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Chemical and Bio-Based Demulsifiers for Crude Oil-Water Emulsions: A Comprehensive Review of Mechanisms, Performance and Sustainable Solutions

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ABSTRACT

Crude oil-water emulsions pose significant challenges in the petroleum industry due to their stability, which is enhanced by natural surfactants like asphaltenes, resins, and waxes. Effective demulsification is essential to mitigate operational inefficiencies, corrosion, and increased viscosity. This review compares chemical and natural-based demulsifiers, evaluating their performance under laboratory and industrial conditions. Chemical demulsifiers, such as surfactants and polymers, are widely used for their efficiency and adaptability but raise environmental concerns. Natural demulsifiers derived from plant extracts, waste oils, and biopolymers offer sustainable alternatives, though their effectiveness varies with conditions. The study highlights the mechanisms of emulsion formation and stabilization, demulsification techniques (mechanical, chemical, thermal, and electrical), and factors influencing the process, such as temperature, droplet size, and interfacial films. While chemical demulsifiers remain dominant in industrial applications, natural alternatives show promise, particularly in eco-sensitive contexts. Future research should focus on optimizing natural demulsifiers and validating their scalability under industrial conditions.

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Introduction

Crude oil extraction and production are frequently associated with the formation of emulsions, typically water-in-oil emulsions, which arise when water is dispersed as droplets in crude oil. These emulsions, formed mostly during extraction and transportation, consist of two immiscible liquids (oil and water), where one liquid (dispersed phase) is suspended as small droplets within another (continuous phase) [1]. Shear forces and pressure changes during production, especially at valves, pumps, and wellheads, cause emulsions to form in crude oil. They increase oil viscosity, reduce the efficiency of transportation and processing, and lead to operational issues such as equipment corrosion and fouling [2].

The natural surface-active components in crude oil, such as asphaltenes, resins, and waxes, act as stabilizers, leading to the formation of stable emulsions which are difficult to handle [3-5]. These natural surfactants (asphaltenes, resins, and fine solids) in crude oil form rigid interfacial films around water droplets, which prevent coalescence and increase the emulsion stability [5,6].

Crude oil emulsions, particularly water-in-oil emulsions, pose significant challenges during production, transportation, and refining. Emulsions account for ~30% of operational costs in offshore production. Effective demulsification is crucial to separate the water phase from crude oil and reduce issues like corrosion, increased viscosity, and operational inefficiencies. This review article compares demulsification methods described in various studies, focusing on the differences between natural extract-based demulsifiers and typical chemical demulsifiers, evaluating their performance under laboratory and industrial conditions.

Crude Oil Emulsion: Types, Characteristics and Stability

An emulsion can be defined as a structure whereby an immiscible liquid state is distributed as globules (dispersed state) in another immiscible liquid state (continuous state) [6]. There are three main types of emulsions produced in the petroleum industry [5,7,8]. They are classified based on which liquid is dispersed in the other. A schematic of two of these types of emulsion is shown in Figure 1

Water-in-Oil (W/O)

This emulsion is also called regular emulsion. The water droplets are dispersed within the continuous oil phase. It is the most common emulsion type encountered during crude oil production [1,3,5]. W/O emulsions can be tight or loose based on the stability and length of the separation time. Tight emulsions are particularly difficult to break and may remain stable for extended periods.

Oil-in-Water (O/W)

This less common type consists of oil droplets dispersed in the continuous water phase, often referred to as "reverse emulsions" [5,8]. These emulsions are encountered in processes involving significant water co-production.

Multiple Emulsions (W/O/W and O/W/O)

Multiple emulsions could be water-oil-water or oil-water-oil emulsions. They are more complex with small droplets suspended in bigger droplets that are suspended in a continuous phase [1]. For example, W/O/W emulsions comprise tiny water droplets embedded in larger oil droplets in a continuous water phase [5].

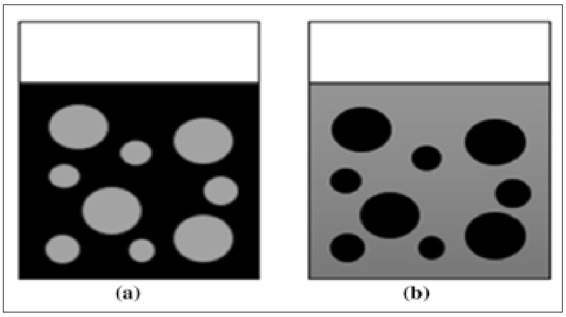

Figure 1: A Schematic Representation of Emulsions (Black - Oil; Grey - Water) (a) Water-in-Oil (b) Oil-in-Water [1].

