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Review

Research and Application Progress of Crude Oil Demulsification Technology

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Abstract: The extraction and collection of crude oil will result in the formation of numerous complex emulsions, which will not only decrease crude oil production, raise the cost of extraction and storage, and worsen pipeline equipment loss, but also seriously pollute the environment because the oil in the emulsion can fill soil pores, lower the soil's permeability to air and water, and create an oil film on the water's surface to prevent air–water contact. At present, a variety of demulsification technologies have been developed, such as physical, chemical, biological and other new emulsion breaking techniques, but due to the large content of colloid and asphaltene in many crude oils, resulting in the increased stability of their emulsions and oil–water interfacial tension, interfacial film, interfacial charge, crude oil viscosity, dispersion, and natural surfactants have an impact on the stability of crude oil emulsions. Therefore, the development of efficient, widely applicable, and environmentally friendly demulsification technologies for crude oil emulsions remains an important research direction in the field of crude oil development and application. This paper will start from the formation, classification and hazards of crude oil emulsion, and comprehensively summarize the development and application of demulsification technologies of crude oil emulsion. The demulsification mechanism of crude oil emulsion is further analyzed, and the problems of crude oil demulsification are pointed out, so as to provide a theoretical basis and technical support for the development and application of crude oil demulsification technology in the future.

Keywords: crude oil emulsion; demulsification technology; chemical demulsification; demulsification mechanism

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1. Crude Oil Emulsion

As an important strategic resource, oil is known as the "blood" of industry. Due to its widespread application value, the demand for it from countries around the world is still growing [1]. In order to meet the demand for petroleum in human life and industrial production, various technologies have been adopted to extract crude oil, including chemical flooding, hybrid flooding and other chemical means to improve crude oil recovery [1]. However, the mixing of groundwater and the addition of chemicals will increase the degree of oil–water emulsification in the produced liquid, resulting in the stronger stability of crude oil emulsion, higher costs for crude oil gathering, transportation and storage, and more serious wear and tear on pipeline equipment [2]. Even in the subsequent refining stage, it may increase the probability of catalyst poisoning [3]. In addition, a large amount of emulsified oily wastewater will inevitably be produced in the process of crude oil production, refining, storage and transportation, causing serious pollution to ecosystems, plants, soils and water bodies [4]. The American tanker Amoco Cadiz lost power after hitting the rocks in the waters near Brittany Peninsula, France. After this, 246,000 tons of light crude oil carried on the ship flowed into the English Channel, killing more marine life than any oil spill at that time. Therefore, the oil–water separation of crude oil emulsions, namely, demulsification, is of great significance.

As the term suggests, the process of crude oil demulsification involves disrupting the stability of the preexisting oil–water emulsion, thereby facilitating phase separation. The stability of crude oil emulsion depends on multiple factors, including the tension of oil–water interface, the film of oil–water interface, interface charge, and so on [5]. Therefore, changing the interfacial energy between oil and water, the strength of the oil–water interfacial film and the interfacial charges are all important ways to achieve demulsification. At present, researchers both domestically and internationally have developed a range of emulsion breaking technologies, including physical emulsion breaking, chemical emulsion breaking, biological emulsion breaking, as well as other novel emulsion breaking techniques [6,7]. Different demulsification technologies are suitable for different types of crude oil emulsions, and the selection of a suitable demulsification technology needs to be comprehensively considered according to the characteristics of crude oil emulsions, demulsification efficiency, cost and environmental protection requirements. At the same time, during the demulsification of crude oil, it is necessary to monitor and control the demulsification process to ensure the separation efficiency and product quality [8,9]. However, in comparison, the physical method has lower efficiency, the biological method is still immature, and the chemical method, with its low cost and simple equipment, is widely used at present. Although there are many demulsification technologies to choose from, it is still a challenge to achieve the efficient, widely applicable and environmentally friendly demulsification of crude oil emulsion due to the complexity of crude oil chemical composition and the difficulty of deriving a demulsifier suitable for all types of emulsions and the improvement of environmental protection requirements. Therefore, the research and development of more efficient, widely applicable and environmentally friendly crude oil lotion demulsification technology is still the research direction in the field of oil development and application. In this work, we will discuss the formation of crude oil emulsion; in terms of properties, we will analyze in detail its physicochemical properties, such as stability, interfacial tension, and so on; in terms of hazards, we will focus on the negative impacts on petroleum extraction, transportation, processing and the environment. As for the development and application of emulsion breaking technology, it will cover the evolution of traditional emulsion breaking technology and the innovation of new emulsion breaking technology, and analyze the advantages and shortcomings of various technologies. Through in-depth analyses of the mechanism of emulsification, the key factors and mechanisms in the process of emulsification will be revealed, so as to lay the foundation for the development of more efficient and environmentally friendly crude oil emulsification technology.

1.1. Formation, Types, and Hazards of Crude Oil Emulsions

The production of crude oil emulsions is mainly achieved in two ways. On the one hand, during the process of crude oil extraction, a large amount of formation water will be mixed in, and under the enormous pressure of pipelines and valves, the crude oil and formation water will mix, resulting in the production of stable emulsions of crude oil. On the other hand, it is caused by the complex nature of crude oil itself. Crude oil contains not only natural interfacial active substances such as asphaltenes, resins, naphthenic acids, and waxes, but also amphiphilic fine solid particles that are both hydrophilic and lipophilic [10]. These active substances possess the characteristics of surfactants [11]. As a result, crude oil emulsions are prone to form during the extraction and production process of crude oil.

The types of crude oil emulsions primarily include water-in-oil (W/O), oil-in-water (O/W), water-in-oil-in-water (W/O/W), oil-in-water-in-oil (O/W/O), and various other types (Figure 1). Among them, the most common are the first two types of emulsions, namely, emulsions with water dispersed in oil and emulsions with oil dispersed in water. In the latter two types of composite emulsions, the dispersed phase of the W/O/W type is the

W/O emulsion, where uniformly dispersed oil droplets exist within the water phase, and within these oil droplets, uniformly dispersed water droplets are also present. The O/W/O type, on the other hand, refers to a system where uniformly dispersed water droplets exist within the oil phase, and within these water droplets, there are further uniformly dispersed oil droplets.

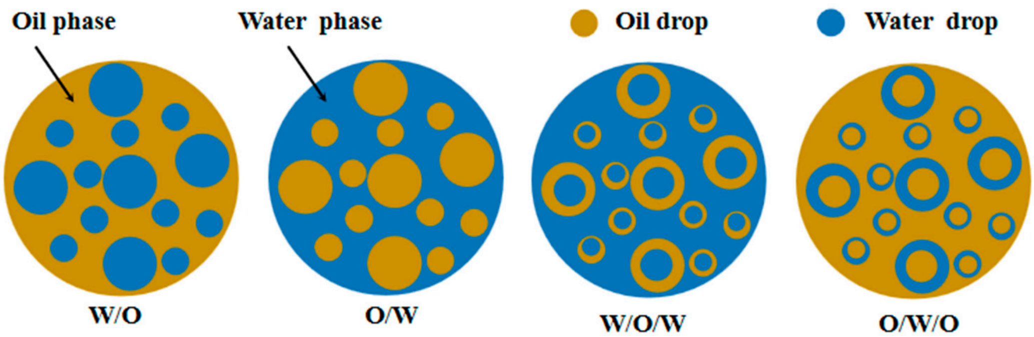

Figure 1. Types of the crude emulsion.

The presence of crude oil emulsions can have various hazardous impacts on subsequent processes, such as reducing production efficiency [12]. It can increase the viscosity of fluids in pipelines, pumps, and other equipment, leading to increased operating resistance and consequently requiring more energy for transportation and processing [13]. This, in turn, increases energy consumption and production costs, thereby reducing production efficiency [14]. Furthermore, the water and impurities present in the crude oil emulsion will further contaminate the crude oil, causing quality issues in subsequent processes and impacting the overall quality of the final products. In addition, it can make water turbid, adversely affecting the survival and reproduction of aquatic organisms, and ultimately leading to the imbalance of aquatic ecosystems. Particularly in marine environments, it poses a significant threat of serious pollution and damage to marine ecosystems [15].

