REVIEW

Trending approaches on demulsification of crude oil in the petroleum industry

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Received: 28 March 2021 / Accepted: 5 September 2021 / Published online: 15 September 2021
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Abstract

The complicated nature of crude oil emulsions is part of the major setbacks associated with the postulation of methods for phase separation and demulsification in the oil industry. Despite the increasing efforts in generating efficient and dependable demulsification methods, the majority of emulsions cannot be shattered in reduced times. This review examines the trending techniques of crude oil demulsification in the petroleum industry. Several approaches have been examined to discover the best method of demulsification. Hence, this report reviewed the past studies on the emulsion, formation of oil emulsions, methods of demulsification, characteristics of demulsifier, mechanism of demulsification, kinetics in demulsification, operating parameters influencing the demulsification processes, the structure of demulsifier, and formulations that are involved in the demulsification. The formulations of crude oil demulsification have been investigated to unveil adequate demulsifiers for crude oil. Therefore, demulsification approaches have several applications due to wider varieties of crude oil, separation equipment, brines, chemical demulsifiers, the method in which demulsifiers is been formulated, and product specifications.

Keywords Emulsion · Demulsification · Crude oil · Coalescence · Flocculation · Kinetics

Introduction

Emulsions of crude oil-in-water are very difficult to handle due to the fact they stabilize through different surface-active materials that occur naturally, these include asphaltenes and resins [1, 21]. Generated water in the crude oil centres different challenges such as the poisoning of downstream in catalysts associated with the downstream refinery, the corrosion of pumps, pipe works and downstream overhead distillation column, and cost of transporting or pumping water through tankers or pipelines [1, 60]. Hence, there exists a large variety of industrial and working characteristics for casting off water emulsification from crude oil. As the result, the parameters that either reduce or improve the stability of crude oil emulsion are most essential in the oil industry. According to Abdulredha et al. [1], an emulsion is a crucial challenge in the petroleum industry from the time of production till refining processes are carried out. Most of the time, petroleum operators choose to stop the formulation of emulsion or elimination to preclude the challenges associated with the environment. Besides, the therapy used in resolving water-in-crude oil emulsions entails the application of chemical, electrical, thermal, and mechanical techniques [3, 54].

The complicated nature of crude oil emulsion is part of the major setbacks associated with the postulation of methods for phase separation and demulsification in the oil industry. Despite the increasing effort in generating efficient and dependable demulsification methods, the majority of emulsions cannot be shattered in reduced times [54]. In refineries, the operation of demulsification is the main approach to evacuate water from crude oil in refineries [50]. The elimination of water from oil until adequate degrees are achieved requires dehydration (demulsification) steps within the desalting plant; this is mostly seen in petroleum refineries, environmental technology, coating, and painting.

Demulsification requires the breaking down of crude oil into water and oil states [53]. This is described as a system of breaking emulsion to distinguish oil from water, this is part of the initial stages in crude oil processing [54]. Presently, accessible approaches utilized in demulsification can be classified as physical (electrical, mechanical and thermal) and chemical (addition of demulsifier). Chemical
demulsification is broadly employed in the treatment of oil-in-water and water-in-oil emulsions; it entails using chemical additives to speed up the breaking of emulsions. Moreover, formulating a demulsifier for a certain petroleum emulsion is very complex [3]. A chemical demulsifier is generally utilized in the breaking of crude oil emulsions in different instances; this demulsifier is toxic, can alter the wellbeing of the operating personnel and generate environmental issues [1, 53, 54]. The use of chemicals is not only limited to the removal of water from an emulsion but aid in the reduction of operating costs. Also, it improves the plant efficiency and profits associated with material recovery. Hence, this review discusses the trending techniques use in the demulsification of crude oil in the petroleum industry.

**Emulsion**

The emulsion is a colloid whereby one state is distributed in some other states. The distribution state is known as the interior state whilst the other state is known to be exterior or continuous. One of the two liquid states needs to be distributed in form of small droplets to generate an emulsion. The dispersed state’s droplet is draped into the continuous state due to its resistance to separation and coalescent. The stability in terms of separation resistance is typically due to the occurrence of an agent at the interface of two states [38]. Generally, emulsions are seen in everyday existence including yoghurt, milk, mayonnaise, cream, butter, paints, pharmaceutical, and others. Hence, emulsion water, oil, energy, and surfactant are established [62].

