Synthesis of Sodium Ligno Sulfonate (SLS) Surfactant from Black Liquor Waste and The Potential Test for EOR in Ledok Field Cepu

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Abstract. Chemical injection in Enhanced Oil Recovery (EOR) with surfactants is known to reduce the value of Interfacial Tension (IFT) of oil and water which can increase oil mobility. EOR has been considered a promising technology to increase national oil production through the revitalization of existing wells in Indonesia, particularly in the Ledok field, Cepu. This study aims to test core flooding on a laboratory scale with EOR surfactant from biomass waste pulp industry, Black Liquor, from Sodium Lignosulfonate (SLS) on porous sandstone media. SLS is produced from lignin which is isolated from Black Liquor waste. In this study, crude oil from Ledok, Cepu, Central Java was used which was characterized first. To determine the effectiveness of surfactant performance before core flooding, several tests such as water stability test, IFT test, CMC (Critical Miselization Concentration) test, and filtration test have been carried out. For the core flooding test, a 1.5% surfactant concentration is injected continuously at 70 °C. The core flooding results show that the compatibility test shows that SLS is compatible with Ledok's natural formation water. Filtration tests show that SLS using membrane 42 produces larger FR solutions. The core flooding test results showed the best reservoir temperature for SLS surfactants was formulated at 70 °C with a recovery of 87%. Therefore, the results show that SLS surfactants show promising results for sandstone media. Important for this research is the hydrodynamic study, studying the correlation flow rate of 4.06 Cm/sec, giving the Reynold value in the best porous medium of 0.3, and the best yield of 75% w/w. Keywords: Sodium Lignosulfonate (SLS); EOR; Core Flooding; Sandstone

1. Introduction

Along with economic and population growth, energy demand in Indonesia continues to increase. Various sources have stated that the highest final energy consumption between 2000 and 2014 occurred in the industrial sector, followed by households and transportation, and the lowest was commercial and others [1] [2], [3]. Indonesia, even though it is a country that has large oil reserves, has continued to decline from year to year [4]. Petroleum is the main energy source in Indonesia with a consumption rate of 1.2 million kiloliters per day. The existence of old wells causes the current exploitation stage to be not optimal due to the limited use of technology. Various efforts to increase the production of these old wells need to be made to provide thrust from the reservoir so that the fluid rises to the surface. Injection of
external chemicals is also known to increase oil production. This technology itself is known as Enhanced Oil Recovery (EOR) [5].

The application of the EOR method in Indonesia is currently very limited due to the limited ability of researchers, so based on available data in the literature, Indonesia is trying to develop EOR technology [6]. Indonesia applies EOR with imported chemicals so that it becomes less economical and less efficient. Surfactants are compounds that can reduce the interface stress of two fluids that do not mix between solids and fluids attached to rocks. Thus, the main function of surfactants is to reduce Interfacial tension (IFT) to increase oil recovery.

The surfactants that are applied in various tests in Indonesia are usually petroleum-based commercial surfactants. This study used a surfactant based on sodium lignosulfonate (SLS) whose raw material was obtained from lignin from pulp mill biomass waste, namely black liquor. The lignin obtained is then sulfonated to produce SLS. This cheap and abundant raw material is expected to increase the efficiency of EOR and be environmentally friendly [7]. The surfactants will then be tested in core flooding on a synthetic sandstone-type core.

Studies of making SLS from biomass have been carried out by many previous researchers, for example from oil palm empty bunches (Ismiyati, et al., 2012; Rachim, Mirta and Thoha, 2012, oil palm husk dust (Mulyawan, et al., 2015); bagasse (Setiati et al. 2016); rice straw (Murni et al., 2013, Rifatus Saufiyah, 2015; Anwar Ma’ruf, 2017).

Several studies related to SLS surfactants for EOR applications have been discussed by previous researchers, including by Novita and Wa, (2011), Abdurrahman (2017), Damanik, et al. (2018) and Anggara et al. (2019). The reference of researchers who refer to the study of surfactant injection on 35 mesh sized synthetic sandstone rocks, among others, is the study of Anggara et al. (2019). The SLS compatibility test used in this study has met the requirements as a surfactant, as a fluid in the core flooding, it can increase oil recovery by 87% crude oil from the Ledok field using natural formation water from the same field. The success of SLS surfactant injection can be seen from several other criteria such as the filtration test, the filter ratio is less than 1.2, has a stable emulsion phase, IFT can reach $10^{-1}$ dyne / Cm occurs at a concentration of natural formation water of 5000 ppm and a concentration of 1.5% v/v SLS.

This study aims to test core flooding on a laboratory scale with EOR surfactant from biomass waste pulp industry, black liquor, from Sodium Lignosulfonate (SLS) on porous sandstone media. SLS is produced from lignin which is isolated from black liquor waste. In this study, crude oil from Ledok, Cepu, Central Java was used which was characterized first.

### 2. Materials and Method

#### 2.1. Materials

Sodium lignosulfonate (SLS) which is isolated from lignin from the black liquor of PT. Indah Kiat Pulp and Paper Mill in Pekanbaru, Riau, West Sumatra. Aqua dest were obtained from the Integrated Laboratory of Diponegoro University, Semarang. Crude oil and natural formation water are obtained from LDK 154 well, Ledok village, Cepu, Central Java, Indonesia.