Stability of Crude Oil Emulsions

Emulsions are generally considered a special liquid-in-liquid colloidal dispersion. From a purely thermodynamic point of view, they are unstable systems because of their tendency to separate and reduce their interfacial area. However, most emulsions are kinetically stable over a long period [5]. Their stability is largely influenced by factors such as temperature, pH, agitation, salinity, and the nature of surface-active agents (naturally occurring or added during production) [7]. The stabilizers hamper the mechanism involved in breaking the emulsions (demulsification). Asphaltenes and resins make up the majority of the interfacial active components in crude oil. They are large polyaromatic and polycyclic condensed ring compounds containing heteroatoms [9].

The heavy or high boiling fractions of crude oil contain a large number of natural stabilizers such as asphaltenes, resins and oil soluble organic acids. Asphaltenes reside at the oil//water interface because of their surface-active properties. This accumulation of asphaltenes at the interface results in the formation of rigid films which act as barriers to droplet coalescence. They are polar molecules insoluble in aliphatic hydrocarbons but soluble in aromatic hydrocarbons [2]. Studies have suggested that crude oil emulsion stability is influenced by the solubility state of asphaltenes in the crude oil. This solubility state is determined by the resins-to-asphaltenes ratio and the concentration of the polar functional groups in the resin and asphaltenes.

The role of resins in emulsion stability has been debated by several researchers. They believe that they tend to associate with asphaltenes and form micelles, which play a key role in stabilizing the emulsion. They have a smaller molecular volume compared to asphaltenes, and their molecules do not aggregate. The asphaltene/resin ratio is responsible for the type of film formed and therefore, influences the stability of the emulsion [2,5].

Waxes are high molecular weight paraffin substances that crystallize out when crude oil is cooled beyond its cloud point. Waxes on their own do not form stable emulsions since they are soluble in oil. However, in the presence of asphaltenes, they interact to form stable emulsions. Waxes tend to form stable emulsions when they are present as fine solids in the emulsion [5].

The presence of fine solid particles in crude oil is capable of stabilizing emulsions. Their effectiveness is influenced by factors such as particle size, interparticle interactions and wettability. Solid particles stabilize emulsion by diffusing to the oil/water interface to form rigid films. The particles should be smaller than the emulsion droplets to act as emulsion stabilizers, and if they are charged, this may also enhance the stability of the emulsions.

Methodology

Techniques of Demulsification

Demulsification can be defined as the process of breaking emulsions or separating emulsified water from oil [10]. This process of breaking emulsions is essential for the separation of water from oil before the crude oil can be transported or refined. Various techniques are employed in the industry, categorized broadly into mechanical, chemical, thermal, and electrical methods. The selection of demulsification techniques depends on the characteristics of the crude oil and the type of emulsion, requiring a careful balance between operational costs, efficiency, and environmental impact.

Mechanical Methods

Mechanical demulsification involves the application of external forces such as centrifugation, filtration, or gravitational settling to separate water from oil [5]. Centrifugation, for example, accelerates the separation process by increasing the settling rate of water droplets. Gravity settling tanks, centrifugal contactors, free water knock-out drums, and/or a desalting tank are some equipment used for mechanical demulsification. Generally, mechanical demulsification is environmentally friendly as it does not involve chemicals and is useful for the initial stages of separation in combination with other methods. However, mechanical methods are ineffective for stable emulsions with small droplet sizes, are not always effective for tight emulsions, and may require supplementary techniques to achieve complete separation. The process may also require large equipment and high energy consumption [1].

Chemical Methods

Chemical demulsification is the most widely used method in the industry, where chemical agents called demulsifiers or emulsion breakers are added to destabilize the interfacial film around water droplets, allowing them to coalesce and separate from the oil [3,4]. Common demulsifiers include surfactants, resins, and copolymers, which reduce the interfacial tension and enhance water droplet coalescence. They are highly effective for stable emulsions and can be tailored to specific crude oil characteristics [6]. They also increase efficiency and reduce operational costs by accelerating the separation process. Chemical demulsifiers can be toxic, leading to environmental concerns, and their overuse or incorrect formulation of demulsifiers can lead to excessive costs [4].

Thermal Methods

Thermal methods involve heating the emulsion to reduce its viscosity and enhance the coalescence of water droplets. The increase in temperature decreases the interfacial tension and accelerates the separation process [1]. Heating is often combined with chemical methods to break highly stable emulsions and improve efficiency. Thermal demulsification involves high energy consumption, making it expensive for large-scale operations. There is also the risk of heat damage to certain crude oil components, such as asphaltenes [3].

