Synthesis of Sodium Lignosulfonate (SLS) Surfactant and Polyethylene Glycol (PEG) as Surfactants in Enhanced Oil Recovery (EOR)

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Abstract. The process of extracting oil from oil wells still uses the premier and secondary methods, another method that is not optimal is the tertiary method to increase oil recovery. The tertiary method is by chemical injection with surfactants, polymers, and alkalis, among others. Surfactants (surface active agents) can change the interface tension of insoluble liquids. One of the surfactants that can be used is sodium lignosulfonate (SLS). In this study, sodium lignosulfonate surfactant was made from lignin as raw material isolated from black liquor. In this study, the surfactant sodium lignosulfonate was reacted with polyethylene glycol (PEG) as a polymer so that it became a polymeric surfactant. The surfactant polymer that has been synthesized can control oil mobility due to its viscous nature in aqueous solutions. This study examines the effect of the molecular weight of polyethylene glycol and sodium lignosulfonate, temperature, the concentration of ammonium persulfate catalyst, the weight ratio of polyethylene glycol and sodium lignosulfonate. FTIR test results on sodium lignosulfonate surfactant have a wavelength of 3369 cm⁻¹ hydroxyl groups -OH, 1593 cm⁻¹ -C=O aromatic groups, 1456 cm⁻¹ -S = O groups, 1423 cm⁻¹ -CH aromatic groups, 1216 cm⁻¹ asymmetric SO₂ groups, =C= S, and 1102cm⁻¹ symmetric groups SO₂=C=S. The compatibility test of enhanced oil recovery (EOR) shows that SLS is compatible with the formation of water. Filtration test of enhanced oil recovery shows that SLS using membrane 42 produces greater FR solution.

Keywords: Sodium lignosulfonate (SLS) surfactant, polyethylene glycol (PEG), polymeric surfactant, enhanced oil recovery (EOR).

1. Introduction
Petroleum production in Indonesia during the last ten years from 2009 – 2018 shows a downward trend from 346 million barrels (949 thousand barrels of oil per hour) in 2009 to around 283 million barrels (778 thousand barrels of oil per hour) in 2018 [1]. The use of fuel oil as the main fuel source has not been replaced until now, making it possible to do a chemical injection, one of which is by using surfactants to maximize oil recovery. Surfactant injection is a method in the process of
maximizing the removal of residual oil in the reservoir that cannot be extracted, using the primary or secondary method which is caused by the large oil and water interface stress [2].

One of the surfactants that are being developed in enhanced oil recovery (EOR) is the surfactant sodium lignosulfonate (SLS). Sodium lignosulfonate surfactant is a surface-active agent that can reduce the interfacial tension between oil and water, it can be obtained from sulfonation of lignin with sodium bisulfite [3]. The addition of surfactant reduces the interfacial tension (IFT) between the oil and formation water, decreasing capillary action. While polymer surfactants can reduce interfacial tension (IFT), they can also increase the viscosity of the solution which is very important for increasing sweeping efficiency so that oil absorption increases, reducing the permeability of porous media [4]. One of the most difficult problems in using flooding surfactants for enhanced oil recovery is the frequent loss of surfactants due to adsorption on formation rocks or trapped in the pores of carbonate or sandstone rocks. Polymers can be used for mobility control, namely the interaction between polymer and surfactant which is influenced by pH, ionic strength, type of crude oil, polymer properties, and the nature of the surfactant itself [5].

According to Abidin et al. [6] researched polymer surfactants that are injected into the reservoir, can reduce the interfacial tension between oil and water and allow it to release trapped oil in rocks making it easier for the oil extraction process. Yin and Zhao [7] studied the effect of viscosity on polymer surfactants, a higher the concentration of the polymer would increase the viscosity so that the polymer surfactant solution could only flow in water and was less effective for oil uptake. Rita et al. [8] studied the injection mechanism of polymer surfactants that can sweep the oil contained in the low permeability zone by about 4%. This research will study the polymer surfactant synthesis process and identify the sodium lignosulfonate surfactant. The surfactant used in this study is sodium lignosulfonate that is made from black liquor raw material after which polymer will be added in the manufacture of polymer surfactants, it is called polymeric surfactants. The polymer used is polyethylene glycol (PEG). This research will examine the effect of polyethylene glycol molecular weight, polymeric surfactant temperature, the weight ratio of polyethylene glycol and sodium lignosulfonate, and concentration of ammonium persulfate catalyst to produce polymeric surfactants.