1.2. Stability of Crude Oil Emulsion

The stability of crude oil emulsion refers to the ability of crude oil emulsion to maintain its dispersed state and resist demulsification or stratification. It is influenced by many factors, including oil–water interfacial tension (refers to the force on the interface between oil and water, which is caused by the different interaction forces between liquid molecules) [16], interfacial facial mask [17], interfacial charge (refers to the charge on the surface of oil droplets and water droplets) [18], crude oil viscosity [19], dispersity [20] and natural surfactant [21]. These factors interact with each other and affect the stability of emulsions. Therefore, in the development and application of demulsification technology, it is necessary to comprehensively consider these factors so as to achieve efficient and sustainable crude oil demulsification. Crude oil emulsions have certain phase interfaces and interfacial energies, which are the driving forces for emulsion polymerization [22]. When droplets coalesce, the interfacial area of the emulsion decreases, resulting in a reduction in the system's energy and causing the liquid to tend towards a thermodynamically stable state. This is because the formation of polymerization droplets makes the originally dispersed droplets larger, thereby reducing the interfacial area and surface free energy, making the entire system energy more stable. Therefore, in practical applications, even if it is stored for a relatively long time, the stability of crude oil emulsions remains excellent, and there will be no separation of oil and water. Research has indicated that by increasing the oil–water interfacial energy and altering the oil–water interfacial tension, the stability of emulsions can be effectively reduced [23]. This is because the increase in oil–water interfacial energy and the change in tension raise the energy of the interface, making droplet coalescence more likely to occur, which in turn reduces the stability of the emulsions. When emulsifiers are present in emulsions, they not only reduce the interfacial tension between oil and water, but also strongly adsorb at the oil–water interface, forming a viscoelastic oil–water interface film that hinders the coalescence of dispersed phase droplets and thereby enhancing the stability of the emulsion [24]. The tighter the arrangement of emulsifier molecules is, the greater the strength of the interface film will be. This makes it more difficult for emulsion droplets to coalesce, and thus the oil–water emulsion tends to be more stable. In crude oil emulsions, the presence of negatively charged natural surface-active substances, polymers, or solid particles at the oil–water interface leads to their aggregation at this interface. This aggregation causes the oil droplets of the water-in-oil emulsion to acquire a negative charge and form a double layer around each oil droplet [25]. When oil droplets are close, the electrostatic repulsion arising from the overlapping of the double layers makes it difficult for the droplets to coalesce, thereby enhancing the stability of the emulsion.

In addition to the oil–water interfacial energy and interfacial tension, the viscosity, dispersion, and natural surfactants contained in crude oil are also important factors affecting the stability of crude oil emulsions. As the viscosity of crude oil increases, the movement resistance of droplets will increase, leading to a decrease in their movement rate. This will reduce the stratification, flocculation and polymerization rate of the emulsion and affect the stability of the emulsion. The greater the dispersion of the crude oil, the lower the settling rate of the particles, thus enhancing the stability of the emulsion. In addition, interfacial active substances such as asphaltenes, colloids, and solid particles also affect the stability of oil–water emulsions [26]. These interfacial active substances adsorb onto the interface to form an interfacial film, which significantly impacts the interactions between droplets in the continuous fluid phase, interface properties, and the performance of the emulsion.

2. Demulsification Technology and Application of Crude Oil Emulsion

The blending of groundwater with the implementation of various oil displacement techniques, including water injection and polymer injection, can result in the creation of crude oil emulsions during the oil recovery process, ultimately impacting crude oil production. Therefore, relevant technologies need to be used to demulsify crude oil emulsions to meet the requirements of on-site dehydration. At present, researchers at home and abroad have developed various emulsion breaking technologies, such as physical [27], chemical [28], biological [29], and other new emulsion breaking technologies [30] (Figure 2). Physical demulsification techniques typically include mechanical [31], thermal [32], microwave [33], electrical [34], ultrasonic [35], and membrane demulsification methods [7]. These technologies are based on different principles and mechanisms, and can be used to break the interactions between droplets in emulsions, that is, to eliminate or weaken the mutual attraction or stabilization conditions between oil droplets and water droplets in emulsions through specific methods or means, so that these droplets can be more easily separated, thereby achieving emulsion breaking. Chemical demulsification technology primarily encompasses the use of surfactants, electrolytes, ionic liquids, nanoparticles, and so forth, depending on the diverse chemical demulsifiers that are added to crude oil emulsions [2,36,37]. Biological demulsification technology is a method of breaking down emulsions by utilizing biological surfactants produced by the growth and metabolism of microorganisms in crude oil emulsions, achieved by disrupting the interactions between droplets. This method usually requires adding microorganisms to the emulsion. Droplets in the emulsion are broken through the metabolic action of microorganisms and the biological surfactants produced by fermentation to achieve the purpose of demulsification. In addition, with the development of science and technology, researchers have also developed new demulsification techniques such as high-frequency radiation demulsification and CO_2 demulsification in recent years. These techniques are described in detail below.

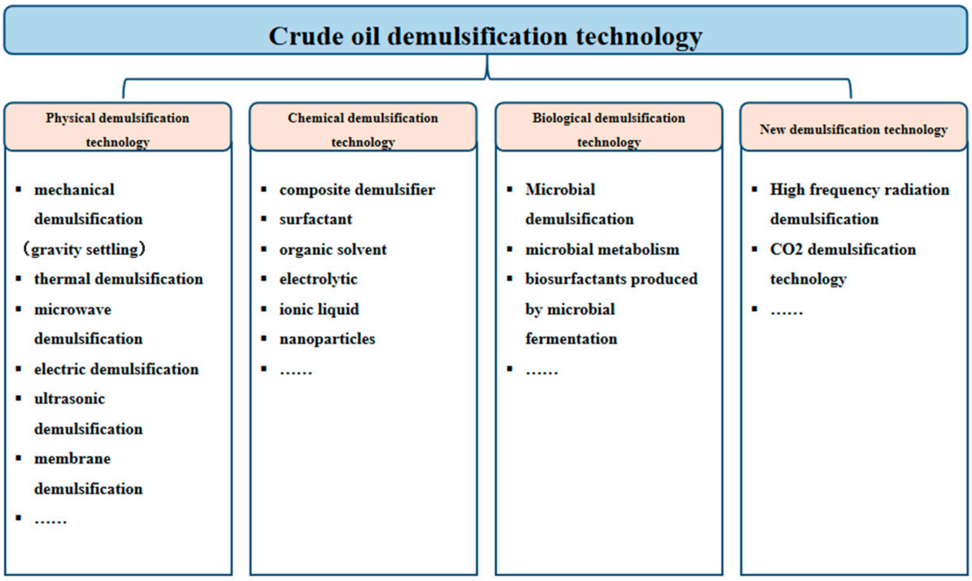

Figure 2. Demulsification techniques for crude emulsion.

2.1. Physical Demulsification Technology

Physical demulsification technologies employ many methods. This paper will introduce mechanical demulsification, microwave demulsification, electric demulsification, ultrasonic demulsification and membrane demulsification (Figure 3). Among these, mechanical demulsification methods mainly refer to centrifugal separation [38] and gravity sedimentation [39]. Although these methods have different principles and have their own advantages and disadvantages, their appearance has promoted the development of the demulsification of crude oil emulsions.

