial dilatational rheology. J. Colloid Interface Sci. 297, 785–791.
Dol, S.S., Wong, S.F., Wee, S.K., Lim, J.S., 2018. Experimental study on the effects of water-in-oil emulsions to wall shear stress in the pipeline flow. J. Appl. Fluid Mech. 11, 1309–1319.
El-Ashtoukhy, E.S.Z., Fouad, Y.O., 2014. Oil removal from oil-water emulsion by electrocoagulation in a cell with rotating cylinder anode. Electrochemistry 82, 974–978.
Fajun, Z., Zhexi, T., Zhongqi, Y., Hongzhi, S., Yanping, W., Yufei, Z., 2020. Research status and analysis of stabilization mechanisms and demulsification methods of heavy oil emulsions. Energy Sci. Eng. 8, 4158–4177.
Fakher, S., Ahdaya, M., Elturki, M., Imqam, A., 2020. Critical review of asphaltene properties and factors impacting its stability in crude oil. J. Pet. Explor. Prod. Technol. 10, 1183–1200.
Fakhru'l-Razi, A., Pendashteh, A., Abdullah, L.C., Biak, D.R.A., Madaeni, S.S., Abidin, Z.Z., 2009. Review of technologies for oil and gas produced water treatment. J. Hazard Mater. 170, 530–551.
Ferreira, B.M.S., Ramalho, J.B.V.S., Lucas, E.F., 2013. Demulsification of water-in-crude oil emulsions by microwave radiation: effect of aging, demulsifier addition, and selective heating. Energy Fuels 27, 615–621.
Fingas, M., 1995. Water-in-oil emulsion formation: a review of physics and mathematical modelling. Spill Sci. Technol. Bull. 2, 55–59.
Fingas, M., Fieldhouse, B., 2009. Studies on Crude Oil and Petroleum Product Emulsions: Water Resolution and Rheology. Colloids and Surfaces A : Physicochemical and Engineering Aspects, 333, 67–81.
Gazali, A.K., Alkali, A.N., Mohammed, Y., Djauro, Y., Muhammed, D.D., Kodomi, M., 2017. Environmental impact of produced water and driiling waste discharges from the Niger Delta petroleum industry. IOSR J. Eng. 7 (6), 2250–3021.
Hadidi, H., Manshadi, M.K.D., Kamali, R., 2019. Numerical simulation of a novel non-uniform electric field design to enhance the electrocoalescence of droplets. Eur. J. Mech. B Fluid 80, 206–215.
Hajivand, P., Vaziri, A., 2015. Optimization of demulsifier formulation for separation of water from crude oil emulsions. Braz. J. Chem. Eng. 32, 107–118.
Hao, M., Bai, Z., Wang, H., Liu, W., 2013. Removal of oil from electric desalting wastewater using centrifugal contactors. J. Petrol. Sci. Eng. 111, 37–41.
Hassanshahi, N., Hu, G., Li, J., 2020. Application of ionic liquids for chemical demulsification: a review. Molecules 25.
Hazrati, N., Akbar, A., Beigi, M., Abdouss, M., 2018. Demulsi fi cation of water in crude oil emulsion using long chain imidazolium ionic liquids and optimization of parameters. Fuel 229, 126–134.
Hjartnes, T.N., Mhatre, S., Gao, B., Sørland, G.H., Simon, S., Sjöblom, J., 2020. Demulsification of crude oil emulsions tracked by pulsed field gradient NMR. Part II: influence of chemical demulsifiers in external AC electric field. Colloids Surfaces A Physicochem. Eng. Asp. 586, 124188.
Ho, T.M., Razzaghi, A., Ramachandran, A., Mikkonen, K.S., 2021. Emulsion characterization via microfluidic devices: a review on interfacial tension and stability to coalescence. Adv. Colloid Interface Sci. 102541.
Huang, B., Wang, J., Zhang, W., Fu, C., Wang, Y., Liu, X., 2019. Screening and optimization of demulsifiers and flocculants based on ASP flooding-produced water. Processes 1–15.
Ichikawa, T., 2007. Electrical demulsification of oil-in-water emulsion. Colloids Surfaces A Physicochem. Eng. Asp. 302, 581–586.
Javadian, S., Sadrpoor, S.M., 2019. Demulsification of water in oil emulsion by surface modified SiO 2 nanoparticle. J. Petrol. Sci. Eng. 106547.
Johannes Karl Fink, 2015. Demulsifiers. Pet. Eng. Guid. To Oil F. Chem. Fluids, pp. 787–808.
Johnsen, E.E., Rønningen, H.P., 2003. Viscosity of "live" water-in-crude-oil emulsions: experimental work and validation of correlations. J. Petrol. Sci. Eng. 38 (1–2), 23–36.
