Improvement of bagasse become lignosulfonate surfactant for oil industry

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Abstract. The aim of this research is to use bagasse as a raw material as an effort to enhance petroleum acquisition. There are two steps of processing bagasse into surfactant lignosulfonate which are the separation process of lignin from bagasse and the sulfonation process of lignin into lignosulfonate. The formation of surfactant lignosulfonate is a result of reaction between ion lignin with bisulfit. The sulfonate group/cluster at lignosulfonate are hydrophilic group which causes lignosulfonate to have amphipathic structure (surfactant). The comparison uses infrared test result against the formed component in surfactant sodium lignosulfonate from bagasse. With the two crude oil samples used in phase test, it turned out that at some light petroleum sample which were mixed with surfactant lignosulfonate formed a middle phase emulsion, with middle phase emulsion stability happening after the second day with a comparison of 10 – 50%. Meanwhile the heavy crude oil did not form a middle phase emulsion at all. Therefore, it can be concluded that bagasse has enough potential to be processed into surfactant lignosulfonate and to be used as injection fluid in the EOR process in oil industries.

Keywords: bagasse, enhanced oil recovery, lignosulfonate, surfactant injection

1. Introduction
Currently in Indonesia there are 63 sugar mills which, 53 factories are state-owned companies while the other ten private-owned sugar factories. So it is necessary for the development of sugarcane plantations and sugar factories in order to meet the needs of the sugar. Actually, based on statistical data, extensive sugar cane crop in Indonesia 395,399.44 hectares, which is spread over an area of 99,383.8 hectares island of Sumatra, Java, covering an area of 265,671.82 hectares, an area of 13,970.42 hectares of Kalimantan, and Sulawesi area of 16,373.4 hectares [12]. It is estimated that each hectare of sugar cane plant capable of producing 100 tons of bagasse. Then the potential of bagasse available from total area of sugarcane plants reached 39,539,944 tons per year. This is taken into consideration for the selection of bagasse processed since sugar cane land in Indonesia is quite large, spread from western Indonesia to East Indonesia, ranging from North Sumatra, Palembang, Lampung, Java, and Sulawesi, so it can be said that natural resources has provided. The development of sugar plantations will support the needs of the sugar industry, which will produce enough sugarcane waste too much. Total production of bagasse annually is relatively abundant, easily available and cheap. Based on data from the Indonesian Sugar
Plantation Research Center (P3GI), bagasse obtained as much as 32% of the weight of cane milled or about 10.2 million tonnes/year or milled per season in Indonesia [13].

Bagasse is the waste from the extraction process cane into sugar products after experiencing five times the milling process. Known as waste because after the mill, there is no more liquid sugar that can be utilized. The rest is sugar cane fibers that are usually considered as goods that are no longer useful are only used as a furnace fuel in the sugar mills or as a mixed fodder. Currently bagasse mostly just as a fuel in boilers, paper-making raw material, or as a source of animal feed. In general, the sugar factory in Indonesia utilizes bagasse as fuel for the plant itself, after the experience bagasse drying process.

Based on the research results done, in the bagasse consist of lignin, cellulose and hemicellulose. In particular, lignin is the basic material of lignosulfonate. Sulfonation processed using bisulfite sodium, so that lignin ion be binded with bisulfite ion to form lignosulfonate. Lignosulfonates containing hydrophilic group (group sulfonate, hydroxyl phenyl and hydroxyl alcohol) and hydrophobic groups (carbon chain) that belong to the group of anionic surfactants [8].

| No | Nabati Waste | Cellulose | Hemicellulose | Lignin |
|----|--------------|-----------|---------------|--------|
| 1. | The wood of width$^1$ | 40 - 55 | 24 - 40 | 18 - 25 |
| 2. | The wood of needle$^1$ | 45 - 50 | 25 - 35 | 25 - 35 |
| 3. | Leave$^2$ | 15 - 20 | 80 - 85 | 0 |
| 4. | Lump Corn$^2$ | 45 | 35 | 15 |
| 5. | Nut shell$^2$ | 23 - 30 | 25 - 30 | 30 - 40 |
| 6. | Grass of wheat$^3$ | 30 | 50 | 15 |
| 7. | Bagasse$^3$ | 50 | 25 | 25 |
| 8. | Palm empty bunch$^3$ | 41.30 – 46.50 | 25.30 – 33.80 | 27.5060 – 32 |