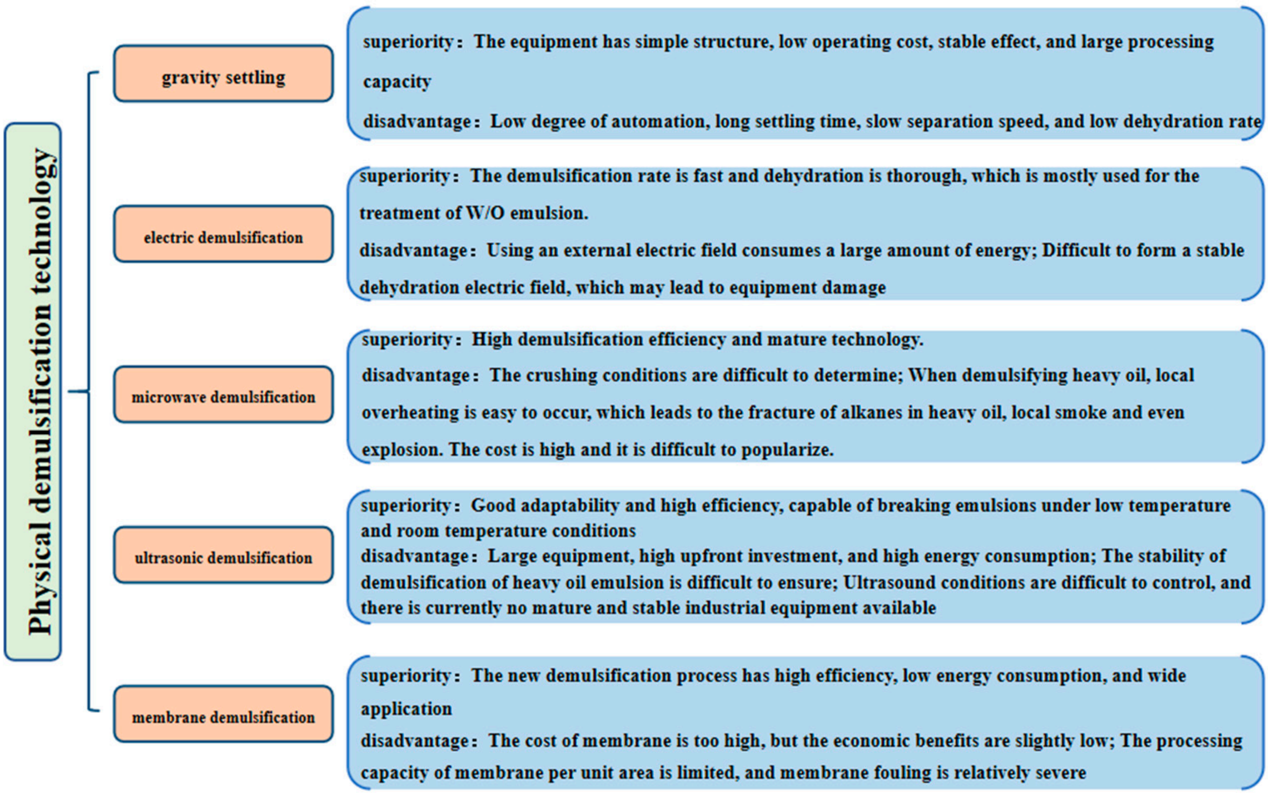

Figure 3. Comparison of physical demulsification methods for crude oil emulsions.

2.1.1. Mechanical Demulsification

The gravity settling method is the most commonly used method of mechanical emulsion breaking; the principle is that in the emulsified state, water molecules are dispersed in the crude oil in the form of tiny water droplets. As the settling time passes, gravity will prompt these droplets to aggregate with each other, so that the emulsion droplet particle size increases, which leads to sinking. The method boasts the advantages of a simple equipment structure, stable effects, and a large processing capacity. For example, Li Jun's research group at Sichuan University employed the gravity sedimentation method to demulsify emulsions, and investigated the influence of sedimentation time on both the demulsification rate and the droplet size of the emulsions. They pointed out that increasing the droplet size would accelerate droplet sedimentation and intensify collisions during sedimentation, thereby reducing the difficulty of emulsion phase separation [40]. Through unremitting efforts, they effectively combined gravity settling with agitation shear demulsification methods, accelerating the demulsification process of emulsions. However, compared to other demulsification techniques, gravity settling demulsification technology currently suffers from a lower degree of automation, longer settling times, slower separation speeds, and lower dehydration rates. Centrifugal separation for demulsification is also one of the important methods of mechanical demulsification. The centrifugal force generated by rotation simulates and enhances the effect of gravity. Centrifugal force effectively accelerates the settling of particles (e.g., water droplets) in liquids in a much shorter period of time than the effect of gravity [41]. However, the centrifugal separation method requires special centrifugal equipment, and the operation is relatively complicated, requiring professional technicians to operate and maintain, and the cost is high. The gravity settling method only needs a simple settling tank or container, which is simple to operate, easy to master and low in cost. To sum up, when choosing between the gravity sedimentation method and centrifugal separation method, it is necessary to comprehensively consider demulsification requirements, cost factors, emulsion characteristics, operation and maintenance, and make appropriate choices according to specific conditions.

2.1.2. Electrical Demulsification Method

Electric demulsification is a method that utilizes high-voltage direct current [42] (DC) and alternating current [43] (AC) electric fields to achieve emulsion demulsification. Under the influence of the electric field, the opposite ends of the liquid droplets become charged with opposite charges, leading to electrostatic attraction. This electrostatic attraction causes the charged liquid droplets to approach, touch, and coalesce with each other, ultimately resulting in demulsification. This method boasts high demulsification efficiency, thorough dehydration, and mature technology, making it more suitable for demulsifying heavy oil. However, it also has drawbacks, such as the requirement for an external electric field that consumes significant amounts of electrical energy. Additionally, it can lead to conductive currents between electrodes, potentially causing short circuits that are detrimental to the formation of a stable dehydration electric field, and may result in equipment damage. Ren et al. [44] used a simple and novel Bidirectional Pulsed Electric Field (BPEF) method to emulsify oil–water emulsions. The results indicate that BPEF can promote the formation of specific rotational flow patterns in oil–water emulsions, which causes the movement and aggregation of oil droplets. Specifically, BPEF can induce the formation of chain-like structures among liquid droplets, which subsequently coalesce into larger oil droplets. To explain the mutual attraction and coalescence phenomenon of oil droplets under BPEF, they proposed the hypothesis of surface charge redistribution of oil droplets within BPEF, and established a charge redistribution model based on the adsorption phenomenon exhibited by oil droplets. The behavior of oil droplets in BPEF can be successfully explained through the use of assumptions and models. Yang et al. [45] investigated the demulsification performance of oil–water emulsions under different electric fields and demonstrated that the oil droplets were polarized by the electric field, aligning themselves parallel to the direction of the electric field. Furthermore, an increase in electric field intensity was found to accelerate the aggregation of oil droplets, which is advantageous for demulsification.

2.1.3. Microwave Demulsification

Microwave demulsification is a method that involves heating crude oil emulsions using microwave radiation at high temperatures [46]. The Zeta potential at the oil–water interface is disrupted by changes in the surface charge of the droplets under the influence of the microwave electric field, thereby facilitating collision and aggregation between droplets [47]. Specifically, microwave electric fields can cause polar molecules or charged droplets on the surface of droplets to shift or rapidly rotate, resulting in changes in the potential between droplets and a decrease in resistance, thereby promoting collisions and aggregation between droplets. Due to the differing microwave absorption properties between water and oil, the higher the heating rate and volume of water exposed to microwave radiation, the greater the pressure exerted on the interfacial film. The thinner the interfacial film becomes, the more conducive it is to droplet aggregation, thereby facilitating oil–water separation. In other words, microwaves can reach a high temperature in a short time, heat the emulsion, reduce its external viscosity, accelerate the coagulation and aggregation of emulsion, shorten the separation time of oil–water lotion, and promote the separation of oil–water emulsion. Chan et al. [48] systematically studied the impact of emulsification conditions and microwave operation parameters on the demulsification rate and separation efficiency of W/O emulsions. Their findings reveal that both the demulsification rate and separation efficiency increased with the enlargement of droplet size, as well as with the increase in carrier and acid concentrations. However, as the concentration of the surfactant (Span 80) and the volume ratio of oil phase to water phase (O/W) increased, the demulsification rate and separation efficiency exhibited a downward trend. In addition, there is a special extreme phenomenon in the influence of electrolyte concentration. Under the condition of an electrolyte concentration of 0.5 mol, microwave demulsification achieves the highest demulsification rate and separation efficiency. In addition, the optimal microwave radiation power is 420 W, and the optimal microwave irradiation time is 12 s. This indicates that, under these optimal conditions, microwave demulsification technology can optimize the demulsification effect and separation efficiency, while simultaneously minimizing energy consumption and costs. Heriberto Díaz Velázquez et al. [49] summarized the research progress made on microwave-assisted fragmentation of oil/oil emulsions and oil/water emulsions in oilfield applications, and compared the combined use of demulsifiers for demulsification. This method exhibits high demulsification efficiency and a mature technology. This method also has its limitations, such as the difficulty in determining the optimal crushing conditions. During the demulsification of heavy oil, local overheating is prone to occur, leading to the fracture of alkanes in the heavy oil, which may result in localized smoking and, in severe cases, even explosions. Additionally, the high cost of this method makes it difficult to promote widely.

