Application of Sodium Ligno Sulphonate as Surfactant in Enhanced Oil Recovery and Its Feasibility Test for TPN 008 Oil

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Abstract. One of enhanced oil recovery (EOR) methods is using surfactants to reduce the interfacial tension between the injected fluid and the oil in old reservoir. The most important principle in enhanced oil recovery process is the dynamic interaction of surfactants with crude oil. Sodium ligno sulphonate (SLS) is a commercial surfactant and already synthesized from palm solid waste by another researcher. This work aimed to apply SLS as a surfactant for EOR especially in TPN 008 oil from Pertamina Indonesia. In its application as an EOR’s surfactant, SLS shall be passed feasibility test like IFT, thermal stability, compatibility, filtration, molecular weight, density, viscosity and pH tests. The feasibility test is very important for a preliminary test prior to another advanced test. The results demonstrated that 1% SLS solution in formation water (TPN 008) had 0.254 mN/M IFT value and was also great in thermal stability, compatibility, filtration, molecular weight, viscosity and pH test.

1 Introduction

The development of chemicals for the enhanced oil recovery (EOR) in Indonesia has been done by many researchers [1]. A surfactant can be used to reduce the interfacial tension between the injected fluid and the oil in the reservoir. However, Indonesian national oil industries are still using surfactants which are imported from other countries that in fact, the price is very high. Therefore, cheap and well-performing surfactants are urgently needed[1].

The dynamic interaction between the surfactants and the oil in the reservoir is the basic principle in EOR process [2]. The surfactant should interact very well with the oil, and it can be seen from the interfacial tension values. A surfactant with low IFT value and low adsorption on the reservoir rock material is a good candidate before continuing to core flooding process [3]. Interfacial tension analysis is very important as the initial analysis prior to preliminary tests such as core flooding and another advanced test.

Sodium ligno sulphonate is a well known commercial surfactant that can be synthesized from lignin [4] which is isolated from the waste of crude palm oil industry [5][6][7][8]. This surfactant is very potential if applied in the Indonesian oil field considering that Indonesia have big palm oil industry. However, sodium ligno sulphonate has not been tested for the feasibility to Indonesian crude oil. This study is very
important for tested the feasibility as an EOR agent through IFT, compatibility, phase behavior, thermal stability, filtration, molecular weight, viscosity and pH test. Surfactants with low prices and sustainable raw material can be obtained. This study can be a novelty in the field of surfactants in Indonesia, especially for TPN 008 oil.

2 Experimental
All chemicals used were of analytical grade from Merck and Co. Inc (Ethanol, Methanol, NaHSO₃, NaOH, and H₂SO₄). Chemicals with technical grade are oil palm empty fruit bunches from PT Asiatic Persada Sungai Bahar, Jambi, aquadest from CV Progomulyo, dead oil TPN-008 and formation water sample with code TPN-008 from Pertamina Indonesia. The instruments used in this study included infrared spectrophotometer (FT-IR, Shimadzu Prestige-21), IFT Meter TX500D Spinning Drop Tensiometer, and Viscosity kinematic P 906 size 150.

Lignin isolation from oil palm empty fruit bunches isolated by using batch method with reaction temperature, system pressure, concentration of NaOH, the ratio of fibers to solvents and reaction time of 170 °C, 15 atm, 1% (w/v), 9% (w/v), respectively, and the reaction was carried out for 5 hours. The black liquor was acidified until the pH reached 1, and the formed solid lignin was filtered and dried [5].

Synthesis of SLS was carried out by refluxing lignin to NaHSO₃ solution for 4 hours. The reaction was conducted under reflux conditions at 97 °C and the mass ratio of lignin to the NaHSO₃ solution, concentration of NaHSO₃ solution, reaction temperature, and reaction time were 0.3 M, 0.1 M 97 °C, respectively [4]. The 1% of SLS in formation water TPN 008 tested for feasibility as an EOR agent through IFT (temperature of test of 60 °C and root speed of 6000 r/min), compatibility (temperature of test of 60 °C), phase behavior (temperature of test of 60 °C), thermal stability test (temperature of test of 60 °C), filtration rate (0.45 µm), molecular weight (viscometer), viscosity (ASTM D 445-07) and pH test.