#### 2.2. Report on the Analysis of Crude Oil from Ledok

The report on the results of the analysis of crude oil from Ledok was obtained from the Ministry of Energy and Mineral Resources of the Republic of Indonesia. Human Resources Development Agency for Energy and Mineral Resources Development Center for Oil and Gas Human Resources 'Testing Laboratory' Jalan Sorogo No.1 Cepu 58315, Blora Regency - Central Java, based on letter Number: Analysis Number: 790/08/20, dated August 27, 2020

| NO | Parameters               | Unit | Result | Testing Methods         |
|----|--------------------------|------|--------|-------------------------|
| 1  | Base Sediment and Water  | % v / v | 0      | ASTM D 4007-11 (reapproved 2016) |
Kinematic Viscosity \( \text{mm}^2 / \text{sec} \) 2,232 ASTM D 445-17a
Pour Point °C -3 ASTM D 5853-11
Water Content % Volume trace ASTM D 95-13 (reapproved 2018)
Sediment Content % wt. 0 ASTM D 473-07 (reapproved 2017)
Density 15 °C kg/m\(^3\) 833.8 ASTM D 1298-18
Salt Content lb / 1000 bbl (PTB) <0.2 ASTM D 3230-13
API Gravity
SG 60/60 °F 38.1 ASTM D 1298-18
0.8342 ASTM D 1298-18

The report on the results of the analysis of natural formation water from Ledok was obtained from the Ministry of Energy and Mineral Resources of the Republic of Indonesia. Human Resources Development Agency for Energy and Mineral Resources Development Center for Oil and Gas Human Resources 'Testing Laboratory' Jalan Sorogo No.1 Cepu 58315, Blora Regency - Central Java, based on letter Number: Analysis Number: 791/08/20, dated August 27, 2020

| NO | Parameters | Unit | Result | Testing Methods |
|----|------------|------|--------|----------------|
| 1  | Calcium (Ca\(^{2+}\)) | mg/L | 131.9 | AAS |
| 2  | Magnesium (Mg\(^{2+}\)) | mg/L | 217.6 | AAS |
| 3  | Carbonate (CO\(_3\)^{2-}\)) | mg/L | 0 | Titrimetric |
| 4  | Hydrogen Carbonate (HCO\(_3\)-) | mg/L | 34.4 | Titrimetric |
| 5  | Chloride (Cl\(^-\)) | mg/L | 10.444 | APHA 4500-Cl\(^-\), 23rd Ed 2017 |
| 6  | Sulfate (SO\(_4\)^{2-}\)) | mg/L | 5.35 | APHA 4500- SO4\(^{2-}\), 23rd ED 2017 |
| 7  | Iron (Fe\(^{3+}\)) | mg/L | <0.0808 | SNI 6989-84-2019 |
| 8  | pH | | 8.73 | SNI 6989.11:2019 |
| 9  | SG Water | | 1.014 | Pycnometry |

2.3. Characterization Methods
FT-IR spectrophotometer (SHIMADZU with DRS-8000) was used to analyze infrared spectroscopy using KBr 6 pellets. KBr pellets consist of 300 mg KBr and 0.1 mg fine powder SLS samples. The scans were recorded from 400 to 4000 cm\(^{-1}\) at a resolution of 16 cm\(^{-1}\). [13].

2.4. Optimization Method
The Square Methodology (RSM) Response Software is used for the optimization program according to Statistica 6, [17], SLS is made at the optimum condition, namely Temperature 79.7 °C; The bisulfite lignin ratio of 4.6 w / w and a pH of 8.3 obtained Yield of SLS 89.96% w/w.

3. Results and discussions
3.1. FTIR Test
The identification of SLS sulfonation results using an FTIR spectrophotometer is intended to see the mechanism of the lignin sulfonation reaction to form SLS. The reaction mechanism for lignin sulfonation is by substituting SO\(_3\) with –OH groups; C = as well as the guaiacil (methoxyl) group contained in lignin at the absorption wavenumber 2924; 2852 cm\(^{-1}\) and absorption band 1708.93 cm\(^{-1}\). The success of lignin sulfonation is evidenced by the formation of sulfonate groups (SO\(_3\)) which is indicated by the presence of an absorption band at wave number 1219; 1128 cm\(^{-1}\) and the S = O and SO ranges shown in the wavenumbers range 1006.84 cm\(^{-1}\) and 902.69 cm\(^{-1}\), as in Figure 3.2.
Figure 3.1. FTIR Results of commercial Sodium Lignosulfonate

Figure 3.2. FTIR Results of Sodium Lignosulfonate from Black Liquor

The SLS formed has similarities with standard sodium lignosulfonate (SLS) from PT. Aldrich (Figure 1) which has a sulfonate group (SO$_3^-$) vibration range at wave number 1120 - 1230 cm$^{-1}$ and asymmetric S = O group at wavenumbers 1005 - 1055 cm$^{-1}$ and an SO range at wavenumber 750-1000 cm$^{-1}$ (Ismiyati, et al., 2019). The characteristics of SLS include purity, moisture content, reducing sugar, pH, and density. The characteristics of the SLS resulting from the sulfonation have similarities with the commercial standard SLS which is the characteristic of lignosulfonate as a commercial dispersing agent (Table 3.1).

