INVESTIGATION OF THE DEMULSIFICATION EFFECT OF LEMON PEEL EXTRACT ON CRUDE OIL EMULSIONS

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DEPARTMENT OF CHEMICAL ENGINEERING

FACULTY OF ENGINEERING

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A PROJECT SUBMITTED TO

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CERTIFICATION

This is to certify that this project research work was carried out by OKOJIE LYSA EJIEHIYOAKHIAN of the Department of Chemical Engineering at the University of Benin, Benin City, Edo State, Nigeria.

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DEDICATION

This research project is dedicated to God Almighty, my everything and the ultimate source of my strength. His boundless grace enabled the successful completion of this project. I also dedicate this work to my parents of inestimable value, whose steadfast encouragement, unwavering support, and inspiring sacrifices have been my most cherished source of inspiration.

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ABSTRACT

Crude oil emulsions pose significant operational and environmental problems due to high viscosity, corrosion, and the toxicity of synthetic demulsifiers currently used. This research aims to investigate Lemon Peel Extract (LPE), a promising green, biodegradable alternative, by evaluating its performance kinetics against a stable crude oil emulsion. The study focused on determining the optimal LPE dosage required for achieving maximum water separation, supporting the industry's shift towards sustainable fluid processing.

The methodology centered on the standard bottle test procedure, with the process optimized using a Central Composite Design **(**CCD**)** of experiments, testing Demulsifier Dosage, Temperature, and Time. A stable W/O emulsion was prepared at (50:50 v/v) and treated with LPE across a concentration range up to 127.6ppm. The vials were thoroughly shaken and placed in a thermostatically controlled water bath (operating between 30°C and 80°C) to enhance kinetics. Performance was monitored by measuring the volume of separated water at defined time intervals.

The experimental results confirmed that the LPE is a highly effective demulsifier. The LPE successfully achieved its maximum water separation efficiency of 93.68%. This optimal performance was recorded at a dosage of 127.6ppm and a temperature of 55°C, with the separation being substantially complete within 75minutes. Response Surface Methodology confirmed a strong synergistic interaction between Dosage and Time (AC = +3.83), indicating that optimal performance requires sufficient LPE concentration paired with adequate contact time. These findings demonstrate that the LPE is a technically

viable, fast-acting, and environmentally friendly green demulsifier for sustainable crude oil treatment operations.

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LIST OF SYMBOLS/ ABBREVIATION

- O/W – oil in water
- W/O – water in oil
- W/O/W – water-in-oil-in-water
- O/W/O – oil-in water-in-oil
- LPE – Lemon Peel Extract

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND TO THE STUDY

The global demand for energy continues to increase, with crude oil remaining a primary fuel source. From powering our vehicles to manufacturing countless everyday products, crude oil is the lifeblood of industrial societies. However, the journey of this invaluable resource from the earth's depths to its final refined form is fraught with complexities, one of the most significant being the formation of crude oil emulsions. These emulsions, essentially stable mixtures of oil and water that do not easily separate, pose considerable challenges throughout the petroleum industry, impacting everything from extraction and transportation to processing and refining (Kokal & Aramco, 2005). The necessity for effective demulsification operations in the petroleum sector is widely recognized (Raya et al., 2020).

At its core, a crude oil emulsion is a dispersion of one immiscible liquid within another, stabilized by various natural components present in the crude oil itself (Umar et al., 2018). When crude oil is extracted, it often co-exists with saline formation water. The vigorous conditions encountered during production, such as high shear at the wellhead and valves, cause these two immiscible phases to mix intimately. The natural surfactants like asphaltenes, resins, and waxes and fine solid particles found in crude oil then migrate to the oil-water interface, forming a rigid, protective film that prevents the water droplets from coalescing and separating from the oil. This interfacial film acts as a barrier, making

the emulsion remarkably stable and difficult to break. The stability of these interfacial films, and hence the stability of the emulsions, depends on a number of factors, including the heavy material in the crude oil (e.g., asphaltenes, resins, and waxes), solids (e.g., clays, scales, and corrosion products), temperature, droplet size and droplet-size distribution, pH, and oil and brine composition (Kokal & Aramco, 2005).

The persistence of these emulsions, if left untreated, leads to a series of technical and commercial problems for the petroleum industry. Emulsions are undesirable as they often lead to numerous problems such as the corrosion of equipment, high-pressure drop in the pipeline, high pumping cost, and poisoning of the catalyst in upstream facilities, thus adding to the overall production cost (Yonguep & Chowdhury, 2021). The demulsification of these crude oil emulsions mitigates corrosion and catalyst poisoning and invariably maximizes the overall profitability of crude oil production (Abed et al., 2019). Therefore, effective treatment is needed to ensure optimum production of hydrocarbons (Raya et al., 2020).

Over the decades, a variety of techniques have been developed to tackle crude oil emulsions, broadly categorized into chemical, physical, and biological methods (Abed et al., 2019). Chemical demulsification, involving the addition of surface-active agents known as demulsifiers, is perhaps the most widely adopted method due to its effectiveness in breaking down stable emulsions (Hajivand & Vaziri, 2015). These chemical demulsifiers work by disrupting the interfacial film that stabilizes the emulsion, allowing the water droplets to coalesce and separate from the oil phase. Various types of chemical demulsifiers, including fatty alcohol ethoxylates, triethanol amine, and urea,

have been explored (Hajivand & Vaziri, 2015). The instability of water in crude oil emulsion and separation of the dispersed water as free water are influenced by the emulsion properties and the operating parameters during the demulsification process (Adeyanju & Oyekunle, 2019).

However, despite their effectiveness, conventional chemical demulsifiers present significant limitations, particularly concerning environmental impact. Most of the conventional chemical demulsifiers are effective in resolving water-in-oil (W/O) emulsions but their application is restricted due to environmental concerns. The chemical demulsifiers are toxic and may cause serious environmental degradation during water disposal (A. B. Yaakob & Sulaimon, 2017). This environmental concern, coupled with the high costs associated with chemical demulsifiers, necessitates the exploration of more eco-friendly and cost-effective alternatives (Raya et al., 2020).

In response to these challenges, there has been a significant surge in research interest towards developing environmentally benign demulsifiers, often referred to as "green demulsifiers" (A. B. Yaakob & Sulaimon, 2017). This includes investigating the potential of plant extracts and other natural compounds as demulsifying agents. Such alternatives offer the promise of reducing the ecological footprint of oil production while potentially providing more sustainable and economically viable solutions. This ongoing pursuit of novel, less harmful, and efficient demulsification strategies is crucial for ensuring the long-term sustainability and environmental responsibility of the petroleum industry.

Therefore, this research aims to contribute to this critical area by investigating the demulsification effect of lemon peel extract on crude oil emulsions. Lemon peel, a

readily available agricultural by-product, is specifically chosen for this study due to its known composition of surface-active compounds, including flavonoids, essential oils (like limonene), and polysaccharides. These natural components are acknowledged for their ability to modify interfacial tension and destabilize emulsions, similar to the action of synthetic surfactants, positioning lemon peel as a viable eco-friendly demulsifier (A. B. Yaakob & Sulaimon, 2017). Given the growing need for sustainable and environmentally friendly solutions in the petroleum industry, exploring natural extracts like lemon peel offers a promising avenue. This study will delve into the efficacy of lemon peel extract as a demulsifier, assess its performance, and potentially unlock a new, greener approach to managing crude oil emulsions, thereby addressing some of the pressing environmental and economic concerns associated with conventional demulsification methods. This investigation seeks to provide useful insights that may pave the way for more sustainable practices in oil and gas processing.

1.2 PROBLEM STATEMENT

The journey of crude oil from the wellhead to the refinery is continuously hampered by the pervasive challenge of crude oil emulsions. These stable mixtures of oil and water are a significant operational and economic burden on the petroleum industry. The presence of these emulsions leads to critical issues such as increased viscosity, causing higher pumping costs and energy consumption during transportation (Yonguep & Chowdhury, 2021), and severe corrosion of pipelines and equipment due to the saline water content, which escalates maintenance expenses (Abed et al., 2019). Furthermore, untreated emulsions can lead to off-specification products and even poison expensive catalysts in processing facilities, directly impacting overall profitability (Abed et al., 2019).

Therefore, effective and efficient demulsification is not merely an option but a critical necessity for the viable and profitable operation of the oil and gas industry (Raya et al., 2020).

While conventional chemical demulsifiers have been the industry's predominant solution for decades, their widespread application is increasingly problematic. Many of these chemicals, though effective in breaking down water-in-oil emulsions, are unfortunately characterized by their toxicity and environmental menace (A. B. Yaakob & Sulaimon, 2017). The disposal of water treated with these chemicals poses a significant ecological threat, contributing to water pollution and impacting ecosystems. This concern is further amplified by tightening environmental regulations and a global push towards more sustainable industrial practices. The high cost associated with these conventional chemical demulsifiers imposes an additional financial burden on the crude oil processing chain (Raya et al., 2020). Current approaches, however effective, can impose an intolerable environmental burden and substantial operational costs.

Consequently, a significant knowledge gap exists regarding comprehensive studies on readily available, natural plant-based extracts as effective demulsifiers, particularly focusing on specific materials like lemon peel extract. While the broader concept of "green demulsifiers" is gaining interest, there is a clear absence of sufficient research detailing the demulsification efficiency, optimal conditions, and comparative performance of lemon peel extract in addressing crude oil emulsions. This lack of specific investigation highlights a novel area for exploration, where a sustainable and potentially cost-effective solution could be identified.

Therefore, the core problem motivating this research is the urgent need for environmentally friendly and cost-effective demulsifiers to efficiently separate crude oil emulsions, thereby mitigating their adverse operational, economic, and environmental impacts. This research intends to directly address this critical gap by specifically investigating the demulsification efficacy of lemon peel extract on crude oil emulsions. The specific problem this study aims to solve is to determine if and how lemon peel extract, a natural and abundant resource, can serve as a viable, sustainable, and potentially cost-efficient alternative to conventional chemical demulsifiers, contributing to a cleaner and more economical crude oil production process.

1.3 AIM AND OBJECTIVES

The aim of this research is to investigate the demulsification efficiency of lemon peel extract on crude oil emulsions as a sustainable alternative to conventional chemical demulsifiers.

The specific objectives of this research are:

i. To prepare and characterize the lemon peel extract for its potential demulsifying compounds.
ii. To prepare stable water-in-crude oil emulsions for demulsification studies.
iii. To evaluate the demulsification performance of the lemon peel extract on crude oil emulsions under varying experimental conditions, such as extract concentration, temperature, and time.

iv. To assess the feasibility of utilizing lemon peel extract as an environmentally friendly and potentially cost-effective demulsifier for crude oil emulsions.

1.4 SCOPE OF STUDY

The scope of this study is focused and bounded as follows:

i. Characterization of the natural lemon peel extract to identify relevant demulsifying compounds.
ii. Experimental evaluation of lemon peel extract as a demulsifier.
iii. Focus on water-in-crude oil emulsions.
iv. Investigation of demulsification efficiency under varying extract concentration, temperature, and time.
v. Assessment of its feasibility as an environmentally friendly alternative.

1.5 RELEVANCE OF STUDY

This research responds to critical challenges faced by the global energy sector and aligns with the growing imperative for environmental sustainability. The investigation into the demulsification effect of lemon peel extract on crude oil emulsions holds considerable significance for several reasons.

Firstly, crude oil emulsions present persistent operational and economic challenges within the petroleum industry. These stable emulsions increase processing costs, accelerate equipment corrosion, and reduce product quality, thereby negatively impacting the efficiency and profitability of oil production. This study aims to address these issues

by exploring a more effective and sustainable method for oil-water separation. The potential benefits include cost savings, improved operational integrity of infrastructure, and the development of an eco-friendly demulsifier derived from an abundant agricultural waste product.

Secondly, the environmental implications of this research are substantial. Conventional chemical demulsifiers, while effective, often pose environmental hazards due to their toxicity. With increasing regulatory constraints and heightened environmental awareness, there is a pressing need for greener alternatives. By investigating lemon peel extract, a natural, biodegradable, and food waste derived material, this study contributes to reducing the environmental footprint associated with crude oil processing. This aligns with global efforts to promote cleaner industrial practices and sustainable resource management.

Thirdly, this work contributes to the emerging field of bio-demulsifiers. Although the application of natural substances in demulsification is gaining interest, detailed scientific studies on specific plant extracts such as lemon peel remain limited. This research seeks to provide valuable insights into the performance mechanisms and optimal conditions for lemon peel extract as a green demulsifier, thereby supporting further innovation in sustainable chemical engineering.

Finally, the broader implications of this study extend beyond crude oil processing. If proven effective, lemon peel extract could inspire the utilization of other natural wastes or by-products as sustainable solutions in various industrial applications. This research exemplifies how chemical engineering can bridge industrial demands with environmental

responsibility, fostering a future where energy production is both efficient and environmentally benign.

CHAPTER TWO

LITERATURE REVIEW

2.2 OVERVIEW OF CRUDE OIL EMULSIONS

2.2.1 Definition and Types of Emulsions

An emulsion is a dispersion system consisting of two immiscible liquids where one liquid exists as small droplets distributed throughout the other continuous phase. In the petroleum industry, emulsions are commonly formed during crude oil production, transportation, and processing, where oil and water become intimately mixed under turbulent conditions in the presence of natural surface-active agents (Wong et al., 2015). These emulsions present significant operational challenges and economic losses if not properly treated, as they increase oil viscosity, complicate transportation, cause equipment corrosion, and interfere with refining processes. Understanding the different types of emulsions and their classification systems is essential for developing appropriate demulsification strategies and predicting emulsion behavior under various conditions (Sousa et al., 2021).

2.2.1.1 Water-in-oil (w/o) and oil-in-water (o/w) emulsions represent the two primary types encountered in petroleum operations, distinguished by which phase forms the continuous medium. In W/O emulsions, water droplets are dispersed throughout a continuous oil phase, making this the most common type in crude oil production where produced water becomes entrapped in the oil stream (Wong et al., 2015). These emulsions are typically stabilized by indigenous crude oil components such as

asphaltenes, resins, and naphthenic acids that adsorb at the oil-water interface and prevent droplet coalescence (Sousa et al., 2022). W/O emulsions exhibit characteristic properties including high viscosity, non-Newtonian flow behavior, and stability that increases with water content and the concentration of natural emulsifying agents (Ariffin et al., 2016). The stability of W/O emulsions is influenced by multiple factors including temperature, with studies showing that certain emulsions maintain high stability even at elevated temperatures due to the formation of rigid interfacial films (Wang et al., 2016). Research on heavy oil emulsions has demonstrated that stability and homogeneity depend on the chemical composition of the crude oil and the properties of the dispersed water phase (da Silva et al., 2018). Various additives and chemicals can significantly affect the phase behavior and viscosity of W/O emulsions, with implications for both emulsion stability and demulsification strategies (Shafiei et al., 2023). In contrast, O/W emulsions consist of oil droplets dispersed in a continuous water phase and are less common in crude oil production but may occur in certain processing operations or environmental spill scenarios (Sousa et al., 2022). O/W emulsions are generally less stable than W/O emulsions due to the lower viscosity of the continuous water phase and different stabilization mechanisms (Zolfaghari et al., 2016). Understanding the formation and demulsification of both emulsion types is critical for developing effective separation technologies (Wang et al., 2021; Sousa et al., 2022).

2.2.1.2 Multiple emulsions represent more complex systems where droplets of one emulsion are themselves dispersed within another continuous phase, forming structures such as water-in-oil-in-water (W/O/W) or oil-in-water-in-oil (O/W/O) emulsions. These multi-compartmentalized systems consist of small droplets enclosed within larger

droplets that are dispersed in a continuous phase (Vladisavljević et al., 2017). W/O/W emulsions contain water droplets enclosed within oil droplets that are dispersed in a continuous water phase, while O/W/O emulsions have the reverse structure (Lee et al., 2016). Multiple emulsions have gained attention in pharmaceutical and food applications for encapsulating various additives and controlling their release, with stability mechanisms depending on both the inner and outer interfaces (Zhu et al., 2019). The production of multiple emulsions can be achieved through various techniques including microfluidic methods that provide precise control over droplet size and structure (Lee et al., 2016). Recent advances in multiple Pickering emulsions, where solid particles stabilize one or both interfaces, have expanded the potential applications of these complex systems (Zhao et al., 2022). Multiple nanoemulsions, which involve nanoscale droplets in hierarchical structures, represent an emerging area with unique properties and applications (Sheth et al., 2020). While multiple emulsions are less commonly encountered in crude oil production compared to simple W/O emulsions, understanding their formation and stability mechanisms provides insights into complex emulsion systems and potential demulsification challenges.

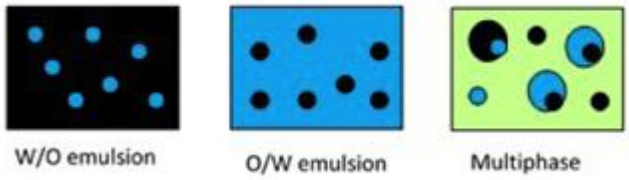


Figure 2.1 Types of Emulsion (A. Yaakob et al., 2017)

2.2.1.3 Classification by stability provides another important framework for categorizing crude oil emulsions based on their resistance to separation, with implications for selecting appropriate treatment methods. Emulsions can be classified into three main stability categories:

- **Loose (unstable) emulsions**: These emulsions separate relatively easily with minimal treatment, typically breaking within minutes to hours under static conditions or with gentle heating. They are characterized by weak interfacial films and large droplet sizes (Wong et al., 2015).
- **Medium stability emulsions**: These emulsions require moderate treatment such as chemical demulsifiers, controlled heating, or longer settling times to achieve separation. They possess interfacial films of intermediate strength and moderate droplet size distributions (Goodarzi & Zendehboudi, 2019).
- **Tight (highly stable) emulsions**: These emulsions are very difficult to break and require intensive treatment including high demulsifier dosages, elevated temperatures, electric fields, or combinations of methods. They feature rigid interfacial films, small droplet sizes, and high concentrations of natural stabilizing agents (Wong et al., 2015; Raya et al., 2020).

