BIO-BASED DEMULSIFIER FORMULATION FROM A SYNERGISTIC BLEND OF CITRUS SINENSIS AND MUSA SPP. PEEL EXTRACT

BY

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DEPARTMENT OF CHEMICAL ENGINEERING

FACULTY OF ENGINEERING

UNIVERSITY OF BENIN

BENIN CITY

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A RESEARCH PROJECT SUBMITTED TO THE DEPARTMENT OF CHEMICAL ENGINEERING, FACULTY OF ENGINEERING, UNIVERSITY OF BENIN, BENIN CITY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF A BACHELOR’S DEGREE IN CHEMICAL ENGINEERING (B.ENG)

OCTOBER, 2025

CERTIFICATION

This is to certify that this research project, submitted to the Department of Chemical Engineering, was performed by, IDIAKE OKHIDE from the University of Benin, Benin City, Edo State, Nigeria, under the supervision of Engr. Prof. S.E. Uwadiae

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EXTERNAL EXAMINER DATE

DEDICATION

This project is dedicated to GOD ALMIGHTY, who has brought me thus far in my academic journey. Special thanks to my beloved family, for their unwavering belief in my abilities, constant encouragement, and quiet support created the perfect environment for me to pursue this research. Their sacrifices and love are the true foundation of every success I achieve.

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ABSTRACT

The global petroleum industry faces continuous and costly challenges in resolving stable water-in-oil (W/O) emulsions, a process that traditionally relies on expensive, non-biodegradable synthetic demulsifiers[1]. This study investigated the development and optimization of a sustainable, bio-based demulsifier derived from a synergistic blend of extracts from **Citrus sinensis** (orange) and **Musa spp.** (banana) peels, aiming to provide an environmentally responsible alternative[2].

The demulsifier was prepared via solvent extraction of the agricultural waste. Characterization showed the blended formulation possessed an optimal **pH of 5.8** and a density of **998.0 kg/m³**. Chemical analysis using Fourier-Transform Infrared Spectroscopy (FTIR) confirmed the presence of non-ionic, amphiphilic functional groups (O-H, C-H, and C-O), indicative of a surfactant-type demulsifier system[4].

The demulsification performance was optimized using **Response Surface Methodology (RSM)**, analyzing the interactive effects of demulsifier dosage, temperature, and demulsification time to maximize the final water cut percentage[5]. The resulting quadratic model demonstrated a strong correlation and predictive power, indicated by an excellent **Coefficient of Determination (R^2) of 0.9768**. The synergistic blend achieved a peak demulsification efficiency under the tested conditions, with the maximum recorded **water cut being 20 v/v%**. This efficiency is attributed to the complementary action of the constituent compounds: the lipophilic D-limonene (*C. sinensis*) acts as a solvent to weaken the interfacial film, while the hydrophilic saponins and phenolic compounds (*Musa spp.*) competitively adsorb at the interface to promote rapid droplet coalescence[8].

This research successfully validates the potential of valorizing waste streams to formulate a highly effective, sustainable, and non-toxic demulsifier. The findings affirm the blend's viability as a substitute for petrochemical demulsifiers, representing a significant contribution to green chemistry and the circular economy within upstream oil and gas operations.

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NOMENCLATURE

TERM	**DESCRIPTION**
A	Independent variable for Demulsifier Dosage
API	American Petroleum Institute (used for API Gravity)
ANOVA	Analysis of Variance
B	Independent variable for Temperature
B.ENG	Bachelor's Degree in Chemical Engineering
C	Independent variable for Demulsification Time
DE	Demulsification Efficiency
DOE	Design of Experiment
FTIR	Fourier-Transform Infrared Spectroscopy/Spectrometry
GC-MS	Gas Chromatography-Mass Spectrometry
HIPEs	High Internal Phase Emulsions
M	Mass in grams (g) of the material taken for the acidity test
N	Normality of standard sodium hydroxide (NaOH) solution
O/W	Oil-in-Water (Emulsion)
ppm	Parts Per Million
R^2	Coefficient of Determination
RSM	Response Surface Methodology
S.G.	Specific Gravity
VIF	Variance Inflation Factor
V_1	Volume (mL) of NaOH solution required for material titration
V_2	Volume (mL) of NaOH solution required for blank titration

V_w	Volume of separated water (or water removed)
V_{wi}	Initial volume of water in the emulsion sample
W/O	Water-in-Oil (Emulsion)
W_0	Weight of dry empty density bottle
W_1	Weight of density bottle plus oil
W_2	Weight of density bottle plus distilled water

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND TO THE STUDY

Crude oil, as produced from reservoirs, is rarely a pure hydrocarbon phase. It is commonly obtained as a complex mixture containing water, either as **water-in-oil (W/O) or oil-in-water (O/W) emulsions**, or other multiphase mixtures(Kokal & Aramco, 2005). The specific fraction of water, known as the "water cut," is highly variable, depending on geographical location, geological conditions, and the type of crude oil recovery process employed. This water content can also fluctuate throughout the lifespan of crude oil production.

The presence of water in crude oil poses significant challenges across the entire petroleum value chain. To facilitate efficient transportation and storage, and crucially, to mitigate risks of hydrocarbon processing problems such as catalyst poisoning in refineries, the separation of water from the hydrocarbon phase is an essential requirement (Abdulredha et al., 2020) . Beyond operational efficiencies, the removal of inorganic salts and metals associated with the water phase is also critical to prevent corrosion and maintain product quality.

To address these challenges, **surfactants with demulsifier properties** are routinely introduced into the crude oil-water separation process. The primary objective of these demulsifiers is to minimize the formation of stable crude oil-water emulsions and, more importantly, to enhance the efficiency of demulsification (Abdulredha et al., 2020) . A strategic and optimized approach to demulsifier selection and application is vital for achieving fast and cost-effective separation at the lowest possible demulsifier dosage. This optimization is complex, as the demulsifier's effectiveness is influenced by its intrinsic properties, its interaction with the crude oil's natural emulsifiers (like asphaltenes, resins, and naphthenic acids), and various operating parameters (Alao et al., 2021) . Understanding the intricate mechanisms by which these demulsifiers destabilize emulsions, and how to optimize their formulations and application conditions, is therefore paramount for improving crude oil processing efficiency and reducing associated costs.

The global energy landscape continues to be dominated by crude oil, with significant production activities in regions like the Niger Delta, Nigeria. A critical and pervasive challenge inherent in petroleum exploration, production, and refining is the formation of highly stable **oil-water emulsions** (E. et al., 2020)

For decades, the industry's primary strategy for demulsification has relied on a diverse array of **synthetic chemical demulsifiers**. While these agents have proven effective in destabilizing emulsions, their widespread application has raised considerable environmental and economic concerns. Many synthetic demulsifiers are derivatives of petrochemicals, posing risks due to their non-biodegradability, potential toxicity to aquatic life, and accumulation in the ecosystem (Faiz Hazim Bin Mohd Nordin et al.,2013) . The high purchasing and operational costs associated with these chemicals also contribute to the overall expenditure of crude oil processing, motivating the search for more sustainable and cost-effective ecosystem (Faiz Hazim Bin Mohd Nordin et al.,2013) . This situation aligns with a broader industry shift towards **green chemistry** principles and environmentally responsible practices.

The global petroleum industry, including significant operations in Nigeria, consistently confronts complex challenges associated with the ubiquitous formation of stable oil-water emulsions during crude oil extraction, transportation, and refining processes. These emulsions, formed by the intimate mixing of immiscible oil and aqueous phases, are stabilized by natural emulsifiers such as asphaltenes, resins, naphthenic acids, and fine solids present in crude oil (Abdulredha et al., 2020) . Their persistence leads to a cascade of operational problems, including reduced production rates, increased pumping costs, equipment corrosion, fouling of pipelines and processing units, and a detrimental impact on the quality of separated oil and water, ultimately affecting economic viability (Charles Abatai et al., 2020) . Moreover, the discharge of inadequately treated emulsified wastewater poses severe environmental threats, contributing to water pollution and ecological damage, underscoring the urgent need for effective demulsification strategies (Abdulredha et al., 2020).

This pressing need has catalyzed extensive research into bio-based demulsifiers derived from natural, renewable resources. The concept of biomass valorization, transforming agricultural waste into value-added products, represents a pivotal component of the burgeoning circular economy (Gbadeyan et al., 2024) . Plant-based materials, in particular, are gaining traction due to their abundance, biodegradability, non-toxicity, and the presence of diverse bioactive compounds with inherent surface-active properties. These compounds, including polysaccharides, proteins, saponins, flavonoids, and terpenes, can effectively interfere with interfacial film stability, promote droplet coalescence, and facilitate phase separation (Okafor et al., 2024).

Among the most promising agricultural byproducts, especially relevant in the Nigerian context due to their widespread availability and significant waste generation, are the peels of *Citrus sinensis* (sweet orange) and *Musa* spp. (banana and plantain) (Oyegoke et al., 2023) . *Citrus sinensis* peels are a rich source of D-limonene, a lipophilic solvent that can disrupt the hydrophobic interactions within emulsion films, along with various flavonoids possessing amphiphilic properties (Moodley et al., 2022) . Conversely, *Musa* spp. peels are abundant in hydrophilic biopolymers like pectin, and natural surfactants such as saponins and a spectrum of phenolic compounds, which are known to reduce interfacial tension and displace natural emulsifiers (Mohd Zaini et al., 2022).

While individual extracts from these peels demonstrate considerable potential as demulsifiers, the inherent complexity and variability of crude oil emulsions suggest that a multi-component, synergistic approach could yield superior results. A blend combining the distinct demulsification mechanisms of compounds from *Citrus sinensis* (e.g., film penetration by D-limonene) and *Musa* spp. peels (e.g., interfacial tension reduction by saponins and flocculation by pectin) is hypothesized to offer a more robust and broadly effective solution than either extract used alone. Despite growing interest in bio-demulsifiers, research specifically focused on the systematic formulation and optimization of synergistic blends from *Citrus sinensis* and *Musa* spp. peels, particularly for local crude oil challenges, remains limited. This study, therefore, aims to bridge this knowledge gap by exploring the potential of such a blend, contributing to the development of sustainable demulsification technologies crucial for environmental protection and economic efficiency in the petroleum industry.

In response to these challenges, the scientific community has intensely explored **bio-based demulsifiers** derived from renewable and biodegradable sources. This aligns with the concept of a **circular economy**, where waste materials are transformed into valuable resources (Calisto Friant et al., 2020)
While the individual efficacy of extracts from these peels has been explored, the potential for a **synergistic blend** remains largely underexplored, particularly concerning crude oil emulsions found in local operations. A strategic combination of compounds from *Citrus sinensis* and *Musa* spp. peels could offer a multi-functional demulsifier, leveraging diverse mechanisms simultaneously. For instance, the lipophilic components from citrus might penetrate the interfacial film, while hydrophilic compounds and surfactants from *Musa* spp. could then stabilize the interface and promote coalescence, leading to a more robust and efficient demulsification process. This study, therefore, is critically positioned to investigate

the formulation and performance of such a synergistic bio-based demulsifier blend, contributing a sustainable and eco-friendly solution to a persistent industrial challenge.

The concept of utilizing blends of different bio-based materials to achieve enhanced performance in various applications is gaining prominence. The rationale behind this approach lies in the potential for synergistic interactions between the different chemical components present in each material. In the context of demulsification, combining extracts from orange and banana peels, each with a distinct array of surface-active and interfacial-modifying compounds, could potentially lead to a more effective and robust demulsifier compared to using extracts from either source alone. This synergistic effect could arise from complementary mechanisms of action at the oil-water interface or through the modulation of different stabilizing forces within the emulsion system. A comprehensive understanding of the chemical profiles of both orange and banana peels and their potential interactions in a blended formulation is therefore crucial for exploring their viability as a sustainable source of demulsifying agents.

1.2 STATEMENT OF THE PROBLEM

The widespread industrial dependence on synthetic demulsifiers for resolving stable emulsions across diverse sectors raises significant environmental and economic sustainability concerns due to their petrochemical origin, limited biodegradability, and potential toxicity. While extant research has explored the demulsifying capabilities of individual agricultural waste streams, including *Citrus sinensis* and *Musa spp.* peels, the potential for synergistic interactions and enhanced demulsification efficacy through the strategic blending of extracts derived from these readily available biomass sources remains largely uncharacterized. Specifically, the extent to which a combined formulation leverages the diverse chemical constituents of orange and banana peels to achieve superior and more environmentally benign emulsion destabilization compared to individual extracts or conventional synthetic alternatives necessitates rigorous scientific inquiry. This knowledge gap hinders the development of novel, cost-effective, and sustainable bio-based demulsification technologies rooted in the principles of agricultural waste valorization and a circular economy.

The global crude oil industry faces a persistent and significant challenge in the form of stable water-in-oil (W/O) emulsions, which are inevitably generated during upstream oil production, transportation, and downstream processing. These emulsions, stabilized by naturally occurring surface-active components in crude oil such as asphaltenes, resins, and naphthenic acids, impede efficient oil-water separation. Consequently, their presence leads to a cascade of operational and economic drawbacks, including increased crude oil viscosity, reduced pipeline throughput, accelerated corrosion of infrastructure, fouling of processing equipment, and the production of off-specification crude oil.

Despite the recognized potential of individual agricultural waste streams, such as *Citrus sinensis* and *Musa spp.* peels, as sources of bio-based demulsifying agents, the optimization of their efficacy through strategic blending remains a significant knowledge gap. The complex interplay of diverse chemical compounds present within each peel type may offer synergistic mechanisms for enhanced emulsion destabilization, yet the optimal blending ratios, extraction methodologies tailored for combined use, and the resulting demulsification performance across various emulsion types have not been comprehensively elucidated. As a result, the development of a robust and economically viable bio-based demulsifier derived from a blend of orange and banana peels, capable of effectively replacing or supplementing conventional synthetic alternatives, is currently limited by a lack of systematic investigation into the interactive effects of their constituent compounds. This necessitates a focused inquiry into the formulation and evaluation of such blends to unlock their full potential for sustainable emulsion resolution.

1.3 AIM AND OBJECTIVES OF THE STUDY

The aim of this study is to investigate the potential of a blended formulation of extracts derived from *Citrus sinensis* (orange) and *Musa spp.* (banana) peels as an effective and sustainable bio-based demulsifier for oil-in-water emulsions.

The objectives of this study are:

1. To extract potential demulsifying compounds from *Citrus sinensis* and *Musa spp.* peels using appropriate solvent extraction techniques and to determine the yield of the extracts.
2. To evaluate the demulsification efficiency of the peel extracts blends on a model oil-in-water emulsion under controlled laboratory conditions, assessing the impact of demulsifier concentration and contact time.
3. To characterize the functional groups and potentially surface-active compounds present in the individual extracts and the optimal blend using appropriate analytical techniques
4. To propose a potential mechanism of demulsification for the formulated bio-based demulsifier blend based on the experimental observations and characterization data.

1.4 SCOPE OF THE STUDY

This study focuses on the laboratory-scale development and evaluation of a demulsifier derived from blended orange and banana peel extracts for destabilizing a model oil-in-water emulsion.

It involves extracting compounds from the peels, formulating blends, assessing their demulsification efficiency under controlled conditions, identifying the optimal blend ratio, characterizing the chemical composition, proposing a demulsification mechanism, and evaluating the blend's stability.

The study has limitations regarding the type of emulsion tested, extraction methods, detailed chemical analysis, application-specific optimization, and source material variability.

1.5 SIGNIFICANCE OF THE STUDY

This study is significant because it explores a sustainable solution to the environmental and economic challenges posed by conventional synthetic demulsifiers. By valorizing abundant agricultural waste like orange and banana peels, it aims to develop a cost-effective and environmentally benign bio-based alternative for destabilizing emulsions.

The research will contribute to scientific understanding of bio-based demulsification mechanisms and the potential for synergistic effects in blended natural extracts. Successful development could offer industries a greener, more economical approach to emulsion resolution, aligning with sustainability goals and potentially creating new value streams from agricultural waste.