| Parameter                  | SLS Sulfonation | SLS Commercial |
|----------------------------|-----------------|----------------|
| Purity, % w/w              | 80,05           | 96             |
| pH: 20% solution           | 7,20            | 7,50           |
| Reducing sugar, %          | 1,07            | 7,00           |
| Water content, %           | 3,00            | 7,00           |
| Spec gravity, kg/m$^3$     | 368,42          | 402,40         |

FTIR spectroscopy is used to determine hydroxyl groups (OH) with sulfonate groups (-SO$_3^-$), it can be seen in Figures 3.1 and 3.2 that in general sodium lignosulfonate synthesized from black liquor is not the same but has almost the same groups, namely 3369 cm$^{-1}$ hydroxyl group -OH, 1593 cm$^{-1}$ -C=O aromatic group, 1456 cm$^{-1}$ -S=O group, 1423 cm$^{-1}$ -CH aromatic group, 1216 cm$^{-1}$ asymmetric SO$_2$ group, =C=S and 1102 cm$^{-1}$ symmetric groups SO$_2$=C=S.
The identification of SLS sulfonation results using an FTIR spectrophotometer is intended to see the mechanism of the lignin sulfonation reaction to form SLS. The reaction mechanism for lignin sulfonation is by substituting SO3 with –OH groups; C = as well as the guaiacil (methoxyl) group contained in lignin at the absorption wave number 2924; 2852 cm\(^{-1}\) and the absorption band 1708.93 cm\(^{-1}\) (Figure 3.2). The success of lignin sulfonation is evidenced by the formation of sulfonate groups (SO3\(^{-}\)) which is indicated by the presence of an absorption band at wave number 1219; 1128 cm\(^{-1}\) and the S = O and S-O ranges shown in the wavenumbers range 1006.84 cm\(^{-1}\) and 902.69 cm\(^{-1}\).

The SLS formed has similarities with the standard sodium lignosulfonate from Aldrich (SLSAldrich) which has a vibrational range of the sulfonate group (SO3) at wave number 1120 -1230 cm\(^{-1}\) and a symmetric S = O group at wave number 1005 - 1055 cm\(^{-1}\), and the SO range at wavenumbers 750-1000 cm\(^{-1}\).

### 3.2. Optimization Test

The SLS synthesis process was carried out by reacting to 2 grams of lignin from black liquor with 1.7 mL of 40% bisulfite solution and 60 mL of distilled water. The pH is adjusted from 9 to 9.5 with NaOH. The SLS solution is evaporated at 100 °C. The concentrated solution which is formed is then filtered through a Buchner funnel using a vacuum pump. The filtrate obtained was SLS containing lignin and bisulfite residue. The filtrate is mixed with methanol to precipitate the insoluble bisulfite, shaken vigorously, and then filtered over a Buchner funnel. SLS filtrate and residual lignin were evaporated to thicken SLS. The concentrated SLS obtained is dried at 60 °C to a constant weight, this is the result that will be obtained optimized by Responsibility Surface Methodology (RSM).

The experimental design by optimizing the synthesis of sodium lignosulphonate (SLS) from pulp and paper biomass waste was carried out using RSM with Central Composite Design (CCD). The ranges and independent variables are given in Table 5.3. The response of each variable and the interaction of the variables was evaluated using the quadratic polynomial equation model. The equation of the quadratic polynomial is described in Eq. (1).

\[
Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_1^2 + \beta_5 X_2^2 + \beta_6 X_3^2 + \beta_7 X_1X_2 + \beta_8 X_1X_3 + \beta_9 X_2X_3 + \varepsilon
\]

The relationship between the Y response and the independent variable X is:

\[
Y = f(X_1, X_2, ..., X_3) + \varepsilon
\]

Where Y is the response or dependent variable, Xi is the independent variable/factor (i = 1, 2, 3, ..., k) and \(\varepsilon\) is the error.

Analysis using the RSM method was carried out to study the effect of temperature (X1), lignin, and sodium bisulfite ratio (X2) and pH (X3) on SLS yield. The research data are as follows:

| Variables (X) | Range and levels | Range | -α | -1 | 0 | +1 | +α |
|---------------|------------------|-------|----|----|---|----|----|
| Temperature (X1), °C | 71.63 | 75.00 | 80.00 | 85.00 | 88.37 |
| Ratio lign/bisulfite (X2), g/g | 2.33 | 3.00 | 4.00 | 5.00 | 5.67 |
| pH (X3) | 6.33 | 7.00 | 8.00 | 9.00 | 9.67 |

The data used to assess the effect of process variables on the synthesis of SLS from lignin black liquor and sodium bisulfite are given in Table 5.3. Table 5.3 shows that the SLS results are in the range of 39.38% to 89.96%. Quadratic regression analysis was applied to experimental data. The correlation of the response variable and test variable is determined by the second-order polynomial equation according to the coded value as expressed by Eq. (3):
With the correlation coefficient, $R^2 = 0.9942$. Where $Y$ is the yield of SLS and is calculated using a regression model, $X_1$, $X_2$, and $X_3$ are variables that represent temperature, ratio, and pH. From equation (3) the order of the most influential variables are pH, ratio, and temperature. The significance of each variable and the interaction of the variables was evaluated with a p-value at 95% significance. Analysis of variance (ANOVA) using the Fisher F test was used to assess each model obtained. STATISTICA 6 is used to analyze the model. The observed and predicted value of the SLS yield.