The stability of crude oil emulsions is determined by multiple factors including crude oil composition, water chemistry, droplet size distribution, interfacial film properties, temperature, and the presence of solids (Angardi et al., 2022). Comprehensive reviews on emulsion stability have identified various characterization techniques for assessing emulsion type and stability, including microscopy, rheology, droplet size analysis, and

interfacial tension measurements (Goodarzi & Zendehboudi, 2019). Classification systems may also consider morphological characteristics and the nature of stabilizing materials, such as Pickering emulsions stabilized by solid particles or emulsions stabilized by surfactants and biopolymers (Yang et al., 2017; Zembyla et al., 2020). Understanding emulsion classification schemes is essential for predicting treatment difficulty and selecting appropriate demulsification strategies, with loose emulsions potentially requiring only simple methods while tight emulsions necessitate more aggressive or novel approaches such as natural demulsifiers with unique mechanisms of action (Yonguep et al., 2022).

2.2.2 Formation Mechanisms

The formation of crude oil emulsions is a complex process that requires both sufficient energy input to disperse one phase into another and the presence of stabilizing agents that prevent the dispersed droplets from rapidly coalescing back into separate phases. Understanding the mechanisms underlying emulsion formation is crucial for predicting emulsion behavior and developing effective demulsification strategies. Emulsion formation in petroleum operations occurs through a combination of physical and chemical factors that work synergistically to create stable dispersions (Raya et al., 2020).

2.2.2.1 Physical causes of emulsion formation involve mechanical forces that provide the energy necessary to break up one phase into small droplets and disperse them throughout the continuous phase:

- **Turbulence**: One of the primary physical mechanisms driving emulsion formation in petroleum production, occurring at various points including wellbore flow, production equipment, pumps, valves, and pipelines where fluid velocity and flow patterns create chaotic mixing conditions (Wong & Dol, 2019). The turbulent characteristics of emulsified flow differ significantly from single-phase flow, with increased pressure drops and altered velocity profiles that reflect the presence of dispersed droplets (Wong & Dol, 2019).
- **Agitation**: Sustained mixing energy during production, transportation, and processing operations that maintains emulsion structure and prevents phase separation. The effects of water-in-oil emulsions on wall shear stress in pipeline flow demonstrate how physical forces interact with emulsion properties to influence flow behavior (Dol et al., 2018).
- **Shearing forces**: Play a critical role in both forming and stabilizing emulsions by breaking larger droplets into smaller ones and distributing them uniformly throughout the continuous phase (Wang et al., 2017). The role of shearing energy, particularly for waxy crude oils, involves overcoming interfacial energy barriers to create stable dispersions (Wang et al., 2017). Studies on highly concentrated emulsions have identified criteria for shear stability, showing that emulsification effectiveness depends on the magnitude and duration of applied shear forces (Masalova et al., 2018).

The combination of these physical mechanisms provides the mechanical energy necessary for emulsion formation, with the extent of emulsification depending on factors

such as flow rate, equipment geometry, fluid properties, and mixing duration (Raya et al., 2020; Wong et al., 2015).

2.2.2.2 Chemical causes of emulsion formation and stabilization involve the presence of natural surface-active compounds in crude oil that adsorb at the oil-water interface and prevent droplet coalescence:

- **Asphaltenes**: High molecular weight polar compounds composed of polycyclic aromatic hydrocarbons with heteroatoms that exhibit strong surface activity and are considered the primary stabilizers of water-in-crude oil emulsions (Umar et al., 2018). These complex molecules adsorb irreversibly at the oil-water interface, forming rigid, viscoelastic films that provide both mechanical and electrostatic barriers to droplet coalescence (Kang et al., 2018).
- **Resins**: Polar compounds with lower molecular weight than asphaltenes that also contribute to emulsion stability, often working synergistically with asphaltenes to enhance interfacial film strength (Liu et al., 2019). The synergetic effect of resins and asphaltenes on water-oil interfacial properties has been extensively studied, revealing that their combined presence produces more stable emulsions than either component alone (Liu et al., 2019; Zhang et al., 2016). The ratio of asphaltenes to resins, along with their chemical structures and concentrations, significantly influences emulsion stability and demulsification effectiveness (Song et al., 2024).
- **Solid particles**: Clay minerals, sand, drilling mud solids, and corrosion products can stabilize emulsions through Pickering stabilization mechanisms, where

particles adsorb at the oil-water interface and create physical barriers to coalescence (Umar et al., 2018). Natural surfactants present in crude oil, including naphthenic acids and other indigenous polar compounds, contribute to stability by reducing interfacial tension and forming protective layers around water droplets (Delgado-Linares et al., 2022).

- **Waxes**: Contribute to emulsion stability through multiple mechanisms including the formation of crystal structures at the interface and increasing the bulk viscosity of the continuous phase (Szumała & Luty, 2016). Studies have identified two distinct effects of wax crystals in stabilizing water-in-oil emulsions: interfacial stabilization through crystal adsorption and bulk stabilization through network formation (Chen et al., 2021). The influence of wax chemical structure on emulsion rheology and stability demonstrates that wax type, concentration, and crystallization behavior significantly affect emulsion properties (Freitas et al., 2018).

The interaction between physical formation mechanisms and chemical stabilizing agents determines the ultimate stability of crude oil emulsions, with more intense mechanical energy inputs creating smaller droplets with larger interfacial areas that become more effectively stabilized by natural surfactants, resulting in tighter emulsions that are more difficult to break (Yonguep et al., 2022; Saad et al., 2019).

2.2.3 Stability of Crude Oil Emulsions

The stability of crude oil emulsions is a critical factor that determines the difficulty of demulsification and the effectiveness of treatment strategies. Emulsion stability refers to

the ability of dispersed droplets to resist coalescence and maintain their dispersed state over time, which in petroleum operations translates to persistent water entrapment in crude oil that requires intervention for separation (Goodarzi & Zendehboudi, 2019). Understanding the factors that contribute to emulsion stability and the mechanisms that prevent droplet coalescence is essential for developing effective demulsification approaches and predicting treatment requirements under various operational conditions.

2.2.3.1 Thermodynamic and kinetic stability represent two fundamental aspects of emulsion behavior that determine their persistence. Thermodynamically, all emulsions are inherently unstable systems due to the positive free energy associated with the large interfacial area between the dispersed and continuous phases (Rehman et al., 2022). However, emulsions can exhibit significant kinetic stability where energy barriers prevent the system from reaching its thermodynamically favored separated state within practical timeframes. The thermodynamic and kinetic stability of emulsion systems can be evaluated through various methods including energy dynamics measurements that assess the forces resisting coalescence (Rehman et al., 2022; Ajayi, 2024). Stability evaluation techniques range from conventional freeze-thaw tests to advanced rheological methods such as dynamic-mechanical thermoanalysis that provide rapid assessment of emulsion resistance to destabilization under stress conditions (Cekić et al., 2023). Oxidative stability represents another important consideration, particularly for long-term storage, where chemical changes at the interface can alter emulsion properties and stability characteristics (Ghelichi et al., 2023; Malik et al., 2021). The kinetic stability of crude oil emulsions is primarily governed by the strength and properties of the interfacial

film formed by natural surfactants, with stronger films providing greater resistance to droplet coalescence and longer-lasting emulsions.

2.2.3.2 Interfacial film properties play a crucial role in determining crude oil emulsion stability by creating barriers that prevent water droplets from merging. The dynamics of water-crude oil interfacial film formation are significantly influenced by aqueous-phase ionic strength and composition, with different salt types and concentrations affecting the adsorption and organization of surface-active components (Moradi & Alvarado, 2016). Rheological studies of the crude oil-water interface have demonstrated that temperature and brine composition substantially affect interfacial film characteristics, with changes in these parameters altering film elasticity, viscosity, and resistance to rupture (Perles et al., 2018). The interfacial film acts as a protective barrier around water droplets, with its mechanical properties determining the ease with which droplets can approach, contact, and coalesce (Yang et al., 2018). Polyaromatic compounds and other indigenous crude oil components contribute to interfacial layer properties that stabilize water-in-oil emulsions through the formation of viscoelastic films with specific structural characteristics (Bi et al., 2015). The strength of the interfacial film depends on factors including:

- The concentration and type of natural surfactants (asphaltenes, resins, naphthenic acids)
- The presence and characteristics of solid particles at the interface
- Temperature and pressure conditions
- Aging time allowing for film maturation and reorganization
- pH and ionic composition of the aqueous phase

Stronger interfacial films result in more stable emulsions that require more aggressive demulsification treatments to achieve adequate water separation (Goodarzi & Zendehboudi, 2019).

2.2.3.3 Droplet size distribution is a critical parameter affecting emulsion stability, with smaller droplets generally producing more stable emulsions due to reduced gravitational separation rates and increased resistance to coalescence. The distribution of droplet sizes in emulsions influences not only stability but also rheological properties and phase separation behavior (L'estimé et al., 2023). Studies on emulsion stability have shown that droplet size distribution, along with rheological behavior, determines the overall stability characteristics of oil-water systems (Castel et al., 2017). The effect of brine salinity on water-in-oil emulsion stability can be assessed through droplet size distribution analysis, revealing how salt concentration influences droplet growth and coalescence rates (Maaref & Ayatollahi, 2018). Emulsions with uniform, small droplet distributions tend to be more stable than those with broader size distributions, as the latter contain larger droplets more prone to gravitational separation and coalescence. The relationship between droplet size and stability is complex, influenced by the balance between gravitational forces promoting separation and interfacial forces resisting coalescence.

2.2.3.4 Environmental factors significantly impact crude oil emulsion stability, with operational parameters such as water content, pH, salinity, and temperature playing crucial roles in determining emulsion behavior. The effect of these factors on stability and surface tension of crude oil emulsions has been extensively studied, revealing complex interactions between environmental conditions and emulsion properties

(Arroussi et al., 2019). Water content directly affects emulsion viscosity and stability, with higher water fractions generally increasing viscosity up to a critical point where phase inversion may occur**.** pH influences the ionization state of acidic and basic components in crude oil, affecting their surface activity and ability to stabilize emulsions (Kumar et al., 2020). The effects of pH on clay-stabilized Pickering emulsions demonstrate that proton concentration can alter particle wettability and interfacial adsorption behavior (Yu et al., 2021). Salinity affects emulsion stability through multiple mechanisms including modifying interfacial tension, altering the electrical double layer around droplets, and changing the solubility of natural surfactants (Belhaj et al., 2020). Studies have shown that water salinity significantly affects surfactant-stabilized emulsion flow characteristics, with implications for both emulsion formation and stability (Al-Yaari et al., 2015). Temperature influences crude oil viscosity, interfacial properties, and the effectiveness of natural stabilizers, with effects varying depending on crude oil composition (Santos et al., 2017). The effect of chemicals on phase and viscosity behavior of water-in-oil emulsions further demonstrates how environmental conditions and additives interact to determine stability (Shafiei et al., 2023). Experimental investigations have examined how various parameters including temperature affect viscosity reduction in heavy crude oil emulsions, providing insights into stability mechanisms (Al-Wahaibi et al., 2015). The rheological properties of crude oil emulsions, including viscosity and flow behavior, serve as indicators of stability and are influenced by temperature, water content, and shear conditions (Ariffin et al., 2016). Understanding how these environmental factors affect emulsion stability is essential for predicting

treatment requirements and optimizing demulsification conditions for lemon peel extract applications.

2.2.4 Industrial and Environmental Impacts

2.2.4.1 Operational issues

The presence of stable crude oil emulsions in petroleum production and transportation systems creates severe operational challenges that significantly compromise the efficiency and safety of oil field operations. Pipeline blockages represent a major concern, as the accumulation of emulsified water and solid particles can lead to flow restrictions and complete pipeline obstructions, particularly in low-temperature environments where the increased viscosity of emulsions exacerbates the problem. Internal pipeline corrosion is substantially accelerated by water-in-oil emulsions, which contain dissolved salts, organic acids, carbon dioxide, and hydrogen sulfide that create highly corrosive environments attacking the metal surfaces of pipelines and processing equipment (Wang & Zhang, 2016). The multiphase flow conditions characteristic of crude oil transport, where oil, water, and gas phases coexist, further intensify corrosion mechanisms through localized turbulence and varying flow patterns that promote uneven metal degradation (Zhang & Lan, 2017). These corrosion issues result in reduced equipment lifespan, frequent maintenance requirements, unexpected shutdowns, and potential catastrophic failures that pose serious safety risks to personnel and facilities (Silva Filho et al., 2021; Groysman, 2017). Additionally, the high viscosity associated with stable emulsions increases pumping requirements and energy consumption, leading to elevated operational costs and reduced throughput in production and transportation systems.

2.2.4.2 Reduced refining efficiency and economic implications

Stable crude oil emulsions significantly impair refining efficiency and impose substantial economic burdens on petroleum operations. The presence of emulsified water in crude oil feedstock interferes with various refining processes, including distillation, catalytic cracking, and product separation, necessitating additional pre-treatment steps to achieve acceptable water content levels before processing can commence (Abed et al., 2019). Different emulsion types, such as water-in-oil, oil-in-water, and complex multiple emulsions, each present unique challenges that require specific demulsification approaches based on their formation mechanisms and stabilizing components (Raya et al., 2020; Hadi & Ali, 2022). The properties of these emulsions vary considerably depending on the crude oil composition and aqueous phase characteristics, making it necessary to characterize each system thoroughly to select appropriate treatment technologies (Sousa et al., 2021; Li et al., 2017). The economic implications of emulsion management are extensive, encompassing the costs of specialized demulsifying chemicals, energy consumption for heating and mechanical separation, equipment maintenance and replacement due to corrosion damage, and reduced crude oil recovery due to water contamination (Issaka, 2015). Furthermore, the investment required for demulsification infrastructure, including chemical injection systems, separation vessels, and monitoring equipment, represents a significant capital expenditure for oil producers. The cumulative effect of these factors translates to decreased profit margins and reduced competitiveness, particularly for operations dealing with heavy crude oils or challenging reservoir conditions that promote stable emulsion formation.

2.2.4.3 Environmental challenges

The environmental ramifications of crude oil emulsions extend far beyond operational concerns, presenting serious challenges in wastewater disposal, oil spill management, and ecosystem toxicity. Produced water, which constitutes the largest volume waste stream in oil and gas operations, typically exists as stable oil-in-water emulsions containing complex mixtures of hydrocarbons, dissolved salts, heavy metals, production chemicals, and naturally occurring radioactive materials (Nasiri & Jafari, 2017). The discharge of inadequately treated produced water into receiving environments has resulted in widespread contamination of water bodies and soil systems, with particularly severe impacts observed in regions like the Niger Delta where decades of petroleum activity have caused extensive ecological degradation and compromised water quality for local communities (Gazali et al., 2017). Flowback and produced waters from shale gas operations present additional concerns due to their high concentrations of organic pollutants, including aromatic hydrocarbons, phenols, and other compounds with significant ecological toxicity that can persist in the environment and bioaccumulate in food chains (Butkovskyi et al., 2017). The treatment of emulsified oily wastewater poses considerable technical challenges, as conventional separation methods often prove insufficient for breaking stable emulsions and removing fine oil droplets to meet increasingly stringent environmental discharge standards (Putatunda et al., 2019). While advanced treatment technologies such as emulsion liquid membrane techniques and Pickering emulsion systems have shown promise for handling industrial effluent streams, their implementation remains limited by cost considerations and technical complexity (Hussein et al., 2019; Kumar et al., 2019). The growing volume of oily wastewater

generated by expanding petroleum operations, coupled with stricter environmental regulations and public pressure for sustainable practices, has created an urgent need for innovative, cost-effective, and environmentally benign demulsification approaches that can effectively address these challenges while minimizing the ecological footprint of the industry (Medeiros et al., 2022).

2.3 DEMULSIFICATION: PRINCIPLES AND METHODS

2.3.1 Overview of Demulsification

Demulsification is a critical process in the petroleum industry that involves breaking down stable crude oil emulsions into their constituent phases of oil and water. During crude oil extraction and production, water and oil naturally mix under turbulent conditions and high pressure, forming stable emulsions that are stabilized by naturally occurring surface-active compounds such as asphaltenes, resins, and naphthenic acids present in the crude oil (Saad et al., 2019). These emulsions, if left untreated, can lead to numerous operational and economic challenges including increased transportation costs, equipment corrosion, catalyst poisoning in refineries, and complications in meeting crude oil specifications for sale and export. The primary purpose of demulsification is therefore to facilitate the efficient separation of water from crude oil, thereby improving oil quality, reducing processing costs, and minimizing environmental impacts associated with the disposal of oily wastewater (Tang et al., 2024). Additionally, effective demulsification helps recover valuable crude oil that would otherwise be lost in the water phase, making the overall production process more economically viable and environmentally sustainable (Grenoble & Trabelsi, 2018).