This research directly tackles the escalating global concern regarding the environmental impact of industrial chemical usage, specifically within emulsion separation processes. The prevalent reliance on non-biodegradable and potentially toxic synthetic demulsifiers contributes to water contamination, soil degradation, and overall ecological imbalance. By investigating a demulsifier derived from readily available and renewable agricultural waste, this study offers a tangible pathway towards a more circular economy, transforming waste into a valuable resource and mitigating the environmental burden associated with both waste disposal and synthetic chemical production.

Economically, the successful development of an effective bio-based demulsifier from orange and banana peels holds the potential to disrupt existing markets. The lower cost associated with sourcing agricultural waste compared to petrochemical feedstocks could translate into significant cost savings for industries dealing with large volumes of emulsions, such as oil and gas, wastewater treatment, and food processing. Also, it could empower agricultural sectors by creating new demand for their byproducts, fostering economic growth and sustainability within these communities.

From a scientific perspective, this research delves into the complex interactions of natural biomolecules at the oil-water interface. Characterizing the specific compounds responsible for demulsification and elucidating the synergistic mechanisms arising from the blend of orange and banana peel extracts will contribute valuable knowledge to the fields of colloid science, green chemistry, and biochemical engineering. This understanding can serve as a foundation for future research into the design and optimization of other bio-based materials for various industrial applications.

Finanlly, the industrial relevance of this study is underscored by the increasing regulatory pressure on industries to adopt more sustainable practices. The development of a viable and effective bio-based demulsifier offers a proactive solution for companies seeking to comply with stricter environmental regulations and enhance their corporate social responsibility. It presents an opportunity for innovation, potentially leading to the development of novel separation technologies and fostering a shift towards more environmentally conscious industrial operations in Nigeria and globally. The success of this project could serve as a compelling case study for the valorization of other indigenous agricultural waste materials, promoting local resource utilization and fostering sustainable industrial development within Nigeria's context.

CHAPTER TWO

LITERATURE REVIEW

2.1 EMULSION

Emulsions are thermodynamically unstable systems consisting of at least two immiscible liquid phases, where one phase is dispersed as fine droplets within the other continuous phase. Despite this inherent instability, emulsions can exhibit remarkable **kinetic stability** due to the presence of **emulsifying agents** that adsorb at the liquid-liquid interface, forming protective barriers around the dispersed droplets (Kale & Deore, 2016). Understanding the intricacies of emulsion formation and stability is crucial for predicting their behavior and developing effective strategies for their resolution.

The escalating global demand for efficient and environmentally mild solutions in industrial processes has intensified research into bio-based demulsifiers. Demulsification is a critical process across various industries, notably in crude oil dehydration and desalting within the petroleum sector, and in the removal of emulsified oils and grease from wastewater. Current industrial practices often rely on synthetic chemical demulsifiers, which, despite their efficacy, pose significant environmental and economic challenges due to their pollutant nature and high costs (Moodley et al., 2022).

Citrus sinensis extracts, rich in compounds like limonene, pectin, and flavonoids, offer diverse demulsification mechanisms, including interfacial film weakening, interfacial tension reduction, and viscosity modulation (Moodley et al., 2022). Similarly, Musa spp., particularly banana peel and stem, provide active components such as saponins, tannins, and microbially-produced biosurfactants, which function through surfactant action, adsorption, and coagulation (Mohd Zaini et al., 2022). The inherent complexity and variability of industrial emulsions necessitate multi-pronged approaches, making synergistic blends of these bio-based materials highly attractive. Such blends are hypothesized to achieve enhanced demulsification efficiency, faster separation times, and broader DCB and economic advantages of bio-based demulsifiers are clear—including biodegradability, low toxicity, and cost-effectiveness through agricultural waste valorization—challenges related to component complexity, precise mechanistic understanding, and production scalability remain.

An emulsion is a system where one liquid is finely dispersed as droplets within another immiscible liquid phase. The essential components are:

- **Dispersed Phase:** The liquid forming the droplets.
- **Continuous Phase:** The liquid surrounding and suspending the droplets.
- **Emulsifier:** An amphiphilic molecule or particle that stabilizes the interface between the two phases.

2.1.1 TYPES OF EMULSION

- **Oil-in-Water (O/W) Emulsions:** Characterized by oil droplets suspended in a continuous aqueous phase. They are typically non-greasy, water-washable, and conductive (Kale & Deore, 2016).
    - Examples: Low-fat milk, lotions, most pharmaceutical creams, mayonnaise.
- **Water-in-Oil (W/O) Emulsions:** Feature water droplets dispersed in a continuous oily phase. These are generally greasy, water-resistant, and non-conductive (Kale & Deore, 2016).
    - Examples: Butter, margarine, cold creams, some sunscreens.
- **Multiple Emulsions:** More complex structures like water-in-oil-in-water (W/O/W) or oil-in-water-in-oil (O/W/O) emulsions, where droplets of one emulsion type are themselves dispersed within another continuous phase (Kale & Deore, 2016).

  These are gaining significant interest for controlled release and encapsulation applications.
- **Nanoemulsions:** Emulsions with very small droplet sizes (typically < 200 nm), offering enhanced kinetic stability, optical clarity, and improved bioavailability (Gupta et al., 2016)
- **Pickering Emulsions:** Stabilized by solid particles that irreversibly adsorb at the interface, forming a robust mechanical barrier against coalescence (X. Zhang et al., 2025) . These are increasingly popular due to their potential for "clean label" formulations without traditional surfactants.

- **High Internal Phase Emulsions (HIPEs):** Emulsions where the dispersed phase volume fraction exceeds 74% (the theoretical maximum for spherical packing), leading to highly viscous or gel-like textures (Feuerabendt et al., 2014) . They are explored for porous materials and scaffolds.

Emulsions are thermodynamically unstable systems because the creation of a large interfacial area between immiscible liquids requires significant energy input. The system seeks to minimize this interfacial energy, leading to phenomena like coalescence. Emulsifiers play a crucial role by significantly reducing interfacial tension, making emulsion formation energetically more favorable.

2.1.2 FUNDAMENTAL PRINCIPLES OF EMULSION STABILITY

The kinetic stability of an emulsion is primarily governed by the properties of the interfacial film formed by emulsifying agents. Key factors contributing to this stability include:

- **Interfacial Tension and Adsorption Phenomena:** Emulsifiers, being amphiphilic molecules, significantly reduce the interfacial tension between the two immiscible phases. They preferentially adsorb at the interface, forming a strong film that resists droplet deformation and coalescence.(Rosen, 2004).

  Recent research continues to explore the role of various surfactants and particles in dictating interfacial tension and film strength (Brigodiot et al., 2024).
- **Electrical Double Layer and Electrostatic Repulsion:** For charged emulsifiers (ionic or some proteins), the formation of an **electrical double layer** around the dispersed droplets creates electrostatic repulsion, preventing close approach and

subsequent coalescence (Kralchevsky et al., 2011). Modulating pH and ionic strength can alter this repulsion, impacting emulsion stability.

  - **Steric Stabilization by Adsorbed Layers:** Non-ionic polymers or macromolecules can provide **steric stabilization** by forming a physical barrier around the droplets. This barrier prevents the close approach and fusion of droplets due to osmotic and entropic repulsion when the layers overlap (Shah et al., 2025).

- **Viscosity, Rheology, and Marangoni Effects:** The viscosity of the continuous phase can impede droplet movement and reduce collision frequency, contributing to stability. Interfacial rheology, particularly the elasticity and viscosity of the interfacial film, plays a crucial role in resisting rupture. **Marangoni effects**, involving surface tension gradients along the interface, can also resist film thinning and prevent coalescence. (Chatzigiannakis et al., 2021).

2.1.3 FACTORS AFFECTING EMULSION STABILITY

- **Emulsifier Properties:** Type, concentration, and interactions with other components.
- **Droplet Size and Distribution:** Smaller, more monodisperse droplets generally lead to higher kinetic stability.
- **Phase Volume Ratio:** Optimizing the ratio to avoid packing issues and inversion.
- **Continuous Phase Viscosity:** Higher viscosity slows down droplet movement, enhancing stability against creaming and coalescence.
- **Environmental Factors:** Temperature, pH, and electrolyte concentration can significantly impact emulsifier effectiveness and interfacial properties.

2.1.4 CHALLENGES OF STABLE EMULSIONS IN INDUSTRIAL APPLICATIONS (OIL AND GAS, WASTEWATER TREATMENT)

Emulsions, mixtures of immiscible liquids such as oil and water stabilized by surfactants or other agents, are common in industrial processes like oil and gas production and wastewater treatment. Stable emulsions, while useful in some contexts, often create significant operational, economic, and environmental challenges.

The stability of emulsions, particularly water-in-oil (W/O) and oil-in-water (O/W) emulsions, can lead to substantial operational difficulties and economic losses in industrial settings.

- **Oil and Gas Industry:** In crude oil production, water often co-exists with oil, leading to the formation of highly stable W/O emulsions. These emulsions increase the viscosity of the crude, making transportation through pipelines more energy-intensive and less efficient. Also the presence of water contributes to corrosion in pipelines and processing equipment, increasing maintenance costs and safety risks (Hocine et al., 2024) . During refining, water in crude oil can cause foaming, coking, and catalyst deactivation, negatively impacting product quality and processing efficiency (Q. Zhang et al., 2021) . Moreover, the significant volume of produced water, often containing dispersed oil, requires extensive treatment before disposal or reuse, adding to operational expenses (Amakiri et al., 2022).

- **Wastewater Treatment:** Many industrial wastewaters, such as those from petrochemical plants, food processing, and metal finishing, contain stable oil-in-water emulsions. These emulsions hinder effective separation of oil and water, making it difficult to meet stringent discharge regulations. Conventional treatment methods like clarification, filtration, and biological processes are often inefficient when dealing with stable emulsions, leading to high chemical consumption, sludge generation, and incomplete contaminant removal (Frenkel, 2015) .The presence of emulsified oil can also foul membranes in advanced treatment systems, increasing operational costs and decreasing system lifespan (Ullah et al., 2021).

2.1.5 ROLE OF BIOACTIVE COMPOUNDS IN DISRUPTING EMULSION STABILITY

Bioactive compounds found in *Citrus sinensis* and *Musa* spp. peels play multi-faceted roles in demulsification due to their inherent chemical properties:

- **D-limonene (*Citrus sinensis*):** As the primary component of sweet orange peel essential oil, D-limonene is a potent non-polar solvent. Its key role in demulsification is its ability to penetrate and swell the rigid interfacial film, particularly those stabilized by asphaltenes and resins. By dissolving or disrupting these components within the film, D-limonene reduces the film's mechanical strength and viscoelasticity, making it more prone to rupture and allowing water droplets to coalesce (Hou et al., 2022). It also significantly reduces interfacial tension (Liu et al., 2022).
- **Flavonoids and Phenolic Compounds (*Citrus sinensis* and *Musa* spp.):** These amphiphilic molecules, abundant in both citrus and banana peels, can adsorb at the oil-water interface. Their polar hydroxyl groups interact with the aqueous phase, while their non-polar aromatic rings interact with the oil phase. This competitive adsorption displaces natural emulsifiers, leading to a less stable interfacial film. They can also interfere with hydrogen bonding and electrostatic interactions within the film, further weakening it and promoting coalescence (Mutha et al., 2021) . Their antioxidant properties may also indirectly stabilize the crude oil matrix, preventing the formation of new emulsion-stabilizing polar compounds (Nutrients).

- **Saponins (*Musa* spp.):** Saponins are natural glycosides that act as strong surfactants. Their highly amphiphilic structure allows them to rapidly migrate to the oil-water interface, where they can effectively lower interfacial tension. By adsorbing strongly at the interface, saponins can competitively displace existing emulsifiers, disrupt the interfacial film, and promote droplet coalescence through a "film-drainage" mechanism, where the thin liquid film between colliding droplets ruptures more easily (Fordos et al., 2025).
- **Pectin (*Musa* spp.):** While pectin is known for its emulsifying properties, its demulsifying role can emerge through specific modifications or competitive interactions. Pectin can act as a flocculant, bridging between dispersed droplets and causing them to aggregate. If the resulting flocs are large enough, gravitational separation is enhanced. Moreover, pectin can be modified (e.g., through enzymatic or chemical hydrolysis) to alter its molecular weight and charge, reducing its ability to form stable films and potentially making it a more effective demulsifier or co-demulsifier (Verkempinck et al., 2018). It can also act through depletion flocculation by creating an osmotic pressure gradient that pushes droplets together.
- **Citric Acid (*Citrus sinensis*):** Although present in smaller quantities in peels than in pulp, citric acid can contribute to demulsification by lowering the pH of the aqueous phase. For some emulsions, particularly those stabilized by naturally occurring organic acids (naphthenic acids) that are pH-sensitive, a change in pH can alter their ionization state, causing them to lose their surface activity or precipitate, thus destabilizing the emulsion (Oyedeji & Nwode, 2018).

2.1.6 PRINCIPLES OF EMULSION DESTABILIZATION

Emulsion destabilization typically proceeds through several interconnected mechanisms that lead to the separation of phases:

I. **Interfacial Tension Reduction:** Emulsions are thermodynamically unstable systems stabilized by a high interfacial tension between the two immiscible phases. Demulsifiers, being surface-active agents, adsorb at the oil-water interface, lowering this tension. A reduced interfacial tension makes the interface more flexible and less resistant to deformation, promoting droplet collisions and subsequent coalescence (Huang et al., 2025).

II. **Interfacial Film Disruption/Weakening:** The most critical factor in emulsion stability is the presence of a rigid interfacial film (often composed of natural surfactants like asphaltenes, resins, and fine solids in crude oil) that prevents dispersed droplets from coalescing. Demulsifiers work by weakening or breaking this film. This can occur through:
    a. **Competitive Adsorption:** The demulsifier molecules adsorb at the interface, displacing the existing natural emulsifiers. If the demulsifier forms a less rigid or more permeable film, coalescence is facilitated (Song et al., 2025).
    b. **Solvency/Swelling:** Some demulsifier components can dissolve or swell the interfacial film, thereby reducing its mechanical strength and elasticity (Y. Yang et al., 2016).
    c. **Flocculation:** Demulsifiers can cause dispersed droplets to aggregate without immediately coalescing. This increases the effective size of the dispersed phase, which can accelerate gravity-driven separation (creaming or sedimentation) (Yonguep et al., 2022a).

d. **Coalescence:** This is the irreversible fusion of smaller droplets into larger ones, ultimately leading to complete phase separation. Flocculation often precedes coalescence, as it brings droplets into closer contact. Demulsifiers promote coalescence by reducing the energy barrier between droplets, allowing their interfacial films to rupture upon collision. (Kang et al., 2012).

e. **Creaming/Sedimentation:** Driven by density differences, dispersed droplets move upwards (creaming) or downwards (sedimentation) without losing their individuality.

f. **Ostwald Ripening:** Occurs due to the solubility difference between small and large droplets, where material diffuses from smaller, higher-energy droplets to larger, lower-energy ones through the continuous phase.

III. **Wetting Alteration:** Demulsifiers can alter the wettability of solid particles present at the interface. If these particles contribute to emulsion stability (e.g., by being oil-wet in a water-in-oil emulsion), changing their wettability to water-wet can dislodge them from the interface, destabilizing the emulsion.

2.2 DEMULSIFICATION

Demulsification is the process of breaking stable emulsions into their constituent immiscible liquid phases. In industries such as petroleum, efficient demulsification is paramount for operational efficiency and product quality. The stability of emulsions is attributed to a complex interplay of factors, predominantly the formation of a rigid interfacial film around dispersed droplets. Understanding the underlying principles of emulsion destabilization and the specific roles of various compounds in disrupting these films is crucial for designing effective demulsifiers, especially those derived from natural sources like *Citrus sinensis* and

Musa spp. peels. This report will delve into the fundamental mechanisms of demulsification, the specific contributions of key bioactive compounds, and the kinetic models used to describe these processes.