An emulsion can be defined as a structure whereby an immiscible liquid state is distributed as globules (dispersed state) in another immiscible liquid state (continuous phase) [37]. The emulsion has a steady distribution of liquid droplets of a particular size in another immiscible liquid. The emulsion is generated as two immiscible liquids like oil and water are exposed to shear force alongside a surface-active substance [62]. Various levels of crude oil manufacturing cause emulsion because water is introduced to supplant the fluids in the reservoir. Additionally, emulsion generation appears that the participated oil and water reach valves and chokes through enormous pressure differences in the processing pipes [37]. Different kinds of emulsions are multiple, oil-in-water (O/W) and water-in-oil (W/O) emulsion. The water-in-oil emulsion is generated through the dispersion of water globules in the continuous state (Fig. 1a); oil-in-water is generated through the dispersion of oil globules in the continuous state (Fig. 1b); multiple emulsion is an elaborate emulsion structure in which O/W or W/O emulsions are distributed for the duration of other immiscible phases [31]; it consists of oil-in-water-in-oil (O/W/O) and water-in-oil-in-water (W/O/W) emulsions [54]. Two sorts of emulsions are observed in the oil industry; these include oil-in-water (O/W) and water-in-oil (W/O). The latter is mostly observed in the production water whilst the former is regularly encountered during the production of oil. In the transport and processing of crude oil, the setback emanating from excessive water contents in the oil unfavourably reduces the purity of oil [54]. Moreover, increased contents of the water-in-oil is a challenging problem because the export quality standard needs water lesser than 0.5% [24].

The treatment of emulsion by utilizing chemicals can be distinguished into two types, these are demulsifiers and non-demulsifiers. Non-demulsifiers is introduced in the last step to erupt existing emulsion; however, demulsifier serves as a preventive measure when introduced into oil to cease the formation of emulsions [46]. Another study by Sjoblom et al. [57] pointed out that the separation of emulsion occurs due to collisions between droplets, this promotes either coalescence through drainage potential of the separating oil films or droplet flocculation through external association to the thin oil films within them. The occurrence of flocs can enlarge the rate of sedimentation [57]. Understanding the flocculation kinetic is critical due to its ability to comply with the adjustments in emulsion characteristics that mostly precedes droplet coalescence [38].

An emulsion can be produced to minimise viscosity and enhance the flow of oil. For example, the transportation of produced concentrated oil-in-water over a prolonged distance [53, 61]; and transportation of the oil-in-water emulsion from the off-shore drilling site to an on-shore processing

![Fig. 1 Water-in-oil (a) and oil-in-water emulsion (b) [31]](image)
site where the emulsion can be re-emulsified for other usages [1]. In doing this, the emulsion should be surfactant-stabilized to ensure stability during the transport (nevertheless, it should not be too stable to enable its breakage when exiting the pipeline). Both natural and synthetic surfactants are being utilized [35, 53, 54]. Also, stability is required in the emulsions under flowing and static conditions in case there is a shutdown of the pipeline for a duration of time; there will be an incomplete breakdown of emulsion with consequently increased pressure drop and phase separation.

**Formation of oil emulsion**

The contact between water and oil with adequate mixing in the presence of emulsifier or emulsifying agent generate crude oil emulsions. The presence of emulsifiers and mixing quantity are important during the oil emulsion formation [1, 45, 53]. The production of crude oil requires diverse sources of mixing (called amount of shear), these include bottom-hole perforation/pump; flow across reservoir rock; production headers; flow lines and flow through tubing; chokes, fittings and valves; generated gas bubbles due to phase changes; and surface equipment [23]. The amount of mixing is a function of different properties. Generally, mixing is inversely proportional to the distributed water droplets in the crude oil and emulsion tighter [1, 53]. A previous study on emulsions had suggested that the droplets of water fall within 1 and 1000 µm [27]. Furthermore, the presence of an emulsifier is another important factor; the nature, amount and presence of the emulsifier outline the tightness and nature of an emulsion [1, 38]. The natural emulsifier in crude oil occurs in form of heavy fractions because there exist exceptional kinds of crudes as the crude comprises precise quantities of heavy components. Crude containing a reduced volume of emulsifier reflects a steady emulsion and significantly separate effortlessly. Base on a previous study, there are three essential characteristics in the formation of crude oil emulsion [1]:

- There should be contact between two immiscible liquids;
- The surface-active components must be present as an emulsifying agent; this is often contributed through the means of resins and asphaltenes;
- Adequate mixing strength must be provided to distribute a liquid into another in form of droplets.

During the formation of emulsion (Fig. 2), the deformation of a droplet is adversarial through the pressure gradient between the internal (concave) and external (convex) components of an interface [30]. The velocity or pressure gradient for the formation of emulsion requires essential furnish through agitation. The massive amount of energy required to produce an emulsion of small droplets can be furnished with the useful resources of very immoderate agitation, which desire a lot of energy. Moreover, there can be an addition of adequate surfactant or surface-active component to the system to minimise the required agitation energy in the production of precise droplet size. The emulsification process is facilitated by the surfactant film formation around the droplets that can achieve a minimised agitation energy using a factor of 10 or more [30].

