



The Characteristics of *Sapindus Rarak* Green Surfactant Injection to Enhance Oil Recovery

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ABSTRACT - Green surfactants are surfactants derived from natural materials such as plants, animals, and microorganisms. *Sapindus Rarak* contains saponins, one type of natural surfactant that is widely known. This study evaluated the effectiveness of surfactant injection using *Sapindus Rarak*. This study involved laboratory experiments and analytical design with variations in salinity of 6,000 and 10,000 ppm and six variations of *Sapindus Rarak* surfactant concentrations from 0.5% to 3.0% using Berea sandstone cores at a temperature of 60°C. Compatibility testing based on water stability and phase behavior tests showed that only three samples of surfactant solutions, namely *Sapindus Rarak* surfactant concentration of 2.0% at a salinity of 6,000 ppm and surfactant concentrations of 2.5% and 3.0% at a salinity of 10,000 ppm, were homogeneous. The two best samples were selected based on the largest middle phase emulsion volume for each salinity, namely *Sapindus Rarak* surfactant concentration of 2.0% at a salinity of 6,000 ppm and surfactant concentration of 2.5% at 10,000 ppm. The wettability test of the two selected samples showed strongly water wet properties with contact angles of 26.86° and 23.28°, respectively. The results of the interfacial tension (IFT) test for the two selected samples were 2.15 x 10⁻¹ and 1.71 x 10⁻¹ mN/m, respectively. Based on the thermal stability test, the IFT values after 12 weeks for the two selected samples were smaller, namely 5.81 x 10⁻² and 1.51 x 10⁻¹ mN/m, respectively. Oil recovery factor (RF) for water injection showed that the use of 6,000 ppm salinity was better than 10,000 ppm salinity, which were 35.35% and 25.00%, respectively, while for surfactant flooding, the RF for the two selected *Sapindus Rarak* solution samples were 14.14% and 23.49%, respectively. This study offers a great opportunity to include green alternatives to improve conventional chemical-enhanced oil recovery techniques.

Keywords: biosurfactant, *Sapindus Rarak*, salinity, surfactant injection, recovery factor.

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INTRODUCTION

The use of surfactants aims to reduce the interfacial tension between two immiscible fluids. This causes the orientation of the intermolecular attraction on the water surface to change, which is previously oriented downward (into the water) to upward (towards the oil) after the surfactant is added. The upward attraction activates the molecules on the water surface so as to attract other molecules on its surface (Gbadamosi et al., 2019). Surfactant flooding involves the use of chemical surfactants and natural surfactants or biosurfactants. The achievement of ultra-low IFT is usually accompanied by the presence of a middle phase microemulsion in the surfactant phase behavior test (Alli & Tobing 2016; Alli et al. 2018).

The green-surfactant in this study was obtained from a natural raw material namely Lerak fruit (*Sapindus Rarak*). Lerak fruit (*Sapindus Rarak*) is a plant that is used as a raw material for natural soap because its seeds contain saponins. The bioactive and physicochemical properties of natural saponins have been shown to be better than synthetic saponins, making them a promising source of natural surfactants, for both research and commercial purposes (Rai et al. 2021). *Sapindus Rarak* contains saponins because mixing and stirring soapberry fruit with water will produce soap foam called 'saponin'. Utilizing organic resources more efficiently will make a positive contribution to a greener environment (Budhya et al. 2018).

Saponins contain anti-bacterial and anti-fungal properties so they are safe for all types of cleaning product industries in terms of content and efficacy (Darwis 2021). Saponins are a well-known type of plant surfactant. This type of surfactant can be produced with quite large added value and it is cost effective; it can be used in environmental control efforts such as industrial emulsion processing, oil pollution control, industrial wastewater detoxification and bioremediation of contaminated soil (Hajimohammadi et al. 2017).

Soapnut is a tropical plant that is widely found in various countries including Indonesia and is abundant in Java and its surroundings. The leaves are 6 to 16 inches long with white fruit protected by brown skin in a round shape with a diameter of 1-2 cm. This fruit is known as a commodity that produces many derivative products such as soap, detergent and surface active agent (surfactant) (Fatimah et al. 2020). *Sapindus Rarak* contains saponins, flavonoids,

alkaloids, tannins, steroids, and triterpenes (Artha et al. 2022). Before knowing green-surfactants as cleaning agents, most conventional detergents used surfactants in the form of phosphates, alkyl benzene sulfonates, and alkyl phenoxy diethanolamine. However, all these compounds are included in the group of compounds that are harmful to the environment and toxic and come from non-renewable resources, namely oil.

Saponins are natural secondary metabolites from plants with surfactant properties, which are synthesized by plants and some marine organisms. In terms of chemical structure, saponins are classified as glycosides. The name saponin comes from its soapy nature, where the Latin word '*sapo*' means 'soap'. Saponin is able to reduce IFT from 48 to 9 dynes/cm, allowing saponin to have the same ability as conventional surfactants commonly used in chemical injection processes. It has an average contact angle of 50.24° which is in the relatively hydrophilic range (Shahri et al. 2012). Saponin contains a pH in the range of 8-11 and foam stability in the range of 13-200 mm (Nurrosyidah et al. 2023).

In aqueous solution, saponin reduces the surface tension of water and exhibits foam-forming properties. The detergent properties of saponin come from its amphiphilic structure, which consists of a hydrophobic skeleton known as aglycone (or sapogenin) and a hydrophilic sugar group (glycone) (Putri et al. 2023). The two glycoside-forming parts are the basis of the structural variation of saponins in nature. The glycone part consists of one or more sugar chains, which are then bound to the aglycone through a glycosidic bond. The O-glycosidic bond separates the two structural parts of the saponin, acting as a boundary as shown in the figure below. Saponins are mainly classified based on differences in aglycone structure or the number of sugar chains. The basic classification is based on the skeletal structure that distinguishes two main groups, namely steroids and triterpenoids.

