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Synthesis and Performance Evaluation of Green Demulsifiers for Water-in-Crude Oil Emulsion Treatment

Godwin A. Udourioh[1]*, Chisom C. Ezeh[1], Moses M. Solomon[2]
[1]Department of Pure and Applied Chemistry, Faculty of Natural and Applied Sciences, Veritas University Abuja, Nigeria
[2]Department of Chemical and Environmental Engineering, University of Nottingham Ningbo China, Ningbo, China

***Corresponding Author's email:** udouriohg@veritas.edu.ng

ABSTRACT

The crude oil production industry faces a persistent challenge in the form of water-in-oil emulsions, necessitating the development of cost-effective and eco-friendly demulsification methods. This study presents a unique approach by synthesizing and characterizing green demulsifiers derived from coconut and soybean oils through a condensation reaction with diethanolamine catalyzed by p-toluene sulfonic acid. Characterization techniques, including Gas Chromatography-Mass Spectrometry (GC-MS), Fourier Transform Infrared Spectroscopy (FT-IR), and Thermogravimetric Analysis/Differential Thermal Analysis (TGA/DTA), were utilized. The demulsifiers' separation efficiency was evaluated through bottle tests with varying settling times, demulsifier dosage, and temperature. Results demonstrate the complete separation of stable water-in-oil emulsions by both Coconut Oil-Based Synthesized Demulsifier (COSD) and Soybean Oil-Based Synthesized Demulsifier (SOSD), albeit with differing kinetics. COSD exhibited superior separation kinetics, achieving 100% separation within 360 minutes at a 3 mL dosage, compared to 960 minutes required by SOSD under identical conditions. At 70°C with a 1 mL dosage, COSD achieved 100% separation in 30 minutes, while SOSD required 40 minutes. A comparative analysis with a chemical demulsifier (ethylene glycol) underscores the efficiency and viability of bio-based demulsifiers for emulsion breakage in the petroleum industry. These green demulsifiers offer environmental sustainability and cost-effectiveness. COSD demonstrates notably shorter separation times and lower required dosages, presenting a sustainable solution to the challenges posed by water-in-crude oil emulsions.

KEYWORDS: Green demulsifiers, Petroleum Flow Assurance, Emulsion treatment, Demuslsification, Coconut/Soyabean oil.

1. INTRODUCTION

The global crude oil industry continuously grapples with the challenge of water-in-crude oil emulsions, which reduce operational efficiency, increase costs, and pose environmental risks.[1–4] During crude oil production, water is often produced alongside the oil, forming water-in-oil emulsions. These emulsions, consisting of water droplets dispersed throughout the crude oil, can cause several problems, such as increased viscosity, equipment corrosion, and flow obstruction in pipelines.[5] Traditional methods for demulsification rely heavily on synthetic chemical demulsifiers, which are often expensive, non-biodegradable, and toxic to the environment.[6–8]

The quest for greener alternatives has led to the development of demulsifiers from natural sources.[1,9,10] Green demulsifiers derived from plant extracts and vegetable oils are becoming increasingly popular due to their low environmental impact and biodegradability. This study focuses on the synthesis and characterization of two such green demulsifiers, derived from coconut oil (COSD) and soybean oil (SOSD). By leveraging the natural surfactant properties of these oils, this research aims to provide a sustainable solution to the water-in-oil emulsion problem in crude oil processing.

2. MATERIALS AND METHODS

2.1. Materials

Soybean seeds and coconut fruits were sourced from the National Institute for Pharmaceutical Research Development (NIPRD), Abuja, Nigeria. Crude oil was obtained from the Nigerian National Petroleum Cooperation (NNPC) in Port Harcourt, Nigeria. The reagents, p-toluene sulfonic acid, diethanolamine,

petroleum ether, sodium chloride, and hexane, were of analytical grade, and procured from Finland Chemical Ltd, a subsidiary of Sigma-Aldrich.

2.2. Extraction of Soybean and Coconut Oils

Soybean oil was extracted using a Soxhlet extractor with hexane as the solvent. A total of 50 g of crushed soybean was placed in a thimble, and hexane was continuously cycled through the sample for 15 minutes. The extracted oil was recovered via rotary evaporation. For coconut oil, a hot extraction process was employed, where 1kg of blended coconut was mixed with 2.5L of water, filtered, and allowed to separate over 6 hours.[9,11] The separated coconut oil was then purified through heating and filtration.

