Laboratory Evaluation of Red Onion Skin and Orange Mesocarp Extracts as Oilfield Emulsion Breakers

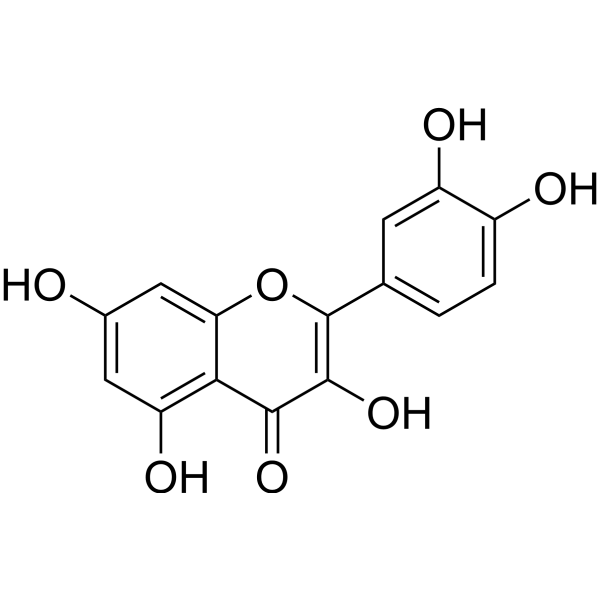
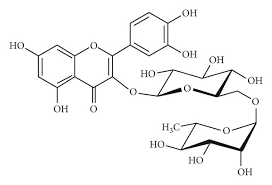
**Abstract**

Oilfield emulsions, particularly water-in-oil types, pose significant processing challenges. The efficient resolution of these emulsions is essential for enhancing crude oil quality, minimizing production losses, and meeting regulatory standards in the oilfield industry. Conventional demulsifiers, often synthetic, pose environmental risks, and natural extracts like red onion skin and orange mesocarp offer a sustainable alternative. This study evaluates the potential of red onion skin extracts (ROSE) and orange mesocarp extracts (OME) as bio-based emulsion breakers under controlled laboratory conditions. Both extracts were assessed for water separation efficiency via bottle testing under various conditions. The physicochemical properties of the crude oil and seawater samples were characterized to simulate oilfield conditions. ROSE demonstrated comparable and, in some cases, superior performance relative to a commercial demulsifier at optimal conditions (70°C and 80% water content). These findings support the adoption of environmentally friendly alternatives in the petroleum industry.

**Introduction**

Emulsions in crude oil production pose significant challenges, necessitating effective demulsification methods. These emulsions, typically water-in-oil (W/O), can adversely affect production efficiency, reduce pipeline flow, increase processing costs, and pose significant challenges in separating oil and water. To address these issues, emulsion breakers, also known as demulsifiers, destabilize and break the emulsions, facilitating phase separation. Traditionally, synthetic chemical demulsifiers have been widely used due to their efficiency and rapid action. These chemicals, though efficient, have raised environmental concerns due to their toxicity, low biodegradability, and potential harm to aquatic and terrestrial ecosystems, which have prompted a shift toward exploring greener alternatives1.

Demulsifiers are typically categorized into four main groups: polymers, amines, alcohols, and polyhydric alcohols. Polymeric demulsifiers are particularly effective for water-in-oil emulsions, while the other types are more suitable for oil-in-water emulsions2. Developing sustainable, cost-efficient, and ecologically friendly demulsifiers remains a critical area for future research in the oil industry. Recent research has explored the potential of plant-based extracts as eco-friendly demulsifiers for crude oil emulsions. Studies have investigated various plant sources, including *Nicotiana tabacum*3, *Calotropis procera*, *Citrus limonum*, *Jathropha curcas*, and *Thevetia ferifolia*4. These natural extracts contain hydrophilic and hydrophobic components, effectively breaking down emulsions3. Researchers have also developed novel green demulsifiers through the esterification of fatty acids, demonstrating excellent surface-active properties and demulsification efficiency comparable to commercial products5. The performance of these plant-based demulsifiers is influenced by factors such as temperature, concentration, pH, and settling time4,6. While some plant-derived demulsifiers have shown promising results, their effectiveness may still be lower than conventional chemical demulsifiers in some instances4. Nevertheless, these green alternatives offer environmental benefits by reducing toxicity and improving biodegradability7.

