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DEMULSIFICATION METHODS FOR HEAVY CRUDE OIL EMULSIONS. A REVIEW

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Abstract. Demulsification (dehydration) is one of the most important problems in the oil industry. The peculiarity of heavy oil emulsions is their high stability since heavy crude contains a significant quantity of resins and asphaltenes. This paper provides an overview of the issue of heavy oil emulsion dehydration, emphasizing the importance of understanding their properties to develop appropriate demulsification methods. The use of environ-mentally friendly demulsifiers was an object of special attention. The analysis of ongoing research in this area would be useful for researches and engineers.

Keywords: heavy oil; demulsification; environmentally friendly demulsifier; microwave irradiation; ultrasound.

1. Introduction

The formation of oil emulsions is one of the main economic problems of the oil industry; depending on the production scheme, about 80 % of the world's oil is produced in emulsified form[1]. Demulsification is necessary to avoid problems that arise mainly during the transportation and refining stages[2]. The lack of efficient and effective separation of oil-water mixtures can lead to many problems[3–5] (Fig. 1).

Heavy crude oil emulsions are considered to be more difficult to break than light and medium crude oil emulsions. Markedly different from other types of crude oil (heavy oils are characterized by high density and viscosity[6]), the difficulty of heavy oil concerning emulsification is due to the surface-active components contained in the oil, such as low molecular weight fatty acids, naphthenic acid, humic acids and asphaltenes[7]. The aforementioned components are responsible for the molecular weight, chemical structure, and the value of the hydrophilic-lipophilic balance of heavy oil. Emulsions of crude heavy oil may also contain inorganic solids (such as clay) and gases, which can further contribute to the stability of the emulsion. Demands for heavy crude oil, which is unconventional crude oil, are increasing due to the growth in consumption of petroleum products and the gradual depletion of exploited oil fields.

It should be noted that the estimated reserves of heavy crude oil vary from 650 billion tons to 1 trillion tons, which is almost five times higher than those of light and low-viscosity oils, which are only 162.3 billion tons[8]. Oil companies are showing significant interest in unconventional oil as an alternative resource for energy supply[9]. The oil industry is expected to invest huge sums in heavy crude oil production and infrastructure in the coming years, up to about $1 trillion over the next decade alone. The involvement of unconventional crude oil in international energy markets faces serious challenges that require certain technological developments in production, refining, and transportation[10].

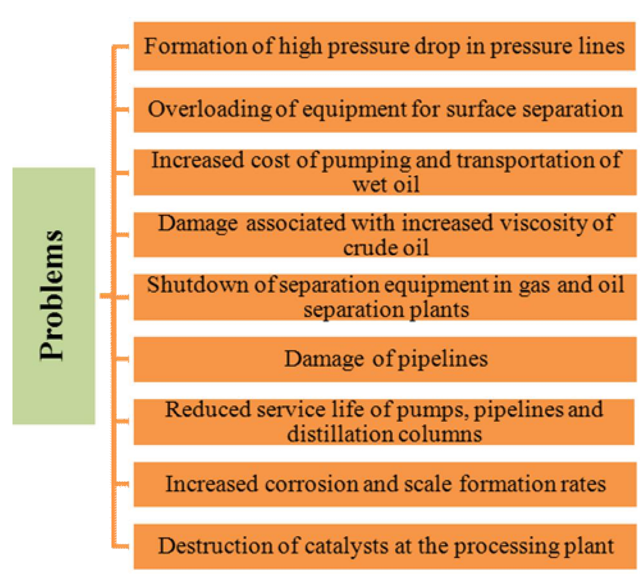

Fig. 1. Problems arising from emulsion formation

Therefore, the research on effective methods for demulsifying heavy crude oil emulsions is highly relevant.

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It is extremely topical, because the production of heavy crudes with high asphaltenes content increases, the water and salt content increases accordingly. Washing operations to remove salts dispersed in crude oil also involve the formation of new emulsions and, consequently, further dehydration operations[11].

Nowadays, the methods mostly used to break emulsions of conventional crude oil, are: thermal (heating and microwave irradiation), mechanical (gravity settling, centrifugation, filtration, membrane, and ultrasonic treatment), chemical, biological, electrical, and magnetic. The combination between heating and chemical demulsifiers is the most broadly used technique.[1] Several reviews[2,9,12–19] describe these methods of oil dehydration with their respective advantages and disadvantages.

Chemical demulsification is one of the most widely used and flexible methods of demulsifying various types of emulsions. Its essence lies in the addition of chemical substances (demulsifiers) to destabilize emulsions. Since the demulsifier is a surface-active compound, when added to the emulsion, it migrates to the oil-water interface and destroys the rigid film, which leads to coalescence of water droplets[16]. The main disadvantages of chemical demulsification are contamination of the separated products, as well as the toxicity and non-biodegradability of chemical substances in the water extracted during demulsification. In addition, this method is not always economically feasible for demulsifying all types of oil emulsions[9].

Another recently developed method applied for crude oil emulsions is biological demulsification[20,21]. A biodemulsifier is a type of biologically active substance that helps to destabilize a crude oil emulsion. Biodemulsifiers are environmentally friendly, and their use does not lead to secondary pollution. One of the main advantages of using biodemulsifiers is that they can be obtained from agricultural and industrial waste[14]. However, despite being more environmentally friendly and cost-effective, this method is time-consuming and very sensitive to operating conditions[22]. Heavy crude oil emulsions were rarely used in these studies[23].

Membrane separation is one of the effective and relatively new methods of separating oil and water. The main advantages of this process are the non-involvement of any chemicals, high separation efficiency, cost-effectiveness and compactness of the plant. However, its application is limited by high capital costs required for large volumes of wastewater, degradation of polymer membranes and pollution during operation[12]. To date, membrane technology is used mostly for the separation of oil-in-water emulsions or straight emulsions, such as industrial wastewater contaminated with hydrocarbons[14].