2.3. Synthesis of Demulsifiers

Following the procedure previously reported,[12,13] the demulsifiers were synthesized using a condensation reaction of the extracted oils with diethanolamine, catalyzed by p-toluene sulfonic acid. The reaction was carried out at temperatures between 140°C and 180°C for COSD, and between 60°C and 150°C for SOSD. The reaction products were purified and stored for further analysis.

2.4. Characterization of Demulsifiers

All characterizations were performed at the Multi-User Science Research Laboratory of Ahmadu Bello University, Zaria, Nigeria. FT-IR and GC-MS were employed to characterize the molecular structure of the demulsifiers. Agilent FT-IR with Agilent MicroLab, transmittance against wavelength was analyzed at 8 resolution and 4000 – 650 range. The sample scan was done at 30 while the background scan was at 16. Similarly, Agilent GC-MS, 7890B model of GC and 5977 model MS were used with 99.999 percent Helium as carrier gas. Column: Agilent 19091S-433UI, HP-5ms Ultra Inert; 0°C—325 °C (350 °C): 30 m x 250 µm x 0.25 µm. Oven: the initial temperature of the oven was 40 °C with 2 min hold time, 1 min equilibration time and 325 °C maximum temperature. Thermal stability and degradation profiles were examined using TGA and DTA techniques. PerkinElmer thermal analyzer was used to analyze 19.876 mg 19.201 mg of COSD and SOSD demulsifiers respectively. The initial heating started at 30.00 °C to finial temperature at 750.00 °C at the rate of 10.00 °C/min for the demulsifiers.

2.5. Demulsification Bottle Tests

The demulsification process was carried out following the procedure by Saad et al.[3] and Yaakob and Sulaimon.[14] The performance of the synthesized demulsifiers (SOSD and COSD) was tested on a water-in-crude oil emulsion prepared with a 30:70 water-to-oil ratio. Bottle tests were conducted by adding varying amounts of demulsifiers (1 mL, 2 mL, 3 mL) to 10 mL of emulsion in 15 mL centrifuge tubes. The tubes were agitated and heated to 60°C in a water bath before allowing the emulsion to settle. The amount of separated water was recorded over time.

3. RESULTS AND DISCUSSION

3.1. Characterization Data of the Synthesized Demulsifiers

The characterization of the synthesized demulsifiers (COSD and SOSD) was conducted using several analytical techniques, including Fourier Transform Infrared Spectroscopy (FT-IR), Gas Chromatography-Mass Spectrometry (GC-MS), and Thermogravimetric Analysis/Differential Thermal Analysis (TGA/DTA). Each technique provided valuable insights into the chemical composition, functional groups, and thermal stability of the demulsifiers, confirming their suitability for applications in emulsion treatment.

3.1.1. Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR analysis was performed to identify the functional groups present in the synthesized demulsifiers. The spectra (Fig. 1) revealed characteristic peaks associated with hydroxyl (-OH), ester (C=O), and amine (-NH) functional groups, which are crucial for the surfactant properties of the demulsifiers. The

presence of these functional groups indicates that the synthesis process effectively converted the coconut and soybean oils into functional demulsifiers. The peak intensities and positions can also give insights into the degree of substitution and the effectiveness of the condensation reaction with diethanolamine. FTIR spectra for COSD showed prominent peaks such as: 3362.1 cm^{-1}: O-H stretch of alcohols, 2922.2 cm^{-1} and 2855.1 cm^{-1}: C-H stretch of alkanes, 1736.9 cm^{-1}: C=O stretch of esters, and 1461.1 cm^{-1}: C=C stretch of aromatics. For SOSD, key peaks included: 3291.2 cm^{-1}: N-H stretch of amides, 2922.2 cm^{-1} and 2851.4 cm^{-1}: C-H stretch of alkanes, 1744.4 cm^{-1}: C=O stretch of ketones, 1200.2 cm^{-1} and 1237.5 cm^{-1}: =C-O-C stretch of ethers. Both results align with literature, confirming the presence of functional groups like esters, alcohols, and amides.[12,15]

