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Impact of Rhamnolipid Biosurfactants on Chemical Composition, Rheology, and Imbibition Performance of Crude Oils

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ABSTRACT - The application of biosurfactants in enhanced oil recovery (EOR) has generated significant interest due to their biodegradability, low toxicity, and effectiveness in modifying oil–rock–brine interactions. Rhamnolipids glycolipid biosurfactants synthesized by bacterial species exhibit a distinctive amphiphilic structure that can alter crude oil characteristics at both molecular and macroscopic levels. This study provides a novel, integrative evaluation of rhamnolipid-induced changes in the chemical composition, rheological properties, and imbibition efficacy of medium and light crude oils using gas chromatography–mass spectrometry (GC–MS), viscosity assessments, interfacial tension (IFT) measurements, and spontaneous imbibition experiments. These analyses allow simultaneous examination of compositional, rheological, IFT, and cAmerican petroleum institute llarity-driven displacement mechanisms across two crude oil categories, contrasting prior studies focused only on either compositional or interfacial properties of a single crude oil type. The results are expected to enhance understanding of biosurfactant-mediated EOR mechanisms, refine rhamnolipid application strategies, and help relate molecular alterations to core-scale oil recovery efficacy. This integrated approach provides a framework for customizing biosurfactant formulations for specific crude oil types, aiming to improve recovery while supporting environmental sustainability.

Keywords: rhamnolipids, biosurfactant, chemical composition, imbibition, enhanced oil recovery.

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INTRODUCTION

Biosurfactants, especially rhamnolipids made by Pseudomonas spp., have emerged as eco-friendly agents for Enhanced Oil Recovery (EOR) due to their low toxicity, biodegradability, and ability to alter oil–brine–rock interactions (Rita et al., 2025; Syafrizal et al., 2020). Recent research shows that rhamnolipids lower surface tension and stabilize oil-water dispersions. This action helps mobilize trapped hydrocarbons while supporting sustainability principles (Ahmad et al., 2021; Zeng et al., 2018; Zhao et al., 2015).

Although extensive research has established the efficacy of rhamnolipids in reducing interfacial tension (IFT), creating emulsions/nanoemulsions, and facilitating hydrocarbon dispersion, the mechanistic connections between molecular-level compositional changes in crude oil and core-scale imbibition performance are still inadequately investigated—particularly in the context of light versus medium crude oils. Most studies focus on either (i) compositional or remediation endpoints (e.g., Gas chromatography - Mass Spectrometry (GC-MS) fingerprints during biodegradation) or (ii) petrophysical outcomes such as wettability alteration and spontaneous imbibition, but seldom combine both across different crude grades using a single biosurfactant chemistry (Lu et al., 2023; Sharma et al., 2023; H. Wang et al., 2023).

Recent findings show rhamnolipids adsorb to oil-coated mineral surfaces, orienting hydrophilic heads outward, decreasing hydrophobicity, and promoting water-wet conditions—key for cAmerican petroleum institute llary-driven recovery in tight or mixed-wet rocks (Marhaendrajana et al., 2025; Sari & Kussuryani, 2013). Atomic force microscopy and surface analysis clarify how biosurfactants (rhamnolipid and surfactin) affect adhesion and contact angle, providing insight into improved imbibition (Udoh & Vinogradov, 2019; Y. Wang et al., 2011).

Recent advances explain the physics of imbibition and important design factors like surfactant type, salinity, and hybrids with nanoparticles. Research on sandstone and carbonates shows that using surfactants improves oil recovery by altering wettability and lowering interfacial tension. Methodological updates, such as testing optimal surfactant concentration with spontaneous imbibition before forced methods or CO_2 co-injection, further improve outcomes. Still, few studies link these methods with biosurfactant-specific, GC–MS–validated changes in crude composition (Austad & Standnes, 2003; Standnes, 2001).

Biosurfactants can reduce crude oil viscosity and improve flowability by dispersion and emulsification. Rhamnolipid-stabilized oil-in-water nanoemulsions show these effects under different pH and salinity levels. However, a direct and comparative assessment of viscosity changes in rhamnolipid–crude mixtures across light and medium crude oils is missing. This is especially true for studies using concurrent compositional and imbibition metrics under EOR-relevant ionic conditions (Ahuekwe et al., 2016; Gayathiri et al., 2022; Hadia et al., 2019).

GC–MS is the benchmark for analyzing total petroleum hydrocarbons, including n-alkanes, cycloalkanes, branched alkanes, and aromatics. Recent studies use GC–MS to track changes in hydrocarbon classes during biosurfactant-assisted processes. However, the specific relationships between rhamnolipid dosage, GC–MS compositional changes, and core-scale imbibition in reservoir-like brines for two crude classes remain inadequately documented (Abidin et al., 2023; Pandey et al., 2022).

Despite much research on rhamnolipids for enhanced oil recovery (EOR), significant gaps remain. Specifically, comparative assessment of rhamnolipid effects on light versus medium crude oils—integrating GC-MS compositional changes, mixture viscosity, spontaneous imbibition, and cAmerican petroleum institute llarity-driven displacement—remains limited. This work examines these topics by performing GC–MS profiling, viscosity analysis of oil-oil-oil-rhamnolipid mixtures, and imbibition experiments. The study specifically contrasts medium and light crudes under controlled ionic conditions. By connecting molecular compositional shifts to core-scale recovery, this work introduces a framework for tailoring biosurfactant use to specific crude categories and advances scientific understanding and practical EOR optimization.

