JJMIE

Volume 19, Number 4, Dec. 2025
ISSN 1995-6665
Pages 721– 731
https://doi.org/10.59038/jjmie/190403
Editor-in-Chief: Prof. Faris M. AL-Oqla

Jordan Journal of Mechanical and Industrial Engineering

Effect of Natural Demulsifier on the Efficiency of Ultrasonic Assisted Oil Emulsion Separation

Hind A. Sami*, Raheek I. Ibrahim, Manal K. Odah

Electromechanical Engineering Department University of Technology, Baghdad-Iraq.

Received 11 April 2025 *Accepted 8 September 2025*

Abstract

Heavy fuel oil is a complicated amalgamation typically formulated with saline water to produce stable emulsions. The coproduced water is emulsified as it traverses pipelines and choke valves, resulting in emulsions (termed water-in-oil emulsions) that can be stabilized by naturally occurring substances in heavy oil, including asphaltenes, resins, wax, and particulates. The presence of water in heavy fuel oil might result in pipe damage and elevate transportation expenses. A fuel oil emulsion consisting of 40% water and 60% oil was exposed to low-frequency ultrasonic waves (28 KHz) for 10 minutes to evaluate its effectiveness in emulsion separation. To improve separation performance, natural particles derived from date pit (approximately 10-100 μm) were included at concentrations of 3000, 5000, 10000, and 15000 ppm. Tests were performed at 85° C with ultrasonication power levels of 100, 400, 600, and 800 W, with treatment durations of 2, 4, 6, 8, and 10 minutes. Date pit powder effectively separates oil and water within 24 hours, demonstrating its utility in the rapid destabilization of water-in-oil emulsions due to its distinctive wettability and surface structure. Demulsification efficiency may attain 83% with a dosage of 10000 mg/L and a settling duration of 10 minutes at 85°C. The amalgamation of date pit particles and ultrasonic waves demonstrated a cost-effective, efficient, rapid, and ecologically friendly method for the separation of water-in-oil emulsions.

Keywords: Oil-water separation, Ultrasonic waves, Demulsification, Heavy fuel oil emulsion, Separation efficiency.

1. Introduction

A principal challenge in heavy oil production is the separation of water-in-oil (W/O) emulsions. Emulsified water not only increases the susceptibility of pipelines and equipment to corrosion[1], but also enhances the viscosity of heavy oil, resulting in energy loss during transportation. Demulsification can be achieved by many combinations of physical, chemical, or biological mechanisms, as is commonly acknowledged[2]. The heavy oil business extensively employs procedures such as demulsifier addition and electrostatic treatment. An appropriate demulsifier is often employed to facilitate the demulsification process[3]. The major purpose of the chemical additions is to destabilize the emulsifying agents. Demulsifiers enhance droplet coalescence in emulsions by adhering to and destabilizing the oil-water interface [4]. Mechanical demulsification entails using density disparities between the aqueous and oleaginous phases or disrupting physical barriers. Consequently, an efficient, economical, and environmentally benign demulsification technique is needed[5]. Consequently, the amalgamation of heavy oil and salty water must undergo demulsification, or division into two distinct phases, before the heavy oil is transported or processed [6].

Acoustic cavitation dynamics are used in ultrasonic emulsification processes. The formation, growth, and implosive collapse of tiny bubbles in a liquid media subjected to intense ultrasonic vibrations is known as acoustic cavitation. Due to the fact that the collapse of these bubbles results in large local pressure and temperature variations, the medium also alternately compresses and expands due to the propagation of ultrasonic waves[7]. This creates high shear forces, shock waves, and micro-jets that can break up large particles and agglomerates into smaller pieces. Despite the small displacement and velocity, the ultrasonic-induced media particle's motion shows a significant acceleration proportional to the square of the ultrasonic vibration frequency, sometimes exceeding tens of thousands of times the acceleration caused by gravity. This significant acceleration is enough to produce a noticeable mechanical effect in the medium, as illustrated in figure (1) [8].

Ultrasonic treatment, now the subject of substantial investigation, can alleviate the limitations inherent in traditional extraction methods such as solvent extraction, distillation, and pressing[10]. The basis of ultrasonic demulsification is as follows: increased droplet oscillation accelerates droplet collisions, facilitating their coalescence [11], while heat transfer from partial acoustic energy reduces emulsion viscosity and interfacial layer strength.

* Corresponding author e-mail: eme.22.45@grad.uotechnology.edu.iq.

Moreover, droplets might enhance the efficacy of coalescence by creating droplet bandings in ultrasonic standing waves (USWs) and aggregating directionally towards pressure nodes or anti-nodes [12].

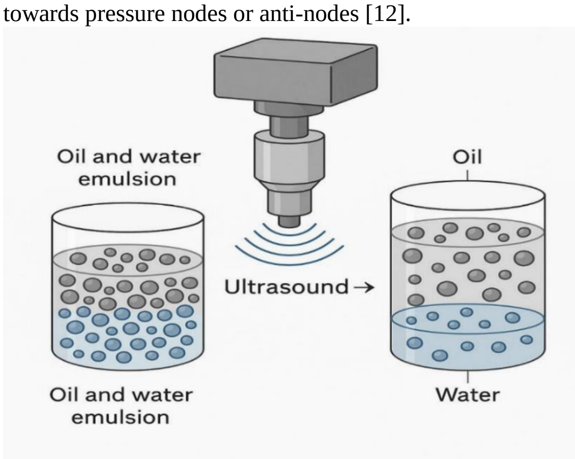

Figure 1. Mechanism of ultrasonic activity in emulsion separation[9].

Environmental and human health are jeopardized by oil pollution, especially with water emulsions. This is elucidated by the difficulty of collecting such little oil droplets [13]. Consequently, it is essential to continue investigating novel methodologies and procedures, efficient oil capture systems, and advanced wastewater treatment technologies, particularly for the separation of water and oil emulsions. Ultrasonic treatment is regarded as an effective technique for transforming residual oil, facilitating further processing in oil refineries. Furthermore, it consumes less energy while enhancing the outcomes of physicochemical processing [14]. Ultrasonic treatment is crucial for enhancing heavy molecules, since it induces thermal scission of bonds in heavy oil, resulting in the generation of hydrogen atoms. It is essential to pursue the exploration of more efficient solutions, potentially through the integration of various wettability types with suitable porous substrates, as prevalent methods, such as electroflotation and electrocoagulation, exhibit drawbacks including substantial material demands, costly apparatus, and elevated energy consumption [6].

