

# An Overview of Recent Advances in State-of-the-Art Techniques in the Demulsification of Crude Oil Emulsions

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## **Abstract:**

The processing of crude oil often requires the extraction of a large amount of water. Frequently, crude oil is mixed with water to form water-in-crude oil emulsions as the result of factors such as high shear at the production wellhead and surface-active substances that are naturally present in crude oil. These emulsions are undesirable and require demulsification to remove the dispersed water and associated inorganic salts in order to meet production and transportation specifications. Additionally, the demulsification of these crude oil emulsions mitigates corrosion and catalyst poisoning and invariably maximizes the overall profitability of crude oil production. Recently, there has been growing research interest in developing workable solutions to the difficulties associated with transporting and refining crude oil emulsions and the restrictions on produced water discharge. Therefore, this paper reviews the recent research efforts on state-of-the-art demulsification techniques. First, an overview of crude oil emulsion types, formation, and stability is presented. Then, the parameters and mechanisms of emulsification formation and different demulsification techniques are extensively examined. It is worth noting that the efficiency of each of these techniques is dependent on the operating parameters and their interplay. Moreover, a more effective demulsification process could be attained by leveraging synergistic effects by combining one or more of these techniques. Finally, this literature review then culminates with propositions for future research. Therefore, the findings of this study can help for a better understanding of the formation and mechanisms of the various demulsification methods of crude oil to work on the development of green demulsifiers by different sources.

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Review

# An Overview of Recent Advances in State-of-the-Art Techniques in the Demulsification of Crude Oil Emulsions

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**Abstract:** The processing of crude oil often requires the extraction of a large amount of water. Frequently, crude oil is mixed with water to form water-in-crude oil emulsions as the result of factors such as high shear at the production wellhead and surface-active substances that are naturally present in crude oil. These emulsions are undesirable and require demulsification to remove the dispersed water and associated inorganic salts in order to meet production and transportation specifications. Additionally, the demulsification of these crude oil emulsions mitigates corrosion and catalyst poisoning and invariably maximizes the overall profitability of crude oil production. Recently, there has been growing research interest in developing workable solutions to the difficulties associated with transporting and refining crude oil emulsions and the restrictions on produced water discharge. Therefore, this paper reviews the recent research efforts on state-of-the-art demulsification techniques. First, an overview of crude oil emulsion types, formation, and stability is presented. Then, the parameters and mechanisms of emulsification formation and different demulsification techniques are extensively examined. It is worth noting that the efficiency of each of these techniques is dependent on the operating parameters and their interplay. Moreover, a more effective demulsification process could be attained by leveraging synergistic effects by combining one or more of these techniques. Finally, this literature review then culminates with propositions for future research. Therefore, the findings of this study can help for a better understanding of the formation and mechanisms of the various demulsification methods of crude oil to work on the development of green demulsifiers by different sources.

**Keywords:** crude oil; emulsion; demulsification; stability; mechanism

## 1. Introduction

One major challenge often encountered during the production and transportation of crude oil in petroleum industries is the formation of complex and extremely stable emulsions with saline water [1–4]. These emulsions are droplets of water or brine dispersed in a continuous phase of crude oil: hence, they are known as water-in-oil (W/O) emulsions [5]. The emulsions encountered during crude oil production are complex in nature, and they can be grouped into water-in-oil (W/O), oil-in-water (O/W), and water-in-oil-in-water (W/O/W) emulsions [6–9]. Amongst these emulsion types, the water-in-oil emulsion has been reported to predominate, whereas the other types are present in insignificant proportions [2,10,11]. The formation of water-in-oil emulsions is often linked to pressure and shear

forces [12–14]. The presence of emulsified water often results in several difficulties during crude oil processing [12]. The difficulties reported in the literature range from constrained flow line pressure, decreased production, pipeline corrosion, pump malfunctions, poisoning of downstream refinery catalysts, and other problems associated with the production equipment and overhead distillation column [15,16]. The profit margin and productivity of petroleum industries are usually impeded by the myriad challenges associated with emulsified water [17,18]. Hence, to prevent economic losses and operational challenges, there is a need to separate the mixture of saline water and crude oil into two separate phases in a process known as demulsification before the transport or refining of crude oil [19]. The demulsification process is often accomplished using a suitable demulsifier [20–22]. Several techniques for crude oil demulsification have been reported in the literature [23–25], and they can be grouped into three broad categories, namely, chemical, physical (mechanical, thermal or microwave, electrical, ultrasonic, and membrane), and biological [19]. Amongst these techniques, chemical demulsification has been the most widely applied and reported in the literature, which involves the addition of demulsifier to crude oil emulsions [26–28]. The main function of the chemical additives is to destabilize the emulsifying agents [5]. Demulsification by mechanical means entails the disruption of physical barriers or the application of density variation between the water and the oil phases for demulsification processes [29,30]. Mechanical demulsification of crude oil emulsion can be carried out using series of mechanical equipment such as free-water knockout drum, two- and three-phase separators (low- and high-pressure traps), desalters, and settling tanks [31,32]. Demulsification by thermal treatment refers to the separation of oil and water phase in crude oil emulsion by increasing the temperature of the emulsion [33]. A heater is usually employed to achieve the raise the temperature of the crude oil emulsion before they enter a horizontal flow to be treated. Demulsification by electrical techniques entails the application of electric fields for separation of oil and water in crude oil emulsions [26]. The demulsification of crude oil emulsion by ultrasonic technique works based on the principle of condensation and viscosity-reducing impact of ultrasound on crude oil [34]. The ultrasound facilitates clumping together of the water droplets in the crude oil, thereby facilitating the separation of the oil–water phases. The membrane demulsification of crude oil emulsion works based on the tendency of low pressure to push the dispersed phase thereby permeating through a membrane into a continuous phase [35]. Bio-demulsifier is a form of biosurfactant with a characteristic feature to destabilize a crude oil emulsion. Biodemulsifier is environmentally friendly, and its usage does not result in secondary pollution [36].

A few review papers have examined the formation, mechanisms, and performance optimization of the demulsification process and the influence of emulsion formation on petroleum industries [12,37]. The present study provides an overview of recent advances in state-of-the-art techniques of the chemical, biological, mechanical, and physical demulsification of the crude oil emulsions and discusses potential synergies between these demulsification techniques that would enhance the overall process performance. This could assist researchers to understand enough of the parameters, suitable conditions and types of demulsifiers used to continue in development of the demulsification process of crude oil and avoid the problems and the unsuitable conditions which affect demulsification efficiency. Since recent advances are of interest, the literature reviewed for this study was restricted to research articles published from 2010 to 2018. First, an overview of crude oil emulsion types, formation, and stability is presented. Then, the parameters and mechanisms of emulsification formation and different demulsification techniques are extensively examined with short tables of the studies through the last eight years. In the last section of the review, some propositions for future research are given. Figure 1 shows the general sketch of the problem and steps of the demulsification process.