Jones, T.J., Neustadter, E.L., Whittingham, K.P., 1978. Water-in-Crude oil emulsion stability and emulsion destabilization by chemical demulsifiers. J. Can. Pet. Technol. 17, 100–108.
Juntarasakul, O., Maneeintr, K., 2018. Evaluation of stability and viscosity measurement of emulsion from oil from production in northern oilfield in Thailand. IOP Conf. Ser. Earth Environ. Sci. 140 (1).
Kang, W., Xu, B., Wang, Y., Li, Y., Shan, X., An, F., Liu, J., 2011. Stability mechanism of W/O crude oil emulsion stabilized by polymer and surfactant. Colloids Surfaces A Physicochem. Eng. Asp. 384, 555–560.
Katepalli, H., Bose, A., 2014. Response of surfactant stabilized oil-in-water emulsions to the addition of particles in an aqueous suspension. Langmuir 30, 12736–12742.
Kato, S., Kawasaki, J., 1988. Continuous demulsification of O/W emulsions by A mechanical technique. J. Chem. Eng. Jpn. 21, 321–323.
Kobayashi, I., Yasuno, M., Iwamoto, S., Shono, A., 2002. Microscopic Observation of Emulsion Droplet Formation from a Polycarbonate Membrane. Colloids and Surfaces A Physicochemical and Engineering Aspects, 207(1-3), 185–196.
Kokal, S.L., Al Ghamdi, A., 2006. Oil/water separation experience from a large oil field. SPE Prod. Oper. 21, 365–371.
Kovaleva, L., Zinnatullin, R., Musin, A., Gabdrafikov, A., Sultanguzhin, R., Kireev, V., 2021. Influence of radio-frequency and microwave electromagnetic treatment on waterin-oil emulsion separation. Colloids Surfaces A: Physicochem. Eng. Asp 614, 126081.
Krebs, T., Schroën, C.G.P.H., Boom, R.M., 2012. Separation kinetics of an oil-in-water emulsion under enhanced gravity. Chem. Eng. Sci. 71, 118–125.
Kumar, S., Pandey, A., Trifkovic, M., Bryant, S.L., 2021. A facile and economical configuration for continuous generation and separation of oil in water emulsions. Separ. Purif. Technol. 256, 117849.
Kusumastuti, A., Anis, S., Ahmad, A.L., Ooi, B.S., Shah Buddin, M.M.H., 2020. Emulsion liquid membrane for heavy metals removal: emulsion breaking study. J. Teknol. 82, 51–57.
Lv, X., Song, Z.L., Yu, J., Su, Y., Zhao, X.Q., Su, J., Mao, Y.P., Wang, W.L., 2020. Study on the demulsification of refinery oily sludge enhanced by microwave irradiation. Fuel 279, 118417.
Ma, S., Kang, Y., Cui, S., 2014. Oil and water separation using a glass microfiber coalescing bed. J. Dispersion Sci. Technol. 35, 103–110.
Ma, J., Li, X., Zhang, X., Sui, H., He, L., Wang, S., 2019. A novel oxygen-containing demulsifier for efficient breaking of water-in-oil emulsions. Chem. Eng. J. 123826.
Maaref, S., Ayatollahi, S., 2018. The effect of brine salinity on water-in-oil emulsion stability through droplet size distribution analysis: a case study. J. Dispersion Sci. Technol. 39, 721–733.
Maia Filho, D.C., Ramalho, J.B.V.S., Lucas, G.M.S., Lucas, E.F., 2012. Aging of water-in-crude oil emulsions: effect on rheological parameters. Colloids Surf. A Physicochem. Eng. Asp. 405, 73–78.
Masalova, Irina, Fabrice, K.K., Tshilumbu, N.N., George, N., Malkin, A.Y., Kapiamba, F., Tshilumbu, N.N., Malkin, A.Y., 2018. Emulsification of highly concentrated emulsions—a criterion of shear stability. J. Rheol. 62, 781–790.
Masalova, I., Kapiamba, F., Tshilumbu, N., Malkin, A.Y., 2018. Shear stability of highly concentrated emulsions. Colloid J. 80, 54–58.
Mateos, R., Vera, S., Valiente, M., Díez-Pascual, A.M., San Andrés, M.P., 2017. Comparison of anionic, cationic and nonionic surfactants as dispersing agents for graphene based on the fluorescence of riboflavin. Nanomaterials 7.
Mohammadian, E., Suriya, T., Ari, T., Azdarpour, A., Hamidi, H., Yusof, S., Sabet, M., Yahya, E., 2018. Demulsi fi cation of light Malaysian crude oil emulsions using an electric field method. Ind. Eng. Chem. Res. 57 (39), 13247–13256.
Mohammed, S.A.M., Mohammed, M.S., 2013. The Application of Microwave Technology in Demulsification of Water-In-Oil Emulsion for Missan Oil Fields. Iraqi Journal of Chemical and Petroleum Engineering, 14, 21–27.