This study aims to quantify compositional changes in medium and light crudes induced by rhamnolipids using GC–MS. It will assess viscosity variations in oil-rhamnolipid mixtures and measure IFT. Spontaneous imbibition in core plugs will be analyzed to establish mechanistic links among composition, rheology, and cAmerican petroleum institute llarity.

Rhamnolipids are proposed to selectively

alter hydrocarbon-class distributions, such as by increasing the solubilization of specific aromatics or n-alkanes. At the same time, they reduce mixture viscosity and interfacial tension (IFT). These effects enhance displacement performance through spontaneous imbibition. The comprehensive, multi-scale methodology developed in this study guides formulation strategies in biosurfactant-assisted enhanced oil recovery (EOR) and ensures direct applicability to field operations.

METHODOLOGY

Materials

Two crude grades (light, American petroleum institute >43.45°, and medium, 33.1°) are tested with a 4:1 formula of rhamnolipid biosurfactant. The mixture is stirred for 30 minutes. It is then tested for GC-MS and viscosity over three weeks. IFT testing is carried out on both crude grades with 0, 0.5%, 1%, and 1.5% rhamnolipid concentrations at 10,000 ppm brine salinity. The imbibition test uses synthetic cores and brine with 10,000 ppm salinity at the Critical Micelle Concentration (CMC).

Rhamnolipids

Rhamnolipids (Figure 1) are produced by Pseudomonas aeruginosa. These biosurfactants feature two hydrophilic head groups: carboxylate groups that give rhamnolipids their anionic character and rhamnosyl groups that contribute to the bulkiness of the head group. Furthermore, rhamnolipids are relatively more hydrophilic than synthetic surfactants (Nguyen et al., 2010).

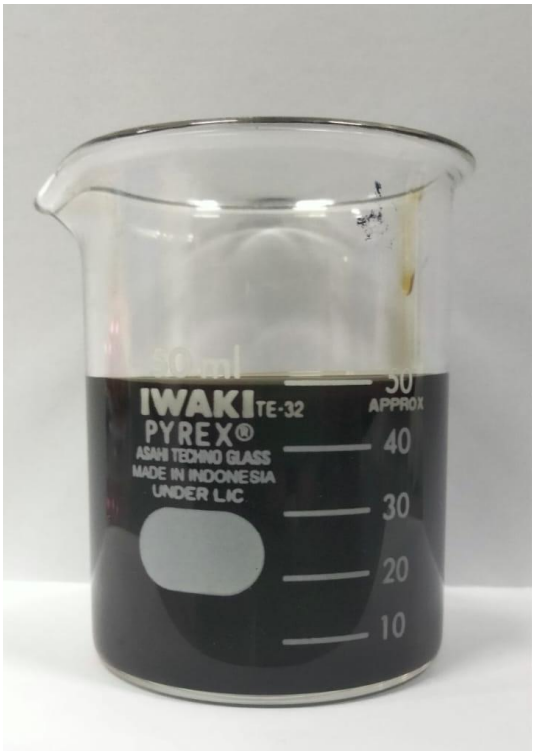


Figure 1. Rhamnolipid Samples for experimental testing in viscosity, interfacial tension, and imbibition studies.

Building on this, the molecular structure of rhamnolipids can vary depending on the bacterial strain producing them and their growth conditions. The basic structure of rhamnolipids consists of a hydrophobic fatty acid chain and a hydrophilic rhamnose sugar. A key difference among rhamnolipids produced by various bacterial strains is the number of rhamnose sugar molecules they contain. Some rhamnolipids have a monorhamnolipid structure, while others have a dirhamnolipid structure or a more complex arrangement.

Measurements

GC–MS quantifies compositional changes in samples prepared under two conditions: with and without rhamnolipid biosurfactants. For each condition, oil and rhamnolipid were mixed in a 4:1 ratio (oil: rhamnolipid) and soaked together for 3 weeks. This sample preparation matches the conditions used for measuring mixture viscosity. The rheological properties of the mixtures were assessed using a rotational rheometer or Brookfield viscometer at 60 °C, reporting viscosity in centipoise (cP). For interfacial tension (IFT) measurements, each mixture was tested with a Spinning Drop Tensiometer at 60 °C, 6000 rpm for 30 minutes, using saline conditions (10,000 ppm) and varying rhamnolipid concentrations (0%, 0.5%, 1%, and 1.5%).

Imbibition and analysis

Spontaneous imbibition uses synthetic sandstone core plugs. These are cleaned, brine-saturated, and oil-aged, and then submerged in rhamnolipid brine at 60 °C. Oil recovery (%OOIP) and ejected volume are tracked over time until reaching a plateau. This gives ultimate recovery and imbibition rate. A multi-criteria desirability function finds the best rhamnolipid dosage and salinity for each crude grade. Quality assurance covers GC–MS, viscosity, and imbibition to ensure reproducibility and safety compliance. Figure 2 shows the research flow chart for this study. This study was performed at the Enhanced Oil Recovery (EOR) laboratory of UPN Veteran Yogyakarta. The procedure starts with crude oil, rhamnolipid, and brine. These are mixed for