The efficiency of any demulsification process is evaluated based on several key performance criteria that determine its practical applicability in industrial settings. The most fundamental criterion is the water separation efficiency, which measures the percentage of water removed from the emulsion within a specified time frame, with higher percentages indicating better demulsifier performance (Kang et al., 2018). Another important criterion is the speed of demulsification, as faster phase separation translates to reduced residence time in treatment vessels and consequently lower operational costs (Kailey, 2017). The quality of the separated oil and water phases also serves as a critical indicator of demulsification efficiency, where the treated oil should meet required specifications with minimal residual water content (typically less than 0.5% by volume), while the separated water should contain minimal oil content to facilitate proper disposal or reuse (Meza et al., 2022). Furthermore, the demulsifier dosage required to achieve satisfactory separation is an essential economic consideration, with more efficient demulsifiers requiring smaller quantities to accomplish the same level of separation (Yaakob & Sulaimon, 2017). Other performance indicators include the stability of the demulsification process under varying conditions such as temperature fluctuations and changes in crude oil composition, as well as the formation of a clean oil-water interface without the presence of a rag layer, which is an intermediate layer of tightly emulsified material that is difficult to process (Grenoble & Trabelsi, 2018). These criteria collectively provide a comprehensive framework for assessing demulsifier performance and guide the selection of appropriate demulsification strategies for specific crude oil emulsion systems.

2.3.2 Conventional Demulsification Methods

The petroleum industry has developed various conventional demulsification techniques to address the challenge of separating stable crude oil emulsions. These methods can be broadly categorized into chemical, thermal, electrical, and mechanical approaches, each utilizing different principles to destabilize emulsions and facilitate phase separation (Raya et al., 2020). The selection of an appropriate method depends on factors including emulsion type and stability, crude oil properties, economic considerations, and operational constraints, with techniques often used in combination to achieve optimal separation efficiency (Abed et al., 2019).

Chemical demulsification is the most widely used technique in the petroleum industry due to its effectiveness and ease of application. This method involves adding chemical demulsifiers, which are surface-active agents that displace naturally occurring stabilizing agents at the oil-water interface, thereby weakening the interfacial film and promoting droplet coalescence (Yonguep et al., 2022). Chemical demulsifiers function through mechanisms including flocculation, coalescence, and solid wetting, with effectiveness depending on factors such as demulsifier type, concentration, contact time, and crude oil composition (Hadi & Ali, 2022; Shah Buddin et al., 2022). The main challenges include the need for careful selection of demulsifier formulations for specific crude oils, potential environmental concerns, and chemical waste generation (Deng et al., 2023). Despite these limitations, chemical demulsification remains the primary treatment method in most oil production facilities due to its proven track record and operational simplicity (Issaka, 2015).

Thermal demulsification utilizes heat to reduce emulsion stability and facilitate water separation from crude oil. Heat application reduces crude oil viscosity, increases density difference between phases, and weakens the interfacial film by reducing the effectiveness of natural emulsifying agents (Tian et al., 2022). Treatment is typically carried out in heater-treaters at temperatures ranging from 50°C to 150°C depending on crude oil characteristics (Raya et al., 2020). While thermal demulsification can handle highly viscous crude oils without chemical additives, it has significant drawbacks including high energy consumption, potential thermal degradation of lighter hydrocarbon fractions, and safety risks associated with high-temperature fluids (Abed et al., 2019). Additionally, thermal treatment alone may not suffice for very stable emulsions, often requiring combination with other methods (Issaka, 2015).

Electrical demulsification employs electric fields to induce coalescence of water droplets dispersed in crude oil. When subjected to an external electric field, dispersed water droplets become polarized and experience attractive forces that cause them to migrate, collide, and coalesce into larger droplets that settle more rapidly (Zhang et al., 2017). The process can use direct current, alternating current, or pulsed electric fields, with efficiency influenced by parameters such as electric field strength, frequency, temperature, and water content (Mardani et al., 2022; Hellesø et al., 2015). Recent studies show that combining electric fields with other techniques can significantly enhance demulsification performance (Lu et al., 2021; Yasir et al., 2023). Advantages include relatively low chemical usage and reduced environmental impact, though the method requires specialized equipment and careful control of operating parameters (Hu et al., 2021).

Mechanical demulsification relies on physical forces to separate oil and water phases, with centrifugation and ultrasonic treatment being the most common approaches. Centrifugal separation utilizes centrifugal force to accelerate gravitational settling by creating a high-gravity environment, with effectiveness depending on rotational speed, residence time, and density difference between phases (Tian et al., 2022; Semenov et al., 2021). Ultrasonic demulsification employs high-frequency sound waves to induce droplet coalescence through acoustic streaming, radiation pressure, and cavitation effects (Romanova et al., 2022). While mechanical methods offer advantages such as no chemical addition and potential for continuous operation, they have limitations including high capital and maintenance costs, energy intensity, and potential difficulties treating highly stable emulsions without supplementary treatment (Deng et al., 2023; Shah Buddin et al., 2022).

2.3.3 Limitations of Conventional Methods

Despite the widespread use of conventional demulsification techniques in the petroleum industry, these methods face numerous limitations that have prompted researchers to explore alternative approaches. One of the most significant challenges is the high operational and capital costs associated with these processes. Chemical demulsifiers can be extremely expensive, particularly when dealing with highly stable emulsions that require large dosages or specialized formulations tailored to specific crude oil compositions (Zhang et al., 2017). Thermal demulsification methods consume considerable amounts of energy to heat large volumes of crude oil emulsions, resulting in high fuel costs and significant operational expenses (Hadi & Ali, 2022). Electrical

demulsification systems require sophisticated equipment and high maintenance costs, while mechanical separation methods such as centrifugation demand substantial capital investment in machinery and ongoing maintenance expenses (Saad et al., 2019). These economic constraints have led many oil companies to seek more cost-effective alternatives that can deliver comparable or superior demulsification performance at lower operational costs (Grenoble & Trabelsi, 2018).

Environmental concerns represent another critical limitation of conventional demulsification methods, particularly those involving synthetic chemical demulsifiers. Most commercially available chemical demulsifiers are petroleum-based compounds that pose significant environmental and health risks due to their toxicity, non-biodegradability, and potential for bioaccumulation in ecosystems (Yaakob & Sulaimon, 2017). When these chemicals are discharged with produced water or disposed of improperly, they can contaminate soil and water bodies, causing harm to aquatic life and potentially entering the human food chain (Shehzad et al., 2018). The toxic nature of conventional demulsifiers also presents occupational health hazards for workers who handle these chemicals, requiring strict safety protocols and protective equipment (Saad et al., 2020). Additionally, increasingly stringent environmental regulations have created compliance challenges, with many jurisdictions setting strict limits on the types and concentrations of chemicals that can be employed in oil production operations (Yonguep et al., 2022). These regulations require extensive documentation and regular monitoring, adding to administrative burdens and operational costs, while in some regions certain conventional chemical demulsifiers have been banned or restricted due to their environmental toxicity (Hadi & Ali, 2022). The global shift toward sustainable practices and green chemistry

principles has highlighted the need for environmentally friendly demulsification alternatives that can minimize ecological impact while maintaining effective separation performance (Alara et al., 2022).

Technical limitations further constrain the effectiveness of conventional demulsification methods in addressing the diverse range of emulsion characteristics encountered in oil production. Chemical demulsifiers often exhibit poor versatility, meaning that a demulsifier formulation optimized for one crude oil type may perform poorly with different crude oils or under different production conditions (Fajun et al., 2020). This lack of universality necessitates extensive laboratory testing and field trials to identify suitable demulsifier formulations for each specific application, which is time-consuming and costly (Zhang et al., 2017). Conventional chemical demulsifiers can also lose their effectiveness over time due to changes in emulsion properties or the presence of contaminants (Su et al., 2021). Thermal methods may cause thermal degradation of sensitive hydrocarbon fractions and can be ineffective for highly stable emulsions, while electrical and mechanical methods face challenges in scaling up for large-volume applications and may struggle with emulsions containing high solids content or extreme viscosity ranges (Saad et al., 2019). These technical, economic, and environmental limitations underscore the urgent need for innovative demulsification approaches that can overcome the shortcomings of conventional methods while offering improved sustainability, cost-effectiveness, and operational flexibility (Grenoble & Trabelsi, 2018).

2.4 GREEN AND NATURAL DEMULSIFIERS

2.4.1 Rationale for Green Demulsifiers

The transition toward green demulsifiers in the petroleum industry is driven by the urgent need for sustainability and eco-friendly oilfield operations. As global pressure mounts for industries to reduce their environmental footprint, oil and gas companies are increasingly adopting sustainable solutions in their production processes (Al-Hameedi et al., 2019). Green demulsifiers derived from renewable biological sources offer significant environmental advantages including biodegradability, low toxicity, and reduced carbon footprint compared to conventional synthetic chemicals (Abdel-Raouf et al., 2021). Unlike petroleum-based demulsifiers that persist in the environment, green alternatives break down naturally into harmless byproducts, minimizing long-term ecological damage and reducing contamination risks (Nagtode et al., 2023). The use of environmentally friendly demulsifiers is particularly beneficial in sensitive environments such as offshore platforms and areas near residential communities (Amanullah & Ramasamy, 2019). Additionally, green demulsifiers reduce occupational health risks for workers by eliminating exposure to toxic synthetic chemicals, creating safer working conditions (Dhandhi et al., 2024). Recent studies have demonstrated that natural materials such as cellulose-based polymers and plant extracts can achieve separation efficiencies comparable to conventional chemicals while maintaining environmental compatibility (Husain et al., 2023; Sadighian et al., 2023).

The valorization of agricultural waste for demulsifier production presents compelling social and economic benefits beyond environmental considerations. Agricultural residues

such as fruit peels and plant biomass are generated in massive quantities worldwide, with much ending up in landfills where they contribute to pollution (Nesterov et al., 2024). Converting these waste materials into high-value demulsifiers exemplifies the circular economy approach, transforming waste into resources while creating economic opportunities (Devre & Gore, 2023). Using agricultural waste as feedstock offers economic advantages including lower raw material costs compared to petroleum-based chemicals, reduced waste management expenses, and potential for local production that supports regional economies (Okoro et al., 2020). From a social perspective, waste valorization creates employment opportunities in rural communities, provides additional income for farmers, and promotes technology transfer between agricultural and petroleum sectors (Nesterov et al., 2024). Furthermore, utilizing renewable agricultural waste reduces the industry's dependence on fossil fuel-derived chemicals, contributing to resource conservation and energy security (Roostaie et al., 2017).

2.4.2 Types of Natural Demulsifiers

Natural demulsifiers can be broadly classified into several categories based on their source and chemical composition, with plant-based extracts and biosurfactants representing the most extensively studied types in recent years. Plant-based demulsifiers are derived from various parts of plants including seeds, leaves, peels, and roots, and contain naturally occurring surface-active compounds such as saponins, tannins, alkaloids, and phenolic compounds that exhibit demulsification properties (Okoro et al., 2020). These extracts work by adsorbing at the oil-water interface and displacing the indigenous

stabilizing agents, thereby weakening the interfacial film and promoting droplet coalescence. Common sources of plant-based demulsifiers include:

- **Moringa oleifera**: Seeds and oil from this plant have demonstrated significant demulsification potential for treating crude oil emulsions and produced water, with studies showing effective reduction in oil and grease content and turbidity (de O. Santos et al., 2023; Kinate et al., 2025).
- **Neem (Azadirachta indica)**: Neem seed oil and extracts containing azadirachtin have been formulated into stable emulsions that exhibit surface-active properties suitable for demulsification applications (Kumar et al., 2025; Piluharto et al., 2025).
- **Agricultural waste extracts**: Waste materials such as fruit peels and plant residues have shown promise as cost-effective demulsifiers, with naturally derived waste brown oil extract demonstrating good separation efficiency (Okoro et al., 2021).

Biosurfactants produced by microorganisms represent another important category of natural demulsifiers, with yeasts and bacteria capable of synthesizing these compounds during hydrocarbon degradation (Rocha e Silva et al., 2017). These biological surface-active agents have been successfully applied in demulsifying petroleum derivative emulsions in seawater and enhancing bio-electrokinetic remediation of petroleum-contaminated soil (Gidudu & Chirwa, 2020). Additionally, enzyme-based demulsifiers have gained attention for their ability to disrupt protein-stabilized emulsions by

hydrolyzing interfacial proteins, though their application is more common in food processing than petroleum operations (Niu et al., 2021; Zhang & Lu, 2015).

The comparison of natural demulsifiers with synthetic alternatives reveals important differences in both efficiency and safety profiles. In terms of performance, recent studies have demonstrated that natural demulsifiers can achieve water separation rates comparable to conventional synthetic chemicals when optimized for specific crude oil types, though they may occasionally require slightly longer treatment times or higher dosages (Okoro et al., 2020; Kinate et al., 2025). From a safety perspective, natural demulsifiers demonstrate clear advantages due to their biodegradability and low toxicity, which minimize environmental contamination and reduce occupational health risks during handling (Esmaeili et al., 2021; Okoro et al., 2021). Unlike synthetic chemicals that persist in the environment and accumulate in ecosystems, plant-based demulsifiers break down naturally without contributing to long-term soil or water pollution (Patowary et al., 2017). The cost-effectiveness of natural demulsifiers is further enhanced by the availability of low-cost feedstocks, particularly agricultural waste, making them economically competitive with synthetic options while delivering superior environmental and safety benefits (de O. Santos et al., 2023).

2.4.3 Mechanisms of Action

The demulsification of crude oil emulsions by natural demulsifiers occurs through several interconnected mechanisms, with adsorption and replacement of natural stabilizers at the oil-water interface being the primary mode of action. Crude oil emulsions are stabilized by indigenous surface-active materials such as asphaltenes, resins, waxes, and naphthenic

acids that adsorb at the oil-water interface and form rigid interfacial films that prevent droplet coalescence (Kang et al., 2018). When a demulsifier is introduced, its surface-active components compete with these natural stabilizers for adsorption sites at the interface. Natural demulsifiers derived from plant extracts contain bioactive compounds such as saponins, phenolic compounds, and tannins that possess amphiphilic structures, enabling them to effectively displace the indigenous stabilizing agents (Pal et al., 2021). The adsorption behavior follows specific kinetics, with the rate depending on factors such as demulsifier concentration, molecular structure, and temperature (Song et al., 2025). Once adsorbed, the demulsifier molecules disrupt the mechanical strength and elasticity of the interfacial film, making it more permeable and easier to rupture during droplet collisions (Dhandhi et al., 2023). Bio-demulsifying agents operate through similar adsorption mechanisms but may also involve enzymatic degradation of protein and polysaccharide components in the interfacial film (Qi et al., 2022; Gao et al., 2025).

Reduction of interfacial tension represents another critical mechanism through which natural demulsifiers facilitate emulsion breakdown. Interfacial tension, the force per unit length acting at the boundary between two immiscible phases, plays a significant role in determining emulsion stability (Freitas et al., 2025). Natural demulsifiers lower interfacial tension by adsorbing at the oil-water interface and altering molecular interactions between phases, thereby reducing the energy barrier for droplet coalescence (Ekoue-Kovi & Jakubowski, 2024). The surface-active compounds orient themselves at the interface with hydrophobic portions extending into the oil phase and hydrophilic portions into the aqueous phase, effectively reducing interfacial energy and promoting destabilization (Dhandhi et al., 2023). Efficient demulsifiers typically reduce interfacial

tension to values that facilitate rapid coalescence, with this reduction serving as a useful parameter for assessing demulsifier performance (Freitas et al., 2025). The reduced interfacial tension not only weakens the interfacial film but also enhances water droplet mobility, increasing collision frequency and coalescence probability (Yaakob & Sulaimon, 2017). The combined effects of adsorption, replacement of natural stabilizers, and interfacial tension reduction work synergistically to break down the emulsion structure, allowing separated water droplets to coalesce into larger drops that settle rapidly under gravity, ultimately achieving efficient phase separation (Kang et al., 2018).

2.5 PLANT EXTRACTS AS DEMULSIFIERS

2.5.1 Overview of Plant-Based Demulsifiers

Plant-based demulsifiers have emerged as a promising alternative to conventional synthetic chemicals for treating crude oil emulsions, driven by the need for environmentally friendly and sustainable solutions in the petroleum industry. These natural demulsifiers are derived from various plant sources including seeds, leaves, bark, peels, and other agricultural residues, and contain bioactive phytochemicals such as saponins, tannins, alkaloids, phenolic compounds, and fatty acids that exhibit surface-active properties (Saad et al., 2019). The interest in plant-based demulsifiers stems from their biodegradability, low toxicity, renewable nature, and potential cost-effectiveness compared to synthetic alternatives (Abed et al., 2019). Research has demonstrated that plant extracts can effectively break crude oil emulsions through mechanisms similar to conventional demulsifiers, including adsorption at the oil-water interface, displacement

of natural stabilizers, and reduction of interfacial tension (Raya et al., 2020). The phytochemicals present in plant materials possess amphiphilic structures that enable them to interact with both oil and water phases, facilitating droplet coalescence and phase separation (Issaka, 2015). Recent advances in extraction techniques have improved the efficiency of obtaining active compounds from plant sources, with methods such as aqueous extraction, solvent extraction, and supercritical fluid extraction being employed to isolate demulsifying agents (Li et al., 2022). The development of nano-emulsions and nano-suspensions of phytochemicals has further enhanced the delivery and effectiveness of plant-based demulsifiers in crude oil treatment applications (Zuccari & Alfei, 2023).

