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Review

Petroleum Emulsion Stability and Separation Strategies: A Comprehensive Review

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Abstract

Crude oil emulsions continue to pose significant challenges across production, transportation, and refining due to their inherent stability and complex interfacial chemistry. Their persistence is driven by the synergistic effects of asphaltenes, resins, acids, waxes, and fine solids, as well as operational factors such as temperature, pH, shear, and droplet size. These emulsions increase viscosity, accelerate corrosion, hinder catalytic activity, and complicate downstream processing, resulting in substantial operational, economic, and environmental impacts—underscoring the necessity of effective demulsification strategies. This review provides a comprehensive examination of emulsion behavior, beginning with their formation, classification, and stabilization mechanisms and progressing to the fundamental processes governing destabilization, including flocculation, coalescence, Ostwald ripening, creaming, and sedimentation. Separation techniques are critically assessed across chemical, thermal, mechanical, electrical, membrane-based, ultrasonic, and biological domains, with attention to their efficiency, limitations, and suitability for industrial deployment. Particular emphasis is placed on hybrid and emerging methods that integrate multiple mechanisms to improve performance while reducing environmental impact. By uniting fundamental insights with technological innovations, this work highlights current progress and identifies future directions toward greener, more efficient oil–water separation strategies tailored to diverse petroleum operations.

Keywords: petroleum emulsions; emulsion stability; demulsification; destabilization mechanisms; sustainable oil–water separation

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1. Introduction

The occurrence of emulsions is a recurrent challenge in crude oil production, arising at multiple stages of the extraction process. Crude oil extraction is generally categorized into three stages—primary, secondary, and tertiary recovery—each designed to progressively maximize production efficiency through different mechanisms. Primary recovery relies mainly on natural reservoir energy but yields only a limited fraction of the oil. Secondary recovery enhances production by injecting water or gas into the reservoir, while tertiary recovery (enhanced oil recovery, EOR) employs advanced techniques, such as chemical, thermal, or microbial methods, to further increase yield. At each of these stages, emulsions can form due to a variety of mechanisms, including oil flow through porous media, shear forces within choke valves, pumping-induced pressure drops, and intentional water injection or chemical additives during EOR operations [1–3].

Beyond extraction, emulsions may be intentionally generated. For example, water is sometimes blended with heavy or extra-heavy crude oils to reduce viscosity and thereby facilitate transportation through pipelines. Similarly, controlled water addition is a central step in the desalting of crude oil, which removes inorganic salts before refining [4]. Despite these operational advantages, the presence of water in crude oil systems introduces significant economic and technical complications. Coproduced water raises transportation and pumping costs, accelerates corrosion in pipelines, pumps, and refining units due to chloride ions, and necessitates the installation of supplementary treatment facilities to comply with export standards [5–7]. Furthermore, dispersed water droplets can increase crude oil viscosity and deactivate refinery catalysts, thereby complicating downstream refining processes and reducing overall efficiency [8,9]. Given these challenges, efficient demulsification emerges as a crucial requirement for ensuring both crude oil quality and sustainable processing.

Demulsification represents a complex operation owing to the inherent stability of oilfield emulsions, which are essentially liquid–liquid colloidal systems. These emulsions consist of a dispersed or internal phase, a continuous or external phase, and naturally occurring or added emulsifying agents that localize at the oil–water interface. To achieve effective separation, a demulsification method must be capable of disrupting or weakening the interfacial stability of these emulsions, ultimately enabling the segregation of the immiscible phases. In practice, demulsification strategies are broadly categorized into three classes: physical, chemical, and biological. Physical techniques encompass gravitational settling, centrifugation, thermal treatment, flotation, filtration, electro-coalescence, membrane separation, ultrasonic methods, and shear-based processes. However, physical treatments alone often fail to achieve satisfactory destabilization, leading to their frequent integration with chemical or biological methods to form hybrid approaches that enhance overall separation efficiency [10–12].

This review addresses the persistent challenge of stable emulsions in petroleum production, which hinder efficient oil–water separation. It provides a comprehensive review of emulsion formation, stability mechanisms, and strategies for destabilization and separation. Its key contribution is an integrative approach that consolidates theoretical insights while critically evaluating thermal, mechanical, chemical, electrical, membrane, ultrasonic, and biological demulsification methods. Emphasis is placed on hybrid techniques that combine multiple methods for improved efficiency and sustainability. By linking fundamental mechanisms with applied technologies, the study advances scientific understanding and industrial practice, supporting the development of cost-effective, environmentally compatible demulsification strategies.

2. Formation and Classification of Petroleum Emulsions

In petroleum production, crude oil is most frequently obtained in the form of emulsions, making their formation and stabilization a critical concern for the industry [13]. The emergence of such emulsions results from the competing processes of droplet disruption and coalescence, which govern the overall stability of the system [14]. Crude oil–water emulsions are typical multiphase dispersions in which one phase, present as fine droplets, is termed the dispersed or discontinuous phase, while the surrounding liquid constitutes the continuous medium [15].

2.1. Emulsion Formation

The formation of emulsions requires three fundamental conditions [16]. First, two immiscible liquids—oil and water—must coexist within the system. Second, an Emulsifying agent must be present to prevent rapid separation and stabilize the oil–water interface.

The solubility of the emulsifier in either medium dictates the emulsion type: preferential solubility in oil promotes water-in-oil emulsions, whereas solubility in water favors oil-in-water emulsions. Finally, external energy input, typically through stirring, agitation, or shear, is necessary to disperse one liquid throughout the other. Such mechanical action reduces droplet size, thereby enhancing the kinetic stability of the emulsion. Figure 1 depicts the mechanism of oil–water emulsion formation. As shown in Figure 1a, dispersed droplets are generated in the presence of emulsifiers. Their stability depends on both the emulsifier concentration and the rate at which they diffuse and adsorb at the droplet interface. Newly formed droplets may become stabilized immediately or coalesce if insufficiently protected. Figure 1b illustrates variations in interfacial tension (IFT) during droplet formation. Emulsifier adsorption progressively reduces IFT, a process described as dynamic IFT, until equilibrium is reached, where the fully covered interface reflects the equilibrium IFT value [17].

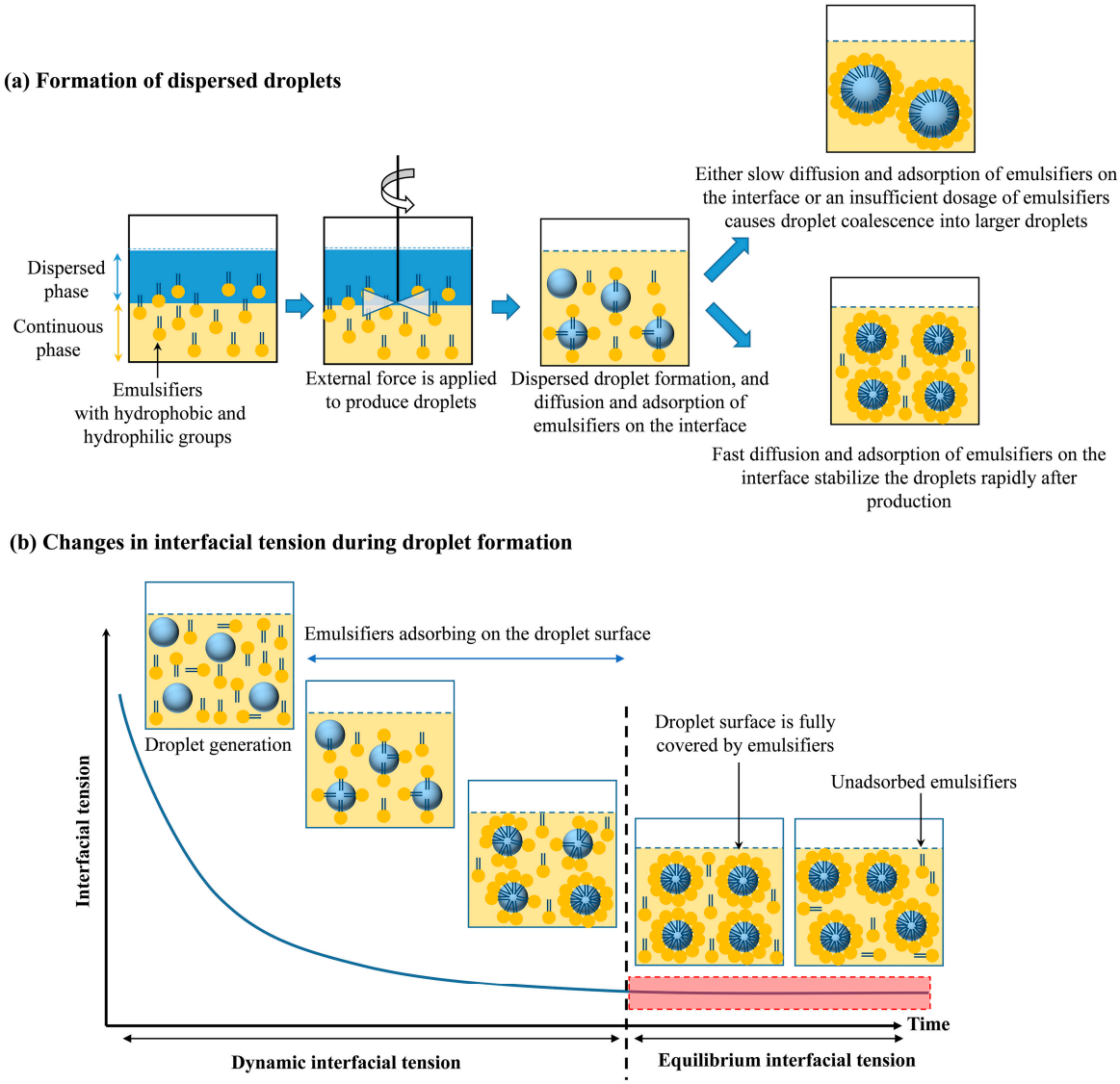


Figure 1. Formation and stabilization of oil–water emulsions [17].

Petroleum emulsions are complex systems that form predominantly during crude oil production from reservoirs, where oil and formation water initially exist as separate phases. Intense mixing occurs as multiphase fluids move through porous rock, wellbores, and surface flowlines, with mechanical agitation, turbulence, shear stresses, and pressure

fluctuations dispersing water droplets within crude oil [18]. Unlike simple laboratory emulsions stabilized by externally added surfactants, petroleum emulsions are inherently stabilized by indigenous surface-active compounds naturally present in crude oil, including asphaltenes, resins, waxes, organic acids, and fine mineral solids. These materials adsorb at the oil–water interface, forming rigid interfacial films that prevent droplet coalescence and confer exceptional stability. The resulting emulsions are predominantly water-in-oil. Their formation and persistence significantly influence production and downstream operations, leading to elevated viscosity, reduced flow efficiency, increased pumping costs, and complications in desalting, dehydration, and refining processes [19,20]. Understanding the mechanisms of emulsion generation—from reservoir conditions to surface handling—is therefore essential for developing effective demulsification strategies, improving process efficiency, and mitigating operational challenges.