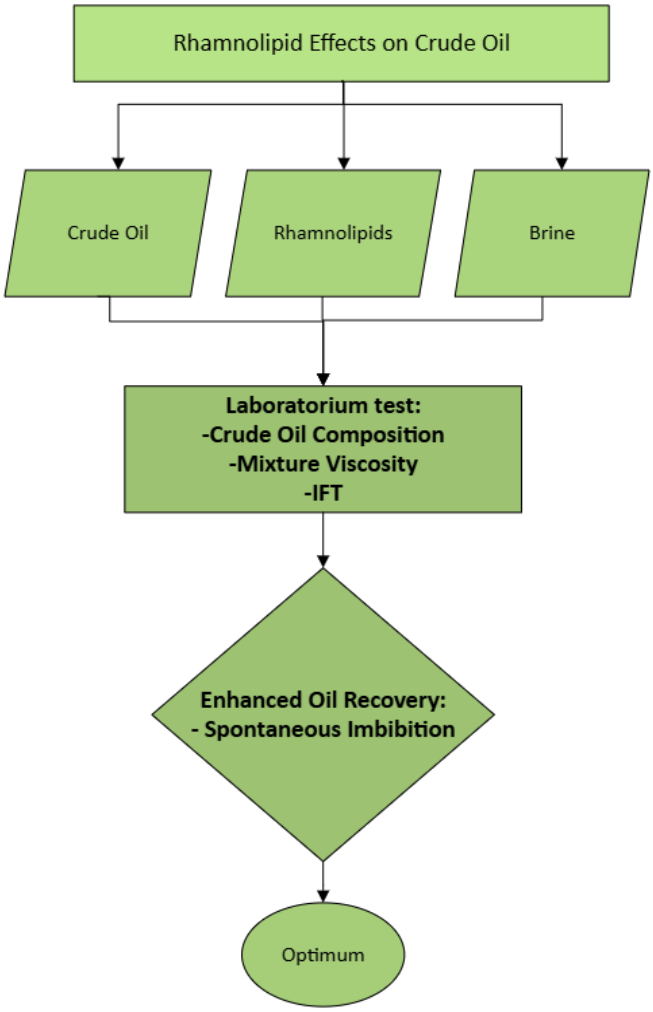


Figure 2. Research workflow

laboratory analysis. Tests include crude oil content, viscosity of the mixture, and interfacial tension (IFT). The results of these tests help judge rhamnolipid's effectiveness in Enhanced Oil Recovery (EOR) through spontaneous imbibition. The final step is to find the best conditions for maximizing oil recovery using the biosurfactant abilities of rhamnolipid.

RESULTS AND DISCUSSION

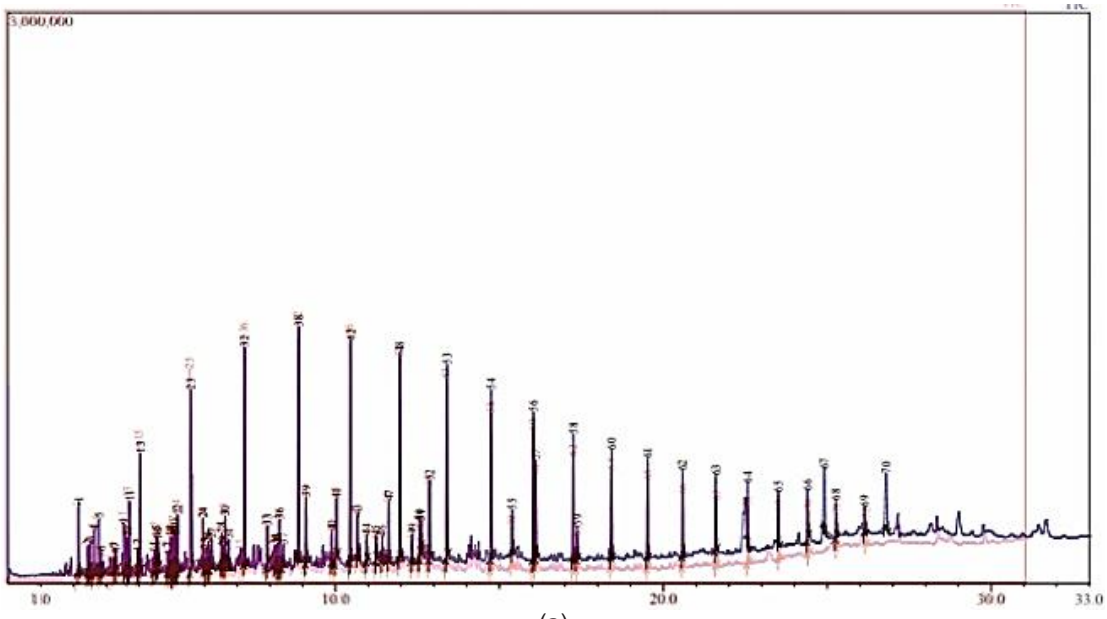
Crude oil composition

A qualitative analysis of retention time (RT) GC–MS for light and medium oils was performed at baseline and after 3 weeks of rhamnolipid immersion (Figure 3). In light oil, the baseline chromatogram is dominated by sharp peaks at RT 5–20 minutes, showing mostly light to medium fractions; peaks above RT 20 minutes are minor. After 3 weeks, intensity at RT 5–18 minutes increases and becomes more distinct, while peaks at higher RT flatten. For medium oil, the baseline shows more contribution at RT 18–33 minutes, indicating heavier/resinous fractions. After rhamnolipid treatment, two trends are observed: (i) increased signal at RT 5–15 minutes, indicating more light fractions; (ii) decreased signal at RT >25–33 minutes, showing fewer heavy fractions as they disperse or move into the microemulsion phase. As in light oils, peak RT positions remain stable, but the proportion between RT windows shifts. This pattern shows a shift toward lighter, more mobile fractions, especially in medium oils. The main mechanism is rhamnolipids forming O/W aggregates or microemulsions, enhancing the solubilization of short-chain hydrocarbons and partially breaking up heavier fractions. Rhamnolipids are not oxidizers, so major chemical changes are unlikely; the changes seen result from partitioning and solubilization, as shown by stable RT and shifting