Research by (Rai et al. 2021) explains that the two classes of saponins (steroidal saponins and triterpenoid saponins) have different numbers of molecules. There are molecules with 27 C atoms in steroidal saponins and 30 C atoms in triterpenoid saponins. There are 2 types of steroidal saponins, namely furostanol type and spirostanol type. Saponins from several families such as Solanaceae have steroidal glycoalkaloids as the aglycone backbone. In addition to steroids, there are 3 types

of triterpenoid saponins, namely: oleanane saponins (for example, *Sapindus mukorossi*, and *Camellia oleifera*), ursolic acid saponins, for example, *Ilex paragariensis*, and dammarane saponins, for example, ginseng (*Panax* genus).

The purpose of the study was to analyze whether the *Sapindus Rarak* surfactant solution is compatible with brine and light crude oil solutions based on aqueous stability testing, phase behavior testing, and wettability testing. In addition, this study aimed to observe the thermal stability of *Sapindus Rarak* surfactant solution based on thermal stability and IFT tests. Furthermore, the main objective was to determine the oil recovery factor of surfactant flooding using *Sapindus Rarak* for light crude oil.

METHODOLOGY

This research included collecting materials and equipment for conducting laboratory experiments. The results of the experiments were used to evaluate the characteristics and performance of *Sapindus Rarak* surfactants in increasing oil recovery (Ristawati et al. 2019; Sainuka et al. 2021).

Materials

The following are the materials used in the study, namely: surfactant from *Sapindus Rarak* fruit. Surfactant solutions were made with various concentrations of *Sapindus Rarak*. Synthetic brine (NaCl solution) used to dissolve surfactants was made with low salinities. The crude oil used was light crude oil with a specific gravity of 42.92 ° API. The core sample used in the study was Berea core.

Equipment

The equipment used was in the laboratory of the Petroleum Engineering Department of Trisakti University such as the Enhanced Oil Recovery Laboratory, Reservoir Rock Analysis Laboratory, and Reservoir Fluid Laboratory. In addition, some research processes were also conducted in the Oil and Gas Recovery Research for Indonesia Laboratory at Bandung Institute of Technology (OGRINDO ITB).

Laboratory Experiments

The studies conducted include: 1). Preparation of *Sapindus Rarak* solution; 2). Measurement of fluid physical properties; 3). Measurement of core physical properties; 4). Filtration test; 5). Aqueous stability test; 6). Phase behavior test; 7). Wettability

test; 8). IFT and thermal stability test and 9). Core-flooding test.

The surfactant solutions were made with variations in *Sapindus Rarak* concentrations of 0.5%, 1%, 1.5%, 2%, 2.5%, and 3%. Meanwhile, the salinity of the brine used was 6,000 ppm and 10,000 ppm. The first to sixth experiments were carried out for screening solutions with various combinations of concentrations and salinities (Sugihardjo & Eni 2022).

RESULT AND DISCUSSION

Preparation of *Sapindus Rarak* Solution

The surfactant solution was made with a combination of concentration and salinity. The concentration variations of *Sapindus Rarak* ranged from 0.5% to 3%. Meanwhile, the salinity of the brine used was 6,000 ppm and 10,000 ppm. Therefore, there were twelve fluid samples used in the experiment as shown in Table 1.

Measurement of Physical Properties of Fluids

The physical properties of the surfactant solution that were measured were specific gravity

Table 1
Twelve surfactant solutions with various combinations of surfactant concentration and salinity.

Solution	Concentration %	Salinity ppm
1	0.5	6,000
2	1	6,000
3	1.5	6,000
4	2	6,000
5	2.5	6,000
6	3	6,000
7	0.5	10,000
8	1	10,000
9	1.5	10,000
10	2	10,000
11	2.5	10,000
12	3	10,000

and viscosity. The results of the specific gravity and viscosity measurements for the twelve fluid samples are given respectively in Figures 1 and 2.

Based on Figures 1 and 2, the specific gravity

and viscosity increased with increasing concentration of surfactant solution. The average increase in specific gravity was 0.48% for every 1% increase in concentration. In addition, Figure 1 shows that the effect of salinity on the specific gravity of the solution was greater with increasing salinity.

Figure 2 displays the findings of the viscosity computations for different concentrations at salinities of 6,000 ppm and 10,000 ppm. The surfactant solution's viscosity ranged from 1.2190 cP to 2.6347 cP at a salinity of 6,000 ppm, as shown in the figure. With a salinity of 10,000 ppm, the viscosity varied from 1.5215 cP to 2.7473 cP, which was slightly higher.

The formation of micelles and the solution's viscosity can both be significantly impacted by the addition of salt to the surfactant solution. This is because electrolytes, like salt, can encourage the creation of additional micelles by reducing the critical micelle concentration (CMC) when they are present in the aqueous phase. As a result, the

viscosity will initially rise as the NaCl concentration in the surfactant system increases until it reaches a particular maximum value because of the creation of micelles. Nevertheless, the viscosity will drop once more if the NaCl content rises above a particular point. This is thought to be caused by the breakdown of the micelle network structure and the decrease in hydration capacity, which causes the viscosity to drop (Jin et al. 2023). This implies that the maximum increase in viscosity can be achieved at an ideal salinity value.

The viscosity calculations for different concentrations of *Sapindus Rarak* surfactant solutions with salinities of 6,000 ppm and 10,000 ppm are displayed in Figure 2. The viscosity values are directly correlated with the flow time, and the size of the surfactant concentration affects viscosity. The viscosity of the fluid increases with surfactant content. Salinity has a fluctuating impact.

