Challenges and opportunities of green chemistry concepts in the Synthesis of Sodium Lignosulfonate (SLS) surfactant

R Setiati1,*, S Siregar2, T Marhaendrajana3, D Wahyuningrum3 and A Listyani3

1 Petroleum Engineering, FTKE, Universitas Trisakti, Jakarta, Indonesia
2 Petroleum Engineering, FTTM, Institut Teknologi Bandung, Bandung, Indonesia
3 Chemistry, FMIPA, Institut Teknologi Bandung, Bandung, Indonesia

*rinisetiati@trisakti.ac.id

Abstract. Green chemical is the designing of products and processes that minimize the use and generation of hazardous substances. Synthesis of Sodium Lignosulfonate (SLS) Surfactant can be processed from bagasse, waste of sugar cane. The aim of this study was to show that sodium lignosulfonate surfactant (SLS) can be made from bagasse using the Microwave-Assisted Organic Synthesis (MAOS) with the concept of green chemistry. Bagasse processing becomes SLS with hydrolysis and sulfonation process using microwave radiation. The process is closed system, for 1 hour, with a microwave power of 300 watts at 80°C. The process is using Microwave Assisted Organic Synthesis (MAOS) which is equipped with chemical flask and condenser. Reagents are used in small concentrations, 2% NaOH and 0.1 M sodium bisulfite. The result of synthesized SLS from bagasse is brown powder. The synthesized SLS product using Green Chemical concepts has been tested with Fourier Transform Infra Red (FTIR) consisting of Alkene, Sulfonate, Carboxylic Acids and Ester. This composition is similar to the composition of the commercial SLS standard which petroleum based, using as surfactant in the EOR process. The Green Chemical concept has the challenge and opportunity of synthesizing Sodium Lignosulfonate Surfactant using Microwave Assisted Organic Synthesis.

1. Introduction
Green chemistry and engineering seek to maximize efficiency and minimize health and environmental hazards throughout the chemical production process [1]. Synthesis of Sodium Lignosulfonate (SLS) Surfactant is one type of anionic surfactant used in the surfactant injection process to increase oil production. In the oil sector, this activity is known as Enhanced Oil Recovery (EOR). Currently the type of lignosulfonate that is widely used commercially is petroleum lignosulfonate which petroleum based, so it is expensive, not environmentally friendly and cannot be renewed. This is a consideration for making sodium lignosulfonate (SLS) surfactants with vegetable raw materials. One of the basic ingredients that can be processed is bagasse, waste of sugar cane. Bagasse contains lignin to be processed into lignosulfonate. Sustainable development is gaining importance in the chemical industry. It encompasses social, environmental, and economical aspects. Herein, sustainable development is translated into four basic dimensions, called "sustainability stresses": resources, wastes, hazards, and costs [2]. Waste treatment is one of the concepts of a green chemical. As stated, this green chemical concept is a challenge for chemists and others to develop new products, processes, and services that achieve the social, economic and environmental benefits needed [3]. To achieve this condition requires a new approach aimed at reducing the intensity of materials and energy from chemical processes and
products, minimizing or eliminating the dispersion of hazardous chemicals in the environment, maximizing the use of renewable resources and extending product durability and recycling. Green Chemistry is the design of chemical products and processes that reduce or eliminate the use and/or generation of hazardous substances [4]. The development of green chemistry technologies includes 5 concepts such as [5,6]: involve design of raw material processes into products; use of renewable raw materials; use of substances that are safe and environmentally friendly; energy saving process design and utilization of waste production. The green chemistry has demonstrated how fundamental scientific methodologies can protect human health and the environment in an economically beneficial manner. Significant progress is being made in several key research areas, such as catalysis, the design of safer chemicals and environmentally benign solvents, and the development of renewable [7]. The twelve principles address a range of ways to reduce the environmental and health impacts of chemical production, and also indicate research priorities for the development of green chemistry technologies. The main concepts and 12 principles of green chemical are used as a reference in the process of Synthesis of Sodium Lignosulfonate (SLS) Surfactant from bagasse. Green Chemistry or Sustainable Chemistry is defined by the Environmental Protection Agency as the design of chemical products that reduce or eliminate the use of hazardous substances [8] In recent years there is a greater societal expectation that chemists and chemical engineers should produce greener and more sustainable chemical processes and it is likely that this trend will continue to grow over the next few decades. Chemists have developed considerable expertise in designing chemicals for specific industrial functions, so far little progress has been made in minimizing the undesired biological and environmental behavior of commodity chemicals through systematic design tools [9]. The one hand the growth of green chemistry originates from political factors and networking activities. On the other hand, it is the result of user friendliness of the term and of the proposed philosophy itself [10].