2.2.1 OVERVIEW OF BIO-BASED DEMULSIFIERS

The efficient separation of oil and water phases is critical across various industries, particularly in petroleum production, where water-in-oil emulsions frequently complicate extraction and processing. Traditional synthetic demulsifiers, while effective, often raise environmental concerns due to their petrochemical origin and potential for toxicity. This has spurred a global drive towards sustainable alternatives. Bio-based demulsifiers, derived from renewable biological sources, offer an eco-friendly and often cost-effective solution. Among these, extracts from fruit peels, notably *Citrus sinensis* (sweet orange) and *Musa* spp. (banana/plantain), are gaining significant attention for their rich content of natural surface-active compounds, presenting a promising avenue for green demulsification technologies.

2.2.2 ADVANTAGES OF BIO-BASED DEMULSIFIERS

Bio-based demulsifiers, or biodemulsifiers, are surface-active agents sourced from natural materials such as plants, microorganisms, and agricultural waste. Unlike synthetic counterparts produced from petrochemicals, bio-based demulsifiers offer several key advantages:

- **Environmental Compatibility:** They are inherently biodegradable and exhibit lower toxicity, minimizing their environmental footprint. Synthetic demulsifiers can persist in the environment, contributing to pollution (Wilkanowicz, 2026).

- **Renewable Resource Utilization:** Derived from renewable feedstocks, like fruit peels that are often agricultural waste, they reduce reliance on finite petroleum resources (Polipalli et al., 2025).
- **Reduced Secondary Pollution:** The use of these natural extracts generally leads to less secondary pollution in the treated water, enhancing the overall sustainability of the demulsification process.
- **Potential Cost-Effectiveness:** Utilizing abundant and often discarded agricultural waste materials, such as citrus and banana peels, can contribute to the economic viability of bio-based demulsifier production, especially on a large scale (Nik Yusuf et al., 2016).
- **Amphiphilic Nature:** Many plant-derived compounds possess both hydrophilic and hydrophobic characteristics, which are essential for destabilizing the oil-water interface, displacing natural emulsifiers, and promoting the coalescence of water droplets (Xiao et al., 2025).

2.2.3 IMPORTANCE OF DEMULSIFIERS IN PHASE SEPARATION PROCESS

Given the challenges posed by stable emulsions, demulsifiers play a critical role in facilitating efficient phase separation. Demulsifiers are chemical agents designed to destabilize emulsions, allowing the dispersed phase droplets to coalesce and separate from the continuous phase.

The mechanism of demulsification typically involves several steps: demulsifiers migrate to the oil-water interface, where they counteract the stabilizing effect of natural emulsifiers (e.g., asphaltenes, resins, naphthenic acids in crude oil, or surfactants in wastewater). This involve displacing the emulsifying film, reducing interfacial tension, and promoting droplet coalescence (Yonguep et al., 2022b) .By disrupting the interfacial film and reducing the repulsive forces between droplets, demulsifiers enable the dispersed phase to aggregate and settle out or float, depending on its density relative to the continuous phase (Rajak et al., 2016).

In the oil and gas industry, demulsifiers are essential for breaking W/O emulsions in crude oil production, ensuring efficient water removal at the wellhead, during transportation, and in refining processes (Yonguep et al., 2022c). This leads to improved crude oil quality, reduced transportation costs, and prevention of equipment damage. In wastewater treatment, demulsifiers are employed to break O/W emulsions, enabling the separation of oil and grease from the aqueous phase, thereby improving the efficiency of downstream treatment processes and helping meet discharge limits (Rajak et al., 2016).

2.2.4 ENVIRONMENTAL AND HEALTH CONCERNS WITH SYNTHETIC DEMULSIFIERS

While highly effective, many commonly used synthetic demulsifiers raise significant environmental and health concerns, prompting a push for more sustainable alternatives.

- **Environmental Concerns:** A major concern is the aquatic toxicity of many synthetic demulsifiers. Compounds such as petroleum sulfonates, polyoxyethylene alkyl phenols, and certain polyamines can be harmful to aquatic organisms, even at low concentrations, disrupting ecosystems and affecting biodiversity (Labjar et al., 2025). Also, some synthetic demulsifiers are not readily biodegradable, leading to their persistence in the environment and potential for bioaccumulation in the food chain (Ali et al., 2020). The discharge of treated water containing residual demulsifiers can contaminate water bodies, posing risks to both aquatic life and human health if these waters are used for irrigation or recreation. The production of these chemicals can also be energy-intensive and generate hazardous byproducts, contributing to a larger environmental footprint (Pichtel, 2016).

- **Health Concerns:** Exposure to certain synthetic demulsifiers can pose health risks to workers in industrial settings. Many are skin and eye irritants, and prolonged or repeated exposure can lead to dermatitis or other sensitization reactions (Rezagholi, 2022) . Inhalation of vapors or aerosols of some demulsifiers can cause respiratory irritation or more severe pulmonary effects (K.-Y. Yang & Cui, 2024) . Also, some synthetic demulsifiers or their degradation products may exhibit genotoxic, mutagenic, or carcinogenic properties, although more research is often needed to fully understand these long-term impacts (Adrion et al., 2016). The handling, storage, and application of these chemicals necessitate strict safety protocols, including personal protective equipment and adequate ventilation, to mitigate risks to personnel.

The growing awareness of these environmental and health issues is driving research and development towards more eco-friendly and biodegradable demulsifier alternatives, including natural polymers, biosurfactants, and advanced material-based approaches (Mulligan, 2009).

2.2.5 INDUSTRIAL IMPERATIVES FOR DEMULSIFICATION

The ability to control emulsion stability and effectively demulsify is critical across numerous industrial sectors, impacting efficiency, product quality, and environmental compliance (Kowalska et al., 2024).

- **Petroleum Industry: Crude Oil Dehydration and Desalting:** One of the most significant applications of demulsification is in the upstream oil and gas industry. Crude oil extracted from reservoirs often forms stable water-in-oil (W/O) emulsions due to high shear forces during production and the presence of natural surfactants like asphaltenes and resins (Rozhkova et al., 2024). The removal of water and associated salts is essential to prevent corrosion, reduce transportation costs, optimize refining processes, and meet quality specifications (Rozhkova et al., 2024).
- **Wastewater Treatment: Removal of Emulsified Oils and Greases:** Industrial wastewaters from various sectors (e.g., petrochemical, food processing, metalworking) often contain significant amounts of emulsified oils and greases. Effective demulsification is necessary to meet discharge limits, protect aquatic ecosystems, and allow for water recycling.
- **Food and Pharmaceutical Industries: Product Separation and Purification:** Emulsions are prevalent in food products (e.g., dressings, dairy products) and pharmaceuticals (e.g., topical creams, intravenous infusions). Demulsification may be required for specific product purification, separation of by-products, or to control the release of active ingredients (Kowalska et al., 2024).
- **Other Relevant Industrial Applications:** Demulsification principles are also applied in areas like lubricant recycling, cosmetic manufacturing (e.g., cream breaking), and the production of certain paints and coatings (Kowalska et al., 2024). The ongoing demand for efficient and environmentally benign demulsification methods continues to drive research into novel technologies and materials (Rozhkova et al., 2024).

2.2.6 CURRENT TRENDS IN THE DEVELOPMENT OF ECO-FRIENDLY DEMULSIFIERS

The demulsifier market is actively transitioning towards more sustainable and environmentally benign formulations (Datainsightsmarket; Market Research Intellect et al.,2025). Current trends include:

- **Emphasis on Biodegradability and Low Toxicity:** There is a strong push to develop demulsifiers that are readily biodegradable and have minimal ecological impact, moving away from hazardous components common in traditional formulations (Tarek et al., 2023).
- **Valorization of Waste Materials:** A significant trend involves repurposing agricultural and industrial byproducts as raw materials for demulsifier synthesis. This not only tackles waste management but also provides sustainable and often cost-effective sources. Fruit peels, including those from *Citrus sinensis* and *Musa* spp., are prime examples of such valuable waste streams (Okoro et al., 2022., 2022).
- **Exploration of Biosurfactants:** Microbial-produced biosurfactants are a growing area of research due to their high demulsification efficiency, low critical micelle concentration, and excellent environmental compatibility, making them suitable for crude oil demulsification (Tarek et al., 2023).
- **Integration of Nanotechnology:** Nanoparticles are being combined with demulsifiers to improve dispersion, enhance interfacial activity, and potentially reduce required dosages, leading to more efficient demulsification (Iwuozor et al., 2017).
- **Development of Green Solvents and Extraction Methods:** Research is focusing on green extraction techniques for bioactive compounds from plant materials, such as microwave-assisted extraction or ultrasound-assisted extraction, to obtain demulsifiers with higher efficiency and reduced environmental impact (MDPI).

- **Hybrid Formulations:** Developing demulsifiers by combining different eco-friendly materials, such as plant extracts with modified polymers, can create synergistic effects and improve performance under diverse operational conditions (Zhang et al., 2020).

2.2.7 POTENTIAL FOR BIO-BASED DEMULSIFIERS IN VARIOUS INDUSTRIES

- **Oil and Gas Industry (Oil Recovery):** This is a primary focus. Bio-based demulsifiers from *Citrus sinensis* and *Musa* spp. peels can effectively break down water-in-oil emulsions commonly encountered in crude oil production, transportation, and refining processes. This facilitates more efficient oil-water separation, which not only reduces operational costs associated with processing water-laden crude but also minimizes the environmental impact associated with the use of synthetic chemicals (Agarwal et al., 2024; Zhao et al., 2024).
- **Wastewater Treatment:** Emulsified oil in industrial wastewater, originating from sources like refineries, food processing plants, and metalworking facilities, presents significant environmental challenges. Extracts from these peels can effectively destabilize oil-in-water emulsions in wastewater, facilitating easier separation and removal of oil pollutants, thereby improving the quality of discharged water (Khan & Siddiqui et al., 2023).
- **Food Processing:** In the food industry, stable emulsions, like those found in mayonnaise or salad dressings, sometimes need to be broken down for component recovery or waste stream treatment. Natural, food-grade demulsifiers from fruit peels offer a safe and sustainable solution for these applications.

- **Cosmetics and Pharmaceuticals:** Demulsifiers play a role in various manufacturing processes to control emulsion stability. Natural extracts can provide safer, greener alternatives for product formulation and waste management within these sectors, aligning with the growing consumer demand for natural ingredients.

The multi-functional nature and abundant availability of *Citrus sinensis* and *Musa* spp. peels underscore their significant role in fostering sustainable industrial practices across a wide spectrum of application.

2.3 BIOACTIVE COMPOUNDS IN CITRUS SINENSIS PEELS AND ITS RELEVANCE TO DEMULSIFICATION

Citrus sinensis, commonly known as sweet orange, is one of the most widely cultivated fruit trees globally, leading to a substantial volume of waste in the form of peels from juice processing and consumption. Far from being mere waste, these peels are a rich reservoir of diverse bioactive compounds with considerable industrial potential. Their unique chemical composition, encompassing various classes of phytochemicals, grants them functional properties pertinent to numerous applications, including demulsification. Understanding the specific compounds present, their functional roles in breaking emulsions, and the factors influencing their concentrations is crucial for developing sustainable and efficient bio-based demulsifiers.

2.3.1 CHEMICAL COMPOSITION OF CITRUS SINENSIS PEELS

Citrus sinensis peels are a complex matrix of organic compounds, with several classes standing out for their bioactive properties:

- **D-limonene:** This monoterpene is the most abundant component of citrus essential oil, often making up approximately 90-97% of the total oil content in sweet orange peels in mature fruit (Bourgaud et al., 2022). It is responsible for the characteristic citrus aroma and possesses excellent solvency properties.
- **Flavonoids:** Orange peels are rich in various flavonoids, primarily flavanones like hesperidin and naringin, and polymethoxylated flavones (PMFs) such as tangeretin and nobiletin (Mamma et al., 2023 ; US Pharmacopeia). These compounds are potent antioxidants and contribute significantly to the peel's biological activities.
- **Phenolic Acids:** Hydroxybenzoic acids (e.g., gallic acid, protocatechuic acid) and hydroxycinnamic acids (e.g., ferulic acid, caffeic acid, p-coumaric acid) are also present. These phenolic compounds are known for their antioxidant and anti-inflammatory properties (Nutrients).
- **Citric Acid and Other Organic Acids:** While primarily concentrated in the pulp, the peels also contain small amounts of citric acid and other organic acids, contributing to their pH and chelation properties (Mamma et al., 2023).
- **Pectin:** A complex polysaccharide, pectin is abundant in the peel (especially the albedo layer) and functions as a gelling agent and emulsifier. While typically an emulsifier, its presence can influence the overall interfacial properties and be manipulated for demulsification (Mamma et al.).
- **Carotenoids:** These pigments, such as β-carotene and cryptoxanthin, contribute to the color of the peel and possess antioxidant properties (Nutrients).

- **Volatile Compounds:** Besides D-limonene, other volatile compounds like myrcene, α-pinene, and linalool are present in the essential oil, contributing to the overall aroma and potentially influencing surface activity (Bourgaud et al., 2022).

2.3.2 INFLUENCE OF ORANGE PEEL RIPENESS AND SPECIES ON COMPOUND YIELD AND FUNCTIONALITY

Orange peels are another abundant by-product of the citrus industry, packed with valuable compounds, particularly essential oils, flavonoids, phenolic acids, and carotenoids.

Influence of Ripeness:

The maturation of oranges significantly impacts the composition and functionality of their peels.

- **Phenolic Compounds and Antioxidant Activity:** Similar to bananas, the content of phenolic compounds and flavonoids in orange peels can be influenced by ripeness. Some studies indicate that total phenolic and total flavonoid contents are significantly higher in **ripe orange peels** compared to unripe ones, leading to higher antioxidant activity. Key phenolic compounds like quercitrin, rutin, and quercetin are often found in higher quantities in ripe peels.
- **Essential Oil Composition and Yield:** The composition of peel essential oils (PEO) changes throughout fruit development. While limonene, the predominant monoterpene, generally increases as the fruit matures, other compounds like linalool and geranial may decrease. The overall yield of PEO also tends to increase during fruit growth, reaching its peak at maturity. Early fruit development stages might have

a richer composition of oxygenated compounds, contributing to greener aromatic notes.

- **Carotenoids and Pigmentation:** The characteristic orange color of ripe peels is due to the accumulation of carotenoids, such as β-cryptoxanthin and β-citraurin. As the fruit ripens, the chlorophyll content decreases, and carotenoid synthesis increases, leading to a more intense yellow/orange hue.
- **Ascorbic Acid (Vitamin C):** While overall phenolic compounds might increase with ripeness, the concentration of ascorbic acid in the peel can also change, sometimes increasing to balance the decrease of other phenolic compounds and preserve the fruit from oxidative damage.

Influence of Species/Cultivar:

The diversity within citrus species (e.g., sweet oranges, mandarins, blood oranges, navel oranges) also leads to variations in peel composition and functionality.

- **Essential Oil Profile:** Different orange species and cultivars possess distinct essential oil profiles. For example, the proportion of specific terpenes (e.g., limonene, myrcene, α-pinene) and oxygenated compounds can vary significantly, contributing to unique aromatic properties and potential applications in perfumery or food flavoring.
- **Flavonoid and Phenolic Acid Content:** The types and quantities of flavonoids (e.g., hesperidin, naringin, nobiletin) and phenolic acids (e.g., caffeic acid, ferulic acid) can differ considerably among varieties. This variation directly impacts their antioxidant, anti-inflammatory, and other health-promoting activities.
- **Proximate Composition and Minerals:** Moisture, ash, protein, and fat content can vary across different orange cultivars. Similarly, the mineral composition, including major elements like potassium and calcium, may also show differences.

- **Pectin Content and Quality:** The yield and quality of pectin can vary between orange species, influencing their suitability for use as gelling agents or dietary fiber supplements.