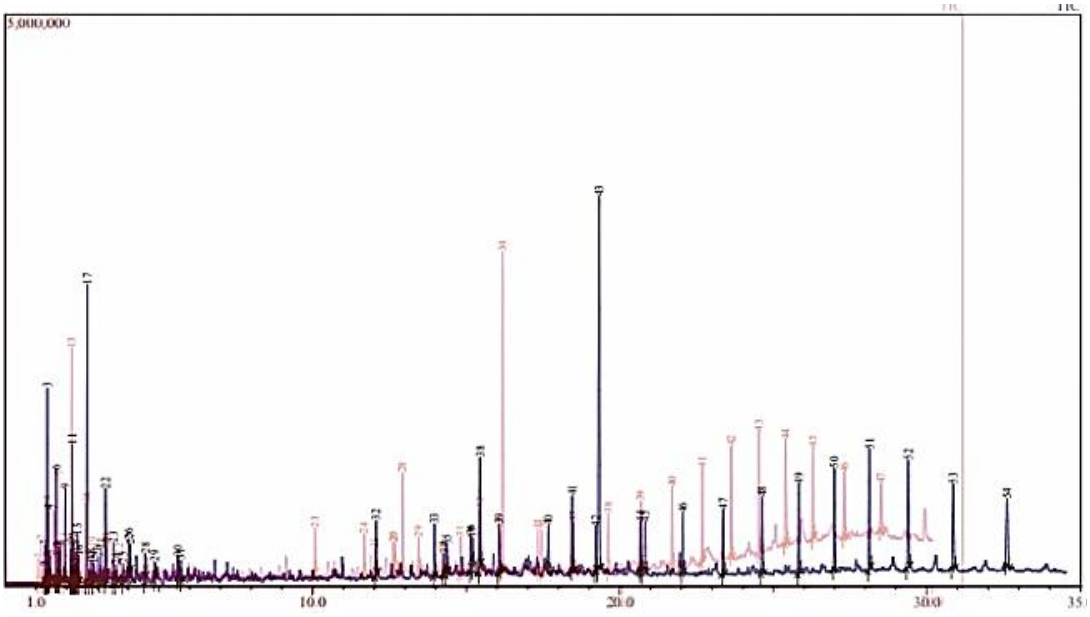
peak areas. For flow and oil recovery, these changes reduce viscosity and improve imbibition. Shifting the area to earlier RTs means a less heavy fraction, so viscosity drops, IFT decreases, and wettability shifts toward water, promoting higher imbibition. This effect is greater in medium oil, which has heavier fractions to improve.

Viscosity Analysis

Figure 4 (a and b) shows the viscosity of light oil and medium oil versus time with three temperature conditions. In panel (a) (lower viscosity) and panel (b) (higher viscosity, representing heavier/ medium oil), the time pattern is consistent: the most significant decrease in viscosity occurs from Day-1 to Day-7, followed by stable/marginal changes until Day-14. This means that rhamnolipids are most effective at reducing viscosity in the first 1–2 weeks, and medium oils benefit relatively more than light oils. The subtle rebound pattern in the third week indicates emulsion/microemulsion restructuring or phase distribution changes after prolonged aging. On the curve representing measurement temperature, the order of lines 70 °C > 60 °C > 50 °C makes sense as a consequence of droplet coarsening and/or system dehydration at higher aging temperatures (e.g., slight

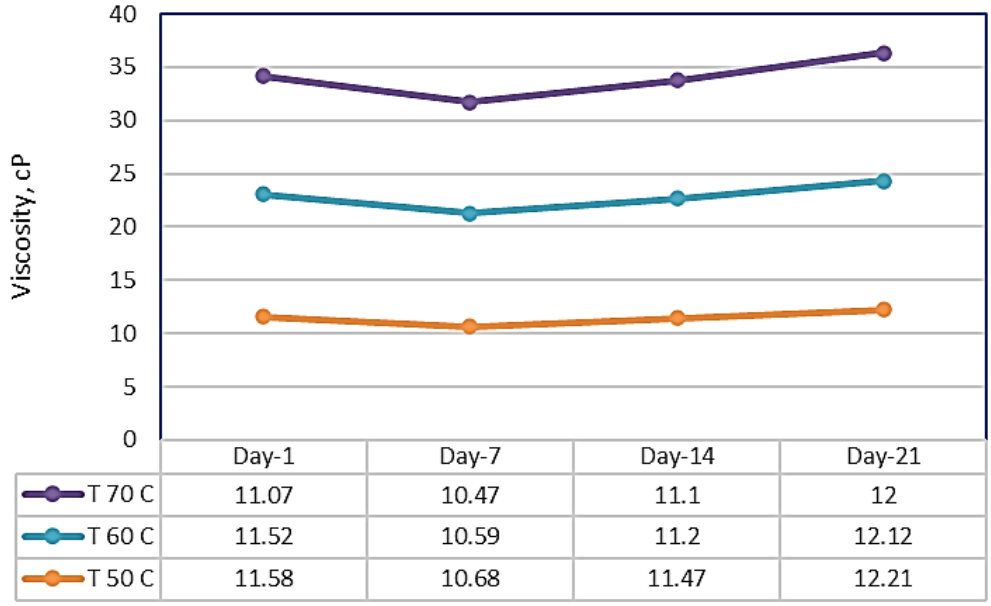


(a)