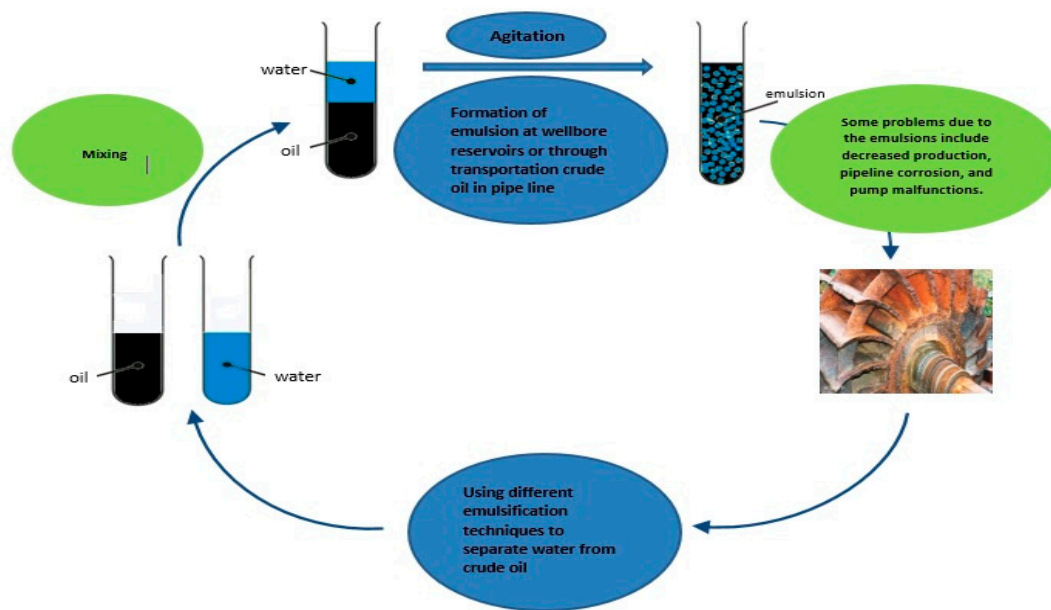


Figure 1. The general sketch of the problem.

## 2. Methodology

The literature review for this study was performed in accordance with the method proposed by Gupta et al. [38], with a slight modification. The modified literature review process included journal/database selection, keyword searches, a review of abstracts, inclusion/exclusion criteria, and a full-text review. The Web of Science citation database was selected for the literature search in order to obtain high-quality journal articles [39,40]. The search keywords were carefully selected to prevent the unintentional limitation of the research articles retrieved. Keywords such as “crude oil emulsion”, “demulsification”, “oil–water separation techniques”, and “demulsifier” were employed during the literature search. The first search using “crude oil emulsion” resulted in 2463 articles indexed from 2000–2018. Since the main aim of this study was to examine recent advances in state-of-the-art techniques for the demulsification of crude oil emulsions, the indexing year was refined to 2010–2018. Moreover, the document types were restricted to research articles. After modifying the search criteria, the number of articles obtained was reduced to 1348. An additional search using “demulsification of crude oil emulsion” reduced the search results to 226 articles. The titles of each of the 226 articles were scanned for their suitability to the study topic, and this further downsized the number of articles to 128. At this point, the abstracts of each of the 128 articles were thoroughly examined to ensure that they were in line with the objectives of this review. This resulted in 78 articles, which were thoroughly reviewed in full for this study.

The next section presents a detailed review of the formation, stability, and demulsification of crude oil emulsions.

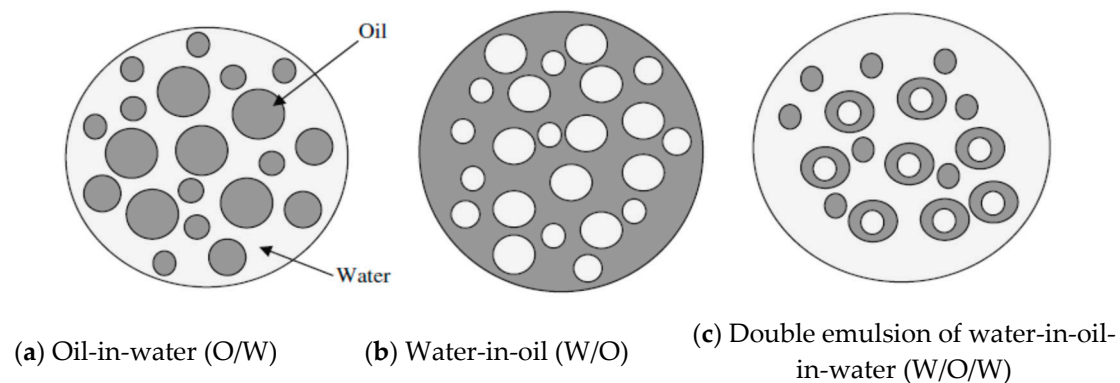
## 3. Emulsions

An emulsion comprises two phases that do not mix under normal conditions, as is the case for oil and water. In an emulsion system, one phase is dispersed as globules in the second phase. The phase that appears in the shape of globules is often referred to as the sparse or dispersed phase, while the continuous phase is the medium that holds the dispersed-phase droplets [41]. There is substantial research interest in the science of emulsions because they have a wide range of applications in areas such as the food, cosmetics, pulp and paper, pharmaceutical, and agricultural industries [14]. Outside of petroleum industries, crude oil emulsions may not be as common as other emulsion types; however, they represent an important phenomenon that plays a vital role in crude oil commercialization [42]. In

the crude oil processing stages, such as drilling, production, and transportation, crude oil emulsions are often encountered. A proper understanding of the characteristics of the crude oil emulsion is vital for monitoring and enhancing crude oil production at all stages. In view of this, several investigations have been conducted to better understand the complex nature of crude oil emulsions.

### 3.1. Types and Structure of Crude Oil Emulsions

Crude oil emulsions consist of complex colloidal structures, with the dispersion of fine droplets of one liquid in another liquid. The two liquid phases that constitute an emulsion are mutually immiscible [43]. A crude oil emulsion is often produced when the oil and water phases are vigorously stirred; nevertheless, once the stirring is stopped, there is an immediate breakdown in the emulsion [42]. Crude oil emulsions can be classified according to the nature of the dispersed phase; thus, an O/W emulsion refers to oil droplets in water, and a W/O emulsion refers to water droplets in oil. There are also multiple emulsions, such as oil-in-water-in-oil (O/W/O) and water-in-oil-in-water (W/O/W) as shown in Figure 2. The composition of oil and water varies in different emulsion types, depending on the nature of the crude oil. Studies have shown that W/O emulsions have  $\leq 50\%$  water, whereas oil-in-water emulsions contain  $\geq 80\%$  water. In some specific conditions, the water content in O/W emulsions may be  $\geq 20\%$  [44]. The characteristics of each of the crude oil emulsion types are presented below.



**Figure 2.** Types of emulsions [45].

#### 3.1.1. Oil-in-Water Emulsions (O/W)

In this type of emulsion, the oil phase is usually the dispersed phase, and the dispersion medium (continuous phase) is water. According to Arab et al. [46], oil-in-water emulsions are preferable to water-in-oil emulsions in heavy oil systems since water-in-oil emulsions require a significant high-pressure gradient to achieve typical flow rates, and this is impractical.

#### 3.1.2. Water-in-Oil Emulsion (W/O)

The water-in-oil emulsion occurs when the dispersed phase mainly consists of water, and the dispersion medium is oil [43]. One of the major challenges in the transportation of crude oil is the presence of water-in-oil emulsions [47]. For ease of flow, a water-in-oil emulsion needs to be broken down into separate phases prior to transporting the crude oil to the refinery.

### 3.1.3. Multiple Emulsions

O/W/O denotes a double emulsion in which oil droplets are dispersed in water droplets that are, in turn, dispersed in a continuous oil phase [48]. In the processing and transportation of petroleum, the presence of certain emulsions can be desirable or undesirable, depending on the conditions. Table 1, based on the work of L.L. Schramm [49], summarizes some of the desirable and undesirable emulsions.