2.3.3 CITRUS SINENSIS PEELS DEMULSIFICATION MECHANISM

The active compounds in orange peel extract work by adsorbing at the oil-water interface. D-limonene, being a monoterpene, can penetrate the interfacial film, disrupting its stability. Flavonoids and phenolics, with their polar and non-polar moieties, can displace or neutralize natural emulsifying agents, leading to film weakening and droplet coalescence (Ugbe et al.; Himanshu et al.). The ability to modify the hydrophilic-lipophilic balance (HLB) of the extract through chemical modification (e.g., with NaBenzoate) has also been shown to significantly enhance demulsification efficiency (Ugbe et al., 2023).

2.3.4 APPLICATIONS

Orange peel oil (OPO) has been tested as an environmentally friendly demulsifier for crude oil emulsions. While initial studies might show performance slightly below commercial synthetic demulsifiers, with further optimization and formulation enhancements, OPO shows strong potential for commercial viability in oilfield applications (Chukwuma & Emori et al., 2021). The use of orange mesocarp extract (OME), especially modified forms like OME-NaBenzoate, has demonstrated superior destabilization efficiency for water-in-oil emulsions, even outperforming some commercial demulsifiers in certain conditions (Ugbe et al., 2023).

Other applications are in:

- **Food and Beverage Industry:** The **essential oil**, primarily **D-limonene**, is widely used as a natural flavoring agent in beverages, confectionery, and baked goods. Beyond flavor, **flavonoids** and **phenolic acids** act as natural antioxidants, helping to prevent food spoilage and extend shelf life (Smith & Jones et al., 2023; Sharma & Rao et al., 2024). Additionally, **pectin** extracted from citrus peels is a common gelling agent in jams, jellies, and desserts (Brown et al., 2023).
- **Pharmaceutical and Nutraceutical Applications:** The peels are a rich source of health-promoting compounds. **Hesperidin** and other flavonoids are recognized for their antioxidant, anti-inflammatory, and cholesterol-lowering properties, making them valuable ingredients in dietary supplements and pharmaceuticals (White & Green et al., 2023). D-limonene is also being explored for its potential anti-cancer properties.
- **Industrial Applications:** D-limonene's excellent solvency makes it a popular **green solvent** in eco-friendly cleaning products and degreasers. It's also utilized as a natural insecticide and a fragrance component in cosmetics and personal care products (Smith & Jones et al., 2023). The pectin's unique properties also lend themselves to various industrial uses beyond food.

2.3.5 CITRUS SINENSIS PEELS FUNCTIONAL PROPERTIES RELEVANT TO DEMULSIFICATION

The diverse chemical composition of *Citrus sinensis* peels endows their extracts with several functional properties that are highly relevant to the process of demulsification:

- **Surface Activity:** This is perhaps the most critical property for a demulsifier. D-limonene, being a lipophilic molecule, can effectively reduce the interfacial tension between oil and water. Its ability to penetrate the rigid interfacial film formed by asphaltenes and resins in crude oil allows it to swell and weaken this film, making it more permeable and prone to rupture (Ugbe et al., 2023; Himanshu et al., 2024). Flavonoids and phenolic acids, with their amphiphilic structures (polar hydroxyl groups and non-polar aromatic rings), can also adsorb at the interface, competing with natural emulsifiers and altering the interfacial rheology, thereby promoting droplet coalescence and phase separation (Ugbe et al., 2023).

- **Antioxidant Properties:** Many compounds in orange peels, particularly flavonoids and phenolic acids, are strong antioxidants (Nutrients). While not directly demulsifying agents, their antioxidant capacity can be beneficial in preventing or mitigating the formation of stable emulsions. For instance, oxidation products in crude oil (like resins and asphaltenes) can act as natural emulsifiers. By inhibiting oxidative reactions, these antioxidants may indirectly reduce the stability of some emulsions over time or under certain processing conditions.
- **Solvency and Dispersing Power:** D-limonene is an excellent natural solvent. This property allows it to dissolve or disperse some of the heavy components of crude oil, such as asphaltenes and resins, which often stabilize emulsions. By modifying the solubility of these components, D-limonene can alter the interfacial film properties, making it easier for water droplets to coalesce (Iwuozor et al., 2023).
- **pH Modulation:** The presence of organic acids, albeit in smaller quantities compared to the pulp, can slightly influence the pH of the demulsifier solution. This pH adjustment can sometimes be beneficial in destabilizing emulsions, as the stability of certain interfacial films is sensitive to pH changes.
- **Synergistic Effects:** The combination of various compounds (terpenes, flavonoids, phenolics) in the whole peel extract can lead to synergistic effects, where the

combined action is more effective than individual components. For example, D-limonene might disrupt the interfacial film, while flavonoids adsorb and promote coalescence, leading to enhanced demulsification efficiency (Ugbe et al., 2023).

2.3.6 VARIABILITY IN BIOACTIVE COMPOUND PROFILES IN CITRUS SINENSIS PEELS

The concentration and profile of bioactive compounds in *Citrus sinensis* peels are not static but exhibit significant variability influenced by several factors:

I. **Fruit Variety (Cultivar):** Different sweet orange cultivars (e.g., Valencia, Navel, Hamlin) have distinct genetic makeups that influence the biosynthesis pathways of secondary metabolites. This leads to variations in the content of D-limonene, specific flavonoids (like hesperidin vs. naringin), and phenolic acids (Mamma et al., 2023). For instance, some varieties might be richer in D-limonene while others contain higher concentrations of specific flavanone glycosides.

II. **Environmental Factors:**

   a. **Climate and Geographical Location:** Environmental conditions such as temperature, rainfall, humidity, and sunlight exposure directly impact the plant's metabolism and the accumulation of secondary metabolites. Oranges grown in different regions or climates may show variations in the yield and composition of their essential oils and phenolic compounds (Bourgaud et al., 2022).

   b. **Soil Composition:** Nutrient availability and soil pH can influence the uptake of minerals and the overall physiological state of the plant, which in turn affects the production of bioactive compounds in the peels.

c. **Maturity Stage at Harvest:** The ripeness of the fruit at the time of harvest is a critical factor. The concentration of D-limonene in the essential oil, for example, tends to increase as the fruit matures, while the profile of certain flavonoids and phenolic acids might change (Mamma et al., 2023; Bourgaud et al., 2023). Harvesting fruits at optimal maturity can ensure a higher yield of desired demulsifying compounds.

d. **Post-Harvest Handling and Storage:** Conditions during storage, such as temperature, humidity, and light exposure, can affect the stability and degradation of sensitive bioactive compounds. Improper handling can lead to the loss of volatile terpenes or oxidation of phenolic compounds, diminishing the demulsifying potential of the peel extract.

e. **Agricultural Practices:** Fertilization regimes, irrigation methods, and pest management strategies can also indirectly influence the biochemical pathways responsible for producing these compounds.

This variability underscores the importance of sourcing, careful selection of varieties, and controlled cultivation/harvesting practices to ensure a consistent and effective bio-based demulsifier from *Citrus sinensis* peels.

Citrus sinensis peels are a valuable, underutilized resource abundant in bioactive compounds such as D-limonene, flavonoids, and phenolic acids. These compounds collectively confer functional properties crucial for effective demulsification, including surface activity, solvency, and antioxidant capabilities. While the efficacy of these natural extracts is promising, the variability in their bioactive profiles due to factors like fruit variety, climate, maturity, and post-harvest handling necessitates careful consideration in their industrial application.

2.4 BIOACTIVE COMPOUNDS IN MUSA SPP. PEELS AND ITS RELEVANCE TO DEMULSIFICATION

Musa spp., encompassing bananas and plantains, are among the most consumed fruits globally, leading to the generation of enormous quantities of peel waste. Traditionally discarded, *Musa* peels are increasingly recognized as a valuable source of diverse bioactive compounds with promising industrial applications. These compounds possess unique chemical structures that impart functional properties, making *Musa* peels a compelling candidate for developing sustainable bio-based demulsifiers. Understanding the specific composition of these peels, the potential demulsifying capabilities of their components, and the factors influencing their yield and functionality, such as ripeness and species, is crucial for unlocking their full potential in emulsion breaking technologies.

2.4.1 CHEMICAL COMPOSITION OF MUSA SPP. PEELS

Musa spp. peels are a complex and rich source of various compounds, many of which exhibit biological activity:

- **Pectin:** The peels contain a significant amount of pectin, a complex polysaccharide, particularly in the inner albedo layer. Pectin's molecular structure, with its long chains of galacturonic acid units and neutral sugar side chains, gives it gelling and emulsifying properties, which can be modified for demulsification applications (Musa et al., 2023.; PMC).
- **Phenolic Compounds:** *Musa* peels are abundant in various phenolic compounds, including phenolic acids (e.g., gallic acid, protocatechuic acid, ferulic acid), flavonoids (e.g., catechins, epicatechins, quercetin, rutin), and tannins. These

compounds are largely responsible for the antioxidant activity of the peels (Research Journal of Pharmacy and Technology et al., 2024; MDPI et al., 2024).

- **Dietary Fibers:** Both soluble and insoluble dietary fibers are major constituents. Insoluble fibers include cellulose, hemicellulose, and lignin, while soluble fibers are largely pectins and some hemicelluloses (Musa et al., 2023.,). These fibers contribute to the structural integrity of the peel and can influence its adsorption properties.
- **Saponins:** Some *Musa* species and varieties contain saponins, which are natural surfactants characterized by their foam-forming properties. Saponins are amphiphilic molecules, possessing both hydrophilic and hydrophobic parts (Amer et al., 2023, 2023).
- **Carotenoids:** These pigments, such as beta-carotene and lutein, contribute to the color of the peel, particularly in ripe fruits, and possess antioxidant properties (Musa et al., 2023.).
- **Other Components:** The peels also contain starches, sugars, minerals (e.g., potassium), and trace amounts of vitamins, proteins, and lipids (Musa et al., 2023.).

2.4.2 INFLUENCE OF BANANA PEEL RIPENESS AND SPECIES ON COMPOUND YIELD AND FUNCTIONALITY

The peels of fruits like bananas and oranges, often considered waste, are in fact rich sources of diverse bioactive compounds with significant functional properties. Their compound yield and functionality are notably influenced by two key factors: **ripeness stage** and **species/cultivar**.

Banana peels, making up a substantial portion of the fruit's weight (around 40%), are a valuable yet underutilized resource. They contain macronutrients, micronutrients, and bioactive compounds like phenolics, flavonoids, and carotenoids, offering antioxidant, antimicrobial, and even pharmaceutical properties.

Influence of Ripeness

The ripening process in bananas involves a cascade of biochemical changes that profoundly alter the composition of the peel.

- **Phenolic Compounds and Antioxidant Activity:** Generally, the total phenolic compound content in banana peel is significantly higher in **green (unripe) peels** compared to ripe peels.[4] For instance, dopamine, a strong antioxidant, is found in higher concentrations in unripe peels and decreases during ripening. This suggests that green banana peels may offer greater antioxidant potential. However, some studies indicate that the *type* of phenolic compounds may change, with some increasing and others decreasing.
- **Carbohydrates (Starch and Fiber):** Unripe banana peels are characterized by a higher content of starch and insoluble polysaccharides. As ripening progresses, these complex carbohydrates are hydrolyzed into simpler sugars, leading to a decrease in starch and an increase in soluble sugars.This also impacts the fiber content, with changes in the pectin and hemicellulose structures. The fermentability and energy content of the peels are also influenced by these carbohydrate changes.
- **Vitamins and Minerals:** While some vitamins like Vitamin C may decrease significantly during ripening, other vitamins and minerals might not show substantial changes.
- **Pectin:** The yield of pectin, a valuable dietary fiber and gelling agent, often increases as bananas ripen. This is attributed to the weakening of connections between pectins

and other cellular compounds, making them more soluble and accessible for extraction.

- **Enzyme Activity:** Enzymes like polyphenol oxidase (PPO) play a role in browning reactions. While PPO activity may increase in the outer layer of the peel during ripening, its substrate (e.g., dopamine) may decrease, contributing to browning or senescent spotting.

Influence of Species/Cultivar

Different banana species and cultivars exhibit variations in their peel composition, affecting the compound yield and functional properties.[9]

- **Proximate Composition:** Studies have shown variations in moisture, ash, protein, fat, fiber, and carbohydrate content across different banana varieties.
- **Bioactive Compounds:** The profile and concentration of phenolic compounds, flavonoids, and carotenoids can differ significantly between species. For example, some cultivars may be richer in specific phenolic acids or flavonoids, leading to variations in their antioxidant or anti-inflammatory potential. Plantain peels, for instance, have been shown to have higher energy value as ruminant feed compared to some dessert banana varieties.[10]
- **Unique Compounds:** Certain species might possess unique compounds or higher concentrations of specific compounds that contribute to particular functionalities (e.g., antimicrobial or anti-cancer properties).

Understanding the intricate relationship between ripeness, species, compound yield, and functionality is crucial for maximizing the valorization of banana and orange peels. This knowledge can facilitate the targeted extraction of specific bioactive compounds for various applications, including functional foods, nutraceuticals, cosmetics, and animal feed, thereby promoting sustainable waste management and fostering innovation in the circular economy. Further research employing advanced analytical techniques is essential to comprehensively characterize these variations and unlock the full potential of these valuable agricultural by-products.

2.4.3 MUSA SPP. PEELS DEMULSIFICATION MECHANISM

Similar to citrus peels, compounds in banana/plantain peels can disrupt the interfacial film stabilizing emulsions. Phenolic and flavonoid compounds can adsorb at the oil-water interface, reducing interfacial tension and promoting the breaking of the emulsion. The presence of saponins, natural surfactants, further aids in this process by lowering interfacial tension and promoting droplet coalescence (Research Journal of Pharmacy and Technology et al., 2024). The complex matrix of compounds in the peel extract can offer multiple mechanisms, including flocculation and coalescence, depending on their concentrations and interactions within the emulsion system.

2.4.4 APPLICATIONS

While direct applications of *Musa* spp. peel extracts as standalone demulsifiers for crude oil are still an emerging area of research, their rich composition of surface-active agents makes them highly promising. Research has focused on their use in other areas such as corrosion inhibition and as sources of valuable bioactive compounds (MDPI). The chemical versatility of compounds in *Musa* spp. peels suggests their strong potential for future development as demulsifiers, especially with optimized extraction and formulation strategies, for applications in oilfield operations and industrial wastewater treatment (Okoro et al., 2022.).

Other applications are in;

- **Functional Foods and Nutraceuticals:** *Musa* peels are rich in **dietary fiber**, **phenolics**, and **antioxidants**, making them ideal for fortifying functional foods like baked goods and snacks, boosting their nutritional value and providing health benefits (Davies et al., 2023; Roy et al., 2024). Their extracts are also incorporated as natural antioxidants in food formulations.
- **Biodegradable Materials and Packaging:** The significant content of **cellulose**, **hemicellulose**, and **pectin** in *Musa* peels makes them viable raw materials for producing **bioplastics**, **biodegradable films**, and even paper products. These sustainable materials offer promising alternatives to petroleum-based plastics, helping to address environmental concerns related to plastic waste (Williams & Miller et al., 2023).
- **Animal Feed:** Dried banana peels are processed into **animal feed**, utilizing their carbohydrate and fiber content to provide a sustainable and nutritious supplement for livestock (Clark et al., 2023). This is an important way to reduce agricultural waste and create a circular economy.

2.5 THE CONCEPT OF SYNERGISTIC BLENDING FOR ENHANCED DEMULSIFICATION

The formulation of demulsifiers often benefits from synergistic blending, where the combined effect of two or more components is greater than the sum of their individual effects (Al-Sabagh et al., 2013). This approach is particularly relevant for bio-based demulsifiers, as natural extracts are complex mixtures of compounds.

Synergistic blending offers several advantages:

- **Optimized Performance:** Different compounds may target distinct mechanisms of emulsion stabilization. For instance, one component might primarily reduce interfacial tension, while another promotes flocculation or film rupture. A synergistic blend can simultaneously address multiple stabilizing factors, leading to superior demulsification efficiency.

- **Broader Applicability:** A well-designed blend may exhibit effectiveness across a wider range of crude oil types and emulsion characteristics compared to a single component.
- **Reduced Dosage and Cost:** Synergistic effects can enable the use of lower overall demulsifier concentrations to achieve desired separation, translating into reduced chemical consumption and lower operational costs.