According to Azubike et al. [15]conducted an assessment of the efficacy of demulsifiers derived from tobacco seed oil, leaf extracts, and stem ash in disrupting crude oil emulsions. Hydrophilic and hydrophobic demulsifier components were identified in the physicochemical properties of Nicotianatabacum seed oil, the phytochemical analysis of Nicotianatabacum leaf extracts, and the potash concentrations of Nicotianatabacum stalk ash extract. The properties of the formulated demulsifier are analogous to those of commercial demulsifiers. The outcomes of the bottle tests indicated that the demulsifier's formulation may disrupt medium- and high-density crude oil emulsions. The efficacy of the developed demulsifier was comparable to that of the commercial variants.Yuan et al. [16] synthesized an environmentally benign RHC-0.5 demulsifier by a simple one-step hydrothermal procedure employing rice husk (RH) as the principal ingredient. Characterization was performed via Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, field-emission scanning electron microscopy, energy dispersive X-ray spectrometry, and thermogravimetric analysis. A maximum DP of 95.01% was attained using 300 mg/L of RHC-0.5 at 70 °C overa duration of 10 minutes. Moreover, RHC-0.5 exhibited notable salt resistance, even at a salinity level of 40,000 mg/L. Furthermore, its DP was juxtaposed with those of commercial demulsifiers like SP169, CH-66, and AR-32. Parvasi et al. [17] demonstrated the impact of low-frequency ultrasonography on the demulsification process in a crude oil wastewater unit with a low crude oil concentration (500 mg/L). Subsequently, research has been conducted without chemical demulsifiers with a laboratory ultrasonic bath at frequencies of 25 kHz and 45 kHz. Perform experiments to assess the impact of wastewater temperature, ultrasonic power, frequency, and irradiation time on separation efficiency. The findings indicated that, under ideal conditions, the efficiency of crude oil emulsion separation improved by 72%.Nadirov et al. [18]performed a comparative analysis of the demulsifying efficacy of original and newly milled quartz (FMQ) particles derived from river sand, in the absence of an emulsifier. Alongside conventional solid-liquid characterization techniques, employ rheological measurements, surface tension assessments, and demulsification experiments to examine the impact of 75-micron mesh-sized quartz on emulsion stability. Following 100 minutes of deposition, a demulsification efficiency of 97% was achieved with the incorporation of 3 weight percent FMQ, in contrast to 140 minutes for unmodified quartz. The objective of grinding quartz is to enhance water permeability, hence elevating the local pH level, which results in decreased emulsion stability and eventual dissolution. Chen et al. [19]examined the impact of several operational factors, including acoustic power intensity, operating temperature, ultrasonic radiation duration, and chemical dispersant doses, on the extraction of water from crude oil by ultrasound. The optimal operating parameters for ultrasonic-assisted crude oil desalination were identified as follows: acoustic power intensity of 300 W, operating temperature of 90°C, ultrasonic irradiation duration of 75 minutes, and chemical demulsifier dose of 54 mg/L. Moreover, it was determined that temperature was the paramount operational parameter, succeeded by the intensity of acoustic power, the length of ultrasonic irradiation, and the quantities of chemical demulsifiers. Sadighian et al. [20] produced ecologically benign demulsifiers for the disruption of water-in-oil (W/O) emulsions, employing click chemistry to develop new and versatile derivatives of imidazolium ionic liquids (ILs) including a triazole moiety [SIm-TazCn][Br]. The bottle test was employed to assess the impact of each demulsifier's type and concentration on phase separation and dehydration efficiency (DE). The CEL[SIm-TazC6][Br] derivative at 4000 ppm exhibited a satisfactory DE of 79% after 5 minutes, increasing to 82% after 24 hours, according to the bottle test results. The interfacial tension (IFT) of the derivatives was evaluated at different concentrations. After 24 hours, CEL[SIm-TazC6][Br] with a shorter alkyl chain at 4000 ppm exhibited the lowest interfacial tension value of 16.3 mN/m. The collaboration of imidazolium and triazole moieties significantly enhanced the demulsification of W/O emulsions by the environmentally friendly and efficient CEL-based surfactants. Abdullah et al.[21] concentrated on employing oleic acid (OA), a readily available natural compound, to synthesize two innovative ionic liquids (ILs) and apply them to disrupt water-in-oil (W/O) emulsions. EAPA-IL and EATA-IL exhibited effective performance, achieving 100% across several concentrations of demulsifier. The results indicated that as their focus increased over time, their performance also improved. Furthermore, pure water was isolated using EAPA-IL and EATA-IL. Qian et al. [22]employed a straightforward two-step procedure to effectively produce two ionic liquid demulsifiers, PEDA-Br and GEDA-Br. The objective was to enable the efficient and successful treatment of water-in-oil emulsions at low temperatures. Nuclear magnetic resonance hydrogen spectra (1H NMR) and Fourier-transform infrared spectroscopy (FT-IR) were employed to characterize the structure of the demulsifiers. Their demulsification efficiency (DE) in water-in-oil (W/O) emulsions was subsequently evaluated by bottle tests. The results indicated that after two hours, at a temperature of 50 °C and a concentration of 500 mg/L, GEDA-Br achieved a DE of 98.92%. Moreover, at a salinity concentration of 10,000 mg/L, both PEDA-Br and GEDA-Br had DE values above 95%, and both shown effectiveness throughout a broad pH range of 4 to 12. Mirzadeh et al. [23] examined the determinants influencing the variables of the dual-component demulsifier formulation. The efficiency of five demulsifier combinations with identical surfactant coefficients was assessed using the hydrophilic-lipophilic deviation concept. The effect of including alcohol (c-butanol) on the separation of water in crude oil emulsions was evaluated. The combination of lauryl-myristyl-alcohol-3ethoxylate (KELA3) and sodium dodecyl sulfate (SDS) exhibited the maximum water separation efficiency at 75%, as per the data. The second segment was to evaluate the predictive usefulness of the HLD-NAC (network average curvature) model regarding the demulsification performance of heavy crude oil emulsions in surfactant and oil-water systems containing different salts. Mi et al.[24]introduced an environmentally benign ionic liquid emulsion, cotton cellulose-dodecylamine (CCDA), with exceptional demulsification efficiency at low concentrations. Dodecylamine was utilized to hydrophobically modify natural cotton, resulting in CCDA. FT-IR, 1H NMR, 13C NMR, and SEM were utilized to analyze the chemical structure and surface morphology. The demulsification studies demonstrated that CCDA-6 exhibited remarkable salt tolerance, achieving an oil removal rate of 99.78% and a light transmittance of 87.56% at a concentration of 20 mg/L. The studies demonstrate that CCDA-6 facilitates electrostatic neutralization and replaces natural surfactants at the interface to improve demulsification. Thus, CCDA-6 has considerable potential for the remediation of oily wastewater and introduces a novel method for using biomass materials in demulsification. The objective of this study is to devise an eco-friendly method utilizing low-frequency ultrasonic waves to inhibit emulsions, aided by inexpensive and locally sourced date pits particles. The influence of operational factors is a critical factor in ultrasonication demulsification. The research enhances separation efficiency by developing more effective procedures in petroleum processing, so facilitating future inquiries into other factors that may positively impact this process. The study examines the impact of sonication duration and intensity, with date pits content, on the separation of W/O emulsions.

2. Materials and Methods

2.1. Heavy FulOil (HFO):

Heavy fuel oil is a kind of fuel oil distinguished by a viscosity akin to that of tar. HFO comprises the byproducts from petroleum sources after the extraction of superior-quality hydrocarbons by techniques like thermal and catalytic cracking [25]. HFO is characterized by its physical, processing, and end-use properties owing to its diverse makeup. HFO, the ultimate output of the cracking process, consists of varying mixes of chemicals, including paraffins, cycloparaffins, aromatics, olefins, asphaltenes, and molecules containing sulfur, oxygen, nitrogen, and/or organometals[26].

The Daura refinery in Baghdad, Iraq, which generated water-in-oil emulsions, supplied the heavy fuel oil emulsion apparatus utilized in this investigation. The physical characteristics of this oil are presented in Table 1.

Table 1. Physical Characteristics of Basra Heavy Oil. Al-Doura Refinery.