**a.**  **b.**

**Figure 1:** Structure of Quercetin (left) and Rutin (right)

Red onion (*Allium cepa*) skin and orange (*Citrus sinensis*) mesocarp are two agricultural by-products that have shown considerable promise in various applications due to their rich phytochemical content. The outer skins of onions, including red onions, and the mesocarp of orange are often considered waste material in the food industry. The extract, derived from these outer layers, contains compounds such as phenolics, flavonoids, and antioxidants, which may contribute to its potential applications as an emulsion breaker in the oil industry8,9,10. These compounds, especially quercetin and its derivatives, exhibit various biological activities such as antioxidants, anti-inflammatory, anti-diabetic, and anti-cancer properties11,12. Red onion skin extract (ROSE) and Orange mesocarp extract (OME) have shown promise as natural surfactants for enhanced oil recovery, demonstrating compatibility with reservoir conditions and effective heavy oil displacement13-15.

Recent research highlights the growing interest in biobased chemicals as sustainable alternatives to petroleum-based demulsifiers in oilfield operations. These green demulsifiers offer environmental benefits, including reduced carbon footprint and improved biodegradability16. Natural sources like cashew nutshell liquid derivatives have shown promise in formulating effective green demulsifiers for water-in-crude oil emulsions17-20. A study on Sesamum indicum-based demulsifiers demonstrated excellent performance, achieving 85 % efficiency within 10 minutes and 100 % efficiency in 60 minutes at 70 °C, outperforming commercial alternatives21. Factors affecting demulsification include settling time, temperature, and demulsifier concentration. Despite the advantages, challenges remain in scaling production, ensuring cost-competitiveness, and addressing regulatory considerations1. Ongoing research focuses on improving the efficacy and applicability of biobased chemicals in oilfield production processes, promoting a more sustainable approach to oil and gas production. Recent studies have also explored environmentally friendly alternatives to conventional chemical demulsifiers for breaking oil-water emulsions. Plant extracts and bio-based surfactants have shown promise as green demulsifiers, with some outperforming commercial chemical options7, 13-15, 22. A waste brown oil extract demonstrated superior demulsification efficiency compared to a chemical demulsifier, achieving 85.6% water separation under optimal conditions22. Bio-demulsifiers derived from sources like soapwort, coconut betaine, and lauryl glucoside have been evaluated for their effectiveness in breaking water-in-oil emulsions23. Additionally, red onion skin extract (ROSE) and its chemically modified derivative have shown potential as scale inhibitors24, biomass-based enhanced oil recovery agents, and surface-active agents for tertiary oil recovery, with the modified ROSE exhibiting superior performance in hard brine conditions13-14. These studies highlight the growing interest in sustainable, eco-friendly alternatives for oilfield applications.

While previous studies on emulsion breakers have been conducted, a research gap exists in the use of orange mesocarp extracts. Thus, this study aims to fill this gap by evaluating the potential of Red Onion Skin and Orange Mesocarp Extracts and their benzoate-modified derivatives as Oilfield Emulsion Breakers and bio-based demulsifiers under controlled laboratory conditions. The performance of these extracts will be compared to conventional synthetic demulsifiers by examining key parameters such as separation efficiency, rate of demulsification, and dosage requirements.

The novelty of this study lies in the use of bio-based extracts, especially orange mesocarp extracts, which have not been extensively studied for this purpose. The findings of this study could have significant implications for the oil and gas industry by introducing a more sustainable and environmentally friendly approach to emulsion management, minimizing waste handling costs, and contributing to the circular economy by creating value from agricultural residues.

1. **Experimental**

2.1. ***Materials***

Red onion skin (ROS) and orange mesocarp were sourced locally from Oil mill market located 4.8585 ˚N, 7.0648 ˚E in Obio-Akpor Local Government Area of Rivers State, Nigeria. Analytical-grade reagents such as sodium hydroxide and sodium benzoate were purchased from local suppliers and used as received without further purification. Some equipment/apparatus used include a Fourier transform infrared (FTIR) spectrometer, conductivity meter, pH meter, thermostatic water bath, emulsion homogenizer, glassware, and demulsification test bottles.