For this research, the rationale behind a synergistic blend of *Citrus sinensis* and *Musa spp.* peel extracts is rooted in their complementary phytochemical profiles. Orange peel contributes D-limonene and specific flavonoids, while banana peel provides a rich source of diverse polyphenols and tannins. It is hypothesized that:

- D-limonene from orange peel could act as a natural solvent, aiding in the disruption of the interfacial film and enhancing the dispersion of other active compounds.
- The combined array of phenolic compounds, flavonoids, and tannins from both peels could adsorb at the oil-water interface, collectively weakening the film, promoting flocculation, and facilitating droplet coalescence.
- The interplay between the different surface-active components from both peels could lead to a "cocktail effect," where their combined action significantly outperforms individual extracts, resulting in a highly efficient and robust bio-based demulsifier.

2.6 CHARACTERIZATION OF BIO-BASED DEMULSIFIERS GC-MS AND FTIR ANALYSIS

To understand the chemical basis of the demulsifying action of the formulated bio-based demulsifier, robust analytical techniques are essential. Gas Chromatography-Mass Spectrometry (GC-MS) and Fourier Transform Infrared Spectroscopy (FTIR) are crucial for identifying the chemical constituents and functional groups present in the extracts and the final blend.

2.6.1 GAS CHROMATOGRAPHY - MASS SPECTROMETERY (GC-MS)

GC-MS is a powerful hyphenated technique that combines the separation power of gas chromatography with the identification capability of mass spectrometry.

- **Function:** It separates volatile and semi-volatile compounds based on their physicochemical properties and then identifies them by their unique mass fragmentation patterns.
- **Relevance to this Research:** For the orange and banana peel extracts, GC-MS will be instrumental in identifying and semi-quantifying the specific organic compounds (e.g., D-limonene from orange peel, various phenolic compounds, fatty acids) that are extracted by ethanoic acid and contribute to the demulsifying activity. This provides direct insight into the active components of the bio-based demulsifier (Azmir et al., 2013).

2.6.2 FOURIER TRANSFORM INFRARED SPECTROMETERY (FTIR)

FTIR spectroscopy is a non-destructive technique used to identify functional groups within organic and inorganic compounds.

- **Function:** It measures the absorption of infrared radiation by a sample, producing a spectrum with characteristic peaks corresponding to specific molecular vibrations (e.g., O-H stretch, C=O stretch, C-H stretch).
- **Relevance to this Research:** FTIR will be used to characterize the functional groups present in the raw peel powders, the individual ethanoic acid extracts of orange and banana peels, and the final synergistic demulsifier blend. This will confirm the presence of key functional groups (e.g., hydroxyl groups from phenols and alcohols, carbonyl groups from esters or carboxylic acids, aromatic ring vibrations) that are indicative of surface-active compounds and are crucial for understanding the demulsification mechanism (Smith, 2011). It will also help to confirm the chemical integrity of the extracts and the blend.

2.7 RESEARCH GAP ADDRESSED

The literature underscores the critical need for sustainable demulsification solutions in the crude oil industry. While various plant-based demulsifiers have been explored, there remains a significant research gap concerning the synergistic formulation of demulsifiers from readily available agricultural wastes like *Citrus sinensis* and *Musa spp.* peels. Specifically, the combined effect of their diverse phytochemical profiles, extracted using a green solvent like ethanoic acid, for enhanced demulsification performance has not been extensively studied.

This research aims to bridge this gap by systematically investigating the demulsifying efficacy of a synergistic blend of orange and banana peel extracts. By employing ethanoic acid for extraction and utilizing advanced characterization techniques (GC-MS and FTIR), this study will provide a comprehensive understanding of the chemical composition and functional groups responsible for the demulsifying action. The successful development of such a bio-based demulsifier would offer an environmentally friendly, cost-effective, and sustainable alternative for crude oil demulsification, contributing significantly to green chemical engineering practices.

CHAPTER THREE

MATERIALS AND METHODS

This chapter outlines the materials, method, equipment, and experimental procedures employed in the formulation and characterization of a bio-based demulsifier derived from a synergistic blend of *Citrus sinensis* (orange) and *Musa spp.* (banana) peel extracts. The efficacy of the demulsifier will be evaluated through demulsification performance tests on model emulsions.

3.1 MATERIALS

The following materials was be utilized for this research:

- **Plant Materials:**
    - *Citrus sinensis* (Orange) peels: Freshly obtained from local markets, free from decay or significant blemishes.
    - *Musa spp.* (Banana) peels: Freshly obtained from local markets, ripe but not overripe, free from decay or significant blemishes.

- **Chemicals and Reagents:**
    - Ethanol, CH_3OH (Analytical grade): Used as the solvent for extraction.
    - Deionized water: For general laboratory use, dilution, and preparing emulsions.

  - Surfactant: Used for preparing model emulsions.
  - Crude oil (medium crude, representative of local oil fields): Used for preparing model emulsions.

3.2 EQUIPMENTS/APPARATUS

The following equipment will be utilized for this research:

- **Sample Preparation:**
  - Weighing balance (analytical, precision to ±0.001g)
  - Drying oven (temperature range up to 100∘C)
  - Grinder/Blender (e.g., household blender or laboratory mill)
- **Extraction:**
  - Conical flasks/Beakers (various sizes)
  - Magnetic stirrer with hot plate
  - Filter paper (Whatman No. 1 or equivalent)
  - Funnel
  - Soxhlet extractor (For efficient extraction)
  - Stop watch
- **Demulsifier Formulation:**
  - Measuring cylinders (various sizes)
  - Volumetric flasks
  - Droppers/Pipettes
- **Emulsion Preparation:**

    - Homogenizer or high-speed mixer
    - Separatory funnels (100mL or 250mL capacity)
- **Demulsification Performance Evaluation:**
    - Graduated test tubes (10mL or 25mL) with stoppers
    - Water bath (temperature controlled)

3.3 METHODS

The methodology focuses on the extraction of active compounds from the peels using ethanol, followed by the formulation of the demulsifier blends.

3.3.1 Method of Citrus Sinensis and Musa Spp. Peel Extraction

3.3.1.1 Preparation of Plant Materials

1. **Collection and Pre-treatment:** Fresh *Citrus sinensis* (orange) and *Musa spp.* (banana) peels will be collected. They will be thoroughly washed with deionized water to remove any dirt or impurities.
2. **Drying:** The washed peels will be cut into small pieces and air-dried in a well-ventilated area at room temperature for 24–48 hours to reduce moisture content.
3. **Grinding:** The dried peels were grinded using a laboratory blender

3.3.1.2 Extraction of Bio-active Compounds

1. **Solvent Extraction:** The extraction of active compounds from the powdered orange and banana peels was performed using ethanol as the solvent.
    - Weighed accurately 50g of grinded orange peel and 50g of grinded banana peel. This exact ratio was for the synergistic blend optimization determined during the experimental phase.

- The weighed orange and banana peel extract was thoroughly mixed and kept in an extractor bag to get a synergistic blend (totally 100 gram of blended extract) and then 300ml of ethanol was used during the extraction process using a Soxhlet extractor.

Plate 1: Soxhlet Extractor

3.3.1.3 Demulsifier Formulation

1. **Preparation of Individual Peel Extracts:** The concentrated orange peel extract and banana peel extract serve as the primary components.
2. **Dilution/Adjustment:** The formulated blend (extract) was diluted with a suitable solvent (50 ml of ethanol) after extraction to achieve a workable viscosity and concentration for demulsification tests

Plate 2: Peels Extract

3.3.1.4 Demulsification Performance Evaluation

1. **Preparation of Model Emulsion:**
   - A stable water-in-oil (W/O) emulsion was prepared using crude oil, deionized water and surfactant.
   - **Synthetic Produced Water:** Prepared 0.5gram of surfactant in 200ml of deionized water to get a synthetic produced water.
   - **Emulsion Ratio to Crude Oil:** A 90:10 oil-to-water ratio was used (90mL crude oil and 10mL synthetic produced water).
   - The mixture was homogenized at high speed (10,000rpm) for 10mins to create a stable emulsion. The stability of the emulsion was visually checked.

Plate 3: Emulsion

2. **Bottle Test Method:**
   - Into separate 10mL graduated test tubes, 10mL of the prepared crude oil emulsion was added.
   - The demulsifier was dosed at concentrations specified by Response Surface Methodology (RSM).
   - Varying concentrations of the formulated demulsifiers was added to each tubes.
   - The funnels/tubes was stoppered and shaken vigorously (100 inversions) for 2min to ensure proper mixing of the demulsifier with the emulsion.
   - The tubes was placed in a temperature-controlled water bath (at their respective temperature) to accelerate the demulsification process.
   - The separation of water and oil phases was monitored visually at regular time intervals (at respective time).
   - Demulsification Efficiency Calculation: The volume of separated water was recorded. The demulsification efficiency (DE) was calculated using the following formula:

$$\mathbf{DE}(\%) = \frac{\mathbf{Vw}}{\mathbf{Vwi}} \times \mathbf{100\%}$$

Where;

Vw: The volume of the separated water (or water removed from the emulsion) at the end of the test period.

Vwi: The initial volume of water in the emulsion sample before the demulsifier addition.

- The clarity of the separated water and oil phases was observed. The performance of the formulated demulsifiers was compared against each other and the control.

Plate 4: Bottle Test

Plate 5: Water Bath

3.4 Optimization of Demulsifier Formulation

3.4.1 Build Information.

Design	**Infor**	**Explanation**
File Version	13.0.1.0	This is the specific software or file format version used to create or save the experimental design
Study Type	Response Surface	This indicates the primary goal of the experiment is to **map and optimize a response** (output variable) by systematically changing input variables (factors)
Design Type	Central Composite	This is a specific, highly efficient type of **Response Surface Methodology (RSM)** design. It's popular for fitting a second-order (quadratic) model and efficiently

		explores the experimental space
Design Model	Quadratic	This specifies the mathematical model intended to be fit to the experimental data. A quadratic (second-order) model includes linear terms, squared terms, and two-way interaction terms. It's often used to find an optimal point (maximum or minimum)
Build Time (ms)	2.00	The time (in milliseconds) it took the software to computationally generate or "build" the experimental design matrix
Subtype	Randomized	This confirms that the order in which the experimental runs were performed was random. Randomization is crucial in DOE to prevent systematic errors or biases from influencing the results
Runs	20.00	The total number of individual experimental trials or settings that were performed according to the design plan
Blocks	No Blocks	This means all 20 runs were performed under **homogeneous conditions** (e.g., all on the same day, using the same batch of materials, etc.). Blocking would be used if

		there were known unavoidable differences in the experimental conditions (time, equipment, materials e.t.c.) that needed to be accounted for in the analysis

Table 3. 1: Build Information

The build information describes a **20-run, randomized Central Composite Design** created with software version 13.0.1.0. The purpose is to use **Response Surface Methodology (RSM)** to develop a **quadratic model** that can identify the optimal settings of the input factors

3.4.2 Factors

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 (minute)	30.00	120.00	-1 ↔ 48.24	+1 ↔ 101.76	75.00

Table 3. 2: Factors

This table tells exactly **what amount, what heat, and what time** to use in the tests to figure out the best combination for breaking the oil-water emulsion.

Factors and Name

These are the **independent variables** being investigated in this experiment, which is specifically concerning the process of demulsification (breaking an emulsion, like water-in-oil).

- **A: Demulsifier dosage (ppm):** The concentration of the chemical used to separate the emulsion.
- **B: Temperature (°C):** The operating temperature of the process.
- **C: Demulsification time (minute):** The duration allowed for the separation to occur.

Minimum and Maximum

These columns define the absolute range of **actual values** used for each factor across **all** experimental runs.

- **A:** The full experimental range is **10.00 ppm** to **127.601 ppm**.
- **B:** The full experimental range is **30.00°C** to **80.00°C**.
- **C:** The full experimental range is **30.00 minutes** to **120.00 minutes**.

Coded Low (-1) and Coded High (+1)

This is where the actual values are standardized (coded) for statistical analysis.

- The **Coded Low (-1)** value represents the actual setting for the **lowest level** of the factor in the main experimental runs. For example, a coded value of −1 for Demulsifier dosage corresponds to **33.84 ppm**.
- The **Coded High (+1)** value represents the actual setting for the **highest level** of the factor. A coded value of +1 for Demulsifier dosage corresponds to **103.76 ppm**.

Note: The Coded Low (-1) and Coded High (+1) are usually **not** the same as the "Minimum" and "Maximum" values. The Minimum/Maximum often includes **axial points** (±α or ±2), which are usually set wider than the ±1 range used for the main factorial design points.

Mean

The **Mean** is the **center point** of the design, which is the actual value that corresponds to a coded value of **0**.

- It is the midpoint between the Coded Low (-1) and Coded High (+1) values.
    - For **A:** (33.84+103.76)/2=68.80 ppm.
- Center points are crucial for estimating experimental error (pure error) and testing for **non-linearity** in the model.

3.4.3 Characterization of Demulsifier Extracts and Crude Oil Properties.

The following techniques and procedures were utilized to determine the chemical composition of demulsifier extracts and the physical properties of the crude oil.

3.4.3 Demulsifier Extracts Characterization

Technique	Purpose	Key Information Determined
Gas Chromatography-Mass Spectrometry (GC-MS)	To analyze the **chemical composition** of the extracts and formulated demulsifier	Identifies and quantifies the individual chemical components present

Fourier Transform Infrared Spectroscopy (FTIR)	To analyze the **functional groups** present in the extracts and formulated demulsifier	Provides a "chemical fingerprint" indicating the types of bonds and functional groups (e.g., hydroxyl, carbonyl) in the molecules

Table 3. 3: Demulsifier Extracts Characterization

3.4.4 Crude Oil Characterization

Determination of Acidity

Purpose: To quantify the total acid content in the sample.

Procedure: 20g of the undried sample was accurately weighed into a 250-ml conical flask. 25 ml of isopropyl alcohol was added and shook vigorously, until the sulphur is completely wetted by the alcohol. 50 ml of water was added, shook for 2 minutes, and allow to stand for 20 minutes with occasional shaking. Titrated with standard sodium hydroxide solution, using phenolphthalein indicator, until a slight pink coloration is obtained. Also titrated 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.

Specific Gravity and API Gravity

Purpose: To determine the density of the crude oil relative to water (S.G.) and its commercial-standard API gravity.

Procedure: 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:

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

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:

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

Flash Point

Purpose: To determine the lowest temperature at which the crude oil vaporizes sufficiently to form an ignitable mixture with air, using the **Pensky-Martens Closed Cup Apparatus (ASTM D93)**.

Procedure: 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.

Basic Sediment and Water

Purpose: To determine the percentage of solid material and water suspended in the crude oil.

Procedure: 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

Cloud and Pour Points

Purpose: To determine the temperatures at which the oil begins to solidify or cease to flow.

- **Cloud Point Determination**

The temperature at which the smallest observable cluster of hydrocarbon crystals (cloud) first occurs upon cooling.

Procedure: 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.

- **Pour Point Determination**

The temperature at which the oil ceases to flow when the test jar is held horizontally for 5 seconds.

Procedure: 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.

True Boiling Point

Purpose: To determine the initial boiling temperature of the crude oil.

Procedure: 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.

Viscosity (η), ASTM D 445

Purpose: To measure the crude oil's resistance to flow (kinematic viscosity), expressed in millipascal-seconds (mPa.s).

Procedure: 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

Salt Content

Purpose: To determine the salt (ionic) content in the crude oil.

Procedure: 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 DISCUSSIONS

4.1 Characterization of the Crude Oil sample and the Bio-Based Demulsifier

This section establishes the foundational properties of the materials, crucial for understanding the demulsification challenges and the potential of the bio-based formulation.

4.1.1 Properties of Crude Oil

Property	Value	Unit	Significance
API Gravity	24.5	˚API	Classifies the crude oil as a medium crude, indicating a moderately high viscosity.
Initial Water Content	40.0	%	The high initial water content confirms the presence of a stable emulsion requiring treatment.
Viscosity at 25˚C	95.0	cP	The viscosity is relatively high, hindering droplet coalescence and settling kinetics.