Heavy fuel oil properties	
sp. gr at 15.6 ºC	0.8724
API at 15.6 ºC	15.8
Density at 15 ºC (g/Cm^3)	0.9657
Kinematc Viscosity at 50ºC cst (mm^2/s).	183
Pour point ºC	+3
Carbon residue %w/w	8.1
Sulfur content %w/w	4.5
Water & sediment %v/v	<0.025
Asphaltenes content (wt %)	3.09%
Calorific Value (gross) Keal/kg	10441

2.2. Salt Water:

This study employed natural water (tap water). A certain volume of sodium chloride solution (5500 ppm) was mixed with various prepared samples in 100 ml beakers containing 40% water. Table (2) delineates the water parameters[27].

Table 2. Physical characteristics of water.

water properties	
Physiologic (pH)	9.8
Electrical conductivity (EC)	3460 µs/cm
Temperature ºC	Between 20 and 25°C
Viscosity at 25°C	mPa/s

2.3. Natural Demulsifier:

The natural material employed in the separation process is date pits with a particle size of around 10-100 µm. The date pits were extracted, purified, dehydrated, and sun-dried for one week. The specimens were then placed in an electric oven at 80°C and ground using a 1000-watt grinder.

2.4. Experimental Apparatus:

The Lab Scale Ultrasonic Probe Sonicator (HC-SG-28800). The main components of the ultrasonic vibrating rod are the ultrasonic transducer, ultrasonic horn, and ultrasonic generator. The features of the ultrasonic apparatus used in the experiment are listed in Table 3.

Table 3. specifications of the ultrasonic machine

Specifications	Value
Type	HC-SG-28800
Input voltage	220V 50-60 Hz
Frequency	28 kHz
Rated power	100-400-600-800 W
Power adjustment	50-100% gear adjustable
Working ambient temperature	+5 to +50℃
Tool head material	Titanium alloy
Length of the tool head	182 mm
Maximum operating temperature	150 degrees
Weight	16 Kg
Power supply size	380×285×135 mm
Real-time display	Resonance, current
Cooling device	Transducer fan cooling
Connecting length	5 m
Reference processing capacity	1000

2.5. Emulsion Preparation:

Samples were produced using a rigorous technique to ensure experimental uniformity and reproducibility of results. Experimental reactors consisted of pristine 100-ml glass beakers. A 40% brine and 60% oil combination by volume formed a biphasic system that replicates actual separation circumstances. The components were carefully mixed using a magnetic stirrer to ensure equal dispersion before ultrasonication. All preparations were executed under controlled settings to ensure repeatability and analytical accuracy[27].

Figure 2 illustrates the process of applying ultrasonic waves to petroleum emulsions within a 300 ml beaker. Following separation, the water content is expelled into a 500 ml conical flask via a controlled tap located at the base of a borosilicate glass 500 ml conical separatory funnel.

To ensure the stability of the emulsion, the containers holding the oil/water emulsion were let to rest for a full day before being allocated for each experiment. A measurement is acquired following the exposure of the materials to ultrasonography and a subsequent five-minute interval. The initial water content in the emulsion before ultrasound (IWC) and the final water content after ultrasonic exposure (FWC) were used in determining the demulsification efficiency (ED) for each experiment where water-emulsion separation was achieved. The subsequent equation was employed to do this:

$$ED\% = (I\_WC - F\_WC)/I\_WC \times 100 \qquad (1).[28]$$

Where:

I_WC: The emulsion's initial water content prior to ultrasonography.

F_WC: The ultimate water content measured during ultrasonic exposure.

Cannon-Fenske-Routine Viscometer was used to determine the kinematic viscosity of heavy oil. The relationship applied to calculate the kinematic viscosity is

$$\nu = K \times t \qquad (2)[29]$$

The instrument constant k refers to the timing marks during the visual survey of the meniscus passage.

It comes to: $k=0.02688$ 〖mm〗$^2/S^2$.

3. Result

In this study, date pit particles of different concentrations (3,000, 5,000, 10,000, and 15,000 ppm) were incorporated into the emulsion at 85°C with an operating frequency of 28 kHz. The results demonstrate the effect of these concentrations on demulsification efficiency when ultrasonic was employed in conical glass reactors. The separation efficiency improved with increasing date pit content, attaining an 83% water removal rate from the emulsion at 10,000 ppm, especially when subjected to ultrasonic treatment. The separation efficiency varied at different concentrations, indicating an interaction between the applied energy level and the amount of additive. Furthermore, it was shown that ultrasound-induced friction increased the emulsion temperature with prolonged processing time, hence facilitating the separation process. Experiments demonstrate that with increased energy levels, the separation process speeds; nevertheless, more explanations have been conducted to understand the impact of different concentrations on properties such as viscosity and color.

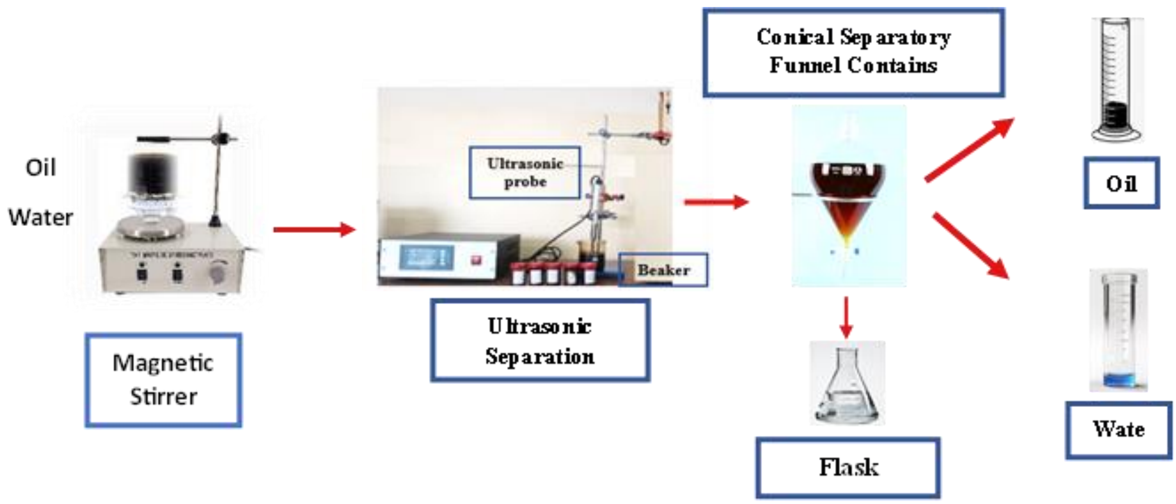

Figure 2. Diagram of emulsion separation process.

3.1. Effects of Adding a 3000 ppm Concentration of Date Pits Particles:

Upon introducing date pits at a concentration of 3000 ppm and subjecting the sample to ultrasound irradiation over a duration of 10minutes at varying power levels (100, 400, 600, 800 W), all curves exhibited a progressive increase in the concentration of separated water with prolonged ultrasound exposure time, demonstrating the efficacy of the technique in augmenting the separation of water from heavy oil. At a low power of 100 W, the separation initially occurs at a slower rate compared to 400 W, 600 W and 800 W. At 600 W and 800 W, the separation occurs more rapidly and attains greater levels in a reduced timeframe, suggesting that increased power amplifies the efficacy of ultrasound in disrupting the emulsion. At the conclusion of the duration (10 min), the findings are comparatively clustered at 600 and 800 W, suggesting the existence of an energy threshold beyond which no substantial enhancement in separation occurs, as seen in Figure (3). The date pit particles enhance separation efficiency by influencing emulsion stability, either by absorption at the water-oil interface or by serving as a catalyst in the ultrasonic cracking process. Prior to the incorporation of the natural material, the separation efficiency was markedly low.