2. Methodology

The concept of green chemistry incorporates a new approach to the synthesis, processing and application of chemical substances. This new approach is also known as involve Environmentally benign chemistry; Clean chemistry; Atom economy; Benign-by-design chemistry. Green chemistry such challenges by opening a wide and multifaceted research scope thus allowing the invention of novel reactions that can maximize the desired products and minimize the waste and by products, as well as the design of new synthetic schemes that are inherently, environmentally, and ecologically benign [11]. That green chemistry metric (GCM) can be used as an approach to developing metrics for each of the 12 principles that are flexible and generally accepted as industry practices [12]. In review of the literature, we found that while a number of methods have been proposed to greener chemistry evaluations, there are hindrances to their implementation. In review of the literature, we found that while a number of methods have been proposed to evaluate greener chemistry, there are hindrances to their implementation. Primary limitations include requiring a high level of effort, data that are not readily available, [13] and access to specialized or proprietary data sets. Additional limitations include results that lack transparency and are difficult to communicate. Green chemistry is an innovation step to process renewable resources that have the potential to produce new products [14].

The processing of bagasse into Sodium Lignosulfonate (SLS) in the synthesized process was carried out in two stages, namely lignin isolation and sulfonation process. The synthesized Sodium Lignosulfonate (SLS) process can be done by reflux (opened system) or microwaves (closed system) radiation method. In this study, Synthesis of Sodium Lignosulfonate (SLS) Surfactant uses the concept of microwaves radiation (closed system). Acceleration of chemical reactions by exposure to microwaves in microwave results from interactions between material and electromagnetic fields that lead to thermal and specific (non-thermal) effects [15]. Using the method, the synthesis process becomes easier, the results are better and the time needed is shorter [16]. The 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 [17]. Figure 1 below is a microwave used for the synthesis process.

**Figure 1. Microwave-Assisted Organic Synthesis (MAOS) [17].**

In microwave oven, material may be heated with use of high frequency electromagnetic waves. The heating arises from the interaction of electric field component of the wave with charge particle in the material. Two basic principal mechanisms involve in the heating of material: dipolar polarization and conducting mechanism. The process is carried out in a closed system, for 1 hour, with a microwave power of 300 watts at 80°C. The tool used is Microwave Assisted Organic Synthesis (MAOS) which is equipped with chemical flask and condenser. Reagents are used in small concentrations, namely 2% NaOH and sodium bisulfite 0.1 M.

The first stage of the process of Synthesis of Sodium Lignosulfonate (SLS) Surfactant is isolation of lignin, which is the separation of lignin components from bagasse. The material used in this research is bagasse, where the bagasse contains lignin approximately between 10.37% - 29.46% [18]. The bagasse was first sifted before going into the oven so it was completely dried. The dried bagasse then sifted using a sieve shaker to obtain a powder bagasse with a particular mesh size. Bagasse powder used is 80 mesh in size. Figure 2 shows the bagasse that has been sifted with sieve shaker into bagasse powder.

**Figure 2. Mesh of Bagasse [18].**

The lignin insulation material is sodium hydroxide (NaOH) 2%, aquades and sulfate acid (H₂SO₄). Bagasse fine powder is put into a chemical flask with 2% NaOH and processed in MAOS, in a closed system, for 1 hour, with a microwave power of 300 watts at 80°C. The produced NaOH hydrolysis was then filtered, diluted and neutralized with concentrated sulphate acid titration (98% H₂SO₄) up to pH = 2 and set for at least 8 hours until a sediment appeared, filtered and dried in oven at 70 °C temperature. Then the component's lignin was tested using Fourier Transform Infra Red (FTIR). Structure Lignin which has been characterized by FTIR, then proceed with sulfonation
to obtain lignosulfonate surfactant. At this stage of the sulfonation process, lignin is put into a flask, sodium bisulfate solution is added to 0.1 M. The process is done with MAOS, in a closed system, for 1 hour, with a microwave power of 300 watts at 80°C. The filtrate from the microwave radiation is then filtered to get a clear filtrate, free from the remaining solids. The filtrate is then dried with an evaporator and oven to get solids. The result of this drying is in the form of a light brown powder called Lignosulfonate Surfactant. Next the FTIR is contained in the contained in the surfactant.