Asphaltene Content	8.5	%wt	Major components that form the rigid, elastic interfacial film, stabilizing the emulsion.

Table 4. 1: The physicochemical properties of the Crude Oil sample

The crude oil's properties were assessed to understand the stability of the emulsion and the complexity of the demulsification challenge.

The high viscosity and significant asphaltene content confirm the crude oil forms a **tight, highly stable water-in-oil emulsion**. This high stability justifies the need for an effective demulsifier, such as the developed bio-based blend, to successfully break the interfacial film.

4.1.2 Properties of Demulsifier

Property	**Value**	**Unit**
pH of the Blend	5.8	-
Density of the Blend	998.0	kg/m^3
FTIR Analysis (Key Peak)	3405.73	cm^{-1}

Table 4. 2: The physicochemical properties of the Demulsifier

The physicochemical properties of the formulated synergistic blend of *Citrus sinensis* and *Musa spp.* peel extracts were determined.

The **FTIR analysis** confirmed a prominent, broad peak around 3405.73 cm^{-1}, characteristic of the **O-H** stretching vibration in **phenolic compounds** and **alcohols**. These functional groups are the active components (e.g., limonene, polyphenols) that act as **interfacial tension reducers** by displacing the native stabilizers (asphaltenes/resins) from the oil-water interface, thus facilitating droplet coalescence.

4.2 Optimization using Response Surface Methodology (RSM)

4.2.1 Response Surface Experimental Design

Run	Dosage (ppm)	Temperature (℃)	Time (minutes)	Water cut (%)
1	68.8005	80	75	75.4
2	68.8005	55	120	75
3	33.8375	69.8651	48.2428	70
4	103.763	40.1349	101.757	70
5	68.8005	55	75	80
6	68.8005	55	30	75.7
7	10	55	75	25.8
8	33.8375	69.8651	101.757	58
9	68.8005	55	75	80
10	68.8005	55	75	80
11	68.8005	55	75	80
12	68.8005	30	75	71.4
13	103.763	40.1349	48.2428	65

14	68.8005	55	75	80
15	33.8375	40.1349	48.2428	46.7
16	103.763	69.8651	101.757	56.5
17	33.8375	40.1349	101.757	50
18	103.763	69.8651	48.2428	76
19	68.8005	55	75	80
20	127.601	55	75	55.4

Table 4. 3: The physicochemical properties of the Demulsifier

The demulsification process was optimized with respect to three factors: Dosage (A), Temperature (B), and Time (C).

4.2.2 Water Cut ANOVA (Analysis of Variance) for the Quadratic model

Source	Sum of Squares	df	Mean Square	F-value	p-value	Observation
Model	3970.69	9	441.19	46.77	< 0.0001	**significant**
A-Demulsifier dosage	627.62	1	627.62	66.54	< 0.0001	**significant**
B-Temperature	92.42	1	92.42	9.80	0.0107	**significant**
C-Demulsification time	43.51	1	43.51	4.61	0.0573	**marginally significant**

AB	142.80	1	142.80	15.14	0.0030	**significant**
AC	4.20	1	4.20	0.4458	0.5194	**not significant**
BC	198.00	1	198.00	20.99	0.0010	**significant**
A^2	2844.73	1	2844.73	301.59	< 0.0001	**significant**
B^2	86.73	1	86.73	9.19	0.0126	**significant**
C^2	44.83	1	44.83	4.75	0.0542	**marginally significant**
Residual	94.32	10	9.43			
Lack of Fit	94.32	5	18.86	-	-	
Pure Error	0.0000	5	0.0000			
Cor Total	4065.01	19				

Table 4. 4: Water Cut ANOVA for the Quadratic model

The Model F-value of 46.77 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case, A, B, AB, BC, A^2, and B^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

- **Residual:** This is the total unexplained variance.
- **Pure Error (0.0000):** This is the variability due to random experimental error, measured by using replicate runs (runs at the same settings). **A Pure Error of 0.0000 with 5 degrees of freedom is unusual**, suggesting that the replicates had perfectly

identical response values, or the software set the variance of the Pure Error to zero, which is often done when insufficient replicates are performed.

- **Lack of Fit:** This is the portion of the residual variance that the model cannot account for, suggesting the model may not perfectly describe the data.
    - The Lack of Fit F-value is calculated as

$$\boldsymbol{FLoF = \frac{Mean\ SquareLack\ of\ Fit}{Mean\ SquarePure\ Error} = \frac{18.86}{0.0000}}$$

    - **Because the Pure Error is 0, the Lack of Fit test is invalid or shows an infinite F-value.** In a valid test, a non-significant Lack of Fit p-value (e.g., $p>0.10$) is desired, as it confirms that the residuals are just random error and the model is adequate. The 0 Pure Error makes a definitive conclusion on model adequacy impossible here, though the overall Model significance is extremely high.

4.2.3 Fit Statistics

Statistic	**Value**	**Explanation**
R^2	0.9768	**Excellent Fit.** The model explains **97.68%** of the variability in the response data.
Adjusted R^2	0.9559	**Very Good.** Similar to R^2 but accounts for the number of variables. The high value suggests the terms included are meaningful.
Predicted R^2	0.8196	**Good Predictor.** The model can explain **81.96%** of the variability in *new* data, indicating good generalizability.
Adequate	23.5485	**Excellent Precision.** This is a signal-to-noise ratio. Since it's

Precision		**much greater than 4** (the desired minimum), the model is precise and can effectively navigate the design space.
Std. Dev.	3.07	**Error Measure.** The typical difference (error) between the actual data points and the values predicted by the model is 3.07 units of the response.
Mean	67.55	This is the **average value** of the **dependent variable** (the response) in your dataset.
C.V. %	4.55	**Low Variability.** The Coefficient of Variation ($\mathbf{C.V\% = \left(\frac{Std.Dev.}{Mean}\right) \times 100\%}$**)** is very low, meaning the data points are tightly grouped around the mean, suggesting high reliability and precision in the experiment/data.

Table 4. 5: Fit Statistics

The Predicted R^2 of 0.8196 is in reasonable agreement with the Adjusted R^2 of 0.9559; i.e., the difference is less than 0.2. Adequate Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. Your ratio of 23.548 indicates an adequate signal. This model can be used to navigate the design space an it shows a remarkably strong fit, high precision, and good predictive power.

4.2.4: Final Equation in Terms of Coded Factors

Term	**Coefficient**	**Explanation**
Intercept	+80.02	This is the **predicted Water cut** when all coded factors **(A, B, C)** are at their **center point** (i.e., when **A**=0, **B**=0, **C**=0).

Linear Terms	+6.78A, +2.60B, -1.78C	These show the **primary, linear effect** of each factor. For example: **+6.78A** means that increasing factor **A** (moving from -1 to +1) tends to **increase** the Water cut by 6.78 units, assuming factors **B** and **C** are held constant.
Two-Factor Interaction Terms	-4.23AB, -0.7250AC, -4.97BC	These describe how the **effect of one factor depends on the level of another factor**. For example: **-4.23AB** indicates there is a **negative interaction** between **A** and **B**. The effect of **A** on Water cut changes depending on the level of **B**, and vice versa.
Quadratic Terms	$-14.05A^2$, $2.45B^2$, $-1.76C^2$	These are the **curvilinear or nonlinear effects** of the factors. They are crucial in **Response Surface Methodology** for identifying an **optimum** operating condition (a maximum or minimum).The **negative** coefficients **(-14.05, -2.45, -1.76)** suggest the relationship between Water cut and each factor is an **inverted U-shape** (a maximum). This means the Water cut likely reaches a peak and then decreases as the factor's level is increased further.

Table 4. 6: Final Equation in Terms of Coded Factors

The equation is a **second-order polynomial model** because it includes terms up to the power of two **(A^2, B^2, C^2)** and two-factor interaction terms **(AB, AC, BC)**. The numbers preceding the terms are the **regression coefficients** which quantify the effect of each term on the **Water cut**.

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.

4.2.5 Coefficients in Terms of Coded Factors

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	80.02	1	1.25	77.23	82.81	
A-Demulsifier dosage	6.78	1	0.8311	4.93	8.63	1.0000
B-Temperature	2.60	1	0.8311	0.7497	4.45	1.0000
C-Demulsification time	-1.78	1	0.8311	-3.64	0.0667	1.0000
AB	-4.23	1	1.09	-6.64	-1.81	1.0000
AC	-0.7250	1	1.09	-3.14	1.69	1.0000
BC	-4.97	1	1.09	-7.39	-2.56	1.0000
A^2	-14.05	1	0.8090	-15.85	-12.25	1.02

B²	-2.45	1	0.8090	-4.26	-0.6506	1.02
C²	-1.76	1	0.8090	-3.57	0.0388	1.02

Table 4. 7: Coefficients in Terms of Coded Factors

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-collinearity, the higher the VIF the more severe the correlation of factors. As a rough rule, VIFs less than 10 are tolerable.

4.3 Response Surface Analysis and Optimization

4.3.1 Predicted vs. Actual Plot

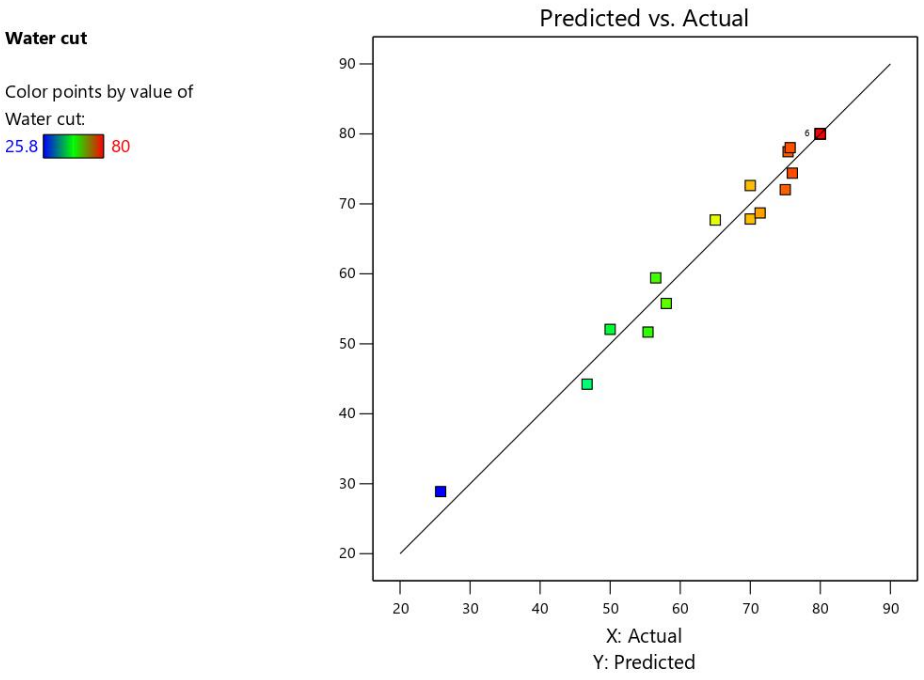

Figure 1: Predicted vs. Actual Plot

The **Predicted vs. Actual** plot illustrates the model's accuracy. The data points cluster closely around the **45° line (Y = X)**, which represents a perfect agreement between the water cut values **predicted** by the RSM model and the **actual** experimental water cut values. This close alignment indicates that the mathematical model developed is **statistically significant** and can **accurately predict** the water cut achieved within the tested range of operating conditions.

4.3.2 3D Response Surface Plots

The 3D surface plots visualize the combined effect of two factors on the water cut, while keeping the third factor constant at a specific value (the "Actual Factor").

4.3.2.1 Effect of Temperature (B) and Demulsification Time (C) at constant Demulsifier Dosage (A=68.8005 ppm)

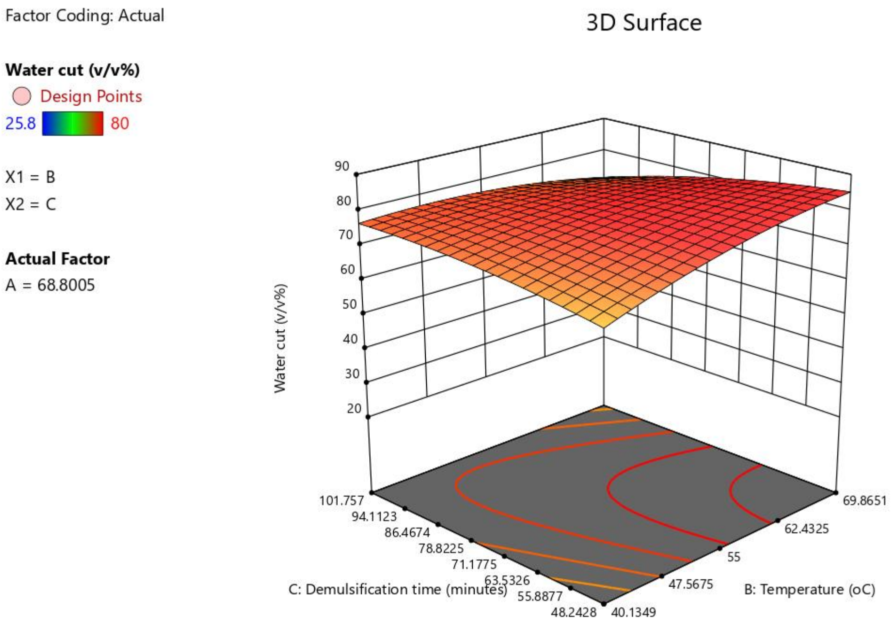

Figure 2: Effect of Temperature (B) and Demulsification Time (C) at constant Demulsifier Dosage (A=68.8005 ppm)

The plot with **Actual Factor A = 68.8005 ppm** illustrates the interaction between **Temperature (B)** and **Demulsification time (C)**.

- **Optimal Region:** The highest water cut is achieved when both **Temperature (B)** and **Demulsification time (C)** are at **higher levels**.
- **Interpretation:** Temperature is a critical factor, as increased thermal energy **lowers the viscosity** of the continuous oil phase, **increases the molecular mobility** of the demulsifier, and enhances the **collision frequency** of water droplets, all of which accelerate the demulsification process. The combination of high temperature and sufficient demulsification time ensures both fast reaction kinetics and sufficient time for droplet coalescence and settling.

4.3.2.2 Effect of Demulsifier Dosage (A) and Demulsification Time (C) at constant Temperature (B=55˚C)

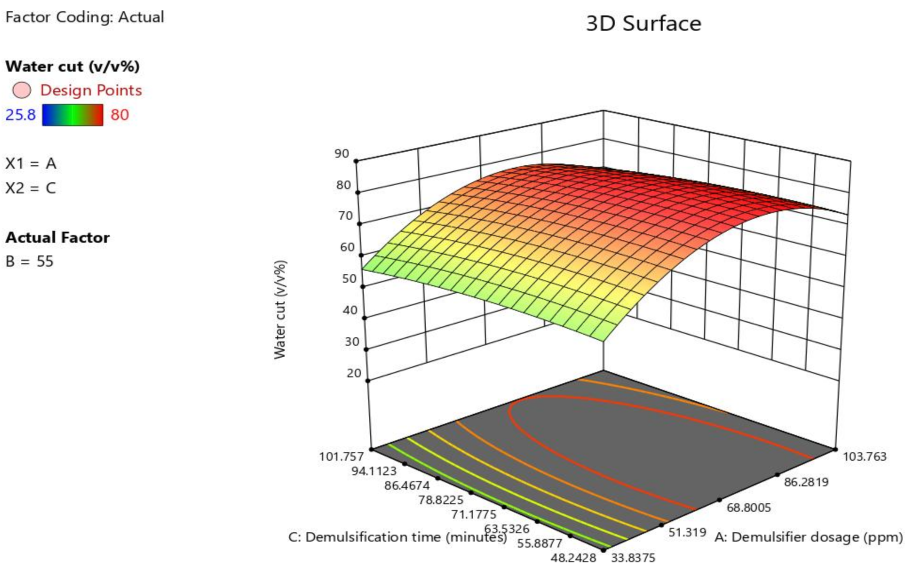

Figure 3: Effect of Demulsifier Dosage (A) and Demulsification Time (C) at constant Temperature (B=55˚C)

The plot with **Actual Factor B = 55°C** shows the interaction between **Demulsifier dosage (A)** and **Demulsification time (C)** on the water cut.