Source : [5], [3], [14], [9], [15]

| Reference | Lignin | Cellulose | Hemicellulose |
|-----------|--------|-----------|---------------|
| [1]       | 13     | 40        | 29            |
| [2]       | 18     | 45        | -             |
| [4]       | 24.2   | 52.7      | 20            |
| [11]      | 21     | 37        | 28            |
| [12]      | 29.46  | 58.39     | 17.99         |

The anionic surfactant formed because of sulfonate group in the molecule lignosulfonates. Lignosulfonate is one type of anionic surfactant which is widely used in the oil industry as an injection fluid to the reservoir in an effort to enhanced oil recovery. This lignosulfonate surfactants have the performance to decrease interfacial tension on the water - oil so that oil can move to be produced. From table 1 shows several other waste which also has a content of lignin, cellulose and hemicellulose. Of these, it appears that one of material, bagasse is containing enough lignin. Table 2 show the result of previous studies of lignin, cellulose and hemicellulose contained in bagasse. Data of components of lignin, cellulose and hemicellulose enough to be reprocessed and these things into consideration that the bagasse can be used as raw material for the manufacture of surfactants with the concept of biomass because it uses vegetable raw materials derived from plants.

Surfactant Lignosulfonate is one of lignosulfonate components that made based raw material lignin with reagent sodium hydroxide and sodium bisulfite, so its called Surfactat Sodium Lignosulfonate. Sulfonate is known with the formula R-SO$_3$Na as the simplification of sulfat R-O-SO$_3$Na [6]. The standard formula is shown below.
R is the group of carbon atom aromatic C₈ – C₂₂ which constitutes the group of hydrophilic whilst group of hydrophobic consists of carboxilat, sulfonate, fosfat or other acid. The Lignosulfonate Surfactant is categorized as surfactant anionic because it has a group of sulfonate and salt (−NaSO₃−) which constitutes anion (head) and group of hidrocarbon as the tail. For lignosulfonate, there is propanoid phenyl compounds as the basis of lignosulfonate compound [7]. The Lignosulfonate Surfactants which being used as an injection fluid in EOR process are still commercial petroleum based surfactants (petroleum lignosulfonate). Surfactants are used as injection fluids since surfactants could lower the oil-water interface tension so that the oil could easily move for production. Surfactant is a surface active substance that could lower the oil-water interface tension to a much lower level.

Surfactant–water–oil mixture could form a bottom phase emulsion (dissolve in water), middle phase emulsion/micro emulsion (dissolve in oil and water phase) and top phase emulsion (dissolve in oil). Meanwhile in the EOR process, the expected emulsion is the middle phase emulsion (micro emulsion) because one of the phases in this condition became a continuous phase (external phase) and the others forms granules (discontinuous phase). Due to this condition, the surfactant needs to have a suitable character with petroleum, among others is the ability to form a stable middle phase emulsion. With the ability of forming a stable middle phase emulsion, some of the surfactant could integrate with water and some with oil. This thought is what became a consideration to use bagasse as a raw material in this research as an effort to enhance the petroleum acquisition.

2. Research Method

Materials used are derived bagasse from sugar mills that were previously sifted and dried. Then bagasse already sifted back with a sieve shaker to obtain powder size bagasse with certain mesh. The equipment used is a sieve shaker, reflux (flask and condenser), magnetic stirrer, hot plate, filter paper and oven.

Methods of processing bagasse into lignosulfonate done through two processes, namely the process of isolation lignin from bagasse and process of lignin sulfonation becomes sulfonate. Insulating material for isolation lignin are water, sulfuric acid (H₂SO₄) and sodium hydroxide (NaOH), and for the lignin sulfonation process using sodium bisulfite (NaHSO₃).