The use of a natural emulsifying agent stops the distribution of water droplets emanating from coalescent because of the connection to the water droplets' surface [38]. In another study, it was outlined that the occurrence of resins and asphaltenes contents in the crude oil had been the main source of emulsion formation [7]. Moreover, it had been stated that asphaltenes are the principal materials that maintain resins and W/O emulsions [14]. Generally, every kind of emulsion comprises two immiscible liquids in which one distributes in form of droplets (droplet or internal phase) into the other (continuous phase). Mostly, the two phases are stable through a third phase known as emulsifying agent (emulsifier, surface-active agent or surfactants). In the case of W/O emulsions, the distributed droplets of water are enclosed in an oil matrix [38, 51]. Emulsions generated from each pure element of water and oil phases cannot be stable except with the addition of emulsifying agent; within

![Fig. 2 Process of forming an emulsion: Water, oil, emulsifier, and mixing are needed (Oluwatosin 2016)](image-url)
a short time, the emulsion can break up to form the initial phases (oil and water). This might be because of increased interfacial tensions between oil and water. Increased interfacial tension can propel the required forces to attract the neighbouring droplets of water which will quickly join together and later split into two distinct phases (oil and water). Thus, an emulsifier or surface-active agent is needed to maintain interfacial film and the entire system. Crude oil emulsion maintains its stability using resins and asphaltenes that are partially soluble and possess a stronger potential of migrating to sediment between the interface of an oil phase and water droplet.

**Methods of demulsification**

Industrially, emulsions of crude oil require nearly completed separation before transporting for further processing. Destabilization of the emulsifying film is needed during the emulsion separation into water and oil. This procedure can be achieved using any or combinations of the following techniques:

- Addition of chemical demulsifier;
- Improving the emulsion temperature;
- Application of electrostatic field which promotes coalescence;
- Minimising the flow of velocity that enhances the gravitational separations of gas, water and oil.

**Thermal methods**

The heating process involves during the crude oil emulsion generate several impacts including reduction in interfacial and oil viscosity, increasing the water settling rate, destabilizing the rigid films, and increasing the coalescence frequency because of increasing energy from the droplets. Thus, heating improves the emulsion separation that fastens the involving process. However, there are some setbacks associated with an increase in temperature; these include the high cost of heating, increasing volume of oil and reduction in API gravity. Besides, it can generate increasing scale deposition and corrosion. The design of a water heater is presented in Fig. 3. Thermal demulsification entails using heat in promoting emulsion breakdown in a refinery or oil field. Based on a laboratory scale, the impact may be influenced by an elevated temperature.

![Image](image-url)

Elevated thermal energy from the droplets improves the coalescence frequency amidst water films. Besides, elevated thermal energy from the droplets improves the coalescence frequency amidst water droplets. In this study, thermal demulsification infrequently secures the problem associated with emulsion alone rarely fixes the emulsion issue alone. Nevertheless, elevated temperatures can have some destructive influences as well. Mainly, the higher cost is associated with stream heating. Next, it can result in the deprivation of crude oil’s lighter fractions by reducing its API gravity and volume. Because of an elevated temperature, the treating vessels are highly inclined to scale deposition and corrosion. Hence, heating due to demulsification should be done after examining the comprehensive economic analysis of the treatment facility.
Chemical methods

The most common technique of emulsion treatment involves the addition of demulsifiers. These chemicals are modelled to counteract the stability impact of the emulsifying agents. A previous study reported the use of experimental data to reflect the impact of diverse kinds of chemical demulsifiers on the stability and demulsification of emulsion [2]. The authors used three different groups of demulsifiers with different functional groups including polyhydric alcohol, alcohol and amines. The results showed the efficacy of a chemical breaking agent in destabilizations of a water-in-oil emulsion. In another study, the combined technique of chemical demulsifiers and ultrasound at temperature differences of 40, 60 and 70 ºC were investigated [68], the results generated showed that combining chemical and ultrasound demulsifiers had the best demulsification impact, followed by the chemical demulsifier. Using an ultrasound without a chemical demulsifier had a minimum influence on the demulsification process. Moreover, the effect of temperature, treatment time and ultrasonic power on demulsification of crude oil using the combined technique of chemical and ultrasound demulsifiers was investigated. The outcomes show that the final rate of dehydration rose with increasing temperatures, while ultrasonic power was insignificant with increasing ultrasonic treatment time [68].

The study carried out by Abdurahman et al. [3] presented that the declined order of amine demulsifier efficiency might
be because of the higher factor of molecular weight; forming floculant interaction and adsorption activities. An environmental friendly oil soluble demulsifier generally reduce the interfacial viscosity and gradient interfacial tension that reflects an improvement in the film thinning rate and decline in time taken for the film to obtain a possible thickness as suggests by way of dioctylamine, hexylamine and octylamine [43]. Amine group demulsifiers are mostly utilized in the study of crude oil emulsion since it presents best outcomes in emulsion separation. Using an oil-soluble demulsifier is appropriate for water-in-oil emulsion [44]. Amines are greatly surface-active and can be absorbed on the interface of oil–water because of their direct absorption in a continuous water phase [44]. Nevertheless, the demerit of this group is in their capacity to change the salinity or pH of the aqueous phase of an emulsion [44]. This property can improve the stability of emulsion and reduces the demulsification efficiency of the applied demulsifiers [5].

