Ligno Sulphonate [SLS] Laboratory Testing
For the Recovery of Residual Oil at Ledok Oil Field

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ABSTRACT
Fossil energy much still needed and exhaled in demand every year on industrial sector, household, and transportation in Indonesia. In the other hand, oil gas production has decreases as many of oil and gas reservoirs have saturated with water breakthrough. Therefore, Enhance Oil Recovery [EOR] as one of proposed solution is adopted to optimize the remaining reserves of oil wells exploitation, especially from mature field that has lesser production capacity towards production problems. Ledok field Cepu district, Central Java Indonesia has many mature wells that produce liquids with its water cut higher than 90 %.

The objective of study is to determine which variables that are involve on black liquor or Sodium Ligno Sulphonate [SLS] application as surfactant for EOR on laboratory measurements. Core flooding measurements had been developed and measured. Crude, formation water, and SLS surfactant were injected into the artificial cores. FTIR test show appearance of Sulphonate and Ether alkyl in its composition. Preliminary results show the surfactant has optimum performance to recover oil up to 79% with IFT value 10^{-1} dyne/cm.

Keywords: Laboratory study; surfactant, core flood; crude exploration; EOR

ARTICLE HISTORY
Received: 16 May 2022
Revised: 06 Jun 2022
Accepted: 05 Jul 2022

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1. Introduction
The last few years, the industry in Indonesia, especially in the transport industry increased, so the need for fuel is also increased. The main source of fuel reserves for Indonesia and the world, generally derived from petroleum. However, the world’s oil reserves are running low. One of the efforts that can be done to solve the problem is to optimize the mature wells, such as wells in the Field Ledok, the Town of Cepu through the acquisition of the tertiary recovery method, which is called Enhanced Oil Recovery (EOR). EOR is a technique to enhance remaining oil reserves from the field that are already in production with the method of production of primary and secondary. The EOR methods that commonly has been used is chemical injection, where the chemicals are injected into the production layers. This method uses a surfactant and/or a polymeric material and alkaline, which serves to change the physical properties of the oil in the reservoir, making it easier for the oil to flow to the surface[1].

Injection with surfactant is one of the EOR methods which a very attractive alternative, because it will be beneficial to the process of EOR can be run effectively and efficiently. Surfactants, especially in this study, the use of SLS to increase the viscosity of the fluid in water, and simultaneously surfactants can reduce the voltage of the interface or as an emulsifier[2].
Arjmand and Kalbasi (2018)[3], have examined the injection of surfactants with the addition of the polymer. The results showed that the injection (flooding) a mixture of polymers and surfactants is very good, because of the addition of polymer can increase the viscosity of the fluid so that it can absorb more oil.

The purpose of this research is to study the best variable from the synthesis of SLS, as well as studying the results of the synthesis of surfactant materials as chemical injection on the process of Enhanced Oil Recovery (EOR).

2. Materials and Methods

Sodium Lignosulfonate (SLS) which was synthesized from black liquor from PT. Indah Kiat Pulp and Paper Industry in Pakanbaru, Riau, West Sumatra. Sulfuric acid and sodium hydroxide as a raw material for isolating lignin from black liquor obtained from PT. Indrasari Semarang. Crude oil and natural formation water are obtained from LDK XYZ well, Ledok Field, Cepu, Central Java, Indonesia. Commercial lignin and sodium lignosulfonate under the PT. Aldrick Yogyakarta and aquadest were obtained from the Integrated Laboratory of Diponegoro University Semarang, Central Java [9].

The analysis reports of crude oil Field Ledok obtained from the 'Laboratory Testing' Center for Human Resources Development (PPSDM), Oil and gas, Road Sorogo No.1 Cepu 58315, Blora Regency, Central Java.

FT-IR Spectrophotometer (SHIMADZU with DRS-8000) is used to analyze the infrared spectroscopy using pellets of KBr (6). Pellet KBr consisting of 300 mg of KBr and 0.1 mg of the fine powder samples of the SLS. Scanned were recorded from 400 to 4000 cm\(^{-1}\) at a resolution of 16 cm\(^{-1}\).[5]
Software Response Methodology Meter (RSM) is used for optimization program according to the Statistics[6], and SLSnya made on the optimum conditions, namely Temperature 79,7 oC; the Ratio of lignin bisulfite 4,6 w/b and pH 8.3; so that the obtained Yield SLS 89,96 % w/w.