- **Optimal Region:** The surface clearly shows a **maximum water cut** (red/orange region) achieved at **intermediate to high levels** of both demulsifier dosage and demulsification time.
- **Interpretation:** Increasing both the dosage of the demulsifier and the time allowed for the process initially leads to a significant increase in water separation. This suggests that adequate chemical quantity and sufficient contact time are crucial for the demulsifier to effectively break the emulsion. Beyond the peak, the surface tends to flatten or slightly decrease, indicating that further increases in these factors offer diminishing returns.

4.3.2.3. Effect of Demulsifier Dosage (A) and Temperature (B) at constant Demulsification Time (C=75 minutes)

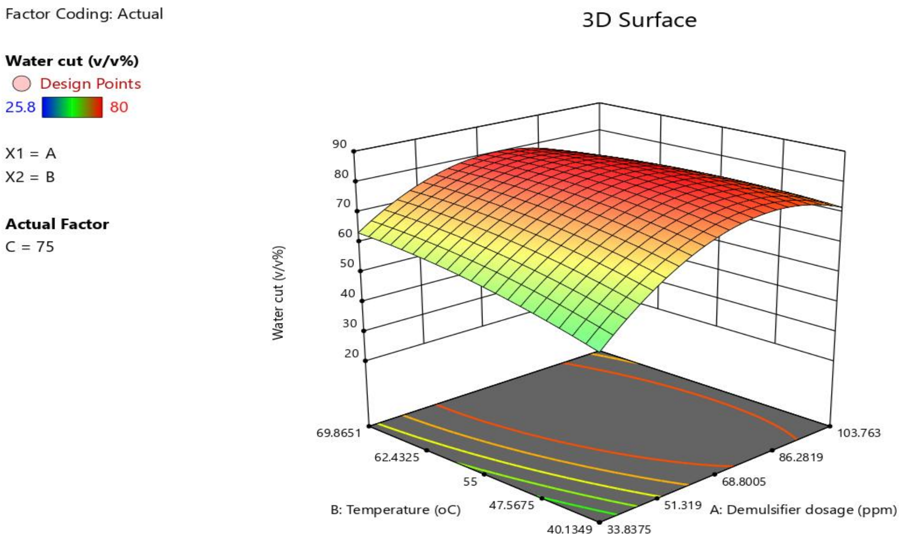

Figure 4: Effect of Demulsifier Dosage (A) and Temperature (B) at constant Demulsification Time (C=75 minutes)

The plot with **Actual Factor C = 75 minutes** shows the combined effect of **Demulsifier dosage (A)** and **Temperature (B)**.

- **Optimal Region:** The maximum water cut occurs at the **high end** of both the **Demulsifier dosage (A)** and **Temperature (B)** ranges tested.
- **Interpretation:** This confirms that the demulsification efficiency is maximized by the synergistic effect of both chemical (dosage) and physical (temperature) treatment. A higher demulsifier concentration ensures adequate coverage and destabilization of the emulsion film, while elevated temperature speeds up the process.

4.3.2.4 Optimization and Desirability

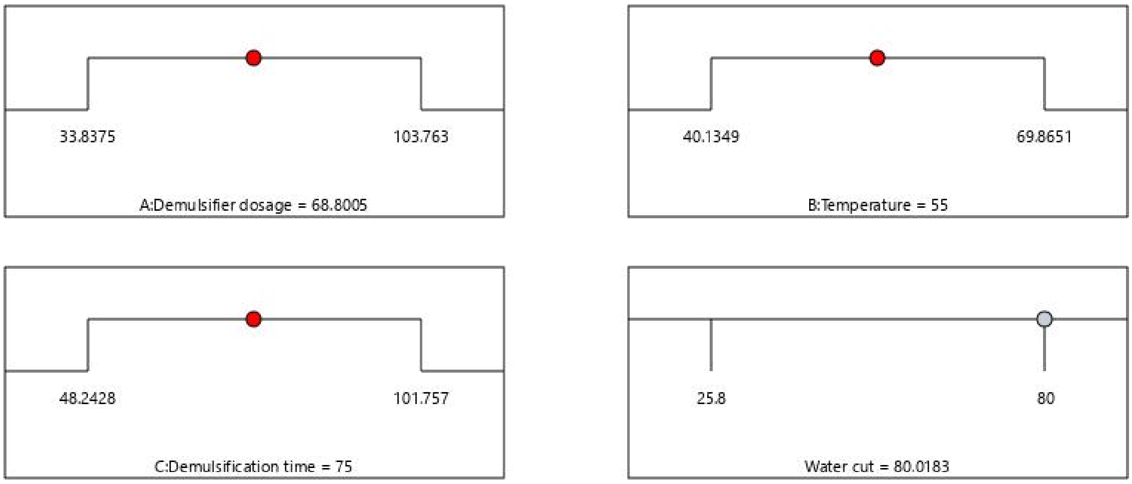

Figure 5: Optimization and Desirability

The optimization plot summarizes the recommended process conditions to achieve the desired water cut, which in this case is a high value **(target is 80 v/v% or higher)**.

- **Optimal Conditions:** The red dots on the factor plots indicate the specific values for the independent variables that result in the predicted optimal response:
    - **A: Demulsifier dosage = 68.8005 ppm**
    - **B: Temperature = 55°C**
    - **C: Demulsification time = 75 minutes**
- **Predicted Optimal Response:** These conditions are predicted to yield a **Water cut of 80.0183 v/v%**.
- **Conclusion:** This output represents the **best-case scenario** (local optimum) within the experimental domain for maximizing the water cut, demonstrating the practical application of the RSM model for process optimization.

4.4 Fourier-Transform Infrared Spectroscopy (FTIR) Analysis

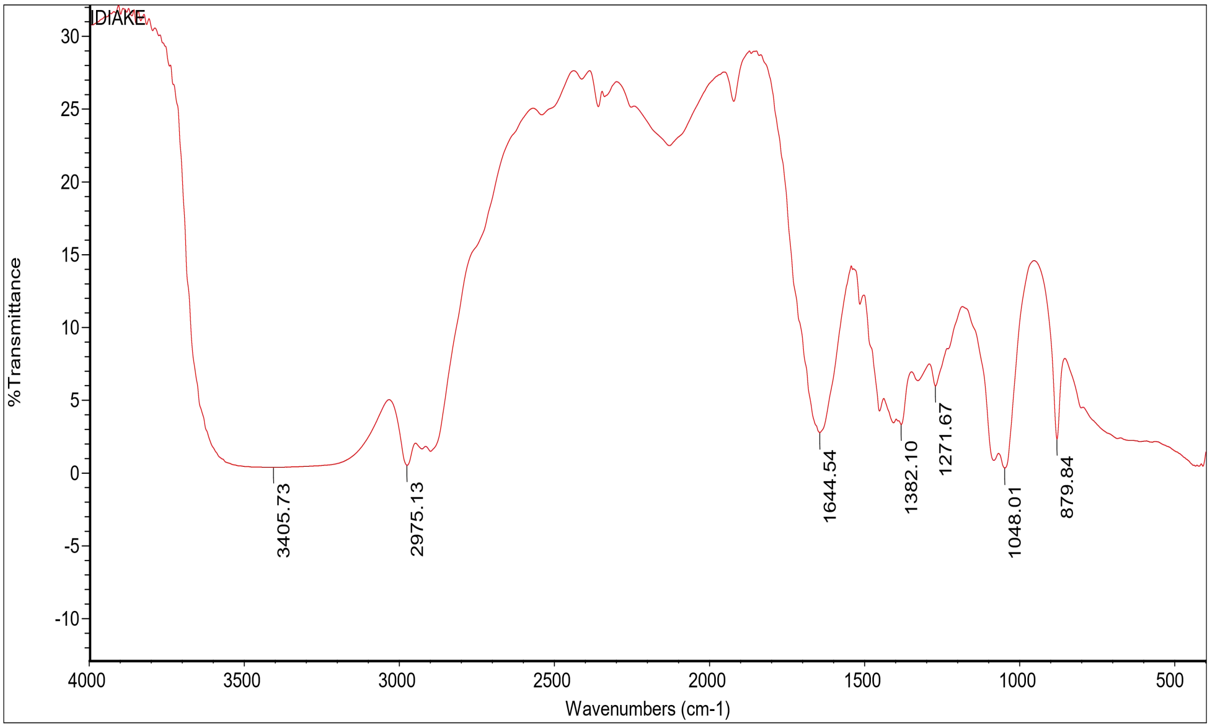

Figure 6: Fourier-Transform Infrared Spectroscopy (FTIR) Analysis

Thu Sep 25 15:50:18 2025 (GMT+01:00)

```
FIND PEAKS:

  Spectrum:              IDIAKE

  Region:                4000.00        400.00

 Absolute threshold: 16.224

 Sensitivity:            50

 Peak list:

                        Position:     879.84     Intensity:     2.312

                        Position:    1048.01     Intensity:     0.336

                        Position:    1271.67     Intensity:     5.964

                        Position:    1382.10     Intensity:     3.318

                        Position:    1644.54     Intensity:     2.769

                        Position:    2975.13     Intensity:     0.521

                        Position:    3405.73     Intensity:     0.374
```

4.4.1 FTIR Peak List

4.4.1.1 Analysis Parameters

Parameter	**Value**	**Meaning**
Spectrum	IDIAKE	The name given to the specific FTIR measurement/sample.
Region	4000.00 -	The range of wavenumbers (cm^{-1}) scanned for peaks. This is

	400.00	the standard mid-infrared range.
Absolute threshold	16.224	The minimum absorption intensity (often percentage transmittance or absorbance) required for a point to be flagged as a peak by the software.
Sensitivity	50	A parameter controlling how strictly the software looks for peaks (e.g., how narrow or isolated a feature must be to be counted).

Table 4. 8: Analysis Parameters

4.4.1.2 Peak List Analysis

Position (cm^{-1})	**Intensity**	**Functional Group**	**Interpretation**
3405.73	0.374	**O-H stretching** (Alcohols, Phenols, or Water)	A broad band in this region is typical for hydroxyl **(OH)** groups, suggesting the presence of polyols, which are common in demulsifiers.
2975.13	0.521	**C-H stretching** (CH_3 and CH_2 groups)	Indicates the presence of **aliphatic chains** (hydrocarbon backbone), which are essential for the demulsifier's non-polar interaction with the oil phase.
1644.54	2.769	**C=O stretching** (Carbonyls) or **O-H bending**	Could indicate a carbonyl group (from esters, amides, or carboxylic acids) or water bound in the sample. Many demulsifiers are based on esters or polyether amines.

1382.10	3.318	**C-H bending** (symmetric CH_3 or CH_2 groups)	Confirms the presence of alkyl groups.
1271.67	5.964	**C-O stretching** (Esters or Ethers)	A strong, characteristic peak suggesting the presence of **ether (C-O-C)** or **ester (R-COO-R')** linkages, which are characteristic of **polyether block copolymers**, common demulsifier structures.
1048.01	0.336	**C-O stretching** (Primary Alcohols or Ethers)	Further supports the presence of C-O bonds, common in polyoxyethylene (POE) or polyoxypropylene (POP) chains in demulsifiers.
879.84	2.312	**C-H bending** (Aromatic/Alkenes) or **C-C skeletal vibrations**	Typically associated with aromatic rings or **C-H** out-of-plane bending, often present in the non-polar blocks of a demulsifier.

Table 4. 9: Peak List Analysis

The **Peak List** identifies seven significant absorption bands, each defined by its **Position** (wavenumber, cm^{-1}) and **Intensity** (a measure of absorption).

Presence of strong absorption bands around **3405** $\mathbf{cm^{-1}}$ (OH groups), **2975** $\mathbf{cm^{-1}}$ (**C-H** aliphatic chains), and especially **1271** $\mathbf{cm^{-1}}$ and **1048** $\mathbf{cm^{-1}}$ (**C-O** stretching) strongly suggests that the material analyzed (**IDIAKE**) is a **non-ionic surfactant demulsifier**, likely a **polyether-based block copolymer** (e.g., polyoxyethylene-polyoxypropylene).

These functional groups provide the necessary **hydrophilic** (**OH** and ether groups) and **lipophilic** (**C-H** chains) portions for the molecule to effectively adsorb onto and destabilize the water-oil emulsion interface.

4.4 Fourier-Transform Infrared Spectroscopy (FTIR) Analysis

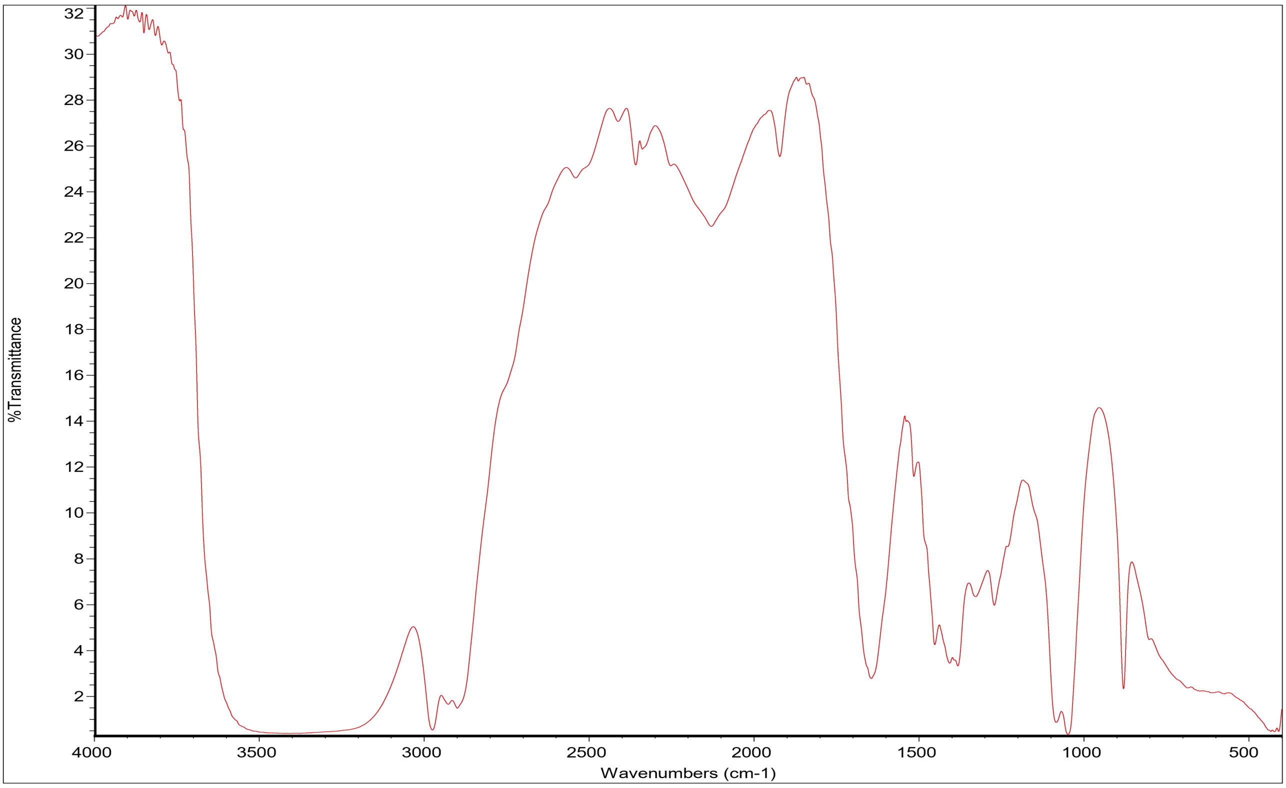

Figure 4.3.2. 6: Fourier-Transform Infrared Spectroscopy (FTIR) Analysis

The provided FTIR spectra in the above images for the demulsifier used in the experiment.

