Characterization and Purification of Surfactant Sodium Ligno Sulfonate (SLS) From Biomass Waste in The Application Of Enhanced Oil Recovery (EOR)

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Abstract. The waste of pulp and paper industry in the form of Black Liquor still contained a large amount of lignin (12-46%). The high lignin content had the potential to make Sodium Ligno Sulfonate (SLS) Surfactants by reacting Lignin with Sodium Bisulfite. Isolation of Lignin From Black Liquor was carried out at room temperature of 30°C, using sulfuric acid (H₂SO₄) and 1N NaOH. The purpose of this study was to characterize SLS formed both physically and chemically. Characteristics of SLS were formed compared to commercial SLS. The SLS purification results were carried out by comparing the SLS results of the experiments with commercial SLS using Fourier Transform Infra Red (FTIR) equipment, and the purity was tested by UV-Vis. For Enhanced Oil Recovery (EOR), SLS was tested based on its characteristics using screening tests.

Keywords: Biomass Waste, Characterization, Purification, SLS, EOR

1. Introduction.
Balck Liquor was a pulp and paper industry waste, containing 30-45% lignin. Lignin from Black Liquor ([1], [2]), had the potential to produce Sodium Ligno Sulfonate (SLS) surfactants by reacting Lignin with Sodium Bisulfite. Lignin was synthesized with Sodium Bisulfite ([3], [4], [5]) to form SLS. Industrial development in the world was followed by increasing demand for surfactants. Unfortunately, the need for these surfactants was not followed by increased production.
The purpose of the sulfonation process was to change the hydrophilicity of lignin by introducing a sulfonate group as a hydrophilic group. The sulfonation process that occurred was reacting lignin with sodium bisulfite (Denli, 2010). The sulfonate group in lignosulfonate made lignosulfonate possess an amphipatic (surfactant) structure. Sulfonate was known as the general formula R-SO₃Na which was a simplification of R-O-SO₃-Na sulfate ([7], [8]). R was a C8-C22 aromatic carbon atom group which was a hydrophobic group, while a hydrophilic group consists of carboxylic, sulfonate, phosphate or other acids. Sodium lignosulfonate surfactant was categorized in anionic surfactant because it had sulfonate and salt groups (-NaSO₃-) which were anions (heads) and hydrocarbon groups were tail ([8], [9], [4]).

These Research Objectives were Reviewing SLS Characterization and Purity, Tests and Assessing the best operating conditions of the sulfonation process in the manufacture of sodium lignosulfonate (SLS) surfactant.
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amphipatic (surfactant) structure. Sulfonate was known as the general formula R-SO3Na which was a simplification of R-O-SO3-Na sulfate ([7], [8]). R was a C8-C22 aromatic carbon atom group which was a hydrophobic group, while a hydrophilic group consists of carboxylic, sulfonate, phosphate or other acids. Sodium lignosulfonate surfactant was categorized in anionic surfactant because it had sulfonate and salt groups (-NaSO3-) which were anions (heads) and hydrocarbon groups were tail [8,9,4]. The novelty of this research was that surfactants for the petroleum industry (non renewable) were obtained from biomass waste (renewable) and involved the role of groups in their functional studies.

2. Experimental
2.1. Materials
Black Liquor was purchased from PT. Indah Kiat Pulp and Paper Factory at Pekanbaru, Riau, West Sumatra, Indonesia. Sodium Ligno Sulfonate (SLS) was obtained from lignin of Black Liquor synthesised by using sodium bisulfite. Sulfuric acid, sodium hydroxide, Sodium Bisulfite 40% and demineralized water (aquadest) obtained from PT. Indra Sari Semarang, Central Java, Indonesia. The reaction occurred between the lignin which had been acidified with sulfite salt (Denli, 2010). There were several types of salt sulphites which could be used in the sulfonation. In US Patent No.4,892,588 sulfite salt used was sodium bisulfite [10, 11]. Crude oil used was purchased from Kawengan, Cepu, Central Java, Indonesia.

2.2. Synthesis Process of SLS
This synthesis process was the most important step to produce lignosulfonic salt. The reaction between lignin which had been acidified with bisulfite salt [6]. There were several types of sulfite salts which could be used in sulfonation. In US Patent No.4,892,588 the sulfite salt used is sodium bisulfite [10,11]. Two grams of lignin from black liquor were reacted with 1.7 ml of 40% bisulfite solution, diluted with 60 ml of aquadest. Optimization study using the SLS synthesis Response Surface Methodology (RSM) was obtained at a temperature of 79.67°C, pH 8.32, and Ratio of Lignin and Bisulfite 4.58, a time of 2 hours and a stirring speed of 290 rpm [12,13,14]. The SLS liquid phase was evaporated at a temperature of 100°C. The concentrated solution formed was then filtered through a buchner funnel using a vacuum pump. The filtrate obtained was SLS which contains lignin and bisulfite residue. The filtrate was mixed with methanol to precipitate the insoluble bisulfite, shaken vigorously, and then filtered with a buchner funnel. The SLS filtrate and the remaining lignin were evaporated to concentrate SLS. The concentrated SLS obtained was dried at 60°C to a constant weight, this was the result to be characterized by FTIR and purified by shaken vigorously with methanol solution.