2.2. Types of Petroleum Emulsions

Based on the nature of the dispersion medium, crude oil–water emulsions encountered during production are generally classified into three categories (Figure 2) [21]:

- water-in-oil (W/O) emulsions;
- oil-in-water (O/W) emulsions;
- multiple emulsions, where both types coexist in more complex structures.

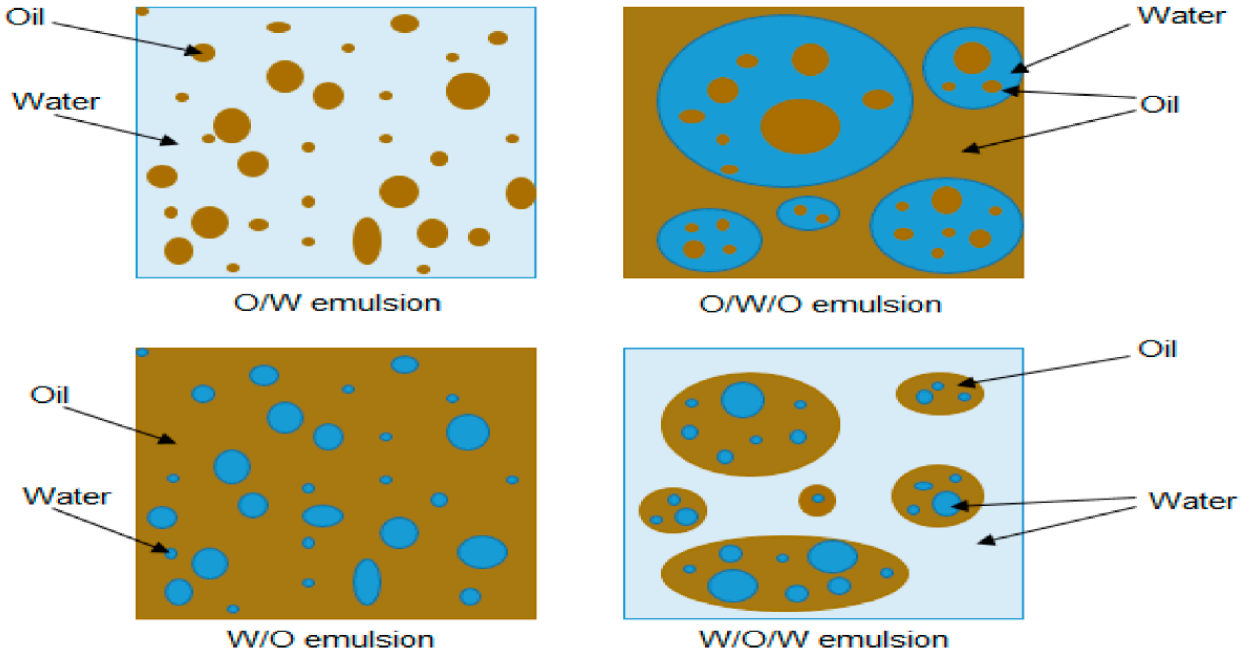


Figure 2. Types of Petroleum Emulsions [19].

W/O emulsions represent the most prevalent emulsion type encountered in petroleum production, accounting for more than 95% of all oilfield emulsions [22,23]. In these systems, the aqueous phase exists as finely dispersed droplets within a continuous oil phase. Their stability is primarily attributed to the presence of naturally occurring surface-active compounds such as carboxylic acids, resins, and asphaltenes, or to surfactants and polymers intentionally introduced in injection or flooding fluids [24]. Fingas and Fieldhouse [25,26] proposed a classification scheme for W/O emulsions based on their degree of stability and tendency toward spontaneous breakdown. This scheme identifies four categories: entrained water, unstable emulsions, stable emulsions, and mesostable emulsions. While entrained water and unstable systems lack the defining characteristics of true emulsions and

are therefore excluded from consideration [18], stable and mesostable emulsions demonstrate distinct lifetimes. Mesostable emulsions typically persist for 1–3 days, whereas stable emulsions can remain intact for several weeks, often exceeding four weeks [18]. The enhanced persistence of stable emulsions has been linked to higher concentrations of naturally occurring stabilizers, with reported compositions including 5–30% resins and 3–20% asphaltenes, alongside a typical asphaltene-to-resin ratio of approximately 0.74 [26]. Additional parameters such as crude oil density, viscosity, salinity, and water content further influence emulsion stability [27,28]. Moreover, the addition of synthetic emulsifiers with hydrophilic–lipophilic balance (HLB) values below 7 has been shown to reinforce the stability of W/O emulsions, thereby extending their persistence [29].

In contrast, oil-in-water (O/W) emulsions, where the oil droplets are dispersed within a continuous aqueous medium, are less frequently observed in oilfield operations [30,31]. Despite their lower natural occurrence, these emulsions have important industrial applications. One of their significant uses lies in ex situ enhanced oil recovery (EOR) techniques, where they can be engineered to improve oil displacement efficiency [31]. Additionally, O/W emulsions have been employed to reduce the viscosity of heavy and extra-heavy crude oils, thereby improving their flow properties and lowering associated pumping and transportation costs [32]. Unlike W/O emulsions, O/W systems require surfactants with higher hydrophilic–lipophilic balance values, typically ranging from 8 to 16, to maintain stability [33]. This difference in stabilizing requirements underscores the importance of surfactant selection in designing emulsions for specific applications, as it determines both the dispersion behavior and the practical feasibility of the emulsion system.

Beyond these binary systems, multiple emulsions—or complex emulsions—represent a more sophisticated class in which one type of emulsion is further dispersed within another immiscible phase. For example, dispersing an O/W emulsion into a continuous oil phase generates an O/W/O structure, while incorporating a W/O emulsion into an aqueous medium form a W/O/W configuration. The stabilization of these complex systems is highly dependent on surfactant selection: W/O emulsions typically require surfactants with hydrophilic–lipophilic balance (HLB) values below 7, whereas O/W emulsions necessitate surfactants with HLB values above 7. Effective formulation of multiple emulsions generally requires at least two emulsifiers with contrasting HLB values to ensure stability at both internal and external interfaces, making their preparation more challenging than that of simple emulsions [34]. These systems are distinguished by their enhanced structural stability and prolonged lifetimes, which make them particularly suitable for applications demanding durable emulsions. Additionally, their multiphase architecture enables the encapsulation of active substances within internal droplets, providing controlled release and protection—features that are especially advantageous in precision applications, such as industrial processes requiring stable, long-lasting emulsions [35].

Multiple emulsions such as W/O/W and O/W/O systems are increasingly relevant in enhanced oil recovery, but their demulsification is considerably more complex than that of simple emulsions because destabilization requires the sequential rupture of both outer and inner interfaces [36,37]. Mechanistic studies indicate that interfacial film thinning, rupture, and competitive adsorption of demulsifiers govern the destabilization process. Chemical demulsifiers act by displacing native stabilizers (asphaltenes, resins, or surfactants) to lower interfacial tension and elasticity, but in multiple emulsions this action must occur selectively at either inner or outer interfaces depending on their solubility and hydrophile–lipophile balance [38]. Recent advances have highlighted the potential of demulsifiers with dual or multifunctional capabilities, which can simultaneously interact with different interfaces and promote stepwise droplet coalescence, thereby enhancing overall efficiency [39,40]. Interfacial rheology studies further show that viscoelastic films can prevent droplet coalescence,

making effective demulsification highly dependent on the ability of additives to weaken or rupture these rigid layers. Complementary physical strategies—including electrocoalescence, thermal treatment, and ultrasonics—facilitate droplet deformation, accelerate film thinning, and simplify the nested emulsion structure [41]. Mechanical separation methods (e.g., centrifugation, membranes, coalescers) are generally applied after internal droplets have been destabilized, while nanoparticle-assisted approaches are emerging as promising tools to alter interfacial rheology and promote controlled coalescence [42]. Collectively, these mechanistic and physical insights underscore the greater complexity of destabilizing multiple emulsions and highlight the need for tailored hybrid strategies in EOR operations [43].

3. Stability of Petroleum Emulsions

Crude oil emulsions are thermodynamically unstable systems, inherently inclined to minimize free energy as small droplets collide and coalesce into larger droplets, eventually separating into two distinct phases [44]. Nevertheless, these emulsions often display dynamic stability under practical conditions [45]. The persistence and interfacial characteristics of oil–water emulsions are largely determined by both crude oil composition and environmental parameters. Among these, the presence of surface-active components such as asphaltenes, resins, and acidic species, along with factors including temperature, pH, mixing and droplet size distribution, play pivotal roles in controlling emulsion stability [46–48]. The influence of these determinants on interfacial properties and overall emulsion behavior is elaborated further in the subsequent sections.

3.1. Crude Oil Composition and Interfacial Components

3.1.1. Role of Asphaltenes

Asphaltenes are a distinct fraction of crude oil that dissolve in aromatic solvents such as toluene but remain insoluble in paraffinic solvents, including n-heptane, n-hexane, and n-pentane [49–51]. Structurally, asphaltene molecules consist of polycyclic aromatic cores substituted with saturated hydrocarbon chains and various polar functional groups, including amines, hydroxyls, carboxyls, and sulfur-containing moieties [52,53]. Schuler et al. [54] pioneered a method using atomic-resolution imaging and molecular orbital techniques to directly elucidate the asphaltene molecular architecture. Atomic force microscopy (AFM) and scanning tunneling microscopy (STM) revealed that asphaltene molecules possess polycyclic cores of approximately seven fused rings, connected to linear or branched hydrocarbon chains. These structural features confer pronounced interfacial activity, making asphaltenes the primary stabilizers of oil–water emulsions, with stabilization times potentially exceeding one year [55]. Understanding their stabilization mechanism is crucial, as it provides foundational guidance for the development of effective demulsification strategies. Yang et al. [56] demonstrated that even a small number of asphaltene molecules can form a robust interfacial film, with adsorption mediated through hydrogen bonding and cross-linking with other interfacially active species.

Figure 3 illustrates how varying asphaltene concentrations influence the stability of a W/O emulsion. The emulsion was prepared with 20 mL of solution containing different asphaltene levels (0.01–11.00 g/L) in a 7:3 toluene-to-n-heptane mixture, along with 6 mL of water [57]. Results show that as asphaltene concentration increased, the percentage of dewatering decreased and the time to achieve equilibrium became longer. This indicates that asphaltenes play a significant role in reducing water separation, thereby enhancing emulsion stability [58]. At the highest concentration of 11.00 g/L, the system displayed complete resistance to dewatering, suggesting a relatively stable emulsion state. Complementing this, Figure 4 highlights the microstructural changes in the emulsions

with increasing asphaltene dosage. Microscopy images demonstrate that higher asphaltene levels result in smaller, more uniform droplets, further confirming the improved stability of the emulsion system [59].