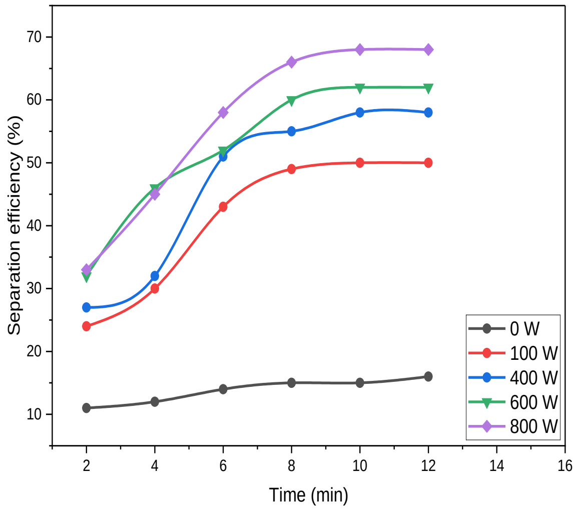

Figure 3. Effect of time on the separation efficiency using 3000 ppm of date pits.

3.2. Effect of Adding Date Pits Particles at A concentration of 5000 ppm.

Upon augmenting the concentration of date seed particles by 5000 ppm, as illustrated in Figure (4), and applying ultrasound waves to the sample over a duration of 10 minutes at varying intensities, an enhancement in the separation rate was observed. However, in certain instances, the elevated concentration may induce detrimental effects due to the potential for particle agglomeration or an increase in the system's viscosity. Date pits powder is abundant in phenolic compounds and tannins that diminish emulsion stability, and it also has fatty acids, including lauric acid, which lowers particle surface tension and aids in the separating process. Increasing the concentration of date seed particles from 3000 ppm to 5000 ppm enhanced the separation; nevertheless, it may attain a saturation threshold beyond which no significant increase is observed.

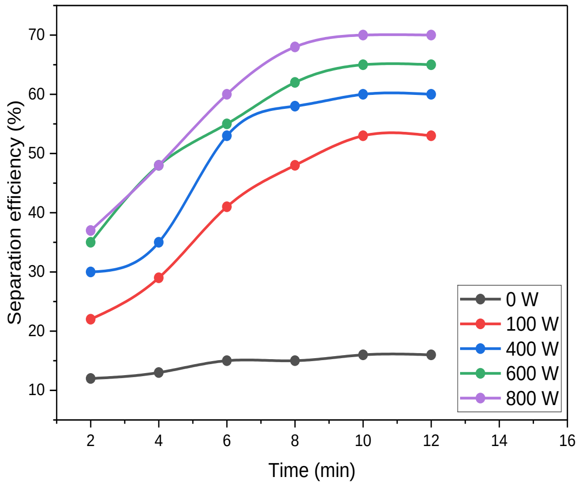

Figure 4. Effect of time on the separation efficiency using 5000 ppm of date pits.

3.3. Effect of Adding Date Pits Particles at A concentration of 10000 ppm.

Figure (5) shows that increasing the concentration to 10000 ppm resulted in an increase in the separated water concentration over time at all powers, confirming the continued effect of ultrasound in improving separation over time and when increasing the concentration. At 10 min, the separated water concentration reached its highest value, especially at 800 W, it reached 83% indicating that this power enhances the separation efficiency at this concentration.

The effect of increasing the concentration of date pits (10000 ppm) compared to the previous two concentrations (3000 and 5000 ppm) A greater improvement in the separation rate was observed, especially at high capacities (600 and 800 W), where it exceeded the previous values seen at 3000 and 5000 ppm.

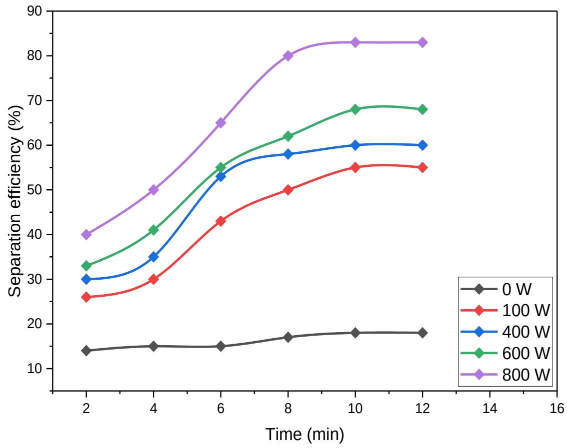

Figure 5. Effect of time on the separation efficiency using 10000 ppm of date pits.

3.4. Effect of Adding Date Pits Particles at A concentration of 15000 ppm.

Consistent with prior research, the concentration of separated water augmented with time at all power levels, demonstrating that the efficacy of ultrasound in emulsion separation persisted, as seen in Figure (6). At 10 minutes, the separation attained its peak value, particularly at 800 W; nevertheless, the rate of enhancement appeared less significant in comparison to the concentration of 10,000 ppm. Comparing these results with 10,000 ppm revealed that at elevated concentrations, the particles may begin to agglomerate, potentially impacting their efficacy in emulsification disruption. A concentration of 10,000 ppm was identified as near optimal, beyond which issues such particle aggregation and the development of a viscous network may arise. A saturation limit was identified, beyond which increasing particle concentration did not significantly enhance separation efficiency, likely due to the agglomeration of surplus particles, which diminishes their efficacy in emulsification disruption. In certain instances, substantial quantities of particles can elevate viscosity, therefore impeding the unobstructed passage of droplets within the oil-water combination and complicating their separation, resulting in a less effective separation process.

3.5. Effect of Concentrations of Date Pits Particles:

Elevated power enhances the emulsification of water inside the oil, likely due to the fragmentation of water droplets into smaller sizes and their augmented stability in the oil medium, as seen in Figure (7). At 100 W, the concentration discrepancies are minimal; but, as the power escalates, the disparities become increasingly evident. At 800 W, the maximum water concentration is 10,000 ppm, whereas the other concentrations (3,000, 5,000, and 15,000 ppm) are comparatively lower yet similar.

This indicates that at lower concentrations (3000 and 5000 ppm), the percentage of water incrementally rises with increased power, but at a slower rate compared to higher concentrations. At 10,000 ppm, a significant rise in water concentration with elevated energy was observed, suggesting that this concentration may enhance emulsification stability more than others. At 15,000 ppm, there is no substantial enhancement over 10,000 ppm, suggesting the existence of a threshold beyond which further concentration increases yield diminishing returns, inversely correlating with rising oil viscosity, which impairs separation efficiency[30].

The combination of ultrasound with date seed powder improved the speed and efficiency of water-oil separation, enhancing the role of ultrasound in breaking emulsions when there is an effective natural substance such as date seed.

From all these results for date seed particles, the following was shown:

1. Ultrasound increased the speed of breaking emulsions due to acoustic cavitation, which led to strong turbulence within the emulsion and helped to quickly break up water droplets.
2. Date seed powder enhanced separation efficiency by:
   - Absorbing water molecules and helping them aggregate.
   - Reducing oil viscosity by interacting with heavy compounds such as asphaltenes.
   - Interacting with oil under the influence of ultrasound, which led to a change in color and facilitated the separation process.
3. The reduction in viscosity may result from:
   - the fragmentation of large oil molecules into smaller, more fluid components.
   - Enhanced oil flow resulting from the degradation of asphaltenes and resins, hence reducing its density.