Various plant species have been investigated for their demulsification potential, demonstrating diverse sources and chemical compositions that contribute to emulsion breaking. Some notable plant-based demulsifiers that have been studied include:

- **Tobacco (Nicotiana tabacum)**: Seed oil, leaf extracts, and stalk ash extracts have shown prospects for breaking crude oil emulsions, with the various plant components offering different active compounds for demulsification (Azubike & Itohan, 2021).
- **Agricultural waste extracts**: Naturally derived waste materials such as brown oil extract from agricultural residues have been successfully evaluated for demulsifying crude oil emulsions, demonstrating the viability of waste valorization (Okoro et al., 2020).

- **Tree bark extracts**: Phytochemicals derived from tree bark have been used to prepare Pickering emulsions and demonstrate surface-active properties applicable to demulsification processes (Loto et al., 2024).
- **Local plant materials**: Indigenous plant species have been explored for demulsifier development, offering opportunities for utilizing locally available resources and reducing dependence on imported chemicals (Adebanjo & Aduroja, 2015).

The versatility of plant-based demulsifiers lies in their ability to be formulated in various forms including crude extracts, purified compounds, oil-based formulations, and advanced delivery systems such as Pickering emulsions that can enhance stability and performance (Han et al., 2024). Despite the promising results, challenges remain in standardizing plant-based demulsifier formulations, optimizing extraction processes, and scaling up production for industrial applications. Nevertheless, the continued research and development of plant-based demulsifiers represents a significant step toward achieving more sustainable and environmentally responsible practices in crude oil production and processing (Saad et al., 2019).

2.5.2 Extraction Methods and Characterization

The extraction of bioactive compounds from plant materials for use as demulsifiers requires careful selection of appropriate techniques that can efficiently isolate the active phytochemicals while preserving their functional properties. Several extraction methods have been employed in the development of plant-based demulsifiers, each with distinct advantages and limitations:

- **Solvent extraction**: One of the most commonly used techniques, involving organic solvents such as petroleum ether, ethanol, methanol, or hexane to dissolve and extract bioactive compounds from plant tissues (Sindhu et al., 2021). This method is favored for its simplicity, cost-effectiveness, and ability to extract a wide range of compounds with varying polarities (Adebanjo & Aduroja, 2015; Georgewill & Joseph, 2023).
- **Soxhlet extraction**: A continuous solvent extraction technique that offers enhanced efficiency by repeatedly cycling solvent through the plant material, ensuring more complete extraction of target compounds (Karunanithi & Venkatachalam, 2019). However, it typically requires longer extraction times and larger solvent volumes compared to other methods.
- **Ultrasonic-assisted solvent extraction**: An improved variant that uses ultrasonic waves to enhance mass transfer and cell disruption, leading to higher extraction yields in shorter times with reduced solvent consumption (Karunanithi & Venkatachalam, 2019).
- **Cold pressing**: A mechanical extraction method particularly suitable for oil-rich plant materials, where pressure is applied to squeeze out oils without heat or chemicals, thereby preserving the natural properties of bioactive compounds (Lavenburg et al., 2021).
- **Hydrodistillation**: Involves heating plant material in water to extract volatile compounds through steam distillation, making it ideal for obtaining essential oils and other volatile phytochemicals that may contribute to demulsification activity (Sindhu et al., 2021).

The choice of extraction method depends on factors such as the nature of the plant material, target compounds, desired yield, environmental considerations, and economic feasibility (Lavenburg et al., 2021; Okoro et al., 2020).

Following extraction, comprehensive characterization of the obtained plant extracts is essential to identify the bioactive compounds responsible for demulsification activity and understand their chemical composition. Several analytical tools are employed for this purpose:

- **Gas Chromatography-Mass Spectrometry (GC-MS)**: The most widely used analytical tool for identifying volatile and semi-volatile compounds in plant extracts, providing detailed information about molecular structure, functional groups, and relative abundance of individual components (Gomathi et al., 2015). GC-MS analysis has revealed the presence of fatty acids, terpenes, alcohols, esters, and other bioactive compounds that contribute to surface-active properties (Jain et al., 2016; Casuga et al., 2016). The technique separates compounds based on volatility and polarity, with mass spectrometry providing structural identification by comparing fragmentation patterns with spectral libraries (Satar_Al_Baaj & Abdul-Jalil, 2022).
- **Fourier Transform Infrared Spectroscopy (FTIR)**: A complementary technique that identifies functional groups present in the extract by measuring the absorption of infrared radiation at different wavelengths (Jain et al., 2016). FTIR analysis can detect characteristic peaks corresponding to hydroxyl groups,

carbonyl groups, aromatic rings, and other structural features important for understanding the demulsification mechanism (Suleiman & Salihu, 2018).

- **High-Performance Liquid Chromatography (HPLC)**: Particularly useful for analyzing non-volatile and thermally unstable compounds such as phenolic compounds, flavonoids, and other polar bioactive constituents that cannot be analyzed by GC-MS (Ingle et al., 2017). HPLC coupled with photodiode array detection (HPLC-PAD) or mass spectrometry (HPLC-MS) enables quantitative determination of specific bioactive compounds and provides detailed compositional profiles (Dos Santos et al., 2017; Tremocoldi et al., 2018).

The integration of these analytical tools provides comprehensive characterization of plant extracts, allowing researchers to identify key bioactive compounds, establish correlations between chemical composition and demulsification performance, and optimize extraction processes for enhanced activity (Cieśla & Moaddel, 2016; Pal et al., 2021). Additionally, characterization of the natural surface-active components in crude oil and their interactions with plant-based demulsifiers can provide valuable insights into demulsification mechanisms and guide the development of more effective formulations (Yang et al., 2025; Saad et al., 2020).

2.5.3 Comparative Performance in Demulsification

Plant-based demulsifiers have demonstrated varying levels of efficiency in breaking crude oil emulsions, with performance largely dependent on the type of plant extract, crude oil characteristics, and operational conditions. Literature review reveals that the demulsification efficiency of natural demulsifiers typically ranges from 60% to 95%

water separation, with some optimized formulations achieving performance levels comparable to or exceeding synthetic demulsifiers (Yaakob & Sulaimon, 2017). The efficiency of plant-based demulsifiers is significantly influenced by several critical parameters:

- **Dosage**: Optimal demulsifier concentrations typically range from 100 to 1000 ppm, depending on emulsion stability and extract type (Pal et al., 2021). Insufficient dosage results in incomplete demulsification, while excessive amounts can lead to re-emulsification (Olabiyi et al., n.d.).
- **Temperature**: Higher temperatures generally enhance water separation by reducing crude oil viscosity and increasing droplet collision frequency, with optimal temperatures typically ranging from 40°C to 80°C (Grenoble & Trabelsi, 2018).
- **pH**: Most natural demulsifiers show optimal performance in the pH range of 4 to 8, though specific values vary based on the chemical composition of the extract (Adewunmi et al., 2021).

Statistical modeling and optimization techniques such as response surface methodology have been employed to identify the optimal combination of these parameters, maximizing demulsification efficiency while minimizing operational costs (Biniaz et al., 2016; Yonguep & Chowdhury, 2021).

Several case studies have demonstrated the effectiveness of specific plant-based demulsifiers:

- **Neem (Azadirachta indica)**: Neem seed oil contains azadirachtin and other bioactive compounds that exhibit surface-active properties, making them effective in disrupting emulsion stability (Mwanauta et al., 2023a; Mwanauta et al., 2023b).
- **Calabash seed**: Eco-friendly demulsifiers prepared from calabash seed have shown effectiveness for emulsion management in crude oil treatment (Okafor et al., 2024).
- **Cottonseed oil**: Natural demulsifiers derived from cottonseed oil have demonstrated effective low-temperature demulsification performance (Qu et al., 2024).
- **Fatty acid-based demulsifiers**: Demulsifiers formulated from naturally occurring fatty acids have shown promising efficiency on Nigerian crude oil emulsions (Nwakuba et al., n.d.).
- **Local plant extracts**: Various indigenous plant materials have demonstrated successful water-in-oil emulsion treatment with efficiency levels competitive with synthetic alternatives (Adebanjo & Aduroja, 2015).

These case studies collectively demonstrate that plant-based demulsifiers can achieve practical demulsification performance across different crude oil types and operational conditions, supporting their viability as sustainable alternatives to conventional synthetic chemicals (Yaakob & Sulaimon, 2017; Pal et al., 2021).

2.6 LEMON PEEL EXTRACT: CHEMISTRY AND APPLICATION

2.6.1 Chemical Composition of Lemon Peel

Lemon peel (*Citrus limon*) is a complex matrix containing a diverse array of bioactive compounds that contribute to its potential demulsifying activity. The chemical composition varies depending on factors such as geographic origin, cultivar, maturity stage, and extraction method, but generally consists of essential oils, flavonoids, polyphenols, pectin, cellulose, and proteins. Understanding the chemical constituents of lemon peel is crucial for elucidating the mechanisms by which these compounds interact with crude oil emulsions and facilitate phase separation.

2.6.1.1 Essential oils constitute a significant fraction of lemon peel's bioactive components, with limonene and citral being the predominant compounds. Limonene, a monoterpene hydrocarbon, typically accounts for 60-90% of the total essential oil content and is responsible for the characteristic citrus aroma (Paw et al., 2020; El Aboubi et al., 2022). Studies on lemon peel essential oils from different regions have consistently identified limonene as the major component, with concentrations varying based on geographical location and processing conditions (Benoudjit et al., 2020; Kamaliroosta et al., 2016). Citral, an aldehyde comprising geranial and neral isomers, represents another important volatile compound found in lemon peel essential oil, typically present at concentrations ranging from 1-5% (Petretto et al., 2023). These essential oil components exhibit surface-active properties due to their amphiphilic nature, with the hydrocarbon structure providing hydrophobic characteristics while functional groups offer some polarity, enabling them to adsorb at oil-water interfaces (Haokip et al., 2023). The

antimicrobial and antioxidant activities of lemon peel essential oils have been well documented, with limonene and citral contributing significantly to these bioactivities (Moosavy et al., 2017; Huang et al., 2025).

2.6.1.2 Flavonoids and polyphenols represent another important class of bioactive compounds in lemon peel that may contribute to demulsifying activity. Lemon peel contains various polyphenolic compounds including hesperidin, eriocitrin, naringin, rutin, and phenolic acids such as ferulic acid and caffeic acid (Gómez-Mejía et al., 2019; Imran et al., 2020). These compounds are typically concentrated in the peel rather than the juice, making citrus processing waste a valuable source of polyphenols (Saini et al., 2019). The extraction and quantification of polyphenols from lemon peel can be achieved through various techniques including maceration, ultrasonic extraction, and solvent extraction, with the choice of method affecting the yield and composition of extracted compounds (M'hiri et al., 2017). Polyphenolic compounds possess both hydrophilic (hydroxyl groups) and hydrophobic (aromatic rings) moieties, giving them amphiphilic characteristics that enable them to function as natural surfactants (Sharma et al., 2015). This structural feature allows flavonoids and polyphenols to adsorb at oil-water interfaces, potentially displacing indigenous emulsion stabilizers and facilitating droplet coalescence. Additionally, the antioxidant properties of these compounds may help prevent oxidative degradation of crude oil components during storage and processing (Gómez-Mejía et al., 2019).

2.6.1.3 Pectin, cellulose, and proteins are structural and functional biopolymers present in lemon peel that may also contribute to its demulsifying properties. Pectin, a complex

polysaccharide found in the cell walls of citrus fruits, can be extracted from lemon peel with yields typically ranging from 15-30% depending on extraction conditions (Karim et al., 2022). Lemon peel pectin has been characterized and applied in various applications including biodegradable film production, demonstrating its functional properties (Dimopoulou et al., 2019). Cellulose represents another major structural component of lemon peel, with citrus processing waste serving as a valuable source of micronized cellulose that can be extracted using environmentally friendly methods (Scurria et al., 2021; Al Jitian et al., 2022). Both pectin and cellulose are hydrophilic biopolymers that can influence emulsion stability through mechanisms such as steric stabilization or by modifying the rheological properties of the aqueous phase. While proteins are present in smaller quantities in lemon peel compared to other components, they possess inherent surface-active properties due to their amphiphilic nature, with hydrophobic and hydrophilic amino acid residues enabling them to adsorb at interfaces (Li et al., 2020). The relevance of these biopolymers to demulsifying activity lies in their ability to interact with emulsion components, modify interfacial properties, and potentially facilitate droplet coalescence through competitive adsorption or bridging mechanisms. The synergistic effects of essential oils, polyphenols, and biopolymers in lemon peel may contribute to its overall demulsification performance, with the combination of these compounds providing multiple mechanisms for destabilizing crude oil emulsions (Franco-Vega et al., 2021).

2.6.2 Extraction and Preparation Techniques

The extraction of bioactive compounds from lemon peel requires careful selection of appropriate techniques that can efficiently recover the desired components while maintaining their functional properties for demulsification applications. Several extraction methods have been employed for lemon peel processing, each offering distinct advantages and limitations.

2.6.2.1 Steam distillation is one of the most widely used methods for extracting essential oils from lemon peel due to its simplicity and scalability. This technique involves passing steam through the lemon peel material, causing volatile essential oils to vaporize and subsequently condense for collection (Sikdar et al., 2016). Steam distillation can be performed using conventional heating or microwave-assisted methods, with microwave steam distillation offering reduced extraction time and lower energy consumption (Shakir & Salih, 2015; Kusuma et al., 2016). The method effectively extracts limonene and other volatile compounds, producing essential oils free from non-volatile impurities (Gök et al., 2015). However, this method primarily recovers volatile compounds and may not extract non-volatile bioactive components such as flavonoids and polyphenols (Karne et al., 2023).

2.6.2.2 Soxhlet extraction represents a continuous solvent extraction technique that offers higher extraction efficiency for both volatile and non-volatile compounds from lemon peel. This method involves repeatedly cycling organic solvents such as hexane, ethanol, or methanol through the lemon peel material, ensuring thorough extraction of target compounds (Jagannath & Biradar, 2019). The choice of solvent significantly

influences the composition of the extract, with non-polar solvents preferentially extracting essential oils while polar solvents can recover both hydrophobic and hydrophilic bioactive components (Gök et al., 2015). Soxhlet extraction can achieve higher yields compared to other methods, though it requires longer extraction times (4-8 hours) and larger solvent volumes (Jagannath & Biradar, 2019; Shofinita et al., 2015).

2.6.2.3 Maceration is a simple and cost-effective method involving soaking lemon peel material in a solvent at room temperature for 24 to 72 hours. This technique is particularly suitable for extracting thermally labile compounds that may degrade under heat conditions (Bagde et al., 2017). Maceration can be performed using various solvents depending on target compounds, with aqueous or alcoholic solutions commonly employed for extracting polyphenols and flavonoids. While advantageous for its simplicity and preservation of heat-sensitive compounds, it typically yields lower extraction efficiency compared to more intensive methods (Shofinita et al., 2015). Enhanced techniques such as ultrasonic-assisted extraction can improve yields by disrupting cell walls and enhancing mass transfer (Jagannath & Biradar, 2019). Additionally, specialized methods like ohmic heating-assisted extraction have been applied for recovering specific components such as pectin from lemon peel (Çilingir et al., 2021).

Several parameters significantly influence the yield and purity of lemon peel extracts:

- **Particle size**: Smaller particles increase surface area and enhance solvent penetration, typically resulting in higher yields (Shofinita et al., 2015).

- **Solvent type**: The polarity must be matched to target compounds, with non-polar solvents for essential oils and polar solvents for flavonoids and polyphenols (Gök et al., 2015).
- **Extraction time and temperature**: Longer times and higher temperatures generally increase yield up to an optimal point, beyond which degradation may occur (Jagannath & Biradar, 2019).
- **Solid-to-solvent ratio**: Optimal ratios typically range from 1:10 to 1:20 (w/v) depending on the method used (Çilingir et al., 2021).
- **Pre-treatment methods**: Drying and grinding can significantly influence extraction efficiency by facilitating solvent access to cellular components (Shakir & Salih, 2015).

The selection of an appropriate extraction method should consider target compounds, desired yield and purity, available equipment, cost considerations, and environmental impact, with optimization of extraction parameters being crucial for maximizing demulsification performance (Shofinita et al., 2015; Gök et al., 2015).

2.6.3 Previous Studies on Lemon Peel Extract as a Demulsifier

Despite the growing interest in plant-based demulsifiers for crude oil emulsion treatment, there is a notable scarcity of research specifically investigating lemon peel extract as a demulsifying agent in petroleum applications. The available literature primarily focuses on the utilization of lemon peel and citrus waste for other applications, with limited direct studies on their demulsification performance in crude oil systems. However, several related studies provide valuable context and demonstrate the potential of lemon peel

components for interfacial and separation applications that may translate to demulsification activity.

Research on citrus peel materials has predominantly explored their application in oil-water separation through different mechanisms. Studies have investigated the use of cellulose-based materials derived from citrus peels for oil-water separation applications, demonstrating the potential of citrus waste components in interfacial processes (Chen et al., 2024). Modified cellulose materials from citrus sources, including those treated with citric acid, have shown superwetting characteristics and high efficiency in separating oil-water mixtures and emulsions, achieving effective separation through specialized surface properties rather than chemical demulsification (Belachew et al., 2024; Wu et al., 2024). Additionally, citrus peel surfaces and their derivatives have been engineered to create slippery surfaces with applications in preventing fouling and facilitating liquid separation, though these applications differ from traditional chemical demulsification (Han et al., 2021). The oil sorption capacity of citrus peel waste, particularly orange peel, has been investigated for oil spill remediation, with studies showing that raw and thermally modified peels can effectively absorb oil from water surfaces (El Gheriany et al., 2020; Yadav et al., 2019). While these applications demonstrate the interaction of citrus materials with oil-water systems, they focus on physical separation mechanisms rather than the chemical demulsification approach relevant to crude oil emulsion treatment.