The average increase in viscosity at low surfactant concentrations (0.5–1.5%) was caused

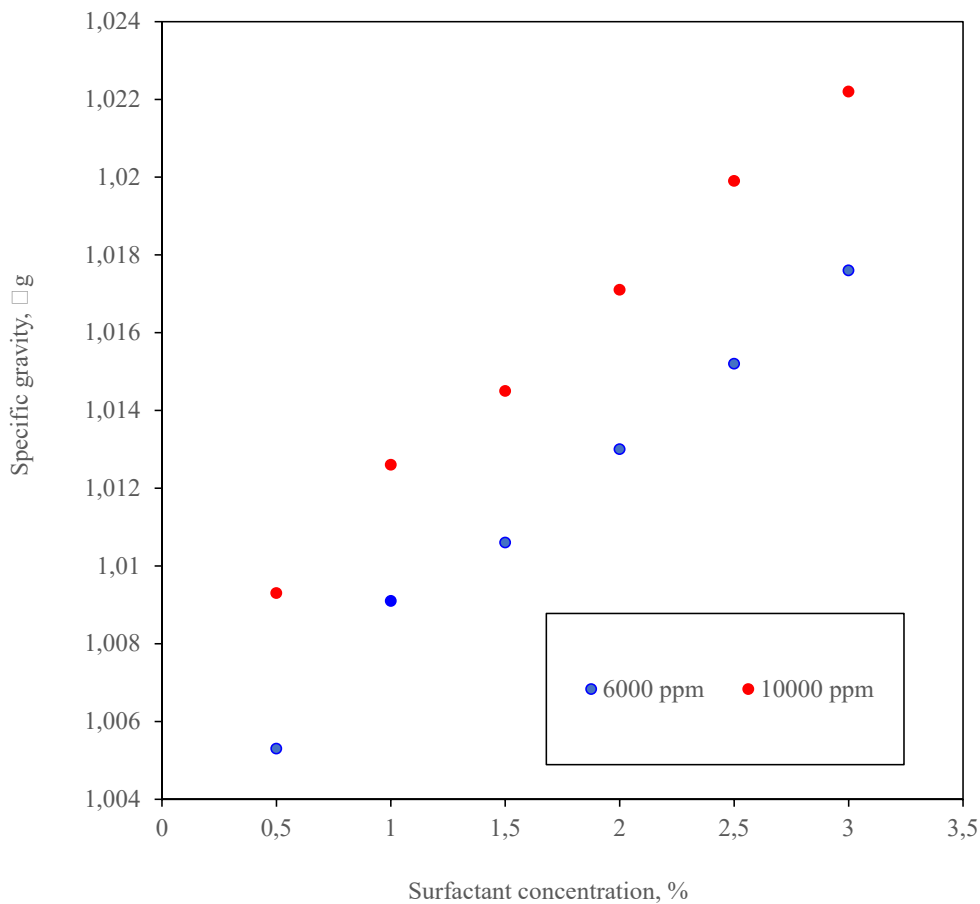


Figure 1
Specific gravity of surfactant solutions

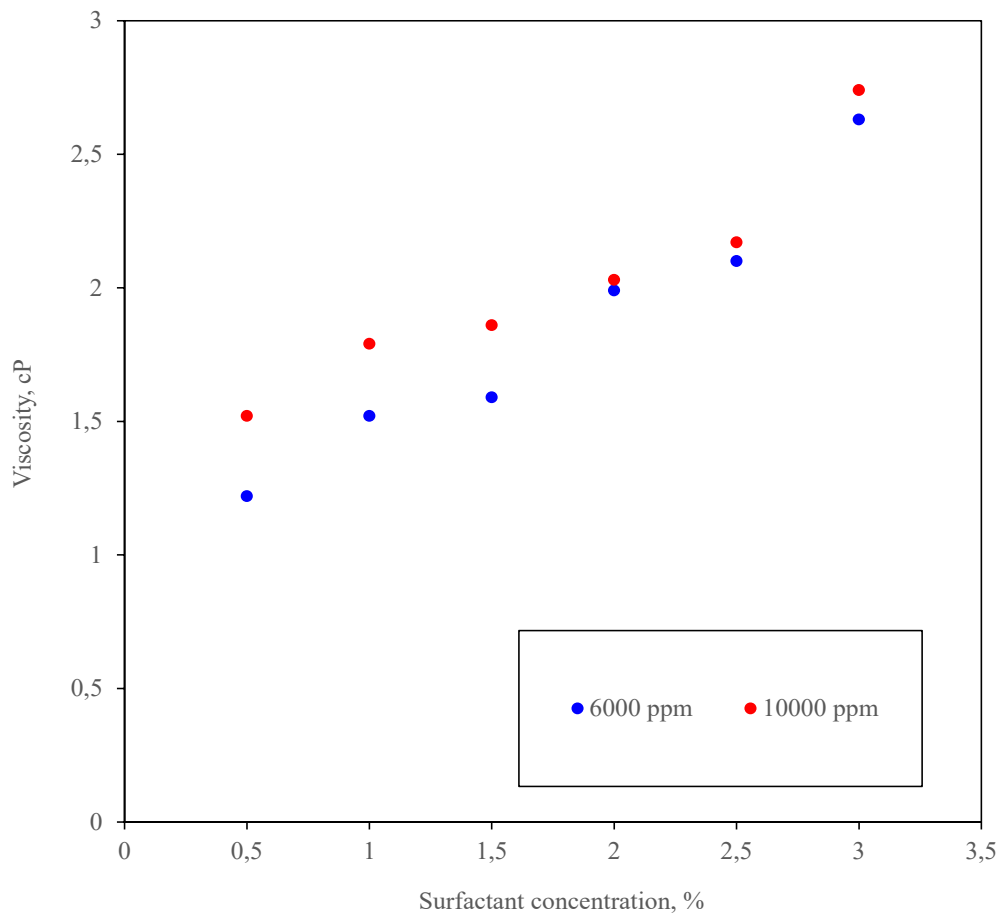


Figure 2
Viscosity of surfactant solutions

by the change in salinity from 6,000 ppm to 10,000 ppm. On the other hand, the increase in viscosity due to the change in salinity from 6,000 ppm to 10,000 ppm in salinity only led to an average of 0.08 cP for higher surfactant doses, ranging from 2.0% to 3.0%. This suggests that surfactant concentration also affects the ideal salinity value for raising viscosity. Furthermore, the findings demonstrated that the surfactant solutions with high concentrations had a lower ideal salinity value than those with low concentrations.