**Table 1.** Some desirable and undesirable emulsions.

Emulsion Description	Type of Emulsion	Desirable	Undesirable
Heavy oil pipeline emulsions	O/W	√	
Oil flotation process emulsions	O/W	√	
Emulsion drilling fluid: oil-emulsion mud	O/W	√	
Oil-base mud	W/O	√	
Asphalt emulsion	O/W	√	
Enhance oil recovery from in situ emulsions	O/W	√	
Fuel oil emulsion (70% heavy oil)	O/W	√	
Wellhead emulsions	W/O		√
Fuel oil emulsions	W/O		√
Oil flotation process froth emulsions	W/O or O/W		√
Oil flotation process diluted froth emulsions	O/W/O		√
Oil spills mousse emulsions	W/O		√

Source: Reference [49].

### 3.2. Emulsion Formation

Emulsions can be formed during nearly all phases of oil production and processing. Range emulsions, for example, can be created inside oil reservoirs, in the wellbore throughout production, or in the pipelines during transportation. Emulsion formation and stability have been extensively investigated with respect to their relevance in several technological areas, such as the petroleum, coating, food, cosmetic, and pharmaceutical industries, among many others [6,7,10]. The factors that affect crude oil emulsions and their stabilities during emulsification have been thoroughly investigated [50]. Several studies have shown that the formation of crude oil emulsions is strongly dependent on the composition of the crude oil, which often consists of natural emulsifying agents, such as asphaltenes, acidic compounds (naphthenic acids, fatty acids, aromatic acid), and resins [43]. The asphaltene fraction is characterized by a high percentage of heteroatoms such as oxygen, sulfur, and nitrogen. In addition, it also contains organometallic constituents such as nickel, vanadium, and iron in crude oil. Acidic compounds like naphthenic acids are non-polar hydrocarbons, without double bonds, but including straight-chain and branched, and aromatics are formed of structures containing aromatic ring these components could be connected to all oil types. The resins contain a solubility group and interfere with the aromatic constituents [51–53]. This characteristic assists the natural emulsifiers in the formation of a rigid layer around the dispersed droplets that prevent coalescence from happening and make the emulsion more stable [54]. These natural emulsifiers are abundant in heavy and extra heavy crude oils. The formation of a crude oil emulsion is initiated when there is contact between two immiscible liquids in the presence of an emulsifying agent, provided that there is adequate blending or agitating in order to disperse one liquid in the form of droplets into the other. Wen et al. [25] reported that full and partial crude oil emulsification can occur below the critical value of the water fraction and high-water fraction, respectively. The authors established that the emulsion formation and behavior vary from one crude oil to another. A follow-up study by Delgado-Linares et al. [55] revealed that the natural surfactants in crude oil reduce the IFT of oil–water, leading to the formation of an interfacial film. This interfacial film, which is characterized by its mechanical strength, serves an important function in the formation and stability of the emulsion [56]. Studies by Ostertag et al., Bauer et al., Solans, and Sole have identified the different routes by which oil droplets can be produced for the



formation of emulsions. These routes include the use of devices such as dispersing machines, rotor stators, colloid mills, or high-pressure homogenizers that apply high shearing stresses; additionally emulsification can be achieved by using a membrane and applying ultrasonic waves [57–59]. Chemical reactions or the nucleation of one phase in another as a result of low temperature can lead to immediate crude oil emulsification [60].

### 3.3. Stability of the Emulsions

Crude oil consists of several components. The main elements in crude oil are carbon and hydrogen, with small quantities of nitrogen and oxygen gases, sulfur, and trace amounts of common metals (iron, vanadium, and nickel) [61]. Therefore, the variation in crude oil composition might contribute to the significant differences found in emulsification behavior. During the emulsification process, each natural surfactant plays a unique role. Asphaltene, which consists of myriad non-hydrocarbon compounds, improves the emulsion stability as a result of its good interfacial activity [62]. Kilpatrick [63] revealed that asphaltenic aggregates (7–20 nm) were responsible for the formation of the stabilizing interfacial film of the crude oil emulsion. Moreover, Fan et al. [64] reported that emulsion stabilization was significantly increased by asphaltene aggregation and its concentration. Similar to asphaltene, resin consists of various macromolecular non-hydrocarbon compounds and plays a significant role in the formation of crude oil emulsions [65]. Unlike asphaltene, the emulsion formed by resin exhibits less stability as a result of the low thickness of the interfacial film [66]. However, the presence of both asphaltene and resin could have a synergistic effect on the formation and stability of crude oil emulsions. According to Kar et al. [65], the addition of resins can result in the deteriorated stability of emulsions formed by asphaltenes.

The presence of an acidic compound in crude oil has been reported to play an important role in the stability of emulsions. These compounds decrease the interfacial tension of the oil–water interface and thereby stabilize the interface and the emulsion [67]. This was confirmed by Waraho et al. [68], who discovered that the adsorption of acidic compounds onto the oil–water interface significantly stabilized the oil–water emulsions. Acids with lower molecular weights, such as carboxylic and aliphatic acid, were observed to be the most effective in reducing the interfacial tension of oil–water [69]. Acids with a higher molecular weight were observed assist the stabilization of the emulsion.

Factors such as phase ratios, the viscosity ratio, surfactant types and concentrations, temperature, stirring speed, and the average droplet diameter of water-in-oil have been reported to have significant effects on water-in-oil emulsions [70,71].

### 3.4. Emulsification Methods

#### 3.4.1. Gel-Emulsification Method

There has been growing interest in the formation of crude oil emulsions using the gel-emulsification method for its potential as an energy-efficient process [72]. Also, oil viscosity and interfacial tension have negligible effects on the drop breakup process during the gel-emulsification method. Moreover, the gel-emulsification method is highly suitable for emulsifying viscous oils: gel emulsions with a high viscosity favor very efficient emulsification of the added phase with low energy input [47,73]. Several research efforts have been conducted to characterize the gel-emulsification method. Fallah et al. [72] investigated the effect of surfactant type and concentration on gel emulsification and direct mechanical emulsification. The study revealed that the gel-emulsification method is more effective than the direct mechanical emulsification method for the production of nanosized drops [73].

### 3.4.2. Direct Mechanical Method

The direct mechanical method is commonly used for the formation of crude oil emulsions in industry [74]. This method involves the use of a mechanical device with a stirring head that has a set of blades operating at a high speed [72]. Mechanical stirring creates a significant external force that disrupts the interfacial tension between dispersed and continuous phases. Moreover, during the stirring process, large viscous liquid drops are broken into small liquid droplets, the generation of which invariably leads to the formation of an emulsion. The use of this device enables the vigorous agitation of the liquid phases, and it stimulates emulsification by creating larger shearing forces between the oil, water, and surfactant phases. Nevertheless, the major disadvantage of the mechanical method is that the dispersed droplets in the emulsions tend to form assemblies that then separate into the water and oil phases, regardless of how thoroughly the mixture is stirred.

### 3.4.3. Emulsification by Ultrasound

Emulsification by ultrasound involves the use of ultrasonic waves to stir and mix liquids [75]. Studies have shown that high-frequency ultrasonic waves applied to a water and oil mixture cause a considerable vibration as a result of cavity effects [76]. One major advantage of using the ultrasound method is the shortening of the emulsion process time and the formation of smaller droplets of the dispersed phase of the emulsion. Studies have shown that during emulsification by ultrasound, the processing time is shorter and the average drop size of the dispersed phase is smaller compared with that generated by the mechanical method [77].