Electrical Methods

In this method, an electric field is applied to induce the coalescence of water droplets through electrostatic forces [6]. The electric field disrupts the stabilizing interfacial film, allowing the water droplets to combine and settle more rapidly. This method is highly effective for tight emulsions. It is non-chemical and environmentally friendly. Some major drawbacks are that it requires specialized equipment, leading to high operational costs and may not be effective for highly viscous emulsions [4].

Demulsification is a critical process in the petroleum industry for efficient crude oil processing and transport. While mechanical and thermal methods provide environmentally friendly options, chemical demulsification remains the most effective due to its adaptability and efficiency. However, environmental concerns and the need for optimal formulation pose challenges. Electrical demulsification offers a promising alternative, particularly for stable emulsions, but its high-cost limits widespread adoption.

Mechanism of Demulsification

Demulsification occurs progressively through sedimentation, flocculation, and coalescence. The process flowchart in Figure 2 illustrates the stages. Then, Table 1 presents the comparison of the demulsification mechanisms.

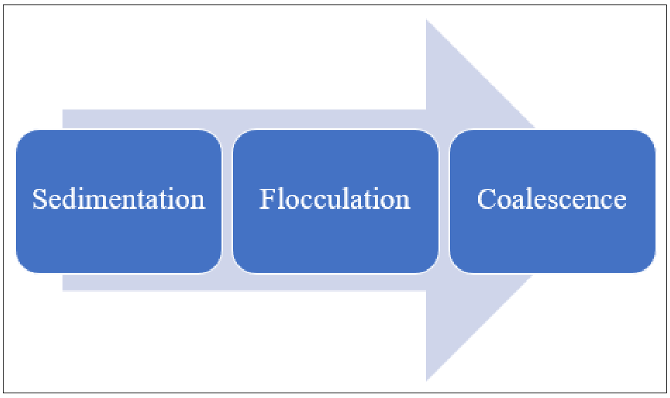

Figure 2: Mechanism of Demulsification

Table 1: Comparison of Demulsification Mechanisms

Mechanism	Time Scale	Energy Input	Key Influencing Factors	Industrial Applicability	Key References
Sedimentation/ Creaming	Hours to days	Low (gravity-driven)	- Density difference between phases - Droplet size - Viscosity of continuous phase - Interfacial film strength	Used in primary separation (e.g., settling tanks); slow but cost-effective for loose emulsions.	[2,8,5]
Flocculation	Minutes to hours	Moderate (mixing/ agitation)	- Van der Waals forces - Temperature - Water content - Oil viscosity - pH/salinity	Common in pretreatment; requires chemical aids (e.g., polymers) to enhance droplet aggregation.	[2,5,8]
Coalescence	Seconds to minutes	High (thermal/ mechanical/chemical)	- Interfacial tension - Temperature - Demulsifier chemistry - Droplet collision frequency	Critical for tight emulsions; often combined with thermal/chemical methods in refineries.	[2,4,8]

Factors Affecting the Demulsification Process

Separating emulsified water from crude oil is influenced by several factors related to the physical, chemical, and operational characteristics of the emulsion system. The effectiveness of the demulsification process depends on factors such as the chemical structure of demulsifiers, temperature, droplet size distribution, interfacial films, pH levels, and water and oil content. Understanding these factors is crucial for optimizing demulsification strategies and improving oil-water separation efficiency in the petroleum industry. Each factor plays a unique role, and the selection of appropriate emulsion breakers and operating conditions must be tailored to the specific properties of the emulsion.

Chemical Structure of Demulsifiers

The structure of demulsifiers plays a crucial role in determining their efficiency in breaking down emulsions. Demulsifiers are surface-active agents that modify the interfacial tension between oil and water phases. They generally consist of a hydrophobic backbone and a hydrophilic head, and the balance between these components determines the demulsifier's ability to interact with the emulsion [4]. Its molecular weight and hydrophilic-lipophilic balance (HLB) significantly impact its performance. High-molecular-weight demulsifiers tend to show lower mobility, which can reduce their effectiveness, while optimal HLB values enhance the coalescence of water droplets [3,4].

Temperature

Temperature is a critical factor influencing the demulsification process. Increasing the temperature reduces the viscosity of oil, accelerates the movement of water droplets, and weakens the interfacial films that stabilize emulsions [5]. At higher temperatures, the rate of film drainage increases, enhancing the coalescence of droplets and speeding up the separation of water and oil. However, excessive temperatures can reduce the efficiency of some chemical demulsifiers, as they may degrade or lose their effectiveness under heat [1]. Optimal temperatures for demulsification generally range between 50°C and 70°C.