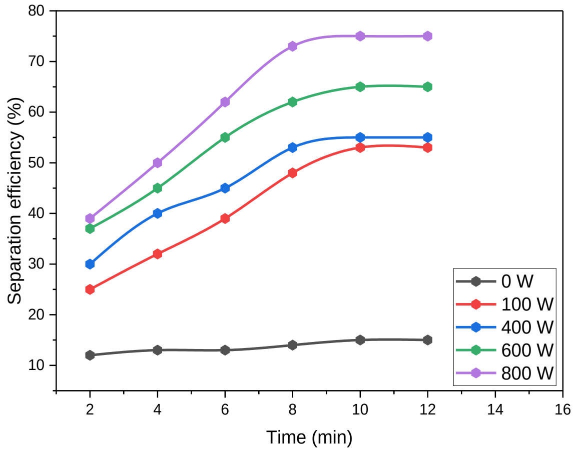

Figure 6. Effect of time on the separation efficiency using 15000 ppm of date pits.

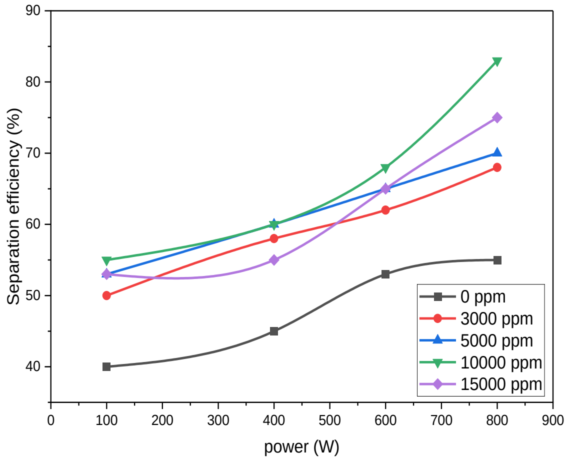

Figure 7. Effect of date pits particles addition at different concentrations.

3.6. Morphological Analysis of Date PitsParticles Using Scanning Electron Microscopy (SEM):

Figure 8a shows clusters of particles with sharp edges and an irregular surface at a magnification of 100x. There is also agglomeration in the structure with some particles showing obvious porosity. The particle size ranges from tens to hundreds of micrometers (10-100), indicating that the rough and porous surface may be useful in adsorption or surface interactions.

Figure 8b shows the spread of particles over a wider range of approximately 50 - 500 micrometers at a magnification of 500x, with variation in size and shape reflecting the grinding or heat treatment the material may have undergone. Some of the larger particles appear more pronounced and may contain various impurities or components that enhance physical or chemical reactions when used as an additive or catalyst. The bottom surface appears relatively smooth compared to the diffuse particles. Additionally, they have a higher probability of interacting successfully with water droplets, either through adsorption or by shaping interfacial phenomena. Their rough and porous surfaces can enhance surface interactions and water retention, potentially reducing water permeation through separation membranes. Small particles range from 10 to 50 micrometers, medium particles from 50 to 200 micrometers, and large particles from 200 to 500 micrometers.

Figure 8c shows the particles in irregular structures with sharp and jagged edges at a magnification of 1000x. There are also clustered areas of particles, suggesting that agglomeration may have occurred naturally or as a result of grinding the material. Small particles range from 5 to 20 micrometers, medium particles from 20 to 40 micrometers, and large aggregates from 40 to 100 micrometers. Figure 8d the particles exhibit irregular structures, measuring approximately 500 micrometers when viewed at a magnification of 2000x.

The characteristics imply that ground date seed particles have promising potential as additives or active layers in oil–water separation membranes, especially in systems where control of surface wettability and interfacial dynamics is critical[31].

3.7. X-ray Diffraction (XRD) Analysis to Determine the Crystal Structure of Date Pits Particles:

Figure (9) illustrates the XRD curve analysis of the date sample, with the horizontal axis (Theta-2Theta) denoting the angle 2θ, which provides insights into the crystal structure. The vertical axis (Intensity - CPS) denotes the intensity of the scattered X-rays, reflecting the degree of material organization. Sharp peaks are observed in the area between 10° and 30°, indicating a partly crystalline structure. The extensive tail beyond 30° shows the existence of an amorphous phase. The sample has a composition of both crystalline and amorphous components[32].

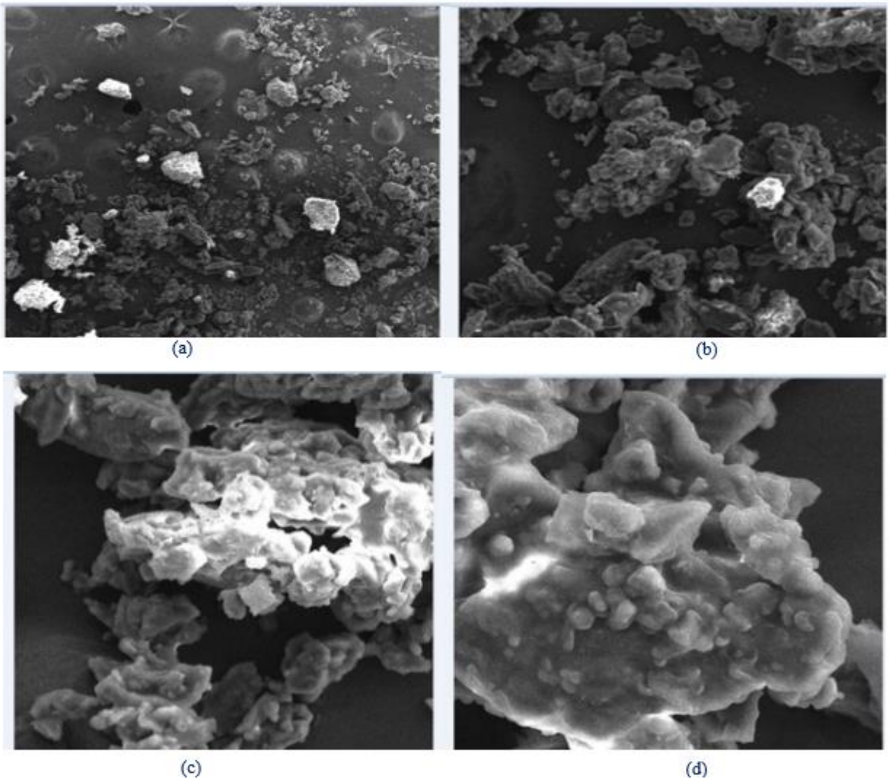

Figure 8. SEM images of date pit particles at magnifications of (a) 100x, (b) 500x, (c) 1000x, and (d) 2000x.

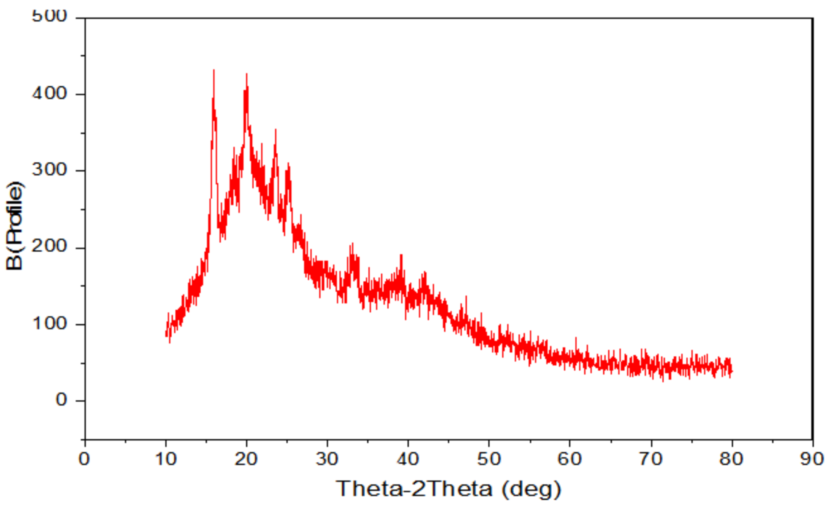

Figure 9. X-ray diffraction (XRD) examination of an oil sample before exposure to ultrasound.