Measurement of Core Physical Properties

The results of the measurement of the core's physical properties are shown in Figure 3. Based on Figure 3, it can be seen that all cores used had almost similar physical characteristics, with an average porosity ranging from 20% - 22%, which according to (Febrian et al. 2015), was categorized as very good.

Filtration Test

Based on (Tobing & Hestuti 2013), if the sediment or impurities are found to be largely retained on the filter paper, then the surfactant is said to be not good because the filtration results will reduce the concentration of the surfactant. Therefore, the results of the filtration test will determine the quality of the surfactant. Any surfactants that can successfully pass through the filter (filter paper) and do not clog are surfactants that can function effectively in the EOR process.

Figure 4 shows the results of the filtration test on a surfactant solution that has a relatively small filtration rate. The *Sapindus Rarak* surfactant had an inconsistent line slope, showing a tendency for the surfactant molecules to clog when the surfactant dissolves across the membrane. From the results of the study, the *Sapindus Rarak* surfactant solution had good performance as seen in the figure where the FR value obtained was close to the expected FR value, i.e., ≤ 1.2 .

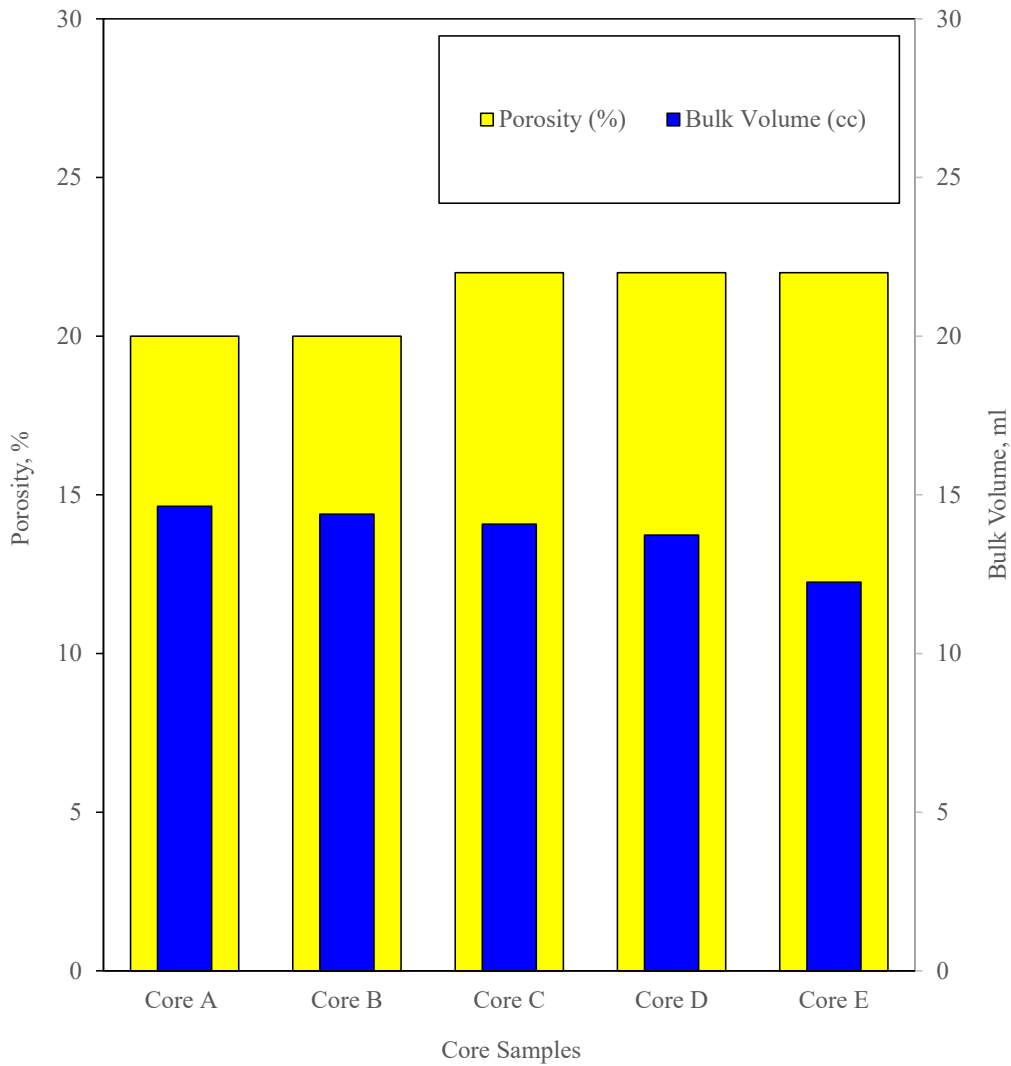


Figure 3
Porosity and bulk volume of five core samples

Aqueous Stability Test

Aqueous stability testing was one of the initial stages in the surfactant screening process, where the test was carried out for 7 days. Aqueous stability measurement is a visual measurement to obtain qualitative measurements. For this reason, quantitative measurements are needed, namely transmittance tests (%). This is to identify whether there are deposits, colloids, or coarse particles that cannot be completely dissolved in the surfactant solution. The test was carried out using a pipette tube with an oven temperature of 60 °C. Below is Table 2 below shows the results of the aqueous stability test for the 12 surfactant solutions.