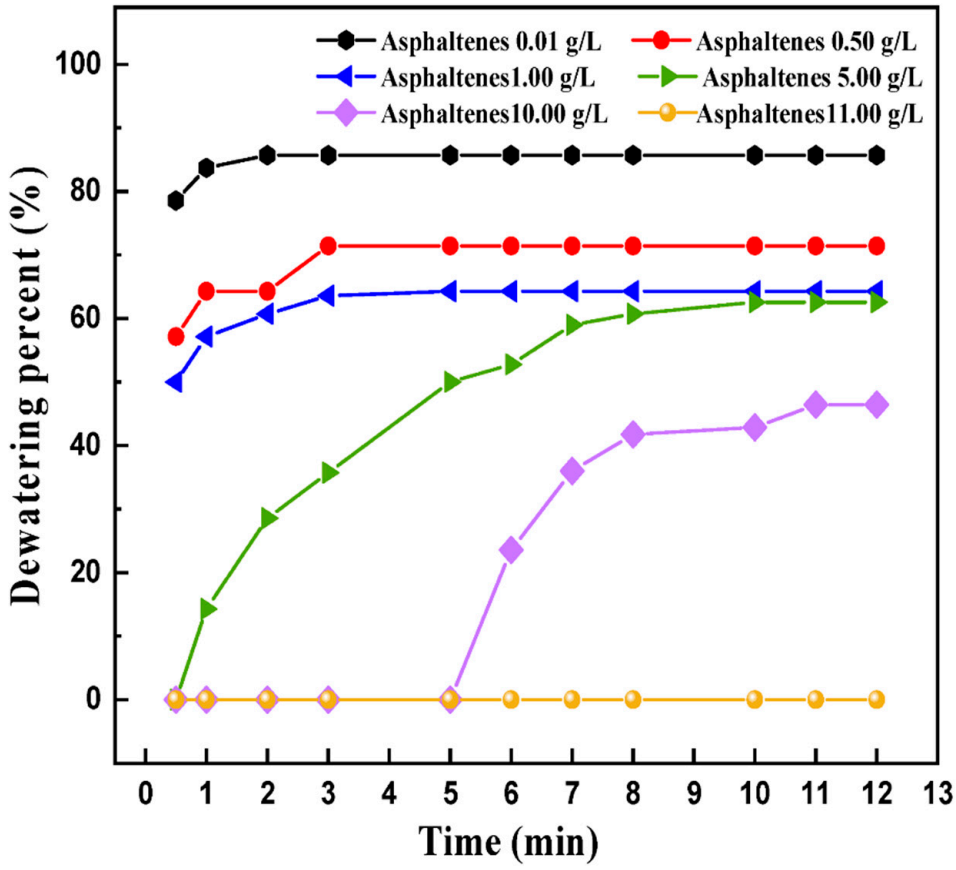


Figure 3. Effect of varying asphaltene concentrations on the stability behavior of W/O emulsions [57].

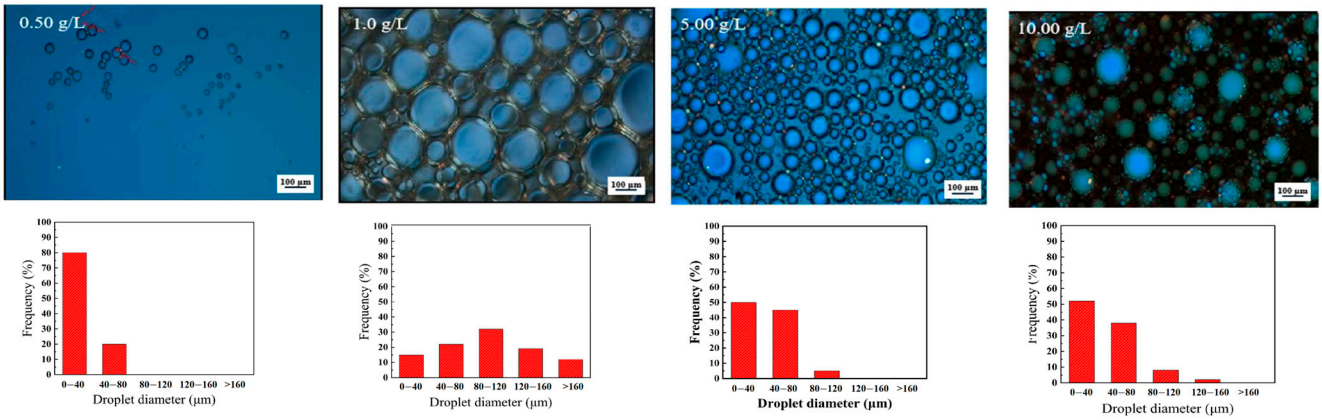


Figure 4. Effect of asphaltene concentration on the microstructural evolution of W/O emulsions, based on microscopic observations taken 15 min after emulsion formation [57].

The polarity of asphaltenes, largely influenced by the length and number of aliphatic chains, significantly affects their interfacial behavior [60]. Longer or more numerous aliphatic chains reduce molecular polarity, leading to poor retention at the interface and the formation of weak, unstable films under external forces. Conversely, highly polar asphaltenes tend to aggregate excessively, limiting their ability to occupy interfacial space. Only moderately polar asphaltenes can persist at the interface, reorganizing at the molecular

scale to generate a rigid, solid-like film that resists compression and prevents coalescence of droplets [61,62].

Asphaltene composition varies considerably across crude oil sources, influencing solubility and aggregation behavior [63]. Spiecker et al. [64] reported that asphaltenes with low hydrogen-to-carbon ratios, elevated nitrogen, vanadium, nickel, and iron contents, and high polarity and hydrogen-bonding capacity exhibit limited solubility in toluene–n-heptane mixtures, promoting substantial aggregation. Under conditions approaching precipitation, nano-scale asphaltene aggregates display heightened interfacial activity [65], with intermolecular interactions at the precipitation threshold maximizing adsorption at the oil–water interface and facilitating the formation of high-strength interfacial films [66].

Although Figures 3 and 4 demonstrate that increasing asphaltene concentration enhances emulsion stability, it should be emphasized that asphaltene polarity and aggregation state are equally critical. Highly polar and well-dispersed asphaltenes adsorb more efficiently at the interface, forming rigid and elastic films, whereas large aggregates adsorb slowly and produce weaker films. This suggests that destabilization can also be promoted by modifying the solvency conditions of crude oil to alter aggregation behavior, rather than solely by reducing asphaltene concentration. Therefore, practical demulsification strategies may benefit from targeting polarity and aggregation state as indirect but effective mechanisms for weakening the interfacial film [18,40,67].

3.1.2. Role of Resins

Resins, another naturally occurring interfacially active component in petroleum, are polar polynuclear molecules composed of aromatic rings, aliphatic side chains, and various heteroatoms [68,69]. Structurally, resins resemble asphaltenes but possess lower molecular weights, fewer aromatic rings, and reduced heteroatom content [70,71], which enhances their solubility in organic solvents. The combination of hydrophilic and hydrophobic groups within resin molecules imparts significant interfacial activity. Highly polar resins can form hydrogen bonds with water molecules, adsorbing at the outer layer of water droplets. As resin concentration increases, the oil–water interfacial tension decreases while interfacial film strength improves, accompanied by rises in interfacial viscosity, storage modulus, and loss modulus. Additionally, aromatic structures within resins allow π-π stacking interactions, forming dense interfacial films that hinder water droplet coalescence [72,73].

Resins exhibit higher diffusion efficiency and faster adsorption at interfaces compared with asphaltenes, substantially lowering interfacial tension and contributing to emulsion stabilization [74]. Cao et al. [75] demonstrated that water-in-oil emulsions containing resins exhibited lower interfacial tension, higher interface al viscosity, and greater stability than those stabilized by asphaltenes alone. The combined effect of chain structures and hydrogen bonding strengthens resin adsorption at the interface [76], consistent with findings by Yudina et al. [77].

Despite these properties, resins alone are generally insufficient to stabilize oil–water emulsions but significantly enhance the stabilizing performance of asphaltenes [72,78]. Resin adsorption is often reversible, yet its rapid accumulation at the interface provides a foundation for the slower, more persistent adsorption of asphaltenes [79]. Moreover, resin–asphaltene interactions disrupt polar bonds and π-π stacking among asphaltenes, increasing their solubility and reducing aggregate size [80]. Yang et al. [74] observed that the presence of resins accelerates asphaltene interfacial film formation, as smaller asphaltene–resin complexes diffuse and adsorb more rapidly at the oil–water interface, enhancing overall emulsion stability.

3.1.3. Influence of Acidic Compounds

Acidic compounds in crude oil, including naphthenic acids, carboxylic acids, and aromatic cyclic acids, significantly contribute to the stabilization of oil–water emulsions by accumulating at the interface through strong ionization [81]. These interfacially active acids can interact with asphaltene molecules via hydrogen bonding and π-π stacking, forming robust interfacial films with high mechanical strength [82]. Wu et al. [83] reported that low concentrations of organic acids enhance the rigidity of asphaltene interfacial films. However, at higher acid concentrations, competitive adsorption occurs between acids and asphaltenes, resulting in a more flexible interfacial layer and reduced emulsion stability. Thus, the balance between acidic species and asphaltene adsorption is critical in determining the structural strength of oil–water interfacial films.

3.1.4. Effect of Wax Crystals

In addition to acids, wax crystals can adhere to the oil–water interface, acting as Pickering stabilizers that reinforce interfacial film strength and modify the rheological behavior of emulsions [84,85]. At low temperatures, small wax crystals precipitate to form a reticular network that increases oil viscosity, slows the diffusion of water droplets, and enhances emulsion stability. Simultaneously, other wax crystals remain at the interface, providing a physical barrier that inhibits droplet coalescence and maintains emulsion integrity.

3.1.5. Solid Particulates and Inorganic Species

Solid particulates such as clay aggregates, silica (SiO_2), and metal-containing compounds can adsorb at the oil–water interface, interacting with polar groups of asphaltenes and resins. These particles stabilize emulsions via Pickering-type mechanisms, forming a rigid interfacial layer that prevents droplet aggregation and enhances resistance to demulsification [86,87]. Collectively, acidic species, waxes, and solid particulates play synergistic roles in enhancing the mechanical and structural stability of oil–water emulsions, complicating separation processes.

3.2. Operational and Environmental Factors

3.2.1. Temperature Effects

Temperature plays a crucial role in modulating the stability of oil–water emulsions. An increase in temperature generally reduces the viscosity of the oil phase, amplifies the density difference between the dispersed and continuous phases, promotes more frequent droplet collisions, and weakens the stabilizing interfacial films surrounding the droplets, all of which can facilitate phase separation [86,88]. Concurrently, elevated temperatures enhance the diffusion of asphaltenes to the oil–water interface due to a decrease in the bulk viscosity of crude oil, potentially affecting interfacial film formation [61,89]. The influence of temperature on surfactants is also significant and varies with surfactant type: the relative solubility of nonionic surfactants in water typically decreases with increasing temperature, whereas the solubility of anionic surfactants rises [90]. Consequently, for oil-in-water emulsions, higher temperatures may reduce the interfacial adsorption of anionic surfactants, thereby diminishing emulsion stability [91]. These combined effects highlight the complex interplay between temperature, interfacial phenomena, and the physicochemical behavior of emulsion components.