2.2. ***Methodology***

The study was conducted in the following sequence: agro-waste collection (Red onion Skin; ROS, and Orange Mesocarp; OM), biomass preparation and extraction, characterization of the extracts (Red onion Skin Extract; ROSE, and Orange Mesocarp Extract; OME), crude oil and seawater sampling, emulsion preparation, demulsifier formulation, demulsifier evaluation, and comparative evaluation of the formulated demulsifier with a commercial demulsifier via static bottle test.

2.1. *Biomass Preparation, Extraction and Characterization*

Red onion skin (ROS) and Orange mesocarp (OM) were sorted, cleaned, oven-dried at 40 ℃ for 3 hours, ground to fine powder, labeled, and stored in airtight containers before extraction. A 1 % stock solution of sodium hydroxide (NaOH) was prepared to extract the phytochemicals in ROS and OM at ambient temperature. Pre-weighed amounts of ground ROS and OM were macerated for 24 hrs in 1 % NaOH solution with intermittent agitation. The solutions were vacuum-filtered, and the resultant filtrate was labeled “ROSE” and “OME” respectively. A portion of these extract solutions was separated, and 1g of sodium benzoate was added to the ROSE and OME solutions and labeled “ROSE-NaB” and “OME-NaB,” respectively. The extracts were characterized using an Agilent Fourier transform infrared (FTIR) spectrophotometer scanning in the 4000 – 1000 cm-1 range.

2.2. *Crude oil and Sea water Characterization*

Medium-heavy crude oil was sampled from the Agbada flow station, labeled accordingly, and dispatched to the laboratory for further analysis. Seawater was sampled from the Gulf of Guinea in the Niger Delta region, labeled accordingly, and dispatched to the laboratory for further analysis.

2.3 *Emulsion Preparation and Bottle Tests*

Laboratory-simulated crude oil emulsions of varying crude oil to seawater mixing ratios of 80:20 and 60:40, respectively, were prepared according to the method described by Attah *et al.*25,26. Crude oil was stirred at an ambient temperature of 25 ℃ at high speed using a commercial mixer for 30 minutes with the gradual addition of seawater until both phases became homogenized. Bottle tests were used to assess the efficiency of the demulsifier formulations, ROSE, ROSE-NaB, OME, and OME-NaB, respectively, as described in Al-Sabagh *et al.*27 and Victor-Oji *et al.*18-19. The simulated crude oil emulsions were transferred into graduated 100 ml rubber stoppered demulsification bottles and dosed with the formulated demulsifiers at 1 % w/v, 0.50 % w/v, 0.33 % w/v, 0.25 % w/v, 0.20 % w/v concentrations respectively. A blank was used for each set of experiments. The pre-dosed emulsions were agitated 100 times in a ‘to’ and ‘fro’ motion, placed in a thermostatic water bath set at 70 ℃, and the water drop-out was observed for an initial 5 minutes and subsequently at intervals of 10 minutes for 180 minutes. The demulsifier efficiency was evaluated based on the water separation rate, interfacial layer quality, and water separation volume. The percentage of water drop-out was estimated using the equation below:

1. **Results and Discussion**

*3.1 Physicochemical Characterization of Crude Oil and Seawater Samples*

Tables 1 and 2 show key physicochemical properties of the crude oil and seawater samples used in this study. The crude oil sample had a specific gravity of 0.9065 and an API gravity of 24.59, indicative of medium crude oil. It also had a low sulfur content, 0.308 %, and a minimal water cut of -0.15 %.

**Table 1:** Physicochemical Characterization of the Crude Oil Sample

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Method** | **Value** |
| Specific Gravity (60/60ºF) | ASTM D 1298 | 0.9065 |
| API Gravity at 60ºF | ASTM D 1298 | 24.5949 |
| Kinematic Viscosity at 40℃ (c.St) | ASTM D 455 | 13.75062 |
| Water cut (%) | ASTM D 4006 | 0.15 |
| Sulphur content (wt.%) | ASTM D 4292 | 0.30818 |
| Base, Sediment, and Water (%) | ASTM D 4007 | 0.025 |
| Pour Point (℃) | ASTM D 5853 | >-50 |

The seawater sample pH is mildly acidic. The salinity value, which gives the extent of dissolved salt in the water sample, is approximately 35931.12 ppm. This lies within the salinity range for seawater, 32000 - 37000 ppm, making it a good fit for emulsion preparation. The high salinity content acts as a stabilizer for the oil emulsion.