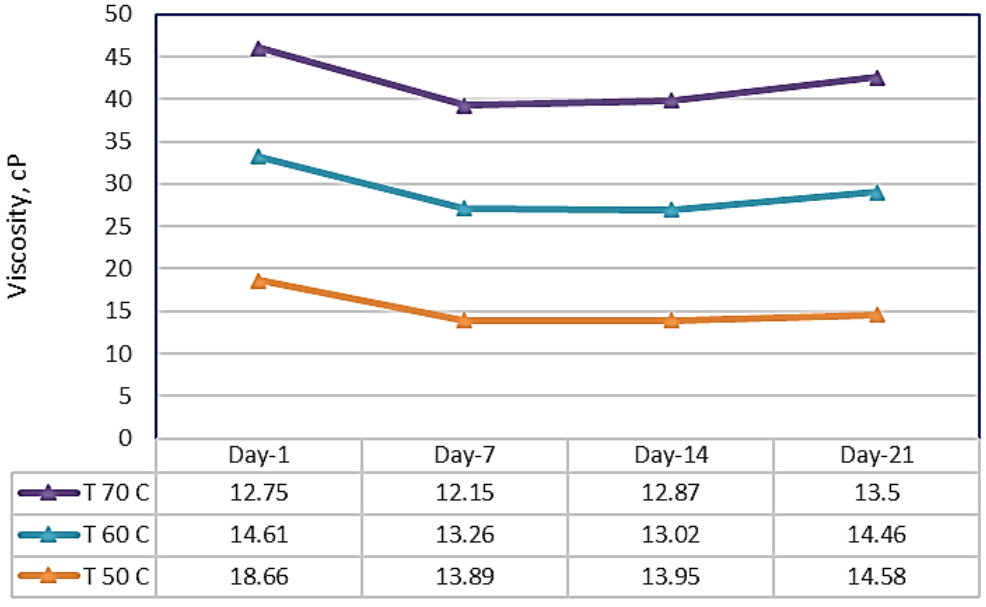
(b)

Figure 3. GC-MS Measurement Baseline and after soaking 3 weeks: (a) light oil, (b) medium oil



	Day-1	Day-7	Day-14	Day-21
T 70 C	11.07	10.47	11.1	12
T 60 C	11.52	10.59	11.2	12.12
T 50 C	11.58	10.68	11.47	12.21

(a)



	Day-1	Day-7	Day-14	Day-21
T 70 C	12.75	12.15	12.87	13.5
T 60 C	14.61	13.26	13.02	14.46
T 50 C	18.66	13.89	13.95	14.58

(b)

Figure 4. Graph of Viscosity Vs Time: (a). Light oil, (b). Medium oil

water loss/surfactant film reconfiguration, leading to increased mixture viscosity). Mechanistically, rhamnolipids form O/W aggregates/microemulsions that reduce flow resistance on days 7–14; thereafter, interfacial relaxation and partial coalescence may slightly increase viscosity again. The chromatograms show no major shift in retention time, but noticeable changes in peak intensity indicate compositional modification toward lighter hydrocarbon fractions after rhamnolipid treatment. Linked to previous GC–MS results, the viscosity decrease coincides with a shift in peak area toward the early–mid RT range (lighter/branched fractions), indicating hydrocarbon solubilization/redistribution that supports flow. Practically, the optimal time window for viscosity benefits is from Day 7 to Day 14; in medium oils, conditions around 60 °C provide the most significant and stable reduction up to Day 14, before a slight

rebound at Day 21. This has positive implications for imbibition: lower viscosity combined with reduced IFT and increased water-wetness will enhance %OOIP and imbibition rate. Viscosity decreased during the first two weeks and then became stable, showing that rhamnolipid was more effective at higher temperatures.