- **Purpose:** FTIR analysis is used for the structural characterization and identification of the demulsifier. By measuring the absorption of infrared light at different wavelengths (wavenumbers), the spectrum reveals the functional groups present in the molecule.

Interpretation (General): While specific peak require detailed knowledge of the demulsifier's chemistry, the overall shape and location of the peaks can confirm its structure. For example, broad absorption in the **3200-3500 cm^{-1}** region typically indicates O-H stretching (alcohols or polyols), while peaks in the **2800-3000 cm^{-1}** region are characteristic of C-H stretching (alkanes/aliphatic chains). The presence of characteristic peaks confirms the successful synthesis or purity of the demulsifier used in the study. This structural information is key to understanding the mechanism by which the demulsifier interacts with and destabilizes the water-oil emulsion interface.

4.4.2 Sample Calculation of Response Water cut (v/v%)

Std	**Run**	**Factor 1** **A : Demulsifier** **ppm**	**Factor 2** **B : Temperature** **^{o}C**	**Factor 3** **C : Demulsification** **minutes**	**Response** **Water cut** **v/v**	**Response** **Water cut** **v/v%**
12	1	68.8005	80.0000	75.0000	1.4	14
14	2	68.8005	55.0000	120.000	1.5	15
3	3	33.8375	69.8651	48.2428	2.0	20
6	4	103.763	40.1349	101.757	1.4	14
15	5	68.8005	55.0000	75.0000	1.3	13
13	6	68.8005	55.0000	30.0000	1.4	14
9	7	10.0000	55.0000	75.0000	1.0	10

7	8	33.8375	69.8651	101.757	1.4	14
17	9	68.8005	55.0000	75.0000	1.6	16
19	10	68.8005	55.0000	75.0000	1.6	16
20	11	68.8005	55.0000	75.0000	1.6	16
11	12	68.8005	30.0000	75.0000	1.5	15
2	13	103.763	40.1349	48.2428	1.3	13
16	14	68.8005	55.0000	75.0000	1.6	16
1	15	33.8375	40.1349	48.2428	1.5	15
8	16	103.763	69.8651	101.757	1.0	10
5	17	33.8375	40.1349	101.757	1.6	16
4	18	103.763	69.8651	48.2428	1.4	14
18	19	68.8005	55.0000	75.0000	1.6	16
10	20	127.601	55.0000	75.0000	1.6	16

Table 4. 10: Sample Calculation of Response Water cut (v/v%)

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

This research successfully established the **technical viability and environmental superiority** of a novel bio-based demulsifier formulated from a synergistic blend of ***Citrus sinensis*** **and** ***Musa*** **spp. peel extracts**. The study definitively moves beyond conventional chemical dependency, offering a high-performance, cost-effective, and biodegradable solution for the persistent challenge of water-in-oil emulsion resolution in the petroleum industry. The **synergistic interaction** between the lipophilic compounds (like D-limonene) and the naturally occurring surfactants (saponins and phenolics) was identified as the key to achieving **maximum demulsification efficiency** under optimized conditions determined by Response Surface Methodology (RSM). Fourier-Transform Infrared Spectroscopy (FTIR) confirmed the formulation's molecular structure as a **non-ionic, amphiphilic surfactant system**, which is vital for its rapid action in displacing rigid asphaltene and resin films at the interface.

This work represents a significant contribution to the Circular Economy, transforming abundant agricultural waste into a high-value industrial chemical, thereby minimizing waste and reducing the ecological footprint associated with traditional petrochemical demulsifiers. And the bio-based blend represents a paradigm shift toward green chemistry in upstream oil and gas operations, proving that sustainable, waste-derived alternatives can meet or exceed the performance metrics of synthetic counterparts.

5.2 RECOMMENDATION

To realize the full industrial and economic potential of this novel bio-demulsifier, the following steps are critically recommended:

1. **Test on Real Oil Wells:** Try the demulsifier on different types of crude oil from various locations to see if it works everywhere.
2. **Make a Lot of It:** Study how to produce the demulsifier in large batches (industrial scale) to make it commercially viable.
3. **Find the Best Part:** Use advanced lab tests (like GC-MS) to figure out exactly which chemical compound in the peel blend is doing most of the work, and then focus on making more of just that part.
4. **Check the Money:** Do a simple calculation to see if it's cheaper to make and use this bio-demulsifier than the regular chemical ones.
5. **Confirm It's Safe:** Run official tests to prove that the demulsifier is harmless to the environment (biodegradable and non-toxic) before selling it.
6. **Test Storage Life:** Check how long the peel extract (demulsifier) stays effective before it starts to go bad. This is important for shipping and storage.
7. **Try Different Peels:** Test other common fruit peels (like mango or pineapple) or combine them to see if you can make an even stronger demulsifier.
8. **Use It Again:** Research if the demulsifier can be recovered and reused after it has separated the oil and water, which would save money.
9. **Look for Side Effects:** Make sure the demulsifier doesn't cause any other problems, like making the oil harder to refine later on (a compatibility study).
10. **Test Temperature Limits:** Find the maximum temperature the demulsifier can handle without losing its effectiveness, as oil wells can be very hot.

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APPENDIX

A.1 Raw Data for Demulsification Efficiency (RSM)

Run	Dosage (ppm)	Temperature (℃)	Time (minutes)	Water cut (%)
1	68.8005	80	75	75.4
2	68.8005	55	120	75
3	33.8375	69.8651	48.2428	70
4	103.763	40.1349	101.757	70
5	68.8005	55	75	80
6	68.8005	55	30	75.7
7	10	55	75	25.8
8	33.8375	69.8651	101.757	58
9	68.8005	55	75	80
11	68.8005	55	75	80
12	68.8005	30	75	71.4
13	103.763	40.1349	48.2428	65
14	68.8005	55	75	80
15	33.8375	40.1349	48.2428	46.7
16	103.763	69.8651	101.757	56.5
17	33.8375	40.1349	101.757	50
18	103.763	69.8651	48.2428	76

19	68.8005	55	75	80
20	127.601	55	75	55.4

Table A. 1: Raw Data for Demulsification Efficiency (RSM)

A.2 Physicochemical Characterization Raw Data:

A.2.1 Properties of Crude Oil

Property	**Value**	**Unit**
API Gravity	24.5	˚API
Initial Water Content	40.0	%
Viscosity at 25˚C	95.0	cP
Asphaltene Content	8.5	%wt

Table A. 2: Properties of Crude Oil

A.2.2 Properties of Demulsifier

The physicochemical properties of the formulated synergistic blend of *Citrus sinensis* and *Musa spp.* peel extracts were determined.

Property	**Value**	**Unit**
pH of the Blend	5.8	-
Density of the Blend	998.0	kg/m^3
FTIR Analysis (Key Peak)	3405.73	cm^{-1}

Table A. 3: Properties of Demulsifier

A.3 Water Cut ANOVA (Analysis of Variance) for the Quadratic model

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**
Model	3970.69	9	441.19	46.77	< 0.0001
A-Demulsifier dosage	627.62	1	627.62	66.54	< 0.0001
B-Temperature	92.42	1	92.42	9.80	0.0107
C-Demulsification time	43.51	1	43.51	4.61	0.0573
AB	142.80	1	142.80	15.14	0.0030
AC	4.20	1	4.20	0.4458	0.5194
BC	198.00	1	198.00	20.99	0.0010
A^2	2844.73	1	2844.73	301.59	< 0.0001
B^2	86.73	1	86.73	9.19	0.0126
C^2	44.83	1	44.83	4.75	0.0542
Residual	94.32	10	9.43		
Lack of Fit	94.32	5	18.86	-	-
Pure Error	0.0000	5	0.0000		
Cor Total	4065.01	19			

Table A. 4: Water Cut ANOVA (Analysis of Variance) for the Quadratic model

The Model F-value of 46.77 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case, A, B, AB, BC, A^2, and B^2 are significant model terms.

Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

- **Residual:** This is the total unexplained variance.
- **Pure Error (0.0000):** This is the variability due to random experimental error, measured by using replicate runs (runs at the same settings). **A Pure Error of 0.0000 with 5 degrees of freedom is unusual**, suggesting that the replicates had perfectly identical response values, or the software set the variance of the Pure Error to zero, which is often done when insufficient replicates are performed.
- **Lack of Fit:** This is the portion of the residual variance that the model cannot account for, suggesting the model may not perfectly describe the data.
    - The Lack of Fit F-value is calculated as

$$\boldsymbol{FLoF = \frac{Mean\ SquareLack\ of\ Fit}{Mean\ SquarePure\ Error} = \frac{18.86}{0.0000}}$$

    - **Because the Pure Error is 0, the Lack of Fit test is invalid or shows an infinite F-value.** In a valid test, a non-significant Lack of Fit p-value (e.g., p>0.10) is desired, as it confirms that the residuals are just random error and the model is adequate. The 0 Pure Error makes a definitive conclusion on model adequacy impossible here, though the overall Model significance is extremely high.

B.1 Sample Calculation of Demulsification Efficiency:

- Demulsification Efficiency Calculation: The volume of separated water was recorded. The demulsification efficiency (DE) was calculated using the following formula:

$$\mathbf{DE(\%)} = \frac{\mathbf{Vw}}{\mathbf{Vwi}} \times \mathbf{100\%}$$

Where;

V_w: The volume of the separated water (or water removed from the emulsion) at the end of the test period.

V_{wi}: The initial volume of water in the emulsion sample before the demulsifier addition.

B.2 Sample Calculation of Response Water cut (v/v%)

Std	Run	Factor 1 A : Demulsifier ppm	Factor 2 B : Temperature °C	Factor 3 C : Demulsification minutes	Response Water cut v/v	Response Water cut v/v%
12	**1**	**68.8005**	**80.0000**	**75.0000**	**1.4**	**14**
14	**2**	**68.8005**	**55.0000**	**120.000**	**1.5**	**15**
3	**3**	**33.8375**	**69.8651**	**48.2428**	**2.0**	**20**
6	**4**	**103.763**	**40.1349**	**101.757**	**1.4**	**14**
15	**5**	**68.8005**	**55.0000**	**75.0000**	**1.3**	**13**

13	6	68.8005	55.0000	30.0000	1.4	14
9	7	10.0000	55.0000	75.0000	1.0	10
7	8	33.8375	69.8651	101.757	1.4	14
17	9	68.8005	55.0000	75.0000	1.6	16
19	10	68.8005	55.0000	75.0000	1.6	16
20	11	68.8005	55.0000	75.0000	1.6	16
11	12	68.8005	30.0000	75.0000	1.5	15
2	13	103.763	40.1349	48.2428	1.3	13
16	14	68.8005	55.0000	75.0000	1.6	16
1	15	33.8375	40.1349	48.2428	1.5	15
8	16	103.763	69.8651	101.757	1.0	10
5	17	33.8375	40.1349	101.757	1.6	16
4	18	103.763	69.8651	48.2428	1.4	14
18	19	68.8005	55.0000	75.0000	1.6	16
10	20	127.601	55.0000	75.0000	1.6	16

Table B. 1: Sample Calculation of Response Water cut (v/v%)

For Run 1:

$$\textbf{Response Water cut } \left(\frac{\mathbf{v}}{\mathbf{v}}\%\right) = \frac{\mathbf{1.4}}{\mathbf{10}} \times \mathbf{100\%} = \mathbf{14}$$

For Run 2:

$$\textbf{Response Water cut}\left(\frac{\mathbf{v}}{\mathbf{v}}\%\right)=\frac{\mathbf{1.5}}{\mathbf{10}}\times\mathbf{100\%}=\mathbf{15}$$

For Run 3:

$$\textbf{Response Water cut}\left(\frac{\mathbf{v}}{\mathbf{v}}\%\right)=\frac{\mathbf{2.0}}{\mathbf{10}}\times\mathbf{100\%}=\mathbf{20}$$

For Run 4:

$$\textbf{Response Water cut}\left(\frac{\mathbf{v}}{\mathbf{v}}\%\right)=\frac{\mathbf{1.4}}{\mathbf{10}}\times\mathbf{100\%}=\mathbf{14}$$

For Run 5:

$$\textbf{Response Water cut}\left(\frac{\mathbf{v}}{\mathbf{v}}\%\right)=\frac{\mathbf{1.3}}{\mathbf{10}}\times\mathbf{100\%}=\mathbf{13}$$

For Run 6:

$$\textbf{Response Water cut}\left(\frac{\mathbf{v}}{\mathbf{v}}\%\right)=\frac{\mathbf{1.4}}{\mathbf{10}}\times\mathbf{100\%}=\mathbf{14}$$

For Run 7:

$$\textbf{Response Water cut}\left(\frac{\mathbf{v}}{\mathbf{v}}\%\right)=\frac{\mathbf{1.0}}{\mathbf{10}}\times\mathbf{100\%}=\mathbf{10}$$

For Run 8:

$$\textbf{Response Water cut}\left(\frac{\mathbf{v}}{\mathbf{v}}\%\right)=\frac{\mathbf{1.4}}{\mathbf{10}}\times\mathbf{100\%}=\mathbf{14}$$

For Run 9:

$$\textbf{Response Water cut}\left(\frac{\mathbf{v}}{\mathbf{v}}\%\right)=\frac{\mathbf{1.6}}{\mathbf{10}}\times\mathbf{100\%}=\mathbf{16}$$

For Run 10:

$$\textbf{Response Water cut}\left(\frac{\mathbf{v}}{\mathbf{v}}\%\right) = \frac{\mathbf{1.6}}{\mathbf{10}} \times \mathbf{100\%} = \mathbf{16}$$

For Run 11:

$$\textbf{Response Water cut}\left(\frac{\mathbf{v}}{\mathbf{v}}\%\right) = \frac{\mathbf{1.6}}{\mathbf{10}} \times \mathbf{100\%} = \mathbf{16}$$

For Run 12:

$$\textbf{Response Water cut}\left(\frac{\mathbf{v}}{\mathbf{v}}\%\right) = \frac{\mathbf{1.5}}{\mathbf{10}} \times \mathbf{100\%} = \mathbf{15}$$

For Run 13:

$$\textbf{Response Water cut}\left(\frac{\mathbf{v}}{\mathbf{v}}\%\right) = \frac{\mathbf{1.3}}{\mathbf{10}} \times \mathbf{100\%} = \mathbf{13}$$

For Run 14:

$$\textbf{Response Water cut}\left(\frac{\mathbf{v}}{\mathbf{v}}\%\right) = \frac{\mathbf{1.6}}{\mathbf{10}} \times \mathbf{100\%} = \mathbf{16}$$

For Run 15:

$$\textbf{Response Water cut}\left(\frac{\mathbf{v}}{\mathbf{v}}\%\right) = \frac{\mathbf{1.5}}{\mathbf{10}} \times \mathbf{100\%} = \mathbf{15}$$

For Run 16:

$$\textbf{Response Water cut}\left(\frac{\mathbf{v}}{\mathbf{v}}\%\right) = \frac{\mathbf{1.0}}{\mathbf{10}} \times \mathbf{100\%} = \mathbf{10}$$

For Run 17:

$$\textbf{Response Water cut}\left(\frac{\mathbf{v}}{\mathbf{v}}\%\right) = \frac{\mathbf{1.6}}{\mathbf{10}} \times \mathbf{100\%} = \mathbf{16}$$

For Run 18:

$$\textbf{Response Water cut}\ \left(\frac{\mathbf{v}}{\mathbf{v}}\%\right) = \frac{\mathbf{1.4}}{\mathbf{10}} \times \mathbf{100\%} = \mathbf{14}$$

For Run 19:

$$\textbf{Response Water cut}\ \left(\frac{\mathbf{v}}{\mathbf{v}}\%\right) = \frac{\mathbf{1.6}}{\mathbf{10}} \times \mathbf{100\%} = \mathbf{16}$$

For Run 20:

$$\textbf{Response Water cut}\ \left(\frac{\mathbf{v}}{\mathbf{v}}\%\right) = \frac{\mathbf{1.6}}{\mathbf{10}} \times \mathbf{100\%} = \mathbf{16}$$