**Table 2:** Physicochemical Characterization of the Seawater sample

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Method** | **Seawater sample** |
| Total Dissolved Solids (ppm) | ASTM D 5907 | 32653 |
| Chloride content (mg/L) | ASTM D 4458 | 1.0189 |
| Density (g/ml) | ASTM D 1429 | 1.0189 |
| Salinity (ppm) | ASTM D 4458 | 35931.12 |
| Specific Gravity @ºF | ASTM D 1429 | 1.0189 |
| pH @ 25℃ | ASTM D 3875 | 8.18 |

*3.2 FTIR Characterization of ROSE and OME*

The formulated solutions were subjected to FTIR spectroscopic analysis to confirm the presence of appropriate functional groups. The FTIR spectra for red onion skin extract (ROSE), red onion skin sodium benzoate extract (ROSE-NaB), Orange Mesocarp extract (OME), and Orange Mesocarp-sodium benzoate extract (OME-NaB) are presented in Figures 2 to 7.

For ROSE, a broad absorption peak due to phenolic O–H stretch vibration was observed at 3265 cm−1, followed by absorption peaks at 2900 cm−1 and 1762 cm−1 due to aromatic C–H and C=O stretch vibrations, which are characteristic of quercetin structure. A mix of aryl conjugated C=C and C=O stretch vibrations were observed at 1620 cm−1 and 1562 cm−1 alongside medium absorption bands at 1462 cm−1 and 1443 cm−1, which match aromatic C=C and =C–H stretch vibrations, the bands observed at 1380 cm−1 and 1339 cm−1 correspond to a combination of aryl O–H deformation and C–O stretch vibrations28-29.



**Figure 2:** FTIR Spectrum of Red Onion Skin Extract (ROSE)



**Figure 3:** FTIR Spectrum of ROSE with Sodium Benzoate (ROSE-NaB)



**Figure 4:** StackedFTIR Spectrum of Red Onion Skin Extract (ROSE) and ROSE with Sodium Benzoate (ROSE-NaBen)

Expectedly, the spectra of the benzoate analog showed peaks in similar domains but with increased transmittance, indicating modification has occurred. For instance, a reduced intensity in transmittance of the C=O and aryl C-H peaks is observed in the spectrum of the ROSE-NaB derivative compared to ROSE. A stacked spectrum of ROSE and ROSE-NaB shown in Figure 4 explains this further29.



**Figure 5:** FTIR Spectrum of Orange Mesocarp Extract (OME)

The FTIR spectra for OME (Figure 5) showed an absorption peak at 3276 cm-1 due to the O-H vibration stretches of phenol and glycosidic sugar bonds. The band's frequency shows possible intermolecular hydrogen bonding. The sharp peaks observed at 1616 cm-1 and 1104 cm-1 can be attributed to the presence of -C=O and -C–O stretches in the quinone ring structure, as seen in the structure of OME15. A weak peak at 1371 cm-1 corresponds to the carboxylate ion, which gives rise to a weak symmetrical stretching band near 1400 cm-1 30. The absorption bands at 2824 cm-1 and 714 cm-1 reveal an out-of-plane deformation vibration stretch of methylene -C-H in various substituted benzene rings and the vibration associated with the C–C moiety, consistent with rutin31-32.



**Figure 6:** FTIR Spectrum of OME with Sodium Benzoate (OME-NaBen)

For OME-NaB, the spectra showed similar bands with slight shifts and increased intensity, indicating modification occurred. For instance, the absorption band ascribed to the carbonyl functional group in the spectrum of OME (1616 cm-1) appears to have shifted to higher wavenumbers (red spectra) in the spectra of the benzoate derivative. An observation that becomes more conspicuous in the stacked spectra (Figure 7).

*3.3 Performance Evaluation Test*

The demulsification potential of the formulated demulsifiers, ROSE, OME, ROSE-NaB, and OME-NaB, were evaluated and compared to that of a commercial demulsifier. The data plots in Figures 8 to 19 illustrate the effect of concentration (0.2 %w/v to 1 %w/v), water content (80 % and 60 %), and modification at a constant temperature of 70 ℃ for a contact time of 180 mins (3 hours) on their water separation efficiency.