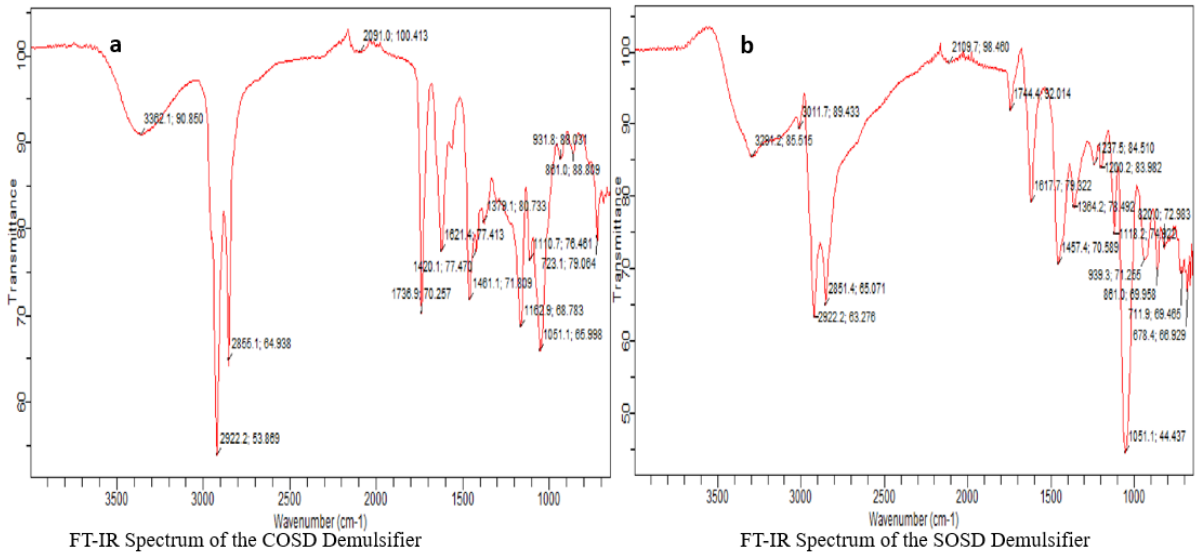

Figure 1: FT-IR Spectra of the Synthesized Demulsifiers (a) COSD (b) SOSD.

3.1.2. Gas Chromatography-Mass Spectrometry (GC-MS)

GC-MS analysis provided detailed information on the molecular composition and purity of the synthesized demulsifiers. The chromatograms (Fig.2) displayed a range of peaks corresponding to various components, confirming the successful synthesis of the desired products. Identifying specific compounds can be linked to the natural oils used and their transformation during the synthesis process. This analysis is critical for verifying the structural integrity of the demulsifiers and ensuring that no unwanted by-products were formed during synthesis. The GC-MS analysis of COSD identified 21 major components, including fatty acids, alcohols, esters, amides, ketones, hydrocarbons, and aldehydes. Notable compounds include octanoic acid (natural to coconut oil) and dodecanamide, N, N-bis(2-hydroxyethyl)-, a key amphiphilic demulsifier component. Similarly, SOSD revealed 15 major peaks, such as 9-eicosenoic acid and 2,3-dihydroxypropyl elaidate, indicating components derived from soybean oil and amidation reactions. Both demulsifiers exhibit hydrophilic and lipophilic regions, essential for effective demulsification. The result of the GC-MS was compared to results of the earlier research[3] and they showed some similarities in the composition. Saad *et al*.[1] reported esters, amines, hydrocarbons, carboxyles, amides, and fatty acids to be present in their corn oil based synthesized demulsifier.