3 Results and Discussion
3.1 FT-IR for determination of lignin and SLS structure
To determine the key functional groups from lignin, the FTIR spectrophotometer was used. The spectra are presented in Figure 1. The existence of OH-stretch (3425 cm⁻¹), CH-stretch (2924 and 2854 cm⁻¹), C=C aromatics (1512 and 1604 cm⁻¹), asymmetry C-H stretch (1458 cm⁻¹), syringyl rings (1327 cm⁻¹), guaiacyl rings (1219 cm⁻¹), C-O either stretch (1033 cm⁻¹), and C-H aromatics (840 cm⁻¹) groups were a sign that the isolation of lignin was successful.

To determine the key functional groups of SLS, determination was conducted by using FTIR spectrophotometer (Figure 2). The existence of OH-stretch (3433 cm⁻¹), CH-stretch (2916 and 2846 cm⁻¹), C=C aromatics (1512 and 1604 cm⁻¹), -SO₂ (1465 cm⁻¹), S=O asymmetric stretch (1118 cm⁻¹), S-O stretch (1) (1026 cm⁻¹), and S-O stretch (2) (825 cm⁻¹) groups were a sign that the synthesis of SLS was successful.
3.2 Analysis of interfacial tension (IFT), phase behaviour, compatibility and thermal stability test

Water and oil are immiscible. However, in the presence of surfactants, they are miscible as the oil can be dissolved in the surfactant micelle nuclei and the surfactant is soluble in water. Combination between oil-water-surfactant mixture can form a lower-phase (water-soluble) emulsion, middle-phase emulsion (called microemulsion, soluble in oil and water), and upper phase emulsion (soluble in oil).

These tests are needed to see the performance of the surfactant as an EOR agent. All test have been done using dead oil and formation water. The results are shown in Table 1. Sodium lignosulphonate will be confirmed to be good as surfactant for an EOR agent when IFT value was obtained on a scale of $10^{-3}$, no precipitate in the compatibility test for 1 to 24 hours, and formed stable microemulsion in the phase.

Figure 1. IR Spectra of lignin

Figure 2. IR Spectra of SLS
behavior test for 24 hours. From IFT, compatibility and phase behavior analysis showed that SLS well performed as an EOR agent. It can be seen by the compatibility phase behavior and thermal stability tests from SLS. There are no precipitate formed in the solution, formed a stable microemulsion and stable in reservoir temperature as surfactant (Figure 3). Nevertheless, IFT value from sodium lignosulphonate was very high (0.254 mN/M).

| Test                      | Results                                      | Explanation                                      |
|---------------------------|----------------------------------------------|--------------------------------------------------|
| IFT (interfacial tension)| 0.254 mN/M                                   | not achieved                                     |
| Compatibility             |                                              | no precipitate                                   |
|                           |                                              | 1 hour                                           |
| Phase behavior            |                                              | no precipitate                                   |
|                           |                                              | 24 hours                                         |
|                           |                                              | Middle layer have formed like a white froth wherein thick and clear. The oil and surfactant are still visibly emulsified after shaking process. |
|                           |                                              | 1 hour                                           |
| Thermal stability         | 0.254-0.0809 mN/M                            | very stable for 3 months                         |
The filtration ratio test was performed to identify the presence of sediment in the surfactant solution. When the surfactant injection process in the reservoir, it is expected that the injected surfactant would not produce precipitates. If the injected surfactant produces precipitates, blocking of the reservoir inlet could occur and inhibit the production process of the oil. Filtration was done using a filtration tool which is designed as Figure 4.

In this filtration process, the flow rate of the surfactant was observed. The filtration test was carried out by passing a fluid (a surfactant liquid) through a 0.45 μm filter (filter membrane) at a constant pressure and calculating the time required by the fluid to reach a given volume. The rate was determined by recording the time per 50 mL of the solution accommodated in the sample container. From this analysis, the streamed sample contained no impurities, the flow rate would tend to be constant so that the filtration ratio (the ratio of filtration time per given volume) would be equal to or close to 1. The results of filtration test on 1% surfactant was given in Table 2 and Figure 5.
Table 2. Filtration ratio of 1% SLS solution to 0.45 µm membrane.

| Volume (mL) | 1st test time (s) | 2nd test time (s) | 3rd test time (s) |
|-------------|-------------------|-------------------|-------------------|
| 50          | 142.91            | 37.56             | 85.13             |
| 100         | 326.44            | 77.06             | 179.56            |
| 150         | 523.2             | 116.71            | 273.13            |
| 200         | 721.26            | 155.95            | 366.71            |
| 250         | 922.75            | 195               | 460.71            |
| 300         | 1123.14           | 234.24            | 554.33            |
| 350         | 1325.25           | 273.91            | 649.53            |
| 400         | 1525.5            | 313.23            | 744.9             |
| 450         | 1727.55           | 354.18            | 839.54            |
| 500         | 1928.6            | 394.73            | 933.9             |