**Figure 7:** StackedFTIR Spectrum of Orange Mesocarp Extract (OME) and OME with Sodium Benzoate (OME-NaB)

* + 1. *Concentration effect*

The concentration of a demulsifier in an emulsion governs adsorption at the interface33. Several sets of experiments were carried out across a range of demulsifier concentrations: 1 % w/v, 0.5 % w/v, 0.33 % w/v, 0.25 % w/v, and 0.2 % w/v, to evaluate its impact on the demulsification process. The water separation data plots show that increasing demulsifier concentration for the formulated emulsion breakers increased water separation efficiency, thus aligning with the findings of the literature34.

ForROSE, the data plot in Figures 8 and 9 reveal that as concentration increases (0.2 % to 1 % w/v), the water separation efficiency improves significantly, with higher concentrations (1 %w/v) leading to faster separation at optimal conditions of 70 ℃ and a contact time of 180 minutes.

**Figure 8**: Water Seperation Plot of ROSE at 80 % Water Content and 70℃

**Figure 9**: Water Seperation Plot of ROSE at 60 % Water Content and 70℃

**Figure 10**: Water Seperation Plot of ROSE-Benzoate at 80 % Water Content and 70℃

**Figure 11**: Water Seperation Plot of ROSE-Benzoate at 60 % Water Content and 70℃

In ROSE-NaB (shown in Figures 10 and 11), this modified formulation achieves superior performance compared to ROSE, especially at concentrations above 0.5 % w/v, due to enhanced destabilization of water-in-oil emulsions arising from the synergetic effect of sodium benzoate. This is because sodium benzoate's surface-active properties seem to improve coalescence by facilitating the aggregation of water droplets, thus leading to faster water drop-out, as highlighted in studies on demulsifier performance35-36. Like ROSE, OME (shown in Figures 12 and 13) displays better separation efficiency at higher concentrations, but the increase in water drop-out levels off beyond 0.2 % w/v suggesting saturation.

**Figure 12**: Water Seperation Plot of OME at 80 % Water Content and 70℃

**Figure 13**: Water Seperation Plot of OME at 60% Water Content and 70℃

**Figure 14**: Water Seperation Plot of OME-Benzoate at 80% Water Content and 70℃

Figures 14 and 15 show that OME-NaBenzoate exhibits the highest efficiency overall among the formulations. The observed increased water dropout with demulsifier concentration mirrors that of ROSE-NaBenzoate.

**Figure 15**: Water Seperation Plot of OME-Benzoate in NaOH at 60% Water Content and 70℃

**Figure 16:** Water Seperation Plot of Commercial Demulsifier/NaOH at 80% Water Content and 70℃

**Figure 17**: Water Seperation Plot of Commercial Demulsifier at 60 % Water Content and 70℃

**Figure 18**: Water Seperation Plot of Commercial Demulsifier-Benzoate at 80% Water Content and 70℃

**Figure 19**: Water Seperation Plot of Commercial Demulsifier-Benzoate at 60% Water Content and 70℃

The commercial demulsifier, though effective across all tested concentrations, as shown in Figures 16 to 19, was outperformed by the sodium benzoate-modified formulations (ROSE-NaB and OME-NaB) at higher concentrations (≥ 0.5 % w/v). In comparison, data showed that OME-NaB was the most effective in its overall high water drop-out rate, and ROSE was the least effective across the formulated demulsifier types. The studied demulsifiers were ranked; thus, OME-NaB > ROSE-NaB > Commercial demulsifier-NaB > Commercial demulsifier/NaOH > OME > ROSE for concentration effect.

* + 1. *Effect of Water Content*

Water content plays a crucial role in demulsiﬁer performance. This study utilized laboratory-simulated crude oil emulsions with 80 % and 60 % water content to evaluate the demulsification efficiency of the formulated demulsifiers. Water seperation plots (Figures 8 to 19) show that ROSE was less effective at 80 % water content than at 60 %, likely due to its hydrophobic nature, which limits its interaction at the water-oil interface. A similar trend was observed for OME (Figure 12). However, it exhibited a more significant water drop-out than ROSE at 80 % water content (Figure 13), suggesting better interfacial interaction due to its chemical structure. ROSE-NaB demonstrated improved separation efficiency at 80 % water content (Figure 10), outperforming the unmodified ROSE. OME-NaB consistently outperformed all formulations at 80 % and 60 %, achieving near-complete separation at shorter contact times for 60 % water content (Figures 14 – 15). The commercial demulsifier, though stable, was less adaptable to changes in water content compared to NaBenzoate-modified formulations.