Electrical separation and microwave irradiation methods can be used due to their relatively low cost and the absence of additional contaminants, while low separation efficiency is the only notable drawback of these methods[15]. Electrical demulsification is considered a better option to chemical and thermal demulsification; however, the way to adapt this method to the different emulsion properties is yet to be understood properly[12]. The microwave heating technique can be applied as a standalone demulsification process in the petroleum sector as it can minimize the use of chemical demulsifiers.

The majority of research works focus on chemical and thermal treatment of oil emulsions. However, there is a lack of research on the combination of various effective and relatively cost-efficient methods, as well as research on the demulsification of high-stable heavy oil emulsions[1,9,19]. Complex methods may include several dehydration techniques, for example, chemical separation involving microwave irradiation, membrane separation, or ultrasonic processing[12,24]. Such studies are still relevant.

The **aim** of this paper is to review the ongoing research on the most effective and advanced methods for breaking precisely heavy crude oil emulsions. The article examines the peculiarities of the formation of heavy oil emulsions and gives an overview of environmentally friendly demulsifiers for water-in-oil and oil-in-water emulsions.

2. Formation of Heavy Oil-Water Emulsions

Since heavy oil contains asphaltenes, resins, solid particles, and other natural surfactants, it will inevitably form an oil-water emulsion during the process of production, storage, and transportation[25]. Due to the high density, high viscosity, and high C/H weight ratio of heavy oil, the breaking of heavy oil emulsions becomes difficult and energy-consuming. Due to the entrapment of salts and solids in the aqueous phase (droplets), these emulsions can lead to corrosion of transportation and process equipment[26].

It is known that asphaltenes are considered key components for stabilizing oil-water emulsions[5,11,26,27], *i. e.*, they have the strongest emulsifying ability. This is mainly due to their self-aggregation properties due to intramolecular and intermolecular interactions, such as π-π stacking, hydrogen bonds, and acid-base interactions. These interactions allow asphaltenes to form nanoaggregates and clusters in the oil phase and can form a rigid interfacial film at the oil-water interface[28]. These rigid interfacial films prevent droplet coalescence, resulting in high stability of heavy oil-water emulsions.

The main task of crude oil dehydration is to break or dissolve the asphaltene-based protective layer, which allows the emulsion droplets to collide and combine. The small droplets then gradually collect and condense into large droplets[7].

In general, the formation of oil-water emulsions is caused by three conditions[14,29]:

− the system has an immiscible oil phase (heavy oil) and an immiscible water phase;

− the oil-water system contains one or more intrinsic surfactants of the heavy oil (*e. g*., asphaltenes, resins, and natural surfactants), with mineral particles and surfactants added from the outside;

− there is a necessary mechanical shear force to cause the immiscible oil phase and water phase to completely mix and form emulsions[29].

Emulsions can be classified into different types based on different criteria. According to their structure criterion, crude oil emulsions can be divided into water-in-oil (W/O) emulsions, oil-in-water (O/W) emulsions, and multiple emulsions (W/O/W or O/W/O). More than 95 % of the crude oil emulsions formed in the oilfield are the W/O type[30].

Natural emulsifying agents affect the stability of W/O emulsions in two ways. One way is to prevent the drainage of the interfacial film to maintain the emulsion stability[19,31,32]. Another way is to affect the strength of the interfacial film. The natural emulsifier contained in crude oil is adsorbed at the oil-water interface, forming a viscoelastic film of a certain strength. As the concentration of natural emulsifiers increases, the number of emulsifier molecules adsorbed at the interface increases, and the number of emulsified molecules adsorbed at the interface increases, which increases the strength of the film. Thus, the water droplets in crude oil are less likely to break when they collide with each other, and the stability of W/O emulsions is improved[33].

For O/W emulsions, stability can be divided into static stability and dynamic stability. Static stability is achieved when the emulsion remains dispersed during standing, without stratification, flocculation, or oil-water separation. The dynamic stability of O/W emulsions simulates the stability and phase-free transformation of emulsions after strong shear in the wellbore, transportation through the pipeline, and passage through pumps[34].

In terms of emulsion stability research, most of the work has focused on W/O emulsions. When studying the stability factors of such emulsions, researchers separated crude oil components according to polarity; they studied the interface properties of asphaltene and other components that can also affect the stability of water-in-oil emulsions[35], including interfacial tension, oil-water interfacial film, interfacial charge effect, viscosity effect, temperature effect, stabilizing effect of polymers, sedimentation, droplet size, and changes in water : oil ratio. Relatively little research has been done on O/W heavy oil emulsions, especially the effect of heavy oil components on emulsion stability[36]. Theoretically, emulsions are thermodynamically unstable due to excess energy at the interfaces. However, emulsions of heavy oil and water are kinetically stable over a long time, from several hours to several months or even longer. In addition, these emulsions also significantly reduce the yield and quality of heavy oil.

In general, in contrast to the demulsification of traditional oil-in-water emulsions, the separation of water-in-heavy oil (W/HO) emulsion is carried out in three stages: (i) demulsifiers with higher interfacial activity diffuse from the oil phase to the oil-water interface; (ii) demulsifiers replace their surfactants and preferentially adsorb at the oil-water interface; (iii) demulsifiers reduce the oil-water interfacial tension and promote the coalescence of water droplets, resulting in oil-water separation. Therefore, the dispersion and diffusion of demulsifiers in the oil phase are crucial[28]. However, for heavy oil, due to the high content of heavy components (asphaltenes, resins), the oil viscosity is very high, which hinders the dispersion and diffusion of demulsifiers in heavy oil. As a result, the efficiency of demulsification of W/HO emulsions with demulsifiers is limited by the low separation rate. To improve oil fluidity, various methods of reducing the viscosity of heavy oil are used, such as heating, dilution with solvents, addition of functional chemicals, *etc*.[37]. However, the relationship between oil viscosity and demulsification efficiency of demulsifiers for W/HO is still unclear.

