Sustainable Green Chemical Processing of Surfactant Synthesized from Bagasse for Enhanced Oil Recovery using Microwave Radiation

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Abstract. The purpose of this research is to show the processing of surfactants from bagasse with the green chemical concept that is using vegetable raw materials. This is a laboratory research method, which synthesized become sodium ligno sulfonate (SLS) surfactant using two processes, hydrolisis and sulfonation with a green chemical process that is using microwave radiation (Microwave-Assisted Organic Synthesis / MAOS). In addition to performing functional group analysis, characterization was carried out by analyzing the structure of the lignin amination product by measuring ¹H-NMR with the results of the formation of alkene groups, sulfonate groups and carboxylates. The Microwave-assisted Organic Synthesis (MAOS) method has succeeded in synthesizing contaminated and alkylated lignin derivative compounds from bagasse lignin and synthesizing lignosulfonic derivatives. Derivatives of lignosulfonate synthesized from bagasse can be done with a green chemical processes that are environmentally friendly. Impact of the research is waste of the bagasse can be used as a product that has added value for the oil sector in Indonesia.

1. Introduction

Green chemistry is a variety of chemical techniques and methodologies to reduce the use or production of raw materials, products, solvents, reagents and so on that are harmful to human health and the environment[1]. This reduction starts from chemical materials and processes designed to reduce or eliminate negative impacts on the environment. Green chemistry is a very effective approach with innovative scientific solutions for the prevention of pollution or pollution in the environment. Green chemistry, also called sustainable chemistry, is an area of chemistry and chemical engineering focused on the designing of products and processes that minimize the use and generation of hazardous substances.

The concept of ‘The Twelve Principles of Green Chemistry’[1], namely: (1) Preventing the emergence of waste, (2) The design of safe chemical products (low toxicity), by changing functional groups or by reducing bioavailability, (3) Design of safe synthesis process, produce substances with low toxicity or not harmful to human health by minimizing the exposure or danger of the use of these chemicals, (4) Synthesis methods are designed to use and renewable raw materials are not consumables which will continue to be thinning and expensive economically, (5) Catalysts as increased selectivity, are able to reduce the use of reagents, and are able to minimize energy use in a reaction, (6) Reducing the process of derivation is not needed (protective groups, protection / deprotection, and temporary
modifications) in physical or chemical processes must be minimized or avoided as much as possible because at each stage of derivatization requires tambahan reagents which later multiply waste. Atomic efficiency, synthesis methods must be designed to maximize the incorporation of all materials used in the process to become final products, Safe solvents and additives, Energy Efficiency for chemical processes and impacts environment, Design for easy degradation and does not accumulate in the environment, Direct analysis to reduce pollution, Minimizing the potential for accidents that can cause the entry of chemicals into the environment, explosions and fire can be avoided. The green chemical process is based on the use of basic ingredients from plants with a non-polluting process to produce other useful products.

The aim of this research is to show the processing of surfactants derived from bagasse waste with the green chemical concept, using bagasse waste. The surfactant used as injection fluid in the enhanced oil recovery (EOR) process is lignosulfonate. Petroleum sulfonate, including one of the commercial anionic surfactants which is essentially petroleum, so it belongs to the category of products that are not environmentally friendly. So the use of bagasse to be a surfactant is one alternative of natural origin that easily obtained. Using twelve principles of green chemistry, bagasse as raw material can prevent the accumulation of waste. The method of synthesis of bagasse is designed to use and renewable raw materials which will continue to be thinning and expensive economically. Synthesis process of bagasse using microwave. The use of microwaves in the synthesis process speeds up processing time so that the energy for the chemical process is more efficient. With the use of microwaves in this research, it have a safer impact on the environment. Because of the closed system, there is no air pollution that disrupts environmental health. This research also produces lignosulfonate which is in accordance with commercial products that have been used in the oil industry. The positive impact of this research is the treatment of waste while maintaining the environment so as not to be polluted by pollution from the synthesis process.

