

Fast Microwave-assisted Pretreatment for Bioconversion of Sawdust Lignocellulose to Glucose

I Nyoman Sudiana^{1,*}, Seitaro Mitsudo², Prima Endang Susilowati³, Desak Ketut Sutiari¹, Made Widana Arsana⁴, Muhammad Zamrun Firihi¹, La Ode Ngkoimani⁵, La Aba¹, Erzam Sahaluddin Hasan¹, Edi Cahyono⁶, Svilen Sabchevski⁷, Haji Aripin⁸, Komang Gde Suastika⁹

¹Department of Physics, Faculty of Mathematic and Natural Science, Halu Oleo University, Kampus Bumi Tridharma Anduonohu, Kendari 93232, Indonesia

²Research Center for Development of Far-Infrared Region, University of Fukui, 3-9-1 Bunkyo, Fukui-shi 910-8507, Japan

³Department of Chemistry, Faculty of Mathematic and Natural Science, Halu Oleo University, Kampus Bumi Tridharma Anduonohu, Kendari 93232, Indonesia

⁴Department of Agrotechnology, Faculty of Agriculture, Halu Oleo University, Kampus Bumi Tridharma Anduonohu, Kendari 93232, Indonesia

⁵Department of Geophysics, Faculty of Earth Sciences and Technology, Halu Oleo University, Kampus Bumi Tridharma Anduonohu, Kendari 93232, Indonesia

⁶Department of Mathematics, Faculty of Mathematic and Natural Science, Halu Oleo University, Kampus Bumi Tridharma Anduonohu, Kendari 93232, Indonesia

⁷Lab. Plasma Physics and Engineering, Institute of Electronics of Bulgarian Academy of Sciences, Bulgaria

⁸Center for Material Processing and Renewable Energy, Faculty of Learning Teacher and Education Science, Siliwangi University, Jl. Siliwangi 24 Tasikmalaya 46115, West Java, Indonesia

⁹Department of Physics Education, Palangka Raya University, Indonesia, 73112

*E-mail: sudiana75@yahoo.com

Abstract. A preliminary study of application microwave energy for bioconversion of cellulosic sawdust to glucose was performed. The effects of the microwave were compared to those of the conventional method for each solvent. It was expected that a broader mechanism responsible for the microwave effects on the chemical processes, especially the pretreatment on the hydrolysis of cellulose can be explained. Reagents used were an acid (HCl), an alkali (NaOH), and distilled water (H₂O). The experimental results showed that the microwave-assisted pretreatment on the lignocellulosic sawdust faster than by using conventional heating (hotplate). Moreover by using microwave a higher glucose content compared to the conventional method was found. With microwave during hydrolysis, high temperatures and high reagent concentrations were not required. Pretreatment with a microwave at 800 Watt and solvent NaOH 22,50 mg/mL at a temperature of 120°C appeared to be most efficient found in this experiment. These results indicate that microwave effective for bioconversion of cellulosic sawdust to glucose. The microstructure evaluation by using SEM and XRD should be performed to understand more detail the effect especially on their cellulosic structural evolution.



1. Introduction

Renewable biomass resources and appropriate energy technology are being developed as alternatives to conventional fuels. Bio-ethanol or bio-hydrogen that can be obtained via the fermentation of starchy sugar is one of the biomass-based energies that can be a renewable and friendly energy source [1]. However, such a use of starch will compete with the fulfillment for food demands. Therefore, the second generation of bio-ethanol by using cellulose containing organic wastes, such as sago wastes, saw dusts, banana trunks, etc. has been developed [2]. Upon the production of the second generation of bio-ethanol, it requires a pretreatment in order to gain cellulose with a low content of lignin and of hemicelluloses. The cellulose is hydrolyzed to form glucose which is then fermented to produce bio-ethanol [3]. The pretreatment can be done by using a physical method (milling), a physical-chemical method (auto hydrolysis, hydrothermolysis, alkali oxidation), chemical method (application of alkali, mixture of acids), biological method (fermentation, addition of enzymes) and heating or combination of the methods above [4]. The use of cellulosic wastes for the production of bio-ethanol still encounters some problems including low amount of product and high cost production. The problems are brought about by the structure of cellulose being covered with lignin that makes it hard to hydrolyze. Therefore, to produce glucose from wood it is required an optimal technology especially at the pretreatment stage [5]. Novianti, *et.al.* studied the use of a conventional heating and reported that the hydrolysis using sulfuric acid (50%) for 2 h on saw dust (8:1, v/w) produced the highest sugar content (43,72%) [6]. In addition, a waste of coconut bunches has also been tested to produce glucose via hydrolysis using HCl (12%) at a temperature of 90-100°C for 30 minutes and resulted in glucose of 12,795 ppm. From the used conventional method, it was found that the produced glucose was still not optimal.