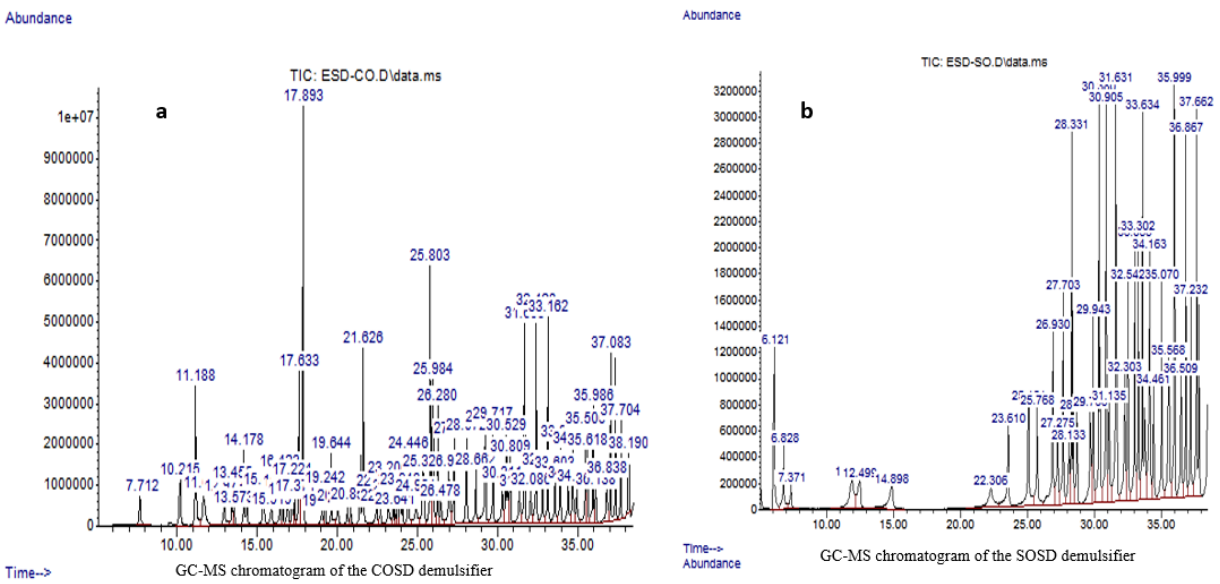

Figure 2: GC-MS Chromatograms of the Synthesized Demulsifiers (a) COSD (b) SOSD.

3.1.3. Thermogravimetric Analysis/Differential Thermal Analysis (TGA/DTA)

TGA and DTA were utilized to assess the thermal stability and decomposition behavior of the synthesized demulsifiers. The TGA thermograms (Fig. 3) indicated the weight loss of the samples as a function of temperature, allowing for the determination of thermal stability. COSD exhibited greater thermal stability compared to SOSD, with decomposition occurring at higher temperatures. This property is significant as it implies that COSD could perform effectively under the high-temperature conditions often encountered in oil production processes. The DTA results provided insights into the thermal transitions, such as melting and decomposition temperatures, which are essential for understanding the operational limits of these demulsifiers in practical applications. COSD remained thermally stable up to 64.48°C, with weight loss phases at 142.38°C (volatile components) and 346.64°C (fatty acid degradation), leaving 13.849% residue. SOSD exhibited similar behavior, stable up to 74.36°C, with decomposition phases at 149.64°C (moisture loss) and 380.33°C (organic degradation), leaving 9.023% residue. Both demulsifiers should avoid temperatures exceeding their degradation thresholds for optimal performance. TGA/DTA curves for both demulsifiers revealed two endothermic transitions: First peak - 91.45°C (COSD) and 104.83°C (SOSD), attributed to moisture vaporization; Second peak - 321.66°C (COSD) and 325.38°C (SOSD), associated with fatty acid decomposition. These transitions, confirmed by literature, emphasize the temperature-sensitive nature of the demulsifiers and their effective performance within stable thermal ranges.[16]