3.2.2. Aqueous Phase pH

The pH of the aqueous phase significantly influences the stability of oil–water emulsions, with effects dependent on both the composition of the oil phase and the brine [92–96].

Oil-soluble organic acids or bases can further modify the demulsification behavior of water-in-oil (W/O) emulsions. Generally, an increase in pH enhances the hydrophilicity of surfactants, favoring the formation of oil-in-water (O/W) emulsions under basic conditions, whereas acidic environments (low pH) promote W/O emulsion formation. Correspondingly, asphaltene-rich interfacial films exhibit maximum rigidity in acidic media and progressively weaken with rising pH, ultimately becoming mobile and unstable under alkaline conditions. In contrast, resin-based interfacial films display greater strength in alkaline environments and are weakest under acidic conditions. Mechanistically, the surface charge of dispersed droplets is modulated by the pH-dependent ionization of surfactants at the oil–water interface, resulting in positively charged droplets in acidic media and negatively charged droplets in basic media [92,97–99]. The so-called "ionization effect" is further enhanced by the presence of salts in the aqueous phase, which interact with interfacially active species to alter droplet charge and film characteristics [96,100]. In systems stabilized by amphoteric asphaltenes, the optimal pH for achieving maximum demulsification efficiency with added demulsifiers is generally reported to be neutral or near-neutral, emphasizing the importance of pH control in emulsion separation processes [99,101].

3.2.3. Droplet Size and Distribution

In oilfield operations, both W/O and O/W emulsions are predominantly classified as macroemulsions, characterized by droplet diameters exceeding 0.1 μm and occasionally surpassing 100 μm. The size and distribution of these droplets play a critical role in determining the rheological properties and overall stability of the emulsion [15,102–105]. Specifically, emulsions composed of smaller droplets with a narrow size distribution exhibit higher viscosity, which enhances resistance to coalescence and delays phase separation. This behavior arises because smaller droplets require longer periods to merge and either sediment in the case of water globules or rise in the case of oil droplets. Conversely, emulsions with larger or more heterogeneously sized droplets tend to display lower viscosity and reduced stability, as coalescence occurs more readily. The application of an effective demulsifier accelerates the merging of dispersed droplets, reducing interfacial tension and promoting phase separation. Consequently, controlling droplet size and distribution is essential for optimizing emulsion stability and designing demulsification strategies in crude oil processing and transport operations [18,19,40,106].

3.2.4. Effect of Mixing Time and Intensity

The stability of petroleum emulsions is significantly influenced by the duration and intensity of mixing during their formation [107,108]. As previously mentioned, emulsification occurs when shear forces disperse one liquid phase into another immiscible phase, creating small droplets that resist coalescence under certain conditions. Longer mixing times generally reduce droplet size by continuously subjecting the dispersed phase to shear stress, thereby increasing the total interfacial area between oil and water [109,110]. Similarly, higher mixing intensity promotes finer droplet distribution and enhances kinetic stability, as smaller droplets possess reduced sedimentation or creaming rates due to lower gravitational settling [44]. However, beyond a critical threshold, excessive mixing may lead to coalescence and phase inversion, as high energy inputs disrupt interfacial films and destabilize droplets. Furthermore, the interaction of mixing dynamics with crude oil composition, particularly asphaltenes and resins, can enhance or hinder emulsion stability by strengthening interfacial films [72,74]. In practice, petroleum production and transportation processes often involve turbulent mixing in pumps, pipelines, and separators, which can unintentionally stabilize water-in-oil emulsions [31]. Therefore, optimizing mixing

parameters is essential to minimize the formation of persistent emulsions that complicate separation and processing.

3.2.5. Demulsifier Concentration

As mentioned above, natural emulsifiers in crude oil adsorb at the oil–water interface, forming rigid films that inhibit droplet coalescence. Higher emulsifier concentrations generally enhance stability by strengthening this interfacial barrier, but excessive amounts can over-stabilize emulsions, making them difficult to break during production and refining [103,111]. Demulsifiers, a distinct class of surface-active agents, are introduced to destabilize these emulsions. They function by displacing or weakening the emulsifying species at the interface, thereby promoting droplet coalescence and facilitating water–oil separation [40,112]. The effectiveness of demulsifiers is highly dependent on their concentration: insufficient amounts fail to disrupt stabilizing films, while excessive dosages may trigger secondary emulsification or increase processing costs without added benefit [113,114]. Achieving the optimal demulsifier concentration is therefore critical for efficient separation, reduced chemical consumption, and cost-effective operations. In practice, the selection and dosage of demulsifier agents must be tailored to the specific crude oil composition, the characteristics of the aqueous phase, and operating conditions [18,40]. Therefore, understanding the concentration-dependent behavior of demulsifiers is essential for optimizing emulsion breakdown.

3.3. Summary of Synergistic Effects on Emulsion Stability

The stability of petroleum emulsions reflects the combined and synergistic actions of chemical constituents and operational conditions [44]. It is important to note that the stabilization of water-in-oil emulsions arises from the combined action of asphaltenes, resins, acidic species, and wax crystals, which may interact in synergistic or competitive ways. Resins typically act as peptizing agents, promoting asphaltene adsorption and strengthening the interfacial film, representing a synergistic effect. In contrast, acidic compounds or other polar species can compete for adsorption sites, partially displacing asphaltenes and yielding softer films with reduced stability. Wax crystals contribute a steric and mechanical barrier, reinforcing the interfacial structure [80,115]. Several studies have further reported that the relative contribution of each fraction depends on crude type: asphaltenes and resins dominate in heavy oils, while acids and waxes can be more influential in lighter crudes [71,108,116]. Environmental and operational factors—temperature, aqueous pH, droplet size, and mixing intensity—further modulate these interactions, influencing film strength, droplet charge, and diffusion rates [117,118]. Small, uniform droplets increase surface area for stabilizer adsorption, whereas pH or temperature variations can either reinforce or weaken interfacial films [103]. These combined chemical and physical effects generate highly persistent emulsions, highlighting the necessity of integrated demulsification strategies that target multiple stabilization pathways simultaneously [119,120]. A comprehensive summary of these factors, their mechanisms, and practical implications is provided in Table 1.

It should be noted that, dynamic optimization of demulsification requires real-time monitoring of emulsion state [121]. Direct assessment of interfacial film strength is difficult in field operations; however, indirect techniques provide valuable proxies [122]. Inline droplet size measurement, using laser diffraction, focused beam reflectance measurement (FBRM), or ultrasonic backscatter, can continuously monitor water droplet size distributions. Conductivity and dielectric sensors give rapid feedback on water cut and phase separation, while turbidity and near-infrared probes offer additional estimates of dispersed water fraction [123]. Collectively, these techniques enable operators to track emulsion

stability and adjust demulsifier dosing or treatment conditions in real time. Such monitoring technologies therefore represent an essential step toward adaptive and sustainable demulsification practices [124].

Table 1. Summary of Factors Influencing Petroleum Emulsion Stability.

Factor Category	Sub-Factor	Mechanism/Effect on Stability	Key Considerations/Implications
Crude Oil Composition	Asphaltenes	Adsorb at interface; form rigid films; H-bonding and π-π stacking	Highly polar asphaltenes enhance stability; aggregation affects film strength
	Resins	Rapid adsorption; enhance asphaltene interfacial films; π-π stacking	Improve emulsion viscosity and resistance to coalescence
	Acidic Compounds	Ionize at interface; interact with asphaltenes; H-bonding	Low concentrations strengthen films; excessive conc. reduces stability
	Wax Crystals	Form network at low temp; steric hindrance	Increase viscosity and prevent droplet coalescence
	Solid Particulates	Clay, silica, metal compounds interact with polar groups	Provide mechanical and steric reinforcement
Operational/ Environmental Factors	Temperature	Reduces viscosity; affects droplet collisions; influences interfacial adsorption	Higher temperature generally decreases emulsion stability by weakening interfacial films
	Aqueous Phase pH	Modulates droplet charge, surfactant ionization, and film rigidity	Acidic favors W/O emulsions; alkaline favors O/W; optimal demulsification near neutral pH
	Droplet Size and Distribution	Smaller droplets increase surface area and viscosity; narrow distribution enhances stability	Directly affects coalescence rate and rheology
	Mixing Time and Intensity	Determines droplet size and kinetic stability	Excessive mixing can destabilize films or cause phase inversion
	Emulsifier/Demulsifier Concentration	Emulsifiers strengthen films; demulsifiers displace stabilizers to promote coalescence	Optimal demulsifier dosing essential to avoid over-stabilization or secondary emulsification

4. Emulsion Destabilization Processes

The stability of emulsions plays a critical role in their practical application and management, being largely governed by the balance between stabilizing and destabilizing forces. Destabilization occurs through several processes, including flocculation, coalescence, Ostwald ripening, creaming, and sedimentation, each of which uniquely contributes

to the breakdown of emulsion structures, as illustrated in Figure 5. Extensive research has investigated these processes, emphasizing their significance in determining emulsion destabilization pathways [18,44,112,114,125–131]. The subsequent subsections provide a detailed discussion of these processes, outlining their underlying principles and roles in the overall destabilization behavior of emulsions.