### 3.5. Parameters Used for the Emulsification Formation Process

The important parameters in the formation of emulsions are summarized in Table 2. These parameters include the water content in the water–oil mixture, mixing time, mixing speed, type of emulsifier, and emulsifier concentration. Studies have shown that the emulsification process is significantly influenced by these parameters, as indicated in Table 2. Investigating the effect of surfactant concentration on the emulsification process, Kumar and Mahto [78] varied the surfactant concentration from 1 wt% to 3 wt% in intervals of 0.5 wt% and found that there was a drastic reduction in the emulsion viscosity of 96%. It was also observed that there was an increase in emulsion stability (from 80% to 100%) as the oil content increased (from 40% to 60%). Furthermore, an increase in the surfactant concentration resulted in a corresponding increase in emulsion stability. Hassanzadeh et al. [79] investigated the influence of factors such as surfactant types, solvents, temperature, pressure, and mixing conditions on emulsions prepared from crude oil storage tanks on Khang Island, Iran. The findings revealed that adjusting the investigated factors could significantly decrease the emulsion viscosity. Moreover, a further investigation of the effect of mixing conditions on the viscosity and stability of the prepared emulsion was conducted. The findings showed that without mixing, the emulsion was too viscous and sticky, while the stability was observed to be homogeneous. Conversely, the emulsions prepared by manual mixing with a mixing time of 30 min and mechanical mixing (500 rpm) with a mixing time of 5 min were observed to have drastically reduced viscosities, and their stabilities were semi-homogeneous.

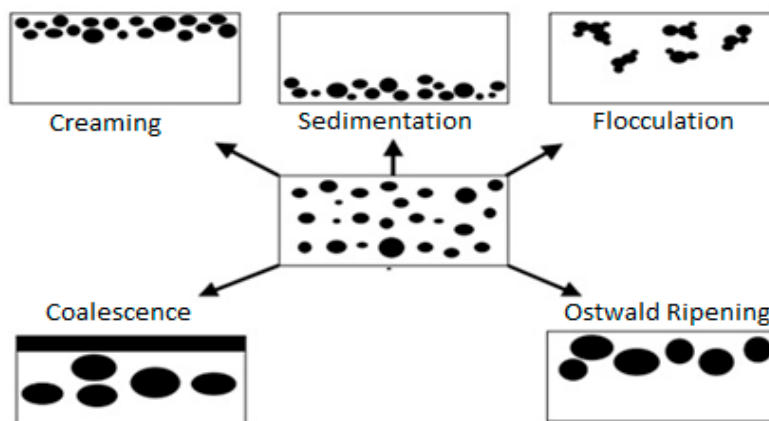


**Table 2.** Summary of important parameters used for the preparation of an emulsion.

Type of Emulsion	Oil/Water Content (v/v)	Mixing Time (min)	Mixing Speed (rpm)	Type of Emulsifier	Emulsifier Concentration	Year of Study	Reference
W/O	Oil content 40 wt%–80 wt%	5–40	1000–15,000	Triton X-100	0.5 wt%–4 wt%	2010	[80]
O/W		60		Triton X-100	0.1%	2010	[81]
O/W	50/50	0.5–1	1000	Ethoxylated nonylphenol family (RENEX) with an ethoxylated amine (Ultramina, five EO groups)	N/R	2011	[82]
O/W	60/30	10	6000	Sodium carbonate (Na <sub>2</sub> CO <sub>3</sub> )	500–15,000 (ppm)	2012	[83]
O/W	69 vol%, 72 vol%, and 66 vol%	5–15	1000–2000	Triton X-100	0.3 wt%–2.5 wt%	2013	[84]
W/O		15	2000	SPAN 83		2014	[85]
W/O	4/1	5	10,000	n-Heptane (analytical grade) and toluene	N/R	2015	[86]
O/W	90/10, 70/30, and 50/50	30	9000			2016	[87]
W/O	70/30	5	1300	SPAN 80	3%	2017	[88]
W/O	50/50	30	15,000			2018	[89]

#### 4. Demulsification Mechanism

During the demulsification process, the emulsions must go through several steps before being separated into water and oil phases. The mechanisms that are involved in this process consist of creaming and sedimentation, flocculation, Ostwald ripening, and coalescence. Figure 3 shows a schematic of the destabilizing mechanisms.



**Figure 3.** Destabilizing mechanisms of emulsions during demulsification. Source: Reference [90].

##### 4.1. Creaming and Sedimentation

Both sedimentation and creaming are caused by the difference in density between water and oil; that is, the density of water is higher than that of oil. Sedimentation is an important mechanism of crude oil demulsification and is characterized by the water droplets in an emulsion settling at the bottom of the continuous oil phase [62]. In contrast, creaming is the rising of oil droplets to the surface of the water phase [91]. Thus, whether sedimentation or creaming occurs is dependent on whether the dispersed phase is water or oil, respectively.

#### 4.2. Flocculation

The water droplets in crude oil emulsions clump together during flocculation, thereby forming aggregates or flocs. The flocculation rate depends on several factors, such as the water content in the emulsion, temperature of the emulsion, viscosity of the oil, the density difference between the oil and the water, and the electrostatic field [17].

#### 4.3. Ostwald Ripening

Ostwald ripening is another process by which crude oil is demulsified. Ostwald ripening is the process by which drops increase in size. The process takes place as soon as the dispersed phase possesses finite solubility in the continuous phase, causing drops of different sizes to migrate toward each other [92]. Faster growth usually occurs in large volume fractions because it is easier for the drops to exchange material. For heavy oil, the solubilities of oil in water or water in oil are low, which slows the drop growth process. The drop growth process via Ostwald ripening plays a crucial role in the stability of oil-in-water emulsions [60].

#### 4.4. Coalescence

Coalescence is an essential step in crude oil demulsification, and it is an irreversible process whereby water droplets fuse or coalesce to form a larger one [21]. The coalescence process often results in fewer water droplets and invariably leads to complete demulsification of the crude oil emulsion [93]. For efficient coalescence, factors such as a high rate of flocculation, absence of mechanically strong films, high interfacial tension and water cut, low interfacial velocity, and high temperature are required [94].

### 5. Crude Oil Demulsification and Different Demulsification Techniques

Having described the processes of emulsification and the formation of crude oil emulsions in the previous sections, it is important to examine recent developments in the demulsification process because of its significance in petroleum industries. Demulsification as a means of breaking crude oil emulsions into separate inhomogeneous water and oil phases has been widely investigated owing to the everyday occurrence of emulsions at every stage of crude oil processing [2]. Factors such as the rate or speed of the phase separation, the volume of water remaining in the crude oil after demulsification, and the water quality left for disposal after the demulsification are vital considerations in crude oil demulsification [12]. For effective demulsification, the separation of the oil and water phases must occur at a fast rate, the residual water content in the crude oil must be low, and the water left for disposal must contain a negligible amount of oil [33]. These qualities are essential because the produced oil must meet the pipeline and company standards and specifications. In a typical crude oil processing facility, produced oil that is ready to be shipped must not exceed (1) 0.2% basic sediment and water and (2) 10 pounds of salt per thousand barrels of crude oil [47]. However, this specification varies, depending on the company and the specifications of the pipeline to be used. A major research objective in crude oil processing industries is to establish an effective technique for the demulsification of crude oil emulsions. The techniques employed to achieve effective demulsification include adding a chemical demulsifier, increasing the temperature of the emulsion, applying an electrostatic field to facilitate coalescence, and reducing the flow velocity for the gravitational separation of oil, water, and gas [28,95]. These techniques can be combined to optimize the demulsification process. The techniques used to demulsify crude oil emulsions are application-specific because of differences in crude oil composition, brine, the separation equipment and chemical demulsifiers used, and the required specifications for the produced oil. Generally, demulsification methods can be classified into chemical, biological, mechanical, thermal, microwave, electrical, ultrasonic, and membrane techniques. The details and recent developments of each of these demulsification methods are discussed in the next sections.