The response ($Y$) is examined and is described in Figure 3.3. This observation is made to determine the suitability between the observed value and the predicted value. The coefficient of determination ($R^2$) of 0.9942 for $Y$ indicates that the observed and predicted values have a good agreement. The quality of conformity of the yield model ($Y$) was tested by analysis of variance (ANOVA) as described in Table 3. Table 3 shows that the F-value of the SLS count is 24.82 from the F distribution table ($F_{(0.95; 7, 16)} = 3.53$) at the 5% significance level. This shows the relationship between process variables and yield.

**Table 3.3. The critical value of the SLS results. (Critical value of various variables)**

| Observasi 1 | Kedatan optimal | Observasi 2 |
|-------------|-----------------|-------------|
| Temperature, °C | 71.63340 | 79.66969 | 88.36660 |
| Ratio, g/g   | 2.323668 | 4.58311 | 5.67332 |
| pH           | 6.326688 | 8.31575 | 9.67332 |

From table 3.3. Using the RSM analysis method, it was found that the optimal operating conditions for making SLS were at a temperature of 79.67 °C, a lignin/bisulfite ratio of 4.6, and a pH of 8.32, and the best yield was at 93.20% w/w. Then it is depicted in Figure 3.3 to visualize the relationship between the three best variables to obtain optimal operating conditions.

**Gambar. 3.3. Respons tiga dimensi: (a) Yield vs suhu dan rasio, (b) Yield vs pH dan rasio. (Pramudono, 2018)**

Based on figure 3.3, it is known that the results of research on making SLS with variations in temperature, lignin/bisulfite ratio, and pH and the response are Yields, [17] found that the higher the yield temperature, the higher the pH, the yield is also getting higher. However, the yield is limited by the ratio of reactants. Finally, the bisulfite-lignin reactant ratio is best achieved at 4.6: 1. Using the RSM software with the Statistica 6 program, the optimal yield was achieved at 89.96% w/w.
The approach (model) proposed after doing the experiment with the theoretical result obtained an equation which can be illustrated in Figure 3.4.

### 3.3. Core Flooding Test

#### 3.3.1. Compatibility Test

The compatibility test is the earliest performance test to determine whether a surfactant is compatible with the brine of a reservoir and is one of the most important considerations in surfactant selection for EOR applications. If the surfactant is completely dissolved and no precipitation is formed, this indicates that the surfactant is compatible with brine. The compatibility test is positive/good if the surfactant and brine can mix completely without lumps in the solution. Negative value / cannot be used as a surfactant formula on EOR if precipitation occurs or does not mix. The test results showed that the surfactant Sodium Ligno Sulfonate against formation water had a positive compatibility test result. Sodium Ligno Sulfonate surfactant is completely dissolved in the absence of precipitation/sediment formed. The surfactant compatibility test results can be seen in Figure 3.5 clear and dissolved.

![Figure 3.5. (a) The results of the SLS black liquor 0.2 compatibility test; 0.3; 0.4; 0.5% in brine](image)

Using the Indonesian National Standardization (SNI) method the results of characterization of SLS black liquor are similar to commercial SLS, meaning that the SLS black liquor character is made similar to commercial SLS (table 3.4).

| No | Parameter          | Unit | SLS Commercial | SLS from black liquor | Method |
|----|--------------------|------|----------------|-----------------------|--------|
| 1  | Water content      | % w/w| 23.96          | 24.62                 | SNI 2012-0813-122059 |
| 2  | Ash content        | % w/w| 31.78          | 32.23                 | SNI11247-0442-2009  |
| 3  | Organic compounds  | % w/w| 39.97          | 41.76                 | SNI 03-2831-1992   |
| 4  | Volatile matter    | % w/w| 4.98           | 5.14                  | SNI 13-3999-1995   |
| 5  | Density (solid)    | g/mL | 1.09           | 1.12                  | SNI 06-2441-1991   |

Table 3.4. Characterization of SLS yield

![Figure 3.4. Experimental results compared theoretically (R² = 0.9942)](image)
(b) The results of the commercial SLS 0.2 compatibility test; 0.3; 0.4; 0.5% in brine

Into 2 ml of surfactant with 8 ml of brine water (3000 ppm) into the test tube, shake the test tube until homogeneous. Observe discoloration and sediment and let stand for 28 days. After 28 days, the results of the compatibility test on SLS 0.5%, 1%, and 1.5% showed that the SLS and brine solutions were completely mixed without any precipitate (figure 3.5). Compatibility is stated positive or good if the surfactant and brine water are completely mixed without clumping in the solution, have a negative value, or cannot be used as a surfactant formula in EOR, if there is precipitation or are not mixed [19].