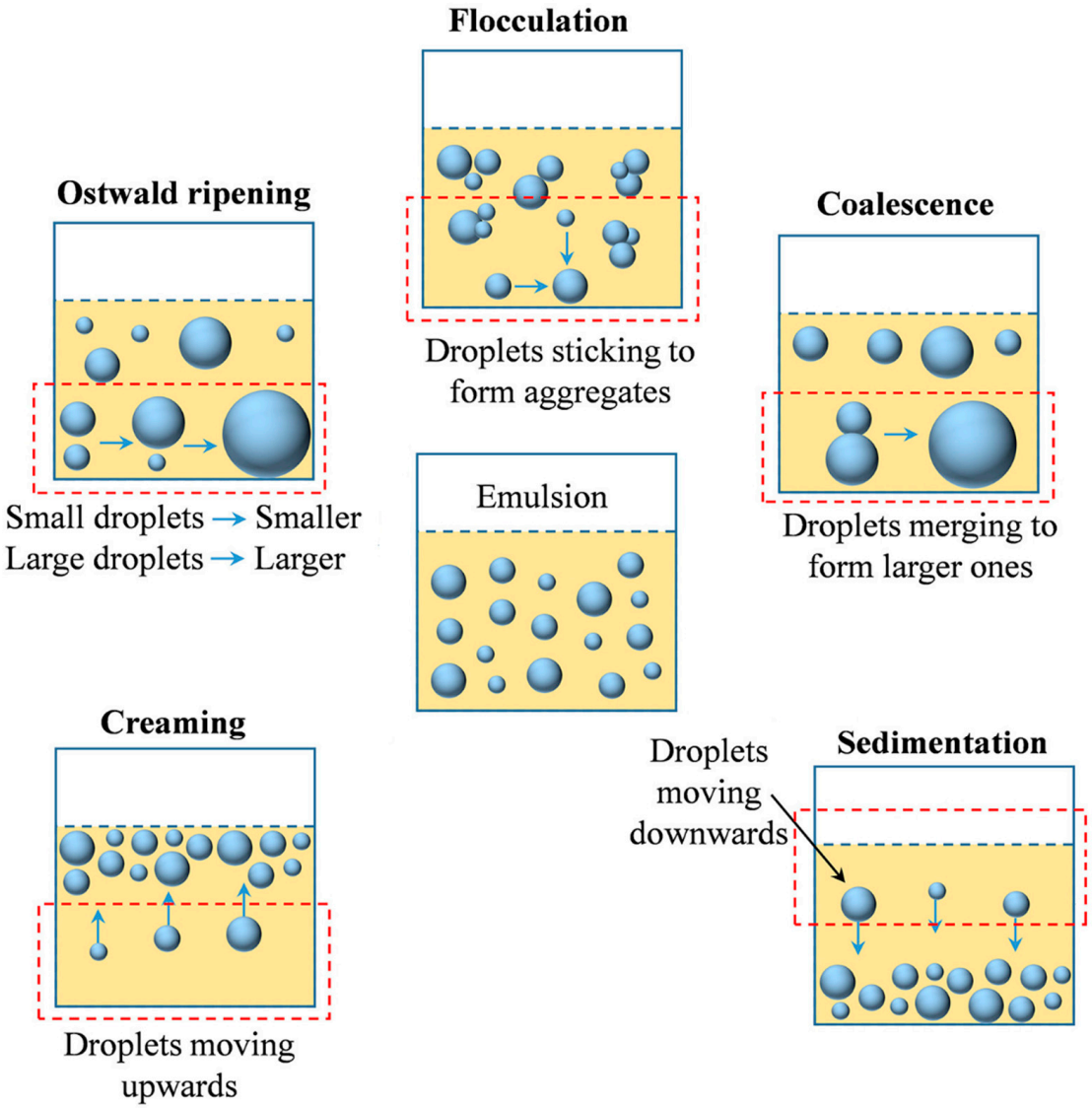


Figure 5. Emulsion destabilization processes [17].

4.1. Flocculation and Coalescence

Flocculation and coalescence represent two fundamental but closely related processes of emulsion destabilization, often occurring simultaneously and influencing each other's progression. Flocculation refers to the clustering of dispersed droplets caused by attractive forces such as van der Waals interactions or depletion forces, resulting in the formation of droplet aggregates, commonly referred to as flocs. Importantly, this process does not involve the actual merging of droplets; instead, it increases the effective hydrodynamic size of the droplet clusters within the emulsion system [132–134]. Depending on the strength and reversibility of the interactions involved, flocculation can either be temporary, where aggregates readily redisperse, or permanent, where droplet clusters remain intact and promote further destabilization.

In contrast, coalescence describes the irreversible merging of two or more droplets into a larger droplet, a process driven by the progressive thinning and eventual rupture of the liquid film that separates adjacent droplets [135]. This phenomenon reduces the total number of dispersed droplets, thereby lowering the overall stability of the emulsion. In systems stabilized by surfactants, however, coalescence can be delayed or suppressed because surfactant molecules adsorbed at the oil–water interface create steric hindrance and electrostatic repulsion that resist film rupture and droplet merging [136,137]. The interplay between flocculation and coalescence is therefore crucial, as initial droplet aggregation through flocculation often accelerates subsequent coalescence, jointly contributing to emulsion breakdown.

4.2. Ostwald Ripening

Ostwald ripening is widely recognized as a key thermodynamically driven process contributing to emulsion destabilization. First described by Wilhelm Ostwald in the late 19th century, this process involves the preferential growth of larger droplets at the expense of smaller ones, gradually shifting the system toward a more energetically stable state [138,139]. The phenomenon arises from the solubility differences between droplets of varying sizes: smaller droplets, owing to their higher curvature, exhibit elevated internal pressures that render them more soluble in the continuous phase than larger droplets [140]. As a result, molecules from smaller droplets diffuse into the surrounding medium and subsequently redeposit onto larger droplets, promoting their growth and leading to a progressive coarsening of the emulsion. In emulsions stabilized by surfactants, Ostwald ripening remains particularly significant. While surfactants reduce interfacial tension and introduce steric or electrostatic barriers that delay coalescence, they also modify the solubility of the dispersed phase, thereby influencing ripening dynamics [141]. When the dispersed phase exhibits high solubility in the continuous medium, the rate of Ostwald ripening increases, resulting in time-dependent droplet enlargement and reduced emulsion shelf life [142]. The specific role of surfactants in this process is complex: strongly adsorbing surfactants can suppress ripening by limiting molecular exchange, whereas surfactants that enhance solubilization of the dispersed phase may accelerate droplet growth, thereby intensifying destabilization [143].

4.3. Creaming

Creaming is a gravitational separation process in which droplets of the dispersed phase migrate upward due to density differences between the two phases. This phenomenon is most commonly associated with oil-in-water (O/W) emulsions, where the oil droplets, being less dense than water, gradually rise to the surface, resulting in the formation of a concentrated upper layer that imparts a “creamed” appearance [144]. Importantly, creaming is distinct from coalescence, as the droplets do not merge but instead maintain their individuality while redistributing spatially within the emulsion. The dynamics of creaming are strongly influenced by droplet size and the viscosity of the continuous phase. According to Stokes’ law, larger droplets ascend more rapidly than smaller ones under gravitational forces, making droplet size reduction a critical factor in enhancing emulsion stability. Similarly, the viscosity of the continuous medium plays a significant role, as higher viscosity provides greater resistance to droplet movement and thereby slows the creaming rate [145–148]. Consequently, strategies aimed at reducing viscosity or encouraging droplet enlargement can be deliberately employed to intensify creaming, thereby supporting more effective oil–water separation and improving the overall performance of demulsification processes.

4.4. Sedimentation

Sedimentation is a gravitational separation process that serves as the inverse of creaming, wherein the dispersed phase droplets migrate downward and accumulate at the base of the emulsion system. This mechanism is predominantly observed in water-in-oil (W/O) emulsions, since water droplets, being denser than the continuous oil phase, settle under gravitational forces and form a concentrated layer at the bottom [31]. Similarly to creaming, the rate of sedimentation is strongly influenced by droplet size, with larger droplets descending more rapidly than smaller ones, a phenomenon quantitatively described by Stokes' law [149,150]. Moreover, the viscosity of the continuous phase exerts a significant influence, as higher viscosity retards droplet motion and thereby enhances resistance against gravitational separation, contributing to emulsion stability. In systems stabilized by surfactants, sedimentation and creaming become particularly critical during storage and handling, as surfactants not only control droplet size distribution but also modify the rheological behavior of the continuous phase [150–152]. Consequently, the interplay between droplet size, phase viscosity, and surfactant properties determines the extent and rate of sedimentation, making it a central factor in evaluating both the stability and destabilization pathways of oil–water emulsions.

5. Demulsification Methods of Oil–Water Emulsions

Demulsification compromises the stability of emulsions by promoting the coalescence of dispersed droplets. This section provides a comprehensive review of the various methods employed for oil–water separation, with particular emphasis on the underlying mechanisms governing their effectiveness.

5.1. Chemical Demulsification

Chemical demulsification is the most widely employed method for separating oil–water emulsions, involving the addition of potent interfacially active chemical demulsifiers to destabilize the emulsion. These agents act by reducing the interfacial tension gradient and lowering interfacial viscosity, thereby promoting droplet coalescence and accelerating film drainage [153–155]. The demulsification can be conceptualized as a two-step process comprising flocculation and coalescence, as shown in Figure 6 [156]. Flocculation mitigates the repulsive forces that maintain emulsion stability, allowing droplets to come closer. Subsequently, coalescence occurs when two or more droplets merge, forming larger, less stable droplets, ultimately resulting in irreversible phase separation [157]. The efficiency of chemical demulsification is influenced by multiple factors, including the type and dosage of the demulsifier, temperature, presence of impurities, and bulk viscosity of the emulsion [158].

Chemical demulsifiers primarily adsorb at the oil–water interface but do not form a strong interfacial film [159,160]. Their function is to alter the interfacial physicochemical properties, disrupt existing interfacial films, and accelerate droplet merging, thereby facilitating phase separation. These agents are versatile and can be applied across a broad spectrum of emulsion types [161]. The key advantages of chemical demulsification include high efficiency, relatively simple operational requirements, cost-effectiveness, and extensive applicability. Research in recent years has focused on understanding the underlying principles of demulsifier action, leading to significant advancements in formulation and application [40,67,114,162]. Table 2 provides a comparative summary of commonly used chemical demulsifiers, highlighting their representative compounds, primary mechanisms of action, notable advantages, inherent limitations, and typical efficiency in demulsification processes. It should be noted that the efficiencies reported in Table 2 largely reflect laboratory conditions. The actual performance of chemical demulsifiers in oilfield opera-

tions can be significantly influenced by salinity, viscosity, and temperature. For instance, high ionic strength may diminish the effectiveness of ionic surfactants, while elevated crude viscosity can hinder the diffusion of large polymeric molecules to the interface [163]. Therefore, laboratory data should be interpreted as indicative, and field-specific screening remains essential.

High-performance demulsifiers achieve their effect by reducing interfacial shear viscosity, enhancing interfacial mobility, and destabilizing water–oil emulsions. Effective demulsifiers must partition between oil and water phases, break down in the oil phase, reach sufficient interfacial concentration to ensure high diffusion flux, and suppress interfacial tension gradients to accelerate film drainage and coalescence [21,106]. As surfactants, demulsifiers possess hydrophilic and hydrophobic groups, and their hydrophilic-lipophilic balance (HLB) critically determines their attraction toward water or oil phases [120,164]. Hydrophilic surfactants (HLB > 10) preferentially migrate to the aqueous phase, whereas lipophilic surfactants (HLB < 10) favor the oil phase. Studies have shown that the HLB, chain length, and balance of hydrophilic and hydrophobic blocks significantly influence the efficiency of emulsion breaking and guide the design of tailored demulsifiers [165–167]. Accordingly, the careful selection of demulsifier type, dosage, and HLB, together with consideration of emulsion characteristics such as viscosity and impurity content, is critical for achieving efficient phase separation. Ongoing research seeks to optimize these formulations to enhance droplet coalescence, reduce interfacial film strength, and improve the overall effectiveness of chemical demulsification across diverse industrial applications.