### 5.1. Chemical Demulsification

The chemical method entails the addition of demulsifiers to crude oil emulsions, and it is one of the most common methods of demulsification [28]. The main function of the chemical additives used for demulsification is to destabilize the emulsifying agents [5]. A demulsifier is a surface-active compound [96], so upon its addition to an emulsion, the demulsifier migrates to the oil–water interface and breaks the rigid film, resulting in the coalescence of water droplets [21]. Studies have shown that the optimum disruption of crude oil emulsions by demulsifiers requires the careful selection of the chemicals for a given emulsion, the appropriate amount of the chemicals, proper mixing of the chemical in the emulsion, and sufficient retention time in the separators to allow the water droplets to settle [19,28]. Also, the emulsion might be completely resolved by the addition of heat, electric grids, and coalescers. In line with this, Razi et al. [28] studied the effect of different demulsifier formulations on the efficiency of chemical demulsification of heavy crude oil. The findings showed that the different surfactant demulsifiers varied in water separation efficiency. The best demulsifier formulation separated a water volume of about 80% in the first several minutes of the experiment. The formulated surfactant was observed to be more efficient in the demulsification of a medium crude oil emulsion compared with that of a heavy crude oil emulsion. This difference in the efficiency of the surfactant was attributed to the medium crude oil having lower asphaltene content than the heavy crude oil. In a follow-up study, Al-Sabagh et al. [97] investigated the effect of five demulsifiers formulated from different ratios of polymers on the demulsification efficiency of W/O emulsions. The findings revealed that there was an increase in the efficiency of the water separation as the molecular weight increased. The use of calcium chloride with cationic poly(dimethylamine-co-epichlorohydrin) (PDcE) and cationic polyacrylamine (CPAM) as demulsifiers for the demulsification of super-heavy oil was investigated by Tong et al. [98]. The demulsifier formulation with a PDcE/CaCl<sub>2</sub>/CPAM ratio of 20:600:1.2 (m/m) was optimal, and it resulted in the effective separation of mineral oil (98.04%) from heavy oil emulsions. Contrary to the work of Tong et al., Flores et al. [99] employed a series of ionic liquids, such as trioctylmethylammonium [TOA]<sup>+</sup> [Y]<sup>−</sup> and the ammonium salt [OCD]<sup>+</sup> [Y]<sup>−</sup>, as demulsifying mediums for the demulsification of super-heavy crude oil. The use of the ionic liquid obtained from the [TOA]<sup>+</sup> [Y]<sup>−</sup> species attained a 95% water removal efficiency. An ionic demulsifier at a concentration of 900 mg/L was employed by Martínez-Palou et al. [7] and resulted in a dewatering efficiency of 89.5%. The disparity in efficiency between Martínez-Palou et al. [33] and Flores et al. [99], who both used ionic demulsifiers, could be attributed to the chemical composition of the demulsifiers and the operating conditions of the demulsification process. However, compared with these two studies, a higher demulsification efficiency (97%) was reported using a high-molecular-weight non-ionic surfactant for the demulsification of multiple high-paraffin oils from Kazakhstan oilfields [100]. In a further study, a non-ionic demulsifier formulated from polyethyleneimine (PEI) with varying ethylene oxide and propylene oxide contents was reported by Duan et al. [101]. According to their findings, increasing the temperature of the emulsion to 50 °C resulted in the enhanced performance of the PEI-formulated non-ionic demulsifier. Adilbekova et al. [102] also observed that a demulsifier formulated from a non-ionic block copolymer based on alkoxyated compounds was very efficient for crude oil demulsification. Ali et al. [103] reported that a low temperature (40 °C) and a demulsifier formulated from kerosene led to the effective demulsification of a crude oil emulsion from the Aksaz field in the study. Zhaoyang You et al. [104] investigated the treatment of emulsified oil-contaminated water with 5000 ppm of demulsifier. In this experiment, a set of inorganic materials were simply compounded with polysilicate aluminum ferric sulfate (PSAFS). The results showed that the effluent oil concentration can be reduced to less than 15 ppm when PSAFS was combined with magnesium sulfate, zinc sulfate, and manganese sulfate.

The use of polymeric chemical species as chemical demulsifiers is gaining increasing attention. Demulsifiers formulated from polymers, such as alkene oxides diester, ethylcellulose (EC), Tween non-ionic polymer, and polyester, have been widely studied for the demulsification of crude oil emulsions [81,103,105]. Variation in the concentration of these polymeric demulsifiers has often resulted in different degrees of demulsification efficiency, with the highest demulsification efficiency of 97.5% recorded within 45 min of the demulsification process using a polyester-based demulsifier. Similarly, magnetic-based chemical demulsifiers, such as magnetic graphene oxide, Janus magnetic submicron particles, oleic acid-coated magnetite nanoparticles, and alginate, have been proven to have a high demulsification efficiency in the range of 95–99.98% [89,106,107]. Ali et al. [108] revealed that the use of a Janus submicron magnetic particle demulsifier at a concentration of 600 ppm and temperature of 60 °C yielded more than a 95% efficiency during demulsification of a water-in-oil emulsion within 2 h of processing. Despite the high demulsification efficiency reported using the above chemical demulsifiers, the process still faces challenges, such as low compatibility and efficiency [28]. Besides these issues, chemical demulsifiers tend to reduce the surface and interfacial tensions by accumulating at the interface between the oil and aqueous phase. Thus, the water extracted by chemical demulsifiers has to be treated to remove refractory organic polymers, which are very harmful to aquatic organisms, prior to being discharged into the environment [109]. Bin Huang et al. [110] studied an orthogonal experiment to treat produced water by using the demulsification–flocculation method. Five major influencing factors of the oil concentration were investigated. Based on the results of the range analysis and the relationship between the factors and oil concentration, the order of important agents was found to be demulsifier dosage > flocculant dosage > settling time > stirring time > stirring intensity, and the optimal demulsification–flocculation treatment conditions were successfully optimized. The toxicity and non-biodegradability of chemical substances in the water extracted during demulsification can be addressed by using biodemulsifiers, which are usually produced by microorganisms. In Table 3 some of the recent studies which use the chemical demulsifiers are summarized, and in the next section, an overview of the biological demulsification of crude oil emulsions is presented.

**Table 3.** Summary of some of the recent studies of chemical demulsifiers from the period 2013–2018.

Type of Emulsion	Type of Demulsification	Emulsifier/Demulsifier Concentration	Ratio and Effect of Demulsifier on Separation	Year of Study	Reference
W/O	Polymer		The efficiency of water separation increases as the molecular weight increases.	2013	[111]
Heavy oil wastewater	CaCl <sub>2</sub> with cationic poly(dimethylamine-co-epichlorohydrin) and cationic polyacrylamine	20:600:1.2 (m/m)	Removal rates for mineral oil (98.04%).	2013	[98]
Super-heavy crude oil	Ionic liquids	1000–1500 ppm	Water removal efficiency of 95–100%.	2014	[99]
W/O	Nonionic surfactant	180, 120, and 80 ppm	A high demulsifying activity 97%.	2014	[100]
Oily wastewater produced from polymer flooding	Non-ionic demulsifiers	250 mg/L	The demulsifiers were mainly affected by temperature.	2014	[101]
W/O	Non-ionic block copolymers		The dewatering was conducted at 80 °C and equal to 51.95%.	2015	[102]
W/O	Janus magnetic submicron particles	600 ppm	More than 95% of emulsifier was separated within 2 h at 60 °C.	2015	[108]
O/W	Ionic demulsifier	900 mg/L	Dewatering efficiency of 89.5%.	2015	[7]
O/W	Oleic acid-coated magnetite nanoparticles (Fe <sub>3</sub> O <sub>4</sub> @OA)	0.10–1.00 g of Fe <sub>3</sub> O <sub>4</sub> @OA	Demulsification efficiency of 97% at a higher dosage.	2015	[107]
W/O	Polymer molecules of alkene oxides diesters	100–600 ppm	Maximum demulsification efficiency was 76%.	2016	[112]
O/W	Ethylcellulose (EC) and EO/PO polymers	200–300 ppm	Addition of 300 ppm of demulsifiers improved the bitumen liberation rate.	2016	[113]
W/O	Tweens (nonionic polymers)	300–1000 ppm	Better demulsification at a dosage lower than 700 ppm.	2016	[114]
W/O	Magnetic demulsifier	0.625 g/L	The dewatering efficiency reached 95%.	2017	[115]
O/W	Hyperbranched poly(amidoamine)	0–40 mg/L	Oil removal ratio reached 92% with a small dosage (<40 mg/L) within 30 min.	2018	[116]
Oily wastewater	Magnetic demulsifier	500 mg/L	The demulsifier had a good demulsification efficiency.	2018	[106]