Filtration Ratio 1.10 1.03 1.00

Figure 5. Graphic of filtration ratio of 1% SLS solution

3.4 Analysis of molecular weight of SLS
Molecular weight measurements of the SLS are according the Mark-Houwink-Sakurada equation where pure solvent of 0.1 M NaCl was used. Then, the SLS solution was applied to the viscometer column until t₀, t₁, t₂, t₃, dan t₄ were obtained. Through calculations, relative viscosity (ηₛ) and specific viscosity(ηₛ$p$) were obtained. Then the graph was ηₛ$p$/C against C was made and by using Huggin’s equation, [η] value can be obtained as an intercept of the graph. The average molecular weight of the polymer can be obtained by following the Mark-Houwink-Sakurada equation: [η] = K (Mₚ)$^{1.3}$ [9]. The result of SLS molecular weight was 21.351 g.mol$^{-1}$ and the calculation are given in Table 3 and Figure 6.
Table 3. Viscosity data of the SLS solution

| C (g/mL) | time (s) | ηr | ηsp | ηsp/C |
|----------|----------|----|-----|-------|
|          | I        | II | III | Average |       |
| 0.0000   | 67.80    | 67.80 | 67.80 | 67.80  |       |
| 0.0002   | 68.75    | 68.76 | 68.85 | 68.79  | 1.01  |
| 0.0004   | 69.30    | 69.33 | 69.35 | 69.33  | 1.02  |
| 0.0006   | 69.02    | 69.04 | 69.05 | 69.04  | 1.02  |
| 0.0008   | 68.44    | 68.42 | 68.43 | 68.43  | 1.01  |
| 0.0010   | 68.61    | 68.63 | 68.63 | 68.62  | 1.01  |

Figure 6. Graphic $\eta_{sp}/C$ versus $C$

Refering to the data presented in Figure 4, calculation of molecular weight of SLS could be calculated by using the following equations.

The relative viscosity ($\eta_r$) is expressed as $\eta_r = \frac{\eta}{\eta_0} = \frac{t}{t_0}$ (1)

The specific viscosity ($\eta_{sp}$) is expressed as $\eta_{sp} = \eta_r - 1$ (2)

The reduced viscosity ($\eta_{red}$) is expressed as $\eta_{red} = \frac{\eta_{sp}}{C}$ (3)

Where $C$ is the concentration of surfactant (g/mL)

Mark-Houwink-Sakurada equation is: $[\eta] = K (M_v)^{\alpha}$.

$K$ value and $\alpha$ for sodium lignosulfonate in 0.1 M NaCl solution is 0.12 mL/g and 0.66. Therefore the ($M_v$) value is 21.351 g.mol$^{-1}$
3.5 Analysis of pH and viscosity of 1% SLS solution

This analysis was conducted to determine the pH and viscosity values of the surfactant (SLS). In common, surfactants should not be alkaline or have a pH above 10 and preferably not too concentrated because it will clog the pores of the rocks. If it happens, the oil cannot be mined. The results of pH and viscosity tests are given in Table 4 and Table 5.

| Table 4. pH value of surfactant and formation water TPN 008 |
|-------------------------------------------------------------|
| Sample                                      | pH         |
| Formation water TPN 008                          | 8,3        |
| 1% SLS solution in formation water TPN 008      | 9,5        |

| Table 5. Kinematic viscosity of 1% SLS solution in formation water TPN 008. |
|-----------------------------|
| Temperature (°C) | Kinematic viscosity (mm²/s) |
|-----------------|-----------------------------|
| 30              | 0,844                       |
| 40              | 0,705                       |
| 50              | 0,673                       |
| 60              | 0,545                       |

From this analysis, it can be concluded that 1% SLS solution in formation water TPN 008 could be applied at an oil reservoir. It can be seen by the pH value of 1% SLS solution in formation water TPN 008 very close with pH value of formation water TPN 008 and still below 10. For kinematic viscosity at reservoir temperature of 60 °C also gave a small value (below 1 mm²/s).

4 Conclusion

In conclusion, we have reported the results of EOR agent feasibility test demonstrated that 1% surfactant solution has 0,254 mN/M IFT value and also great in thermal stability, compatibility, filtration, molecular weight, viscosity and pH test. From this research, it is found that SLS cannot be applied as EOR agent although it fulfill some requirements. It is necessary to modify the SLS either by adding some additive or altering some functional groups to produce a suitable surfactant as EOR agent.

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