3. Results and Discussion

Figure 1 shows the influence of the variables temperature, pH, the ratio of lignin and bisulfite, time and the rate of stirring on the yield of SLS. Based on Table 1, it is seen that the value of the yield 94 % is best achieved at a temperature of 80 °C, pH = 9, the ratio of lignin and bisulfite = 4, time 2 hours and stirring speed of 290 rpm. Table 1 shows the best conditions from the results of the SLS.

Table 1. The Best Conditions of SLS Yield

| Variables               | Best conditions |
|-------------------------|-----------------|
| Temperature, °C         | 80              |
| pH                      | 9               |
| Ratio ligni bisulfite, g/g | 4               |
| Time, hour              | 2               |
| Rate of stirring, rpm   | 290             |

Figure 1. The influence of Temperature (a), pH (b), the Ratio of Lignin/Bisulfite (c), Time (d) and Stirring Speed (e) the Yield of SLS
Figure 2 shows the spectrum of the SLS Reference sample obtained (red line) and the spectrum of the SLS from waste lignin (blue line). The ribbon between the 3425.88-3541.1 cm\(^{-1}\) are characteristic of the hydroxyl group (strain O-H) in the structure of the phenolic and aliphatic. Peak in 2337.72; 2361 and 2337.72; 2360.87 cm\(^{-1}\) shows the strain SO3 C-H MS in the methyl group (-CH3), methylene (= CH2/-CH2-) and methoxy (-OCH3). The peak in 1512.19, 1564.34, 1512.19, 1635.14 show group C-H. In the area of sulfites (SO3), ribbon weak found on 1450.47 cm\(^{-1}\) (blue line) and 1450.57 (red line).

The uptake in the 1512.19 cm\(^{-1}\) is the cluster of aromatic combined with C-H in the deformation field, while 1564.34 and 1635.14 cm\(^{-1}\) is the stretching of C-H aliphatic-CH3 (non-OCH3) and phenolic -O-H. The ribbon on the 1450.47-1450.57 cm\(^{-1}\) shows the SO3. The ribbon at 1111 cm\(^{-1}\) and at 964.41-1033.85 cm\(^{-1}\) (blue line) and the 1033.85 cm\(^{-1}\) in the reference SLS, at 1041 cm\(^{-1}\) at SLS from waste lignin (Prakosa, 2017). The spectrum of FT-IR shows the characteristic spectral SLS, namely the ribbon at a distance of 964.41 and 1450.57 cm\(^{-1}\). The deformation of the S-O aromatic on 948.9 cm\(^{-1}\) and S-O on 1041,56 cm\(^{-1}\) appear as SO3 aromatic on the 1450,47 and 1450,57 cm\(^{-1}\) or <964 cm\(^{-1}\) (figure 2).

In laboratory experiments, 2 ml of the surfactant added with 8 ml of salt water (3000 ppm) into the test tube, shake the test tube until homogeneous. Observed the color and sediment changes then let stand for 28 days. After 28 days, the results of the compatibility test on the SLS of 0.5%, 1%, and 1.5% showed that the solution of SLS and the brine is mixed perfectly without any sediment occurred (figure 3). Compatibility tested positive or better, if the surfactant and salt water mixed perfectly without clumping on the solution. Negative value, or can not be used as a formula of surfactants in EOR, if precipitation occurs or not mixed[10].