## 5.2. Biological Demulsification

On the basis of the research output in recent publications, biological demulsification receives less research interest than chemical demulsification. The demulsification of crude oil emulsions using biological means is typically accomplished with the aid of a biodemulsifier [25]. A biodemulsifier is a form of biosurfactant with features that are conducive to the destabilization of a crude oil emulsion [36]. Biodemulsifiers are environmentally friendly, and their usage does not result in secondary pollution. Biodemulsifiers have the ability to function effectively under extreme conditions and can be used for various compositions of complex crude oil emulsions. One major merit of using a biodemulsifier is that it can be sourced from agricultural and industrial wastes [36,117–119]. Huang et al. [120] reported the isolation of a biodemulsifier produced by bacterial strains in an environment contaminated with petroleum. Studies have shown that the effectiveness of each isolated bacterial strain varies in different environments and is strongly dependent on factors such as temperature, soil properties, type and quantity of contaminants, and demulsification capability. Most of the recent studies of biodemulsification have concentrated on the synergy between the effectiveness of demulsification and properties of the isolated bacteria. In line with this, Coutinho et al. [121] investigated the demulsifying activities of *Pseudomonas aeruginosa* MSJ isolated from petroleum-contaminated soil for the biodemulsification of W/O and O/W emulsions. There was a strong relationship between the demulsification potential of the isolated bacterial, the cellular hydrophobicity, and the culture age. The highest biodemulsifying activity was recorded for cells and supernatants from 96 h cultures. In a similar study by Wen et al. [25], a demulsifying *Alcaligenes* sp. (S-XJ-1) bacterial strain isolated from petroleum-polluted soil was used for the biodemulsification of a W/O emulsion. They achieved a demulsifying efficiency of 81.3% within 24 h using a cell concentration of 500 mg/L. The performance of the isolated bacterial strain was attributed to the highly hydrophobic cell surface and the occurrence of amphiphilic compounds in the cell walls. Although the biological demulsification of crude oil emulsions has rarely been studied, a handful of researchers have employed this technique for the demulsification of crude oil emulsions, as shown in Table 4. It can be seen that organisms or their products (bacterial strains such as *Alcaligenes* sp. S-XJ-1, rhamnolipids, *Paenibacillus alvei* ARN63, and *Candida sphaerica* UCP 0995) isolated from different sources of petroleum-contaminated environments have been employed as demulsifying agents for the biodemulsification of crude oil emulsions. Different concentrations (ranges of 300–6000 mg/L) of cells of isolated strains have been applied in the biodemulsification process, and the resulting dewatering efficiency has ranged from 40% to 90%.

**Table 4.** Summary of some of the recent studies on biodemulsifiers from the period 2010–2018.

Type of Emulsion	Name of Biodemulsifier	Demulsifier Concentration	Ratio and Effect of Demulsifier on Separation	Year of Study	Reference
W/O	S-XJ-1	2550, 100, and 500 mg/L	Emulsion breaking ratio of 81.3% within 24 h.	2010	[25]
W/O	<i>Alcaligenes</i> sp. S-XJ-1	1000 mg/L	The highest demulsification ratio reached 84.5%.	2011	[118]
O/W	Rhamnolipid	1000–2000 mg/L	The dewatering efficiency of the waste crude oil reached over 90%.	2013	[122]
O/W	Rhamnolipid	300–1000 mg/L	The water separation reached 50–80%.	2013	[122]
W/O	<i>Candida sphaerica</i> UCP 0995		The demulsification values reached around 40%.	2015	[36]
W/O	Cellulose-based compounds	100–1500 ppm	The ethylcellulose is efficient at breaking the emulsion, but a low dehydration rate is the main disadvantage of this agent.	2017	[123]
Enhanced oil recovery process	Alpha sulfonated ethyl ester ( $\alpha$ -SEE)		The surfactant shows good wetting characteristics.	2017	[124]
O/W	$\alpha$ -Amylase	0–6000 mg/L	The results show that $\alpha$ -amylase is an efficient biodemulsifier.	2018	[125]
W/O	Biodemulsifier		Biodemulsifier breaks 95% of the emulsion.	2018	[126]



### 5.3. Mechanical Demulsification

Demulsification by mechanical means entails the disruption of physical barriers or the application of density variation between the water and the oil phases [29]. Mechanical demulsification of crude oil emulsions can be carried out using a series of mechanical equipment, such as a free-water knockout drum, two-and three-phase separators (low-and high-pressure traps), desalters, and settling tanks [31]. The presence of relatively large droplets in crude oil emulsions often results in reduced flow velocity, enabling the use of gravitational forces for the separation of oil, water, and small suspended droplets [127], which usually occurs within a short time in large-volume desalters or separators [127,128]. The mechanism of the separator employs flow dynamics to accumulate and concentrate the material and allows for the separation of traces of oil that can be removed from the processed crude oil. The velocity at which oil separates under gravity is one of the crucial factors for using gravity settling tanks for demulsification and is strongly dependent on the concentration of oil in the mixture [129]. The velocity of the oil separation increases by concentrating oil traces in the separator. Usually, the oil is separated in the separator when its concentration in the mixture is very high. One piece of mechanical equipment that is rarely used for demulsification is the centrifuge since its capital cost is high and its capacity is low [130]. In a study by Hao et al. [128], centrifugal contactors were employed to resolve the difficulties of over-standard oil content in electric desalting wastewater. The authors investigated the effects of parameters such as rotor speed, inlet flow rate, water temperature, oil content, and crude oil density on the separation efficiency of the centrifugal contactor. They found that a decrease in the inlet flow rate increased the oil concentration and decreased the oil density, resulting in a corresponding increase in oil removal efficiency.

Unlike the rarely used centrifugal contactor, the gravity settling tank is widely applied in the industry as a mechanical demulsifier [127]. In a gravity settling tank, emulsions sediment by gravity, thereby separating oil and water. During the sedimentation of the emulsion, the dispersed-phase droplets are brought closer together and coalesce. For efficient demulsification, a centrifugal contactor can be combined with a gravity settling tank, as reported by Krebs et al. [127], who investigated the kinetics of demulsification of a model O/W emulsion using a centrifugal field to mimic the force acting on emulsion droplets in O/W separators. The main focus of the study was the growth rate of the separated oil phase, as well as the variation in the mean droplet diameter of the emulsion layer, as a function of centrifugal acceleration and time. They reported a significant improvement in the demulsification of crude oil as the centrifugal acceleration and time increased, with an oil recovery efficiency of 84%.