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. Polyethylene Glycol with molecular weights of 40, 400, 4000, and 6000 was obtained from PT. Indra Sari Semarang, ammonium persulfate as a catalyst under the brand Supelco obtained from Germany and AC2 technical acetone from PT. Hepilab Semarang and aquades were obtained from the Integrated Laboratory of Diponegoro University, Semarang, Central Java.

2.2. Synthesis of Sodium Lignosulfonate
2 g of lignin was reacted with NaHSO₃ with a ratio of 4.58 w/w of lignin and NaHSO₃ and added to 60 ml of aquadest then stirred until homogeneous. The pH was adjusted using a 1N NaOH solution to a pH of 8.32. The solution was then put into a 250 ml three-neck flask and the sulfonation process for two hours at a reaction temperature of 79.6°C. The surfactant solution is then evaporated at a temperature of 100°C until it is concentrated in the evaporation process using a beaker glass. The concentrated solution was filtered, then added 10 ml of methanol, and was shaken to precipitate NaHSO₃. Then filtering it again with a Buchner funnel using a vacuum pump so that the filtrate is obtaining in the form of a concentrated SLS solution. The surfactant sodium lignosulfonate solution was dried on a glass plate at room temperature. This sodium lignosulfonate surfactant will then be polymerized with polyethylene glycol to be formed into polymeric surfactants.
2.3. Synthesis of Polymeric Surfactant
The reaction was carried out with surfactants sodium lignosulfonate (SLS) and polyethylene glycol (PEG) with various molecular weights of polyethylene glycol (40, 400, 4000, 6000) using ammonium persulfate. The weight ratio of sodium lignosulfonate and PEG tested was 0.2 – 0.5 w/w, and the weight ratio of ammonium persulfate catalyst 5 – 20 % wt. For the preparation of the first reaction solution SLS surfactant was dissolved in 80 ml of aquadest, the second was polyethylene glycol in 10 ml of aquadest, ammonium persulfate catalyst in 10 ml of aquadest. Then the sodium lignosulfonate solution and polyethylene glycol solution were added to the three-neck flask. Surfactant polymerization process with temperature variations (60 – 90)°C. Then when the thermocouple reaches the desired temperature, add the ammonium persulfate catalyst. After that start calculating the heating time, heating for 2 hours. The product was then extracted with acetone and oven at 60°C for 12 hours [9]. Then calculate the total weight of the product to calculate the yield in response to the polymeric surfactant.

2.4. 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 [10].

2.5. Characterization Method
In this experiment, the compatibility test and FTIR test were carried out on the synthetic product of Sodium Lignosulfonate from Black Liquor.

3. Results and discussions
3.1. Effect of Polyethylene Glycol Molecular Weight on Yield

![Graph of the relationship between polyethylene glycol molecular weight to yield](image)

Figure 1. Graph of the relationship between polyethylene glycol molecular weight to yield

Figure 1 shows that each increase in the molecular weight of polyethylene glycol yield tends to increase, this is because a large molecular weight can indicate the number of atoms in the compound, so if the molecular weight value is large it will be directly proportional to the yield produced because more the more atoms in the compound will react to produce polymeric surfactant products. Molecular weight is very influential on yield, therefore, to get a yield value that can still be increased, it is necessary to do it in further research. Experiments on making polymeric surfactants with a sodium lignosulfonate: polyethylene glycol ratio of 0.5 (w/w), a temperature of 70°C with a variation of the molecular weight of polyethylene glycol 40,400,4000,6000. Where the molecular weight of polyethylene glycol 40 obtained a yield of 76.7467, the molecular weight of polyethylene glycol 400
obtained a yield of 77.9800, a molecular weight of polyethylene glycol 4000 obtained a yield of 78.7467 and a molecular weight of 6000 obtained a yield of 80.0867. So that the best conditions for variations in the molecular weight of polyethylene glycol in the manufacture of polymeric surfactants are 6000.

3.2. Effect of temperature on Yield

Figure 2. Graphic of the relationship between temperature and yield

Figure 2 shows that the higher the temperature the yield value is lower. The optimum temperature in the surfactant polymeric process to obtain large yields is at 70°C. Meanwhile, when the temperature is raised at 80°C and 90°C, the yield value decreases, this is because the optimum temperature for the product has been passed, so the reaction to form the finished product decreases. In the experiment of making polymeric surfactant, the molecular weight of polyethylene glycol used was 6000 and the temperature in the first experimental design was 60°C, obtained a yield of 75.9667, the next experiment with a temperature of 70°C obtained a yield of 78.4333, the next experiment with a temperature of 80°C obtained a yield of 76.1533 and at temperature 90°C obtained a yield of 69.8067. So that the best temperature for polymeric surfactant is at 70°C with a yield value of 78.4333.