At this research, sugarcane bagasse has processed into lignosulfonate surfactant. The products have component tested using the infra-red with FTIR instruments and lignosulfonate structure tested using NMR test, then the results were compared with standard commercial lignosulfonate.

3. Results and Discussion

This processing begins by entering the bagasse has been sieved with sieve shaker into the flask and refluxed directly in sodium hydroxide solution at a concentration of 2% for five hours. Then results of reflux NaOH is filtered, diluted and neutralized by titration of concentrated sulfuric acid (H₂SO₄ 98%) to pH = 2 and allowed to stand at least eight hours until the precipitate, filtered and dried in an oven at a temperature of 70 °C. The precipitate obtained is lignin isolated from the bagasse. The lignin was further processed by using sodium bisulfite through sulfonation process for five hours at 100°C. The result should be processed through oven drying and heating until it got the brown powder shaped. This powder is surfactant sodium lignosulfonate. To validate sulfonation results will be tested by FTIR, LCMS and NMR. Test with FTIR to obtain the existence of the components contained in the sample. With LCMS test to get the components in detail the visible presence by infra red test. And lastly, using NMR test to obtain the sample's molecular structure.
Figure 2 below, there are several differences among the FTIR result of lignin and surfactant, in which the blue line curve as FTIR Surfactant curve is a peak picking primer on the 1,635.34 cm\(^{-1}\) wave number as stretching vibration Alkena, at 1,384.64 cm\(^{-1}\) wave number as stretching vibration Sulfat, with 1,114.65 cm\(^{-1}\) wave number as stretching vibration Carbonylic Acids, at 462.832 cm\(^{-1}\) wave number as stretching vibration Ester. From the result of the infra-red test, it appears that there has been peak picking of surfactant curve (blue curve) compared to lignin curve (black curve). There is a curve difference through 3-peak picking curves which proved that the lignin surfactant components consists of alkena, sulfat and carboxylic acid.

![FTIR Spectrum](figure.png)

**Figure 2.** The result FTIR of Lignin and Lignosulfonat (from Bagasse) [13].

The FTIR Lignosulfonate Surfactant curve is a peak picking primer on the 1,635.34 cm\(^{-1}\) wave number as stretching vibration Alkena, at 1,384.64 cm\(^{-1}\) wave number as stretching vibration Sulfat, with 1,114.65 cm\(^{-1}\) wave number as stretching vibration Carbonylic Acids, at 462.832 cm\(^{-1}\) wave number as stretching vibration Ester. From the result of infra-red test, wave-length spectrum which read as indicators for peak picking especially sulfat at 1384.64 cm\(^{-1}\) wave number in which the sulfat has peak picking range within 1,350 – 1,450 cm\(^{-1}\) wave number. The appearance of the peak picking indicates that Surfactant LignoSulfonate has completely processed which can be seen on Table 3. The result of infrared spectrum that Lignosulfonate Surfactant has been compared with standart the Lignosulfonate Surfactant of Aldrich products as shown in the Table 3 below.

| No. | Component of Lignosulfonate | Standart Lignosulfonate (Aldrich) | Bagasse’s Lignosulfonate |
|-----|-----------------------------|-----------------------------------|--------------------------|
| 1.  | Alkena C=C                  | 1608.34                           | 1635.34                  |
| 2.  | Sulfate S=O                 | 1365                              | 1384.64                  |
| 3.  | CarboxylicAcids C=O         | 1187.94                           | 1114.65                  |
| 4.  | Ester S-OR                  | 499.831                           | 462.832                  |

From the NMR test results at Figure 3, can be seen the correlation of the H-3 and H-5 to C-5 / C-3, C-1 and C-7; H-7 correlated with C-8 and H-9 correlated with C-8 and C-7. Figure 4 show propanoid
phenyl compounds as the basis of lignosulfonate compound. It could be concluded that the process of sulfonation lignin into lignosulfonates has succeed.

4. Conclusion
Based on the result, it could be concluded from surfactant sulfonation process, that the product is suitable with surfactant standard components that contain four main components such as Alkena, Sulfate, Carboxylic Acids, and Ester. From NMR test, it is found that propanoid phenyl compounds as the basis of lignosulfonate compound at the lignosulfonate surfactant from bagasse. Based on above findings, bagasse has a good potential to be processed into lignosulfonate surfactant.