3. Methods of Heavy Oil Demulsification and Their Characteristics

As mentioned above, many demulsification methods have been proposed for breaking oil-water emulsions, including physical, biological, chemical, and combined methods. A structural chart of the methods reviewed in this article is shown in Fig. 2.

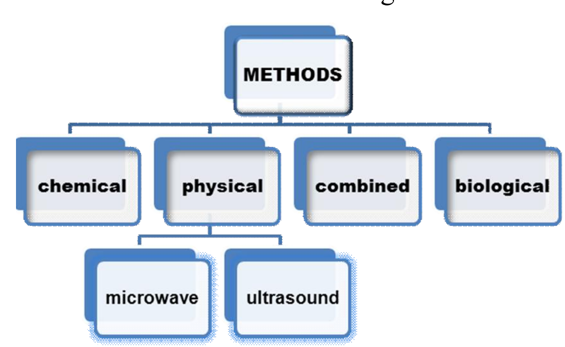

Fig. 2. Structural chart of the demulsification methods for heavy oil emulsions discussed in this review

3.1. Chemical Demulsification

Chemical demulsification is considered to be the most common method of emulsion breaking due to its ease of use and cost-effectiveness. The method uses chemicals or surfactants called demulsifiers, usually in low concentrations. The production of demulsifiers accounts for approximately 40 % of the global market for oilfield chemicals[4].

According to Abdulredha *et al.*[2], demulsifiers or surfactants are organic particles consisting of two parts: a polar part that is attractive to the aqueous phase (hydrophilic) and a non-polar part that is attractive to the oil phase (hydrophobic). Typically, demulsifiers can be divided into four groups: nonionic, ionic, amphoteric, and polymeric surfactants. The necessary choice of demulsifiers or their combination is made after studying many factors, including cost and safety[38].

The ability of a demulsifier to accelerate emulsion breaking and promote droplet coalescence depends mainly on its chemical structure and average molecular weight. The chemical characteristics of crude oil, such as SARA composition, molecular size, and asphaltene content, also strongly influence the demulsification process[11].

Yazdanmehr and Nistor[39] compared 16 types of water- and oil-based demulsifiers for the breaking of heavy Iranian crude oil emulsion. Oil-based demulsifiers were shown to have better demulsification efficiency. For water-based demulsifiers, the pH of the medium plays a crucial role, while other conditions such as dosage and time have less influence.

Zamora *et al.*[11] report the synthesis and evaluation of a series of new acrylic bipolymers as demulsifiers. These bipolymers were prepared by emulsion copolymerization of butyl acrylate (B) and 2-(dimethylamino)ethyl acrylate (Am). The composition and average molecular weight of the bipolymers were varied to evaluate their effect on their demulsifying activity for four heavy crude oils. A random sequence of monomers in the chain and control of the average molecular weight were ensured. It was shown that the efficiency of the synthesized acrylic bipolymers for emulsion breaking, induction of droplet coalescence, and clarification of the residual aqueous phase strongly depends on their alkyl acrylic/amino acrylic ratio in the chain and average molecular weight. The behavior of each BAm bipolymer as a water removal agent was compared with a commercial composition of ethylene and propylene oxide-based block bipolymers, which are widely used in the oil industry. It was shown that the efficiency of the synthesized bipolymers is higher than that of commercial demulsifiers.

The development of demulsifier compositions is currently considered an important aspect in the preparation of heavy oils before processing. The use of composition is in most cases more effective than the use of any compound in its pure form. Gurbanov and Gasimzade[25] studied the compositions with 1:1:1:1 ratio of Dissolvan-4411, Alkan, ND-12, and Gossypol resin reagents (A1) and 3 : 1 ratio of ND-12 and Gossypol resin reagents (A2). The results show that the composition (A2) ND-12+Gosipol resin=3 : 1 has the highest demulsifying effect. It decomposes stable oil-water emulsions at a temperature of 50 °C and reduces the amount of residual water to a minimum.

The advantages of using the demulsifier composition are also confirmed by Kumar *et al.*[40]. The authors experimentally investigated the effectiveness of four inexpensive chemicals with different water solubility as potential O/W demulsifiers for heavy crude oil emulsions, both individually and in combinations. The chemical demulsifiers used, in order of their higher water solubility, were polyethylene glycol 400 (PEG) > polyoxyethylene (20) sorbitan monooleate (Tween-80) > linear alkyl benzene sulfonic acid (LABSA) > *n*-octylamine (OA). As expected, complete demulsification of HO/W emulsions was achieved. The synergistic effect of the interaction between the two respective demulsifiers provided significantly better performance than the independent demulsifiers, resulting in minimizing the demulsifier amount and energy requirement for complete demulsification.

3.1.1. Environmentally friendly demulsifiers

Chemical demulsification is the most effective approach to demulsification that can achieve the desired separation efficiency and meet environmental regulatory standards while imposing a minimal economic burden on the oil industry. However, current demulsification methods using chemical demulsifiers pose the problem of significant secondary pollution, especially after the demulsification process. The water separated by chemical demulsifiers must be treated before being discharged into systems, as it often contains harmful organic compounds that can cause hazardous environmental impacts. In recent years, research has focused on environmentally friendly chemical demulsification methods.

Thus, due to their environmentally friendly properties, non-ionic demulsifiers are gaining more and more attention from the industrial sector. This is the most common type of demulsifier today. Typically, demulsifiers of this type are made by adding ethylene or propylene oxides to organic substances with a mobile hydrogen atom[26].