3.3. Effect of Polyethylene Glycol Ratio on Yield

Figure 3. Graphic of the relationship between the PEG to Yield Ratio
In Figure 3 the experiment was carried out with four variations of the ratio of sodium lignosulfonate: polyethylene glycol 0.2, 0.3, 0.4, and 0.5 (w/w) at a temperature of 70°C and polyethylene glycol which used a molecular weight of 6000. At a polyethylene glycol ratio of 0.2, the yield value was 80.4583, the next experiment with a polyethylene glycol ratio of 0.3 obtained a yield of 77.5077, then a polyethylene glycol ratio of 0.4 obtained a yield of 75.5500 and a concentration ratio of 0.5 to a yield of 76.4333. The higher the polyethylene glycol ratio in the manufacture of polymeric surfactants, the smaller the yield value obtained because the yield can decrease drastically at a low ratio where there is a repulsive force between the polymer or surfactant and there is also a pulling force of the hydrocarbon chains that start to dominate [11]. From these results, it shows that the best condition is the ratio of polyethylene glycol to polymeric surfactant is 0.2 with a yield value of 80.4583.

3.4. Effect of ammonium persulfate catalyst concentration on yield

![Graph of ammonium persulfate catalyst concentration on yield](image)

**Figure 4.** Graphic of ammonium persulfate catalyst concentration on yield.

Figure 4 shows that the higher the concentration of ammonium persulfate catalyst, the higher the yield value produced because the catalyst functions to increase the reaction rate so that the more amount of catalyst added will increase the reaction rate in the amount of sodium lignosulfonate reacted with polyethylene glycol to be converted into polymeric surfactants [12]. The experiment was carried out at a temperature of 70°C, polyethylene glycol used with a molecular weight of 6000, and a ratio of sodium lignosulfonate: polyethylene glycol 0.2 w/w. At a 5% wt ammonium persulfate catalyst concentration, a yield of 71.1750 was obtained, then with a 10% wt ammonium persulfate catalyst concentration obtained a yield of 73.0083, 15% wt obtained a yield of 76.1750 and 20% wt the yield value was 79.7667. So that the best conditions for the concentration of ammonium persulfate catalyst in polymeric surfactants are 20% wt with a yield value of 79.7667.

3.5. Filtration Test

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 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 [13].
Table 1. 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.

3.6. FTIR Test

![FTIR result of commercial Sodium Lignosulfonate](image1)

![FTIR result of Sodium Lignosulfonate from Black Liquor](image2)

FTIR spectroscopy is used to determine the hydroxyl group (OH) with the sulfonate group (-SO₃), can be seen in Figure 7 and Figure 8 in general, sodium lignosulfonate synthesized from black liquor is not the same but has almost the same groups, namely in figure 7 commercial sodium lignosulfonate has a wavelength of 3341 cm⁻¹ is a -OH group, 2932 cm⁻¹ -CH group, 1567 cm⁻¹ -C=O aromatic group, 1115 cm⁻¹ symmetric SO₂=C=S group. In figure 8 sodium lignosulfonate from black liquor has a wavelength, 3369 cm⁻¹ hydroxyl groups -OH, 1593cm⁻¹ -C=O aromatic groups, 1456 cm⁻¹ groups.
S=O, 1423 cm\(^{-1}\) -CH aromatic groups, 1216 cm\(^{-1}\) SO\(_2\) asymmetric groups, =C=S and 1102 cm\(^{-1}\) symmetric SO\(_2\) groups =C=S.

3.7. Compatibility Test

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. 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 [13].

4. Conclusion

The polymeric surfactant produced by reacting sodium lignosulfonate and polyethylene glycol with the addition of ammonium persulfate catalyst with variations in the molecular weight of polyethylene glycol 40, 400, 4000 and 6000, temperature (60 – 90°C), polyethylene glycol ratio 0.2, 0.3, 0.4 and 0.5 (w/w) and catalyst concentrations of 5, 10, 15, 20% wt is reacted for two hours to produce the best operating conditions in the manufacture of polymeric surfactants, namely with a molecular weight of Polyethylene glycol 6000, a temperature of 70°C, a weight ratio of polyethylene glycol 0.2 and a concentration of catalyst weight 20%. And the FTIR test shows that SLS made from Black Liquor synthesis contains hydroxyl and sulfonate groups, the compatibility test shows that SLS is compatible with water formation. The EOR filtration test showed that SLS using membrane 42 produced a larger FR solution.

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