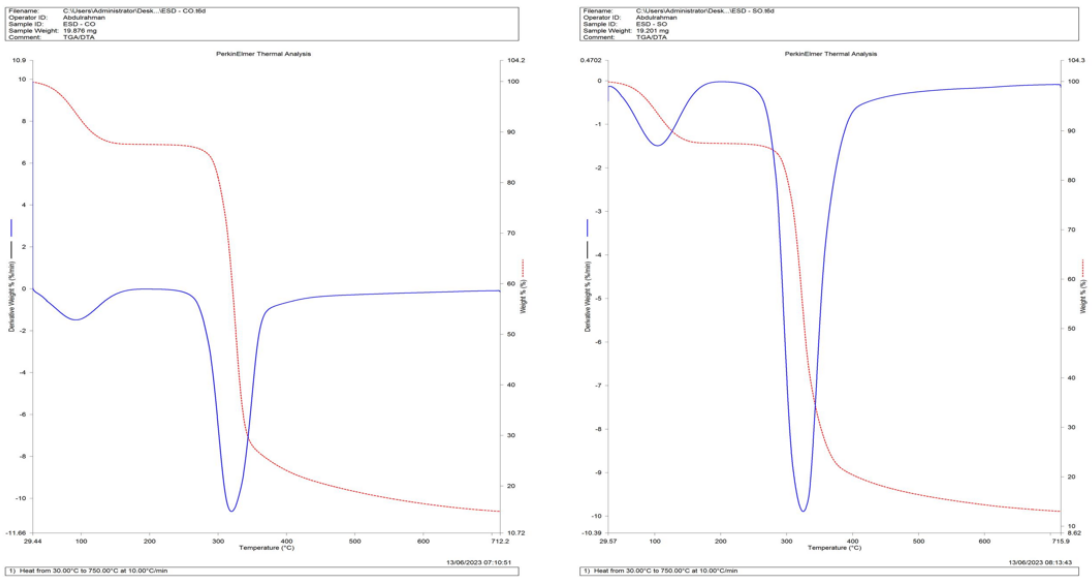

Figure 3: TGA/DTA Thermograms of the Synthesized Demulsifiers (a) COSD (b) SOSD.

3.2. Demulsification Studies

3.2.1. Effect of Dosage

The effect of demulsifier dosage was investigated using 1 mL, 2 mL, and 3 mL dosages. Higher dosages resulted in faster and more efficient separation. COSD achieved complete separation in 360 minutes with a 3 mL dosage, whereas SOSD took 960 minutes under the same conditions (Fig.4). This indicates that dosage plays a critical role in demulsification efficiency, with COSD requiring lower dosages for effective separation.

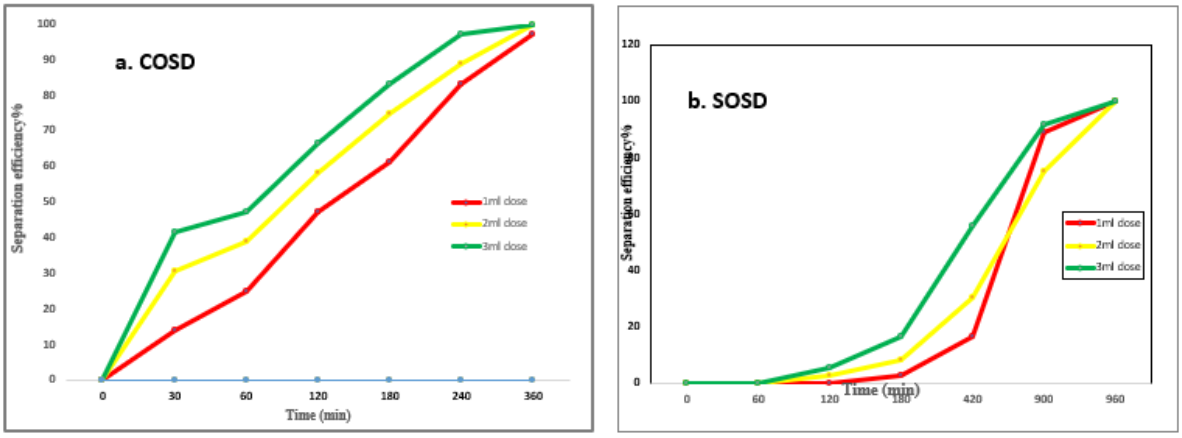

Figure 4: Effect of dosage on separation efficiency for COSD and SOSD demulsifiers

3.2.2. Effects of Settling Time

The settling time was another important factor influencing the separation efficiency of the emulsions. COSD outperformed SOSD in terms of separation speed, achieving complete separation within 360 minutes at the optimal dosage. The longer settling time required by SOSD (960 minutes) suggests that COSD is the more efficient demulsifier in terms of both time and performance (Fig.5).