Droplet Size Distribution

The size and distribution of water droplets in the emulsion affect the stability and ease of separation. Smaller droplets result in more stable emulsions that are harder to break, as the larger surface area of the dispersed phase enhances the effect of stabilizing agents like asphaltenes and resins [3,5]. Large droplets, on the other hand, tend to coalesce more readily, allowing for faster separation. Therefore, emulsions with smaller droplet sizes require longer residence times and higher energy inputs for effective demulsification.

Interfacial Films

The nature and stability of interfacial films surrounding the water droplets play a significant role in emulsion stability. Rigid films, often formed by asphaltenes and resins, act as physical barriers that prevent coalescence. These films are viscoelastic and can significantly hinder the separation of water from oil [5]. Demulsifiers work by weakening these films, allowing water droplets to merge and separate. The mobility of these interfacial films correlates with the ease of breaking the emulsion, where more mobile films promote faster coalescence.

pH

The pH of the water phase in an emulsion affects the stability and type of emulsion formed. Water-in-oil emulsions tend to form in acidic environments (low pH), while oil-in-water emulsions are more stable at higher pH values [1]. The presence of acids or bases can alter the interfacial properties, with acidic conditions typically stabilizing asphaltenic films, making the emulsion more resistant to separation. Conversely, alkaline conditions weaken these films, promoting demulsification.

Water and Oil Content

The ratio of water to oil in an emulsion affects both its stability and the effectiveness of the demulsification process. Higher water content generally facilitates faster separation, as the increased volume of water droplets promotes more frequent collisions and coalescence. On the other hand, higher oil content can stabilize the emulsion, particularly in water-in-oil systems, making it harder to break [11]. Effective demulsifiers are required to manage emulsions with varying water and oil contents, optimizing the separation process based on the specific composition of the emulsion.

Chemical Demulsification Studies

The most common method of breaking emulsions is chemical demulsification [3,6]. These chemicals, commonly called demulsifiers or emulsion breakers, are surfactants (surface active agents).

Reviewed the use of surfactants in crude oil demulsification, their structure, classification, properties, and mechanism for separating water from crude oil [7]. These surface-active agents reduce the interfacial tension between oil and water, promoting the aggregation and coalescence of the water droplets to aid separation. Surfactants contain hydrophobic and hydrophilic components, facilitating their interaction with the oil and water phases. They are usually classified as ionic, cationic, amphoteric (zwitterionic), and non-ionic as described in Table 2. Non-ionic surfactants are more popular due to their stability in various conditions, including salinity [7,9]. They emphasized the importance of selecting surfactants based on specific oilfield conditions to ensure effective separation. The demulsification efficiency depends on the crude oil type, viscosity, water content, salinity, and the nature of the emulsifying agents.

Table 2: Types of Surfactants and Description [7].

Surfactants	Description
Ionic	Negatively charged, present on the active surface of the molecule
Cationic	Transfers a positive shipment on the active surface component of the molecule
Amphoteric	Cationic and anionic-based surfactants, including those that are zwitterionic, possessing repeated charges of each type
Non ionic	Without electric charges which their water solubility is a result of the presence of polar functionalities with the ability of strong hydrogen bonding interactions with water

Demulsifiers are used and/or formulated to counter the stability impact of the emulsifying agents in the crude oil emulsions. Some of the common demulsifiers investigated in literature are polymers (PEG, PEO, etc.), while others have structures comparable to non-ionic emulsifiers. An effective and high-performing emulsion breaker should possess the following qualities [6]:

- Ability to separate emulsion into the oil and water phases.
- Can break down in the oil phase.
- The concentration must be enough to ascertain a high diffusion flux to the film interface.
- Should be able to overcome the interfacial tension, thereby accelerating the rate of film drainage to promote coalescence.

Several studies have been carried out to test the effectiveness of different demulsifiers in breaking crude oil-water emulsions under varying conditions. The study conducted by, investigated the efficacy of three common chemical emulsion breakers – xylene, glycerol, and triethanolamine (TEA) for treating crude oil emulsions obtained from three different oil wells in Delta State, Nigeria [12]. Their analysis showed that glycerol (a polyhydric alcohol) was the most active demulsifier. It achieved up to 72% water separation compared to 70.2% by TEA and 65.7% for xylene. It was suggested that the high solubility of glycerol in oil and water made it the most effective of the chemicals investigated.