Recently, the use of microwave radiation as a substitute for the conventional heating has been reported for sintering ceramic [7-12], synthesizing organic materials [13-15] or speeding up a chemical reaction and drying [16-17]. Microwave radiation is believed to be able to increase the rate of a chemical reaction. The chemical reaction principle with a microwave oven is to make use of the ability of molecules to move and dipole in the materials or conduction ions in a substance that play a role in changing the electromagnetic energy to heat [18-19]. In a conventional method, the thermal energy is transferred to the materials via convection, conduction, or heat radiation from the material surface. On the other hand, the microwave energy is directly transferred to the materials via the interaction between molecules and electromagnetic fields. The *in situ* energy conversion is very interesting for chemical applications and material processing [19]. The heating with a microwave oven depends more on the molecular characteristics and the condition of reactions compared to a conventional heating.

A number of reports states that microwave can speed up a reaction based on the speed and uniformity of the heat transfer produced by the microwave. Microwave irradiation has an effect on the content of cellulose, hemicellulose and lignin. It can increase the percentage of cellulose by reducing the lignin and hemicellulose content. A pretreatment with a microwave oven at a frequency of 2.45 GHz and with a wattage of 950 Watt with varied times and rice straw powder sizes showed a highly significant increase in cellulose content and a highly significant reduction in lignin and hemicelluloses content [2]. Combining microwave pretreatment with NaOH can increase the glucose content and reduce the lignin and hemicellulose content [21]. A pretreatment with a microwave oven combined with NaOH increased the cellulose content of banana stems compared to other treatments. This is because NaOH can interact with the phenolic lignocelluloses and cause the lignocellulose bonds to break [3-4]. Microwave radiation occurring during the pretreatment at an NaOH concentration of 3 M with a duration of exposure of 40 minutes had an effect on the reduction in the lignin and hemicellulose content and an increase in the cellulose content of sugarcane wastes [1]. Pretreatment with NaOH resulted in a higher sugar content compared to Na₂CO₃ and Ca(OH)₂.

Acids and alkalis also significantly increase glucose content. Microwave pretreatment with an acid has advantages at the reaction conditions such as corrosion, high temperatures, and economically cheaper. If the concentration of acid/alkali is increased, the glucose content also increases [21-22] reported that pretreatment with microwave combined with distilled water, NaOH and H₂SO₄ at a temperature ranging from 130 to 200°C on miscanthus showed H₂SO₄ resulted in maximum glucose content at a temperature of 180°C. At 200°C, however, the glucose content significantly decreased. The mechanism of how a microwave increases the chemical reaction has yet to elucidate. A number of authors has proposed a theory as for the presence of ponderomotive force or the emergence of new hot spots in the reacting materials during the radiation process by the microwave. In the current study, the effects of microwave energy on the degradation of saw dust celluloses were observed. Those effects were compared to the effects of the conventional heating. The degradation was expected to be able to break

down the hemicellulosic bonds, reduce the lignin content, and convert crystal structures of the celluloses to simple sugars [20-21]. In addition, it was expected to find a broader explanation of the microwave effects on the chemical processes, especially on the pretreatment for cellulose hydrolysis.

2. Material and Method

2.1 Sample Preparation

Samples of 'Kuma' sawdusts were collected in Kendari, Indonesia. The saw dusts were uniformly dried in the sun for ± 10 h, then sieved with a 20-mesh sieve. The solvent pH of 5 was achieved by adding HCl, a pH of 7 by adding distilled water, and a pH of 9 by adding NaOH.