This test was carried out to find out the compatibility between surfactant and formation water from a reservoir. This test must be performed first before the other tests. If the surfactant was not soluble/compatible, then the surfactant was deemed unfit for the reservoir in question [22]. This is because the sediment will allow blockages or plugging in injection wells which can damage the reservoir. Moreover, good solubility indicates that the surfactant has good capability to decrease IFT, thereby making the oil more water-soluble and easier to recover [27], [28]. Therefore, the compatibility of surfactant is an absolute requirement that must be met to determine the appropriate surfactants as surfactants for EOR applications.

Surfactants that are not completely dissolved or indicate the formation of a precipitate by themselves or are caused by other components in the formation water (brine) forming dissolved solids cannot be used as surfactants for EOR applications. This is because, in addition to the loss of useful material, some deposits may clog or cause plugging in the injection well which can cause reservoir damage. Passing the SLS compatibility test to be used is an absolute requirement that must be met to determine the appropriate surfactant as a surfactant in core flooding in enhanced oil recovery (EOR) if it is compatible/positive and further tests can be carried out on sodium lignosulfonate solution to determine its performance.

The surfactant solution is said to meet the compatibility test as a chemical flooding surfactant is a solution that forms an o / w emulsion, is clear (clear solution), is not cloudy (hazy solution) and does not form a precipitate. The surfactants obtained were stable and met the test because they obtained a solution that was fixed and did not clot during storage. Surfactants can be used for the EOR process when they dissolve in formation water and do not form deposits that can interfere with the flow and can reduce their surface tension (IFT) (Eni, Suwartiningsih and Sugiharto, 2008). The formation of sediment by surfactants can clog the pores in the reservoir, thus blocking the process of taking up the remaining oil.

3.3.2. Filtration Test

The filtration test was carried out by passing 500 ml of surfactant solution through Whatman filter paper sizes 41 and 42 at a pressure of 1.5 bar. Every 50 ml of surfactant solution that passes through filter paper, the time is recorded. Then a volume (ml) versus time (second) graph is made (Hidayati et al., 2012) [13]. In the reservoir, the surfactant will pass through the permeable membrane to the pores of the reservoir rock to move and sweep away the remaining oil due to pressure from the injection well. This allows the surfactants to pass through heterogeneous rock pores which have different permeabilities which affect the flow rate or slow the flow rate of the surfactants in dispersion. The filtration test is attempted to see the fluid flow rate (injected formation water and surfactant formula) through the permeable wall with a certain gap or pore size that represents the formation or condition of the permeable reservoir rock. The following is a graph of the results of filtration tests for synthetic formation water (NaCl) solutions and surfactants with filter membranes 41 and 42 at room temperature.
Based on the graphic (figure 3.7) of the results of the filtration test using various sizes of filter paper, it is known that the results of the filtration test on the injected synthetic formation water solution and the surfactant have differences. The SLS surfactant flow rate is slower than the formation water solution flow rate. The injection formation water filtration test shows a relatively constant slope. This means that the injection formation water does not cause a blockage. Meanwhile, SLS surfactants have an inconsistent line slope, which means that there is a tendency for surfactant molecules to clog when the surfactant dissolves across the membrane. The flow rate of the surfactant formula is slower because the surfactant formula has a solute (micelle) that is filtered and covers the membrane pores. These micelles adhere to and block the porous membrane so that the flow rate of the surfactant formula is slightly inhibited [19].

### Table 3.5. FR values in the filtration test

| Filtration Test on size | FR value |
|------------------------|----------|
| Whatman 41             | 0.711    |
| Whatman 42             | 0.710    |

Surfactants suitable for use in EOR applications have a filtration rate (FR) of less than 1.2. From the research results, it was found that the surfactant solution 0.5% had a good performance on filter paper sizes 41 and 42. This can be seen in Table 1 where the FR value obtained is close to the expected FR.
value, which is less than 1.2. At the smaller pore size, Whatman 42 paper size, has a slightly lower FR value than the larger pore size, Whatman 41 paper size. This test can describe synthetic cores that have a certain permeability that can pass liquids and dissolved materials. Inside it. If a blockage occurs in the membrane used for infiltration so that the flow rate of the solution is inhibited, likely, this will also occur in the injection in the reservoir and can be a factor in reservoir damage.

3.3.3. Phase Behavior Test

In this study, a test tube was carried out to determine the phase behavior, aiming to obtain the optimum concentration of the surfactant solution when the maximum microemulsion was formed in the system between the oil and the surfactant solution. The formation of the maximum microemulsion shows the lowest IFT value so that the optimum yield value can be obtained. In the middle phase emulsion, the emulsion formed is temporary, so that in a short time it can separate back into oil and surfactant solution. Visual observation of the mixed-phase behavior between petroleum and the surfactant formula Sodium Ligno Sulfonate at reservoir temperature (70 °C). The results of the surfactant phase behavior test can be seen in Table 4.3

Table 3.6. Visual Observation Results of the SLS Black Liquor Surfactant Phase Behavior Test

| SLS            | day-0 | day-7 | day-14 | day-21 | day-28 |
|----------------|-------|-------|--------|--------|--------|
| from Black Liquor |       |       |        |        |        |

Into the 7 ml of surfactant into the tube, then added 7 ml of crude oil. Place the tubes on a rack and store them at a reservoir temperature of 70°C. Turn each tube 3 times until the liquid is mixed, do not shake it, and observe and note changes in the interface of the liquid for 1 month. The results of the phase behavior test indicate the presence of a middle phase which indicates the performance of the surfactant, namely the solubility of oil on the surfactant.