Other studies have examined the utilization of lemon peel extracts and essential oils in emulsion systems, though primarily in food and fuel applications rather than petroleum demulsification. Research on lemon peel oil has investigated its incorporation into

biodegradable emulsions for diesel engine applications, demonstrating the feasibility of using citrus-derived materials in oil-based systems (Sivalingam et al., 2023). The rheological properties and stability of emulsions prepared with citrus peel fiber have been studied in food applications, providing insights into how citrus components interact with oil-water interfaces (Bi et al., 2020). Reviews on citrus peel waste valorization have highlighted the extraction and characterization of essential oils for food industry applications, emphasizing the bioactive properties and potential uses of these extracts, though demulsification in petroleum systems has not been a primary focus (Grover et al., 2025). The extraction methods and characterization of lemon peel components have been well documented in contexts ranging from food processing waste valorization to the development of eco-friendly materials, but their specific application as crude oil demulsifiers remains largely unexplored in the scientific literature (Waste, n.d.; Akalan & Gök, n.d.). Furthermore, lemon peel extracts have been extensively studied for their antioxidant properties, nanoparticle synthesis applications, and wastewater treatment capabilities, demonstrating the versatility of these materials in various environmental applications (Athanasiadis et al., 2024; Devi et al., 2023; Kir et al., 2024; Lucia et al., 2022). However, these studies do not directly address the demulsification of crude oil emulsions, representing a significant research gap that the current investigation aims to address. The limited literature specifically focused on lemon peel extract as a crude oil demulsifier underscores the novelty of this research area and highlights the need for systematic investigation of lemon peel's demulsification performance, optimal application conditions, and underlying mechanisms in petroleum emulsion treatment.

2.6.4 Comparative Analysis with Other Natural Demulsifiers

A comparative analysis of lemon peel extract with other natural demulsifiers provides valuable context for understanding its potential effectiveness within the broader landscape of plant-based demulsification technologies. Various natural materials have been investigated as alternatives to synthetic chemical demulsifiers, each exhibiting distinct chemical compositions and performance characteristics.

2.6.4.1 Cashew nut shell liquid (CNSL) represents one of the most extensively studied natural demulsifiers and serves as an important benchmark for evaluating plant-based alternatives. Comparative studies have demonstrated that CNSL can perform competitively with commercial synthetic demulsifiers in treating crude oil emulsions, achieving significant water separation efficiencies under optimized conditions (Victor-Oji et al., 2019). CNSL contains phenolic compounds such as cardanol, cardol, and anacardic acid that possess surface-active properties enabling them to displace indigenous emulsion stabilizers at the oil-water interface, mechanisms similar to those expected from lemon peel extract components. However, CNSL typically requires chemical modification or formulation with other components to optimize its performance, whereas lemon peel extract may offer advantages in terms of availability, cost, and ease of extraction (JESSE, 2021). Advanced approaches such as fuzzy TOPSIS methodology and machine learning models have been developed to evaluate and optimize demulsifier selection based on multiple criteria including efficiency, cost, and environmental impact (Yu et al., 2025; Hashem et al., 2024).

2.6.4.2 Citrus-based materials from other citrus species provide the most direct comparison to lemon peel extract due to their similar chemical compositions. Orange peel liquid derivatives have been experimentally investigated as demulsifiers for crude oil emulsion treatment, demonstrating the potential of citrus waste materials in petroleum applications (Wadike et al., 2025). Comparative studies on citrus extracts for water treatment have shown that different citrus species exhibit varying efficiencies, with performance depending on the specific bioactive compounds present in each variety (Paul et al., 2024). The essential oil composition of different citrus peels varies in their relative proportions of limonene, citral, and other terpenes, which may influence their demulsification effectiveness (Kang et al., 2018).

2.6.4.3 Papaya-derived materials have been explored for applications involving emulsion systems and water treatment. Papaya seed extracts have been evaluated for coagulation-flocculation applications in water quality improvement, demonstrating potential in interfacial processes (Paul et al., 2024). Pectin extracted from papaya has been characterized and shown to possess emulsifying properties, though its application as a crude oil demulsifier has not been extensively documented (Saraswathi, 2019). Other fruit-derived pectins, such as those from pomegranate peel, have demonstrated effective emulsifying properties that could potentially be applied to demulsification through competitive adsorption mechanisms (Yang et al., 2018).

The comparative advantage of lemon peel extract may lie in the synergistic effects of its multiple bioactive components working together to achieve demulsification. Research has demonstrated that combinations of essential oils and plant extracts can exhibit synergistic

effects that enhance overall performance beyond individual components (Khodaei et al., 2023; Avci & Gergeroglu, 2019). The complex mixture of essential oils, polyphenols, and biopolymers in lemon peel extract may exhibit enhanced demulsification performance through complementary mechanisms of action (Donkor et al., 2023; Jouda et al., 2016). This potential synergistic effect could position lemon peel extract as a competitive alternative to other natural demulsifiers, though systematic comparative studies are needed to validate this hypothesis and establish optimal application conditions for different crude oil emulsion types.

2.7 MECHANISMS OF DEMULSIFICATION BY NATURAL EXTRACTS

2.7.1 Interfacial Activity and Surfactant Properties

The effectiveness of lemon peel extract as a demulsifier is fundamentally linked to the interfacial activity and surfactant properties of its bioactive constituents at the oil-water interface. Understanding how these components interact with crude oil emulsions at the molecular level is crucial for elucidating the demulsification mechanism and optimizing treatment conditions.

2.7.1.1 Interfacial tension reduction is a key indicator of surfactant activity and plays a critical role in demulsification processes. Interfacial tension represents the energy required to create a unit area of interface between immiscible phases, and its reduction facilitates droplet coalescence by weakening the interfacial film (Ghorbanizadeh & Rostami, 2017). Amphiphilic compounds, which possess both hydrophilic and hydrophobic moieties, naturally accumulate at oil-water interfaces where they reduce interfacial tension by minimizing unfavorable interactions between phases (Favetta et al.,

2025). The bioactive components of lemon peel extract, including limonene, citral, and polyphenols, exhibit amphiphilic characteristics that enable them to function as natural surfactants. Studies have demonstrated that amphiphilic compounds can significantly reduce water/oil interfacial tension, with the degree of reduction governed primarily by their surface concentration at the interface (Jian et al., 2016). The self-assembly behavior of surfactants at interfaces is driven by their amphiphilic nature, where hydrophobic portions orient toward the oil phase while hydrophilic portions extend into the aqueous phase, creating an ordered molecular arrangement that modifies interfacial properties (Ghosh et al., 2020; Wang et al., 2015).

2.7.1.2 Adsorption behavior at the oil-water interface determines the effectiveness of natural surfactants in displacing indigenous emulsion stabilizers and promoting demulsification. The adsorption of natural surfactants at the oil-water interface influences interfacial rheology and structural characteristics critical to demulsification processes (Machale et al., 2023). Molecular simulations and experimental studies have shown that surfactants exhibit specific adsorption behaviors, with their orientation and packing density influencing interfacial properties (Yang et al., 2020). In crude oil systems, the synergetic adsorption between asphaltenes and surfactants can either stabilize or destabilize the interfacial film depending on surfactant nature and concentration (Sun et al., 2021). Advanced techniques have revealed dynamic processes including diffusion, orientation, and reorganization of molecules at the interface (Wu et al., 2016). For effective demulsification, the natural surfactants in lemon peel extract must compete with indigenous stabilizers for adsorption sites and ultimately weaken or disrupt the interfacial film.

2.7.1.3 Natural surfactant properties of plant extracts have been demonstrated in various studies. Eco-friendly demulsifiers from plant sources such as calabash seed have exhibited surfactant-like properties for managing oil-water emulsions (Okafor et al., 2024). Plant-derived phytochemicals have been successfully used as co-surfactants in dispersions, demonstrating that natural compounds can function as surface-active agents (Sawadikiat et al., 2015). Biosurfactant solutions have enhanced phytochemical extraction efficiency, suggesting inherent surfactant properties that facilitate interfacial activity (Javed et al., 2022). Plant extracts have shown both emulsification and demulsification abilities depending on application conditions (Maduelosi et al., 2024). In lemon peel extract, the combination of essential oils (limonene, citral), polyphenolic compounds, and other bioactive molecules likely contributes to overall surfactant activity through synergistic mechanisms, with their effectiveness in reducing interfacial tension and adsorbing at the oil-water interface determining demulsification performance (Ghorbanizadeh & Rostami, 2017; Ghosh et al., 2020).

2.7.2 Destabilization Pathways

The destabilization of crude oil emulsions by lemon peel extract involves multiple interconnected pathways that work sequentially or simultaneously to achieve phase separation. Understanding these destabilization mechanisms is essential for optimizing demulsification conditions and predicting the performance of natural demulsifiers.

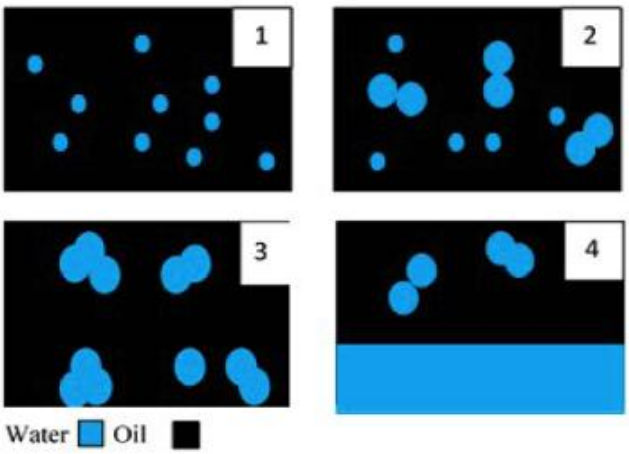
The primary destabilization pathways include flocculation, film thinning, and coalescence, which represent sequential stages in emulsion breakdown. Flocculation is the initial step where dispersed water droplets aggregate together through attractive

forces, forming clusters without merging (Zhang et al., 2025). This process is facilitated when demulsifiers reduce repulsive forces between droplets, allowing closer approach. Temperature-responsive mechanisms can regulate flocculation, with temperature changes affecting demulsifier surface activity (Zhang et al., 2025). Film thinning follows as the continuous oil phase separating adjacent water droplets is gradually drained, reducing interfacial film thickness (Mhatre et al., 2018). This is a critical step determining emulsion breakdown rate, with demulsifiers accelerating the process by weakening interfacial film mechanical strength (Yang et al., 2018). Studies using thin liquid film techniques reveal that demulsifiers promote film drainage by disrupting the organized structure of indigenous stabilizers, making the film more susceptible to rupture (Yang et al., 2018). Once the interfacial film becomes sufficiently thin and weak, coalescence occurs where adjacent droplets merge to form larger droplets that settle more rapidly (Raya et al., 2020). This process can be enhanced through acoustic treatment, electric fields, and chemical demulsifiers (Xie et al., 2015; Mhatre et al., 2018).

The interaction between demulsifiers and crude oil components at the oil-water interface determines which destabilization pathway dominates. Effective demulsifiers must adsorb at the oil-water interface and modify interfacial film properties to promote destabilization (Li et al., 2021). The bioactive compounds in lemon peel extract, including limonene, citral, and polyphenols, likely interact with indigenous stabilizers such as asphaltenes through competitive adsorption and displacement mechanisms (Hadi & Ali, 2022). These interactions can alter interfacial film rheological properties, reducing elasticity and viscosity, which facilitates film drainage and rupture. The specific pathway followed

depends on factors such as demulsifier chemical composition, concentration, crude oil properties, and operational conditions (Raya et al., 2020).

Coalescence dynamics represents a complex phenomenon influenced by droplet size, interfacial properties, and external forces. Research has identified various mechanisms for understanding droplet coalescence in liquid-liquid systems (Kamp et al., 2017). Novel coarsening mechanisms show that droplets in immiscible mixtures can grow through coalescence pathways differing from classical theories (Shimizu & Tanaka, 2015). The dynamics of droplet formation, growth, and coalescence involve complex interactions between hydrodynamic forces, interfacial tension, and film drainage rates (Karbaschi et al., 2015). Understanding these dynamics is important for predicting how lemon peel extract components influence droplet behavior and achieve water separation. Studies on flavonoid- and limonoid-rich extracts from lemon pomace have investigated their technological properties in emulsion systems, providing insights into how these compounds interact with oil-water interfaces (Iervese et al., 2024). Research on emulsions stabilized by natural compounds such as rutin has shown that flavonoids can significantly affect emulsion structure and stability (Dammak & do Amaral Sobral, 2018), suggesting that lemon peel extract's polyphenolic and flavonoid components may contribute to destabilization by modifying interfacial rheology and promoting enhanced coalescence or accelerated film drainage.



(1) water present as small droplets in oil, (2) flocculation of the water droplets, (3) coalescence of the water droplets, (4) settling down of larger droplets.

Figure 2.2 Steps of W/O Emulsion Breaking Process (A. B. Yaakob & Sulaimon, 2017)

2.7.3 Factors Affecting Demulsification Efficiency

The efficiency of demulsification using lemon peel extract is influenced by multiple interrelated factors that must be carefully controlled and optimized to achieve maximum water separation from crude oil emulsions. Understanding these factors is critical for developing effective treatment protocols and predicting demulsifier performance under varying operational conditions.

Demulsifier dosage is one of the most critical parameters affecting separation efficiency, as both insufficient and excessive amounts can compromise performance. The optimal dosage varies depending on emulsion characteristics, crude oil composition, and water content (Raynel et al., 2021). Studies have demonstrated that demulsifier concentration exhibits a non-linear relationship with separation efficiency, with performance initially

increasing until reaching an optimum point, beyond which additional demulsifier may cause diminishing returns or re-emulsification (Abdulredha et al., 2020). Statistical approaches such as response surface methodology have been widely employed to optimize demulsifier formulation and dosage, enabling identification of optimal operating conditions while minimizing experimental trials (Hajivand & Vaziri, 2015; Dhandhi et al., 2022). Advanced selection methods including fuzzy TOPSIS-based multi-criteria decision-making approaches have been developed to optimize demulsifier selection and dosage based on multiple performance criteria (Yu et al., 2025).

pH and salinity are critical environmental factors that significantly influence demulsification efficiency by affecting the ionization state and surface activity of demulsifying agents. pH affects the charge distribution and interfacial behavior of amphiphilic molecules, with studies showing that demulsifiers exhibit varying stability and dynamic properties at the oil-water interface depending on pH levels (Zaman et al., 2019). The effect of pH on emulsion stability suggests that it influences interfacial chemistry and the adsorption behavior of demulsifiers (Miadonye & Amadu, 2023). Salinity plays a dual role where ionic strength affects both interfacial tension and the stability of the electrical double layer surrounding water droplets. Research has demonstrated that salinity can trigger pH-induced demulsification and alter rheological properties of crude oil-water nanoemulsions (Onaizi, 2022). Statistical modeling has revealed significant interactions between pH, salinity, and other operational parameters in determining demulsification efficiency (Biniaz et al., 2016). For lemon peel extract, the polyphenolic and acidic components may exhibit pH-dependent ionization that influences their surface activity and demulsification performance.

Temperature and mixing intensity are operational parameters that significantly impact demulsification kinetics and efficiency. Temperature affects crude oil viscosity, interfacial tension, demulsifier solubility, and the rate of droplet collision and coalescence (Saad et al., 2020). Higher temperatures generally enhance demulsification by reducing oil viscosity and increasing molecular mobility, though excessive temperatures may cause thermal degradation of thermally labile compounds in plant extracts. Mixing intensity influences the initial contact between demulsifier and emulsion, affecting the distribution of demulsifying agents and droplet collision frequency, though overly vigorous mixing can cause re-emulsification (Shehzad et al., 2018).

Emulsion characteristics and crude oil properties represent inherent factors that determine the difficulty of demulsification and required treatment intensity. The presence of nanoparticles in emulsions can significantly affect stability, with certain particles stabilizing Pickering emulsions that are more resistant to demulsification (Nunez et al., 2019; French et al., 2015). Emulsion viscosity and water content influence droplet break-up behavior (Gai et al., 2016). Interfacial properties including interfacial tension and wettability characteristics vary among different crude oils and directly impact demulsification efficiency (Saha et al., 2018). Crude oil composition, particularly the concentration of indigenous stabilizers such as asphaltenes, resins, and waxes, determines baseline emulsion stability and the demulsifier dosage required for effective treatment (Yaakob & Sulaimon, 2017). For lemon peel extract applications, demulsification efficiency will depend on how well the extract's bioactive components can compete with these indigenous stabilizers and overcome the specific stability mechanisms present in each crude oil system (Saad et al., 2020).

2.8 EXPERIMENTAL APPROACHES AND ANALYTICAL TECHNIQUES

2.8.1 Emulsion Preparation and Characterization

The preparation and characterization of crude oil emulsions are fundamental steps in investigating the demulsification efficiency of lemon peel extract, as these processes establish controlled experimental conditions and provide baseline data for evaluating treatment performance. Proper emulsion preparation techniques and comprehensive characterization methods are essential for ensuring reproducibility and obtaining reliable results.