2.2 Hydrolisis and characterization

The study was arranged of varied pH2 and varied microwave wattages. The sample pH consisted of 3 levels- pH 5, pH 7 and pH 9, while the microwave wattages consisted of 400, 560 and 800 Watt. Measurements were conducted with a heating period of 15 minutes for each sample.

Sample hydrolysis was done by using HCl, distilled water, and NaOH. Saw dusts measuring 20 mesh weighing 20 g were thoroughly mixed with 200 mL of a solvent. The samples were heated with a microwave oven having a wattage of 400 Watt for 15 minutes. Data collections were repeated by using a 560 Watt and 800 Watt microwave. After being heated, the samples were cooled down at a room temperature, then sieved with sieve paper to separate the liquid from the saw dusts. The glucose content was determined by using the DNS (3,5-dinitrosalicylic acid) method (BIO BASIC INC). The residues of sieving were dried in the oven at a temperature of 45°C until its water content became zero. Sample hydrolysis without heating was conducted by dissolving 20 g of saw dusts into the solvent at pH of 5, 7 and 9, consecutively. The samples were thoroughly stirred, kept still for 15 minutes, and sieved by sieve paper. The liquid resulting from the sieving was measured for its glucose content by using the DNS method. The sieving remnant was dried in the oven at a temperature of 45°C. Sample hydrolysis using a conventional heating was done by heating bath water, with a treatment on each solvent pH 5, pH 7 and pH 9 for 15 minutes, after which the samples were cooled down and then sieved to separate the remnant from the liquid. Microstructure of samples then characterized by using Scanning electron microscope (SEM) and X-Ray Diffraction (XRD).

3. Results and Discussion

3.1 Effects of Microwave Energy on the Reaction using an Acid

NaOH was used in the current study to find a solvent with a pH of 9. Figure 1 shows that the glucose content increased with wattage in microwave-NaOH pretreatment. The duration of energy exposure used was 15 minutes, while the tested microwave power were 400, 560 and 800 Watt. The results showed that the use of NaOH with microwave assisted energy exposure could increase glucose content from 7,36 mg/mL (without heating) to 16,12 mg/mL (400 Watt), 20,10 mg/mL (560 Watt) and 22,50 mg/mL (800 Watt). In agreement with Dawson, *et.al.*, NaOH degrades the lignin that covers cellulose and hemicellulose by breaking down the lignin per se. The structural damage of the lignin and hemicellulosic bonds could increase the glucose content of the saw dusts [23]. In NaOH-containing saw dusts, the energy could spread through ionic conduction where the movements of the ions produce energy and increase rates of collision that converts kinetic energy to heat.

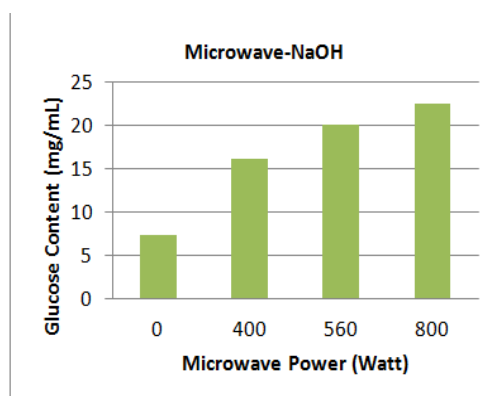


Figure 1 Glucose content vs. microwave power in microwave-NaOH pretreatment

An increase in microwave wattage and temperature could increase the energy and temperature received by any heated material. This causes a faster reaction. That cellulose was hydrolyzed relatively faster at a higher temperature. The interaction between microwaves and the materials brings about the reduced number of hemicelluloses that bind celluloses. This is in agreement with Wu *et al.* (2008) that microwave radiation cause the occurrence of physical explosions on the microfibrers which then result in the disintegration of structures that are hard to degrade such as lignin that protect cellulose [24]. In addition, the electromagnetic fields used in the NaOH-microwave solvent could produce chemical-physical effects that can speed up the disintegration of the crystal structures in celluloses. Therefore, the celluloses found in pretreatment with NaOH-microwave combination produced a higher cellulose content than the cellulose content before being given such a pretreatment.