![Commercial SLS 0.5%, 1%, and 1.5%](image1)

![SLS 0.5%, 1%, and 1.5%](image2)

**Figure 3.8. Results of the phase behaviour test, % SLS in formation water**
The formation of the lower phase/type II (-) microemulsion, the microemulsion formed in the lower phase is indicated by the excess of the surfactant solution in the mixture of oil and surfactant indicating that the type of microemulsion is lower phase/type II (-), which indicates that the surfactant solution is at a low salinity level (low salinity), besides indicating a low level of salinity, it is also thought to be due to the characteristic factors of the SLS oil and surfactant itself. Visual observation of the mixed phase behavior between petroleum and the surfactant formula Sodium Ligno Sulfonate at reservoir temperature (70 °C), concluded that a lower phase/type II (-) microemulsion was formed. The microemulsion formed in the lower phase is indicated by the excess of the surfactant solution in the mixture of oil and surfactant indicating that the type of microemulsion is lower phase/type II (-), which indicates that the surfactant solution is at a low salinity level, apart from indicating a low salinity level, This is also thought to be due to the characteristic factors of the SLS oil and surfactant itself. This indicates that the performance of the surfactant solution is not good until the 30th day. In this test, the solubility ratio of oil and water to heating time is also seen from the calculation seen from the phase behavior test pipettes. The oil solubility is determined by the oil volume from the surfactant volume in the microemulsion. The oil solubility ratio is used for type I and types III phase behavior. During 30 days of observations that have been made it is known that the behavior of the phase formed is the lower phase. In the lower phase, only two phases are formed, namely the water phase and the oil phase, so that the solubility of the oil can be seen concerning heating time.

Based on the results of visual observations of the mixed-phase behavior of petroleum with commercial SLS surfactants and black liquor at reservoir temperature (90 °C), it was concluded that a lower phase/type II (-) emulsion was formed, as in Table 4.3.

The type of emulsion most expected in the EOR / surfactant injection process is the middle phase emulsion (type III phase) or at least the lower phase emulsion (type II phase (-)) (Sugihardjo et al., 2001). In these conditions, the resulting interfacial stress value is a very low IFT value so that the petroleum pressing process can be ascertained to be effective (Nopianto, Hambali, and Suarsana, 2017).

The phase behavior test also calculates the ratio of oil solubility to heating time. The oil solubility ratio is read and measured from the change between the initial water level and excess oil. The oil solubility parameter is calculated by the following calculation:

\[ P_o = \frac{V_o - V_{o'}}{V_s} \]

Where:
- \( P_o \) = Oil solubility
- \( V_o \) = volume of initial oil
- \( V_o' \) = volume of oil during observation
- \( V_s \) = surfactant volume

The ratio of oil solubility to heating time can be seen in Figure 4.3.

![Figure 3.9. Results of SLS phase behavior test](image-url)
good because it can form the bottom emulsion. It can be seen, from various high oil solubility concentrations at a surfactant concentration of 0.5%

3.3.4. CMC Test

The addition of surfactants will cause surface tension to drop to a minimum. The addition of the surfactant concentration will then cause the surfactants to aggregate to form micelles. In micelles, the hydrophobic surfactant groups are directed to the interior of the aggregate, and the polar head groups are directed to the solvent. These micelles are in a dynamic balance between surfactant molecules and are influenced by the molecular structure of the surfactants.

The concentration of micelle formation is called critical micelle concentration (CMC). CMC is an important property of surfactants which indicates the critical concentration limit of surfactants in a solution. The surface tension will decrease until CMC is reached. After CMC is reached, the surface tension will be constant, which indicates that the interface is saturated and micelles are formed (Figure 3.10).

The CMC test can also be done using the conductometric method [13]. Figure 10 shows the relationship between SLS concentration and conductivity. The results showed that the CMC price was 2.5%. The results showed that the higher the surfactant molecular weight, the smaller the CMC. [20], reported that the CMC value of natural surfactants isolated from Zyziphus Spina Christi leaves was 3.35%.

![Figure 3.10. Relationship between concentration and SLS conductivity](image)

3.3.5. Core Flooding Test

The Core Flooding Test is carried out by preparing the core rocks in advance. The rock used is sandstone with a size of 35 mesh. 35 mesh sandstone rock is inserted into the core mold. Sandstone rocks are molded by means of a press with the help of a jack. After the core is installed, a natural water formation solution is injected into the core. This saturation is carried out to condition the media according to the expected salinity until all the pores in the media are filled with a natural water formation solution which is marked by the absence of air bubbles coming out of the porous media. After that, the crude oil is injected to push out the salt solution in it. This is done until there is no more brine solution coming out. The volume of the stored salt solution is considered to be the same as the volume of oil retained in the porous medium. Oil saturation is then carried out for 1 hour. After that, weigh the core. Furthermore, brine injection is carried out until the oil does not come out anymore. The volume of the brine solution and the stored oil was measured. Then inject a surfactant with a base of 500 mL of each concentration, namely 0.5%, 1%, 1.5%. The collected solution is measured for volume, density, and viscosity. Tool for injecting oil, brine, and surfactants. Separation of the retained brine and oil solution after injection of natural formation water.
3.3.5.1. Inter Facial Tension (IFT) Test