A study was conducted to investigate the demulsification of crude oil emulsion traced by pulsed-field gradient (PFG) nuclear magnetic resonance (MNR) [24]. It was explained that the emulsified water droplet required for the transport and economical purposes was extracted from crude oil; this was achieved using chemical demulsification. Four chemicals were tested on the water-in-oil emulsions by employing NMR analysis.

Additionally, Ejikeme et al. [13] investigated the use of urea (commercial demulsifier) and locally formulated demulsifier for the demulsification of emulsified crude oil. The oil was prepared through a mixture of 2.4% salinity synthetic brine and crude oil in 1:1 v/v. The influence of the following process parameters including temperature, demulsifier dosage and time on the chemical demulsification was investigated. Moreover, the FTIR analysis of the demulsified, emulsified, raw crude oil, and formulated demulsified was carried out. It was reported that the process parameters influenced the separated water. Increasing time and temperature enhanced the volume of separated water after demulsification and increasing the dosage of formulated demulsifier improved the volume of separated water within a reduced duration of time with constant separated water at increasing time intervals. Nevertheless, the solvent was insignificant on the separated water. The results from FTIR analysis indicated an anionic formulated demulsifier and cationic urea; the formulated demulsifier was efficient compare to urea in the separation of water. Only 35% of water was separated through urea compare to 65% using formulated demulsifier.

A study was previously conducted on the influence of chemical demulsifiers (breaking agents) on the separation of water and oil from water-in-oil emulsions [44]. Chemical demulsification consisting of the addition of a demulsifier in smaller quantities improved the phase separation. The authors selected four categories of different breaking agents including alcohol, natural, amine, and polyhydric demulsifiers. Each category was studied to determine stable emulsions. The obtained results reflected that amine demulsifiers exhibited the best possible efficiency in breaking the emulsion compared to other categories (natural, alcohol and polyhydric). The results were impacted by the hydrophilicity and hydrophobicity characteristics of the breaking agent. The elements had an impact on the chemical demulsifier solubility. Besides, the molecular weight of the demulsifiers impacted demulsification efficiency.

In another study carried out on the demulsification of crude oil emulsion by utilizing plant extracts as green demulsifiers; the most common method used in breaking water-in-oil emulsion was chemical demulsifier [67]. The plant extracts including coconut oil, olive oil, bio-furfural, pine oil, lemon seed oil, papaya extracts, and cottonseed oil were investigated as suitable green demulsifiers; further tests were done to investigate the eco-friendliness of the extracts. The result generated showed that cottonseed and coconut oils produced the best results, whilst cottonseed oil is more economical compare to coconut oil.

**Mechanical methods**

The mechanical demulsification approach entails using mechanical force in breaking down the physical barriers or differences in the oil and water phase densities to obtain an efficient separation. Different kinds of mechanical equipment can be employed to separate crude oil demulsification, these include gravity settling tanks, cyclones, centrifugal separators, desalters, free-water knockout (FWKO) drums, low-and high-pressure traps (two-and three-phase separators), and others [4, 54]. There is an increase in the velocity of oil separated through the concentration of oil traces in the separator. Mostly, the separated oil is placed in a separator if the mixture concentration is much [19]. Widely, the centrifuge has not been used compared to other approaches for emulsion treatment because of its high capital cost and low capacity [8, 19, 22]. The presence of specifically massive droplets in crude oil emulsions frequently results in diminished flow velocity, enhancing the utilization of gravitational forces to separate small suspended droplets, water and oil; which generally occur within a space of time in the separator or large-volume desalters [22, 54]. Moreover, the mechanism at which the separator works uses flow dynamics to concentrate and accumulate the materials and give room for oil trace separation that can be eliminated from the process oil [65]. The velocity at which the gravity of crude oil separates is one of the indispensable factors for the use of gravity settling tanker in demulsification; this strongly established the concentration of oil in the mixture [5, 50, 54]. A previous study presented a new technique for the mechanical demulsification of oil-in-water (O/W) emulsions; the
authors explained that the establishment of the demulsification method is an important step during the separation of hydrocarbons using liquid membrane permeation for the industrial practices [55]. The demulsification yielded 80% in the batch runs.