3.2 Effects of Microwave Energi on the Reaction using H₂O

According to Lidstroem, *et al.*, H₂O is a polar solvent in which dipolar polarization occurs due to the interaction among electrical field components [25]. When a microwave energy is exposed to a material, polar molecules will follow the electrical fields and adapt themselves to the field phase. However, group of intra polar molecules will undergo inertia and cannot follow the fields. This causes particles to move randomly and such a random interaction will produce hot spots. He also reported that heating with a microwave could increase the rate of a chemical reaction and increase glucose content because of a higher number of disintegrated lignin and hemicelluloses with the microwave heating.

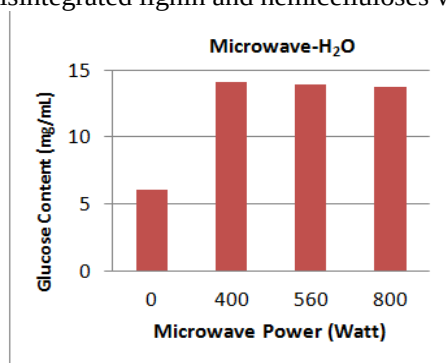


Figure 2 Glucose content vs. microwave power in microwave-H₂O pretreatment

Figure 3 shows effect of microwave power on glucose content for various solvents. Of the three solvents, the highest glucose content (22.50 mg/mL) was found in NaOH at a wattage of 800 W. There was no significant change in the glucose content with HCl and H₂O despite an increase in microwave power. This is concomitant with previous results that pretreatment with microwave heating using different types of solvents resulted in different glucose contents, where NaOH is found to produce the highest glucose content [24-25].

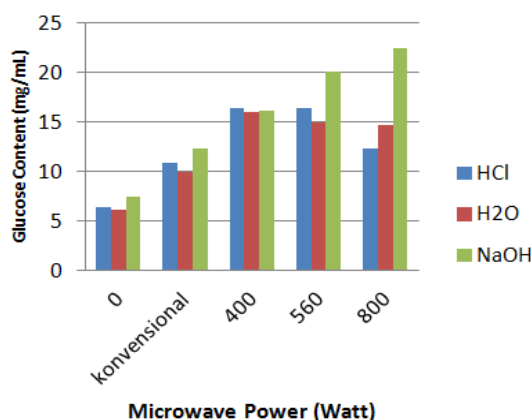


Figure 3 Glucose content vs. microwave power in various solvents pretreatment

An SEM test was used to study the microstructures of saw dusts before and after the pretreatment. The preliminary results indicates that the abundance of bonds of the intact celluloses before treatment and a great number of bonds disappear after being given a microwaves pretreatment. The details of the

microstructure evolution after pretreatment in this investigations will be reported in separated paper. The heat energy of the microwave is produced from a direct interaction between the polar regions of the saw dust biomass and the oscillation of the electromagnetic fields. Microwave irradiation produces an efficient internal heat that can result in a direct and uniform heating on the mixed reactions. The reflection and diffusion on the local barrier cause the occurrence of hot spots and superheating effects as reported previously [7-10, 26-28]. There were also reported that ionic conduction (crystalline) and non-ionic conduction (amorph) occur in celluloses. The structure of hydrogen bonds in the cellulosic crystalline can cause the movements of protons under the electromagnetic fields at suitable conditions. Therefore, the cellulosic crystalline can act as an absorber for the microwave active energy, which can increase biomass decompositions. During this process, lignin/hemicelluloses undergoes disintegration, the effect of microwave absorbance increases and causes the biomass to degrade. This is in agreement with the work of Alvira et al. that pretreatment could break down the lignin that blankets hemicellulose and cellulose, and to reduce the crystal structure of the cellulose [29].

4. Conclusion

The use of microwave for the pretreatment of cellulose hydrolysis was successfully conducted. The reactants used were an acid (HCl), an alkali (NaOH), and distilled water (H₂O). The use of microwave produced a higher glucose content compared to conventional method, especially in the combination with the alkali (NaOH). This indicates that microwave oven is effective for a pretreatment in the conversion of lignocellulose in saw dusts to glucose. The SEM images show the differences in the microstructures of the cellulose surfaces. Microwave-assisted alkali pretreatment showed a reduced number of bonds as a result of a more severe degradation on the microstructures of the cellulose surface compared to other treatments. This is in concomitant with the XRD test where an increase of crystalline index was found from the saw dusts. This result indicates that microwave technology is very promising for converting sawdust lignocellulose to glucose.