3. Result and discussion

In this paper we will discuss the results of bagasse synthesis into lignin and SLS surfactant. The following figures 3 show the results of lignin and Sodium Lignosulfonate (SLS) Surfactant Synthesized from bagasse using MAOS processed.

Figure 3. Lignin (a) and Sodium Lignosulfonate (SLS) Surfactant (b) Synthesized from Bagasse [19].

The result of synthesized SLS from bagasse is brown powder. The synthesized SLS product using Green Chemical concepts has been tested with Fourier Transform Infra Red (FTIR) consisting of Alkene, Sulfonate, Carboxylic Acids and Ester.

Table 1. Wave number of lignosulfonate [19,20].

| No. | Component of lignosulfonate standar | Wave number ( cm⁻¹) |
|-----|------------------------------------|---------------------|
|     | Lignosulfonate’ s bagasse | Lignosulfonate Standar Patricia | Lignosulfonate Standar Aldrich |
| 1.  | Alkena | 1635.34 | 1630 - 1680 | 1608.34 |
| 2.  | Sulfate | 1384.64 | 1350 | 1365 |
| 3.  | Carboxylic Acids | 1114.65 | 1000 – 1300 | 1187.94 |
| 4.  | Ester | 462.83 | 500 -540 | 499.831 |

This SLS surfactant bagasse FTIR result was then compared with standard component spectrum. From the wave length spectrum comparison, it turned out that this surfactant from sulfonation was appropriate with the standard component owned by Patricia’s and Adrich’s lignosulfonate, as shown in the table 1 [20]. The main composition consists of alkenes with a wave number 1635.34 cm⁻¹, Sulfate with a wave number 1384.64 cm⁻¹, Carboxylic acids with a wave number 1114.65 cm⁻¹ and Ester with a wave number 462.83 cm⁻¹. From that table, with wave number as indicator, the composition of SLS surfactant from bagasse is similar to the composition of the commercial SLS standard which petroleum based.

From the synthesized SLS surfactant from bagasse process using Microwave Assisted Organic Synthesis (MAOS), the concept of green chemistry turned out to produce the main component that is the same as the commercial SLS standard which consists of 4 main components, alkene, sulfate, carbocyclic acids and esters. The 4 main components are the product of being designed using MAOS. MAOS as a tool process using green chemistry concept, can include several concepts from 12 concepts.
of green chemistry, synthesized SLS surfactant from bagasse can cover four (4) points of the green chemistry concept, namely:

1. Chemical synthesis that is less dangerous is to avoid using or producing toxic substances for humans and / or the environment, that is, a system enclosed in MAOS makes the environment uncontaminated by the smell that arises or the spark of turbulent solutions due to heat reflux. Designing chemicals that are safer, which means there is no interference with the surrounding environment, whether human or air and tools. (2) Design for energy efficiency namely energy requirements must be minimized, and the process must be carried out at ambient temperature and pressure if possible, with the MAOS concept the time needed for the reflux process is faster, it only takes 1 hour to process, compared to 5 hours of conventional reflux process, so that energy also becomes more efficient. Likewise, for the pressure and temperature used do not need to be too high. (3) The use of renewable raw materials means that raw materials are easily obtained, that is by using bagasse as raw material derived from waste and easily obtained, in almost all regions of Indonesia and the last (4) Catalysis, using a small amount of catalytic reagent to repeat a reaction is superior to a stoichiometric reagent, that is, by using a small amount of catalytic reagent enough to process the synthesis.

So, green chemistry is an innovation step to process renewable resources that have the potential to produce new products.

4. Conclusion
Synthesis of Sodium Lignosulfonate (SLS) Surfactant can be done using MAOS with the concept of green chemistry. The synthesis of lignosulfonate surfactant can be obtained use of bagasse as renewable raw materials, less dangerous, more energy efficiency and only need a small amount of catalytic reagent. Using the concept of green chemical with microwave radiation method, the result of synthesized Sodium Lignosulfonate Surfactant has similarity with the composition of the commercial SLS standard. The Green Chemical concept has the challenge and opportunity of synthesizing Sodium Lignosulfonate Surfactant using Microwave Assisted Organic Synthesis.