2.1.4. Ultrasonic Demulsification

Ultrasonic demulsification is a method that is influenced by many factors. Among them, the multi-factor comprehensive action refers to the mechanical oscillation, cavitation and thermal action of ultrasound [50]. Mechanical oscillation can not only accelerate the vibration speed of small water droplets dispersed in the oil phase and promote their collision, but also disperse the interfacial emulsified active ingredients, reduce the strength of the interfacial film and cause the coalescence of the dispersed phase [51]. Cavitation refers to the positive and negative pressure generated by the propagation of ultrasonic waves in liquid media. Under the action of negative pressure, molecules in the liquid will be stretched and pulled, forming voids or bubbles. These bubbles rapidly expand and rupture under the action of ultrasound. At the same time, more bubbles are generated, forming a cavitation nucleus (this refers to the tiny gas nuclei, impurity particles or tiny gas–liquid interface regions in the liquid, etc., which can become the starting point of cavitation phenomena under the specific conditions of ultrasound). This cavitation phenomenon can cause bubbles to form in liquids. The generation and rupture of foam will not only lead to local high temperature and high pressure, but also form strong shock waves and micro-jets. These phenomena will quickly destroy the interfacial film of the emulsion and accelerate the separation of oil and water. Thermal action refers to the continuous transformation of vibration energy into heat energy through the medium during the transmission of ultrasonic waves. This leads to an increase in emulsion temperature, a weakening of the emulsion phase interface strength, a promotion of the Brownian movement of liquid droplets, a reduction in fluid viscosity, an acceleration of precipitation, and a promotion of demulsification. Xu et al. [52] reported a study on the ultrasound-assisted demulsification and dehydration of crude oil. The results show that the demulsification and dehydration process of crude oil emulsion tends to be stable after 300 min under different ultrasonic irradiation times, which shows that ultrasonic irradiation has a significant effect on the demulsification of crude oil emulsion and can reduce demulsification temperature. With the increase in ultrasonic irradiation time, the demulsification effect is different but not significant, and the final dehydration rate is about 79%. Under different ultrasonic irradiation times, the demulsification and dehydration process of crude oil emulsion tends to be stable after 200 min, and the demulsification effect of ultrasonic irradiation on crude oil emulsion decreases with the increase in temperature, that is, the advantages of ultrasonic application can only be fully exerted at low temperature, and the final dehydration rate can reach 96%. There is a critical value for ultrasound power. When the power falls below this critical level, ultrasound acts as an effective demulsifier. As the power increases, the dehydration rate of crude oil emulsion accelerates significantly. However, once the power exceeds the critical value, the separated oil–water mixture can be re-emulsified. At 75 °C, the final dehydration rate of crude oil emulsion with ultrasonic radiation for 10 min and a demulsifier dosage of 50 mg/L was the highest, and the demulsifier dosages of 25, 100 and 150 mg/L decreased in turn. This shows that ultrasonic demulsification can shorten the settling time and reduce the amount of emulsifier. Under ultrasonic radiation, small water droplets collide and merge into larger water droplets, and then collide and adhere to each other to form larger water droplets, which settle under the action of gravity, and it takes time for these to separate from oil. There are a lot of water droplets in high water-cut crude oil emulsion, and the water droplets more easily coalesce and separate from low water-cut crude oil emulsion, so ultrasound is suitable for the demulsification and dehydration of high water-cut crude oil emulsion. Consequently, there are numerous influencing factors that affect the efficiency of the ultrasonic demulsification method. These include, but are not limited to, the intensity and frequency of the ultrasonic waves, the radiation temperature and duration, the viscosity of the crude oil, and the settling time. This method has the advantages of good adaptability (can be broken at low temperature, room temperature conditions) and high efficiency, but also, ultrasonic conditions are difficult to control, and the large equipment, large upfront investment, energy consumption and other shortcomings mean it cannot be applied in a set of stable industrialized equipment.

2.1.5. Membrane Demulsification Method

Membrane demulsification is a method of breaking crude oil emulsions by placing them in a microporous membrane, allowing oil and water molecules to flow under the action of the membrane, resulting in the aggregation of dispersed droplets and ultimately achieving demulsification. This method harnesses the selective permeation properties of microporous membranes for different substances, enabling the separation of components like oil and water, thus achieving the demulsification effect. For example, Kocherginsky et al. [53] realized the demulsification of surfactant-stabilized water-in-oil emulsion by using a hydrophilic polymer membrane (Figure 4), and pointed out that the success of demulsification depends on the type of emulsion and membrane. The pore size and transmembrane pressure of the membrane have a certain impact on the demulsification efficiency, while other factors such as membrane thickness and initial water content have little or no effect on the demulsification efficiency. Due to the difference in membrane pore size, the separation process is not based on a sieving effect, but is determined by the interaction between droplets and the membrane surface. The membrane demulsification method has high efficiency and low energy consumption, and can be widely used. However, due to the high cost of membranes and the limited treatment capacity of lotion per unit area, this method is feasible for use in practical application, but its economic benefit is low. In addition, serious membrane pollution is inevitable.

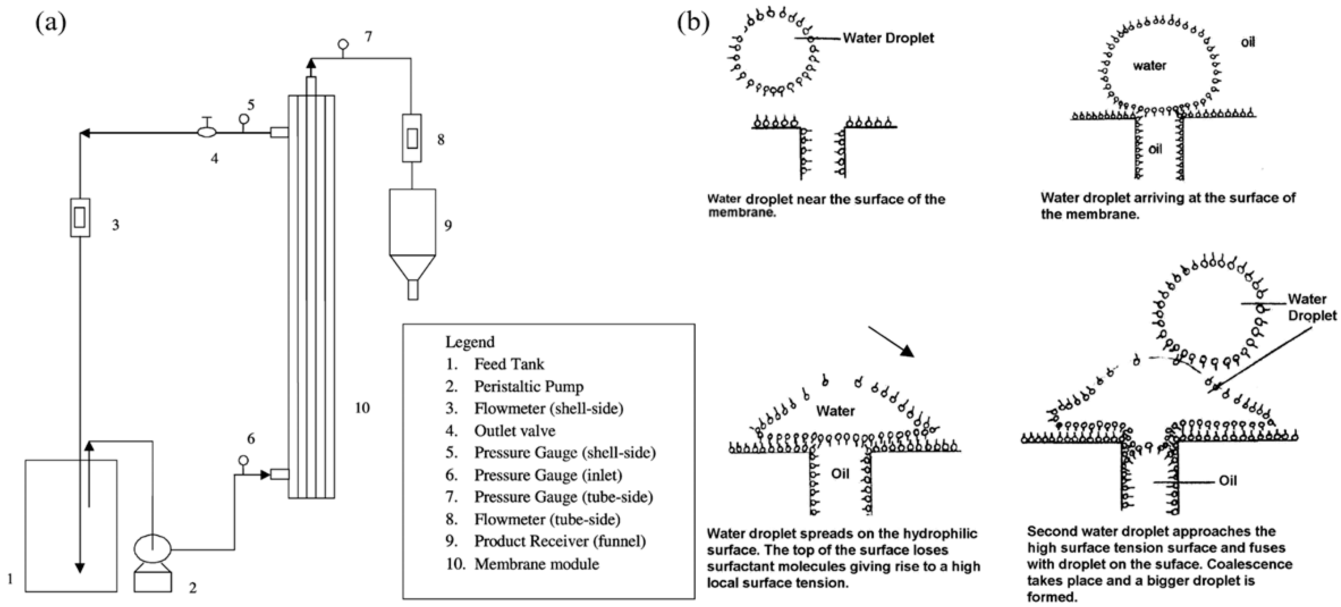

Figure 4. (**a**) Schematic diagram of experimental apparatus for hollow fiber membrane demulsification. (**b**) Schematic diagram of demulsification by hydrophilic nitrocellulose membrane [53].

2.2. Chemical Demulsification Technology

Chemical demulsification technology involves reducing the oil–water interfacial tension by introducing chemical demulsifiers (such as surfactants, electrolytes, ionic liquids, nanoparticles, among others) into the crude oil emulsion. This process enables the demulsifier molecules, which possess high surface activity, to replace the emulsifier particles at the oil–water interface, resulting in the disruption of the interfacial film, thereby achieving demulsification.