The IFT of a fluid is the power required by a fluid to increase the area by one unit area. The greater the face tension of a fluid, the greater the energy required to form a unit of surface area between the liquids. The stress of the oil-water interface is quite large so that the highest primary recover and secondary recover oil. The method used in analyzing IFT is the spinning drop or rotating drop tensiometer method, using the principle of geometric reduction, where the effect of the density difference between two liquids and their rotation determines the IFT value obtained (Salager, 2005). The droplet measurements showed an increase in size as the SLS concentration increased. The surfactant is fed into a rotating horizontal tube containing a drop of curing oil, as the rotation of the tube creates a centrifugal force against the tube wall. The oil droplets will begin to form into elongated shapes. This extension stops when the interfacial tension and centrifugal force are balanced, that’s when the interface stress can be measured by measuring the diameter of the oil that extends, so the smaller IFT value is obtained because the higher the temperature, the increased mobility of the surfactant molecules and the cohesion force between molecules becomes very small where in this study the optimum temperature is 70°C. This is related to the kinetics of the reaction, namely the higher the temperature, the more active the particles are so that the collisions that occur often cause the reaction rate to increase. There is a deviation at a certain temperature depending on the SLS concentration, that is, the IFT value obtained is even small.

The oil contained in the oil reservoir is first pressed with brine. The sweeping process does not produce oil anymore, so the sweeping is continued with the surfactant. The choice of the use of sodium lignosulfonate surfactant because it has good sweeping efficiency which can reduce the interfacial tension of oil and water, it is hoped that the oil trapped in the pores can be pushed out. This phenomenon is predicted because of the small interaction between the surfactants. The measurement of the interfacial tension with the spinning drop tensiometer uses the principle of geometric reduction, where the effect of the density difference between the liquid and its rotation determines the IFT value obtained (Salager, 2005). The mechanism of action of reducing surface tension by surfactants can be from the mechanism of surfactant molecules in the hydrophobic and hydrophilic phases. When oil and water are placed in a container, the difference in interface voltage between the two fluids is so different that they cannot mix. The surfactant is dripped in water, the droplets are round because the surface tension of the oil is different from that of water. The presence of surfactants can reduce the surface tension of these two fluids. The mechanism that occurs when the surfactant is present, the head of the surfactant which is hydrophilic will enter the hydrophilic phase while the tail will enter the hydrophobic phase. After adding the surfactant, the oil droplets will be distributed on the surface, and the shape changes to a flat (widened). The changing shape of the droplets is caused by a decrease in the surface tension of oil and diesel.

During the IFT measurement, sodium lingo sulfonate preparation using NaCl solution aims to create conditions such as in a petroleum withdrawing reservoir. This salt solution can affect the IFT results obtained. The presence of certain salts such as NaCl causes the reduction of the oil-water surface tension to become ineffective. This can occur because NaCl is easily dissociated into its ions, namely Na + and Cl-. Likewise, the surfactant in this area, namely the RSO3H surfactant, is easily dissociated into RSO3- and H +. The consequence that occurs when these ions are formed, they can bind to form HCL and RSO3Na where HCL and RSO3Na are not surface-active substances so they cannot reduce the oil-water surface tension. The reaction mechanism that occurs in the oil well after the surfactant is injected, the surfactant has a hydrocarbon base group and binds to the ends of inorganic compounds (SO3). The chemical formula of the surfactant is RSO3H with the R group being a hydrocarbon chain group. This type of surfactant in water will ionize to form RSO3- and H +. When the RSO3-molecular ion comes into contact with a compound that is nonpolar (oil), the R group tries to exert an adhesion force (oil-surfactant), while the surfactant molecules themselves will work the cohesion force between the RSO3- . The effect of this adhesion force will reduce the resultant value of the cohesion force of the oil itself, which causes the surface force of the oil and water to decrease. There is a repulsive force between the surfactant head which is negatively charged (RSO3-) and the sandstone which is negatively charged because it contains silica compounds (SiO2-). This repulsive force causes the surfactant that binds to the oil in the R group moving away from the rock and this causes the wettability of the rock to turn into water-loving (Ashayer et al, 2000). In general, the IFT formulation shows that low interfacial stress occurs when the radius of the oil droplet is small (Rm), that is, a drop will lengthen and the rotational
speed is slow, while high voltage will require a high rotational speed or a larger radius \((R_m)\) (Dong et al., 2013). The interface voltage spontaneously forms from air and solution and can slowly change over time and then remains constant. This change in interfacial tension is due to the rearrangement of the molecules in the bulk solution. When the interface is formed, the molecular composition at the interface is the composition in the bulk solution. The interface tension then gradually decreases until it stabilizes at a constant level, the IFT value can be seen in Figure 3.11.

**Figure 3.11. IFT values at various temperatures and research concentration SLS**

Based on the graph in Figure 3.11, the higher the temperature and concentration of the study, the smaller the IFT value. The best IFT value in this study was achieved at a temperature of 70°C, at an SLS concentration in natural formation water of 1.5% w/w. In this research, the IFT value is \(10^{-3.3}\).