Adeyanju and Oyekunle tested six different chemical demulsifiers – polyethylene glycol (PEG), polyethylene oxide (PEO), pentylamine, butyl acrylate, ethanol, and butanol - on two types of Nigerian crude oil emulsions. They also performed an optimization study using the response surface methodology (RSM) to optimize the concentration of each chemical demulsifier in a mixture for treating the emulsions. PEG was reported to be the most effective achieving the highest water separation rate, while butanol was the least effective due to its low solubility in the continuous oil phase. This suggests that demulsifiers with low solubility in the water or oil phases do not perform as well as those soluble in both phases. The optimized formulation (comprising optimized concentrations of the six chemicals) separated about 92% and 94% of water from the crude oil samples, exceeding the performance of PEG (57%) and a commercial demulsifier (87% and 90%, respectively). They concluded that it is important to tailor demulsifiers to specific crude oil properties for optimum performance.

The effect of some chemical demulsifiers on the stability and properties of water-in-oil emulsions prepared from crude oil obtained from Petronas refinery was investigated by [9]. These demulsifiers were grouped as amine, polyhydric alcohol, acid and polymeric. The amine group were the most effective in breaking the emulsion compared to the other groups. Decylamine had the highest water separation rate. Amongst the other groups of demulsifiers tested, PEG had the best separation rate for polyhydric alcohols and butanoic acid for the acid group. They pointed out that blended demulsifiers performed better than single demulsifiers.

In a similar study, studied the effect of groups of demulsifiers (amine, natural, polyhydric and alcohol based) on water-in-oil emulsions [10]. The amine group, like the case of, showed the highest efficiency in breaking the emulsions compared to the other groups [9]. They explained that the result was influenced by the hydrophobic and hydrophilic characteristics of the breaking agent. Demulsifiers with HLB numbers below 9.0 are lipophilic, and those greater than 11 are hydrophilic. Amine and natural-based demulsifiers are lipophilic (oil soluble) and are more suitable for water-in-oil emulsions. This, they believed, could be the reason why amine and natural-based demulsifiers performed better than polyhydric alcohol, which is hydrophilic. Their findings also supported the previous postulation that the coalescence rate increased with the higher molecular weight of the demulsifier. This was true for the other groups except the amine group, where the heavier dioctyl amine had a lower oil-water removal rate than octylamine, hexylamine, and pentylamine. For the other groups, the heaviest amongst them (PEG 1000 for the polyhydric alcohol group, heptanol for the alcohol group, and Palm Based Oleyl Amine for, PBOA for the natural group) showed the highest water separation rate.

Natural Extracts as Demulsifiers

Recent research on crude oil-water emulsion focuses on using green or natural demulsifiers. These demulsifiers are derived mostly from plant extracts, and utilize active components like essential oils, fatty acids, or other bio-based compounds to break emulsions. These demulsifiers are environmentally friendly alternatives to synthetic chemicals. Several natural extracts have been investigated to test their efficacy in breaking crude oil emulsions. Some of these extracts and recent works on them are highlighted in this section.

Coconut Extracts and Derivatives

Investigated the potential of using coconut oil and its derivative, coco betaine, for treating water-in-oil emulsions, testing their effectiveness in separating water from oil under a range of conditions, including concentration of demulsifiers, temperature, and the presence of xylene additives [13]. They reported that coco betaine achieved up to 35% separation at optimal conditions of 70 °C and 3 mL dosage. Coco betaine performed better than coconut oil (less than 5% separation). However, its performance is still not comparable to conventional chemical demulsifiers that generally achieve 80% to 90% separation of the emulsion.

Similarly, formulated a biodegradable demulsifier from coconut extracts [14]. This new emulsion breaker called DEMLOCS was synthesized using coconut oil extract, potato starch, camphor and sodium hydroxide. They reported 88% water separation within 24 hours at a dosage of 2000 ppm and a temperature of 45oC. Optimal separation was achieved at a salinity level of 11.7% as higher salt concentrations tended to stabilize the emulsion rather than break it. The demulsifier reduced the interfacial tension between oil and water, promoting the coalescence of water droplets and enhancing water separation. It also contributed significantly to viscosity reduction and was reported to be easily biodegradable. The coconut extract formulation from showed better demulsification properties compared to what was reported by for coconut derivatives [7,14].

Also compared the efficiency of coco amine and palm-based oleyl amine, PBOA [10]. They mentioned that the emulsions completely separated into oil and water when the natural extracts were added. PBOA achieved this in 4 days compared to Coco Amine's 6 days. They explained that the separation was slow at first until the third day, when it was drastic, due to the droplet's coalescence phenomenon. The demulsifier adsorbs into the droplet film, inducing film thinning and leading to rupture.