2.3. Enhanced Oil Recovery (EOR)
Enhanced Oil Recovery (EOR) Method was defined as a method that involved the process of injecting chemicals that could cause changes in the character of the reservoir in the form of rock-oil fluids. By the influence of the injected chemical, in this case the SLS surfactant, oil-rock Interfacial tension (IFT) had decreased significantly and the oil yield obtained had increased. Materials injected into the reservoir could be surfactants, polymers, alkalis or combinations. Although the EOR method was sometimes referred to as tertiary recovery, this did not mean that the EOR method was applied after the secondary phase. Some EOR methods could be applied after the primary phase or even during the oil search process [14]. The use of SLS as a surfactant in this study by assessing TFT and the oil yield obtained. For the IFT study to be obtained up to the smallest, even ultra-value.

2.4. Characterization Methods
Characteristics of SLS as a good surfactant for extracting oil from the earth using tests: Compatibility, Interfacial Tension (IFT), Thermal Stability, Phase Behavior and Filtration. All of these tests were conformity tests with brine. Surfactant Sodium Ligno Sulfonate (SLS) was dissolved in a brine with a concentration of 3000 ppm. Brine was made by dissolving 3 grams of NaCl PA into 1000 ml of
aquadest, then stirring for 4 hours. Add 2 ml of surfactant with 8 ml of brine to the test tube, shake the test tube firmly until it was homogeneous. Observe the discoloration and presence of sediments and then left for 28 days and observed on days 1, 7, 14, 21 and 28 whether the surfactant was soluble in brine. To determine the purity of SLS, UV-Vis Spectrophotometer equipment was used. For the EOR (Enhanced Oil Recovery) characteristic of crude oil from Kawengan, Cepu, Central Java, Indonesia was tested using the ASTM procedure (American Standard Testing Material).

3. Results And Discussion
3.1. Purification And Characterization
The method of UV-Vis spectrophotometry was the most suitable for determining sodium lignosulfonate purity (SLS). The UV spectrophotometer - 1240 pharco - 300 in the integrated laboratory of the University of Diponegoro was analyzed. Sodium lignosulfonate (SLS) had a wavelength, $\lambda = 232$ nm. From figure 1, the UV-Vis test obtained the purity of SLS = 65% wt. The test was carried out using a comparison with commercial SLS which was considered to have 100% purity. The standard curve was made for concentrations of 0.005, 0.01 and 0.02% wt. This concentration was relatively low because the origin of SLS-forming lignin from black liquor was quite difficult to separate the precipitating substances together with SLS was formed during washing with methanol.

Fig. 1 The Purity Of Sodium Ligno Sulfonate (SLS)

Fig. 2. Results of surfactant compatibility test 0.2%, 0.3%, 0.4%, 0.5%

The thermal stability test of SLS was carried out to determine the resistance of surfactant to temperature, especially stability with IFT surfactant test, density, and viscosity at reservoir...
temperature. This test was carried out at the temperature of the reservoir at a temperature range of 60°C, 70°C, 80°C and 90°C. Figure 2 showed the solubility characteristics of SLS at various concentrations of completely dissolved brine. Figure 3 showed the stability characteristics of SLS which dissolve perfectly at reservoir temperatures up to 30 days. The filtration test was carried out by passing 500 ml of the surfactant solution through 40, 41, and 42 whatman filter paper or 0.22 micron pore size with a pressure of 1.5 bar. Each 50 ml of surfactant solution that passed through the filter paper, the time was recorded. Then a graph of volume (ml) versus time (seconds) was made. Figure 3 showed that the relatively stable density value in various concentrations in brine showed that the surfactant formula will be able to maintain its performance in reducing IFT in the reservoir, in addition to many other factors that could reduce the performance of surfactants while in the reservoir, such as reservoir rock adsorption.