### 3.3.5.2. Hydrodynamic Studies

In the oil and gas industry, variations in interfacial tension with temperature and pressure affect the movement of fluid in the reservoir. The total oil recovery obtained at various reservoir temperatures can be seen in Figure 12. The oil recovery values were around 70% to 80% at 60°C, 73% to 84% at 70°C, 76% to 88% at 80°C, and 79% to 89% at 90°C. It is evident that increasing reservoir temperature would increase the oil recovery [22]. Injection of SLS surfactant could increase oil recovery from synthetic core pores due to its ability to reduce the IFT between oil and reservoir rocks. Surfactants could break the interface tension of oil bound to rocks, reduce the occurrence of water blocking and change the wettability of rocks to become water-like [32] [33]. Moreover, it can also be seen that oil recovery increased along with increase in pore volume. On the other hand, the higher the temperature, the smaller the PV would be. This means that the amount of surfactant injected affected the oil yield [34].

**Table 3.6. Oil yield at different conditions**

| Oil Time SLS flow Oil volume (s) rate yield (ml) (cm/s) (%) |
|----------|----------|----------|----------|----------|
| 25       | 30       | 60       | 11.78    |
| 29       | 60       | 6.84     | 69       |
| 31       | 101      | 4.34     | 74       |
| 33       | 115      | 4.06     | 79       |
| 33       | 125      | 3.73     | 79       |
| 33       | 136      | 3.43     | 79       |
Table 3.6 shows the percentage of oil yield during the experiment, at different oil volumes and flow rates. It can be seen that the highest yield was 79%, and the best-operating conditions were obtained using 35 ml of oil, with 115 s injection time and oil flow rate of 4.06 cm/s.

![Figure 3.11. Average oil recovery for each treatment](image)

During the core flooding test at 80 and 90°C, the increase in oil recovery was not significant. Using surfactant injection of 3 PV, oil recovery at 80°C was 88% while oil recovery at 90°C was 89%. It was found that an increase in temperature will increase oil recovery by 11-12%. In terms of working safety, 80°C surfactant injection conditions are better because the operation is safer under normal conditions with oil recovery that is not much different from when the temperature is 90°C. In addition, surfactants are organic compounds which at high-temperature conditions will be more easily degraded. The highest oil yield was recorded at 80°C, indicated by an increase in oil yield by 12%, compared to 11% during surfactant injection at 90 °C. It can be concluded that the best reservoir temperature is 80 °C, in terms of high oil recovery and safety considerations. Similar core flooding test experiment using Thermoviscosifying polymer reported an increase in oil recovery by 13.5% at 85 °C [35].

![Figure 3.12. Curve between flow rate and oil yield](image)
The hydrodynamics study is to study the flow rate of oil in porous media with a value of 4.06 cm/sec. The Darcy equation provides a correlation of flow rates in porous media with a Reynold number of 0.3 occurring at a yield of 75% (Figure 3.12).

![Correlation between SLS Concentration with Reynold and Yield](image1.png)

**Fig. 3.12. Correlation between SLS Concentration with Reynold and Yield**

Figure 3.13 shows the curve between surfactant flow rate and oil yield. It can be implied that higher oil flow rate will decrease the oil yield obtained. Higher oil flow rate resulted in high friction at the rock pores, thereby decreasing the amount of oil exiting the oil discharge hole [22]. According to Allawzi and Al-Jarrah [36], injecting surfactants at a higher flow rate will decrease the contact area between surfactant and oil, causing channeling to occur at various locations in the bed, thereby reducing the oil recovery. Meanwhile, Figure 14 shows the response of dimensionless numbers (Reynold, Schmidt, and Sherwood number) against the oil yield. It can be seen that the lower the value dimensionless numbers, the lower the flow rate would be, thereby increasing the oil yield. This is because a high flow rate will cause friction by rock pores so that the oil that comes out of the oil outlet is getting smaller.

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5. Conclusion

This research studied the synthesis of Sodium Ligno Sulfonate using lignin that has been isolated from black liquor, after which the SLS surfactant was characterized and tested using the Enhanced Oil Recovery method. The SLS yield obtained was 87%, with the IFT value of $10^{-1}$ dyne/cm. Characterization tests of SLS showed good results: the surfactant was soluble in water and showed no lumps or deposits, thermal stability test showed that the surfactant did not form clots during 15-day heating, and during filtration test, the FR values found in this experiment were below 1.2, indicating good performance for EOR applications. The best reservoir temperature for the formulation of SLS was 70 °C with an oil recovery increase of 12%. The best-operating conditions were obtained during the experiment using 35 ml of oil, 115 seconds of testing time, and an oil flow rate of 4.06 cm/s. It was also evident that a higher oil flow rate will decrease the oil yield. Overall, the synthesis of SLS from Lignin contained inside Black Liquor from pulp industry waste showed promising results, with acceptable surfactant characteristics that are suitable for EOR applications. Despite this, there are several suggestions possible for further research, for example by implementing the IFT test to better understand the characteristics of SLS surfactant and also using native core or original reservoir rocks to better illustrate the oil recovery.

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