2.2.1. Types of Chemical Demulsifiers

There are various types of chemical demulsifiers, and their demulsification effects on different crude oil emulsions also vary. According to the specific properties of emulsifiers, they can be classified into different categories (as shown in Figure 5). Among them, based on their solubility properties, demulsifiers can be classified into water-soluble demulsifiers and oil-soluble demulsifiers. According to their ionic properties, emulsifiers can be divided into anionic, cationic, nonionic, and zwitterionic emulsifiers. According to their relative molecular weight, emulsifiers can be divided into low-molecular-weight emulsifiers (<1000), high-molecular-weight emulsifiers (1000–10,000), and ultra-high-molecular-weight emulsifiers (>10,000). According to the number of chimeric segments, emulsifiers can be divided into diblock polymer emulsifiers (a kind of polymer polymerized by two different monomers through chemical reaction, which is mainly used to stabilize and promote the formation of oil–water emulsion) (containing active hydrogen initiators) and triblock polymer emulsifiers (a polymer emulsion composed of three different monomers or units, in which each unit usually has different physical and chemical properties) (which polymerize a segment of epichlorohydrin on top of the diblock polymer) [54]. For demulsification, it is usually necessary to choose a suitable demulsifier, and its HLB value should be determined according to the specific emulsion system. Generally speaking, demulsifiers with low HLB values (3~6) need to be selected for the demulsification of oil-in-water emulsion, because these demulsifiers have strong lipophilicity, which can destroy the oil-in-water interfacial film and demulsify the emulsion. For the demulsification of water-in-oil emulsion, it is necessary to choose a demulsifier with high HLB value (8~18), because of its strong hydrophilicity, which can effectively demulsify water-in-oil emulsion. These classification methods can help people better understand the properties and application scopes of demulsifiers, providing more choices and optimization solutions for demulsification technology in the petroleum industry. This article will focus on introducing demulsifiers with different ionic properties for crude oils.

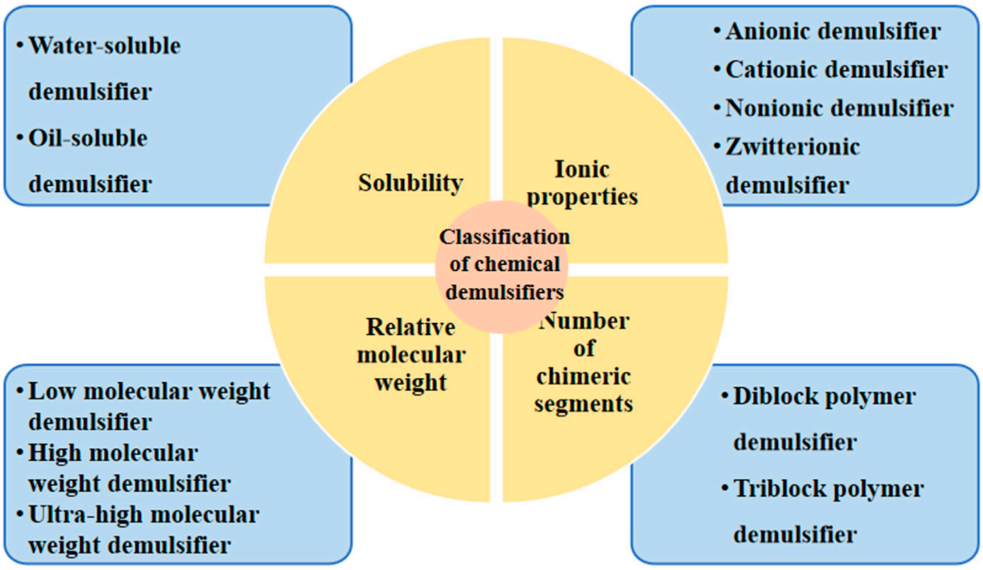

Figure 5. Classification of chemical demulsifiers.

Cationic, anionic, and amphoteric emulsifiers are ionic emulsifiers classified according to the ions of surface-active groups. Among them, cationic demulsifiers can be divided into quaternary ammonium, amine, amide, and polyether types. These demulsifiers can ionize to active cations and adsorb negative charges at the oil–water interface, weakening electrostatic interactions and increasing the probability of oil droplets colliding and condensing with each other, thus achieving demulsification [55]. Compared with other demulsifiers, this type of demulsifier has characteristics such as disinfection, sterilization, and anti-static properties [56]. A new demulsifier was synthesized by the free radical polymerization of acrylate and the cationic monomer. The results show that the copolymer of methyl acrylate (MA) and benzyl dimethyl [2-[(1-oxyallyl) oxy] ammonium chloride (DBC) synthesized in the mixed solvent of dipropylene glycol methyl ether and water had good properties. When the dosage of PMA-co-PDBC is 200 mg/L, the dehydration rate of crude oil emulsion with 50% water content can reach 80% within 4 h at 80 °C. The analysis of structure and interface properties shows that PMA-co-PDBC has a micro-block structure similar to block polyether, which can effectively reduce the strength of the W/O interface film and realize demulsification [57]. Currently, it is widely used in the treatment of oily wastewater and the demulsification of water-in-oil emulsions. However, its application in the demulsification of heavy oil and aged oil is limited. As the first demulsifier to be commercialized, anionic demulsifiers can produce surface-active anions in water, neutralize the positive charge at the oil–water interface, weaken the strength of the interfacial film, and achieve demulsification [58]. This type of demulsifier mainly includes carboxylate salts, phosphate salts, sulfonate salts, and sulfate ester salts. They are commonly used for the demulsification of oil-in-water emulsions. However, in the process of demulsification application, this type of demulsifier is usually used in large quantities, but the effect is not obvious. As a result, it has gradually been marginalized in the market. Two types of ionic emulsifiers [59] (such as betaine and imidazoline) refer to emulsifiers that can exhibit anionic or cationic properties under different medium conditions. This type of demulsifier shows good salt resistance and does not easily react with metal ions, making it suitable for the dehydration and demulsification of emulsions with high salt and mineral contents. Non-ionic demulsifiers are a type of highly stable demulsifier, mainly of the polyether type. They are soluble in water but do not decompose into ions, and always exist in the form of molecules. This type of demulsifier usually has good compatibility and can be mixed with other ionic types. It is currently one of the most widely used demulsifiers, and a hot research topic in the field of demulsifiers.

2.2.2. Mechanism of Chemical Demulsifier

There are many factors that affect the stability of crude oil emulsions. Therefore, the mechanism of action of chemical demulsifiers is also different. So far, mechanisms such as reverse demulsification, solubilization, collision and breaking of the boundary film, folding deformation, and flocculation coalescence are widely considered as the mechanisms by which chemical demulsifiers act on crude oil emulsions [60]. Among them, reverse demulsification refers to the reaction between the demulsifier and the emulsifier present in the initial emulsion, which renders the emulsifier ineffective, thereby achieving oil–water separation. The solubilization mechanism means that the added demulsifier can dissolve the emulsifier, effectively reduce the concentration of the emulsifier at the interfacial film and weaken the strength of the interfacial film to achieve oil–water separation. The mechanism of collision breaking the boundary film involves using external forces such as stirring and heating to promote the collision between droplets and the demulsifier. The demulsifier can not only be adsorbed on the boundary film, but also replace some active substances in the membrane at the same time, thus destroying or reducing the stability of the boundary film to achieve demulsification. Floccultion coalescence demulsification refers to the rapid dispersion of the demulsifier in the emulsion under the action of external force, so that its molecules can be adsorbed on the interface film and weaken the film strength. Due to external forces, the oil droplets in the dispersed phase continuously collide and coalesce into larger particles, ultimately achieving oil–water separation

2.3. Biological Demulsification Technology

Biological demulsification is a method of demulsification performed by adding microorganisms to crude oil emulsions and utilizing their metabolic activity or the production of biosurfactants for demulsification [61]. Biological demulsification technology has the advantages of safe components, wide sources of raw materials and low prices that make the production cost low, and the ability to be compounded with chemical demulsifiers and reduce the environmental impact. The protein biological demulsifier oxalate decarboxylase (*Bacm OxdC*) secreted by *Bacillus Mohavenae XH1* strain can demulsify oil-in-water emulsion [62]. *Bacm OxdC* spontaneously adsorbs at the oil–water interface and rotates its hydrophobic amino acids outward, which increases its hydrophobicity and destroys the emulsion system. In addition, it effectively reduces the oil–water interfacial tension and interfacial film strength, thus reducing the oil–water interfacial energy, and finally realizes demulsification. Salehizadeh et al. [63] isolated a microbial demulsifier strain of *Microbacterium* sp. (Yx/s = 0.663, Yp/s = 0.204, yield = 0.185 g L^{-1} h^{-1}) from oily sludge samples from the southern Iranian island of Siree. Glucose was used as the sole carbon source and yeast extract was added. The optimal temperature for the production of this microbial demulsifier is 25 °C. The optimal inoculation volume is 10^8 CFU mL^{-1}. The optimal pH is 7, and the optimal cultivation time is 24 h. When water-in-oil emulsion is used as emulsion and incubated in a flask at 80 °C for 36 h, the maximum demulsification activity and half-life are 96.4%. When the demulsifier is purified to homogeneity using cold ethanol, 4.33 mg mL^{-1} of partially purified microbial demulsifier has a half-life of 3 h in the W/CO model emulsion.