Testing the filtration is done by passing 500 ml of a surfactant solution through filter paper Whatman size 41 and 42 at a pressure of 1.5 bar. Every 50 ml of a surfactant solution that passes through the filter paper, note the time. Then graph the volume (ml) versus time (seconds) created (Hidayati et al., 2012)[13]. In the reservoir, the surfactant will pass through the membrane permeable towards the pores of the reservoir rock to move and swept the rest of the oil due to pressure from the injection wells. This allows the surfactant pass through the pores of the rocks are heterogeneous, which has a permeability of different influencing the rate of flow or slow flow rate of the surfactant in the dispersion. Testing the filtration is carried out to see the flow rate of the fluid (formation water that is injected and surfactant formula) through the permeable wall with a slit or pore size certain that represents the formation or the condition of the reservoir.
rocks are permeable. Here is a chart of the test results of the filtration of a solution of synthetic formation water (NaCl) and surfactants with membrane filters 42 at room temperature.

![Image](image.jpg)

**Figure 3.** SLS with concentration 0.5%, 1%, and 1.5% mixed with formation water

Based on the graph (figure 4) the results of the testing of filtration 42 size of paper filter, the results of the testing of filtration from the rate of formation water injected and the rate of surfaktan have differences. The flow rate of the surfactant SLS slower than the flow rate of formation water. The test filtration formation water injection shows a slope that is relatively constant. That is, the formation water injection does not cause a blockage. Meanwhile, the surfactant SLS has the slope of the line that is not consistent, meaning that there is a tendency of the molecules of surfactant clogged when the surfactant is soluble across the membrane.

Flow rate formula surfactant is slow because the formula surfactants have dissolved substances (micelles) which is filtered and cover the pores of the membrane. Micellar-micellar is attached to and blocking the porous membrane so that the flow rate formula surfactant slightly inhibited[10].

Surfactants suitable for use on the application of EOR has the filtration rate (FR) of less than 1.2. From the results of the research showed that the surfactant solutions of 0.5 % has a good performance on the filter paper sizes 41 and 42. This can be seen in Table 2, where the value of the FR obtained close to the value of FR is less than 1.2. On the pore size is small, the size of the paper Whatman 42 has a value of FR is slightly lower than the pore size is larger that the size of the paper Whatman 41. This test can be used to describe the core synthetic that has a permeability specific that can pass through the fluid and dissolved materials. In addition, if there is a blockage in the membrane that is used for infiltration, then the flow rate of the solution will be hampered. This is most likely also will occur at the injection on the reservoir and can be a factor causing formation damage.

**Phase Behaviour Test**

In this study, taken 7 ml of the surfactant into the tube, and then is added to 7 ml of crude oil. Place the tube in the rack and save on the temperature of the reservoir 70 oC. Turn each tube 3 times until the liquid is well mixed, not shaken, and watch for changes the interface of the fluid
for 1 month. The results of the test the behavior of the phase indicates the presence of the phase amid a show the performance of the surfactants, namely the oil solubility in the surfactant.

IFT Test

Based on the graph in figure 8, it is seen that the higher the temperature and the surfactant concentration, the smaller the value of IFT. The value of the IFT of the best in this study achieved at a temperature of 70 °C, at a concentration of LS on water a natural formation of 1.5 % b/b. In this study the value of IFTnya is 10-1 dyne/cm.

4. Acknowledgements

This research was supported by the Polytechnic of Energy and Mineral Akamigas Cepu and the Directorate of Research and Community service, Directorate General of Research and Development, Ministry of Research, Technology, and Higher Education fiscal Year 2020.

5. Conclusion

Research on the Synthesis of Sodium Ligno Sulphonate (SLS) examines the lignin has been isolated from the black liquor into SLS. After that the SLS were characterized and tested qualitatively using FTIR. Eligibility as a surfactant for Enhanced Oil Recovery (EOR) are also tested for compatibility, filtrasinya, and IFTnya. The result is a yield of SLS by 87 %, with a value of IFT 10-1 dyne/cm. Compatibility test of the SLS showed good results; wherein the surfactant is soluble in water and showed no clots or sediment. Test thermal stability, showing surfactants do not form lumps during a 28-day warming, and on the test filtration discovered the value of FR in this experiment under 1,2; which shows good performance for the application of EOR. SLS obtained from this research, proved to have the potential to regain the rest of the oil in the wells of the Field Ledok, Cepu, Central Java, and may also potentially to the Field of crude oil in Indonesia.

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