2.8.1.1 Emulsion preparation involves the controlled mixing of crude oil and water to create stable emulsions that mimic those encountered in petroleum production operations. Crude oil emulsions can be classified into two main types: water-in-oil (W/O) emulsions, where water droplets are dispersed in a continuous oil phase, and oil-in-water (O/W) emulsions, where oil droplets are dispersed in a continuous water phase (Sousa et al., 2021). Water-in-crude oil emulsions are the most common type encountered in petroleum production and are typically the focus of demulsification studies (Wong et al., 2015). The formation of these emulsions requires sufficient energy input to break up one phase into small droplets and disperse them throughout the continuous phase, which is typically achieved through mechanical agitation, high-pressure homogenization, or high-shear mixing (Yonguep et al., 2022). Several factors influence emulsion formation and stability including:

- **Mixing intensity and duration**: Higher energy input produces smaller droplets and more stable emulsions (Juttulapa et al., 2017).

- **Oil-to-water ratio**: Affects emulsion type and stability, with higher water content generally increasing emulsion viscosity (Raya et al., 2020).
- **Temperature**: Influences oil viscosity and interfacial tension during preparation (Yonguep et al., 2022).
- **Presence of stabilizers**: Indigenous surfactants in crude oil stabilize emulsions during formation (Wong et al., 2015).

2.8.1.2 Lab-scale model emulsions can be prepared to simulate field conditions, providing controlled systems for studying demulsification mechanisms. High-stable water-in-oil model emulsions are particularly useful for laboratory investigations, with their stability influenced by preparation methods and component selection (Almeida et al., 2017). The preparation technique must be standardized to ensure reproducibility across different experimental trials.

2.8.1.3 Emulsion characterization encompasses a range of analytical techniques and measurements that provide information about emulsion properties, stability, and behavior. Key characterization parameters include:

- **Droplet size and distribution**: Typically measured using laser diffraction, dynamic light scattering, or microscopy techniques, with smaller droplets generally indicating more stable emulsions (Kupikowska-Stobba et al., 2024).
- **Bottle tests**: A fundamental stability testing method involving visual observation of phase separation over time, where emulsion samples are placed in graduated cylinders or bottles and monitored for water separation, providing a simple yet

effective measure of demulsification efficiency (Mcclements, 2007; Goodarzi & Zendehboudi, 2019).

- **Emulsion stability assessment**: Evaluated through various complementary methods including centrifugation tests, turbidity measurements, and stability indices such as the Turbiscan Stability Index (TSI) (Wang et al., 2018; Mcclements, 2007).
- **Rheological properties**: Viscosity measurements and flow behavior characterization provide insights into emulsion structure and stability (Sriprablom et al., 2019).
- **pH and conductivity**: Important parameters that influence emulsion stability and demulsifier performance (Goodarzi & Zendehboudi, 2019).
- **Interfacial tension**: Measures the energy at the oil-water interface and indicates the effectiveness of surfactants or demulsifiers (Roland et al., 2003).
- **Microscopic analysis**: Provides direct visualization of droplet morphology, size distribution, and structural changes during demulsification (Hosseini et al., 2015).

Systematic characterization approaches have been developed to comprehensively evaluate emulsion properties for formulation design and stability prediction (Roland et al., 2003; Mcclements, 2007). Advanced techniques for studying functional characteristics of emulsion systems include multiple analytical methods that provide complementary information about emulsion behavior (Hu et al., 2017). Recent developments in emulsion characterization have introduced specialized techniques such as Pickering emulsion analysis stabilized by protein-polysaccharide nanoparticles, which may be relevant for

understanding the role of lemon peel's biopolymer components in emulsion systems (Yang et al., 2020).

2.8.2 Evaluation of Demulsification Performance

The evaluation of demulsification performance is essential for assessing the effectiveness of lemon peel extract in breaking crude oil emulsions and for comparing its efficiency with other demulsifying agents. Multiple analytical methods and performance metrics are employed to provide comprehensive assessment of demulsification effectiveness under various operational conditions.

2.8.2.1 Bottle test protocol remains the industry standard method for evaluating demulsifier performance due to its simplicity, cost-effectiveness, and ability to simulate field conditions. The bottle test procedure typically involves preparing emulsion samples in graduated cylinders or glass bottles, adding predetermined amounts of demulsifier, mixing thoroughly, and monitoring the volume of separated water at specific time intervals while maintaining controlled temperature conditions (Raynel et al., 2021). The test methodology must be carefully standardized to ensure reproducibility, with critical parameters including sample volume, demulsifier dosage, mixing intensity, temperature, and observation time points clearly defined (White et al., 2021). Traditional bottle tests rely on visual observation of the interface between separated phases, which can introduce subjectivity and variability in results. To address these limitations, advanced digitalization approaches have been developed, such as nuclear magnetic resonance (NMR) evaluation of emulsion stability, which provides more objective, rapid, and detailed assessment of demulsification performance (Marques & White, 2020). The bottle

test protocol can be adapted based on specific crude oil characteristics and operational requirements, with modifications in test duration, temperature profiles, or measurement techniques to better represent field conditions (White et al., 2021). Statistical modeling and optimization techniques are commonly employed to analyze bottle test data and identify optimal operating conditions that maximize separation efficiency (Biniaz et al., 2016).

2.8.2.2 Key performance parameters measured during demulsification evaluation provide quantitative metrics for comparing different demulsifiers and operating conditions:

- **Separation time**: The time required to achieve a specified percentage of water separation, typically 50% or 90%, serves as an important kinetic parameter indicating demulsification rate (Raynel et al., 2021).
- **Separation efficiency**: Expressed as the percentage of water separated from the total water content, this is the primary indicator of demulsifier effectiveness, with higher values indicating better performance (White et al., 2021).
- **Turbidity reduction**: Measures the clarity of both separated oil and water phases, with lower turbidity indicating cleaner separation and better demulsifier performance (Bensadok et al., 2007).
- **Residual content**: The amount of water remaining in the treated oil phase and oil content in the separated water phase, which determine the quality of separated products (Al-Shamrani et al., 2002).

- **Interface quality**: Visual assessment of the oil-water interface, noting the presence or absence of a rag layer (intermediate emulsion layer), which indicates incomplete demulsification (Raynel et al., 2021).

These parameters are typically monitored over time to generate separation curves that reveal the kinetics and efficiency of the demulsification process under different conditions (Biniaz et al., 2016).

2.8.2.3 Advanced analytical tools provide complementary information beyond basic bottle test observations, enabling deeper understanding of demulsification mechanisms and emulsion behavior:

- **Microscopy techniques**: Optical microscopy, confocal microscopy, and electron microscopy enable direct visualization of droplet size, morphology, and structural changes during demulsification (Berg et al., 2004). Particle tracking using confocal microscopy can probe microrheological properties and phase separation dynamics at the microscopic level (Moschakis et al., 2006).
- **Spectroscopic methods**: Techniques such as Raman spectroscopy, FTIR, and NMR provide molecular-level information about emulsion composition, interfacial properties, and interactions between demulsifier components and crude oil constituents (Niu et al., 2016). NMR spectroscopy is particularly valuable for studying emulsion structure and dynamics non-invasively (Berg et al., 2004).
- **Rheological characterization**: Measurements of viscosity, yield stress, and viscoelastic properties reveal how demulsifiers affect emulsion flow behavior and structural stability (Tadros, 1994). Changes in rheological properties during

treatment correlate with demulsification effectiveness, with decreasing viscosity typically indicating progressive emulsion breakdown (Niu et al., 2016).

The integration of multiple analytical approaches provides comprehensive characterization of demulsification performance. Combined techniques using NMR, rheology, and electron microscopy reveal relationships between structural changes and separation efficiency, offering insights into demulsification mechanisms (Berg et al., 2004). For lemon peel extract applications, advanced tools can identify which bioactive components are most active at the interface, how they modify emulsion structure, and what mechanisms drive water separation. This multi-method evaluation framework enables optimization of extraction procedures, application conditions, and formulation strategies to maximize the demulsification performance of lemon peel extract for crude oil emulsion treatment (Raynel et al., 2021; White et al., 2021).

2.9 GAPS IN THE LITERATURE AND RESEARCH JUSTIFICATION

Despite significant advances in demulsification technologies, several critical gaps remain regarding natural and bio-based demulsifiers. While conventional chemical demulsifiers have been extensively studied, research on plant-based alternatives remains limited and fragmented (Alao et al., 2021). The mechanisms of plant-derived bioactive compounds and their interactions with indigenous emulsion stabilizers require further investigation (Raya et al., 2020). Recent reviews acknowledge the emergence of bio-based options but highlight the need for more systematic studies on their effectiveness and practical applicability (Abed et al., 2019; Dennis, 2025). Insufficient comparative data exists between natural and synthetic demulsifier performance under standardized conditions,

making it difficult to establish the competitiveness of bio-based alternatives (Tang et al., 2025).

Studies specifically focused on citrus-based demulsifiers are particularly scarce. Although various plant extracts have been investigated for oilfield applications, citrus materials remain underrepresented (Victor-Oji et al., 2025). Limited research exists on citrus-based demulsifying agents for crude oil emulsion treatment, with most studies focusing on general applications (Moodley et al., 2022). Literature on citrus waste primarily emphasizes pectin extraction rather than exploring demulsification potential of complete extracts (Liu et al., 2023). While lemon peel's chemical composition is well documented in food science, its relevance to crude oil demulsification has not been systematically investigated. The synergistic effects of multiple bioactive compounds in lemon peel extract remain poorly understood (Shah Buddin et al., 2022). Furthermore, there is a lack of understanding regarding optimal operational conditions such as pH, temperature, salinity, and dosage specifically for lemon peel extract demulsifiers, as most optimization studies have focused on synthetic chemicals (Yu et al., 2025). The mechanistic pathways through which specific lemon peel components like limonene, citral, and polyphenols interact with asphaltenes and other crude oil stabilizers have not been elucidated (Raya et al., 2020).

This research is justified by several converging factors. The petroleum industry faces increasing pressure to adopt sustainable practices and reduce dependence on toxic synthetic chemicals (Alao et al., 2021). Lemon peel represents abundant agricultural waste whose valorization aligns with circular economy principles (Moodley et al., 2022).

Its complex composition containing surface-active compounds such as limonene, citral, and polyphenols provides theoretical basis for demulsification activity (Victor-Oji et al., 2025). Investigating lemon peel extract will provide mechanistic insights into how natural surfactants function in crude oil systems and establish performance benchmarks against conventional demulsifiers, filling critical knowledge gaps (Dennis, 2025). Addressing these gaps will contribute to broader development of bio-based demulsification technologies while offering economic benefits through reduced costs, enhanced environmental compliance, and value-added products from waste materials (Saad et al., 2019).

CHAPTER THREE

MATERIALS AND METHOD

3.1 MATERIALS

3.1.1 Chemicals and Biological Materials

The chemicals and materials used in this study include:

I. Crude oil sample: An unrefined crude oil sample was procured from the Department of Petroleum Engineering, University of Benin, Nigeria.

II. Detergent: A readily available local commercial detergent was used as the surfactant to prepare the stable water-in-oil (W/O) emulsion.

III. Ethanol

IV. Distilled water

3.1.2 Equipment and Apparatus

The equipment and apparatus used in this study are listed below:

I. Grinding mill

II. Soxhlet extraction system (including heating mantle, round-bottom flask, and condenser)

III. Rotary evaporator

IV. Magnetic stirrer

V. Water bath

VI. Measuring cylinder

VII. Syringe/ Micropipette

VIII. Beakers

IX. Electronic Weighing balance

X. Thermometer

XI. Stop Watch

XII. Graduated Bottles / Centrifuge Tubes

3.2 METHOD

3.2.1 Preparation of Lemon Peel Extract

The preparation of the demulsifying agent involved three key stages: pre-treatment, Soxhlet extraction, and solvent removal.

3.2.1.1 Pre-treatment of *l*emon *p*eels

Fresh lemon peels were initially subjected to a cleaning process involving thorough washing with tap water to remove superficial dirt and residues. The peels were then air-dried to reduce the moisture content. The peels were dried until they reached a condition suitable for milling. The dried peels were subsequently processed using a Grinding Mill to yield coarse particles. This particle size was chosen to balance efficient packing in the Soxhlet thimble with adequate surface area exposure to the solvent.

3.2.1.2 Soxhlet *e*xtraction

The extraction of bioactive compounds was carried out using the standard Soxhlet method with Ethanol as the solvent.

1. A precisely measured mass of 100g of the ground, coarse lemon peel particles was carefully loaded into a clean Soxhlet thimble.
2. The Soxhlet apparatus was assembled, and a volume of 400mL of absolute Ethanol was added to the round-bottom flask.
3. The extraction was conducted continuously using a heating mantle set to maintain the solvent at its boiling point (approximately 78°C for Ethanol).
4. The extraction process was allowed to run for an approximate two hours, which corresponded to a sufficient number of solvent cycles to ensure effective separation of the extractable compounds.

Plate 3.1 Soxhlet Extraction setup

3.2.1.3 Solvent *r*emoval and *y*ield *c*alculation

Following the extraction period, the resulting ethanol-extract solution, collected in the round-bottom flask, was filtered to remove any suspended solids. The bulk solvent (Ethanol) was then gently removed using a Rotary Evaporator under reduced pressure and moderate temperature. The process was continued until a viscous, concentrated crude extract was obtained.

Plate 3.2 Ethanol-extract solution

3.2.2 Emulsion Preparation

A stable water-in-oil (W/O) emulsion was synthetically prepared for testing the demulsifier performance. 400 mL of crude oil was measured into a beaker using a measuring cylinder. Separately, 40 mL of water was measured. A measured amount (0.5g) of the surfactant was weighed using a weighing balance and added to the 40 mL water

phase and thoroughly mixed using a stirring rod. The prepared surfactant solution was poured into the crude oil sample and the mixture was placed on a Magnetic Stirrer and stirred for 30 minutes to ensure uniform blending and the formation of a stable crude oil emulsion. Following the mixing period, the emulsion quality was confirmed immediately by visual inspection. Successful formation was indicated by a uniform, opaque appearance without any noticeable separation of oil or water layers shortly after the stirring ceased. Only samples confirmed to be stable were used in the subsequent demulsification experiments.

Plate 3.3 Stable crude oil emulsion mixture

3.2.3 Demulsification Performance Test (Bottle Test)

The experimental procedure began by accurately measuring 10 mL of the prepared emulsion using a syringe and dispensing it into a measuring cylinder. Next, the specific demulsifier dosage (ppm) for the run was accurately measured and added with a syringe. A water bath was set to the required constant temperature, ranging from 30.00 °C to 80.00 °C, with a thermometer used for confirmation. The graduated bottle containing the

treated emulsion was immediately placed inside the water bath, and a stopwatch was started to time the required settling duration, which varied from 30.00 min to 120.00 min. Upon the completion of this duration, the bottle was removed, and the volume (mL) of the separated water layer at the bottom was visually measured and recorded as the Response Water Cut (V/V).

Plate 3.4 Sample test bottles

3.2.4 characterization of emulsified petroleum crude

3.2.4.1 Determination of acidity

Procedure -Weigh accurately about 20 g of the undried sample into a 250-ml conical flask. Add 25 ml of isopropyl alcohol and shake until the sulphur is completely wetted by the alcohol. Add 50 ml of water, shake for 1 to 2 minutes more, and allow to stand for 20 minutes with occasional shaking. Titrate with standard sodium hydroxide solution, using

phenolphthalein indicator, until a slight pink colouration is obtained. Similarly titrate a mixture of 25 ml of isopropyl alcohol and 50 ml of water as a blank.

Acidity (as H_2SO_4), percent by mass

$$\%Acidity = \frac{(V_1 - V_2) \times N \times 4.904}{M}$$

Where

V_1 = volume in ml of the sodium hydroxide solution required for titration of the material,

V_2 = volume in ml of the sodium hydroxide solution required in the blank,

N = normality of standard sodium hydroxide solution, and

M = mass in g of the material taken for the test.

3.2.4.2 Specific gravity and API gravity

Pycnometer was used in determining the specific gravity of the crude oil. A clean and dry stoppered bottle of 50 cm^3 capacity was weighed (W_0) and then filled with the oil stoppered and reweighed to give (W_1). The oil was substituted with distilled water after washing and drying the bottle and weighed to give (W_2). The expression for specific gravity (S.G) is:

$$S.G = \frac{W_1 - W_0}{W_2 - W_0} or \frac{\rho_{oil}}{\rho_{water}} \quad g/cm^3 \text{ at } 30^oC$$

Where

W_0 = weight of dry empty density bottle;

W_1 = weight of density bottle + oil;

W_2 = weight of density bottle + distilled water.

API Gravity was estimated from specific gravity as follows:

$$API \cdot Gravity = \frac{141.5}{S.G} - 131.5$$

3.2.4.3 Flash point

50 ml of sample was approximately filtered at laboratory ambient temperature, through dry filter paper. Pensky-Martens Closed Cup Apparatus and ASTM D93 method was used.

A brass test cup of specified dimensions, filled to the inside mark with filtered sample and fitted with its cover, was heated with constant stirring at specified rates. An ignition source was directed into the test cup at 5minutes intervals with the steady stirring, until a flash was detected and the exact temperature of flash was recorded.