2. Methods
This is a laboratory research method, the which synthesized bagasse become sodium ligno sulfonate (SLS) surfactant using two processes, hydrolysis and sulfonation with green chemical process which uses microwave radiation (Microwave-assisted Organic Synthesis / MAOS). Acceleration of chemical reactions by exposure to microwaves in MAOS results from interactions between material and electromagnetic fields that lead to thermal and specific (non-thermal) effects. Using the MAOS method, the synthesis process becomes easier, the results are better and the time needed is shorter. The MAOS method uses microwaves that react directly with reactant molecules so that vibrations and rotations occur which will then produce heat. For microwave heating, compounds must have a dipole moment. Compounds with dipole moments will be sensitive to external electric fields and try to align themselves with the field by rotating (See Figure 1).

Figure 1. Microwave-Assisted Organic Synthesis (MAOS)
The reaction process in a microwave reactor is used a closed vessel. Microwave radiation is given with a power of 300 watts for 60 minutes at 80°C [11]. Power should not be too low because it can cause the reaction to proceed slowly or even not at all because the reaction system is lacking in energy. Meanwhile, using too much power can cause the decomposition of the precursors used due to localized overheating, which can reduce the yield of the product or a side reaction. The synthesis process of bagasse into lignosulfonate consists of several stages: the hydrolysis stage, the lignin amination stage, the alkylation stage of the aminated lignin and the sulfonation stage[6].

2.1 Stage of hydrolysis
The hydrolysis processing is started by inserting bagasse which has been sifted with a sieve shaker into the flask and refluxed in MAOS with sodium hydroxide (NaOH) at a concentration of 2% for 5 hours. The results of reflux NaOH were then filtered, diluted and neutralized by titrating sulfuric acid to pH = 2 and left at least 8 hours until the precipitate appeared, then filtered and dried in an oven at 80°C. The deposit obtained is the result of isolation from the bagasse[9]. The next process is the stage of lignin amination.

2.2 Stage of lignin amination.
The phase of lignin amination aims to add amine groups to lignin. The addition of the amine group will add to the reactive side of lignin because the amine group can form a bridge bond between the alkyl and lignin groups. Amination of lignin goes through the Mannich reaction. The Mannich reaction is an organic reaction used to convert primary or secondary amines and two carbonyl compounds (one cannot form zero species and one can form zero species) into β-amino carbonyl compounds and can occur in an acidic or basic atmosphere [5]. The phase of lignin amination is carried out using the Microwave-assisted Organic Synthesis (MAOS) method because the precursors used are lignin and DETA which have a certain dipole moment so they can absorb energy from microwaves through the polarization mechanism. The next step is the lignin alkylation stage.

2.3 Stage of alkylation
In the C = C double bond polarization of positive and negative charges occurs. A more positive C atom will attack C which has a double bond with an N atom and a phi pair of electrons on the C = N double bond will be transferred to the N atom which is positively charged to form alkyl species[2].

2.4 Sulfonation stage
The amination and alkylated lignin sulfonation stage was carried out by the MAOS method because the precursors used were laminated and alkylated lignin having a functional group with a particular dipole moment so that it was able to absorb energy from microwaves through a polarization mechanism. This step is carried out 4 times under the same reaction conditions, with a temperature of 80°C, a power of 300W and a reaction time of 1 hour. The reaction takes place in a CEM microwave with a closed vessel system[13]. The last step is the lignin sulfonation process into lignosulfonate.

3. Results and Discussion
The stage of hydrolysis, aminated and alkylated lignin
At this stage from the research, the results of lignin amination products are in the form of brown solids (Figure 2). These solids are then tested for the vibrational spectrum of the components contained in them using FT-IR. The produced lignin product along with the commercial lignin (from Aldrich and Kraft) next was structure characterized using Transform Infra Red (FTIR) spectroscopy measurement. The test’s aim is to analyze the function group contained inside the lignin produced from hydrolysis. Similarly to the produced lignin product, it was also tested using FTIR spectroscopy and the result was compared with a standard commercial product[10].
3.1 The alkylation stage of aminated lignin
At this stage alkylated lignin products were obtained in the form of brown solids. This alkylated aminated lignin product can be seen in the following Figure 3. The colour of alkylated aminated lignin ini light brown. This amine component in lignin appears in the wave number 1311 cm⁻¹, the C-N bond [10].