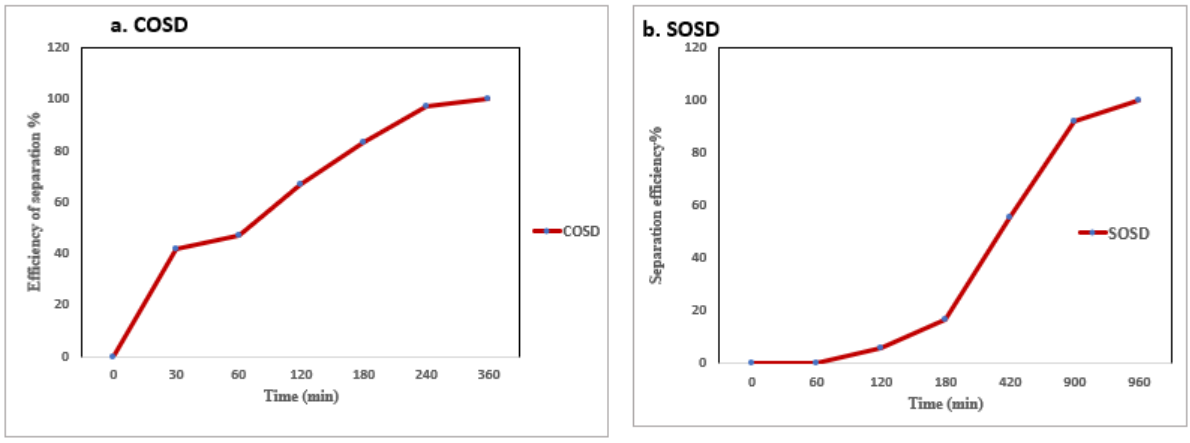

Figure 5: Effect of settling time on separation efficiency for COSD and SOSD demulsifiers

3.2.3. Effects of Temperature

Temperature significantly affected the separation process. At 70°C, COSD achieved 100% separation within 30 minutes at a 1 mL dosage, while SOSD required 40 minutes to reach the same level of separation (Fig. 6). The elevated temperature reduced the viscosity of the oil, allowing for quicker coalescence of water droplets and enhancing the efficiency of the demulsification process.

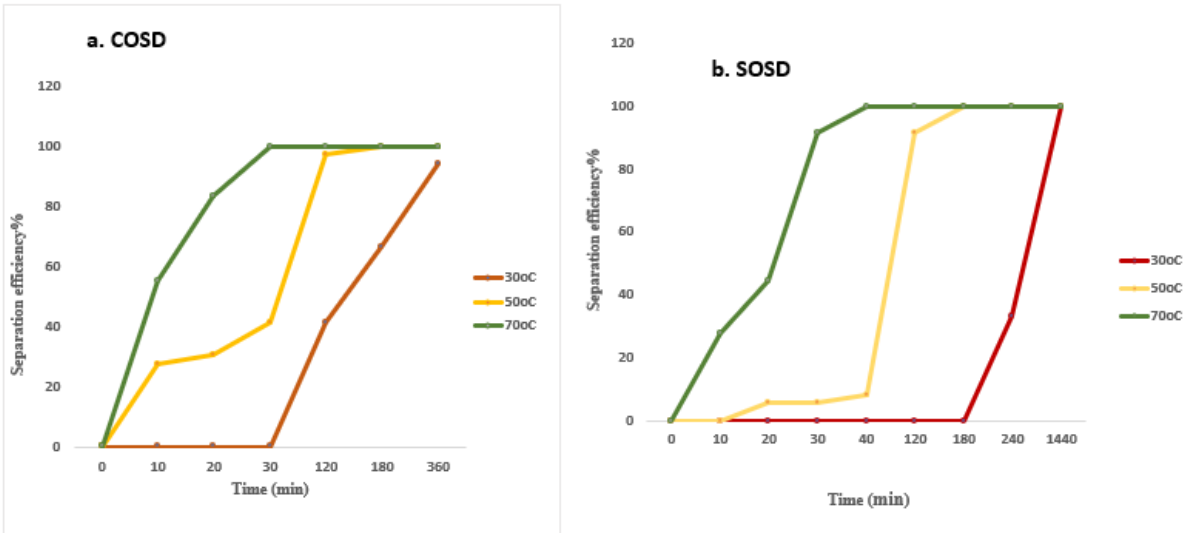

Figure 6 Effect of temperature on the demulsification efficiency of COSD and SOSD demulsifiers

3.3. Performance Evaluation of SOSD, COSD, and Chemical Demulsifiers

A comparative performance evaluation was conducted between COSD, SOSD, and a chemical demulsifier (ethylene glycol) (Fig. 7). COSD consistently outperformed both SOSD and ethylene glycol, particularly at lower dosages. COSD achieved complete separation at a 1 mL dosage and 70°C within 30 minutes, while ethylene glycol required longer times and higher dosages. This highlights the potential of COSD as an eco-friendly and efficient alternative to conventional chemical demulsifiers.