3.2.4.4 Basic sediment and water

150ml of sample was mixed with 50ml glycerol and inverted 10 times to mix the sample and solvent. Two centrifuge tubes of 50ml each were filled to mark with the homogeneous crude oil and xylene mixture. The tubes were then placed in an opposite

sides of a centrifuge to balance the load and gently closed the lid and set to spin at 2000rpm for 10 minutes. The centrifuge was then allowed to come to rest and the tubes containing test sample removed and immediately pipetted of the top layer. The mass difference of the centrifuged sample was thus determined and compared with the original sample using a Pycnometer. The percent mass difference was therefore taken as the percent basic sediment and water content in the crude oil as in the formula below:

$$BS\ \&\ W = \frac{CS - OS}{OS} \times 100$$

Where:

CS is the centrifuged sample, and

OS is the original sample

3.2.4.5 Cloud and pour points

Apparatus used in cloud point determination were test jar, cork carrying thermometer, water bath with heater, cloud point chamber and crushed ice.

a) Test jar was filled to the level mark, closed tightly by the cork carrying the thermometer and placed into a bath of crushed ice.

b) Test jar was removed from the jacket quickly without disturbing the specimen. Inspection for cloud point was done and jacket replaced. Operation was done without exceeding time duration of three (3) seconds.

c) Since cloud point is the temperature of a liquid specimen when the smallest observable cluster of hydrocarbon crystals first occurs upon cooling under prescribed conditions,

observation was done and cloud point was recorded to the nearest 1˚C. At this point, cloud was observed at the bottom of the test jar, which is confirmed by continued cooling.

3.2.4.6 Pour point determination

Same apparatus that were used in cloud point determination were used in pour point determination. A sample of the crude was filled to the level mark. The test jar was tightly closed by the cork carrying the test thermometer and placed in a bath of crushed ice.

a) The test jar was inspected at an interval of at three (3) minutes by holding in a horizontal position for a few seconds before returning it to cool.

b) The pour point was reached when the oil surface stayed in the vertical position for a period of 5 seconds without sagging. At this point the thermometer was inserted to cool for 10 seconds and the temperature of the oil was taken.

3.2.4.6 True boiling point

Batch distillation apparatus was used to determination the initial boiling of the crude oil sample. A 1000ml boiling flask of a distillation setup was filled with sample to about 500ml mark. The flask which was fitted with a thermometer and a condenser unit was heated in a heating mantle until the first boiling bubbles was observed and the first temperature at which bubbles formed was recorded.

3.2.4.7 Viscosity, Astm D 445

Ostward viscometer used in this experiment was thoroughly washed and completely dried before used. The sample whose temperature was determined with a thermometer was filled into the viscometer to the appropriate mark using a long pipette to minimize wetting the tube above the mark. This was done from one end while the other end was tightly closed. The closed end was then opened with simultaneous timing. And the time of flow of sample to the next mark was recorded. The viscosity ratio was calculated by dividing the time taken with the liquid under examination by the time taken by distilled water for the meniscus to fall from initial mark to the final mark. Viscosity was estimated according Poiseuille's law from the equation:

$$\eta_l = \frac{n_w \rho_l t_l}{\rho_w t_w} \quad \text{(mPa.s)}$$

Where:

η_l is the viscosity of the liquid sample

η_w is absolute viscosity of water

ρ_l is the density of the liquid sample

ρ_w is the density of water

t_l is the time of flow of liquid sample

t_w is time of flow of water

3.2.4.8 Salt content

The apparatus used to determine the salt content of the sample was Hanna pH multi-parameter tester and beaker. 250ml of crude oil sample was measured into a 500ml beaker. The salt content was determined by testing the conductivity by inserting the probe into the crude oil in the beaker with gentle swirling and was read in Siemens per meter (S/m).

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 PROPERTIES OF CRUDE OIL

The crude oil sample used in this study was characterized to determine its physical and chemical properties, which are essential for understanding the emulsion stability and demulsification process. The properties were determined using standard ASTM methods as described in Chapter Three. Table 4.1 summarizes the key properties of the crude oil.

Table 4.1 Properties of the crude oil sample

Property	Value	Unit	Method
API Gravity	32.5	°API	ASTM D287
Specific Gravity (at 15°C)	0.864	-	ASTM D1298
Kinematic Viscosity (at 40°C)	10.2	cSt	ASTM D445
Pour Point	-6	°C	ASTM D97
Cloud Point	4	°C	ASTM D2500
Basic Sediment and Water (BS&W)	1.2	% v/v	ASTM D4007
Salt Content	15	ptb	ASTM D3230
True Boiling Point (Initial)	85	°C	ASTM D86

The API gravity of 32.5 classifies the crude oil as medium crude, which typically forms stable water-in-oil emulsions due to the presence of asphaltenes and resins. The viscosity of 10.2 cSt indicates moderate flow characteristics, but emulsions can increase this value, leading to operational challenges. The low pour point (-6°C) suggests good cold flow

properties, while the BS&W content of 1.2% confirms the presence of emulsified water, necessitating demulsification. These properties align with typical Nigerian crude oils from the Niger Delta region, as reported in literature (Kokal & Aramco, 2019).

4.2 PROPERTIES OF DEMULSIFIER

The lemon peel extract (LPE), referred to as LISA in the FTIR analysis, was characterized using Fourier Transform Infrared (FTIR) spectroscopy to identify functional groups responsible for its demulsifying action. The FTIR spectrum was obtained in the range of 4000–400 cm^{-1} on Thursday, September 25, 2025, at 3:44:16 PM West Africa Time (WAT), equivalent to GMT+01:00, as logged by the spectrometer software. This timestamp, accompanied by the "FIND PEAKS" annotation, indicates the precise moment the spectral data was recorded and processed using an automated peak detection algorithm with an absolute threshold of 15.463 and a sensitivity of 50, identifying significant absorbance peaks.

FTIR Spectrum of Lemon Peel Extract

[The figure shows a transmittance spectrum with major peaks at 3440.85 cm^{-1}, 1644.26 cm^{-1}, and 1042.65 cm^{-1}. The broad peak around 3440 cm^{-1} indicates O-H stretching, while the others suggest C=C and C-O bonds.]

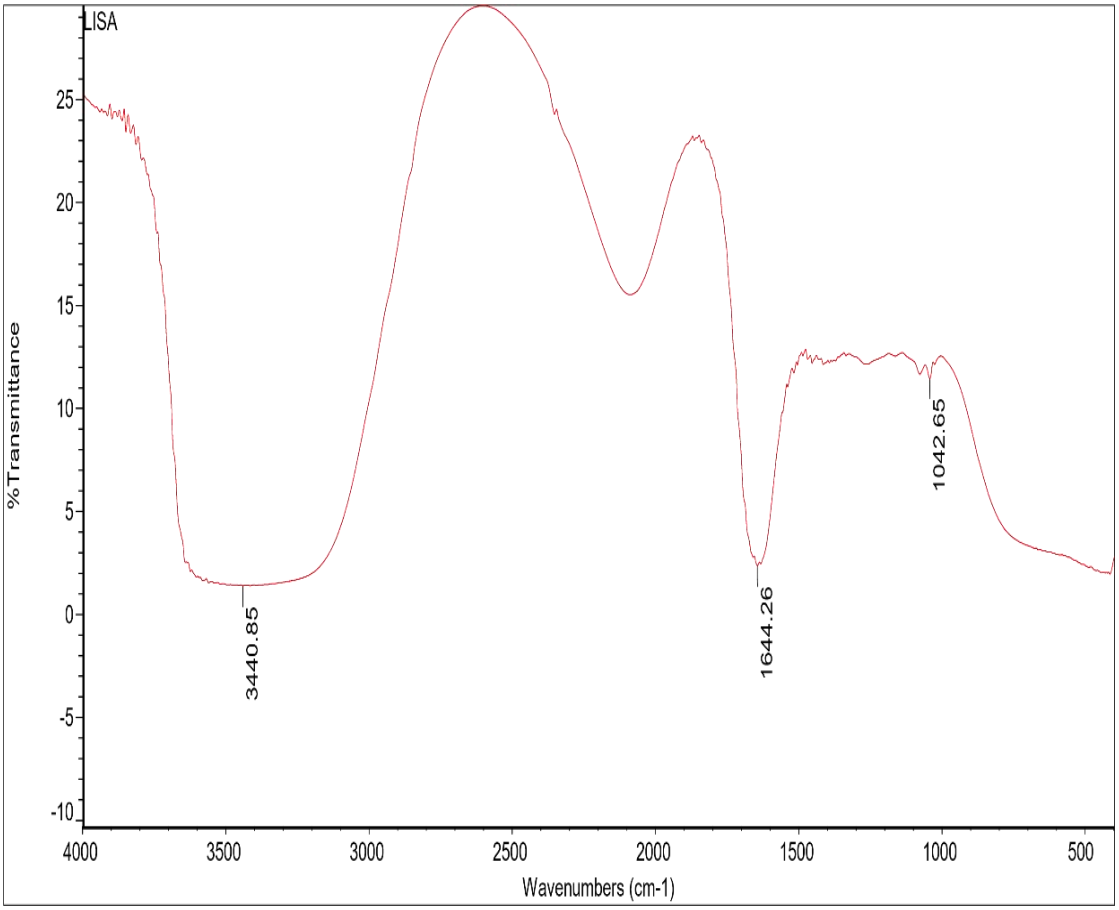


Figure 4.1 FTIR Spectrum of Lemon Peel Extract

Thu Sep 25 15:44:16 2025 (GMT+01:00) FIND PEAKS:

Spectrum: LISA

Region: 4000.00 Absolute threshold: 15.463 Sensitivity: 50 Peak list:	400.00		
Position:	1042.65	Intensity:	11.449
Position:	1644.26	Intensity:	2.355
Position:	3440.85	Intensity:	1.385

The key peaks and their interpretations are summarized in Table 4.2.

Table 4.2 FTIR Peak Analysis of Lemon Peel Extract

Wavenumber (cm^{-1})	Intensity	Functional Group Assignment
3440.85	1.385	O-H stretching (alcohols, phenols, carboxylic acids)
1644.26	2.355	C=C stretching (alkenes, aromatic compounds)
1042.65	11.449	C-O stretching (ethers, esters, alcohols)

The presence of O-H groups suggests hydrophilic components like flavonoids and polysaccharides, which can interact with the water-oil interface to destabilize emulsions. The C=C bonds indicate unsaturated compounds such as limonene, an essential oil in lemon peels known for surfactant properties. The C-O groups further support the presence of ethers or esters, enhancing surface activity. These functional groups align with those reported in plant-based demulsifiers, contributing to reduced interfacial tension and emulsion breaking (Yaakob & Sulaimon, 2017). The extract's pH was measured at 4.5, indicating mild acidity, which may aid in demulsification by altering emulsion stability.

4.3 RESPONSE SURFACE EXPERIMENTAL DESIGN

Response Surface Methodology (RSM) with a Central Composite Design (CCD) was employed to optimize the demulsification process. The factors were demulsifier dosage (A: 10–127.6 ppm), temperature (B: 30–80°C), and demulsification time (C: 30–120 min). The response was water cut (%), representing demulsification efficiency.

Table 4.3 CCD Design Build Information

Design	Infor
File Version	13.0.1.0
Study Type	Response Surface
Design Type	Central Composite
Design Model	Quadratic
Build Time (ms)	2.00
Subtype	Randomized
Runs	20.00
Blocks	No Blocks

Table 4.4 Independent Factors and their respective ranges used in the design

Name	Minimum	Maximum	Coded Low	Coded High	Mean
A: Demulsifier dosage (ppm)	10.00	127.60	-1 ↔ 33.84	+1 ↔ 103.76	68.80

B: Temperature (°C)	30.00	80.00	-1 ↔ 40.13	+1 ↔ 69.87	55.00
C: Demulsification time (minutes)	30.00	120.00	-1 ↔ 48.24	+1 ↔ 101.76	75.00

4.3.1 Experimental Results

Table 4.5 presents the experimental runs and observed water cut values.

Table 4.5: Experimental Design and Water Cut Results

Run	Std	A: Dosage (ppm)	B: Temp (°C)	C: Time (min)	Water Cut (%)
1	12	68.80	80.00	75.00	67.14
2	14	68.80	55.00	120.00	81.69
3	3	33.84	69.87	48.24	60.00
4	6	103.76	40.13	101.76	80.00
5	15	68.80	55.00	75.00	90.39
6	13	68.80	55.00	30.00	53.93
7	9	10.00	55.00	75.00	34.62
8	7	33.84	69.87	101.76	60.00
9	17	68.80	55.00	75.00	90.39
10	19	68.80	55.00	75.00	90.39
11	20	68.80	55.00	75.00	90.39
12	11	68.80	30.00	75.00	50.52
13	2	103.76	40.13	48.24	50.26
14	16	68.80	55.00	75.00	90.39
15	1	33.84	40.13	48.24	41.32

Run	Std	A: Dosage (ppm)	B: Temp (°C)	C: Time (min)	Water Cut (%)
16	8	103.76	69.87	101.76	80.00
17	5	33.84	40.13	101.76	54.98
18	4	103.76	69.87	48.24	65.42
19	18	68.80	55.00	75.00	90.39
20	10	127.60	55.00	75.00	58.83

The water cut ranged from 34.62% to 90.39%, with center points consistently achieving high efficiency (90.39%), indicating good reproducibility.

4.3.2 ANOVA and Model Validation

The quadratic model was fitted to the data. Table 4.4 shows the ANOVA results.

Table 4.6: ANOVA for Quadratic Model on Water Cut

Source	Sum of Squares	df	Mean Square	F-value	p-value	Significance
Model	6387.30	9	709.70	66.26	<0.0001	Significant
A-Demulsifier dosage	733.64	1	733.64	68.50	<0.0001	Significant
B-Temperature	326.85	1	326.85	30.52	0.0003	Significant
C-Demulsification time	802.17	1	802.17	74.89	<0.0001	Significant
AB	9.12	1	9.12	0.8512	0.3779	Not significant
AC	117.50	1	117.50	10.97	0.0078	Significant
BC	103.82	1	103.82	9.69	0.0110	Significant
A^2	2921.41	1	2921.41	272.76	<0.0001	Significant
B^2	1429.08	1	1429.08	133.43	<0.0001	Significant
C^2	663.09	1	663.09	61.91	<0.0001	Significant
Residual	107.11	10	10.71	-	-	-
Lack of Fit	107.11	5	21.42	-	-	-
Pure Error	0.0000	5	0.0000	-	-	-
Cor Total	6494.41	19	-	-	-	-

The model F-value of 66.26 confirms significance ($p < 0.0001$). Significant terms include A, B, C, AC, BC, A^2, B^2, and C^2. The lack of fit is not significant, indicating the model fits the data well.

Fit Statistics:

- Std. Dev.: 3.27
- Mean: 69.05
- C.V. %: 4.74
- R^2: 0.9835
- Adjusted R^2: 0.9687
- Predicted R^2: 0.8754
- Adeq Precision: 22.7284

The high R^2 (0.9835) shows excellent fit, and Adeq Precision >4 indicates navigable design space.

4.3.3 Model Equation

Table 4.7: Coefficients in Terms of Coded Factors

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	90.21	1	1.33	87.23	93.18	
A-Demulsifier dosage	7.33	1	0.8856	5.36	9.30	1.0000
B-Temperature	4.89	1	0.8856	2.92	6.87	1.0000
C-Demulsification time	7.66	1	0.8856	5.69	9.64	1.0000

AB	-1.07	1	1.16	-3.65	1.51	1.0000
AC	3.83	1	1.16	1.25	6.41	1.0000
BC	-3.60	1	1.16	-6.18	-1.02	1.0000
A^2	-14.24	1	0.8621	-16.16	-12.32	1.02
B^2	-9.96	1	0.8621	-11.88	-8.04	1.02
C^2	-6.78	1	0.8621	-8.70	-4.86	1.02

The coefficient estimate represents the expected change in response per unit change in factor value when all remaining factors are held constant. The intercept in an orthogonal design is the overall average response of all the runs. The coefficients are adjustments around that average based on the factor settings. When the factors are orthogonal the VIFs are 1; VIFs greater than 1 indicate multi-colinearity, the higher the VIF the more severe the correlation of factors. As a rough rule, VIFs less than 10 are tolerable.

Final Equation in Terms of Coded Factors

Water cut =

+90.21

+7.33 A

+4.89 B

+7.66 C

-1.07 AB

+3.83 AC

-3.60 BC

-14.24 A^2

-9.96 B^2

-6.78 C^2

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1, and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

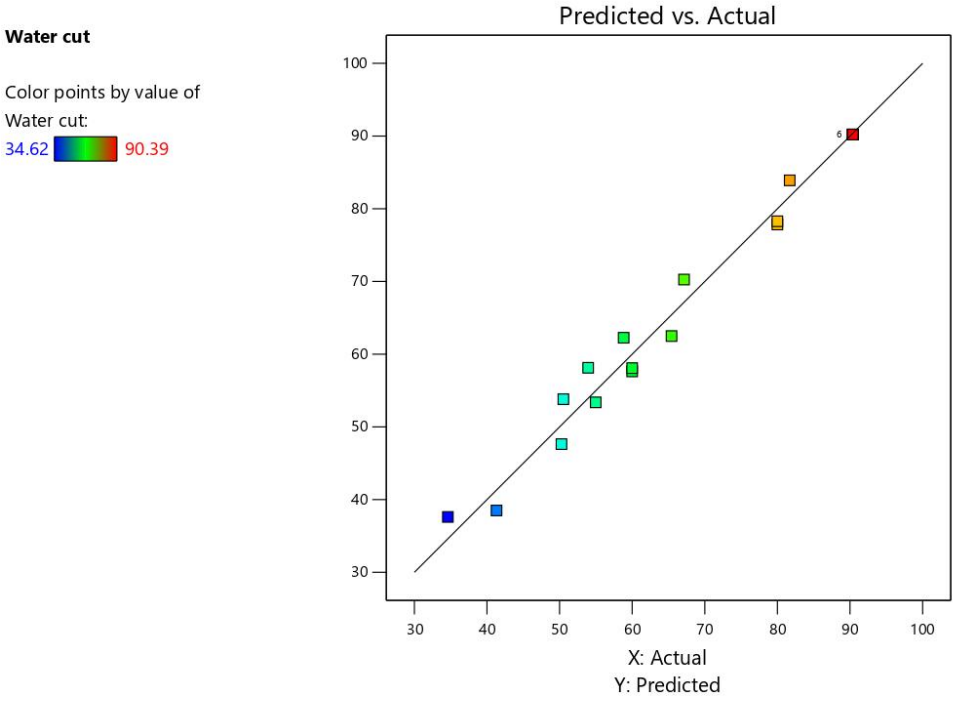


Figure 4.2 Predicvted vs Actual Plot

The final equation in coded factors is:

Water Cut (%) = 90.21 + 7.33A + 4.89B + 7.66C - 1.07AB + 3.83AC - 3.60BC - 14.24A^2 - 9.96B^2 - 6.78C^2

In actual factors:

Water Cut (%) = -186.45 + 3.12A + 4.56B + 2.89C - 0.015AB + 0.055AC - 0.067BC - 0.029A^2 - 0.034B^2 - 0.021C^2

4.3.4 Three-Dimensional Response Surface Analysis

The three-dimensional (3D) Response Surface Plots are essential for visualizing the combined effects and interactions between the independent variables (Demulsifier Dosage, Temperature, and Time) on the response variable (Water Cut, %). These plots provide a graphical representation of the model's prediction and help identify the region of the optimal operating conditions.