2.4. New Demulsification Technology

With the development of science and technology, emerging demulsification technologies such as high-frequency radiation demulsification [60] and CO_2 demulsification [59] have gradually emerged. The former utilizes high-frequency radiation to rapidly heat emulsions, causing an increase in intermolecular spacing (average distance between oil molecules and water molecules), a decrease in cohesion (mutual attraction between adjacent parts in the same substance), a reduction in emulsion viscosity, and accelerating oil and water separation. Compared with traditional demulsification techniques, it has higher efficiency. It can quickly heat the water in the emulsion, accelerate the oil–water separation process, shorten the demulsification time and improve production efficiency, and it is suitable for different types of crude oil emulsions. It has wide applicability and can also achieve good results for high-water-content and high-viscosity crude oil emulsions [64]. The latter utilizes CO_2 to disrupt the stability of the W/O heavy oil emulsion film and achieve a demulsification effect. It uses CO_2 gas for treatment, which reduces the use of chemical agents and is beneficial to environmental protection. The presence of acidic substances, such as cycloalkanoic acid, in crude oil can provide favorable conditions for the formation of surfactants [65]. N, N-dimethylcyclohexylamine (DMCHA) can activate the cyclic acids in crude oil to form surfactants through non-covalent bonding. This process has special significance for the pipeline transportation of crude oil, which forms low-viscosity water-in-oil emulsions. At the same time, due to the CO_2-stimulus response characteristics of surfactants, CO_2 can be used as a demulsifier for the separation of crude oil and water at the end of pipeline transportation. Liu et al. [59] found that water-in-oil emulsions can form, and have good stability. CO_2 has a higher demulsification efficiency in emulsions with lower crude oil content. Under high-oil-content conditions, CO_2 cannot achieve complete demulsification. Due to the corrosive nature of liquids such as sulfuric acid and hydrochloric acid, their application as demulsifiers in crude oil pipeline transportation is not advisable. Organic acids have significantly stronger advantages in this regard. Therefore, they selected citric acid, oxalic acid, acetic acid, and lactic acid as demulsifiers, and confirmed that they all have good demulsification effects in high-oil-content emulsions, with citric acid having the best demulsification effect. Meanwhile, DMCHA can be recycled and reused by adding NaOH to the lower aqueous layer after demulsification. Liu [66] reports a fast CO_2 responsive copolymer emulsifier p [AM—SBMA—DEAEMA]. The synthesized macromolecular emulsifier has excellent emulsification stability and fast CO_2-responsiveness after RAFT polymerization, enabling it to control low-molecular-weight and uniform polydispersity. The CO_2-responsive copolymer nitrogen emulsifier can effectively emulsify crude oil and heavy oil to increase its fluidity, and the viscosity reduction rate reaches 98.6% in highly mineralized water, while the demulsification process can be completed by simple CO_2 treatment. To sum up, compared with the previous demulsification technologies, the new demulsification technologies, such as high-frequency radiation demulsification and CO_2 demulsification, have shown remarkable advantages in terms of high efficiency, environmental protection, adaptability, energy saving, improving crude oil quality, technological innovation and application prospects. These advantages mean the new demulsification technology has higher competitiveness and application value in the crude oil exploitation and processing industry.

3. Summary and Prospect

As one of the most important energy sources in the world, crude oil forms complex emulsions due to various factors during the exploitation process, which reduce the output rate, increase costs, consume equipment, and pollute the environment. Therefore, the development and application of crude oil demulsification technology is of great importance. At present, numerous demulsification technologies have been developed, including mechanical, microwave, electrical, ultrasonic, and membrane demulsification. Each of these technologies has its own unique advantages and disadvantages, making them suitable for different types of crude oil emulsions. Chemical demulsification technology primarily achieves demulsification through the addition of demulsifiers. Due to its various types and complex mechanisms, it is currently one of the most widely used demulsification methods. Biological demulsification technology employs microbial metabolism or biosurfactants for demulsification, boasting advantages in environmental protection and sustainability. However, it is currently not yet fully mature. Emerging demulsification technologies, such as high-frequency radiation demulsification and CO_2 demulsification, offer novel ideas and approaches to crude oil demulsification. In the future, the development of crude oil demulsification technology will prioritize high efficiency, environmental protection, and low cost. In-depth research on the stability and demulsification mechanisms of crude oil emulsions will provide theoretical support for the advancement of new technologies. Additionally, improving and optimizing existing technologies will enhance demulsification efficiency and reduce costs. Furthermore, exploring new areas such as nanotechnology, biotechnology, and supercritical fluid technology will impart fresh momentum in the research into crude oil demulsification. Meanwhile, as petroleum resources dwindle and environmental pressures mount, crude oil demulsification technology must emphasize sustainable development, fostering the transition of the petroleum industry towards green production.

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References

1. Zhou, Y.; Yin, D.; Li, Y.; He, J.; Zhang, C. A review of crude oil emulsification and multiphase flows in chemical flooding. *Energy Sci. Eng.* **2023**, *11*, 1484–1500. [CrossRef]
2. Yonguep, E.; Kapiamba, K.F.; Kabamba, K.J.; Chowdhury, M. Formation, stabilization and chemical demulsification of crude oil-in-water emulsions: A review. *Pet. Res.* **2022**, *7*, 459–472. [CrossRef]
3. Saad, M.; Kamil, M.; Abdurahman, N.; Yunus, R.; Awad, O. An overview of Recent Advances in State-of-the-Art Techniques in the Demulsification of Crude Oil Emulsions. *Processes* **2019**, *7*, 470. [CrossRef]
4. Yao, Y.; Sun, D.; Xu, J.-H.; Wang, B.; Peng, G.; Sun, B. Evaluation of enhanced oil recovery methods for mature continental heavy oil fields in China based on geology, technology and sustainability criteria. *Energy* **2023**, *278*, 127962. [CrossRef]
5. Liu, Z.; Li, Y.; Hejazi, S.H.; Wang, X.; Chen, X.; Luan, H.; Hou, Q.; Liu, L. In-situ emulsification in low-tension surfactant/polymer systems: Impacts on enhanced oil recovery. *Fuel* **2024**, *362*, 130861. [CrossRef]
6. Hu, R.; Tang, S.; Mpelwa, M.; Jiang, Z.; Feng, S. Research progress of viscoelastic surfactants for enhanced oil recovery. *Energy Explor. Exploit.* **2021**, *39*, 1324–1348. [CrossRef]
7. Shah Buddin, M.M.H.; Ahmad, A.L.; Abd Khalil, A.T.; Puasa, S.W. A review of demulsification technique and mechanism for emulsion liquid membrane applications. *J. Dispers. Sci. Technol.* **2022**, *43*, 910–927. [CrossRef]
8. Parsia, Y.; Sorooshian, S. Microbial biodiversity of Tang and Pirgal mud volcanoes and evaluation of bio-emulsifier and bio-demulsifier activities of Capnophile bacteria. *Data Brief* **2017**, *15*, 262–271. [CrossRef]
9. Xu, P.; Wang, Z.; Xu, Z.; Hao, J.; Sun, D. Highly effective emulsification/demulsification with a CO_2-switchable superamphiphile. *J. Colloid Interface Sci.* **2016**, *480*, 198–204. [CrossRef]
10. Schacht-Hernández, P.; Miranda-Olvera, A.D.; Jiménez-Cruz, F.; Morelos-Santos, O.; García-Gutiérrez, J.L.; Quintana-Solórzano, R. Processing and Recovery of Heavy Crude Oil Using an HPA-Ni Catalyst and Natural Gas. *ACS Omega* **2024**, *9*, 34089–34097. [CrossRef]