The synthesis of some new nonionic demulsifiers for the demulsification of extremely stable emulsions of heavy oil and water has been described in several papers[41–44]. Researchers point out the high demulsification efficiency of the compounds studied in these works, but due to the complex components of oil, the principles for selecting effective demulsifiers are still unclear[24], which can lead to laborious testing of demulsifiers for different types of crude oil. In addition, further research is needed on the relationship between demulsification and changes in interfacial rheology, as well as a detailed and quantitative assessment of its mechanism.

Taking into account the positive results obtained by Ma *et al.*[45] regarding the effectiveness of the developed nonionic demulsifier for the rapid demulsification of water-oil emulsions, including water-in-diesel fuel, water-in-crude oil emulsion, water-in-petroleum bitumen emulsion, and water-in-asphaltene solution, Xia *et al.*[46] developed a new type of environmentally friendly demulsifier (a non-ionic polyester modified with hydrophilic groups) for the effective demulsification of stable heavy oil-water emulsions. These hydrophilic groups (such as hydroxyl group, carboxyl group, ester group, and amino group) combined with non-ionic simple polyether can have the following two important advantages in the demulsification of heavy oil-water emulsions. (i) Good amphiphilicity and high interfacial activity. This is useful for promoting the diffusion of demulsifier molecules in the heavy oil-water phases and stable adsorption at the heavy oil-water interface. (ii) A large number of oxygen-containing groups can ensure the rapid breaking of asphaltene-stabilized heavy oil-water interfacial films, to achieve rapid separation of heavy oil and water phases.

The review by Fajun *et al.*[5] describes in detail the mechanism of formation and stability of heavy oil emulsions, discusses the influence of natural surfactants (resins, asphaltenes, solid particles, *etc.*) on the stability of heavy oil emulsions, and summarizes the known technological and methodological developments in the field of heavy oil emulsion demulsification from an economic and environmental point of view. It is reported that ionic liquids are effective and environmentally friendly demulsifiers, and the results of recent research on this topic are discussed.

Ionic liquids (ILs), also known as low-temperature molten salts, are salts composed of anions and cations that are in a liquid state at or near ambient temperature[47]. The results of modern research indicate that the combination and structure of cations and anions play a crucial role in their properties, composition, and hydrophobicity. The asymmetry of certain substituents in their structures allows IRs to resist crystallization and maintain a low melting point. Due to their low melting point, high chemical and thermal stability, and the ability to adjust their properties, they represent a promising research area for use in demulsification[48].

Aburto *et al.*[49] studied the feasibility of using ILs as demulsifiers by preparing an emulsion from Mexican heavy crude oil and then using the IL exchange method to synthesize choline chloride (vitamin B4) and fatty acid salts under microwave irradiation. Four amphiphilic choline carboxylates were tested, and cholic acid palmitate was found to have a good demulsifying effect on O/W emulsions with a demulsification efficiency of over 90 %.

Abdullah and Al-Lohedan[50] synthesized a new amphiphilic ionic liquid based on the glycolysis product of waste polyethylene terephthalate (PET). Bis(2-hydroxyethyl)terephthalate (BHET), obtained from PET glycolysis, was converted to bis(2-chloroethyl)terephthalate (BCET). Glycidyl 4-nonylphenyl ether (GNE) was reacted with ethanolamine (EA) to form the corresponding amine, 1-((2-hydroxyethyl)amino)-3-(4-nonylphenoxy)propan-2-ol, (HANP) and the resulting amine was then ethoxylated using tetraethylene glycol (TEG) to form ethoxylated amine (EHANP). The demulsification efficiency increased with increasing concentrations of EHANP and EHANP-IL. Thus, PET waste can be used not only as a cheap raw material for the preparation of new effective demulsifiers but also help to solve some environmental problems associated with the use of demulsifiers.

New classes of pyridinium ionic liquid demulsifiers were studied by Husain *et al.*[51]. The synthesized 1-butyl-4-methylpyridinium tetrafluoroborate, 1-butyl-4-methylpyridinium hexafluorophosphate, and 1-butyl-4-methylpyridinium iodide effectively removed water from the oil emulsion, and the demulsification efficiency (DE) increased with increasing dosage. BMPT, BMPH, and BMPI achieved the best DE of 84 %, 99 %, and 59 %, respectively, at 1000 ppm after 60 min. The highest water separation was recorded for the PF6- anion due to its high hydrophobic nature. Moreover, demulsifiers can mix with water-oil at the interface, break down asphaltenes and resin molecules, and reduce surface tension.

Ezzat *et al.*[1] investigated the high demulsification efficiency of two new amphiphilic pyridinium surfactants (aminopyridinium bromide ethoxylate, QEP; diquaternized pyridinium bromide, DQEP) in heavy oil-water emulsions. The results showed that the obtained demulsifiers had a high ability to reduce surface and interfacial tension, and successfully break heavy crude oil emulsions. The demulsification efficiency reached 100 % for a crude oil/water emulsion (90/10, v/v).

Among the developments of new types of environmentally friendly demulsifiers, the studies conducted by Dollah *et al.*[52] and Adewunmi *et al.*[53] should be noted.

Dollah *et al.*[52] synthesized magnetic graphene oxide (MGO) from graphene oxide (GO) by a one-step co-precipitation method and studied it as a demulsifier for diluted heavy oil emulsions. Different concentrations of MGO (40, 80, 120, 160, and 200 ppm) were used for different dilutions (20 : 80, 30:70, 50:50, and 60 : 40, v/v).

The demulsification efficiency was 99.98 % at an MGO concentration of 40 ppm due to the high surface area to volume ratio of the nanoparticles and magnetic properties that improve the adsorption capacity for water-oil separation. The interfacial tension of the emulsions during demulsification was also analyzed, where the interfacial tension decreased with increasing MGO concentration.