**Electrical methods**

The electrical method entails droplet deformation and achieving attractive forces between the droplets; resulting in coalescence through the application of an electric field. The utility of the electric-powered field makes it less complicated for small water droplets as they once fuse to form larger ones [4]. There will be deformation in the droplets when using an electric field. As the droplets elongate and deform, the coalescence forms rapidly [36]. Theoretically, it is believed that water droplets possess a charge that if exposed to an electric field, there is a rapid movement in the droplets to enable easy collision against one another and coalesce. Also, the electric field realigns the polar molecule to improve coalescence and minimise the tight film [4]. This is mostly regarded as an efficient way of demulsification. Electrostatic dehydration is not often employed alone in the demulsification but is utilized alongside the chemical and heat treatments. This can minimise the required heat, chemical required, improve fuel economy, and minimise the formation of corrosion and scale.

Electrical techniques of demulsification involve the use of an electric field in separating water and oil from the crude oil emulsions [42]. Using an electrical technique is more sustainable relative to other kinds of demulsification techniques [28, 53, 54]. A previous study on electrocoalescence provided easy media between closely spaced droplets in uniform DC electric fields. It was outlined that treating emulsions with electric fields exhibited about two stages [40]. At first, the droplets aligned into chains followed by coalescence of adjacent droplets into a stage of sedimentation. Furthermore, this study provided that the droplet diameters are smaller compared to a particular dimension; due to this, a constraint was placed on the average total performance of coalescing into bigger droplets during the process [40]. Besides, a study investigated the utilization of the DC electric field in line with diverse kinds of demulsifiers to distinguish analytical electric fields of the crude oil emulsion. This analytical electric field explains the electrical prospect where there is an unstable water–oil interface, bridging of droplets or induction of drop-drop contact [40]. The outcome of this study showed an existing threshold for a higher concentration of demulsifiers. Adding a demulsifier resulted in a better outcome compared to the addition of demulsifiers after emulsification. Moreover, a study was carried out to demulsified light Malaysian crude oil emulsion by utilizing electrical technique; there was undesirable production of crude oil emulsion through natural surfactants and mechanical strength [41]. Nevertheless, the problems emanating from refining oil and its transportation have propelled the use of practical demulsification techniques. Hence, understanding the operating conditions and crude oil rheology is paramount in treating the emulsion. The demulsification rate and rheological behaviour of crude oil emulsion had been investigated; these were evaluated by varying water volume fractions (20, 30 and 40%), shear rate (0.1–1000 s⁻¹) and temperature (30–90 °C) to determine the rheological behaviour of crude oil [41]. At the varied water content of each emulsion, there was a non-Newtonian shear thinning behaviour; this has been appropriately defined by the Herschel–Bulkley model. The outcome from this study showed that there was a significant reduction of temperature in the measured viscosity of crude oil emulsion; nevertheless, the viscosity increased with an increasing volume of water fraction. Furthermore, Mohammadian et al. [41] investigated the demulsification rate of water-in-oil emulsion using a direct current field under diverse conditions through electrochemical cells, there was an increase in the rate of water separation as the salt concentration, water content and applied field were increased. The obtained result suggested that the emulsion separation was controlled through the type of electrode and magnitude of the applied electric field.

**Characteristics of demulsifier**

Demulsifiers are molecules enhancing the separation of oil from water often at a reduced concentration. Demulsifiers avert the occurrence of water in the oil mixture. Some demulsifiers are polymers, others have structures comparable to non-ionic emulsifiers [12]. Demulsifiers are surfactants that are quintessential in breaking the emulsion system [54]. The high-quality demulsifiers can lower the interfacial shear viscosity to extend the interfacial mobility and destabilizing water–oil emulsion. A demulsifier must possess the following characteristic to ensure high-quality performance [53]:

- The demulsifier must be capable to separate into the oil and water phases;
- Can breakdown in the oil phase;
- The demulsifier concentration inform of the droplets must be enough to ascertain higher diffusion flux to the interface;
- The demulsifier should be excessive sufficient to subdue the gradient of interfacial tension; therefore, fast-tracking the rate of film drainage to promote coalescence.

Because demulsifiers are surfactants, it is essential to understand the function of demulsifiers as surface-active
agents. The two categories of demulsifier molecules are hydrophilic (water-liking) and hydrophobic (water-disliking) groups [53].

- The hydrophilic effects are known to be water-preferring (molecule, atom, particle, and droplet). This can be said that a species prefers the aqueous phase more than the oil phase.
- The hydrophobic effects are known to be the water-avoiding nature of a species (molecule, atom, particle, and droplet). This indicates that a species prefers the oil phase to the aqueous phase.