11. Zhu, L.; Tang, Y.; Wang, Y. Constructing surfactant systems with the characteristics of gemini and oligomeric surfactants through noncovalent interaction. *J. Surfactants Deterg.* **2016**, *19*, 237–247. [CrossRef]
12. Alara, O.R.; Abdurahman, N.H.; Tade, M.O.; Ali, H.A.; Alao, K.T. Demulsifier: An important agent in breaking crude oil emulsions. *Chem. Eng. Technol.* **2022**, *45*, 1707–1720. [CrossRef]
13. Lam-Maldonado, M.; Aranda-Jiménez, Y.G.; Arvizu-Sanchez, E.; Melo-Banda, J.A.; Díaz-Zavala, N.P.; Pérez-Sánchez, J.F.; Suarez-Dominguez, E.J. Extra heavy crude oil viscosity and surface tension behavior using a flow enhancer and water at different temperatures conditions. *Heliyon* **2023**, *9*, e12120. [CrossRef] [PubMed]
14. Mironova, M.V.; Ilyin, S.O. Effect of silica and clay minerals on rheology of heavy crude oil emulsions. *Fuel* **2018**, *232*, 290–298. [CrossRef]
15. Gao, Y.; Cai, M.; Shi, K.; Sun, R.; Liu, S.; Li, Q.; Wang, X.; Hua, W.; Qiao, Y.; Xue, J. Bioaugmentation enhance the bioremediation of marine crude oil pollution: Microbial communities and metabolic pathways. *Water Sci. Technol.* **2023**, *87*, 228–238. [CrossRef]
16. Li, Y.; Li, C.; Zhao, Z.; Cai, W.; Xia, X.; Yao, B.; Sun, G.; Yang, F. Effects of asphaltene concentration and test temperature on the stability of water-in-model waxy crude oil emulsions. *ACS Omega* **2022**, *7*, 8023–8035. [CrossRef]
17. Patil, A.; Arnesen, K.; Holte, A.; Farooq, U.; Brunsvik, A.; Størseth, T.; Johansen, S.T. Crude oil characterization with a new dynamic emulsion stability technique. *Fuel* **2021**, *290*, 120070. [CrossRef]
18. Song, F.; Zheng, H.; Li, T.; Fu, X.; Feng, C.; Ma, C.; Jiang, S.; Wang, J.; Huang, Y.; Zhou, F. The influence of asphaltene and resin on the stability of crude oil emulsion and its demulsification mechanism. *J. Mol. Liq.* **2024**, *413*, 125924. [CrossRef]
19. Irfan, M.; Khan, J.A.; Al-Kayiem, H.H.; Waqas, S.; Aleem, W.; Rozali, N.E.M.; Qamar, S.; Ghanim, A.A.J.; Ginter-Kramarczyk, D.; Legutko, S. Characteristics of Malaysian Crude Oils and Measurement of ASP Flooded Water in Oil Emulsion Stability and Viscosity in Primary Separator. *Water* **2023**, *15*, 1290. [CrossRef]
20. Cisneros-Dévora, R.; Cerón-Camacho, R.; Soto-Castruita, E.; Pérez-Alvarez, M.; Ramírez-Pérez, J.; Oviedo-Roa, R.; Servín-Nájera, A.; Buenrostro-Gonzalez, E.; Martínez-Magadán, J.; Zamudio-Rivera, L. A theoretical study of crude oil emulsions stability due to supramolecular assemblies. *Colloids Surf. A Physicochem. Eng. Asp.* **2019**, *567*, 121–127. [CrossRef]
21. Delgado-Linares, J.G.; Pickarts, M.A.; Zerpa, L.E.; Koh, C.A. Outlook on the role of natural surfactants on emulsion stability and gas hydrate antiagglomeration in crude oil systems. *Energy Fuels* **2022**, *36*, 10732–10750. [CrossRef]
22. Santos, L.M.; Dariva, C.; Masso, C.M.; Fortuny, M.; Santos, A.F. Monitoring of Emulsion Polymerization in the Presence of Ionic Liquids Using NIR Spectroscopy. *Macromol. React. Eng.* **2023**, *17*, 2300009. [CrossRef]
23. Shao, P.; Feng, J.; Sun, P.; Ritzoulis, C. Improved emulsion stability and resveratrol encapsulation by whey protein/gum arabic interaction at oil-water interface. *Int. J. Biol. Macromol.* **2019**, *133*, 466–472. [CrossRef] [PubMed]
24. Gao, J.; Xu, X.; Li, T.; Zhang, H.; Xu, J.; Cao, F. Breakup characteristics of water-in-oil emulsion droplets influenced by a rigid interfacial film in the presence of a polymer surfactant. *Energy Fuels* **2022**, *36*, 4339–4347. [CrossRef]
25. Qin, H.; Xu, L.; Lin, S.; Zhan, F.; Dong, K.; Han, K.; Wang, H.; Feng, Y.; Wang, Z.L. Underwater energy harvesting and sensing by sweeping out the charges in an electric double layer using an oil droplet. *Adv. Funct. Mater.* **2022**, *32*, 2111662. [CrossRef]
26. Gorbacheva, S.N.; Ilyin, S.O. Morphology and rheology of heavy crude oil/water emulsions stabilized by microfibrillated cellulose. *Energy Fuels* **2021**, *35*, 6527–6540. [CrossRef]
27. Fajun, Z.; Zhexi, T.; Zhongqi, Y.; Hongzhi, S.; Yanping, W.; Yufei, Z. Research status and analysis of stabilization mechanisms and demulsification methods of heavy oil emulsions. *Energy Sci. Eng.* **2020**, *8*, 4158–4177. [CrossRef]
28. Hippmann, S.; Ahmed, S.S.; Fröhlich, P.; Bertau, M. Demulsification of water/crude oil emulsion using natural rock Alginite. *Colloids Surf. A Physicochem. Eng. Asp.* **2018**, *553*, 71–79. [CrossRef]
29. Deng, Y.; Dai, M.; Wu, Y.; Peng, C. Emulsion system, demulsification and membrane technology in oil–water emulsion separation: A comprehensive review. *Crit. Rev. Environ. Sci. Technol.* **2023**, *53*, 1254–1278. [CrossRef]
30. Zhang, M.; Nan, Y.; Lu, Y.; You, Q.; Jin, Z. CO_2-responsive surfactant for oil-in-water emulsification and demulsification from molecular perspectives. *Fuel* **2023**, *331*, 125773. [CrossRef]
31. Jia, X.; Wang, J. Preparation and characterization of spherical submicron ε-CL-20 via green mechanical demulsification. *J. Energetic Mater.* **2019**, *37*, 475–483. [CrossRef]
32. Nie, C.; Zhang, Y.; Du, H.; Han, G.; Yang, J.; Li, L.; Wang, B.; Wang, X. A molecular modeling and experimental study of solar thermal role on interfacial film of emulsions for elucidating and executing efficient solar demulsification. *J. Mol. Liq.* **2023**, *377*, 121578. [CrossRef]
33. Song, Z.; Pan, W.; Wang, S.; Lv, X.; Zhao, X.; Sun, J.; Mao, Y.; Wang, X.; Wang, W. Microwave demulsification characteristics and product analysis of oily sludge. *Energy Sources Part A Recovery Util. Environ. Eff.* **2021**, 1–20. [CrossRef]
34. Zhang, H.; Bukosky, S.C.; Ristenpart, W.D. Low-voltage electrical demulsification of oily wastewater. *Ind. Eng. Chem. Res.* **2018**, *57*, 8341–8347. [CrossRef]
35. Romanova, Y.N.; Maryutina, T.A.; Musina, N.S.; Spivakov, B.Y. Application of ultrasonic treatment for demulsification of stable water-in-oil emulsions. *J. Pet. Sci. Eng.* **2022**, *209*, 109977. [CrossRef]
36. Hassanshahi, N.; Hu, G.; Li, J. Application of ionic liquids for chemical demulsification: A review. *Molecules* **2020**, *25*, 4915. [CrossRef]