The effectiveness of fly ash (FA) and extracted silica (SC) from sand as natural demulsifiers for breaking stable crude oil emulsions was investigated by Adewunmi *et al.*[53]. A series of stable emulsions was developed, and the oil-water ratio was 4:6. The rheology and interfacial tension characteristics were used to illustrate the demulsification mechanism of FA and SC demulsifiers. According to the bottle test results, the amount of demulsified water increases with the increase in FA concentration. The demulsification efficiency (DE) of 0.25, 0.5, 0.75, and 1 % FA was 35.33 %, 81.99 %, 92.67 %, and 93.77 %, respectively, within 150 min of demulsification. At the same time, all tested SC concentrations (0.25, 0.5, 0.75, and 1 %) reached 90.11 %, 93.87 %, 95.89 %, and 95.89 %, respectively, during the same demulsification period. The reference sample (empty) achieved a DE of only 14.76 %. The rheological characterization showed that the introduction of either FA or SC caused a decrease in the emulsion viscosity, indicating the emulsion breaking and oil-water separation. Interfacial tension measurements showed that FA and SC could migrate and adsorb at the oil-water interface. The addition of FA or SC to the oil-water system resulted in a sharper decrease in the interfacial tension compared to the tension of the oil-water system without FA and SC.

3.1.2. Enhancing the effect of demulsifiers with diluents

Two different strategies were proposed by Zhang and co-workers[28] to improve the demulsification of W/HO emulsions in terms of reconstructing the interfacial surface and adjusting the bulk oil phase. First, to break the rigid interfacial film at the oil-water interface, stronger oxygen-containing groups will be introduced into the polyester demulsifier molecules by polymerization and esterification. This new oxygen-rich TJU-3 demulsifier will play an important role in breaking the asphaltene film and rebuilding a new soft film at the oil-water interface. Secondly, to facilitate the diffusion of demulsifier molecules from the bulk oil phase to the oil-water interface, which is conducive to the demulsification rate, the effect of oil viscosity on demulsification efficiency was investigated. The results showed that when using only one method (heating or dilution under ambient conditions), the demulsification efficiency of W/HO emulsions is limited (no more than 50 %). When combining demulsifiers with diluents and slight heating, complete demulsification (~100 %) of W/HO emulsions was obtained. This synergistic effect is mainly due to the fact that the reduction in viscosity weakens the barriers to demulsifier diffusion and increases the average kinetic energy of the demulsifier's thermal movement.

Ahmadi *et al.*[54] investigated the effect of oil-to-kerosene ratio, volume flow rate, temperature, demulsifier dosage, and amount of flushing water on the demulsification efficiency of heavy crude oil emulsions. The results show that the addition of an optimal amount of kerosene (25 vol. %) to the emulsion can increase the maximum water removal efficiency (WRE) and salt removal efficiency (SRE) by about 17.4 and 8.1 %, respectively. At the same time, the addition of kerosene to oil, in addition to the increase in WRE and SRE, simultaneously decreases the required optimal amount of demulsifier and flushing water from 48 to 27 ppm and from 8.5 to 5.5 vol. %, respectively. The maximum achieved efficiency of water and salt removal from heavy crude oil was found to be 92.89 and 98.73 %, respectively.

A light hydrocarbon diluent (gasoline) was added in different proportions to three samples of heavy Nigerian crude oil emulsions to enhance demulsification.[3] The demulsifiers used for the study were typical ones used in oilfields. The viscosity of the three emulsions under consideration decreased by 38 %, 31 %, and 18 %. It is concluded that an increase in the solvent amount leads to a corresponding decrease in the viscosity value. This, in turn, increases the demulsification rate of the samples.

Mixing heavy and light oils can also significantly reduce the viscosity of heavy oil[55]. However, the technology of demulsification using a mixture has not yet been reported. Zou *et al.*[56] investigated a new process of thermochemical demulsification of heavy oil after mixing with light oil. The results of field tests show that the degree of heavy oil demulsification in this process reaches more than 90 %.

For highly efficient demulsification of oil-water emulsions of heavy high-viscosity oils in the Eastern region of Ukraine, it is proposed to dilute the oil with heavy gas condensate in the amount of 30 %[57]. In this case, the demulsification efficiency increases to 87 % and 95 % when using a demulsifier based on block copolymers of propylene and ethylene oxides, respectively. The authors note that the addition of light gas condensate has a lesser effect on the emulsion viscosity since light condensate dissolves resinous and asphaltene substances less and precipitates them.

3.2. Physical Methods of Demulsification

Physical methods of demulsification include the mechanical method, membrane method, electro-demulsification, microwave radiation, and ultrasonication. The mechanical method consists of applying some external force to the emulsion droplets or achieving oil-water separation by force between the internal molecules of the emulsion, *e. g.* centrifugation, and gravity precipitation[5]. These methods are usually applied to crude oil types with simple structure and chemical composition and are often used in combination with other methods. As a rule, their application for heavy oils is problematic and sometimes impossible[58].

Despite the great versatility and high separation efficiency of the membrane method, the membrane is easily contaminated and the used membrane is difficult to degrade and recycle. Given these challenges, Yao *et al.*[29] report that they have developed flexible and mechanically strong FPI-SiO_2 fiber membranes with different degrees of roughness. These membranes allow the rapid and efficient separation of both light and heavy oil emulsions; in addition, the membranes can be reused.

Common electric demulsification technologies include electrostatic demulsification, electric pulse demulsification, electric vortex demulsification, *etc.*[5]. Electrical demulsification is generally considered to be advantageous in terms of energy consumption compared to other demulsification methods, such as heating or centrifugation, in addition to being environmentally friendly. However, the disadvantage of this process is the formation of small secondary droplets during coalescence, which makes it difficult to separate the resulting small water droplets[37].