**Mechanism of demulsification**

Chemical demulsification takes below non-equilibrium conditions and it is a phenomenon that requires a dynamic approach. This process helps in separating water and decrease viscosity to improve the coalescence of the water droplets in the emulsion. Moreover, the stability of emulsions may be due to the demulsifier that affects the breaking down of the thin film separating droplets in an emulsion containing water and oil, and the existence of surfactant action images at the water/oil interface [53]. Demulsifier acts in suppressing the interfacial tension gradient, together to lower the interfacial viscosity, hence resulting in increasing coalescence and accelerated film drainage [15]. The demulsification mechanism is somehow more complex. Generally, demulsification can be described as a two-step process that includes flocculation and coalescence [1, 53, 54]. The flocculation removes repulsive force that helps in stabilizing the emulsion to create distinct droplets. In coalescence, the method requires two or more droplets coming together to produce less stable and bigger droplets. Splitting of emulsions occurs as various droplets coalesced [53]. Coalescence resulted in the separation of two phases which cannot be reversed. Factors including the presence of any impurity, bulk viscosity, dosage and type of demulsifier, and temperatures can play a vital role in the demulsification efficiency [9].

**Flocculation or aggregation**

Flocculation can best be described as the first motion of demulsifiers on the emulsion. This required a collective combination of flocculation of the small water droplet [25]. During the flocculation, the droplet is closed to one another, forming flocs or aggregates but do not lose their identity [4]. At this stage, coalescence can only occur if the interfacial film surrounding the water droplets is very weak. Factors that can influence the rate of flocculation includes the density difference between oil and water, the viscosity of the oil, temperature and water-cut [4]. Figure 4 illustrates a good example of flocculation. A study on the mechanism of different demulsifiers on the light crude oil emulsion, demulsification performance and behaviour; a chemical demulsifier was widely used for demulsification of crude oil emulsion to form natural stabilizers during the extraction [29]. More so, four classes of non-ionic sodium dodecyl sulphate (SDS), copolymer demulsifiers, ethylene oxide, and propylene oxide; and their dynamic demulsification process on the water/oil light crude oil emulsion were analysed by utilising multiple light scattering techniques. The demulsification mechanism of these demulsifiers was illuminated by measuring the rupture rate, dynamic interfacial viscoelasticity, dynamic interfacial tension and microscopic changes of oil film utilising a single droplet procedure. The outcomes illustrated that demulsification performance did not depend on interfacial tension. An effective demulsifier could have a lower interfacial tension which is around 1 mN/m. Multiple dynamic interfacial tension and light scattering data distinguished the demulsification mechanism of better demulsifiers, adsorption and fast diffusion of demulsifiers, sedimentation, droplet coalescence and palpable change in the interfacial property [29]. The demulsification mechanisms of demulsifiers were dominated by their abilities to decrease the interfacial viscoelasticity and penetrate the interface. The quantitative interpretation of multiple light scattering data showed the demulsification process of various demulsifiers associated with the interfacial viscoelasticity and dynamic interfacial tension [29]. The dynamic rupture process and rupture rate of the oil film between the aqueous phases clearly described differences in the demulsification mechanism. The non-ionic demulsifiers with aromatic groups possessed the best performance and speed because of their similar aromatic groups with those in asphaltenes, which created a less stable oil film [29]. Batista et al. [10] studied the influence of commercial ethylene oxide-b-propylene oxide demulsifier on the demulsification of water-in-crude oil emulsions. During petroleum production, water-in-crude oil emulsions are produced and asphaltenes enhance their stabilization. However, these emulsions were destabilized by adding demulsifiers; hence, the demulsification process
was not known. The effectiveness of commercial ethylene oxide-b-propylene oxide demulsifiers was investigated by utilising asphaltenes in organic solvent (model-system) and synthetic water-in-oil emulsions. The demulsifier induced the asphaltenes and there was no change in the aggregate size when observed. When the asphaltenes aggregated increases, the demulsification performance reduces; thus, it can be deduced that voids between the aggregates adsorbed on the water droplets surface are correlated to the demulsification process.