Chitosan-Based Demulsifier

Demonstrated that chitosan-based demulsifiers achieved 48% separation [15]. FT-IR and 1H-NMR spectroscopy identified C=O, OH, and NH2 as important functional groups in the new demulsifier. The synthesized demulsifier was tested with oil emulsions made from Basra crude oil. Its separation ability was compared to a commercial demulsifier. They reported that the newly formulated demulsifier from natural polymer achieved higher water separation than the commercial demulsifier, especially at higher temperatures. The natural polymer-based demulsifier achieved up to 48 mL water separation at 80 ppm concentration, compared to the 29 mL separation achieved by the commercial demulsifier. The Schiff base demulsifier's thermal gravimetric analysis (TGA) revealed good thermal stability, making it suitable for industrial conditions with elevated temperatures.

Citric Juice Concentrates

Explored biodegradable and cost-effective alternatives to conventional chemical demulsifiers [16]. They investigated the abilities of locally sourced citric juice concentrates extracted from lime, grape, and orange to break down crude oil-water emulsions produced from Basra heavy crude oil. Their results showed that lime juice concentrate was the most effective demulsifier of the juice concentrate. It achieved up to 98% water separation within 5 minutes. They noted that the effectiveness of the lime juice concentrate may be attributed to surfactants present in the concentrate that alter the interfacial film properties, leading to flocculation and coalescence of water droplets. The grape and orange juice concentrates stabilized rather than demulsified the emulsions. They reported that they both caused emulsion inversion from water-in-oil to oil-in-water.

Cashew Nut Shell Liquid Oil

Studied the efficacy of cashew nut liquid oil (CNSL) modified with triethanolamine for demulsification of crude oil-water emulsions [17]. This bio-based crude oil emulsion breaker was prepared from agricultural waste. Three different triethanolamine-CNSL derivatives were made – triethanolamine anacardate (TEA), triethanolamine dianacardate (TED) and triethanolamine (trianacardate) – using a one-pot reaction. These variants were tested and compared to a commercial demulsifier at 60 °C, at concentrations ranging from 10 to 50 ppm, and with different water content in emulsions within 3 hours. They reported that separation improved with increasing concentrations and higher water content in the emulsions. The demulsification trials showed that TED performed better amongst the three variants (TED > TET > TEA). They also investigated the effects of solvent (Butanol and Xylene) in enhancing water separation. TED performed better in butanol than in xylene, achieving water separation of over 80%, comparable to the commercial demulsifier. They explained that the presence of hydroxyl groups in butanol aided the interactions with water molecules, leading to faster separation time compared to xylene, and suggested that butanol may be a sustainable alternative to xylene in demulsifier formulation.

Nicotania Tobacum Extracts and Coal Fly Ash

Formulated a demulsifier from extracts of Nicotiana tabacum seed oil, leaf and stalk ash, which they termed NTLESESAD [18]. Characterization and phytochemical analysis of the extracts showed that the seed oil had a high saponification value, indicating good surfactant properties essential for demulsifiers. The effectiveness of the formulated emulsion breaker was tested on crude oil emulsions from two oil fields (Field X and Field Y) in Nigeria. The formulation had good ability to break both medium and high-density crude oil emulsions, especially for crude oil emulsions with lower viscosity and asphaltenes content. When compared to two commercial emulsion breakers, it was reported that NTLESESAD performed comparably well, but slightly lower than the commercial alternatives. It achieved about 67% and 78% separation of the emulsion samples taken from the two fields, respectively. They concluded that NTLESESAD provides an eco-friendly and cost-effective alternative to synthetic demulsifiers.

In an earlier study by the potency of coal fly ash (CFA) as a demulsifier for water-oil emulsion was investigated [19]. At room temperature, the addition of CFA led to the separation of the water from the oil phase. The highest separation rate of about 96.7% was achieved with concentrations of about 7% CFA in the emulsion. Elevated temperatures improved the efficiency of separation, producing clearer separated water.

Rice Husk Waste Oils

Evaluated the performance of a bio-based emulsion breaker made from waste brown oil of rice husks [20]. The bio-demulsifier was extracted from rice husks using a reflux method with ethanol and n-butanol. The waste brown oil extract was reported to contain significant amounts of fatty acids, including octadecanoic acid and n-hexadecanoic acid, known for their surface-active properties. The performance of the bio-demulsifier was compared with a chemical demulsifier and it was reported that it achieved 85.6% water separation compared to 80.2% achieved by the chemical demulsifier. The effect of temperature, volume, and time was also investigated. Higher temperatures significantly improved separation, while higher demulsifier volume may lead to diminishing returns due to oversaturation. Longer separation times allowed more water to coalesce and separate from the oil phase, improving the overall efficiency.