It seems that for heavy oil emulsions with high water content and complex structure, ultrasonic and microwave demulsification are the most promising methods.

3.2.1. Microwave demulsification

Currently, microwave demulsification of crude oil emulsions is one of the most promising methods of demulsification without generating additional contaminants. Microwave irradiation is a more efficient heating method compared to the traditional thermal method. The mechanism of microwave heating differs from conventional heating and depends on the material's ability to absorb microwaves, whereas in conventional heating, heat is transferred by diffusion from the surface to the material[60]. Microwave-generated dielectric heating is associated with the interaction of radiation and substance at the molecular level. Ionic conduction and dipole rotation provide greater efficiency in microwave heating compared to the conventional method[59].

This highly efficient, environmentally friendly, and new technology can create high temperatures for a relatively short time and heat the emulsion evenly, thus accelerating the coalescence rate of water droplets to improve the overall efficiency of emulsion breaking. Microwaves can also be used for the synthesis of ILs to produce compounds of higher purity[61].

Despite the significant advantages of this method and a sufficient number of published results concerning the microwave demulsification of conventional oils[20,62–67], there is practically no data in the literature on the application of this method to heavy oils. Da Silva *et al.*[59] investigated the use of microwave technology to break water emulsions in heavy crude oil with an emphasis on the identification of acidic substances contained in the aqueous phase removed during microwave demulsification. An experimental study was conducted to assess the effect of operating conditions, including the heating mode (microwaves/conventional heating), process time (30, 60 min), pH of the aqueous phase (pH = 2, 6, 10) and temperature (90, 120, 150 °C). The authors have shown that microwaves can successfully remove water and acidic components from crude heavy oil.

The experiments for the O/W emulsion of the heavy oil from the Xinjiang Oilfield were conducted by Sun et al.[68]. The results showed that microwave demulsification had an optimal power. With increasing microwave power, the water content of the emulsion first increased and then decreased, and the demulsification effect peaked at 600 W. The demulsification efficiency was significantly improved at the synergistic action between magnetic nanoparticles and the microwave. Under the synergistic effect of 50 mg/L γ-Fe_2O_3 and 200 W microwave irradiation, the water separation rate of the emulsion reached 93 % within 60 min, proving that magnetic nanoparticles had a promoting effect on microwave demulsification.

Further experiments in this area are needed. In addition, there are still many theoretical and technical problems in the field of microwave demulsification, including the lack of adequate experimental evidence that allows for precise control of the process parameters[5].

3.2.2. Ultrasonic demulsification

Ultrasonic waves are a type of elastic-mechanical waves that propagate in a medium[69]. Crude oil emulsions are subjected to mechanical, thermal, and cavitational effects of ultrasonic waves. The mechanical action can promote the mechanical vibration of small water droplets and accelerate the collision and merging of water droplets. When ultrasonic waves pass through a crude oil medium containing suspended water particles, the latter ones vibrate together with the crude oil. Since different water particles have different sizes and, accordingly, different relative vibration velocities, they will collide and combine, thus increasing their volume and weight.

Eventually, the particles settle and separate. The ultrasonic waves transfer energy in the form of pulsations and propagate in the emulsion. The emulsion continuously absorbs the vibration energy it carries and converts it into heat energy, which can increase the temperature of the emulsion and promote demulsification and dehydration[56]. In addition, vibration can evenly distribute natural emulsifiers in crude oil, increasing its solubility and reducing the mechanical strength of the oil-water interface film. It also promotes the separation and settling of the aqueous phase.

There are many studies in the literature on the effect of ultrasonic processing technology on the demulsification process of conventional oils[70–77]. The results show that ultrasonic wave plays a positive role in the dispersion of the demulsifier and the demulsification process itself. The separation efficiency of crude oil and water can be >93 %. The application of ultrasonic technology for oil-water demulsification can reduce energy consumption and operating costs, which has good development potential[56].

The effect of crude oil demulsification/dehydration when using ultrasound in combination with chemical or thermochemical methods is significantly higher than when using ultrasonic treatment alone[69,70,75]. Ultrasound can significantly reduce the amount of chemical demulsifiers, decrease the temperature required for demulsification, and reduce the demulsification time[70]. The thermal effect can decrease the crude oil viscosity and the strength of the interfacial film. Boundary friction can increase the temperature at the oil-water interface, which is favorable for interfacial film rupture. Part of the acoustic energy absorbed by the crude oil can be converted into heat energy. The converted heat energy can reduce the viscosity of the crude oil. The mobility of crude oil can be significantly increased after sonication, and its viscosity will not recover after a long time[77].

It is noted that the demulsification effect of the thermochemical method is better than that of the ultrasonic method (without demulsifier), and the demulsification effect of the sonochemical method is better than that of the thermochemical method.

There is a limited number of works in the literature that study the breaking of heavy or extra-heavy oil emulsions. Wang *et al.*[69] conducted a static experiment of demulsification and dehydration of extra-heavy crude oil by ultrasonic treatment at high temperatures. They investigated the effect of factors such as ultrasonic frequency, intensity, sonication time, temperature, and oil:water ratio on the ultrasonic demulsification and dehydration of crude oil. Research results indicate that the dehydration rate increases with the increase in sound intensity but till a certain level; the dehydration rate decreases with the increase in ultrasonic frequency; the effect of ultrasonic demulsification and dehydration becomes better with the increase of temperature; the water ratio has a heavy and complex influence on dehydration rate.

It was noted by Chen and co-workers[71] that the coalescence of water droplets in crude oil is effectively promoted by chemical demulsifiers integrated with ultrasound. However, water droplets in heavy crude oil undergo less aggregation than in light crude oil due to the resistance to mobility in a highly viscous liquid. In the absence of chemical demulsifiers, water droplets coated with natural surfactants seemed to aggregate difficulty due to the occurrence of interfacial tension gradients.