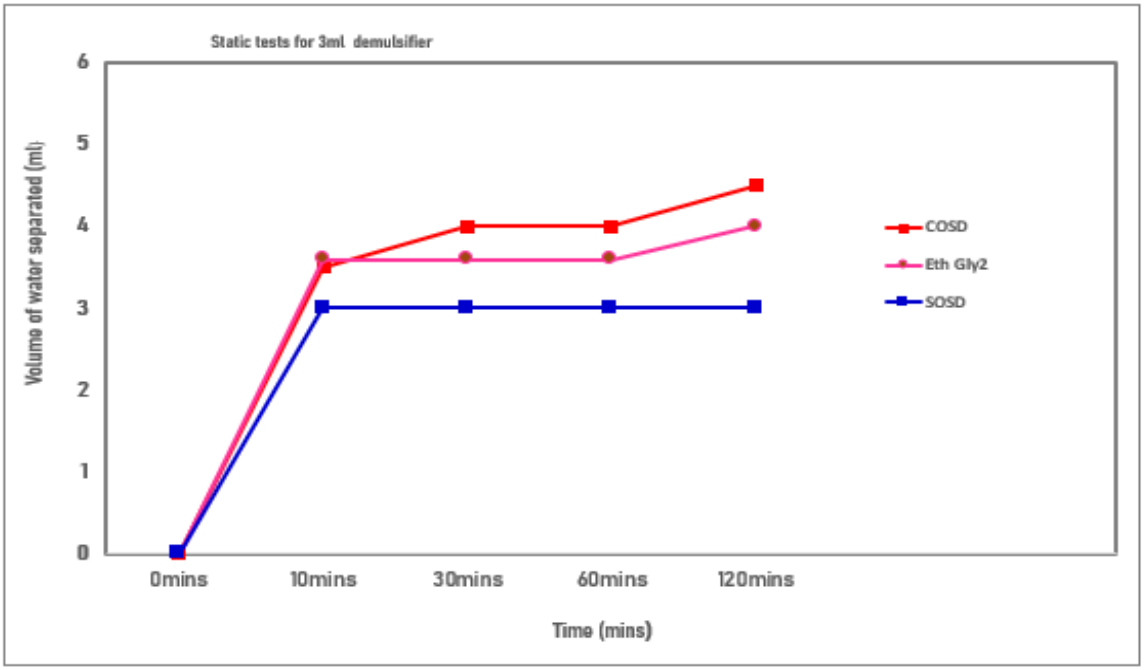

Figure 7: Performance evaluation studies of green and chemical emulsifier

4. CONCLUSION

The synthesis and characterization of COSD and SOSD as green demulsifiers have been successfully demonstrated. COSD, in particular, showed superior performance in terms of separation kinetics and dosage efficiency compared to SOSD and the chemical demulsifier (ethylene glycol). The use of renewable, non-toxic materials in the synthesis of these demulsifiers makes them environmentally friendly alternatives for the oil and gas industry. This study underscores the potential of bio-based demulsifiers in addressing the challenges associated with water-in-crude oil emulsions and supports the shift toward more sustainable industrial practices.

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REFERENCES

(1) Saad, M. A.; Abdurahman, N. H.; Yunus, R. M. Synthesis, Characterization, and Demulsification of Water in Crude Oil Emulsion via a Corn Oil-Based Demulsifier. In *Materials Today: Proceedings*; Elsevier Ltd, 2019; Vol. 42, pp 251–258. https://doi.org/10.1016/j.matpr.2021.01.145.

(2) Raya, S. A.; Mohd Saaid, I.; Abbas Ahmed, A.; Abubakar Umar, A. A Critical Review of Development and Demulsification Mechanisms of Crude Oil Emulsion in the Petroleum Industry. *Journal of Petroleum Exploration and Production Technology*. Springer April 1, 2020, pp 1711–1728. https://doi.org/10.1007/s13202-020-00830-7.

(3) Saad, M. A.; Abdurahman, N. H.; Yunus, R. M. Eco-Friendly Surfactant to Demulsification Water in Oil Emulsion: Synthesis, Characterization and Application. *Chemical Data Collections* **2020**, *30*. https://doi.org/10.1016/j.cdc.2020.100582.

(4) Tong, Q.; Fan, Z.; Liu, Q.; Qiao, S.; Cai, L.; Fu, Y.; Zhang, X.; Sun, A. Research Progress in Nanofluid-Enhanced Oil Recovery Technology and Mechanism. *Molecules*. Multidisciplinary Digital Publishing Institute (MDPI) November 1, 2023. https://doi.org/10.3390/molecules28227478.