Table 2 shows that the transmittance value decreased with increasing concentration and salinity. Increasing the concentration and salinity of the surfactant solution decreased the amount of light

that can pass through the material. In other words, the clearer the solution, the higher the transmittance value. Table 2 also shows that out of the 12 solutions, only 3 concentrations, namely 2.0% concentration at 6,000 ppm salinity, 2.5% concentration and 3.0% at 10,000 ppm salinity, were clear for 168 hours (7 days). This test is very important because unstable surfactants in formation water can disrupt the distribution of surfactants and reduce the performance of surfactants in the EOR process.

Table 2
Aqueous stability test results

Solution	Transmittance %	Condition
1	84.8	Sediment
2	82.4	Sediment
3	80.6	Sediment

Table 2 (continued)
Aqueous stability test results

Solution	Transmittance %	Condition
4	77.2	Clear
5	74.8	Sediment
6	72.5	Sediment
7	83.9	Sediment
8	81.5	Sediment
9	79.3	Sediment
10	76.8	Sediment
11	73.2	Clear
12	70.6	Clear

Phase Behavior Test

Based on the results of the previous experiments of the 12 solutions, 2 best solution samples were selected, namely a solution with a concentration of 2.0% at a salinity of 6,000 ppm and a concentration of 2.5% at a salinity of 10,000 ppm for further testing, namely phase behavior test, wettability test and IFT.

Figure 5 shows the results of the phase behavior

test at a concentration of 2.0% at a salinity of 6,000 ppm. Based on the figure, there was a change in the volume of the emulsion every hour, i.e., from 0 hours there was a full emulsion of 4 ml of surfactant and crude oil solutions, but at 504 hours the emulsion was in the middle phase (Winsor type III) with a volume of 0.08 ml. The total emulsion produced at stable conditions was 2.0%.

Figure 6 shows the results of phase behavior testing of 2.5% concentration at 10,000 ppm salinity. As in the previous solution (Figure 5), there was a change in the volume of microemulsion (Winsor type III), i.e., at 0 hours, the volume of the emulsion was 2.40 ml and decreased to 0.13 ml at 504 hours (3 weeks). The total emulsion produced at stable conditions was 3.30%.

Wettability Test

The test was conducted using a pendant drop tool in the EOR OGRINDO ITB Laboratory. The wettability test results can be seen in Table 3. It is known that the contact angle of the 2.0% *Sapindus Rarak* surfactant and 6,000 ppm brine was 26.86° and the contact angle of the 2.5% *Sapindus Rarak* surfactant and 10,000 ppm brine was 23.28° where $\theta < 90^\circ$ is considered water-wet.