IFT Measurements

FT measurements were performed at a salinity of 10,000 ppm for both light and medium oil samples at various rhamnolipid concentrations. Light oil IFT decreased from 1.36 mN/m (no rhamnolipid) to 0.14 mN/m at ~0.5 (≈−89.7%), plateauing at 0.11 (≈−91.9%) at ~1.0 and 0.10 (≈−92.6%) at ~1.5 (Figure 5). Medium oil IFT began higher at 3.05 mN/m and decreased to 0.90 at ~0.5 (≈−70.5%), then to 0.26 at ~1.0 (≈−91.5%) and 0.25 at ~1.5 (≈−91.8%). Both oils show a strong initial IFT reduction, but after ~1.0, further dosage increases have diminishing returns. The mechanism of rhamnolipid action involves reducing interfacial tension through polar head adsorption at the oil-water interface and forming aggregates/microemulsions to enhance hydrocarbon solubilization. In medium oil, the resulting IFT remains higher (~0.25 mN/m) compared to light oil (~0.10 mN/m) due to more resins, asphaltenes, and polar compounds stiffening the interfacial film. A salinity of 10,000 ppm is sufficient for charge screening and IFT reduction, but not enough to achieve the 'optimum salinity window' (Winsor III) for ultra-low IFT (<0.01 mN/m). Further tuning of ions or co-surfactants may be needed for ultra-low targets. From a practical optimization perspective, the cost-benefit-based optimal rhamnolipid concentration lies between 0.5 and 1.0: for light oils, ~0.5 approaches the IFT plateau; for medium oils, ~1.0 achieves maximum benefit before diminishing returns appear at ~1.5.

Synergistically, these low IFT values are anticipated to enhance results from viscosity and imbibition tests. Lower IFT increases cAmerican petroleum institute llary drive and can boost %OOIP, especially for medium oils, which start with higher IFT.

Spontaneous imbibition test analysis

The imbibition test was performed under initial conditions with a salinity of 10,000, followed by a second treatment incorporating a 0.5% concentration of rhamnolipid (Figure 6. a and b). Biosurfactants, such as rhamnolipids, efficiently enhance spontaneous imbibition and oil recovery rates in tight reservoirs compared to using formation water alone or with conventional surfactants. Rhamnolipids' unique, biodegradable, and environmentally friendly properties make them suitable for sustainability-focused applications, as they decompose organically and reduce potential ecological harm. The imbibition curve for light oil shows two advantages with 0.5% rhamnolipid: faster kinetics and higher final recovery (Figure 7.a). In the first 1–2 days, the green curve (brine + rhamnolipid) rises sharply and reaches ~10% OOIP (Original Oil In Place, a measure of the total recoverable oil) around day 2. It then breaks through ~15% on days 3/4 and stabilizes until the end of the test. In contrast, pure brine plateaus at ~11–12% after day 6/8. This results in an absolute increase of ~3–4 points (≈25–35% relative) in final recovery. The t_{63}% (the time to reach 63% of final recovery) is also shorter for the rhamnolipid system. Mechanistically, this fits a rAmerican petroleum institute d decrease in IFT (interfacial tension, which is the force at the boundary between oil and water) and a shift in wettability (the tendency of a fluid to spread on a solid surface) toward a more water-wet state. As a result, cAmerican petroleum institute llary forces work more effectively to mobilize light oil. His pattern contrasts with the medium oil scenario. Here, brine causes a sharper initial increase, reaching ~15% in about 2 days, so brine's t_{63}% is faster than rhamnolipid's (Figure 7.b. The rhamnolipid curve rises gradually after day 3/4 and, by the test's end, matches or slightly surpasses brine (≈20–21% vs ≈18–19%). This lag before rhamnolipid's full effect likely results from surfactant adsorption, microemulsion formation, and stable wettability reversal. Once the interface stabilizes, the rhamnolipid's advantage emerges as higher final recovery despite a slower start.

Based on these results, in light oil, use 0.5% rhamnolipid for rAmerican petroleum institute d gains and higher final recovery. A soaking time of 3–4 days is already close to the plateau. In medium oil, by contrast, rhamnolipid offers longer-term benefits (slightly higher final recovery) but is less advantageous early on. Thus, it is effective where longer soaking times (≥7 days) are possible. Here, 'plateau' refers to the point at which additional soaking does not increase oil recovery further.