Lotus Leaf Extracts

Used hydrothermally treated lotus leaf (HLLF) to treat water-in-oil emulsions. HLLF was tested on crude oil emulsions from two different oil fields and was reported effective in breaking both types [21]. They explained that the unique micro-nano structure and wettability of the HLLF helped break the rigid interfacial film that stabilized the emulsion. The demulsifier migrates to the water-oil interface, replacing natural surfactants (like asphaltenes), reducing interfacial tension, and promoting the coalescence of water droplets. Higher temperatures improved demulsification, and at an optimal dosage of 1000mg/L and a settling time of 90 minutes, 88.17% water separation was achieved.

Natural Rocks as Demulsifiers

Used alginite, a natural rock in Hungary, for breaking water-in-oil emulsions [22]. The potential of alginite was tested on a water-oil emulsion composed of 50% Brent crude oil and 50% brine. The study found that 0.5 wt% alginite in the emulsion led to rapid demulsification with water content in the oil phase reducing to less than 1% within 2 hours. They explained that alginite contains organic kerogen and carbonates, which weaken the stability of the emulsion by adsorbing natural emulsifiers like asphaltenes and resins, leading to coalescence of water droplets. Water removal efficiency of 98% was reported. This feat is superior to common demulsifiers like polyethylene glycol and polypropylene glycol.

Table 3: Comparison of Chemical vs. Natural Demulsifiers

Parameter	Chemical Demulsifiers	Natural Demulsifiers	References
Separation Efficiency	High (80-95% water separation)	Variable (35-90% depending on type)	[14,19,20]
Separation Time	Minutes to hours	Hours to days	[10,12]
Optimal Concentration	Low (10-500 ppm)	High (500-2000 ppm)	[4,17]
Temperature Sensitivity	Effective at 50-70°C	Often require >60°C for good performance	[1,15]
Environmental Impact	Potentially toxic, slow degradation	Biodegradable, low toxicity	[3,18]
Cost	Moderate to high	Generally lower raw material cost	[5]
Industrial Scalability	Well-established	Limited by production capacity	[6,20]
Mechanism of Action	Disrupt interfacial films via surfactant action	Replace natural surfactants at the interface	[2,21]
Best Application	Tight emulsions, high-throughput systems	Loose emulsions, eco-sensitive areas	[8,22]
Current Limitations	Environmental concerns	Variable performance, scaling challenges	[11,16]

Conclusion

Crude oil-water emulsions, stabilized by natural surfactants like asphaltenes and resins, present significant challenges in the petroleum industry. Chemical demulsifiers, including surfactants and polymers, are highly effective and widely used but pose environmental risks. Natural demulsifiers derived from plant extracts, waste oils, and biopolymers offer eco-friendly alternatives, with some demonstrating comparable or superior performance under specific conditions. However, natural demulsifiers often require higher concentrations and longer settling times, limiting their industrial applicability. The choice of demulsifier must consider emulsion characteristics, operational conditions, and environmental impact. While chemical demulsifiers remain the industry standard, the growing emphasis on sustainability underscores the need for further development of natural alternatives.

Recommendations

This research direction will bridge the gap between laboratory findings and industrial adoption, paving the way for sustainable solutions in crude oil emulsion treatment. However, the following recommendations are made

- **Industrial Validation:** Conduct studies under real industrial conditions to assess the scalability and performance of natural demulsifiers in high-throughput settings.
- **Optimization:** Explore formulations that combine natural and chemical demulsifiers to enhance efficiency while minimizing environmental impact.
- **Novel Materials:** Investigate new natural sources, such as agricultural by-products or microbial extracts, for demulsification potential.
- **Mechanistic Studies:** Deepen understanding of the interactions between natural demulsifiers and interfacial films to improve design and application.
- **Economic and Environmental Analysis:** Evaluate the cost-effectiveness and lifecycle environmental impact of natural demulsifiers compared to synthetic options.
- **Advanced Technologies:** Integrate emerging technologies like nanotechnology or hybrid methods (e.g., electro-chemical) to enhance demulsification efficiency.