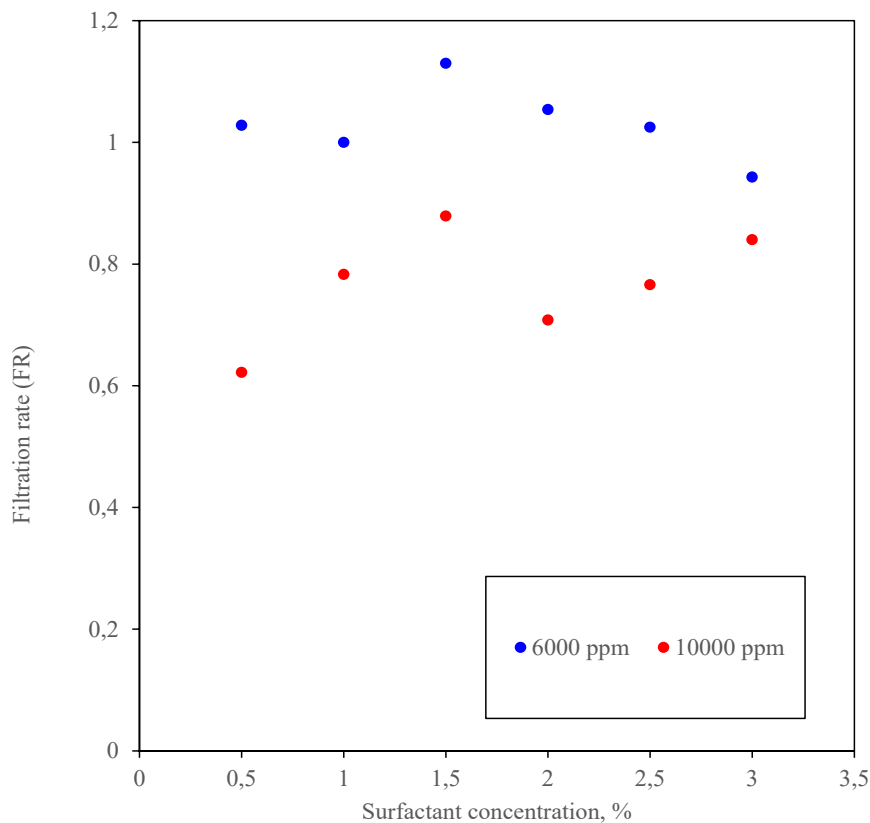


Figure 4
Filtration rate of surfactant solution

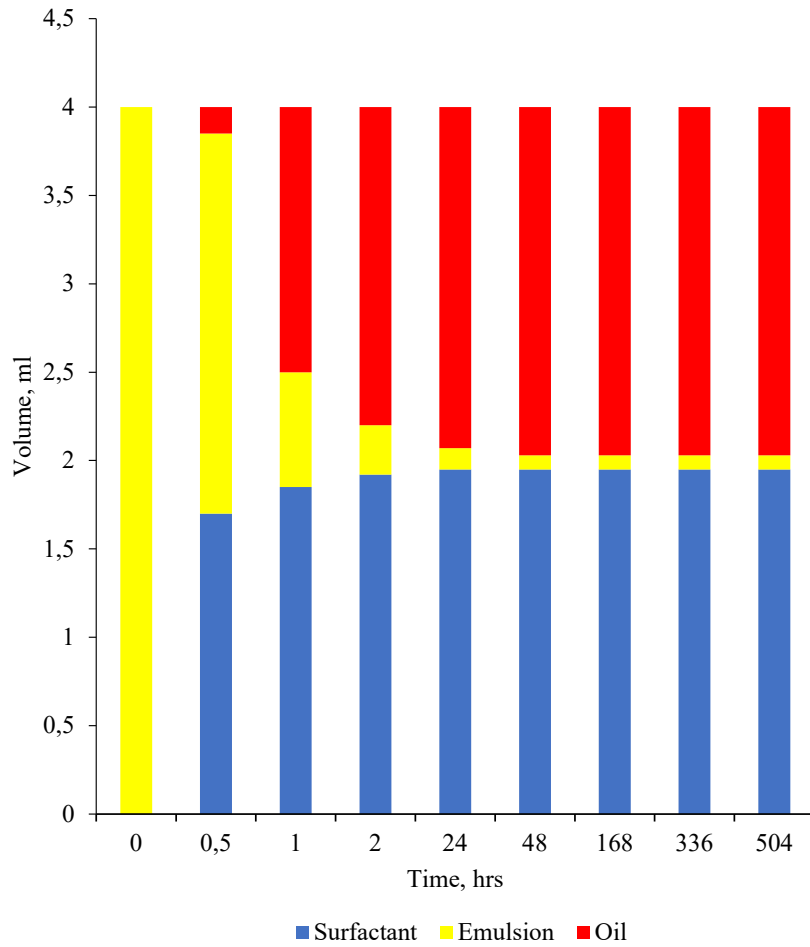
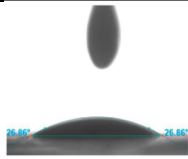
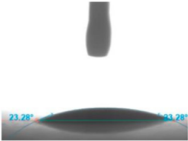


Figure 5
Phase behavior test results at concentration of 2.0% and salinity of 6,000 ppm

Table 3
Contact angle test results

Surfactant Solution	Rock Type	Contact Angel	Visual
2.0%, 6000 ppm	Berea sand stone	26.86°	
2.5%, 10000 ppm	Berea sand stone	23.28°	

Interfacial Tension and Thermal Stability Test

In the IFT test for the *Sapindus Rarak* surfactant, the tool used was a spinning drop tensiometer TX 500D in the OGRINDO ITB laboratory. The test results can be seen in Figure 7. From Figure 7, the IFT value for 6,000 ppm salinity with a concentration of 2.0% was 2.15×10^{-1} mN/m at 0 days and 5.81×10^{-2} mN/m at 12 weeks. There was a significant decrease in the IFT value from 0 days to 2 weeks to 5.16×10^{-2} mN/m and began to stabilize until the 12th week. Time is a benchmark for distinguishing surfactant concentrations and salinities that have good thermal resistance and stability.

Figure 7 shows the IFT results based on thermal stability for 6,000 ppm salinity with 2.0% concentration and 10,000 ppm salinity with 2.5% concentration. The surfactant solution with 2.0% concentration at 6,000 ppm salinity can lead to more significant decrease in surface tension than 2.5% concentration at 10,000 ppm salinity.

Coreflooding Experiments

Figure 8 shows the results of coreflooding tests of the surfactant solutions with a concentration of 2.0% at a salinity of 6,000 ppm and surfactant solutions with a concentration of 2.5% at a salinity of 10,000 ppm based on the waterflooding and surfactant flooding processes.

Figure 8 shows that waterflooding with a salinity of 6,000 ppm obtained a recovery factor of 35.35%. Meanwhile, waterflooding with a salinity of 10,000 ppm obtained a recovery factor of 25%. Therefore, the addition of salinity tends to lower waterflooding recovery factor. Waterflooding with low salinity often produces a higher recovery factor compared to high salinity (Yousef et al. 2012). This phenomenon has been explained in various studies and is influenced by several main mechanisms. Research by (Tang & Morrow 1997) shows that low salinity water injection can increase RF by affecting the petrophysical properties of reservoir rocks. They found that low salinity water injection reduces the capillary tension