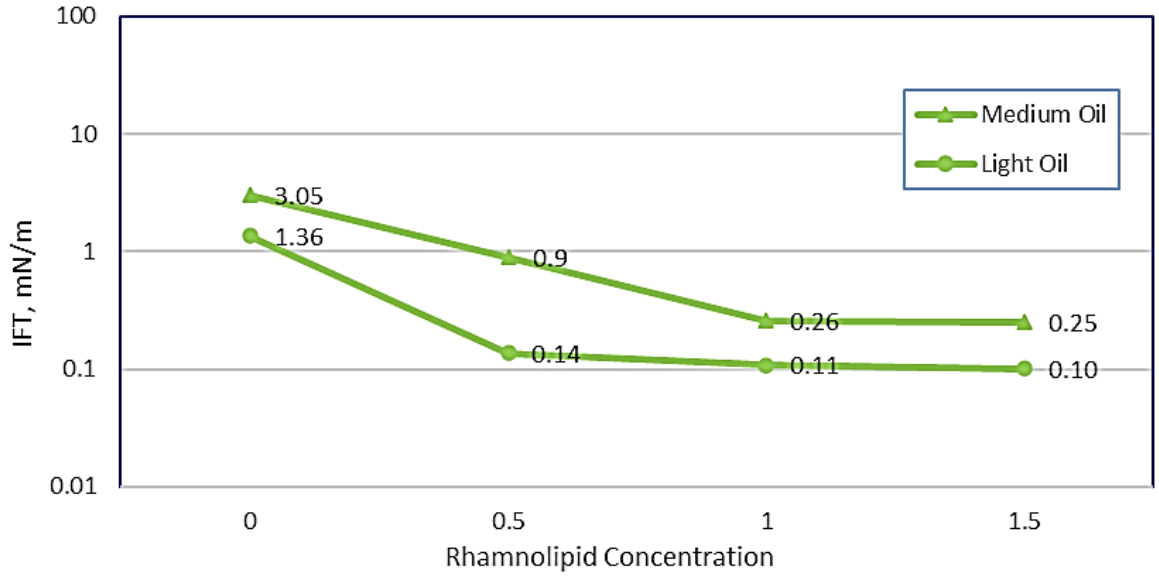
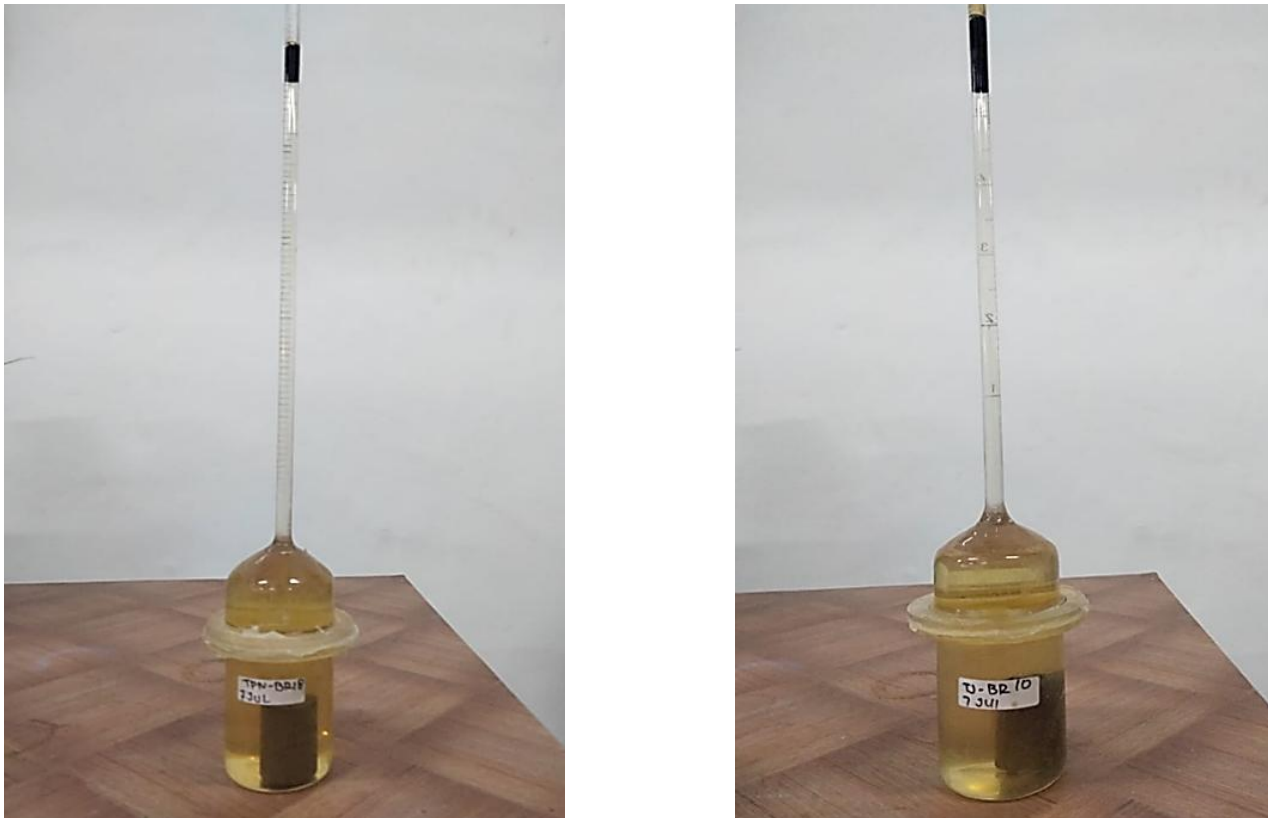
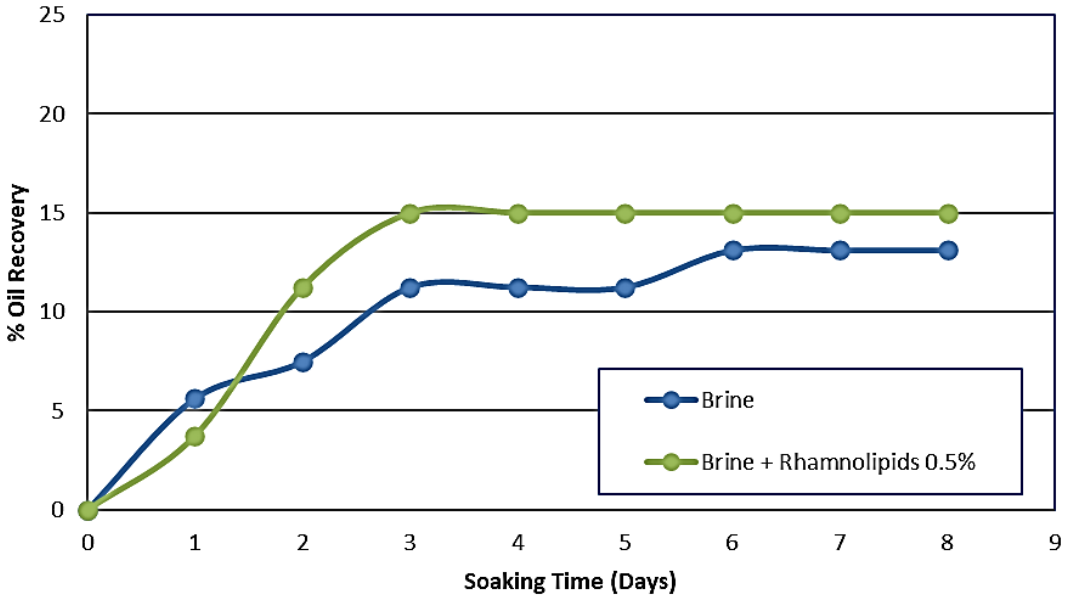