Acknowledgments

This work has been partially supported by the Directorate of Higher Education, at the Ministry of Research Technology and Higher Education, Republic of Indonesia and University of Halu Oleo, Kendari.

References

- [1] Nikolic, S., Mojovic, L., Rakin, M., Pejin, D. dan Savic, D. 2008. A Microwave-Assisted Liquefaction as a Pretreatment for the Bioethanol Production by the Simultaneous Saccharification and Fermentation of Corn meal. *CI and CEO*. Vol 14(4), 231-234.
- [2] Dehani, F. R., Argo, B. D. dan Yuliningsih, R. 2013. Utilization of Microwave Irradiation to Maximize Pretreatment Process Degradation of Lignin Jeremi Paddy. *Jurnal Biopress Komoditas Tropis* Vol.1 No. 1, 175-182 [In Indonesia].
- [3] Jingjing, L. 2011. Isolation of Lignin from Wood. *Saimaa University of Applied Sciences Faculty of Technology*.
- [4] Kumar P, Barrett D.M., Delwiche M.J. dan Stroeve, P. 2009. Methods for Pretreatment of Lignocellulosic Biomass for Efficient Hydrolysis and Biofuel Production, *Industrial and Engineering Chemistry Research* Vol. 48 (8), pp 3713–3729
- [5] Thostenson, E.T. dan Chou, T.W. 1999. *Microwave processing : Fundamental and Applications*, Elsevier Composites Applied Science and Manufacturing: Part A 30, 1055-1071.
- [6] Novianti, Mappiratu dan Musafira. 2013. Utilization Sawdust Waste for Production Bioethanol using yeast cells. *J. of Natural Science*, Vol. 2. No. 3, 9-19 [in Indonesia]
- [7] W. H. Sutton, *Microwave processing of Ceramic Materials, Microwave Solutions for Ceramic Engineers*, American Ceramic Society, (2005), 35-65.
- [8] I.N. Sudiana, Ryo Ito, S. Inagaki, K. Kuwayama, K. Sako, S. Mitsudo, *Densification of Alumina Ceramics Sintered by Using Sub-millimeter Wave Gyrotron*, *J. Infrared, Millimeter, and Terahertz Waves*. 34 (2013), 627-638.
- [9] I. N. Sudiana, S. Mitsudo, M. Z. Firihi, *Effect of Initial Green Samples on Mechanical Properties of Alumina Ceramic*, *Contemporary Engineering Sciences*, Vol. 9, 2016, no. 12, 595-602
- [10] S. Mitsudo, S. Inagaki, I.N. Sudiana, K. Kuwayama, *Grain Growth in Millimeter Wave Sintered Alumina Ceramics*, *Advanced Materials Research*, Vol.789 (2013), pp. 279-282.
- [11] M. Z. Firihi, I.N. Sudiana, *Properties of 2.45 GHz microwave sintered SiO₂ from rice husk ash and*