Mousavi, S.H., Ghadiri, M., Buckley, M., 2014. Electro-coalescence of water drops in oils under pulsatile electric fields. Chem. Eng. Sci. 120, 130–142.
Nasiri, M., Jafari, I., Parniankhoy, B., 2017. Oil and gas produced water management: a review of treatment technologies, challenges, and opportunities. Chem. Eng. Commun. 204, 990–1005.
Niu, Z., Yue, T., He, X., Manica, R., 2019. Changing the interface between an asphaltene model compound and water by addition of an EO – PO Demulsi fi er through adsorption competition or adsorption replacement. Energy Fuels 33, 5035–5042.
Nour, A.H., Anisa, A.N.I., Nour, A.H., 2012. Demulsification ofWater- In-Oil (W/O) Emulsion via Microwave Irradiation : an Optimization. Scientific Research and Essays, 7(2), 231–243.
Oliveira, C.B.Z., Melo, R.L.F.V., Coutinho, R.C.C., Santos, A.F., 2007. Effect of Salinity, Temperature, Water Content, and pH on the Microwave Demulsification of Crude Oil Emulsions. Energy & Fuels, 21(3), 1358–1364.
Ortiz, D.P., Baydak, E.N., Yarranton, H.W., 2010. Journal of Colloid and Interface Science Effect of surfactants on interfacial films and stability of water-in-oil emulsions stabilized by asphaltenes. J. Colloid Interface Sci. 351, 542–555.
Pajouhandeh, A., Kavousi, A., Schaffie, M., Ranjbar, M., 2016. Towards a mechanistic understanding of rheological behaviour of water-in-oil emulsion: roles of nanoparticles, water volume fraction and aging time. S. Afr. J. Chem. 69, 113–123.
Pashakolaie, V.G., Khaleghi, S., Mohammadi, T., Khorsandi, M., 2015. Oil production cost function and oil recovery implementation- evidence from an Iranian oil field. Energy Explor. Exploit. 33, 459–470.
Peng, Y., Liu, T., Gong, H., Zhang, X., 2016. Review of the dynamics of coalescence and demulsification by high-voltage pulsed electric fields. Int. J. Chem. Eng. https://doi.org/10.1155/2016/2492453.

Politova, N., Tcholakova, S., Denkov, N.D., 2017. Factors affecting the stability of water-oil-water emulsion films. Colloids Surfaces A Physicochem. Eng. Asp. 522, 608–620.
Rajak, V.K., Singh, I., Kumar, A., Mandal, A., 2016. Optimization of Separation of Oil from Oil-In- Water Emulsion by Demulsification Using Different Demulsifiers. Petroleum Science and Technology, 34(11-12),1026–1032.
Saad, M.A., Kamil, M., Abdurahman, N.H., Yunus, R.M., Awad, O.I., 2019. An overview of recent advances in state-of-the-art techniques in the demulsification of crude oil emulsions. Processes 7, 1–26.
Salam, K.K., Alade, a.O., Arinkoola, a.O., Opawale, a., 2013. Improving the demulsification process of heavy crude oil emulsion through blending with diluent, 2013 J. Petrol. Eng. 1–6.
Salih, S., Hippmann, S., Roode-gutzmer, Q.I., 2021. Alginite Rock as Effective Demulsifier to Separate Water from Various Crude Oil Emulsions. Colloids and Surfaces A Physicochemical and Engineering Aspects, 611.
Santos, D., da Rocha, E.C.L., Santos, R.L.M., Cancelas, A.J., Franceschi, E., Santos, A.F., Fortuny, M., Dariva, C., 2017. Demulsification of water-in-crude oil emulsions using single mode and multimode microwave irradiation. Separ. Purif. Technol. 189, 347–356.
Schultz, S., Wagner, G., Urban, K., Ulrich, J., 2004. High-pressure homogenization as a process for emulsion formation. Chem. Eng. Technol. 27, 361–368.
Souza, W.J., Santos, K.M.C., Cruz, A.A., Franceschi, E., Dariva, C., Santos, A.F., Santana, C.C., 2015. Effect of water content, temperature and average droplet size on the settling velocity of water-in-oil-emulsions. Braz. J. Chem. Eng. 32 (2), 455–464.
Sun, N.N., Jiang, H.Y., Wang, Y.L., Qi, A.J., 2018. A comparative research of microwave, conventional-heating, and microwave/chemical demulsification of tahe heavy-oil-in-water emulsion. SPE Prod. Oper. 33, 371–381.
Sun, H., Wang, Q., Li, X., He, X., 2020. Novel polyether-polyquaternium copolymer as an effective reverse demulsifier for O/W emulsions: Demulsification performance and mechanism. Fuel, 263, 116770.