3.2. Asphaltene Content Analysis
Crude oil from the earth reservoir contained hydrocarbon compounds, water and minerals. Crude oil from various petroleum wells had a different composition. Crude oil from Kawengan, Cepu, Central Java, Indonesia before being used first was analyzed using the aspalten test. This test was carried out by dissolving crude oil with hexane solvent with a ratio of each crude oil and hexan 1:6, 1:8, 1:10, 1:12 then centrifuged at 3000 rpm. This test aims to determine the presence or absence of the content of aspalten in crude oil, the presence of aspalents indicated that crude oil was polar. Polar oil would bind more water in its formation, making it more easily washed away / carried away by water. Based on this aspal test it was known that Kawengan Cepu crude oil had asphalt content ranging from 6-12%, that was in the ratio of 1:6 asphalt content 6%, bitumen content 1:8 8%, 1:10 bitumen content 8%, 1:12 12% aspalten content. In Figures 4 and 5, proved the presence of deposits in the lower part of the crude oil during the aspalten test.

![Fig.3 Density of SLS at Various Concentration and Temperature of Reservoir](image)

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![Figure 4. Kawengan cepu oil asphalten test results](image)
Table 1. Shows The National Standardization Of Indonesia (SNI) Characteristics, UV-Vis and PT Aldrich of SLS from Biomass Lignin Waste.

| No | Parameter                  | Unit   | SLS Ref | SLS from Waste | Method                  |
|----|----------------------------|--------|---------|----------------|-------------------------|
| 1  | Water content              | % w/w  | 23.96   | 24.62          | SNI 2012-0813-122059    |
| 2  | Ash Content                | % w/w  | 31.78   | 32.23          | SNI 1247-0442-2009      |
| 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        |
| 6  | Purity                     | % w/w  | 46-70   | 65             | UV-Vis                  |
| 7  | Molecular Weight           | mol    | Avg     | Avg            | GC-MS                   |
|    |                            |        | 52,000  | 55,000         |                         |

Table 1 showed that the results of characterization of SLS from waste biomass were compared with SLS reference (commercial). Characterization was carried out using the Indonesian National Standardization (SNI) method, while purity tests using UV-Vis and average molecular weight using SLS PT. Aldrich compared the use of GC-MS for SLS from biomass waste. The purity of SLS using UV-Vis was obtained 65% from the reference SLS 46-70%. The molecular weight of 55,000 was caused by various substances other than SLS, for example organic compounds that were above the SLS reference.

Table 2. Analysis of Crude Oil Kawengan, Cepu, Central Java, Indonesia

| No. | Items                  | Unit | Results | Analysis Method |
|-----|------------------------|------|---------|-----------------|
| 1   | Flash Point PM,cc       | °C   | 115     | ASTM D 93       |
| 2   | Pour Point              | °C   | 27      | ASTM D 97       |
| 3   | Distilasi ASTM IBP      | °C   | 241     | ASTM D 86       |
|     | 10% rec. evap.         | °C   | 297     |                 |
|     | 50% rec. evap.         | °C   | 367     |                 |
|     | 90% rec. evap.         | °C   | *       |                 |

*) Temperature decreases

From table 2 the test was based on the AS1M method. For important characteristics of crude oil, for example Flash Point with ASTM D-93, D-97 for Pour Point, and D-86 for Boiling Point. All results qualify as crude oil, that crude could be poured at 27°C, could be distilled from 241°C 10% distilled, 50% distilled at 297°C, and 90% distilled at 367°C or more.
In figure 4 and figure 5 showed that the higher the concentration of SLS in the brine the IFT decreases to a minimum at IFT less than 10^{-1}. The best was at reservoir temperature of 70°C (figure 5). This showed that for the type of Kawengan Cepu crude oil with SLS the concentration of SLS in the brine had the highest concentration of IFT reduction at reservoir temperature of 70°C.

4. Conclusion
Sodium LignoSulfonate (SLS) could be made by reacting lignin from black liquor biomass waste at optimum conditions temperature of 79.67 ° C, weight ratio of lignin and bisulfite 4.58 and pH 8.32 to get the highest SLS results 89.96%. The correlation of the temperature influence to the constant of reaction rate expressed in arhenius equation as follows k = 0.015 exp (-1408.3/T). In the application for EOR, IFT test results showed that the smallest IFT value was 0.52238 dyne / cm at 5% surfactant concentration at 50°C and there was a tendency for the IFT price to be smaller if the concentration of surfactant was greater. The role of sulfonate group SO3 and hydroxyl OH will increase the hydrophilicity of the surfactants until they will increase their performance in decreasing IFT.

Characterization of SLS was tested by the ASTM and SNI method with results that were relatively similar between SLS of black liquor waste biomass compared to commercial SLS. The purity of SLS was obtained by 65% using UV-Vis purity test equipment. The presence of sulfonate groups in
Sodium Bisulfite was to change the hydrophilicity of lignin by introducing a sulfonate group as a hydrophilic group which in addition to reducing IFT also increases yield.

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