Challenge sodium lignosulfonate surfactants synthesized from bagasse as an injection fluid based on hydrophil lipophilic balance

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Abstract. The aim of this research is to obtain Sodium Lignosulfonate (SLS) surfactant from bagasse as an alternative petroleum sulfonate. The experimental method of the process SLS surfactant from bagasse through two processes, hydrolysis and sulphonation process. Then tested for its characteristics through FTIR test, LCMS test, NMR test and compatibility test. Based on the structure of the sodium lignosulfonate of bagasse with the empirical formula of lignosulfonate monomer is (C11H16O8S)n, have hydrophil and lipophil groups. The calculation of Hydrophilic Lipophilic Balance (HLB), the synthesized SLS surfactant of bagasse has a HLB value of 11.62. From the compatibility test, this SLS surfactant have a good aqueous stability, no turbidity, perfect soluble and clear. This SLS surfactant capable of water wet system and having the category as an O/W (Oil in Water) emulsion, indicating that the surfactant good dissolves in water. The mechanism of the synthesized SLS surfactant of the bagasse produces a good microemulsion between surfactant and oil. HLB is one of the parameters used to determine surfactant function. Based on the characteristic test and HLB value calculation it turns out that bagasse can be used as SLS surfactant. As an injection fluid in the EOR process, the SLS surfactant from bagasse has been in the function as O/W emulsion. So the use of lignosulfonate surfactant synthesized from bagasse is a challenge to be developed futher as a surfactant for the EOR process.

1. Introduction
Bagasse is one type of sugarcane waste that has a high enough lignin content. Sufficient lignin content is a good potential for the bagasse is to be processed into lignosulfonate. Many types of surfactants and their use are surfactants as an oil in water system (O/W system) which means that the surfactant is soluble in water. This classification determination can be obtained by calculation the Hydrophile-Lipophile Balance (HLB) surfactant values.

Bagasse is one of the biomass sources whose utilization is currently mostly only as fuel for boilers, paper making materials, animal feed and as a brick, cement and gypsum reinforcer [1]. Many studies on sodium lignosulfonate have been done. Studies have been conducted on lignin of bagasse to become SLS surfactant [2], but have not achieved the use of SLS surfactants from bagasse as an surfactant injection for oil reservoir. Surfactant is one type of chemical used in the injection process to increase petroleum recovery. Therefore, before using a surfactant as an injection fluid, it should be known that
the surfactant have HLB value so that its use becomes appropriate. For surfactant classification as emulsifier in the O/W system, the surfactant should have a range of values between $8 - 18$ [3]. In the EOR process, an important part of the ternary diagram is the three phase region. This three phase region determines the type of emulsion classification: type II(-) is lower phase emulsion and excess oil phase, type 2(+) is an upper phase emulsion with an excess of water phase, and type 3 is a middle-phase microemulsion [4]. Determination type of emulsion can be done by HLB [5]. The HLB system predict that oil and surfactant will interact. This HLB value indicates the tendency of surfactants as water-soluble or oil soluble to form the emulsion type O/W or W/O. The low HLB indicates that the surfactant is more soluble in water and tends to form the W/O emulsion type. The higher value of HLB indicated that the surfactant more hydrophilic. The lower value HLB indicated that the surfactant more lipophilic. For formation with low salinity, surfactant with low HLB should be chosen, because it can create intermediate phase microemulsion. When high formation salinity, high HLB surfactants make intermediate phase microemulsion. The HLB value 0 for the total hydrophobic molecule and 20 for total hydrophilic. HLB value can be used to estimate surfactant properties.

In general, the process SLS surfactant from bagasse through two processes, hydrolysis and sulphonation process. The surfactant is an amphiphilic organic compound, which contains hydrophobic (tail) and hydrophil (head). Surfactants will spread in water and absorb at the interface between air and water or at the interface between oil and water. The aggregate shape may depend on the chemical structure of the surfactant, taking into account the balance of hydrophobic tail and hydrophilic head, known as HLB. Thus, in this study, SLS surfactant obtained was followed by calculation HLB and surfactant characteristic test. With the result of HLB calculation and known characteristics it can be evaluated the use of SLS surfactant as the injection fluid in the injection surfactant process to core oil reservoir. Thus, the purpose of this study to obtain an alternative SLS surfactant from bagasse can be achieved.