Tchoukov, P., Yang, F., Xu, Z., Dabros, T., Czarnecki, J., Sjöblom, J., 2014. Role of asphaltenes in stabilizing thin liquid emulsion films. Langmuir 30, 3024–3033.
Udonne, J.D., 2012. Chemical Treatment of Emulsion Problem in Crude Oil Production. Journal of Petroleum and Gas Engineering, 3(7), 135–141.
Umar, A.A., Saaid, I.B.M., Sulaimon, A.A., Pilus, R.B.M., 2018. A review of petroleum emulsions and recent progress on water-in-crude oil emulsions stabilized by natural surfactants and solids. J. Petrol. Sci. Eng. 165, 673–690.
Van Schie, L., 2013. Oil/water separation: suparator meets the oil/water challenge. Filtr. Sep. 50, 50–51.
Wang, C., Fang, S., Duan, M., Xiong, Y., Ma, Y., Chen, W., 2015. Synthesis and evaluation of demulsifiers with polyethyleneimine as accepter for treating crude oil emulsions. Polym. Adv. Technol. 26, 442–448.
Wang, D., Yang, D., Huang, C., Huang, Y., Yang, D., Zhang, H., Liu, Q., Tang, T., Gamal El-Din, M., Kemppi, T., Perdicakis, B., Zeng, H., 2021. Stabilization mechanism and chemical demulsification of water-in-oil and oil-in-water emulsions in petroleum industry: a review. Fuel 286, 119390.
Wong, S.F., Dol, S.S., Wee, S.K., Chua, H.B., 2018. Miri light crude water-in-oil emulsions characterization – rheological behaviour, stability and amount of emulsions formed. J. Petrol. Sci. Eng. 165, 58–66.
Xu, L., Song, Z., Yu, J., Su, Y., Zhao, X., Sun, J., Mao, Y., Wang, W., 2020. Study on the Demulsification of Refinery Oily Sludge Enhanced by Microwave Irradiation. Fuel, 279(7), 118417.
Yang, X., Verruto, V.J., Kilpatrick, P.K., 2007. Dynamic asphaltene-resin exchange at the oil/water interface: time-dependent W/O emulsion stability for asphaltene/resin model oils. Energy Fuel. 21, 1343–1349.
Yarranton, H.W., Sztukowski, D.M., Urrutia, P., 2007. Effect of Interfacial Rheology on Model Emulsion Coalescence I. Interfacial Rheology.Journal of Colloid and Interface Science, 310(1), 246–52.
Ye, F., Mi, Y., Liu, H., Zeng, G., Shen, L., Feng, X., Yang, Y., Zhang, Z., Yuan, H., Yan, X., 2021. Demulsification of water-in-crude oil emulsion using natural lotus leaf treated via a simple hydrothermal process. Fuel 295, 120596.
Yi, M., Huang, J., Wang, L., 2017. Research on crude oil demulsification using the combined method of ultrasound and chemical demulsifier. J. Chem. https://doi.org/10.1155/2017/9147926.
Yonguep, E., Chowdhury, M., 2021. Optimization of the demulsification of crude oil-in-water emulsions using response surface methodology. S. Afr. J. Chem. Eng. 36, 105–117.
Yuan, H., Huang, Z., Shen, L., Xu, J., Feng, X., Yang, Y., Zhang, Z., Luo, Y., Yan, X., Mi, Y., 2021. Demulsification of crude oil emulsion using carbonized cotton/silica composites. Colloids Surfaces A Physicochem. Eng. Asp. 617, 126421.
Zaman, H., Ali, N., Shah, A. ul H.A., Gao, X., Zhang, S., Hong, K., Bilal, M., 2019. Effect of pH and salinity on stability and dynamic properties of magnetic composite amphiphilic demulsifier molecules at the oil-water interface. J. Mol. Liq. 290, 111186.
Zargar, G., Gheysari, R.G., Takassi, M.A., Rostami, A., Zadehnazari, A., 2018. Evaluation of a Sulfanilic Acid Based Surfactant in Crude Oil Demulsi Fi Cation : An Experimental Study. Oil & Gas Science and Technology - Revue de l IFP 73, 20.
Zhai, M., Wu, M., Wang, C., Li, X., 2020. A novel silica-supported polyether polysiloxane quaternary ammonium demulsifier for highly efficient fine-sized oil droplet removal of oil-in-water emulsions. RSC Advances, 10(32),18918–18926.
Zhang, H., Bukosky, S.C., Ristenpart, W.D., 2018. Low-voltage electrical demulsification of oily wastewater. Ind. Eng. Chem. Res. 57, 8341–8347.
Zolfaghari, R., Fakhru'l-Razi, A., Abdullah, L.C., Elnashaie, S.S.E.H., Pendashteh, A., 2016. Demulsification techniques of water-in-oil and oil-in-water emulsions in petroleum industry. Separ. Purif. Technol. 170, 377–407.