The data confirms OME-NaB as the most effective demulsifier, achieving the highest water drop-out at higher water content, while ROSE was the least effective. Sodium benzoate alters the hydrophilic-lipophilic balance (HLB), making OME-NaB better suited for high water-cut emulsions37. This HLB optimization enhances the demulsifier affinity for the water phase, improving performance at 80 % and 60 % water content. Water seperation rates increased with higher water content because, at lower water content, water drop-out becomes more difficult due to increased interfacial film stability. At higher water content, the external pressure of the dispersed water phase decreases, leading to interfacial film thinning and improved coalescence17-19. Thus, the formulated demulsifiers were ranked as follows: OME-NaB > ROSE-NaB > OME > Commercial demulsifier-NaB > Commercial demulsifier/NaOH > ROSE, based on the water content effect.

* + 1. *Effect of Chemical Structure*

ROSE comprises a flavone backbone (quercetin) with five hydroxyl groups that enhance hydrogen bonding with the water phase, promoting water droplet coalescence. Its conjugated aromatic system increases lipophilicity, enabling interaction with the oil phase. However, its lipophilic nature results in poor water solubility, limiting its performance in high-water-content emulsions. In contrast, OME has two glycosyl units attached to the flavone backbone, increasing hydrophilicity and improving performance in water-rich emulsions while being slightly less effective in low-water-content emulsion systems. Sodium benzoate enhances the demulsification potential of ROSE and OME by increasing adsorption at the oil-water interface, accelerating water droplet destabilization. Its incorporation adjusts the hydrophilic-lipophilic balance (HLB), improving diffusion and interaction with the oil phase, thereby reducing seperation time. Unmodified ROSE and OME have limited oil solubility, whereas the benzoate modification enhances compatibility with the oil phase, making them more effective in high water-cut emulsions.

Water-in-oil emulsions are stabilized by electrostatic repulsion between droplets; NaBenzoate neutralizes these charges, promoting droplet coalescence. This synergy amplifies demulsification potential by improving solubility, dispersion, and diffusion rates at the water-oil interface, leading to faster seperation kinetics. Studies confirm that NaBenzoate-modified formulations achieve quicker and more efficient water seperation than their modified counterparts1,38-39. Overall, the superior performance of NaBenzoate-modified formulations is attributed to enhanced interfacial activity, reduced electrostatic repulsion, improved synergy, optimized HLB, and faster kinetics. These findings support the optimization of demulsifier formulations through chemical modifications. Thus, based on chemical structure, the formulated demulsifiers are ranked in effectiveness as follows: OME-NaB > ROSE-NaB > OME > ROSE.

1. **Conclusion**

This study evaluated the demulsification potential of ROSE, OME, ROSE-NaB, and OME-NaB in treating oil-in-water emulsion using laboratory-simulated crude oil emulsion, comparing their performance with a commercial demulsifier. Results indicate that increasing demulsifier concentration (0.2 %w/v to 1 % w/v) enhances separation efficiency in emulsions with 80% water content. Contact time had a minimal impact on demulsification performance across all concentrations. Higher water content in crude oil emulsions slows water separation due to increased thinning of the interfacial film. Structural differences among ROSE, OME, ROSE-NaB, and OME-NaB significantly influence their demulsification efficiency. NaBenzoate-modified formulations (ROSE-NaB and OME-NaB) demonstrated superior performance due to enhanced interfacial activity, optimized HLB, and ionic interactions, which improve water separation. Modification with sodium benzoate enhances interfacial adsorption, solubility, and charge neutralization, making OME-NaB and ROSE-NaB the most effective demulsifiers. Among all formulations, OME-NaB exhibited the highest water separation efficiency, comparable to commercial alternatives under optimal conditions. OME-NaBenzoate is a sustainable, non-toxic, less expensive, and renewable bio-based material. This study confirms the viability of red onion skin and orange mesocarp extracts and their modified versions, as eco-friendly oilfield demulsifiers. Adopting these bio-based solutions could improve the sustainability of oilfield operations. In conclusion, biobased demulsifiers present a promising, environmentally friendly alternative for the oil and gas industry, offering effective emulsion control while reducing reliance on petroleum-based emulsion breakers.

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