(5) Abdulredha, M. M.; Siti Aslina, H.; Luqman, C. A. Overview on Petroleum Emulsions, Formation, Influence and Demulsification Treatment Techniques. *Arabian Journal of Chemistry*. Elsevier B.V. January 1, 2020, pp 3403–3428. https://doi.org/10.1016/j.arabjc.2018.11.014.

(6) Alsabagh, A. M.; Hassan, M. E.; Desouky, S. E. M.; Nasser, N. M.; Elsharaky, E. A.; Abdelhamid, M. M. Demulsification of W/O Emulsion at Petroleum Field and Reservoir Conditions Using Some Demulsifiers Based on Polyethylene and Propylene Oxides. *Egyptian Journal of Petroleum* **2016**, *25* (4), 585–595. https://doi.org/10.1016/j.ejpe.2016.05.008.

(7) Alao, K. T.; Alara, O. R.; Abdurahman, N. H. Trending Approaches on Demulsification of Crude Oil in the Petroleum Industry. *Appl Petrochem Res* **2021**, *11* (3), 281–293. https://doi.org/10.1007/s13203-021-00280-0.

(8) Abdullah, M. M. S.; Al-Lohedan, H. A.; Faqihi, N. A. Synthesis and Performance of Two New Amphiphilic Ionic Liquids for Demulsification of Water-in-Crude Oil Emulsions. *ACS Omega* **2023**, *8* (24), 22245–22255. https://doi.org/10.1021/acsomega.3c03246.

(9) Sundrasegaran, S.; Mah, S. H. Extraction Methods of Virgin Coconut Oil and Palm-Pressed Mesocarp Oil and Their Phytonutrients. *eFood*. John Wiley and Sons Inc December 1, 2020, pp 381–391. https://doi.org/10.2991/efood.k.201106.001.

(10) Turki, M. A. J.; Awad, S. H.; Ibrahim, S. K. Synthesis and Characterization of New Demulsifier from Natural Polymer. *Chemical Methodologies* **2022**, *6* (9), 649–660. https://doi.org/10.22034/chemm.2022.336625.1472.

(11) Ng, Y. J.; Tham, P. E.; Khoo, K. S.; Cheng, C. K.; Chew, K. W.; Show, P. L. A Comprehensive Review on the Techniques for Coconut Oil Extraction and Its Application. *Bioprocess and Biosystems Engineering*. Springer Science and Business Media Deutschland GmbH September 1, 2021, pp 1807–1818. https://doi.org/10.1007/s00449-021-02577-9.

(12) Saad, M. A.; Kamil, M.; Abdurahman, N. H.; Yunus, R. M.; Awad, O. I. An Overview of Recent Advances in State-of-the-Art Techniques in the Demulsification of Crude Oil Emulsions. *Processes*. Multidisciplinary Digital Publishing Institute (MDPI) July 1, 2019. https://doi.org/10.3390/pr7070470.

(13) Erfando, T.; Khalid, I.; Bahari, R. Experimental of Alternative Demulsifier Formulation from Corn Oil in Overcoming Water-Oil Emulsion. In *Materials Today: Proceedings*;

Elsevier Ltd, 2019; Vol. 39, pp 1061–1064. https://doi.org/10.1016/j.matpr.2020.05.778.

(14) Yaakob, A. B.; Sulaimon, A. A. Performance Assessment of Plant Extracts as Green Demulsifiers. *Journal of the Japan Petroleum Institute* **2017**, *60* (4), 186–193. https://doi.org/10.1627/jpi.60.186.

(15) Abed, M. M.; Naife, T. M.; Abdel Kawi Ibrahim, M. A. Advancing Green Technology: Demulsifier Preparation and Evaluation for Crude Oil Emulsion Treatment Using Corn Oil. *Iraqi Journal of Chemical and Petroleum Engineering* **2024**, *25* (3), 31–41. https://doi.org/10.31699/IJCPE.2024.3.4.

(16) Gouveia de Souza, A.; Oliveira Santos, J. C.; Conceição, M. M.; Dantas Silva, M. C.; Prasad, S. A THERMOANALYTIC AND KINETIC STUDY OF SUNFLOWER OIL. *Brazilian Journal of Chemical Engineering 21* (02), 265–273.