2. Methodology
The methodology used in this research is laboratory testing. Laboratory tests were performed on SLS surfaces of bagasse which have been produced from sulphonation process using reagent sodium bisulfite [2,6]. Surfactant SLS bagasse was tested its component content using LCMS (Liquid Chromatograph Mass Spectrum) and NMR (Nuclear Magnetic Resonance). From the results of LCMS and NMR test then determined the lipophilic and hydrophilic groups of surfactant components of SLS bagasse. Then based on Myers equation we can calculate the HLB value of surfactant component of SLS of bagasse.

The NMR characterization was tested in the Chemical Analysis Laboratory of LIPI Serpong using NMR brand JEOL JNMECA 500.

![Figure 1. NMR Apparatus.](image-url)
HLB calculations can be determined by the following formula [3]:

$$\text{HLB} = \frac{20M_h}{M_l + M_h}$$

\(M_h\) = molecular weight of hydrophil

\(M_l\) = molecular weight of lipophilic

In the water, the hydrophilic group will attract water molecules in the solution while the hydrophobia group will reject the water molecule. Surfactant reduces the interfacial tension by absorbing the interface of liquid-gas or oil-water. In the liquid phase, surfactant will form aggregates, such as micelles where the hydrophobic tail forms the aggregate core and the hydrophilic head is in contact with the surrounding liquid. The value of HLB is empirically determined, with a scale ranging from 0 – 20 [3]. The higher the HLB value, the more hydrophilic and water-soluble surfactant, called O/W (Oil in Water) emulsion. A lower HLB value indicates that the surfactant is a W/O (Water in Oil) emulsion, which will become more soluble in oil. Likewise, the classification of HLB values based on Nobel Azko's reference.

| HLB Range | General application       |
|-----------|---------------------------|
| 2 - 6     | W/O emulsification        |
| 7 - 9     | Wetting and Spreading     |
| 8 - 18    | O/W emulsification        |
| 3 - 15    | Detergency                |
| 15 - 18   | Solubilization            |

Table 2. Required HLB for a number of applications [7].

| Application                      | Range HLB |
|----------------------------------|-----------|
| Defoaming of aqueous systems     | 1 – 3     |
| Detergency & cleaning           | 12 – 15   |
| W/O emulsification              | 3 – 6     |
| O/W emulsification              | 8 – 28    |
| Solubilization                  | 11 – 18   |
| Wetting                         | 7 – 9     |

3. Result and discussion

Based on the structure of the sodium lignosulfonate of bagasse which has been formed, where in the empirical formula of lignosulfonate monomer is \((C_{11}H_{16}O_8S)_n\), the functional groups in the structure can be grouped as hydrophil or lipophyl groups.

| Classification | Group | Amount |
|----------------|-------|--------|
| Lipophilic     | - CH -| 3      |
|                | - CH2-| 3      |
|                | - CH3 | 2      |
| Hydrophilic    | - SO3Na| 1    |
|                | - OH  | 3      |

As has been explained by Sheng [5], the value of this HLB can also be calculated using the equation as shown in [3], which is described as follows:

$$\text{HLB} = \frac{20M_h}{M_l + M_h}$$
HLB = \frac{20* (M_h)}{(M_l + M_h)}
M_h = (SO_3Na) + (OH) x 3 = (32 + 48 + 23) + 51 = 154
M_l = (CH) x 3 + (CH_2) x 3 + (CH_3) x 2 = 111
HLB = \frac{20* (M_h)}{(M_l + M_h)} = \frac{20 * 154}{(111+154)} = 11.62

The synthesized SLS surfactant of bagasse has a HLB value of 11.62, so based on the Myers table and the Nobel Azko table [7], the SLS surfactant of bagasse has HLB values in range as O/W emulsification, solubilization and detergent. In the field of petroleum, in the enhanced oil recovery process with surfactant injection fluid, the surfactant must function as an oil in water emulsion system, which means that the surfactant is water soluble. Thus, the SLS surfactant of bagasse can be used as an injection fluid because it has an O/W emulsion system and water-soluble. In the injection process, the surfactant is dissolved in formation water and then injected into the reservoir to encourage the oil still trapped in the pores of the rock.