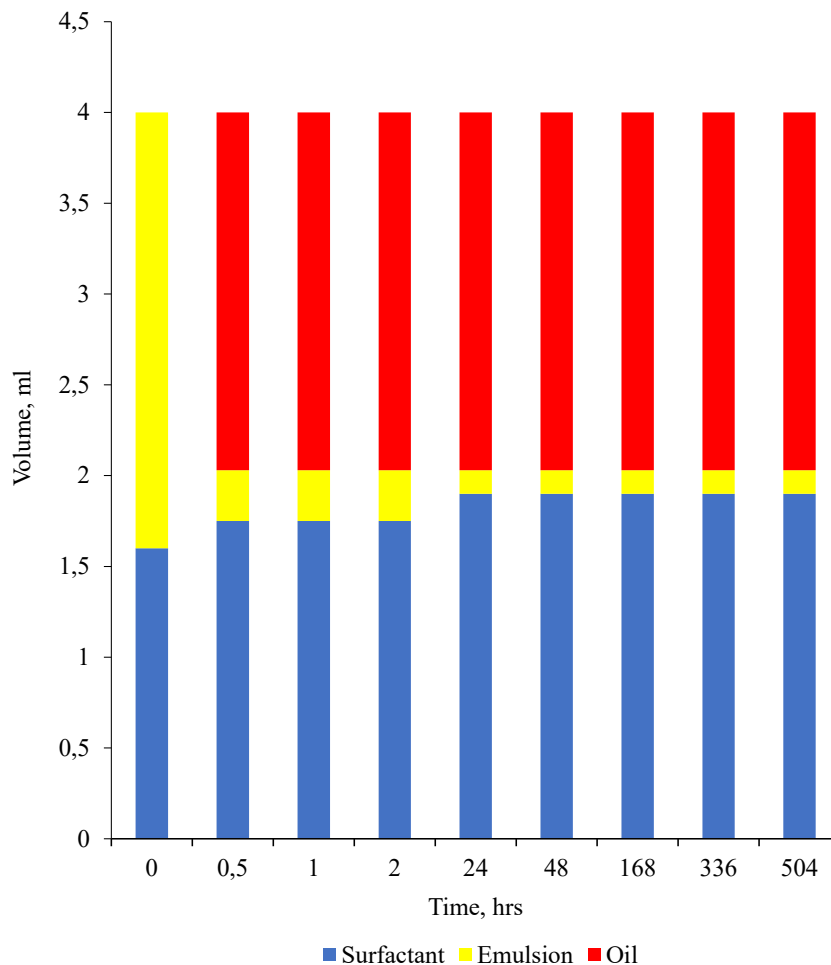


Figure 6
Phase behavior test results at a concentration of 2.5% at a salinity of 10,000 ppm

between oil and rock and increases oil mobility, which contributes to increasing RF (Lager et al. 2008; Tang & Morrow 1997).

Other information that can be obtained from Figure 8 is about the recovery factor based on the surfactant flooding scheme. The application of surfactant injection with a concentration of 2.5% at salinity of 10,000 ppm increased the recovery factor of 23.49%. In this case, the recovery factor for the surfactant concentration of 2.5% at salinity of 10,000 ppm was greater than that of a concentration of 2.0% at salinity of 6,000 ppm with an increase in the recovery factor of only 14.14%. This can be caused

by four factors, namely the volume of the middle phase emulsion, interfacial tension (IFT), viscosity and contact angle (wettability).

Three factors were found in the surfactant solution with a concentration of 2.5% at salinity of 10,000 ppm, namely a larger middle phase emulsion volume, higher viscosity and lower contact angle (strongly water-wet) which were positively correlated to the recovery factor. Meanwhile, the IFT value in the 12-week thermal stability test of the surfactant solution was higher than the solution with a concentration of 2.0% at salinity of 6,000 ppm which was positively correlated to the recovery factor.