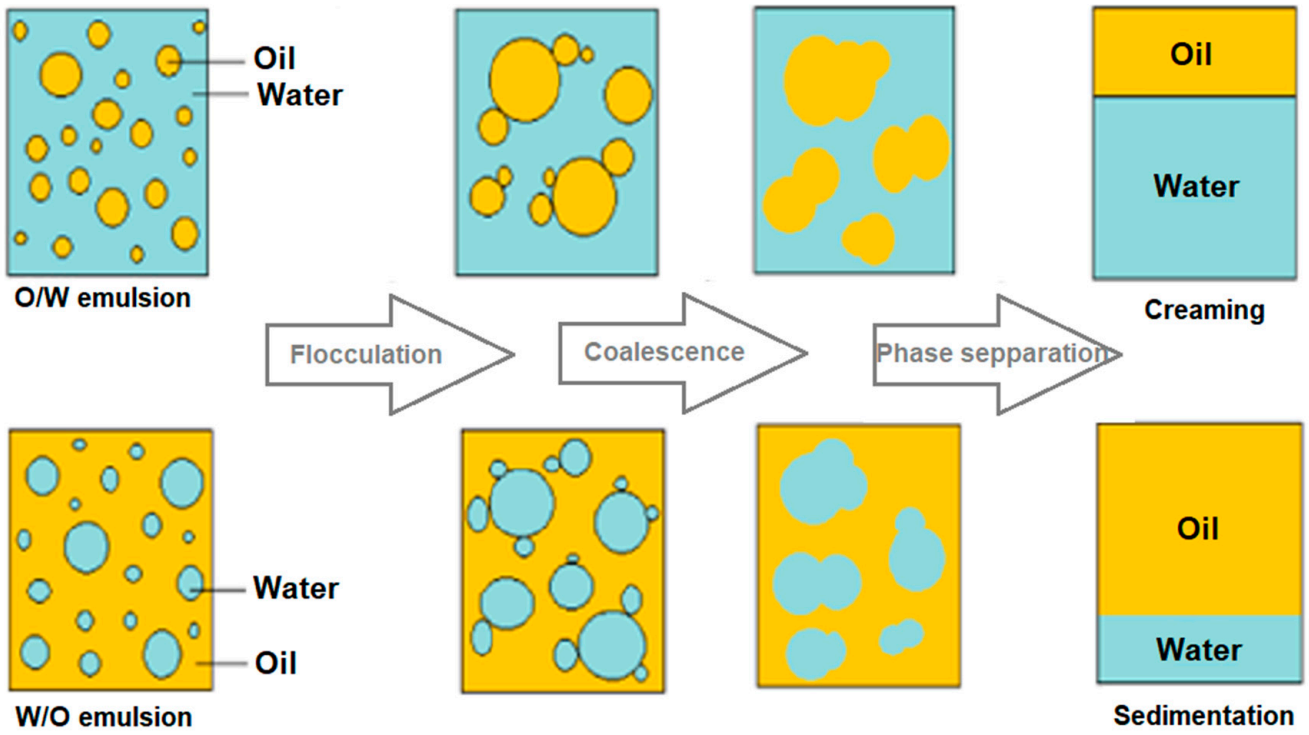


Figure 6. Schematic diagram of the processes involved in chemical demulsification [156].

Table 2. Comparative Overview of Common Chemical Demulsifiers.

Demulsifier Class	Representative Compounds	Dominant Mechanism	Key Advantages	Limitations	Typical Efficiency	Ref.
Anionic	Sodium salts of fatty acids (RCOONa), alkyl sulfonates, alkylnaphthalene sulfonates	Anionic headgroups neutralise positive droplet charges in W/O emulsions; reduce electrostatic repulsion to enable coalescence	Low cost; simple synthesis; effective in low–moderate salinity	High dosage (>100 mg/L); poor high-salinity performance; reduced efficiency in O/W	Moderate efficiency; >100 mg/L often required	[168,169]
Cationic	Quaternary ammonium salts, polyether–polyquaternium (PPA)	Neutralisation of negative charges on O/W droplets; promotes coalescence and possible hydrogen bonding	High O/W efficiency; PPA dehydration 80.6%; some antimicrobial effect	Limited W/O activity; potential aquatic toxicity	80–90% separation at 50–100 mg/L	[170,171]
Ionic Liquids	Glucose-based GC@DA, pyridinium ILs, halide and non-halide variants	Strong interfacial adsorption via electrostatics, π–π stacking, and hydrogen bonding; displace asphaltenes	Tunable amphiphilicity; high activity at low concentration; low volatility	High synthesis cost; limited field-scale validation	>99% removal at ~15 mg/L	[172,173]
Non-Ionic	PO–EO Copolymers: EO–PO–EO and PO–EO–PO (linear, branched, star)	Amphiphilic molecules replace interfacial species and weaken films; steric hindrance prevents re-adsorption	Commercially dominant; EO/PO ratio adjustable; branched forms most effective	High PO ratio reduces performance; less effective for certain high-viscosity oils	High EO type: 20–50 mg/L; high PO type: >100 mg/L	[174,175]
	PDMS Copolymers: EO–PDMS–EO, PO–PDMS–PO	PDMS backbone with EO/PO ends adsorbs at interface, displacing film components	Effective across crude types; hydrophobic PDMS enhances film disruption	Long PDMS chains may stabilise emulsions; higher cost than PO–EO	30–80 mg/L	[176]
	EC Polymer: Ethyl cellulose with β-glucose backbone	Amphiphilicity enables penetration and rupture of asphaltene films	Biodegradable; tunable hydrophilic–lipophilic balance; rapid rupture	Limited data in high-salinity or high-viscosity systems	Rupture in ~20 s at ~50 mg/L	[177,178]
	Dendrimers: Polyamide dendrimers, CHPAMAM	Branched macromolecules penetrate and disrupt films; terminal groups bridge droplets	Strong interfacial activity; functionalisation possible	Slower diffusion at high conc.; complex synthesis	20–40 mg/L typical	[179]
Magnetic	Fe_3O_4–EC (M-EC), NH_2-MNPs, M-mANP	Magnetic nanoparticles adsorb at droplet interface; bridging via surface functional groups; removed by magnetic field	Ultrafast (>98% in 2 min); potential for reuse	High cost; incomplete recovery; synthesis complexity	99.7% at optimal loading	[180,181]

5.2. Physical Demulsification

5.2.1. Thermal Demulsification

Thermal demulsification involves elevating the temperature of oil–water emulsions prior to their introduction into flow treatment units, thereby enhancing droplet collisions and promoting coalescence [19]. By increasing the kinetic energy of the droplets, higher temperatures facilitate agglomeration, ultimately aiding phase separation. This method is typically categorized into conventional heating and microwave-assisted heating. Taylor [87] examined the effect of temperature on asphaltene-stabilized oil-in-water (O/W) emulsions and observed progressive emulsion breakup as the phase temperature approached the cloud point, accompanied by a reduction in the asphaltene–water interfacial tension.

Microwave heating has been shown to improve demulsification efficiency relative to conventional methods. Lv et al. [182] reported a 25.3% increase in the demulsification efficiency of oily sludge using microwave irradiation, along with reductions in both processing time and energy consumption. Similarly, Mowea et al. [183] demonstrated rapid separation of water-in-oil (W/O) emulsions under microwave power of 800–900 W for 150–200 s, highlighting the method's efficiency and environmental advantages. Martínez Palou et al. [184] compared microwave and oil-bath heating for O/W emulsions and confirmed that microwave treatment achieved faster phase separation than conventional heating.

Despite its effectiveness, thermal demulsification has notable limitations. Heating can volatilize light crude oil components, increasing oil density and reducing the efficiency of gravity separation. Moreover, since water has roughly twice the specific heat of oil, a significant portion of input energy is absorbed by the water phase, resulting in inefficiency. To address these challenges, future approaches may focus on minimizing heat loss and combining thermal treatment with complementary methods, such as electrical or chemical demulsification, to enhance overall separation performance and energy efficiency [19,67,185].

5.2.2. Mechanical Demulsification

Mechanical demulsification involves the physical disruption of emulsion stability, typically by exploiting differences in density between the oil and water phases or by breaking interfacial barriers [18]. This method employs various mechanical devices such as free-water knockout drums, low- and high-pressure two- and three-phase separators, desalters, and settling tanks [186]. In crude oil emulsions containing relatively large droplets, reduced flow velocities allow gravitational forces to act effectively, facilitating the separation of oil, water, and suspended droplets. This process is particularly efficient in large-volume separators and desalters, where oil–water separation occurs rapidly [187,188]. The separation mechanism relies on flow dynamics to concentrate oil traces, enhancing the efficiency of gravity-driven settling, which is highly dependent on the oil concentration in the mixture [189]. While centrifuges are capable of mechanical demulsification, their high capital cost and limited capacity restrict widespread industrial use [190]. Hao et al. [191] demonstrated that centrifugal contactors could effectively address high oil content in electric desalting wastewater.

Among mechanical demulsification techniques, gravity settling tanks are the most commonly employed mechanical demulsification technique in the oil industry, allowing emulsions to separate under gravitational forces as dispersed-phase droplets approach one another and coalesce, thereby facilitating efficient phase separation [189]. To further improve performance, centrifugal contactors can be combined with gravity settling tanks, providing additional force to accelerate droplet coalescence. Krebs et al. [189] examined the demulsification kinetics of a model oil-in-water emulsion under centrifugal fields, finding that higher centrifugal acceleration and longer residence times significantly enhanced crude

oil separation, achieving an oil recovery efficiency of 84%. While gravity settling remains the industry standard due to its simplicity and cost-effectiveness, supplementary techniques such as centrifugation can markedly improve separation efficiency under demanding conditions, especially for high oil content or viscous emulsions [31,192,193]. Careful selection and optimization of mechanical equipment thus enable operators to achieve rapid, reliable, and effective demulsification across a wide range of crude oil processing scenarios.

5.2.3. Electrical Demulsification

Electrical demulsification involves the application of electric fields to induce the separation of oil and water in crude oil emulsions [194]. This technique, which has been in use for over a century, is increasingly favored due to its sustainability and minimal environmental impact compared with thermal or chemical methods [30]. Its advantages include reduced sludge formation, simplified equipment requirements, and the avoidance of chemical additives [195]. Typically, electric current is applied to electrodes immersed in crude oil emulsions, producing an in situ coagulant effect that neutralizes the repulsive charges of surfactant molecules, thereby promoting the aggregation of oil droplets into larger flocs that can be easily separated from water [196]. Under the influence of an electric field, droplets become polarized and often align in chains parallel to the field due to induced dipole interactions, while droplet deformation and elongation accelerate coalescence (Figure 7) [197]. Despite its advantages, the adaptation of electrical demulsification to emulsions with varying physicochemical properties remains incompletely understood [198,199]. Electro-demulsification efficiency is closely tied to the physical properties of emulsions. Water-phase conductivity regulates charge relaxation and dipole formation; very low conductivity suppresses polarization, while excessive conductivity promotes joule heating [200]. Droplet size distribution also plays a central role: larger and more polydisperse droplets deform and chain more readily, enhancing coalescence [201]. Furthermore, interfacial charge density influences dipole strength and collision frequency. These sensitivities explain why electro-demulsification performs inconsistently across different crude oils. Coupling this method with pre-treatments such as mild heating or low-dose chemical additives has been shown to alleviate these limitations [201]. Hence, while the method is environmentally favorable, its success relies on careful alignment with the emulsion's intrinsic properties.