Coalescence

During the process of coalescence, the droplets are fused or coalesced to form higher droplets; therefore, reducing the number of droplets and eventually completing demulsification [54]. This is an irreversible process and improved by a high rate of flocculation, absence of mechanically strong films, high interfacial tension, low viscosities, high temperatures, and water cuts [34]. Figure 5 shows an example of the coalescence process. During coalescence, extra droplets are joined collectively to form a single higher unit of a reduced perfect surface area. The coalescence mechanism occurs in two stages; film rupture and film drainage [4, 54]. Film drainage occurs when there are a pressure gradient existence and flow of fluid in the film [4, 54]. A study consisting of the mechanism of 30% Nujol-70% water emulsions with several surfactants and demulsification of oil-in-water emulsion in the centrifuge was investigated utilising a coulter counter to observe the size of the particle at different depths in the cream layer as a function of time centrifugation [20]. It was shown that the cream layers were arranged with different sizes of oil globules along with the centrifuge cell. Coalescence of oil globules exists at the bulk oil–cream interface at high concentrations of spent 221 emulsions and Tween 80, and throughout the body of cream. The bulk oil–cream interface has been seen as the prominent target of coalescence at lower concentrations of Gantrez AN 118 and Tween 80 emulsions. The globule size at the bulk oil–cream interface reaches steady-state particle size, and the rate of oil separation was reduced significantly in all conditions. The plateau state happens as a result of the concentration of Tween 80 and the particle size is enhanced due to an increase in the concentration of Tween 80 [20]. Erica et al. (2014) studied the mechanism of demulsification of asphaltene-stabilized water-in-toluene emulsions using an EO-PO based polymeric demulsifier. Demulsification capacity was detected by utilising bottle tests and in addition to the physical and chemical characteristics of asphaltene interfacial films after the addition of the demulsifier. In the droplet coalescence experiments and bottle tests, the demulsifier gave a strong efficiency at 2.3 ppm in toluene. At increased concentrations, the demulsification efficiency gets reduced because of the intrinsic stabilizing efficiency of the demulsifier caused by the steric repulsion between the water droplets. The inclusion of a demulsifier was seen to decrease the viscoelastic moduli of asphaltene films under both compressional interfacial and shear deformations [49]. The study of the chemical composition and microstructures of asphaltene film at the toluene-water interface after adding demulsifier showed slight perforation of demulsifier into the asphaltene film. The penetration of the demulsifier into the asphaltene film altered the asphaltene interfacial morphology and mobility, as probed with atomic force and Brewster angle microscopy. Besides, a novel strategy was adopted to show the measuring rheological features of a water–oil–water film to study the dynamic interfacial mechanisms for demulsification of water-in-oil emulsions [32]. The published data of various commercial-type demulsifiers showed a high relationship between better performances and dynamic film rheological features, utilising specimens of an actual brine and crude oil emulsion. Investigations of dynamic interfacial tension processes using a traditional drop-volume apparatus affirmed the water–oil–water film results. Detection of static interfacial tension breaks down the relationship with the performance data. The hydrophobic microfiltration membranes are well known to be utilised for demulsification of oil-in-water emulsion because of their coalescence of oil droplets in membrane pores [33]. For the demulsification of surfactant-stabilized water-in-oil emulsion, hydrophilic polymer membranes are used. The demulsification success depends on the type of trans-membrane pressure and emulsions which were seen to have influenced the demulsification mechanism, while initial water content and membrane thickness had slight or no influence [33].

Fig. 5 Process of coalescence (Ruffino et al. 2015)
**Kinetics in demulsification**

The kinetics of the chemical demulsification process has been established to have been triggered using three foremost effects [53]:

- The coalescence of water droplets
- Flocculation
- The displacement of the asphaltene film from the (water/oil) interface with the aid of the demulsifier.

Bhardwaj and Hartland [11] outlined that decreasing adsorption and interfacial tension of demulsifier at the crude water/oil interface is compulsory, again no longer a sufficient circumstance for a successful demulsifier. The most vital features of an acceptable demulsifier include adequate accurate partition and surface pressure between the water phase and oil phase. In a recent study by [9], the influence of different parameters and the presence of different demulsifiers on the kinetics of demulsification of synthetic emulsion were investigated. The influences of demulsifier dosage, temperature, type of demulsifiers on the kinetics of flocculation and coalescence were studied. During the demulsification, the separation performance of emulsion was detected through the measurement of coalescence and flocculation rate constants. The more flocculation and coalescence rate constants were formed, the more successful was demulsification when various demulsifiers were compared. It was observed, as coalescence and destabilization behaviour and temperature increased. Also, it has been shown that an efficient demulsifier concentration is excited to acquire a complete coalescence rate constant.

Thomas [64] carried out a microfluidic approach to study demulsification kinetics. These results illustrated that droplet coalescence in a dense layer of emulsion droplets utilising microfluidic circuits encourages direct observation of coalescence and collision events between the oil droplets dispersed in water. The role of viscosity droplet was measured as the rate of flow in hexadecane-in-water emulsion and a higher speed camera was used to detect droplet concentration of image sequences measured. A trajectory evaluation of colliding droplet pairs allows a comparison of the coalescence $t_c$ and film drainage profile.

**Formulations involve in demulsification**

The overall performance of demulsification and characterization of emulsion stability rely on the temperature, pH, bulk interfacial viscosities, conductivities, and droplet size distribution [1, 4, 54]. These factors are explained in the following subsection.

**Temperature**

Heat displays a significant part and gives both merit and demerit to the emulsion breakdown. The temperature rise enhances the viscosity and differences in density of both crude oil and water [53]. Besides, it produces low oil viscosity and an enormous number of droplets; this can minimise the power of accompanying stabilized agents and give more possibility of settling [4, 54]. In the laboratory scale, the appropriate considered temperature falls within 50 and 70 ºC for the demulsification process, this is close to the exact refinery processes [26]. The increase in temperature will reduce the interfacial viscosity of the internal phase. This might be due to the rate at which film drainage increases in proportion to the temperature [21]. The momentum between two water droplets will lengthen formerly than coalescence [21]. The two stages of immiscible liquids can then separate based on the type of density amongst them. Besides, a reduced interfacial shear viscosity can enhance the diffusion rate of film drainage between adjacent droplets. Nevertheless, higher temperatures will minimise the demulsifier
performance in some cases because the chemical additives are delicate to heat [58].