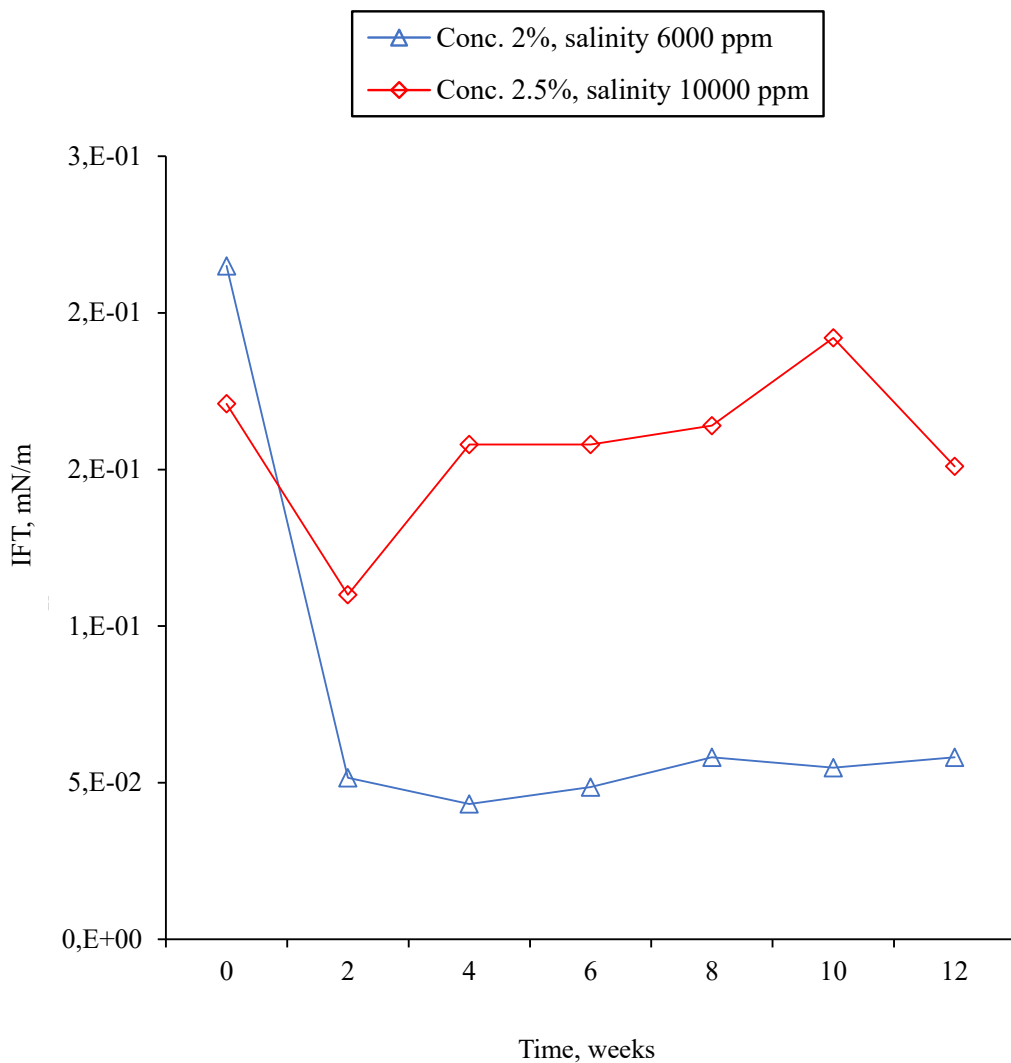


Figure 7
IFT and thermal stability test results

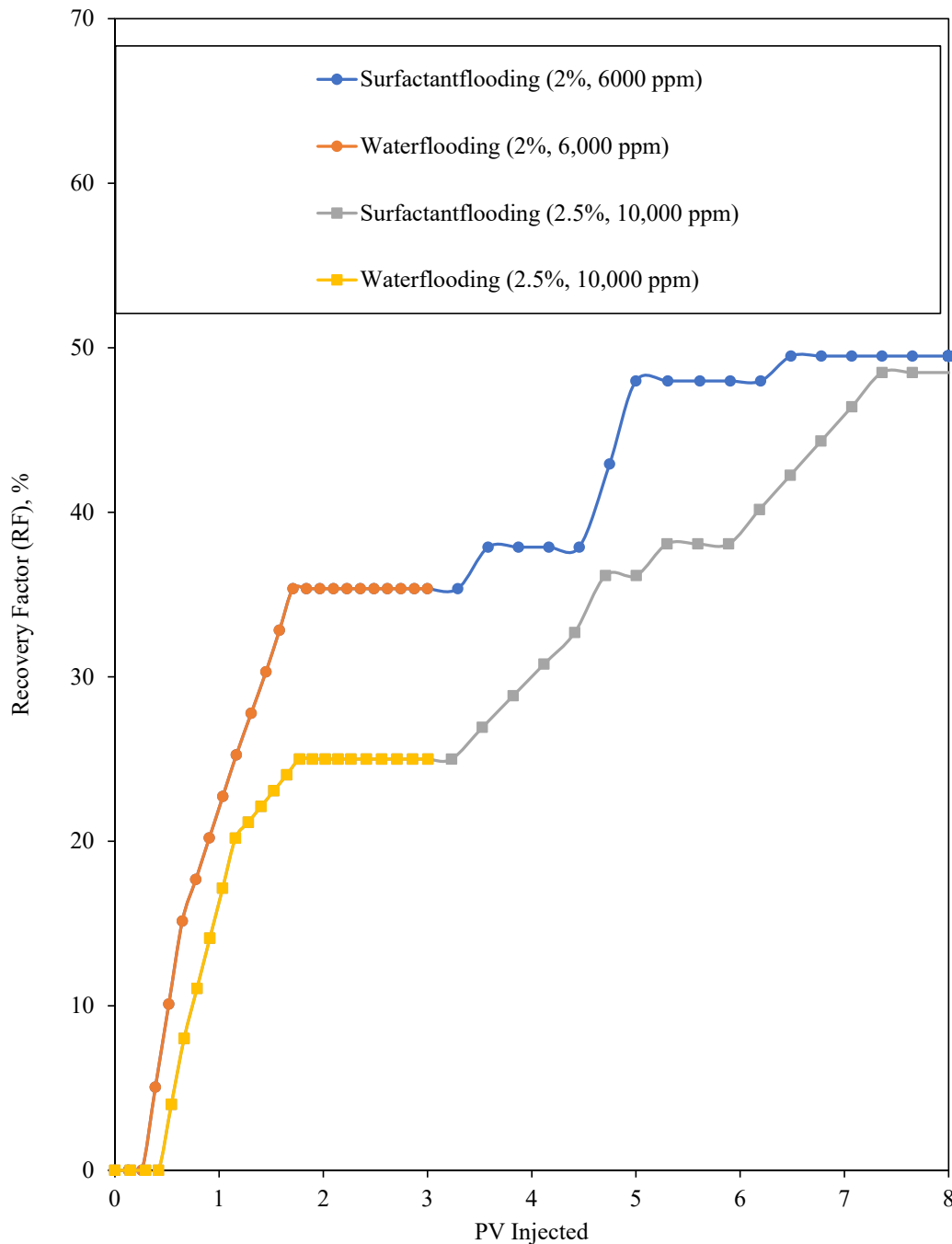


Figure 8
Coreflooding test results

CONCLUSION

Based on the results of the research that has been carried out, several statements can be made as follows. In the aqueous stability test, the concentration of three concentrations of *Sapindus rarak* surfactants containing brine, namely a concentration of 2.0% salinity of 6,000 ppm and a concentration of 2.5% and 3.0% salinity of 10,000 ppm have been run. While in the phase behavior test, surfactants with a concentration higher than 1.5% at

a salinity of 6,000 ppm and a concentration of 2.0% and 2.5% at a salinity of 10,000 ppm produced a middle phase emulsion type. The thermal stability of surfactant concentration of 2.0% salinity 6,000 ppm with oil 42.92° API was concluded to be quite stable in weeks 2 to 12. Meanwhile, the thermal stability of surfactant 2.5% salinity 10,000 ppm with oil 42.92° API was concluded to be quite stable for 12 weeks because it gave relatively the same value. The concentration of *Sapindus rarak*

surfactant and salinity affect wettability. The results of the wettability test of *Sapindus rarak* surfactant at a concentration of 2.0% and a salinity of 6,000 ppm obtained a contact angle of 26.86°. While at a concentration of 2.5% and a salinity of 10,000 ppm the contact angle was 23.28°. The results of the surfactant flooding test at 6,000 ppm salinity and 2.0% concentration increased the recovery factor by 14.14%. While at 10,000 ppm salinity and 2.5% concentration increased the recovery factor by 23.49%. This study offers a great opportunity to include green alternatives to improve conventional chemical-enhanced oil recovery techniques.

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GLOSSARY OF TERMS

Symbol	Definition	Unit
API	American Petroleum Institute gravity	°
V	Volume	ml
	Concentration	%
FR	Filtration Rate	
IFT	Interfacial Tension	mN/m
ϕ	Porosity	%
RF	Recovery Factor	%
	Salinity	ppm
γ_g	Specific Gravity	
μ	Viscosity	cP

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