Extensive research has focused on the mechanisms of droplet formation and coalescence under electrical fields. Mousavi et al. [202] demonstrated that higher frequencies of pulsatile electric fields suppressed secondary droplet formation in the low-frequency domain. Zhang et al. [203] observed that larger water droplets in dielectric oil deformed more under electric fields, with interfacial tension significantly reduced in the presence of surfactants. Mhatre and Thaokar [204] showed that electro-coalescence efficiency varied with the uniformity and symmetry of applied electric fields. Molecular dynamics simulations by Wang et al. [205] revealed that constant DC fields accelerated droplet approach prior to contact. Muto et al. [206] found that alternating electric fields (particularly square-wave) enhanced W/O emulsion demulsification, with the rate further influenced by solvent volume fraction and electrolyte ionic strength. Similarly, Mohammadian et al. [207] reported that water separation rates increased with DC field strength, highlighting the critical role of field magnitude and electrode type in optimizing electrical demulsification of crude oil emulsions.

Although electrical demulsification has been successfully implemented in a range of industrial applications, particularly for the treatment and separation of crude oil emulsions, ongoing research continues to focus on optimizing the process, improving

efficiency, and addressing challenges associated with variable emulsion properties and operational conditions.

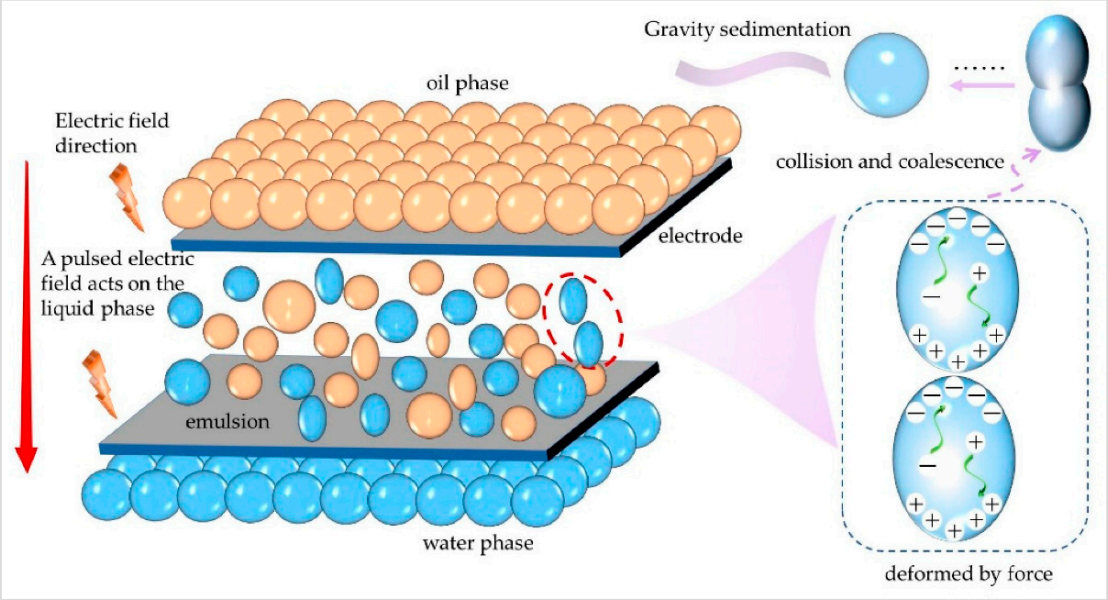


Figure 7. Schematic representation of the electrostatic coalescence process in emulsion systems [208].

5.2.4. Membrane Demulsification

Membrane-based filtration has emerged as a promising technique for demulsifying oil–water emulsions, offering high separation efficiency and low energy requirements [185,209,210]. In this approach, the pore sizes of the membranes are considerably smaller than the emulsion droplets, and the applied pressure forces the droplets through the membrane. During this process, droplets undergo substantial deformation due to the extreme and uneven stresses encountered at the membrane pores, leading to droplet rupture. The resulting smaller droplets are adsorbed onto the membrane surface, where they gradually coalesce into larger droplets that separate from water under gravity. Despite its advantages, membrane fouling remains a primary challenge, reducing flux and operational lifetime while increasing maintenance costs. Wu et al. [211] demonstrated that positively charged membrane surfaces can enhance the demulsification of O/W emulsions, although surface contamination still limits long-term performance. Innovations such as SiO_2 nanosphere-coated membranes have shown exceptional results, achieving W/O emulsion separation efficiencies up to 98% under highly acidic and saline conditions, highlighting their anti-fouling capability [212]. Similarly, polydimethylsiloxane (PDMS)-based membranes, owing to their low surface energy, have been widely employed in oil–water separation and self-cleaning applications [213]. Zhu et al. [214] developed heterogeneous nanofibrous membranes with PDMS shells grafted onto hydrophilic polyacrylonitrile (PAN) cores, allowing oil droplets to slide along the slippery PDMS surface while maintaining continuous water flow through the PAN core. This synergistic core–shell design achieved near-complete water recovery and strong antifouling performance, effectively combining droplet aggregation and release for efficient demulsification.

Hydrophobic surface modification represents a fundamental strategy for enhancing membrane demulsification, particularly in the treatment of petroleum emulsions stabilized by surface-active agents and fine solids. By tailoring surface wettability to favor oil affinity while repelling water, such modifications enable selective permeation of the oil phase and simultaneously promote rapid coalescence of water droplets at the membrane interface [215].

This dual effect facilitates efficient phase separation and lowers the energetic barriers associated with emulsion destabilization. For instance, a superhydrophobic polyvinylidene fluoride (PVDF) membrane fabricated through solute–solvent co-crystallization demonstrated high oil permeance (≈70 $Lm^{-2}h^{-1}Pa^{-1}$) and effective rejection of water droplets in stable water-in-oil emulsions [216]. Similarly, a demulsifier-inspired PVDF membrane modified with Pluronic F127 exhibited underwater superoleophobicity, achieving oil removal efficiencies exceeding 99.1% and maintaining robust structural stability under extreme pH and saline conditions [217]. These findings underscore the capacity of hydrophobic modification to improve demulsification efficiency, mitigate fouling, sustain permeation flux, and extend membrane lifespan. Nevertheless, excessive hydrophobicity may intensify oil fouling, emphasizing the necessity of optimizing surface engineering strategies.

5.2.5. Ultrasonic Demulsification

Ultrasonic demulsification of crude oil emulsions is founded on the principle that ultrasound reduces viscosity while inducing condensation effects, thereby promoting the aggregation of water droplets and facilitating efficient oil–water separation [218]. The method has gained increasing attention because of its simplicity, high efficiency, and potential as a clean separation technology. One of the key mechanisms underpinning this technique is acoustophoresis, where dispersed droplets within an ultrasonic standing wave field experience forces due to differences in density and compressibility between the dispersed and continuous phases, leading to droplet aggregation [19]. Numerous studies have demonstrated the effectiveness of ultrasound in demulsification under varied operating parameters. For instance, Check and Mowla [219] investigated the combined influence of irradiation power, time, temperature, and water injection, reporting an optimal efficiency of 99.8% at 57.7 W, 6.2 min, and 100 °C. Further research into staged ultrasonic irradiation revealed that primary irradiation at 75 W and secondary irradiation at 50 W significantly reduced settling times within 45 s [220]. The utilization of low-frequency ultrasound for crude oil emulsion demulsification has attracted significant and growing research interest. Antes et al. [221] achieved 65% demulsification efficiency using low-frequency irradiation, while Khajehesamedini et al. [221] reported 50% efficiency under conditions of very low frequency, short exposure, and high-intensity ultrasonic waves. Xie et al. [222] highlighted the benefits of pulsed ultrasound, demonstrating enhanced water droplet coalescence that improved separation performance. Similarly, Antes et al. [223] used ultrasonic baths at varying frequencies, achieving 65% efficiency at 25–45 kHz after 15 min, but noting no separation effect beyond 45 kHz. Pedrotti et al. [224] further confirmed the role of intensity and acoustic field distribution, observing efficiencies up to 93% at 100% amplitude after 15 min of sonication, with higher separation performance in more acoustically intense regions. Collectively, these findings underscore ultrasound's potential as a sustainable and adaptable demulsification method. Nonetheless, practical limitations remain, including the need for large and costly equipment and immature application conditions, which currently restrict industrial scalability despite the technique's pollution-free, energy-efficient, and versatile advantages.

5.3. Biological Demulsification

Biological demulsification, compared with chemical methods, has received relatively limited research attention in recent years [18,225]. This approach relies on the action of biodemulsifiers, a class of biosurfactants capable of destabilizing crude oil emulsions [18]. Biodemulsifiers present several advantages, including their environmentally benign nature and the absence of secondary pollution following their application. Moreover, they are functional under harsh operating conditions and adaptable to emulsions of varied and complex

crude oil compositions. A particularly notable merit of biodemulsifiers is their sustainable sourcing, as they can be produced from agricultural or industrial waste streams, thereby contributing to waste valorization [226]. Huang et al. [227] reported the successful isolation of biodemulsifiers produced by bacterial strains thriving in petroleum-contaminated environments. However, studies indicate that the performance of these bacterial strains varies significantly depending on environmental factors such as temperature, soil characteristics, the type and concentration of contaminants, and the inherent demulsification capacity of the microbial strain. This highlights the complexity of optimizing biodemulsification for industrial applications.

Recent research efforts have increasingly focused on examining the synergistic relationship between microbial properties and their demulsification efficiency. For example, Coutinho et al. [228] investigated the activities of Pseudomonas aeruginosa MSJ, a strain isolated from petroleum-polluted soils, in destabilizing both water-in-oil (W/O) and oil-in-water (O/W) emulsions. Their study revealed that the biodemulsification potential was strongly influenced by the cellular hydrophobicity of the strain and the growth stage of the culture. Maximum demulsification activity was achieved using cells and supernatants from 96-h-old cultures, suggesting that both the metabolic state of the microorganism and the extracellular products play a critical role in the efficiency of the process. These findings underline the importance of identifying suitable strains and optimizing culture conditions for effective biodemulsifier production.

Despite its promise, biological demulsification faces practical limitations that hinder widespread adoption. The technique is associated with relatively long cultivation periods required to produce specialized microorganisms, which can restrict its industrial scalability [40,67]. Furthermore, the performance of biodemulsifiers may fluctuate under different field conditions, creating challenges for consistent application. To overcome these barriers, developing high-throughput screening methods capable of rapidly evaluating the efficiency of both natural and engineered microbial strains is essential. Such advancements would accelerate the progress of biotechnology-based demulsification, allowing for systematic selection and enhancement of microbial candidates. Consequently, biological demulsification offers key advantages such as cost-effectiveness, low energy demand, biodegradability, and environmental compatibility [193,229,230]. However, realizing its full potential for large-scale crude oil processing will depend on overcoming current limitations related to microbial cultivation time, performance variability, and process standardization [185,200,231].