3.8. FT-IR laboratory testing of oil samples

The infrared spectra of the compounds prepared using the SHUMADZUFTIR-84005 were recorded as potassium bromide tablets in the region 400 - 4000 cm² at laboratory temperature. Where the device FTIR represents the effect of ultrasonic waves on the physical and chemical properties of oil samples. Figure (10) illustrates a series of peaks for spectral waves, indicating that the wave at (3302-3393) cm^{-1} corresponds to stretching vibrations of the -OH group, maybe associated with adsorbed water or hydroxyl groups on the surface of date pits.

The peak at (2157 cm^{-1}) is a feeble signal indicative of Si-H bonding or potential interference from carbon residues.

The peak at (1636 cm^{-1}) is likely associated with the bending vibrations of the -OH group in the adsorbed water on the surface of date pits. The alteration of the mixture's hue to dark brown post-treatment signifies that oxidation significantly influenced the emergence of this peak.

The peak at (1181 cm^{-1}) signifies stretching vibrations of the Si-O-Si bond, a distinctive hallmark of the date pit's structure.

The prominent peak at (1006 cm^{-1}) signifies the vigorous stretching vibrations of the Si-O-Si group, which is the principal peak indicative of the date pits structure.

The peak at (887 cm^{-1}) often corresponds to Si-OH vibrations, particularly in amorphous formations, signifying the presence of hydroxyl groups on the surface resulting from the use of date pit material.

In form (11), the analysis of oil samples before exposure to ultrasonic waves is depicted, highlighting the spectrum wavelengths and the large peaks observed before ultrasound treatment. (3735 cm^{-1}) and (3404 cm^{-1}) signify O-H vibrations linked to water or hydroxyl groups (alcohols or phenols). Peaks at (2953, 2921, and 2852) cm^{-1} The brief, slender peaks signify the C-H stretching vibrations of methyl ($-CH_3$) and methylene ($-CH_2-$), commonly observed in hydrocarbons. Peak at (1771 cm^{-1}) A distinct peak signifies the C=O vibration, suggesting the existence of carbonyl groups, including carboxylic acids, esters, or ketones. Peak at (1603 cm^{-1})These peaks may be linked to structural vibrations of aromatic rings or C=C bonds in organic molecules. The peaks at (1457 and 1376) cm^{-1} are typically linked to C-H bond bending vibrations in organic compounds, particularly alkanes, signifying the C-H bending vibrations in the $-CH_2-$ and $-CH_3$ groups, as well as hydrocarbons, commonly found in oils and petroleum products, indicating the existence of elongated carbon chains. The alteration (disappearance) of this peak post-treatment signifies the breaking or rearrangement of hydrocarbons, potentially impacting the viscosity or chemical composition of the samples. The peak at (1032 cm^{-1}) is often linked to C-O vibrations, present in alcohols and ethers. The peaks at (808 and 722) cm^{-1} may signify out-of-plane C-H vibrations in aromatic or long-chain hydrocarbon molecules. The strength of this peak diminished following ultrasound exposure, attributed to the breakdown of some aromatic compounds caused by the mechanical and chemical impacts of ultrasound. Peak at (501-432) cm^{-1} These peaks may be associated with the structural vibrations of certain metal oxide complexes[33].

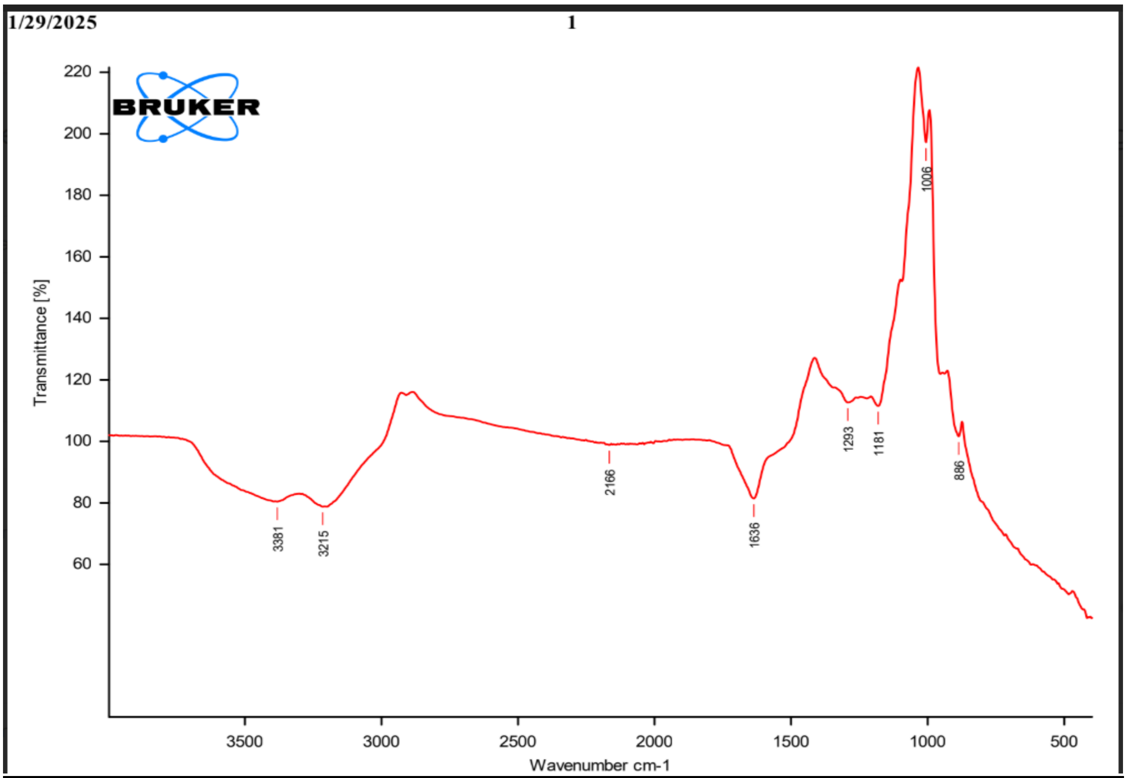

Figure 10. Fourier Transform Infrared (FTIR) Spectral Analysis for Oil Samples Treated with 600 W and 10000 ppm Date Pit Particles.