### 5.4. Thermal (Convective and Microwave) Demulsification

Demulsification by thermal treatment refers to the separation of the oil and water phases in a crude oil emulsion by increasing the temperature of the emulsion [33]. A heater is usually employed to raise the temperature of the crude oil emulsion before it enters a horizontal flow treater. Demulsification of crude oil at high temperature reduces the rigidity of the interface, thereby making it easier for droplets to coalesce on collision. The higher the thermal energy, the higher the rate of collision between the droplets. One major drawback of thermal demulsification is the loss of light ends from the crude oil as a result of the heating and invariable increase in the crude oil density, which has adverse effects on gravity settling [33]. For an improved demulsification process, thermal treatment is often combined with a chemical method of demulsification because the viscosity of the emulsions can be reduced by changes in temperature [131]. The demulsification of a crude oil emulsion by convective and microwave heating was investigated by Akbari et al. [132]. Comparative experiments revealed that a separation efficiency of 100% was attained in a short time by microwave heating demulsification, whereas the separation efficiency by convective heating was 96%. These maximum separation efficiencies by the two heating methods were obtained in optimum conditions in terms of the irradiation time (3 min), microwave power (360 W), and demulsifier concentration (2.5 vol%). Mohammed et al. [3] also employed microwave heating techniques for the demulsification of crude oil in a series of batch

runs. They investigated the effects of operating variables such as irradiation power (700–900 W), water content to oil (20–80%, 30–70%, and 50–50%), and salt content (1000–3000 ppm) on the demulsification performance. The best separation efficiency was attained at 900 W of irradiation power, 50% water content, and 160 s of irradiation time. The effect of temperature on the demulsification of bitumen emulsions was investigated by Taylor et al. who revealed that there was gradual breaking in the bitumen emulsion as the temperature of the phase approached the cloud point. It was also observed that the bitumen–water interfacial tension decreased as the heat increased and became smaller at the cloud point temperature [133]. Al-Sabagh et al. [134] also studied the effect of heating on demulsification efficiency and showed that increasing the temperature to around 70 °C resulted in improved demulsification efficiency for the unbreakable asphaltenic emulsion. Martínez-Palou et al. [33] studied microwave and oil bath heating to compare the water separation time of an oil-in-water emulsion. Microwave dielectric heating of O/W emulsions yielded better water separation in a shorter time than traditional oil bath heating. Binner et al. [29] conducted a comparative study on the separation of W/O emulsions by natural gravity settling and the microwave heating method. They reported that microwave heating resulted in improved water droplet coalescence in water-in-oil emulsions. It was observed that an increase in the salinity of the water phase resulted in a decrease in the settling time for untreated emulsions compared with microwave-heated emulsions.

### 5.5. Electrical Demulsification

Demulsification by electrical techniques entails the application of electric fields for the separation of oil and water in crude oil emulsions [26]. Electrical demulsification techniques are more sustainable compared with other demulsification methods and have been commonly applied for more than a century [14]. The electrical demulsification technique is gaining wide acceptance in the industry as a technological route for the demulsification of crude oil [93]. The advantages of the technique include low sludge production, simple equipment, and a lack of chemical agents [93]. During electrical demulsification, an electric current is typically applied to consumable electrodes that are in contact with the crude oil emulsions, thereby resulting in an in situ coagulant dose [135]. The coagulant dose facilitates the destabilization of the repulsive charges of the surfactant molecule, which in turn enables the trapping of oil droplets and forms larger flocs that can be easily separated from the water. During electrical demulsification, the application of an electric field often causes the droplets to polarize, and drops can align in chains that are parallel to the applied field as a result of the interaction between the induced dipoles [135]. Additionally, the electric fields promote the quick fusion of small water droplets into larger ones. The deformation and elongation of the droplets result in rapid coalescence [136]. Although electrical demulsification has been deemed a substitute for thermal and chemical demulsification, the method for adapting the technique to different emulsions with varying properties is not fully understood [137]. Several studies have reported the electrical demulsification of crude oil emulsions with an emphasis on droplet formation [138]. Mousavi et al. [94] investigated the effect of pulsatile electric fields (PEFs) on secondary droplet formation. The findings revealed that an increase in the frequency of the PEF suppressed the formation of secondary droplets in the low-frequency electric domain. Zhang et al. [139] examined the influence of a demulsifier on the distortion and breakup of hydrous drops in an immiscible dielectric oil under the effect of an electric source. The experimental runs were performed in a single drop microscopic cell under an external electric field. Their results showed that bigger drops were deformed more than smaller drops under the action of an electric field, and the interfacial tension was significantly lower in the presence of a surfactant. In a similar study by Mhatre and Thaokar [140], the relative merits of symmetric and asymmetric non-uniform and uniform electric fields in the electro-coalescence of three types of crude oil emulsions were investigated. They reported that electro-coalescence was affected by the non-uniformity, as well as asymmetry, of the electric field. Wang et al. [141] studied molecular dynamics simulations by investigating the electro-coalescence action of two loaded droplets under stable and pulsed direct current electrical sources. The application of a constant DC electric field accelerated the

droplets' approach to each other before contact when encountering an attractive force. Muto et al. [142] investigated the effect of variables such as the type and volume fraction of an organic solvent and the ionic strength of an electrolyte in the water on the demulsification of crude oil emulsions using an alternating electric current field (square waveform and sine waveform alternating electric field). The demulsification of the crude oil emulsion was more effective under the square waveform alternating electric field than the sine waveform. Besides this observation, the rate of demulsification changed meaningfully when the volume fraction of the organic solvent and the ionic strength of the electrolyte were altered. The authors concluded that crude oil demulsification using an alternating electric field was very effective for W/O emulsions. The rate of demulsification of W/O emulsions in direct current fields was reported by Mohammadian et al. [143], who showed that the rate of water separation increased with the direct current fields. The authors concluded that the demulsification of crude oil emulsions was guided by the magnitude of the applied electric field and the type of electrode.

Although electrical demulsification has been successfully employed for different industrial processes, particularly in the treatment of various industry effluents from paint manufacturing and oilfield-produced water, research efforts are still concentrated on improving the efficiency of the process.

### 5.6. Ultrasonic Demulsification

The demulsification of crude oil emulsions by the ultrasonic technique is based on the principle of condensation and the viscosity-reducing impact of ultrasound on crude oil [34]. The ultrasound facilitates the clumping of water droplets in the crude oil, thereby facilitating the separation of the oil–water phases. The simplicity and efficiency of ultrasound demulsification applied to crude oil emulsions has attracted increasing research attention. During ultrasound demulsification, the acoustophoresis phenomenon often influences the dispersed droplets under an ultrasonic standing wave field. The variation in the density and compressibility of the dispersed droplets and the continuous phase can cause the acoustic standing wave to combine homogeneously suspended droplets [58]. Several studies have reported the application of ultrasound energy for the demulsification of crude oil emulsions. The effect of parameters such as the irradiation input power, irradiation time, temperature, and injected water on the demulsification efficiency was investigated by Check and Mowla [144]. The interaction between the parameters resulted in the highest demulsification efficiency (99.8%) at an optimum input power of 57.7 W, irradiation time of 6.2 min, and temperature of 100 °C. A further investigation [145] focused on the effects of two ultrasonic irradiations, namely, primary and secondary, for the demulsification of crude oil emulsion. The findings showed that the settling time decreased at an irradiation power of 75 W for primary irradiation and 50 W for secondary irradiation at an irradiation time of 45 s. There is a growing interest in the application of low-frequency ultrasound for the demulsification of crude oil emulsions. Antes et al. [146] studied the effect of low-frequency ultrasound on the demulsification of crude oil emulsions in the absence of a chemical emulsifier. They demonstrated that a demulsification efficiency of 65% was attained by low-frequency ultrasound. Khajehesamedini et al. [147] also reported the use of low-frequency ultrasonic waves for the demulsification of crude oil emulsions. They attained a demulsifying efficiency of 50% at a very low frequency, low irradiation time, and high-intensity ultrasonic waves. The use of pulsed ultrasonic irradiation techniques for the demulsification of crude oil emulsions was reported by Xie et al. [148], who observed the pulse irradiation techniques facilitated water coalescence, thereby improving the demulsification efficiency. Antes et al. used ultrasonic baths at different frequencies for the demulsification of crude oil emulsions [149]. Effective demulsification of crude oil with a 65% efficiency was achieved at a frequency range of 25–45 kHz after 15 min. At a frequency of >45 kHz, there was no evidence of crude oil demulsification. In the work of Pedrotti et al. [150], a demulsification efficiency of up to 93% was attained at 15 min of sonication (100% amplitude). Pedrotti et al. [150] proposed the use of indirect low-frequency ultrasonic energy for the demulsification of crude oil. The results showed that a higher demulsification efficiency (up to 93%) was attained in the most intense acoustic regions compared with that positioned in the less intense acoustic field regions.