Antes *et al.*[78] conducted a comprehensive study to evaluate the effect of ultrasonic frequency on the demulsification of crude oil. Synthetic water-in-oil emulsions with water content of 12 %, 35 %, and 50 % were prepared using heavy crude oil. Demulsification of crude oil was achieved at frequencies in the range of 25–45 kHz for all emulsions tested. When frequencies above 45 kHz were used, no changes in the characteristics of the crude oil emulsions were observed. An important aspect is that no chemical demulsifiers were added, and the demulsification efficiency was recognized as high, given that the results were obtained using unconventional crude oil. In contrast to the conventional application of low-frequency ultrasound used for demulsification, the proposed approach seems to be a promising technology for the removal of water from heavy crude oil emulsions.

Thus, further research is needed on the effect of sonication parameters on the demulsification of heavy oil to improve the process efficiency. Moreover, it is necessary to develop new combined processes, which is important for the design of an industrial process. Taking into account the disadvantages of the existing ultrasonic demulsification technology, such as small ultrasonic action area, incomplete demulsification, secondary emulsification after emulsification, *etc.*[73], the development of new equipment and technical support for heavy oil demulsification/dehydration is required.

4. Biodemulsification

Biodegradable demulsifiers are considered potential alternatives to chemically synthesized demulsifiers commonly used in the oil industry. Most of the used chemical demulsifiers, although effective, pollute the environment and do not meet the desired levels of biodegradation. Biodemulsifiers have several advantages, such as high biodegradability, low toxicity, and specific activity within a wide range of temperatures, pH, and salinity. In addition, they can be made from renewable and cheap materials.

From this point of view, the study carried out by Abed and Naife[79] is extremely interesting. A new environmentally friendly biodemulsifier was synthesized from waste corn oil. The maximum demulsification efficiency was 69.3 % at water:oil ratio of 30:70. The dose was 1000 ppm, temperature 70 °C, and time 5 h.

More traditionally, different types of microorganisms (bacteria, yeast, and fungi) are used to create biodemulsifiers[20]. Sabati and Motamedi[22] identified bacteria producing biodemulsifiers from oil-contaminated environments. As a result, several biodemulsifier-producing strains were identified, and it was found that the strain Stenotrophomonas sp. HS7, which produces a cell-associated biodemulsifier, showed the highest demulsification efficiency of 98.57 % for water-in-kerosene and 66.28 % for water-in-crude oil emulsion after 48 h.

As regards the development of biodemulsifiers for heavy oil emulsions, Amirabadi *et al.*[23] studied the demulsifying effect of Paenibacillus alvei ARN63 (*P. alvei*) bacterium. The produced biodemulsifier demonstrated the potential for use in the oil industry as an environmentally friendly and non-toxic material. It had good stability when exposed to salinities up to 20 %, temperatures up to 80 °C, and a wide pH range of 2–12. The demulsification efficiency was close to 77 %.

Many researchers have focused on the study of biodemulsifiers for destabilizing emulsions of O/W type[20]. After the biodemulsifier is added to the emulsion, the interfacial tension between the two phases decreases, which leads to the oil removal from the emulsion[14]. Microorganisms can change the surface charges at the water/oil interface and thus improve the properties of the emulsion[80].

Vallejo-Cardona *et al.*[81] studied the effect of Aspergillus sp. IMPMS7 spores isolated from marine sediments contaminated with petroleum hydrocarbons on the breaking of O/W emulsions of medium, heavy, and extra heavy oils in water (70 : 30). The isolated fungal spores showed a high hydrophobic capacity of 89.3±1.9 %, and at 2 g of spores per liter of emulsion, the half-life for emulsion destabilization was approximately 3.5 and 0.7 h for super-heavy and medium oil, respectively.

Most studies with biodemulsifiers use model emulsions with very low viscosity and low stability, which therefore break easily. In most cases, these emulsions spontaneously break within a few hours of formation without the need for demulsifiers; however, natural emulsions derived from heavy crude oil are much more complex, stable, and difficult to break, so the development of an environmentally friendly method remains a major challenge.

The following Table summarizes the key points of each method discussed in this review, allowing us to compare them, especially in terms of environmental pollution.

Table. Highlights of demulsification methods for heavy crude oil emulsions

In relation to environment	Demulsifiers or parameters under study	Highlights	Ref.
1	2	3	4
Eco-unfriendly	Oil- and water-based demulsifiers	Oil-based demulsifiers have better demulsification efficiency. For water-based demulsifiers, the pH of the medium plays a crucial role	[39]
	Acrylic bipolymers	The demulsification efficiency of the synthesized bipolymers (butyl acrylate and 2-(dimethylamino)ethyl acrylate) is higher than that of commercial demulsifiers	[11]
	Chemical demulsifiers integrated with ultrasound	In the absence of chemical demulsifiers, water droplets coated with natural surfactants aggregated difficulty due to the occurrence of interfacial tension gradients. Coalescence of water droplets in crude oil is greatly promoted by chemical demulsifiers integrated with ultrasound	[71]
	Compositions of ND-12, Gossypol, Disulfan-4411 and Alkan reagents,	ND-12+Gosipol resin (3:1) composition shows a higher demulsification efficiency compared with individual demulsifiers	[25]
	Polyethylene glycol 400, polyoxyethylene (20) sorbitan monooleate (Tween-80), linear alkyl benzene sulfonic acid, *n*-octylamine, and their combinations	The synergistic effect of the interaction between the two respective demulsifiers provided significantly better performance than the independent demulsifiers, resulting in minimizing the demulsifier amount and energy requirement for complete demulsification	[40]
Eco-friend-ly	Pyridinium ionic liquids	Among studied demulsifiers, 1-butyl-4-methylpyridinium hexafluorophosphate had the highest demulsification efficiency (99 %)	[51]