From the characteristic test can be known some of the properties of SLS surfactant from bagasse as seen in the table below.

| No. | Salinity (ppm) | Surfactant Concentration (%) | Middle emulsion (Stable) | IFT (mN/m) | RF SF (%) |
|-----|----------------|----------------------------|--------------------------|------------|-----------|
| 1.  | 10,000         | 1.5                        | 10.00 %                  | 2.73       | 9.25      |
| 2.  | 10,000         | 3.0                        | 7.50 %                   | 1.68       | 9.50      |
| 3.  | 20,000         | 1.5                        | 5.00 %                   | 4.13       | 8.55      |
| 4.  | 20,000         | 4.5                        | 0.00 %                   | 1.27       | 1.05      |
| 5.  | 40,000         | 1.5                        | 6.00 %                   | 4.11       | 1.80      |
| 6.  | 40,000         | 4.0                        | 0.00 %                   | 2.72       | 1.16      |

Surfactant injection aims to decrease the oil-water interfacial tension (IFT). With the decrease of IFT will cause the breakdown of interfacial tension water-oil to form emulsion, i.e. the dissolution of the surfactant in oil and water. Due to the form of emulsions the oil becomes more easily moved and can be removed from the pores of the rock. The surfactant may form micro emulsions due to the surfactant solubility levels both in water and oil.

![Figure 2. Oil and water formation forming micro emulsion](image)

Micro emulsions will greatly affect the performance of surfactant because with the formation of micro emulsion then surfactant can reduce that value of interfacial tension. The lower the interfacial tension, the better the performance of the surfactant. The type of emulsion is also determined by the salinity as shown in the figure 2 above [8].
From the oil recovery data, the salinity proportion of 10,000 ppm of 1.5% oil recovery with surfactant injection (RF SF) reached 9.25% with stable middle phase emulsion up to 10% and IFT value of 2.73 mN/m. This is consistent with the theory that surfactants serve to lower IFT causing a breakdown of the water-to-water interface strength resulting in emulsions being formed up to 10% because they are soluble in oil and water. This microemulsions cause the SLS surfactant to produce the lowest value interfacial tension IFT 2.73 mN/m. This condition is reinforced by the characteristics of the analyzed surfactant, with HLB value = 11.62 indicating that the SLS surfactant of bagasse can function as an oil-in-water emulsion (O/W) meaning SLS surfactant dissolves in water but not mixed. Likewise in a system with a salinity proportion of 10,000 ppm of 3% concentration, yield a stable middle-phase emulsion at 7.5% with an IFT value of 1.68 mN/m. IFT is formed at a proportion of 10,000 ppm 3% lower than the system with a proportion of 10,000 ppm 1.5%. Because IFT value is lower, oil will also be higher until it reaches RF SF 9.50%.

The salinity of 10,000 ppm is almost the same as the salinity of the formation water in the X field where the light crude oil is sampled in this research. The value of EACN (Equivalent Alkaline Carbon Number) of field X is 8.29 with water formation salinity of field X is 8,110 ppm. This condition can be said to be the same, so that the SLS surfactant of bagasse soluble with oil in water formation 10,000 ppm. In this condition there is a balance between oil - water so that the hydrophilic (head) component of SLS surfactant bagasse will go to the surface so that it acts as a Surface Active Agent (surfactant). The EACN value = 8.29 is identical to the carbon chain value that found in the light oil sample (Barakat, 2014). While the SLS surfactant of bagasse has been analyzed has empirical formula (C_{11}H_{16}O_8S)_n which means it contains 11 Carbon components. With the numbers 8.29 and 11 it can be said there is a balance between oil - water by looking at the C component contained in two types of liquids (Creton, 2016). Similarly, a salinity of 10,000 ppm of 3% oil gain reached 9.55% with stable center phase emulsion at 7.5% with an IFT of 1.68 mN/m. In this proportion system there is a balance between hydrophilic (head) and lipophilic (tail) to form a surface active agent (surfactant), which can form microemulsions and lower the interfacial tension.

Different conditions occur in the salinity of 20,000 ppm salinity proportions and salinity of 40,000 ppm. The injection results in this salinity proportion produce only 1% oil. Although the SLS surfactant of bagasse has a HLB value of 11.62 but due to its high salinity there is a non-conformity of EACN value with component C which is owned by surfactant and there is no balance between oil and SLS surfactant in the injection process.

4. Conclusion
Based on the research results can be taken some conclusions are:

- As an injection fluid in the EOR process, the SLS surfactant bagasse has HLB 11.62 which has been in the range of HLB values between 8 - 28 in function as O/W emulsion.
- The successful surfactant of SLS bagasse as an injection fluid is also determined by the suitability of EACN values. Surfactant SLS bagasse has Carbon component of 11, then the performance of surfactant will work well on oil component having EACN close to 11 value.
- Based on the characteristic test and HLB value calculation it turns out that bagasse can be used as SLS surfactant. So the use of lignosulfonate surfactant synthesized from bagasse is a challenge to be developed further as a surfactant for the EOR process.

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