Characterization of aminated alkylated lignin products was carried out by analyzing the functional groups contained in these compounds through FT-IR spectrum measurements. The FT-IR spectrum of the aminated alkyl lignin products can be seen in Figure 4. The absorption and analysis data of the FT-IR spectrum can be seen in Table 1. At this stage an alkylated product of lignin is obtained in the form of brown solids as shown in the figure below.
Characterization of lignosulfonic derivatives was carried out by analyzing the functional groups contained in these compounds through FT-IR spectrum measurements. The FT-IR spectrum of the lignosulfonate derivative can be seen in Figure 4. The absorption and analysis data from the FT-IR spectrum can be seen in Table 1. The result of FT-IR spectrum measurement show that the expected functional groups are have been formed so that the research can proceed in the next stage. From the alkylation stage of aminated lignin, the amine component is obtained which will make lignosulfonate more polar so that it can improve the lignosulfonate function.

Table 1. The Result of Synthesized Lignosulfonate MAOS Method [10]

| No | Lignin amination Component (cm⁻¹) | Alkylated lignin Component (cm⁻¹) | Lignosulfonate Component (cm⁻¹) |
|----|---------------------------------|---------------------------------|--------------------------------|
| 1  | 3419 –NH                          | 3444 –NH₂                        | 3469 and 3414 –NH₂               |
| 2  | 3200 O-H                          | 3148 O-H                         |                                |
| 3  | 2948 C-H alifatic                 | 2926 C-H alifatic                | 2926 C-H alifatic               |
| 4  | 1631 C=C aromatic                 | 1636 -NH                         | 1620 -NH                        |
| 5  | 1502 C=N                          | 1462 C=C aromatic                |                                |
| 6  | 1318 C-N                          | 1350 S=O                         |                                |
| 7  | 1125 C-O                          | 1111 C-O                         | 1165 C-O                        |
| 8  | 617 C-S                           |                                 |                                |

Based on the results of the infrared synthesized lignosulfonate spectrum test on the MAOS (closed system) method compared to the conventional reflux method (open system), it turns out that the MAOS method can extend the lignosulfonate component chain with the amine (NH₂) and alifatic (CH) components, as seen in Table 2 below.
Table 2. Comparison The Results of Synthesized Lignosulfonate (Closed and Opened System)[10]  

| No | Wave number Component of Synthesized Lignosulfonate Bagasse (cm\(^{-1}\)) | MAOS Method (close system) | Reflux Method (open system) |
|----|---------------------------------------------------------------------------|---------------------------|----------------------------|
| 1  | -NH\(_2\)                                                                  | 3469 and 3414             |                            |
| 2  | C-H alifatic                                                               | 2926                      |                            |
| 3  | -NH                                                                        | 1620                      | -C=C                       |
| 4  | C-O                                                                        | 1165                      | C=O                        |
| 5  | S=O                                                                        | 1350                      | S=O                        |
| 6  | C-S                                                                        | 617                       | S-OR                       |

Table 2 can explain that both the closed system uses a microwave and opened system using reflux, producing the same main lignosulfonate component which are alkenes, sulfate, carboxylic acids and ester. The advantage obtained by using MAOS (microwave assisted organic synthesis) is that the processing time is shorter, safer and does not cause pollution. Thus the green chemical process can be fulfilled.

4. Conclusion

Lignosulfonate as one type of anionic surfactant for the EOR process in the oil field can be made from bagasse waste. The Microwave-assisted Organic Synthesis (MAOS) method has succeeded in synthesizing aminated and alkylated lignin derivative compounds from bagasse lignin and synthesizing lignosulfonic derivatives. Derivatives of lignosulfonate synthesized from bagasse can be done with a green chemical processes that are environmentally friendly. Impact of the research is waste of the bagasse can be used as a product that has added value for the oil sector in Indonesia.