### 5.7. Membrane Demulsification

The use of membrane technology for the demulsification of crude oil emulsions is relatively new and receiving increasing research attention. The membrane demulsification of crude oil emulsions is based on the tendency of low pressure to move the dispersed phase, resulting in its permeation through a membrane into the continuous phase. The application of membrane technology for the demulsification of crude oil emulsions has the advantages of being an inexpensive and efficient option for the demulsification of crude oil emulsions. Recently, several studies have been published on the application of membrane technology for the demulsification of crude oil emulsions. Wu et al. [151] investigated the effect of membrane surface charges on crude oil demulsification and fouling resistance. Two membranes, namely, PP-g-pDMAEMA and PP-g-pOEGMA, were employed for the demulsification process. The membranes displayed positive and negative surface charges in water, respectively. A demulsification efficiency increase of 15% was obtained using PP-g-pDMAEMA compared with the use of PP-g-pOEGMA. The authors concluded that the membrane surface positive charges enhanced crude oil demulsification. Nevertheless, membrane damage after the demulsification was exacerbated.

One major challenge faced when using membrane technology for crude oil demulsification is membrane fouling. Fouling reduces the flux and the membrane's lifespan, thereby resulting in expensive maintenance during application. The findings of Liu et al. revealed that both the surface charge and surface hydrophilicity mitigated the irreversible fouling of membranes. The use of superhydrophilic and underwater superoleophobic surfaces using high-surface-energy materials is receiving considerable attention from researchers. This is because these properties enhance the antifouling ability and separation efficiency of the existing membrane. These membranes are electrospun nanofibrous materials with the advantages of having high porosity, high surface area, and easily tunable structures. Because of the exceptional properties of membranes with superhydrophilic and underwater superoleophobic surfaces, Chen et al. [152] employed a silica nanosphere-coated membrane for crude oil demulsification. Application of the membrane for crude oil demulsification resulted in a high efficiency (>98%) for separating oil-in-water emulsions under the harsh influence of strong acidic and concentrated salty conditions. The authors concluded that the membrane had excellent stability since the efficiency did not visibly decrease after several uses. In a similar study, Zhang et al. [135] employed a thermoresponsive poly(*N*-isopropylacrylamide) (PNIOAAm)-modified nylon membrane for the demulsification of crude oil emulsions. The fabricated membrane has the advantages of a rough structure, appropriate pore size, and thermoresponsive wettability and is capable of separating 16 different types of stabilized O/W and W/O crude oil emulsions at different temperatures. At a temperature of approximately 25 °C, the membrane was able to separate any kind of crude oil emulsion. Conversely, at a temperature of approximately 45 °C, the membrane displayed high hydrophobicity and superoleophilicity, which can only be employed for the separation of stabilized crude oil emulsions. In a similar study, Ge et al. [153] developed a novel superhydrophilic and underwater superoleophobic nanofibrous membrane with a hierarchically structured skin for O/W demulsification. The membrane displayed an exceptional separation efficiency, strong antifouling properties, and an extremely high flux that was mainly driven by gravity.

## 6. The Advantages and Disadvantages of Some Demulsification Techniques

The demulsification process can be carried out by four main methods: mechanical, electrical, thermal, chemical and their combinations. The pH adjustment, voltage application, filtration, and membrane separation comprised the available methods. Thermal demulsification may be reached by the use of microwaves [154]. There are many kinds of mechanical separation tools that are typical equipment used in the destabilization of the crude oil emulsion such as cyclones, gravity settling tanks, centrifugal separators and so on. However, this hardware has considerable volume as well as expensive to install on offshore platforms [155]. Electrical demulsification is generally considered advantageous from the perspective of energy consumption as compared with other demulsification approaches, such as heating or centrifugation, in addition to ecological validity [156,157]. However, the

drawback of this process is the formation of fine secondary droplets during the coalescence, making it more burdensome to separate the produced smaller water drops [158].

The application of heat to an emulsion promotes oil/water separation by reducing the viscosity of the oil and water, increasing the mobility and the settling rate of water droplets, and weakening the mechanical strength of the interfacial film [159]. However, heat by itself is not a cure-all and even has some disadvantages, such as loss of light oil fractions from the crude oil, delayed separation efficiency due to formation of air bubbles, the limited availability of temperature sensitive demulsifiers, and increased risk of corrosion of equipment and economical cost [160]. Along with mentioned methods, chemical treatment with demulsifiers (surface active agents) is the most common process for breaking emulsions as the chemical additives accelerate breaking the oil-in-water emulsions process [161]. This treatment is popular because the chemicals are easily applied with reasonable cost, and usually minimize the amount of heat and settling time required [162]. However, chemical demulsifiers must provide full removal of water and salts, must be cheap, accessible, less-toxic and have a small consumption per ton of oil [163].

## 7. Summary and Conclusions

This paper presents an overview of recent advances in state-of-the-art techniques for the demulsification of crude oil. The demulsification of crude oil emulsions using chemical, biological, mechanical, thermal, electrical, ultrasonic, and membrane techniques is examined. It is worth noting that the efficiency of each of these techniques is dependent on the operating parameters and their interplay. Moreover, a more effective demulsification process could be attained by leveraging synergistic effects by combining one or more of these techniques, as discussed in this review. In most of the demulsification techniques, the key factors of interest are the separation efficiency and the rate of demulsification. Moreover, it is also of paramount importance to consider the means of accelerating the interfacial film-thinning process by weakening the stabilizing film that compresses the dispersed drops. It is very clear that each of the demulsification techniques possesses its own merits and demerits. Nevertheless, a favorable demulsification technique is not only robust and applicable to different kinds of emulsions but also environmentally friendly, with minimal impacts on the environment and adherence to environmental standards and regulations. The occurrence of a crude oil emulsion during processing and transportation has been proven to be problematic by increasing the production cost and utilization of chemicals which impacts on the environment. These realities in petroleum industries have aroused the interest of researchers who aim to determine the scientific means of monitoring and preventing crude oil emulsion formation. Therefore, a favorable demulsification technique is not only robust and applicable to different kinds of emulsions but also, must be environmentally friendly, with minimal impacts on the environment, adherence to environmental standards and regulations, and at a lower cost. From the recent literature, it is clear that a proper understanding of the properties and types of crude oil involved in the formation or demulsification of emulsions (either O/W or W/O) would contribute to the formulation of appropriate demulsification methods. In the overview of recent studies, it is apparent that the different techniques employed for the demulsification of crude oil emulsions have different degrees of effectiveness and efficiency. However, most of the researchers have not accounted for the effect of viscosity on the demulsification process. Besides this, most of the case scenarios of crude oil demulsification are based on lab experiments. There is scarce literature on field cases or on-site cases of crude oil demulsification. Hence, research efforts should be geared toward proposing small-scale or pilot-scale on-site demulsification plants implemented with real operating parameters that are used in crude oil processing facilities.

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