Continuation of **Table**

1	2	3	4
Eco-friendly	Amphiphilic pyridinium surfactants	The demulsification efficiency of the synthesized aminopyridinium bromide ethoxylate and diquaternized pyridinium bromide reached 100 % for a crude oil/water emulsion (90/10, v/v)	[1]
	Different types of ionic surfactants	The combination and structure of cations and anions play a decisive role in their properties, composition, and hydrophobicity. The hydrophobic ionic liquid of the long alkyl chain cation generally has a relatively better dehydration efficiency, but the hydrophilic ionic liquid also has a good effect in the face of the emulsion which has a high initial water content	[5]
	Non-ionic polyester modified with hydrophilic groups	A large number of oxygen-containing groups in the synthesized demulsifier ensures the rapid breaking of asphaltene-stabilized heavy oil-water interfacial films and allows to achieve rapid separation of heavy oil and water phases	[46]
	Aliphatic alcohol nonionic polyether	Almost complete dehydration (>97%) to the stable emulsions could be achieved at 60 °C in less than 15 min, that is much faster compared with traditional or commercial demulsifiers	[45]
	Amphiphilic choline carboxylates synthesized under microwave irradiation	Among four synthesized ionic liquids cholic acid palmitate has the best demulsifying effect on O/W emulsions with a demulsification efficiency of over 90 %	[49]
	Amphiphilic ionic liquid based on the glycolysis product of waste polyethylene terephthalate	PET waste can be used not only as a cheap raw material for the preparation of new effective demulsifiers but also help to solve some environmental problems	[50]
	Magnetic graphene oxide	The demulsification efficiency was 99.98 %. Magnetic properties improve the adsorption capacity for water-oil separation	[52]
	Fly ash (FA) and extracted silica (SC) from sand	The introduction of either FA or SC caused a noticeable decrease in the emulsion viscosity	[53]
	Heating mode (microwaves/conventional heating), process time, pH of the aqueous phase and temperature	Microwaves can successfully remove water and acidic components from crude heavy oil. The higher heating rate is achieved in the microwave heating method compared with conventional heating	[59]
	MW power and radiation time, pH value, type and concentration of magnetic nanoparticles	Synergistic action between magnetic nanoparticles and the microwave increases demulsification efficiency. Magnetic nanoparticles have a promoting effect on microwave demulsification	[68]
	Ultrasonic frequency, sound intensity, ultrasonic power, ultrasonic treatment time, sedimentation time, temperature, and water ratio	The increase in sound intensity till a certain level increases the dehydration rate; the dehydration rate decreases with the increase in ultrasonic frequency; the effect of ultrasonic demulsification and dehydration becomes better with the increase of temperature; the water ratio has a heavy and complex influence on dehydration rate	[69]
	Ultrasonic frequency (25–45 kHz)	In contrast to the conventional application of low-frequency ultrasound used for demulsification, the proposed approach seems to be a promising technology for the removal of water from heavy crude oil emulsions	[78]
	Polyimide (PI) nanofiber membrane	The PI fibrous membrane has excellent mechanical robustness and achieved both ultra-high oil-water selectivity and separation performance	[29]
	Biodemulsifier synthesized from waste corn oil	The maximum demulsification efficiency was 69.3 %	[79]
	Bacteria producing biodemulsifiers from oil-contaminated environments	The strain Stenotrophomonas sp. HS7, which produces a cell-associated biodemulsifier was found to be the best with demulsification efficiency of 66.3%	[22]
	Paenibacillus alvei ARN63 (*P. alvei*) bacterium	It had good stability when exposed to salinities up to 20 %, temperatures up to 80 °C, and a wide pH range of 2−12. The demulsification efficiency was close to 77 %	[23]
	Aspergillus sp. IMPMS7 spores isolated from marine sediments contaminated with petroleum hydrocarbons	Breaking of O/W emulsions of medium, heavy, and extra heavy oils in water (70:30). The isolated fungal spores showed a high hydrophobic capacity	[81]

It is evident from the Table that demulsification methods for heavy oil emulsions are different and specific. The issue of rational choice of demulsification method for heavy crude oil emulsion is complicated by the fact that the data on their properties and crude oil composition is incomplete, contradictory, and not systematic.

5. Conclusions

This review provides insight into the progress and status of current research, existing challenges, and applications of heavy oil demulsification methods, each of which has its own advantages and disadvantages, different efficiency, energy and time consumption, and compliance with certain environmental standards. In this regard, a thorough analysis of "positive" demulsification, which is safe for the environment, was carried out.

A proper understanding of the properties and characteristics of heavy oil emulsions for developing appropriate demulsification methods was emphasized. The problems that are not considered by most researchers and require further research are specified, namely the impact of viscosity, lack of field cases or on-site crude oil demulsification cases.

The current review is expected to open up new avenues for researchers and engineers to gain insightful ideas for further development.

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МЕТОДИ РОЗДІЛЕННЯ ЕМУЛЬСІЙ ВАЖКОЇ НАФТИ. ОГЛЯД

Анотація. *Деемульгування (зневоднення) є однією з найважливіших проблем у нафтовій промисловості. Особливістю емульсій важких нафт є їхня висока стабільність, оскільки важка нафта містить значну кількість смол та асфальтенів. У цій статті подано огляд проблеми зневоднення важких нафтових емульсій, підкреслено важливість розуміння їхніх властивостей для розробки відповідних методів деемульгування. Особливу увагу приділено використанню екологічно безпечних деемульгаторів. Аналіз поточних досліджень у цій галузі буде корисним для науковців та інженерів.*

Ключові слова: *важка нафта, деемульгація, екологічно безпечний деемульгатор, мікрохвильове опромінення, ультразвук.*