5.4. Hybrid and Integrated Demulsification Strategies

A comparative overview of the demulsification methods discussed in this study, highlighting their mechanisms, advantages, and limitations, is summarized in Table 3. Petroleum emulsions, stabilized by multiple agents and influenced by variable conditions, are resistant to any single demulsification method, necessitating more versatile approaches. Hybrid strategies have gained attention because they combine the strengths of different methods while compensating for individual limitations [106,232]. For instance, chemical demulsifiers used alongside thermal or ultrasonic treatment accelerate interfacial film disruption and droplet coalescence, while coupling electrical fields with chemical or membrane-based processes enhances separation efficiency and reduces chemical usage [31,185].

Biological methods, though limited by cultivation requirements, can also be integrated with chemical or physical techniques to provide environmentally friendly and cost-effective solutions [190,233]. Hybrid approaches are especially attractive in industrial contexts, where emulsion composition and stability vary widely. Tailoring integrated strategies to specific crude oil properties allows operators to achieve higher efficiency, lower en-

ergy consumption, and improved environmental compliance compared to single-method treatments [106,234].

Consequently, hybrid and integrated demulsification strategies represent a promising direction for research and practice. Their development requires both experimental validation and process modeling to optimize combinations for field-scale application, offering a pathway toward more reliable, sustainable, and adaptable oil–water separation in petroleum production [235].

Table 3. Comparison of Petroleum Emulsion Demulsification Methods.

Method		Mechanism	Advantages	Limitations	Industrial Application
Chemical		Surfactants/displacers alter interfacial films, promote coalescence	High efficiency, cost-effective, widely applicable	High dosage, environmental concerns, secondary pollution	Industry standard
Physical	Thermal	Heating increases droplet collisions, reduces viscosity	Simple, effective with asphaltene emulsions	High energy demand, volatilization losses	Used in combination with chemicals
	Mechanical	Gravity settling, centrifugation, separators	Low cost, simple operation	Limited for small droplets, equipment-intensive	Separators, desalters
	Electrical	Electric fields polarize droplets, promote chain coalescence	Clean, low chemical use, scalable	Sensitive to emulsion properties, electrode wear	Widely used in desalters
	Membrane	Pore filtration ruptures droplets, coalescence on surface	High efficiency, low energy	Fouling, maintenance cost	Emerging field, wastewater treatment
	Ultrasonic	Acoustic waves induce droplet aggregation	Fast, pollution-free, versatile	High equipment cost, scalability issues	Research and pilot plants
Biological		Biosurfactants/ biodemulsifiers displace stabilizers	Eco-friendly, biodegradable, low energy	Slow production, variability, scalability issues	Potential for green processing
Hybrid		Integration of two or more methods	Combines strengths, reduces limitations	Complex optimization, higher costs	Future industrial adoption

6. Environmental and Sustainability Considerations

The sustainable management of petroleum emulsions has become an urgent priority as energy industries face stricter environmental regulations and growing societal expectations for cleaner production [236]. Traditional demulsification techniques, while effective in separating oil and water, often carry significant ecological drawbacks. Chemical demulsifiers, for example, introduce synthetic surfactants, polymers, and solvents that can persist in wastewater, accumulate in ecosystems, and exert toxic effects on aquatic life [165]. Similarly, thermal methods require substantial energy input, increasing both operational costs and greenhouse gas emissions, while mechanical and electrical techniques, although cleaner, demand large-scale equipment and intensive maintenance, indirectly elevating resource consumption [106,237].

A particularly critical environmental challenge is the management of produced water, the largest byproduct of oilfield operations. This effluent contains dispersed oil, salts,

solids, and residual chemicals, all of which can harm soil and groundwater if inadequately treated [238,239]. Contaminated produced water not only threatens aquatic ecosystems but also complicates regulatory compliance, making integrated demulsification and wastewater management strategies essential. Recent research has therefore focused on sustainable approaches, including bio-based demulsifiers derived from microbial metabolites, plant extracts, or agricultural residues [240–242]. These alternatives are biodegradable, low in toxicity, and simultaneously promote resource valorization. Hybrid techniques that combine physical processes with minimal chemical dosages further reduce secondary pollution, while renewable energy–driven thermal or electrical systems offer pathways to lower carbon footprints [19,106].

Embedding sustainability principles into demulsification strategies not only mitigates environmental risks but also enhances long-term economic viability. As the petroleum industry moves toward greener operations, the adoption of low-carbon, biodegradable, and resource-efficient technologies will be critical for achieving environmentally responsible and socially acceptable oil–water separation practices.

7. Smart and Bio-Based Emulsifiers: Relevance to EOR

Emulsion stability is a critical factor in both enhanced oil recovery (EOR) operations and downstream processing. While the main focus of this study is on demulsification methods and reducing the stability of petroleum emulsions, stimuli-responsive ("smart") surfactants, as well as bio-based emulsifiers, play an important role in controlling emulsion formation and stability in EOR processes [243,244]. Understanding their behavior can provide insights into how emulsions can be stabilized during EOR and subsequently broken efficiently during downstream processing.

7.1. Stimuli-Responsive Surfactants

Stimuli-responsive surfactants are increasingly explored in EOR due to their ability to dynamically alter interfacial properties under varying reservoir conditions [243,245–247]. Temperature-sensitive surfactants, such as poly(N-vinyl caprolactam) (PNVCL) and poly(ethylene oxide)-based nonionic surfactants, exhibit reversible phase transitions near their lower critical solution temperature (LCST) or cloud point, enabling controlled surfactant release and reduced interfacial tension at oil–water interfaces, thereby enhancing oil displacement efficiency in reservoirs with fluctuating temperatures [243,248]. Similarly, pH-sensitive surfactants, including N-dodecylpropane-1,3-diamine (DPDA), fatty acid salts, and carboxybetaines, undergo protonation or deprotonation in response to pH changes, modulating their hydrophilic–lipophilic balance (HLB) and improving emulsion stability or demulsification [247,249]. These smart surfactants provide tunable, reservoir-specific responses, enhancing oil recovery while maintaining process control and efficiency.

7.2. Bio-Based Emulsifiers

Bio-based emulsifiers, also referred to as first-generation natural surfactants, are synthesized from renewable resources including plants, animals, microorganisms, or agro-industrial by-products. Unlike conventional petrochemical surfactants, they are biodegradable, biocompatible, and generally less toxic, thereby reducing the environmental footprint associated with surfactant use in various industries [250,251]. Structurally, these emulsifiers consist of amphiphilic molecules in which hydrophilic head groups, typically derived from carbohydrates, glycerol, or amino acids, are chemically or enzymatically linked to hydrophobic fatty acid chains obtained from natural oils or waste by-products [252,253]. This amphiphilic character enables them to effectively reduce interfacial tension, form stable emulsions, and perform functions such as wetting, foaming, and solubilization.

Compared to conventional surfactants, bio-based emulsifiers often exhibit lower critical micelle concentrations (CMC), allowing effective performance at reduced dosages, which translates into both economic and ecological advantages [254]. Several classes of bio-based emulsifiers are of special relevance to EOR, among the most prominent examples are alkyl polyglucosides (APGs), saponins, glycerol-based surfactants, and sucrose esters. APGs, synthesized from glucose and fatty alcohols, combine strong emulsifying power with electrolyte tolerance and have been demonstrated to perform effectively in high-salinity brines, making them suitable for chemical flooding [253,255–257]. Saponins, naturally occurring glycosides found in numerous plants, possess amphiphilic structures that yield significant interfacial activity and stable emulsion formation; their wide availability and functional versatility further support potential applications in petroleum systems [254,258]. Glycerol-based surfactants, obtained through the valorization of biodiesel-derived glycerol, provide cost efficiency alongside emulsification capacity and alkali tolerance, particularly relevant for alkaline flooding processes [259–261].

Looking forward, the development and deployment of bio-based emulsifiers represent a promising direction for sustainable petroleum emulsion management. Their ability to stabilize or destabilize emulsions under high salinity and temperature conditions makes them attractive candidates for enhanced oil recovery and demulsification processes. However, challenges such as high production costs, structural variability, and sensitivity to extreme reservoir environments must be addressed before large-scale application is feasible. Future research should focus on improving biotechnological production pathways, engineering molecular structures for reservoir-specific performance, and integrating bio-based emulsifiers with conventional or hybrid demulsification strategies.

8. Conclusions

This review set out to evaluate the challenges and opportunities associated with crude oil emulsion stability and demulsification, aiming to bridge mechanistic understanding with applied technologies. The analysis confirms that crude oil emulsions, though thermodynamically unstable, can persist for extended periods due to the interfacial activity of asphaltenes, resins, acidic compounds, waxes, and solid particulates. Operational conditions such as temperature, pH, mixing, and droplet size further complicate their separation.

Over the years, a wide array of demulsification strategies has been developed. Chemical demulsifiers remain the industrial standard due to their efficiency and versatility, while thermal, mechanical, electrical, membrane-based, and ultrasonic methods offer complementary approaches, each with limitations in energy use, scalability, or fouling susceptibility. Biological demulsification represents a promising sustainable alternative but is constrained by microbial growth requirements and variable performance under field conditions. Increasingly, hybrid and integrated strategies that combine chemical, physical, and biological methods are emerging as the most effective route to achieve rapid, cost-efficient, and environmentally responsible separation.

Future efforts should focus on integrating green chemistry, advanced materials, biotechnology, and predictive modeling to optimize demulsification under real-world conditions. Innovations such as bio-based demulsifiers, low-energy physical methods, engineered microbes, and smart membranes, coupled with process modeling, can enable tailored strategies that balance operational efficiency with sustainability. By embracing interdisciplinary approaches, the petroleum sector can advance toward more effective, economical, and environmentally responsible management of crude oil emulsions.

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Abbreviations

AFM	Atomic Force Microscopy
APGs	alkyl polyglucosides
CHPAMAM	N-hexadecanoyl hyperbranched poly (amido-amine)
CMC	Critical Micelle Concentration
DC	Direct Current
DPDA	N-dodecylpropane-1,3-diamine
EOR	Enhanced Oil Recovery
EO	Ethylene Oxide
FBRM	Focused Beam Reflectance Measurement
GC@DA	Glucose-based dodecylamine ionic liquid demulsifier
HLB	Hydrophilic–Lipophilic Balance
IFT	Interfacial Tension
ILs	Ionic Liquids
LCST	Lower Critical Solution Temperature
M-EC	Magnetic Ethyl Cellulose
M-mANP	Magnetic nano-modified carboxylated polyether demulsifier
MNPs	Magnetic Nanoparticles
O/W	Oil-in-Water
O/W/O	Oil-in-Water-in-Oil
PDMS	Polydimethylsiloxane
PNVCL	Poly(N-vinyl caprolactam)
PO	Propylene Oxide
PVDF	Polyvinylidene Fluoride
STM	Scanning Tunneling Microscopy
W/O	Water-in-Oil
W/O/W	Water-in-Oil-in-Water

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