- Al₂O₃, ARPN Journal of Engineering and Applied Sciences Vol. 12 No. 19, 2016, pp. 11595-11598
- [12] H. Aripin, S. Mitsudo, I. N. Sudiana, N. Jumsiah, I. Rahmatia, B. Sunendar, L.Nurdiwijayanto, S. Mitsudo, S.Sabchevski, Preparation of Porous Ceramic with Controllable Additive and Firing Temperature, *Advanced Materials Research*, Vol. 277 (2011) pp. 151-158
 - [13] M. Zamrun F., I. N. Sudiana, S. Mitsudo, Microwaves Enhanced Sintering Mechanisms in Alumina Ceramic Sintering Experiments, *Contemporary Engineering Sciences*, Vol. 9, 2016, 5, 237 – 247
 - [14] I.N. Sudiana, S. Mitsudo, T. Nishiwaki, P. E. Susilowati, L. Lestari, M Zamrun Firihi, H. Aripin, Effect of Microwave Radiation on the Properties of Sintered Oxide Ceramics, *Contemporary Engineering Sciences*, Vol. 8 No. 34, (2015), 1607-1615
 - [15] H. Aripin, S. Mitsudo, I.N. Sudiana, T. Saito, S. Sabchevski, Structure Formation of a Double Sintered Nanocrystalline Silica Xerogel Converted From Sago Waste Ash, *Transactions of the Indian Ceramic Society*, DOI: 10.1080/0371750X.2014.980850 (2015)
 - [16] Wu, Y., Zhang, C., Liu, Y., Fu,Z., Dai, B. dan Yin, D. 2012. Biomass Char Sulfonic Acids (BC-SO₃H)-Catalyzed Hydrolysis of Bamboo under Microwave Irradiation. *Bioresources*. 7(4), 5950-5959.
 - [17] M. Z. Firihi, I.N. Sudiana, 2.45 GHz microwave drying of cocoa bean , *ARPN Journal of Engineering and Applied Sciences* Vol. 12 No. 19, 2016, pp. 11595-11598
 - [18] H.M.S. Kingston, H.J. Haswell, 1997. *Microwave-Enhanced Chemistry: Fundamental, Sample Preparation, and Applications*, American Chemical Society.
 - [19] Taylor, M. Atri., S.S. dan Minhas, S. 2005. *Developments in microwave chemistry*. Evalueserve.
 - [20] Stuerge, D. 2006. *Microwaves in Organic Synthesis*, Second Edition. Wiley-VCH.
 - [21] Singh, R., Tiwari, S., Srivastava, M. dan Shukla, A. 2014. Microwave Assisted Alkali Pretreatment of Rice Straw for Enhancing Enzymatic Digestibility. *Hindawi Publishing Corporation Journal of Energy*, Vol. 2014, pp. 1-7. DOI: <http://dx.doi.org/10.1155/2014/483813>
 - [22] Balcu, I., Macarie, C.A., Segneanu, A.E. dan Pop, R.O. 2011. Combined Microwave-Acid Pretreatment of the Biomass. *Progress in Biomass and Bioenergy Production*.
 - [23] L. Dawson and R. Boopathy, 2008. Cellulosic Ethanol Production From Sugarcane Bagasse Without Enzymatic Saccharification, *Bio Resources* 3(2), pp. 452-460
 - [24] Y. Wu, Zhang, C., Liu, Y., Fu,Z., Dai, B. dan Yin, D. 2012. Biomass Char Sulfonic Acids (BC-SO₃H)-Catalyzed Hydrolysis of Bamboo under Microwave Irradiation. *Bioresources*. 7(4), 5950-5959.
 - [25] Lidstroem, P., Tierney, J., Wathey, B. dan Westman, J. 2001. Microwave Assisted Organic Synthesis-a Review. *Tetrahedron*. Vol. 57, pp. 9225-9283.
 - [26] I.N. Sudiana, S. Mitsudo, K. Sako, S. Inagaki, L. O. Ngkoimani, I. Usman, H. Aripin, The microwave effects on the properties of alumina at high frequencies of microwave sintering, *American Institute of Physics (AIP) Conference Proceeding*, **1719**, 030014 (2016); doi: 10.1063/1.4943709
 - [27] I. N. Sudiana, S. Mitsudo, M. Z. Firihi, H. Aripin, Effect of High-Frequency Microwave on Micro Hardness of Alumina Ceramic, *Material Science Forum* , Vo. 872, 2016, pp.114-117.
 - [28] H. Aripin, S. Mitsudo, I Nyoman Sudiana, Bambang Sunendar , Svilen Sabchevski, Structural Characterization of a Glass Ceramic Developed from TiO₂ and a Novel Material-Silica Xerogel Converted from Sago Waste Ash, *Material Science Forum* Vol. 872, 2016, pp.81-86.
 - [29] P. Alvira, E. Tomás-Pejó., M. Ballesteros, and M.J. Negro, 2010. Pretreatment Technologies for an Efficient Bioethanol Production Process Based on Enzymatic Hydrolysis: A review. *Bioresource Technology*, 101(13), pp. 4851–4861.