Acknowledgment
This research was facilitated by the Research Consortium OGRINDO at ITB, Universitas Trisakti, and the Indonesian Directorate General of Higher Education Decentralization Fund for PUPT Fund 2014 Usakti – Dikti, Decentralization Fund 2014 ITB, PUPT Fund 2015 ITB – Dikti and PUPT Fund 2016 ITB – Dikti. We also thank to ISoSUD 2017 who publishes this article, which in turn will benefit the society.

References
[1] Arora DS, Chander M, Gill PK. 2002. Involvement of lignin peroxidase, manganese peroxidase and laccasein the degradation and selective ligninolysis of wheat straw, Int. Bioterior Biodegrad. 50:115 – 120
[2] Bon EPS, Ferara MA. 2007. Bioetanol Production via Enzymatic Hydrolysis of Cellulosic Biomass, FAO. Seminar on the Role of Agricultural Biotechnologies for Production of Bioenergy in Developing Countries, Rome.
[3] Boopathy R. 1998. Biological Treatment of Swine Waste Using An Aerobic Baffela Reactors, Bioresource Technol. 64:1 – 6.
[4] Brady J W, Himmel ME, Ding S H, Johnson D K, Adney W S, Nimlos M R, and Foust, TD. 2007. Biomass Recalcitrance Engineering Plants and Enzymes for Biofuels Production, Science 315:804 – 807.
[5] Cheung SW, Anderson BC. 1997. Laboratory Investigation of Ethanol production from municipal primary wastewater. Bioresource Technol. 59:81 – 96.
[6] Fujimoto T. 1985. New Introducing to Surface Active Agents. Kyoto, Japan: Sanyo Chemical Industries, Ltd.
[7] Lutnaes B F, Myrvold B O, Lauten R A, Endeshaw MM. \(^1\)Hand \(^{13}\)C NMR data of benzylsulfonic acids – model compounds for lignosulfonate, Magnetic Resonance in Chemistry. Willey Interscience. 2007.

[8] Ouyang JM. 2006. Effect of Temperature on growth aggregation of calcium oxalate in presence of various carboxylic acids in silica gel system, Mat. Sci Eng C. 26:679-682.

[9] Pandey A, Soccol CR, Nigam P, Soccol VT, Vandenberghe LPS, Mohan R. 2000. Biotechnological potential of agro-industrial residues, Biorsource Technol. 74(1):81 – 87

[10] Rivai M. 2008. Analisa Kinerja Surfactan Metil Ester Sulfonat (MES) Ramah Lingkungan Dari CPO, CJO dan CNO, Pusat Penelitian Surfactan dan Bioenergi, IPB, Bogor.

[11] Samsuri. 2007. Pembuatan Selulosa Bagas untuk Produksi Etanol Melalui Sakarifikasi dan Fermetasi Serentak dengan EnzymXylanase, Jurnal Makarta Teknologi. 11.

[12] Setiati, R, Wahyuningrum D, Siregar S, Marhaendrajana T. 2015. Studi Laboratorium Pengolahan Ampas Tebu menjadi Lignin sebagai Bahan Baku Surfactan, Prosiding SNITI (Seminar Nasional Inovasi dan Teknologi Informasi), Samosir, Sumatera Utara, Indonesia.

[13] Setiati R, Wahyuningrum D, Siregar S, Marhaendrajana T. 2016. Optimasi Pemisahan Lignin Ampas Tebu Dengan Menggunakan Natrium Hidroksida, Ethos, Jurnal Penelitian dan Pengabdian (Sains dan Teknologi). 4(2):257 – 264, UNISBA.

[14] Sun Ye, Cheng Jiayang. 2002. Hydrolysis of lignocellulosic materials for ethanol production: a review, Bioresource Technology. 83:1 – 11

[15] Syafwina HY, Watanabe T, Kuwahara M. 2002. Pre-treatment of oil palm empty fruit bunch by white-rot fungi for enzymatic saccharification, Wood Res. 89:19-20