37. Wang, D.; Yang, D.; Huang, C.; Huang, Y.; Yang, D.; Zhang, H.; Liu, Q.; Tang, T.; El-Din, M.G.; Kemppi, T. Stabilization mechanism and chemical demulsification of water-in-oil and oil-in-water emulsions in petroleum industry: A review. *Fuel* **2021**, *286*, 119390. [CrossRef]
38. Gong, H.; Yang, Y.; Yu, B.; Luo, X.; Peng, Y.; Jiang, Y. Coalescence characteristics of droplets dispersed in oil subjected to electric and centrifugal fields. *Colloids Surf. A Physicochem. Eng. Asp.* **2022**, *648*, 129398. [CrossRef]
39. Li, C.; Li, J.; Wang, N.; Zhao, Q.; Wang, P. Status of the treatment of produced water containing polymer in oilfields: A review. *J. Environ. Chem. Eng.* **2021**, *9*, 105303. [CrossRef]
40. Chen, J.; Sun, M.; Ni, Y.; Zhu, T.; Huang, J.; Li, X.; Lai, Y. Superhydrophobic polyurethane sponge for efficient water-oil emulsion separation and rapid solar-assisted highly viscous crude oil adsorption and recovery. *J. Hazard. Mater.* **2023**, *445*, 130541. [CrossRef]
41. Cassella, R.J.; Brum, D.M.; Robaina, N.F.; Lima, C.F. Extraction induced by emulsion breaking: A model study on metal extraction from mineral oil. *Fuel* **2018**, *215*, 592–600. [CrossRef]
42. Zhang, J.; Kang, Y. Demulsification of dilute O/W emulsion by DC electric field. *Pet. Sci. Technol.* **2018**, *36*, 1058–1064. [CrossRef]
43. Fang, W.; Tao, Z.; Li, H.; Ma, Y.; Yin, S.; Xu, T.; Wong, T.; Huang, Y. Characteristics of Oil-in-Oil Emulsions under AC Electric Fields. *Langmuir* **2024**, *40*, 2268–2277. [CrossRef] [PubMed]
44. Ren, B.; Kang, Y. Demulsification of oil-in-water (O/W) emulsion in bidirectional pulsed electric field. *Langmuir* **2018**, *34*, 8923–8931. [CrossRef]
45. Yang, S.; Sun, J.; Wu, K.; Hu, C. Enhanced oil droplet aggregation and demulsification by increasing electric field in electrocoagulation. *Chemosphere* **2021**, *283*, 131123. [CrossRef]
46. Li, M.; Li, D. Redistribution of mobile surface charges of an oil droplet in water in applied electric field. *Adv. Colloid Interface Sci.* **2016**, *236*, 142–151. [CrossRef]
47. Lv, X.; Song, Z.; Yu, J.; Su, Y.; Zhao, X.; Sun, J.; Mao, Y.; Wang, W. Study on the demulsification of refinery oily sludge enhanced by microwave irradiation. *Fuel* **2020**, *279*, 118417. [CrossRef]
48. Chan, C.-C.; Chen, Y.-C. Demulsification of W/O emulsions by microwave radiation. *Sep. Sci. Technol.* **2002**, *37*, 3407–3420. [CrossRef]
49. Diaz Velazquez, H.; Guzmán-Lucero, D.; Martínez-Palou, R. Microwave-assisted demulsification for oilfield applications: A critical review. *J. Dispers. Sci. Technol.* **2022**, *44*, 1884–1899. [CrossRef]
50. Ding, L.; Zhao, S.; Liu, L.; Wang, W.; Yao, C.; Chen, G. Characteristics of emulsion preparation in an ultrasonic microreactor: Cavitation, droplet size and energy efficiency. *Chem. Eng. J.* **2024**, *484*, 149462. [CrossRef]
51. Song, Z.; Ren, F.; Wang, S.; Pang, Y.; Zhao, X.; Sun, J.; Mao, Y.; Wang, W.; Yu, J.; Su, Y. Factors influencing demulsification of refinery oily sludge via ultrasonic treatment. *Chem. Eng. Process. Process Intensif.* **2024**, *204*, 109936. [CrossRef]
52. Xu, X.; Cao, D.; Liu, J.; Gao, J.; Wang, X. Research on ultrasound-assisted demulsification/dehydration for crude oil. *Ultrason. Sonochem.* **2019**, *57*, 185–192. [CrossRef] [PubMed]
53. Kocherginsky, N.; Tan, C.L.; Lu, W.F. Demulsification of water-in-oil emulsions via filtration through a hydrophilic polymer membrane. *J. Membr. Sci.* **2003**, *220*, 117–128. [CrossRef]
54. Abdulredha, M.M.; Hussain, S.A.; Abdullah, L.C.; Hong, T.L. Water-in-oil emulsion stability and demulsification via surface-active compounds: A review. *J. Pet. Sci. Eng.* **2022**, *209*, 109848. [CrossRef]
55. Shu, G.; Bu, K.; Zhao, B.; Zheng, S. Evaluation of newly developed reverse demulsifiers and cationic polyacrylamide flocculants for efficient treatment of oily produced water. *Colloids Surf. A Physicochem. Eng. Asp.* **2021**, *610*, 125646. [CrossRef]
56. Zhang, Z.; Wang, Z.; Zhang, H.; Wang, Q.; Tang, Y.; Qu, Q.; Shen, L.; Mi, Y.; Yan, X. An ionic liquid demulsifier with double cationic centers and multiple hydrophobic chains. *J. Mol. Liq.* **2023**, *374*, 121265. [CrossRef]
57. Yuan, S.; Wang, Y.; Wang, X.; Liao, D.; Duan, M.; Fang, S. Preparation of cationic polyacrylate W/O crude oil emulsion demulsifier by free-radical solution polymerization. *J. Appl. Polym. Sci.* **2023**, *140*, e53590. [CrossRef]
58. Yau, Y.-h.; Rudolph, V.; Ho, K.-c.; Lo, C.C.-m.; Wu, K.-c. Evaluation of different demulsifiers for Marpol oil waste recovery. *J. Water Process Eng.* **2017**, *17*, 40–49. [CrossRef]
59. Liu, D.; Suo, Y.; Zhao, J.; Zhu, P.; Tan, J.; Wang, B.; Lu, H. Effect of demulsification for crude oil-in-water emulsion: Comparing CO_2 and organic acids. *Energy Fuels* **2018**, *32*, 757–764. [CrossRef]
60. Yi, M.; Huang, J.; Wang, L. Research on crude oil demulsification using the combined method of ultrasound and chemical demulsifier. *J. Chem.* **2017**, *2017*, 9147926. [CrossRef]
61. El-Sharaky, E.S.A.; El-Tabey, A.E.; Mishrif, M.R. Novel star polymeric nonionic surfactants as crude oil emulsion breakers. *J. Surfactants Deterg.* **2019**, *22*, 779–793. [CrossRef]
62. Hou, N.; Zhao, X.; Han, Z.; Jiang, X.; Fang, Y.; Chen, Y.; Li, D. Dodecenylsuccinic anhydride-modified oxalate decarboxylase loaded with magnetic nano-Fe_3O_4@ SiO_2 for demulsification of oil-in-water emulsions. *Chemosphere* **2022**, *308*, 136595. [CrossRef] [PubMed]
63. Salehizadeh, H.; Ranjbar, A.; Kennedy, K. Demulsification capabilities of a Microbacterium species for breaking water-in-crude oil emulsions. *Afr. J. Biotechnol.* **2013**, *12*, 2019–2026.
64. Sun, N.; Sun, H.; Hu, J.; Xu, S.; Shen, L.; Ma, Y. Using a New Fe_3O_4@ CPAM Magnetic Flocculant and Microwave to Demulsify Heavy Oil-in-Water Emulsions. *ACS Omega* **2024**, *9*, 9202–9215. [CrossRef]

65. Facanali, R.; Porto, N.d.A.; Crucello, J.; Carvalho, R.M.; Vaz, B.G.; Hantao, L.W. Naphthenic Acids: Formation, Role in Emulsion Stability, and Recent Advances in Mass Spectrometry-Based Analytical Methods. *J. Anal. Methods Chem.* **2021**, *2021*, 6078084. [CrossRef]
66. Liu, J.; Li, L.; Xu, Z.; Chen, J.; Zhao, M.; Dai, C. CO_2-responsive zwitterionic copolymer for effective emulsification and facile demulsification of crude heavy oil. *J. Mol. Liq.* **2021**, *325*, 115166. [CrossRef]