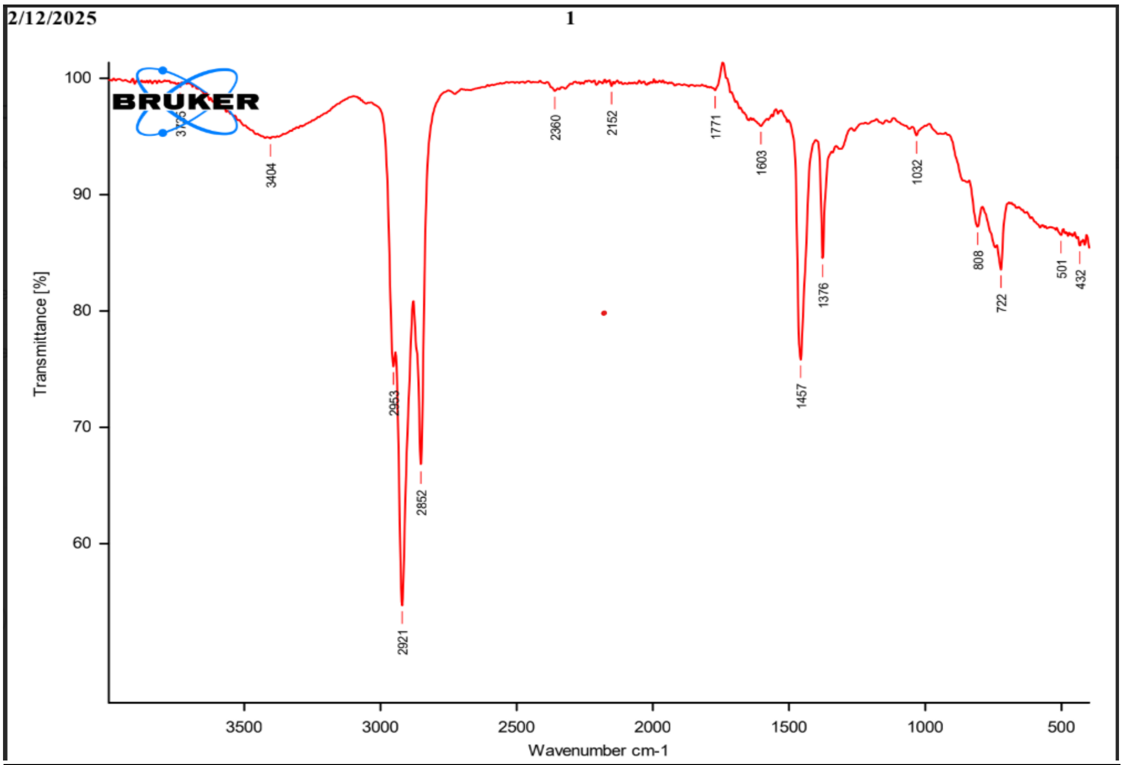

Figure 11. FTIR examination of an oil sample before exposure to ultrasound.

3.9. Commercial Breaker (RQ35) in Breaking Emulsification:

The performance of the commercial emulsification breaker (RQ35) was compared with the natural demulsifier prepared from date pits under similar experimental conditions. As shown in Fig. (12) and Table (4), the commercial breaker exhibited a relatively low separation efficiency, particularly at lower concentrations and moderate temperatures, where the separation did not exceed 20% after 60 minutes. In contrast, the date pit particles achieved a significantly higher efficiency, reaching up to 83% water separation within only 10 minutes at 10,000 ppm and 800 W ultrasound power.

This comparison clearly demonstrates that the natural demulsifier not only performs more effectively than the commercial breaker but also requires lower energy and shorter settling time. Moreover, while the commercial breaker efficiency improved only at higher temperatures, the date pit-based demulsifier maintained high performance under moderate conditions (85°C). These results highlight the advantages of using natural materials such as date pits as an eco-friendly, cost-effective, and efficient alternative to conventional chemical demulsifiers.[34].

Table 4. Emulsification fraction by commercial breaker (35 RQ).

Amount of parasitic substance (ppm)	Amount of water separated (%)					
	Separation time (minutes)					
	10	20	30	40	50	60
500	0	0	0	0	0	5
1000	0	0	0	0	5	10
2000	0	0	5	10	10	15
3000	0	5	10	10	15	20

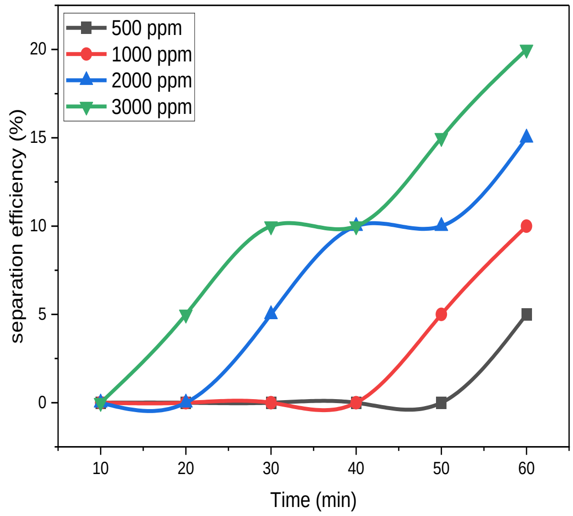

Figure 12. Relationship between separation ratio and time with commercial emulsion breaker (RQ35)

The commercial breaker gave a low separation rate compared to the prepared natural breaker, but when using a high temperature for the commercial breaker (RQ35), its efficiency increases, and this is what happens in most commercial breakers as they need a high temperature more than (70) m. Therefore, the effect of temperature on the commercial breaker and the prepared breakers was studied to increase the separation efficiency. The commercial emulsification breaker was added at concentrations of (500, 1000, 2000 and 3000) ppm and at different temperatures.

Conclusion

The research indicates that employing natural materials such as date pits alongside ultrasonic technology is an effective method for regulating emulsions in heavy fuel oil. This approach may diminish maintenance expenses and improve transportation efficacy in the oil sector. The research findings demonstrate that the use of 10,000 mg/L of date pits as an emulsion solvent, along with low-frequency ultrasound at 800 W for 10 minutes, achieved an 83% separation efficiency. This underscores the efficacy of this technology as a cost-effective and eco-friendly demulsification option. Also, the study found that an emulsification breaker made from natural material (lemon peels) gave the best separation efficiency than using a commercial emulsification breaker (RQ35).

References

[1] Y. Liu, B. Zhang, Y. Zhang, L. Ma, and P. Yang, "Electrochemical polarization study on crude oil pipeline corrosion by the produced water with high salinity," *Eng. Fail. Anal.*, vol. 60, pp. 307–315, Feb. 2016, doi: 10.1016/j.engfailanal.2015.11.049.

[2] A. A. Umar, I. B. M. Saaid, A. A. Sulaimon, and R. B. M. Pilus, "A review of petroleum emulsions and recent progress on water-in-crude oil emulsions stabilized by natural surfactants and solids," *Journal of Petroleum Science and Engineering*, vol. 165. Elsevier B.V., pp. 673–690, Jun. 01, 2018. doi: 10.1016/j.petrol.2018.03.014.

[3] X. Luo, H. Gong, J. Cao, H. Yin, Y. Yan, and L. He, "Enhanced separation of water-in-oil emulsions using ultrasonic standing waves," *Chem. Eng. Sci.*, vol. 203, pp. 285–292, 2019.

[4] F. Betancourt Cardozo, E. Avella Moreno, and C. A. Trujillo, "Structural characterization of unfractionated asphalts by 1H NMR and 13C NMR," *Energy & Fuels*, vol. 30, no. 4, pp. 2729–2740, 2016.

[5] Z. Grenoble and S. Trabelsi, "Mechanisms, performance optimization and new developments in demulsification processes for oil and gas applications," *Adv. Colloid Interface Sci.*, vol. 260, pp. 32–45, 2018.