References

1. Raya SA, Saaid IM, Ahmed AA, Umar AA (2020) A critical review of development and demulsification mechanisms of crude oil emulsion in the petroleum industry. Journal of Petroleum Exploration and Production Technology 10: 1711-1728.
2. Yonguep E, Kapiamba AF, Kabamba KJ, Chowdhury M (2022) Formation, stabilization and chemical demulsification of Crude oil-in-water emulsions: A review. Petroleum Research 7: 459-472.
3. Halim NH, Saaid IM, Panuganti SR (2023) Demulsifier selection guideline for destabilizing water-in-oil emulsion for both non-EOR and EOR applications. Substantia 7: 21-33.
4. Al Sabagh AM, Kandile NG, Noor El Din MR (2011) Functions of demulsifiers in the petroleum industry. Separation Science and Technology 46: 1144-1163.
5. Kokal S (2005) Crude-oil emulsions: A state-of-the-art review. SPE Production & Facilities 20: 5-13.
6. Alao KT, Alara OR, Abdurahman NH (2021) Trending approaches on demulsification of crude oil in the petroleum industry. Applied Petrochemical Research 11: 281-293.
7. Saad MA, Yunus RM, Ali HS (2020) An overview of recent technique and the affecting parameters in the demulsification of crude oil emulsions. IOP Conference Series: Material Science and Engineering 991: 012105.
8. Rajamanickam K (2021) Technologies involved in the demulsification of crude oil. IntechOpen http://dx.doi.org/10.5772/intechopen.99743.
9. Abdurahman H, Nour RMY, Zulkify J (2007) Chemical Demulsification of Water-in-Crude Oil Emulsions. Journal of Applied Sciences 7: 196-201.
10. Nuraini M, Abdurahman HN, Kholijah AMS (2011) Effect of chemical breaking agents on water-in-crude oil emulsion system. International Journal of Chemical and Environmental Engineering 2: 250-254.
11. Zadymova NM, Skvortsova ZN, Traskin VY, Mironova ME (2016) Heavy oil as an emulsion: Composition, structure and rheological properties. Colliodal Journal 78: 735-746.
12. Peretomode JE (2018) Demulsification of Crude Oil Emulsion Using Xylene, Polyhydric Alcohol (Glycerol), and Triethanol Amine (TEA). Journal of Agriculture and Food Environment 5: 68-75.
13. Saat MA, Chin LH, Wong CS (2020) Treatment of crude oil emulsion suing coconut oil and its derivatives as green demulsifiers. Materials Today: Proceedings.
14. Biswadeep P, Kumar R, Tarun KN (2021) Demulsification of crude oil water emulsions using a naturally formulated demulsifier. Petroleum Science and Technology https://www.researchgate.net/profile/Biswadeep-Pal-2/publication/355157089_Demulsification_of_crude_oil-water_emulsion_using_naturally_formulated_demulsifier/links/63046ef2eb7b135a0e55996c/Demulsification-of-crude-oil-water-emulsion-using-naturally-formulated-demulsifier.pdf.
15. Turki MAJ, Awad SH, Ibrahim KS (2022) Synthesis and characterization of new demulsifiers from natural polymer. Chemical Methodologies 6: 649-660.
16. Oyedeji FO, Nwode MC (2018) Effect of some citric juice concentrates on crude oil emulsion. Journal of Petroleum Technology and Alternative Fuels 9: 7-13.
17. Victor Oji CO, Chukwu UJ, Akaranta O (2021) Evaluation of triethanolamine-cashew nutshell liquid derivatives as crude oil emulsion breakers. Applied Petrochemical Research, https://doi.org/10.1007/s13203-021-00273-z.
18. Azubuike AA, Itohan E (2021) Prospects of breaking crude oil emulsions using demulsifier formulated from Nicotiana tabacum seed oil, leaf extracts and stalk ash extracts. Petroleum Science Engineering 5: 44-53.
19. Adewumi AA, Kamal MS (2019) Performance Evaluation of Fly Ash as a Potential Demulsifier for Water-Crude-Oil Emulsion Stabilized by Asphaltenes. November 2019 SPE Production & Operations 821-829.
20. Okoro EE, Nnaji CG, Sanni SE, Ahuekwe EF, Igwilo KC (2020) Evaluation of naturally derived waste brown oil extract for demulsification of crude oil emulsion. Energy Exploration and Exploitation 38: 905-922.
21. Ye F, Mi Y, Liu H, Zeng G, Shen L, et al. (2021) Demulsification of Water-in-Crude Oil Emulsion Using Natural Lotus Leaf Treated via a Simple Hydrothermal Process. Fuel 295: 120596.
22. Hippmann S, Ahmed SS, Frohlich P, Bertau M (2018) Evaluation of a Naturally Derived Waste Brown Oil Extract for Demulsification of Crude Oil Emulsion. Colloid and Surfaces A: Physicochemical and Engineering Aspects. https://doi.org/10.1016/j.colsurfa.2018.05.031.