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References

[1] Anastas, Paul T.; Warner, John C. 1998. Green chemistry: theory and practice. Oxford [England]. New York: Oxford University Press. ISBN 9780198502340.
[2] Areskogh, D. 2011. *Structural Modification of Lignosulfonate*. Stockholm: KTH Royal Institut of Technology, School of Chemical Science and Engineering.
[3] Kremsner, JM., Stadler A., Kappe, CO., 2006, The Scale Up of Microwave Assisted Organic Synthesis, TpoCurrChem, 266: 233-278, DOI 10.1007/128_048 @Springer-Verlag Berlin Heidelberg
[4] Microwave Chemistry Reaction Workstation. www.sineomircrowave.com
[5] Potti ND., Nobles L.W., Studies on the mechanism of the Mannich reaction, 1968, Journal of Pharmaceutical Sciences 57(7):1097-103,DOI: 10.1002/jps.2600570703
[6] Setiati R., Ekarizki Aryani Mandala Putri, Deana Wahyuningrum, Seoptorato Siregar, Taufan Marhaendrajana, Sofa Fajriah, 2016. “Sulfonation of Lignin’s Bagasse into Lignosulfonate Surfactants as Alternative Raw Materials for Injection of Surfactants in the Petroleum Industry”, Proceeding Lignocellulose Seminar, Center for Biomaterial Research LIPI, www.biomaterial.lipi.go.id/epub/index.php/l/prosligno . p. 35 - 41
[7] Setiati R., Deana Wahyuningrum, Seoptorato Siregar, Taufan Marhaendrajana. 2016 ,Infra Red Evaluation of Sulfonation Surfactant Sodium Lignosulfonate onBagasse, The 2nd Materials Research Society of Indonesia (MRS-Id) Meeting 2016 , Bandung.
[8] Setiati, R., 2017, : Synthesis and Characterization of Sodium Lignosulfonate From Bagasse: The Effects of Concentration and Salinity toward the Performance of Oil Injection in Core, [Dissertation], Bandung, Indonesia, Bandung Institute of Technology(ITB); 2017

[9] Setiati, R., Siregar S., Marhaendrajana, T., Wahyuningrum D. 2017. Infra Red Evaluation of Sulfonation Surfactant Sodium Lignosulfonate on Bagasse : The International Journal of Science and Technology, (ISSN 2321 – 919X). 5(3), pp. 137 – 142.

[10] Siregar, S., Marhaendrajana, T., Wahyuningrum D, Setiati R., Anisa AF, Ristawati A., 2018, Study Of Laboratory Identification Of Characteristics Of Sodium Lignosulfonate Surfactants From Cane In EOR Process In Oil Reservoir, Final Report, Leading Research Higher Education, Indonesian Directorate General of Higher Education, Jakarta, Indonesia.

[11] Solhy A, Amer W., Karkouri M., Tahr R., Bouari AE, Bousmina M., Zahouily M, 2011, Bi-functional modified-phosphate catalyzed the synthesis of -'-(EE)-bis (benzyldiene) - cycloalkanones: Microwave versus conventional-heating, Journal of Molecular Catalysis A: Chemical 336, pp. 8–15

[12] Surati, Madhvi A., Jauhari, Smita, Desai KR, 2012, A Brief review: Microwave Assisted Organic Reactions, Scholar Research Library 4(1), pp.645-661

[13] Yaning Zhang, Paul Chen, Shiyu Liu, Liangliang Fan, Nan Zhou, Min Min, Yanling Cheng, Peng Peng Erik Anderson, Yunpu Wang, Yiqin Wan, Yuhuan Liu, Bingxi Li and Roger Ruan, 2017, Microwave Assisted Pyrolysis of Biomass for Bio Oil Production, Intechopen Science, 6(1), pp. 1 -10