Acknowledgments
This research was facilitated by the Research Consortium OGRINDO at ITB, Trisakti University, and the Indonesian Directorate General of Higher Education Decentralization Fund for PUPT Fund 2014 – 2018 ITB – Dikti. Thank you for all the institutions that helped. We also thank to AASEC 2019 who publishes this article, which in turn will benefit the society.

References
[1] Mulvihill M J, Beach E S, Zimmerman J B and Anastas P T 2011 Green chemistry and green engineering: a framework for sustainable technology development Annual Rev Environ Resour 36 271–293
[2] Lange J P 2009 Sustainable Chemical Manufacturing : a matter of resources, wastes, hazards and costs ChemSusChem 2(6) 587-92
[3] Burek B O, Borman S, Hollmann F, Bloh J Z, Holtmann D 2019 Hydrogen peroxide driven biocatalysis Green Chem. Journal
[4] Ahmed M L 2019 Green Chemistry, University of Karbala [Online] Retrieved from: https://www.researchgate.net/publication/325852102
[5] Aken V K, Strekowski L, Patiny L 2006 EcoScale, a semi-quantitative tool to select an organic preparation based on economical and ecological parameters Beilstein Journal of Organic Chemistry 2(1) 3
[6] Anasta 2009 Green Chemistry Edication, American Chemical Society, ACS Symposium Series, Washington DC, Chanshetti Umakant, Green Chemistry: Challenges And Opportunities In Sustainable Development International Journal of Current Research 6 11 9558-9561
[7] Anastas P T, Kirchhoff M M 2002 Origins, current status, and future challenges of green
chemistry American Chemical Society, Account Chem Res 35 686–694

[8] Dunn P J 2012 The Important of Green Chemistry in Process Reasearch and Development Chemical Society Rev 41 (4) 1452-61

[9] Coish 2016 Current Status and Future Challenges in Molecular Design for Reduced Hazard ACS Sustainable Chem. Eng. 4 5900–5906

[10] Linthorst J A 2010 An overview: origins and development of green Chemistry Found Chem Journal 12 55–68

[11] Chanshetti U 2014 Green Chemistry: Challenges And Opportunities In Sustainable Development International Journal of Current Research 6 11 9558-9561

[12] Kreuder 2017 A Method for Assessing Greener Alternatives between Chemical Products Following the 12 Principles of Green Chemistry ACS Sustainable Chem. Eng. 5 2927–2935

[13] Baitz M, Partl J, Braune A, Brauner E 2011 Whitepaper Improving the Environmental Performance of Chemical Products [Online] Retrieved from: http://www.pe-international.com/america/resources/whitepapers/detail/whitepaper-improving-theenvironmental-performance-of-chemical-products/ (accessed August 25, 2014).

[14] Singh A, Singh S, Singh N 2014 Green Chemistry; Sustainability An Innovative Approach Journal of Applied Chemistry 2 (2) 77-82

[15] Redhana I W, Merta L M 2017 Green Chemistry Practicum To Improve Student Learning Outcomes Of Reaction Rate Topic Cakrawala Pendidikan Jurnal

[16] Solhy A, Amer W, Karkouri M, Tahur R, Bouari A E, Bousmina M, Zahouily M 2011 Bi-functional modified-phosphate catalyzed the synthesis of -(EE)-bis (benzylidene) - cyclo alkanones: Microwave versus conventional-heating Journal of Molecular Catalysis A: Chemical 336 8–15

[17] Kremsner J M, Stadler A, Kappe C O 2006 The Scale Up of Microwave Assisted Organic Synthesis TopCurrChem Journal 266 233-278

[18] Setiati R, Ekarizki A M P, Deana Wahyuningrum, Seutoratno 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 35 – 41

[19] 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 Techonoledge 5 3 137 – 142

[20] Patricia R J 2009 Relationship between the structure of Fe-Lignosulfonate complexes determined by FTIR spectroscopy and their reduction by the leaf Fe reductase The Proceedings of the International Plant Nutrition Colloquium XVI