Figure 5. IFT vs Rhamnolipid concentration at light oil and medium oil

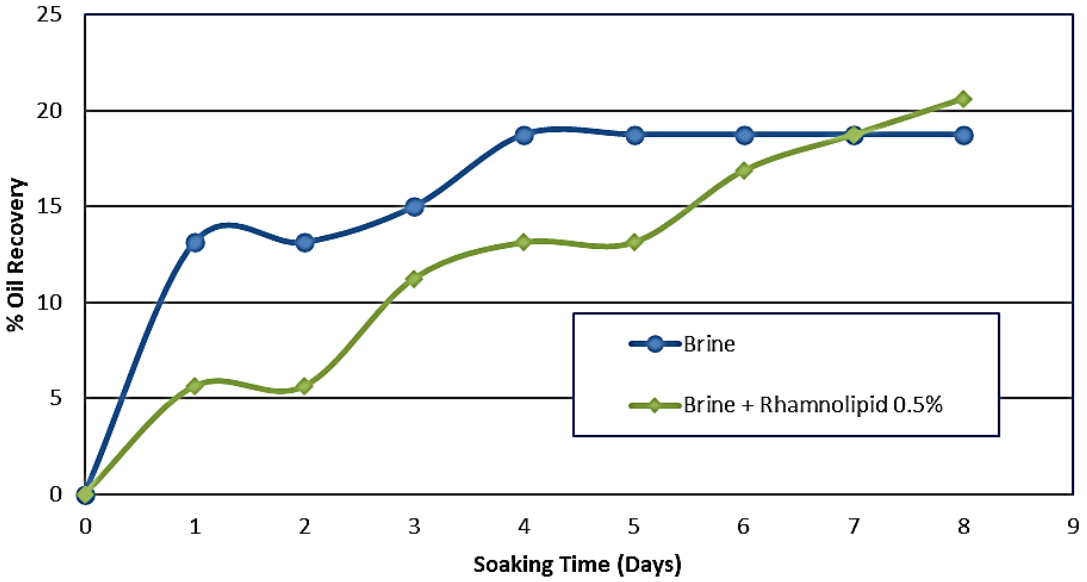


(a) (b)

Figure 6. Amot Imbibition apparatus: (a). Light oil, (b). Medium oil



(a)



(b)

Figure 7. Spontaneous Imbibition test results: (a) light oil, (b) medium oil

From a practical standpoint, select the cost-benefit optimal concentration between 0.5 and 1.0. For light oil, ~0.5 is nearly at the plateau. For medium oil, ~1.0 achieves the most significant reduction before extra benefits level off at ~1.5. These low final IFT values (interfacial tension, or the measure of the force at the oil-water boundary) should synergize with viscosity/imbibition findings. Lower IFT increases cAmerican petroleum institute llary drive and boosts %OOIP (Original Oil In Place), especially for medium oils with higher initial IFT.

CONCLUSIONS

In summary, GC–MS indicated no notable alteration in retention time; nevertheless, variations were seen in peak area—rhamnolipids modified the composition towards lighter fractions (retention time 5–20 minutes), most distinctly in medium oil. This corresponds with the most significant reduction in mixture viscosity during weeks 1–2 (remaining stable until about Day 14, followed by a minor rebound at Day 21), exhibiting a comparatively greater impact on medium oil. Rhamnolipid diminished

interfacial tension (IFT) by one order of magnitude, stabilizing between 0.5–1.0%: light oil reduced from approximately 1.36 to 0.10 mN/m, while medium oil decreased from 3.05 to 0.25 mN/m. The influence on imbibition: light oil demonstrates accelerated kinetics and superior final recovery (15% OOIP compared to brine's 11–12%), whereas medium oil experiences an initial delay but ultimately matches or surpasses at the conclusion (20–21% vs around 18–19%). It is recommended to apply 0.5% rhamnolipid for light oil and approximately 1.0% for medium oil, allowing a soaking period of 7–14 days to optimize the viscosity–IFT–imbibition advantages.

Overall, these findings confirm that rhamnolipid effectively enhances oil recovery through synergistic modification of viscosity and interfacial properties, promoting improved spontaneous imbibition and mobilization of trapped oil. The results highlight the potential of biosurfactant-based EOR as an environmentally sustainable and efficient alternative to chemical surfactants, particularly suitable for medium and light crude systems.

ACKNOWLEDGEMENT

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GLOSSARY OF TERMS

Symbol	Definition	Unit
EOR	Enhanced Oil Recovery	
IFT	Interfacial Tension	mN/m
GC-MS	Gas Chromatography–Mass Spectrometry	
RT	Retention Time	minutes
T	Temperature	º C
RF	Recovery Factor	%

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