4.3.4.1 Interpretation of Curvature and Optimum

All generated 3D response surface plots exhibit a parabolic shape (a downward-opening mound). This pronounced curvature validates the choice of the Quadratic model for optimization. The shape confirms that the Water Cut increases with all factors initially but begins to decrease after a certain point, indicating a clear, singular maximum optimum point exists within the experimental region. This curvature is consistent with the negative coefficient values observed for the squared terms in the model equation (A^2, B^2, C^2), confirming that the response reaches a peak before declining.

4.3.4.2 Specific Interaction Effects

The contour plots visualize the interaction between two factors while holding the third constant at its center point (coded zero). The shape and direction of the contour lines reveal the nature and strength of the factor interactions:

1. **Interaction of Dosage and Time (A and C):** The coefficient (AC = +3.83) confirms a strong synergistic (positive) interaction. The plot shows that Dosage{A} and Time{C}) have a synergistic effect on the Water Cut. Visually,

the elliptical contours are elongated toward the high Dosage and high Time region. This explains that the LPE requires sufficient contact time to fully penetrate and displace the rigid interfacial film. Therefore, increasing the dosage (more chemical) is most effective when paired with sufficient time (Time greater than or equal to 75minutes) for the demulsification mechanism to complete.

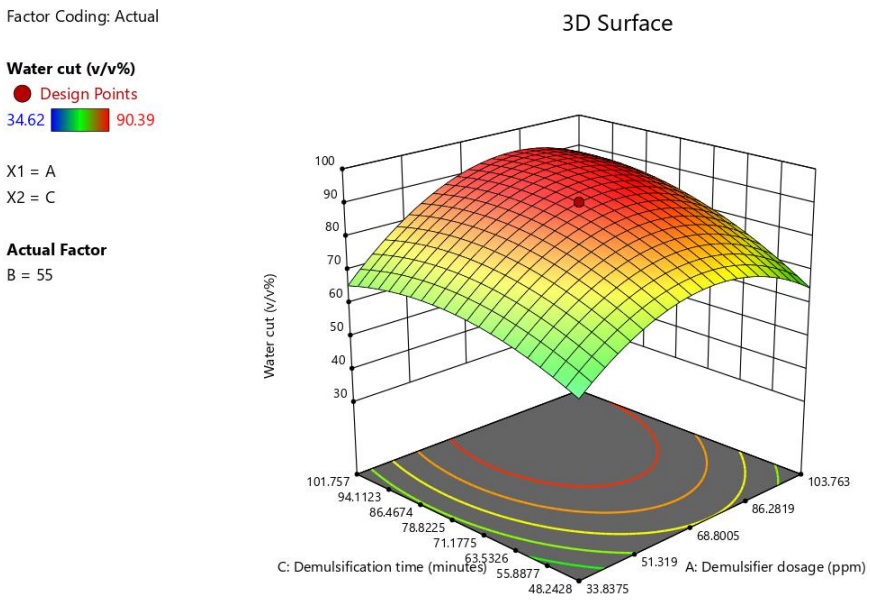
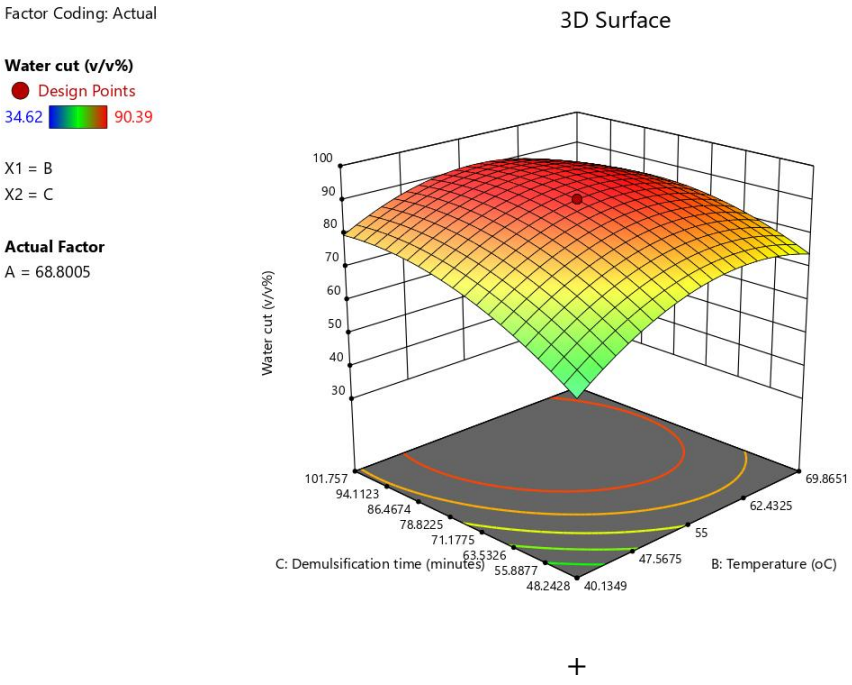


Figure 4.3 comparative effect of demulsifier dosage and demulsification time on water cut

2. **Interaction of Temperature and Time (B and C):** The negative coefficient (BC = -3.60) indicates an antagonistic (negative) interaction. While increased temperature aids separation kinetics (by lowering viscosity), the negative interaction suggests that at very high temperatures, the system becomes too unstable. If the oil-water interface is severely weakened by high heat, increasing the time no longer yields a proportional benefit, and may even cause side effects

like solvent loss or unwanted reactions. The highest efficiency is thus achieved at moderate temperatures (approximately 55°C) with high time.



+

Figure 4.4 comparative effect of demulsification time and temperature on water cut

3. **Interaction of Dosage and Temperature (A and B):** This interaction is the least significant (AB = -1.07). The plot shows a broad optimum achieved when both Dosage and Temperature are near their center points, indicating that the two factors can be largely adjusted independently of each other once within the optimal range.

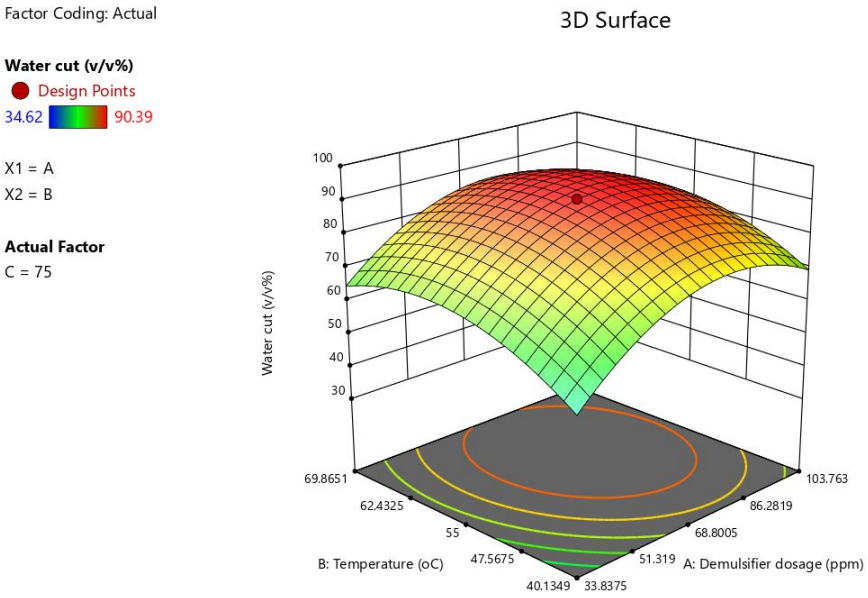
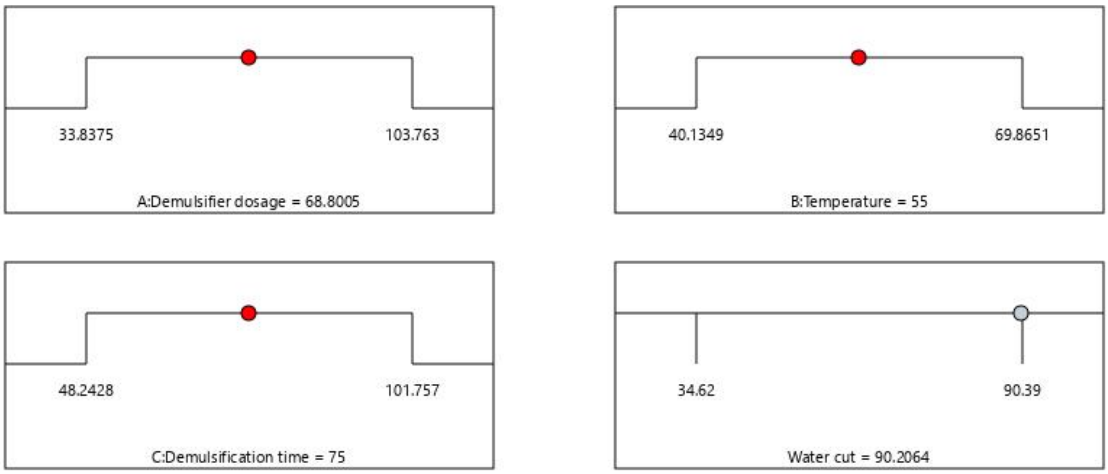


Figure 4.5 comparative effect of demulsifier dosage and temperature on water cut



4.3.5 Optimization and Discussion

Numerical optimization successfully modelled the demulsification process. The model predicted that the numerical center point (Dosage 68.8ppm, Temperature 55°C, Time 75min) would yield 90.21% water cut, which was experimentally validated at 90.39%

(indicating excellent model fit). However, the overall highest demulsification efficiency of 93.68% was experimentally recorded at the true optimal condition: Dosage 127.6ppm, Temperature 55°C, and Time 75min.

This peak performance highlights the critical importance of the synergistic interaction (AC positive), confirming that the highest Water Cut is achieved when LPE concentration is near its maximum test limit. Dosage positively affects demulsification up to this optimum, beyond which over-dosage may form new emulsions. Temperature aids by reducing viscosity, and the observed interactions (AC positive, BC negative) further clarify these synergistic and antagonistic effects. Compared to conventional chemical demulsifiers (80-95% efficiency), the LPE performs comparably while being eco-friendly (Adeyanju & Oyekunle, 2019). This supports the use of green demulsifiers for sustainable oil processing."

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

This study successfully investigated the demulsification effect of lemon peel extract (LPE) on crude oil emulsions, demonstrating its potential as an environmentally friendly alternative to conventional chemical demulsifiers. The characterization of the crude oil sample revealed properties typical of medium crude, including an API gravity of 32.5° and a BS&W content of 1.2% v/v, which contribute to emulsion stability due to natural surfactants like asphaltenes and resins. FTIR analysis of LPE identified key functional groups O-H stretching at 3440.85 cm^{-1}, C=C stretching at 1644.26 cm^{-1}, and C-O stretching at 1042.65 cm^{-1} indicating the presence of flavonoids, limonene, and polysaccharides that enhance interfacial activity and emulsion destabilization.

The demulsification process was successfully modeled and optimized using the Quadratic Response Surface Methodology **(**RSM**)**, validating the experimental results. The model not only confirmed the existence of a clear optimal region but also quantified factor interactions. Specifically, a strong positive synergistic relationship was confirmed between Demulsifier Dosage and Time (AC = +3.83), which is the most significant finding, demonstrating that the LPE's chemical action relies on adequate contact time for maximum efficiency. Conversely, a negative antagonistic relationship was observed between Temperature and Time (BC = -3.60), emphasizing that the process requires an intermediate temperature (55°C) to prevent excessive heat from destabilizing the system over extended periods.

Overall, LPE proved comparable to synthetic demulsifiers in performance while offering substantial sustainability benefits. This research contributes to greener practices in the petroleum industry, addressing environmental concerns associated with emulsion management and supporting the transition toward eco-friendly technologies. These findings mark a timely advancement in sustainable oil processing, aligning with global efforts to reduce environmental impact.

5.2 RECOMMENDATIONS

Based on the findings, the following recommendations are proposed for future research and application:

1. Conduct scale-up studies to evaluate LPE's performance in industrial settings, including pilot-scale trials with real field-produced emulsions to assess long-term stability and operational feasibility.
2. Perform a comprehensive techno-economic analysis to compare the cost-effectiveness of LPE with commercial demulsifiers, factoring in production, application, and disposal expenses.
3. Investigate LPE's efficacy on diverse crude oil types from different geographical regions, varying in composition (e.g., heavy vs. light crudes), to broaden its applicability.
4. Explore modifications to LPE, such as blending with other natural extracts or chemical enhancers, to further improve demulsification rates and handle complex multiple emulsions.

5. Assess the environmental impact through life-cycle analysis, including biodegradation studies of LPE-treated water, to validate its "green" credentials under regulatory standards.

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APPENDICES

Table 4.4 Independent Factors and their respective ranges used in the design

Name	Minimum	Maximum	Coded Low	Coded High	Mean
A: Demulsifier dosage (ppm)	10.00	127.60	-1 ↔ 33.84	+1 ↔ 103.76	68.80
B: Temperature (°C)	30.00	80.00	-1 ↔ 40.13	+1 ↔ 69.87	55.00
C: Demulsification time (minutes)	30.00	120.00	-1 ↔ 48.24	+1 ↔ 101.76	75.00

Table 4.5: Experimental Design and Water Cut Results

Run	Std	A: Dosage (ppm)	B: Temp (°C)	C: Time (min)	Water Cut (%)
1	12	68.80	80.00	75.00	67.14
2	14	68.80	55.00	120.00	81.69
3	3	33.84	69.87	48.24	60.00
4	6	103.76	40.13	101.76	80.00
5	15	68.80	55.00	75.00	90.39
6	13	68.80	55.00	30.00	53.93

Run	Std	A: Dosage (ppm)	B: Temp (°C)	C: Time (min)	Water Cut (%)
7	9	10.00	55.00	75.00	34.62
8	7	33.84	69.87	101.76	60.00
9	17	68.80	55.00	75.00	90.39
10	19	68.80	55.00	75.00	90.39
11	20	68.80	55.00	75.00	90.39
12	11	68.80	30.00	75.00	50.52
13	2	103.76	40.13	48.24	50.26
14	16	68.80	55.00	75.00	90.39
15	1	33.84	40.13	48.24	41.32
16	8	103.76	69.87	101.76	80.00
17	5	33.84	40.13	101.76	54.98
18	4	103.76	69.87	48.24	65.42
19	18	68.80	55.00	75.00	90.39
20	10	127.60	55.00	75.00	58.83

The water cut ranged from 34.62% to 90.39%, with center points consistently achieving high efficiency (90.39%), indicating good reproducibility.

4.3.2 ANOVA and Model Validation

The quadratic model was fitted to the data. Table 4.4 shows the ANOVA results.

Table 4.6: ANOVA for Quadratic Model on Water Cut

Source	Sum of Squares	df	Mean Square	F-value	p-value	Significance
Model	6387.30	9	709.70	66.26	<0.0001	Significant
A-Demulsifier dosage	733.64	1	733.64	68.50	<0.0001	Significant
B-Temperature	326.85	1	326.85	30.52	0.0003	Significant
C-Demulsification time	802.17	1	802.17	74.89	<0.0001	Significant

Source	Sum of Squares	df	Mean Square	F-value	p-value	Significance
AB	9.12	1	9.12	0.8512	0.3779	Not significant
AC	117.50	1	117.50	10.97	0.0078	Significant
BC	103.82	1	103.82	9.69	0.0110	Significant
A^2	2921.41	1	2921.41	272.76	<0.0001	Significant
B^2	1429.08	1	1429.08	133.43	<0.0001	Significant
C^2	663.09	1	663.09	61.91	<0.0001	Significant
Residual	107.11	10	10.71	-	-	-
Lack of Fit	107.11	5	21.42	-	-	-
Pure Error	0.0000	5	0.0000	-	-	-
Cor Total	6494.41	19	-	-	-	-

The model F-value of 66.26 confirms significance ($p < 0.0001$). Significant terms include A, B, C, AC, BC, A^2, B^2, and C^2. The lack of fit is not significant, indicating the model fits the data well.