[6] P. E. E. Maye, Y. Jingyi, Y. Taoyan, and X. Xinru, "The effects of ultrasonic treatment on the molecular structure of residual oil," *China Pet. Process. Petrochemical Technol.*, vol. 4, pp. 82–88, 2017.

[7] G. Shao, H. Li, and M. Zhan, "A review on ultrasonic-assisted forming: mechanism, model, and process," *Chinese J. Mech. Eng.*, vol. 34, pp. 1–24, 2021.

[8] R. van Zwieten, B. Verhaagen, K. Schroën, and D. F. Rivas, "Emulsification in novel ultrasonic cavitation intensifying bag reactors," *Ultrason. Sonochem.*, vol. 36, pp. 446–453, 2017.

[9] D. Ensminger and L. J. Bond, *Ultrasonics: fundamentals, technologies, and applications*. CRC press, 2024.

[10] P. Juliano, M. A. Augustin, X. Q. Xu, R. Mawson, and K. Knoerzer, "Advances in high frequency ultrasound separation of particulates from biomass," *Ultrason. Sonochem.*, vol. 35, pp. 577–590, Mar. 2017, doi: 10.1016/j.ultsonch.2016.04.032.

[11] G. R. Check, "Two-stage ultrasonic irradiation for dehydration and desalting of crude oil: a novel method," *Chem. Eng. Process. Process Intensif.*, vol. 81, pp. 72–78, 2014.

[12] X. Luo, H. Yin, H. Yan, X. Huang, D. Yang, and L. He, "The electrocoalescence behavior of surfactant-laden droplet pairs in oil under a DC electric field," *Chem. Eng. Sci.*, vol. 191, pp. 350–357, 2018.

[13] G. I. Volkova, R. V Anufriev, and N. V Yudina, "Effect of ultrasonic treatment on the composition and properties of waxy high-resin oil," *Pet. Chem.*, vol. 56, pp. 683–689, 2016.

[14] E. E. Banda-Cruz *et al.*, "Crude oil UV spectroscopy and light scattering characterization," *Pet. Sci. Technol.*, vol. 34, no. 8, pp. 732–738, 2016.

[15] A. A. Azubike and E. Itohan, "Prospects of Breaking Crude Oil Emulsions Using Demulsifier Formulated from Nicotiana tabacum Seed Oil, Leaf Extracts, and Stalk Ash Extracts," *Pet. Sci. Eng.*, vol. 5, no. 2, pp. 44–53, 2021.

[16] H. Yuan *et al.*, "Preparation of an environmentally friendly demulsifier using waste rice husk as raw materials for oil–water emulsion separation," *J. Mol. Liq.*, vol. 367, p. 120497, 2022.

[17] P. Parvasi, F. Kamali, and M. R. Talaghat, "An experimental study on low-content crude oil in water emulsion using low-frequency ultrasonic waves," *Brazilian J. Chem. Eng.*, vol. 39, no. 1, pp. 197–205, 2022.

[18] K. Nadirov, M. Zhantasov, Z. Nadirova, N. Otarbaev, G. Bimbetova, and R. Nadirov, "Freshly milled quartz particles obtained from river sand as an efficient natural demulsifier for crude oil emulsions," *Processes*, vol. 10, no. 5, p. 811, 2022.

[19] W.-S. Chen, Z.-Y. Chen, J. Y. Chang, C.-Y. Chen, and Y.-P. Zeng, "Ultrasound-assisted desalination of crude oil: The influence of mixing extent, crude oil species, chemical demulsifier and operation variables," *Ultrason. Sonochem.*, vol. 83, p. 105947, 2022.

[20] H. Sadighian, Z. Mohamadnia, and E. Ahmadi, "Demulsification of crude oil emulsions using versatile and eco-friendly demulsifiers based on cellulose decorated with imidazolium-bearing triazole moiety," *Langmuir*, vol. 39, no. 28, pp. 9627–9637, 2023.

[21] M. M. S. Abdullah, N. A. Faqihi, H. A. Al-Lohedan, Z. M. Almarhoon, and A. M. Karami, "Application of new oleate-based ionic liquids for effective breaking of water in oil emulsions," *Fluid Phase Equilib.*, vol. 568, p. 113737, 2023.

[22] Q. Qu *et al.*, "Two-step synthesis of ionic liquid demulsifiers for demulsification of water-in-oil emulsion," *Sep. Purif. Technol.*, vol. 357, p. 130210, 2025.

[23] M. Mirzadeh, Z. Javadi, and F. Eslami, "Water-in-Oil demulsification with the HLD and HLD-NAC approach and salt effect," *Fuel*, vol. 385, p. 134170, 2025.

[24] Y. Mi *et al.*, "Synthesis of an efficient demulsifier derived from cotton cellulose and its demulsification performance in oily wastewater," *Int. J. Biol. Macromol.*, p. 139839, 2025.

[25] R. H. McKee *et al.*, "The toxicological effects of heavy fuel oil category substances," *Int. J. Toxicol.*, vol. 33, no. 1_suppl, pp. 95S-109S, 2014.

[26] E. DeCola, T. Robertson, M. Fisher, and L. Blair, "Phasing out the use and carriage for use of heavy fuel oil in the Canadian Arctic: Impacts to northern communities," *Nuka Res. Plan. Gr. LLC. Plymouth, MA, USA*, 2018.

[27] W. S. Mowea, R. I. Ibrahim, and M. K. Oudah, "Electromagnetic heating for the separation of water-oil emulsion," *Pet. Chem.*, vol. 64, no. 1, pp. 53–61, 2024.

[28] F. G. Antes *et al.*, "Effect of ultrasonic frequency on separation of water from heavy crude oil emulsion using ultrasonic baths," *Ultrason. Sonochem.*, vol. 35, pp. 541–546, 2017.

[29] D. Montes, F. B. Cortés, and C. A. Franco, "Reduction of heavy oil viscosity through ultrasound cavitation assisted by NiO nanocrystals-functionalized SiO2 nanoparticles," *Dyna*, vol. 85, no. 207, pp. 153–160, 2018.

[30] M. Al-Khalili, N. Al-Habsi, and M. S. Rahman, "Applications of date pits in foods to enhance their functionality and quality: A review," *Front. Sustain. Food Syst.*, vol. 6, p. 1101043, 2023.

[31] M. Nazhipkyzy, D. Assylkhanova, N. Araylim, A. Seitkazinova, G. Özsin, and E. A. Varol, "Effective separation of petroleum oil-water mixtures via flexible and re-usable hydrophobic soot-coated melamine sponge," *J. Water Process Eng.*, vol. 49, p. 103032, 2022.

[32] C.-J. Chang *et al.*, "In situ X-ray diffraction and X-ray absorption spectroscopy of electrocatalysts for energy

conversion reactions," *J. Mater. Chem. A*, vol. 8, no. 37, pp. 19079–19112, 2020.

[33] A. Rohman, M. A. B. Ghazali, A. Windarsih, S. Riyanto, F. M. Yusof, and S. Mustafa, "Comprehensive review on application of FTIR spectroscopy coupled with chemometrics for authentication analysis of fats and oils in the food products," *Molecules*, vol. 25, no. 22, p. 5485, 2020.

[34] Y. M.Hendi and T. A. Mandeel, "Synthesis, identification and evaluated of A Novel Demulsifier of Al-Rashidaiy crude oil (east of Baghdad)," *J. Univ. Anbar Pure Sci.*, vol. 11, no. 1, pp. 58–68, 2017, doi: 10.37652/juaps.2017.141453.