**Droplet size distribution**

In oilfield emulsions, the droplet size distribution can influence the efficiency of the demulsification process. The drop dimension and droplet diameter of every oil-in-water or water-in-oil emulsions are larger than 100 μm and 0.1 μm, respectively. A previous study outlined that a minimum droplet size distribution can result in unrestricted viscosity and concentrated emulsion [69]. Afterwards, a prolonged time will be experienced in the coalescence of the distributed drops that can later float (oil droplets) or sediment (water globules). As the average droplet size reduces, it shows that an extended residence time minimizes the rate at which the droplet sizes are separated [69]. However, an exceptional demulsifier is needed to benefit the coalescence processes; hence, enhancing an adequate demulsification efficiency [17].

**pH**

The oil-in-water emulsion is favoured at reduced pH values between 4 and 6; at the same time, the water-in-oil emulsion is favoured at increased pH values between 8 and 10 [1]. The experimental results indicated that the oil-in-water emulsion was stable conventionally as the pH was prolonged from 4 to 6. On the other hand, increasing the pH from 6 to 8 and eventually, 10 achieved the generation of a more stable water-in-oil emulsion and lesser stable oil-in-water emulsion. When measuring the stability of an emulsion, two main parameters influence the pH of water, they are brine and oil phase compositions in the emulsions [69]. The greater the emulsion value of pH, the greater the surfactant hydrophilicity. Another study presented that water-in-oil emulsions are sustainable in achieving a lower pH environment as the oil-in-water emulsions are favourable in higher pH surroundings. There was an improvement in the demulsification at a pH of 7 [16]. Inconsistent with this outcome, the pH of the emulsion will reduce emulsion stability due to the reality of asphaltene films generated in the acidic medium; nevertheless, there will be unstable emulsion in alkaline environments.

**Oil and water contents**

Apart from resins and asphaltenes, oil and water contents in W/O emulsion are additional important factors that can improve the stability and separation of emulsions. Mainly, the occurrence of demulsifiers can enhance the effectiveness of the demulsification process by improving water content in the emulsions and lower the processing time [54]. The demulsifier concentration is essential to separate water, this depends on if the proportion of water contents fall within 0.3 and 0.7 volumetric fractions [1, 69]. Emulsion with greater water contents can easily break down compared to the one with lower water contents; this implies that higher water content causes more viscous crude oil. Moreover, the rate of coalescence and demulsification improve as the dispersed phase volume increase; this was because of the increased entropy that caused an effective collision between the single-phase droplets [53]. Contrarily, minimising the oil contents to 60% from 90% resulted in a little separation in a stabilized oil-in-water emulsion, while lowering the oil content to 50% can improve the breaking of emulsion promptly [1].

**Surfactant molecular weight**

The molecular weight of a demulsifier makes its diffusion and mobility behaviour produce interfacial adsorption kinetics [18]. It has been reported that the demulsifiers with bigger molecular weights showed lower adsorption kinetics that can make them less active demulsifiers [53]. This may be because the demulsifiers needed to withstand surfactants that occur naturally inside the crude oil. Generally, the adsorption kinetics of asphaltenes in crude oil is as small as > 2–4 wt%; thus, it requires a demulsifier. However, it still requires a demulsifier. A higher molecular weight demulsifier provides adsorption at the interface that reacts with other particles at the interface with average adsorption kinetics [47].

**Conclusion**

The formulation of crude oil emulsion through diverse sources has caused different challenges to the refiners. Given this, this review explains trending approaches to the demulsification of crude oil in the petroleum industry. The essential goal of demulsification is to increase the interfacial film thinning processes through the lowering of stabilizing film strength and incorporating the emulsifier adsorption at the oil–water affiliate. Demulsification approaches are applied specifically due to wider varieties of brines, crude oils, product specifications, separation equipment, and chemical demulsifiers. Moreover, emulsion and its condition can vary over time; this can complicate the treatment processes. Mostly, heat and chemical demulsifiers are the treatment used to enhance destabilization, followed by a set time with an electrostatic grid to enhance separation through gravitation. The mechanisms of demulsification vary from one study to another based on certain parameters such as properties and types of emulsions, characteristics of demulsifier in corresponding to emulsion treatment and function of solid stabilized emulsion. Thus, knowing the emulsion behaviours is more essential in developing an advance strategic
emulsion breaking path to achieve reduced economic challenges in the petroleum industry.

Acknowledgements This study was supported by UIC190806.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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