Microwave Assisted Alkaline Pretreatment of Ramie Decortication Waste for Bioethanol Production

Laeli Kurniasari[#], Suwardiyono[#], Renan Subantoro[*], Indah Hartati[#]

[#]Chemical Engineering Department, Faculty of Engineering, Wahid Hasyim University

[*]Agribusiness Department, Faculty of Agriculture, Wahid Hasyim University, Indonesia

Menoreh Tengah Road X/22 Sampangan, Semarang, Indonesia

[1]laeli_kurniasari@yahoo.co.id

Abstract— **Biofuel production nowadays is developed to change the fossil fuel. Among many raw materials for bioethanol production, lignocellulosic materials are promising alternative feedstocks. One of the lignocellulosic material that can be used for bioethanol production is ramie decortication waste (RDW). There are four steps in producing bioethanol from lignocellulosic materials, they are pretreatment, hydrolisis, fermentation and ethanol purification. Pretreatment is the first and important step. This process is aimed to liberate the cellulose from the lignin and at the same time to reduce the lignin content. In the pretreatment process, microwave can be used to reduce the time needed. In this present study, pretreatment process of ramie decortication waste were done using alkaline and microwave assisted. Two alkaline were used, NaOH and $Ca(OH)_2$ as they represent single and double ion alkali. Ramie decortication waste were immersed in solution of each alkali (3%, 4%, 5%, 6% and 7% b/v) with rasio solid:liquid is 1:10. Solution is pretreated using microwave (power 30% from max power 399W) for 15 minutes. Filtrate is separated and the residue then analyzed its cellulose and lignin content. From the experiment, the result showed that microwave can help the pretreatment process by reducing the time needed. Among the two alkaline, 5% $Ca(OH)_2$ gives the best result in reducing the lignin content (27,4%). SEM analysis also shows that microwave assisted alkali pretreatment can change the structure of samples.**

***Keywords*—alkaline, bioethanol, pretreatment, ramie decortication waste, microwave**

I. INTRODUCTION

Biofuel is an alternative fuel for changing the fossil fuel. Its existency is getting more important since fossil fuel is becoming less. One of the biofuel is bioethanol which can be blended with fossil petrol or used as neat alcohol in dedicated engine [1]. Bioethanol is an attractive biofuel since it is renewable and oxygenated, thereby has potential to reduce particulate emissions in engine [2]. Cellulosic ethanol or ethanol from biomass is also reported to be potential to reduce greenhouse gas emission by 86% [3]. Principally, any material that contain simple/fermentable sugar or can be changed into simple sugar are bioethanol feedstock. Lignocellulosic materials are composed from component that can be changed into simple sugar, hence could be sources for bioethanol production. Nowadays, lignocellulosic materials play important role and seems to be a potential source of bioethanol. These materials are abundant, plentiful, cheap and renewable [4], [5].

One industry that produce lignocellulosic waste is ramie fibre industry. The lignocellulosic waste is produced from decortication process. This process is the first step in producing ramie fibre which separate the fibre from its rod and skin rod. The waste that is produced is abundant, around 75% of the total rod processed. This waste is reported contain high cellulose, around 63% [6] and suitable for bioethanol production. Besides of high cellulose content, ramie decortication waste also reported contain high lignin content.

There are four step in producing bioethanol from lignocellulosic materials, they are : pretreatment, hydrolisis, fermentation and ethanol purification. Pretreatment is the first and also can be the most important step and crucial (Kumar et al, 2009), which will liberate the cellulose from the lignin and at the same time will reduce the lignin content [1], [7]. Pretreatment also will break the rigidity of fibers and making them easy for hydrolisis by altering the cellulose structure that make the enzym can access the carbohydrates polymer to convert them into fermentable sugar. Pretreatment also decrease the cristallinity of cellulose and increase the surface area that will make the hydrolisis process easier [8].

Regarding the importance of pretreatment, the effective process of this step must be achieved. Many pretreatment methods have been developed such as acid/alkali method, oxidative method, organic solvents method and biological method. Among those method, most of the pretreatment process combine the use of acid or alkali with the utilization of heat (thermal energy) to help the bond breaking of the molecule. Alkali pretreatment is one method that increase cellulose digestibility and found more effective for lignin solubilization. Besides that, alkali pretreatment also exhibit the cellulose solubilization than acid or hydrothermal process [7]. But the use of alkaline in pretreatment process consume high energy and time due to long conventional heating [9]. In this case, the use of microwave-assited alkaline is one alternative for improving pretreatment process. The use of microwave will change the conventional heating that is usually need long time process and high energy consumption. Microwave will generate thermal energy through dielectric heating. This apparatus can alter the structure of cellulose, degrade lignin content and increase the enzym capability to convert into fermantable sugar (Gabhane et al, 2014).

This research will observe the use of microwave- assisted alkaline in pretreatment of ramie decortication waste (RDW). Two kind of alkaline will be used, sodium hydroxyde and calcium hydroxide.

II. MATERIALS AND METHODS

A. Materials

Ramie decortication waste (RDW) as lignocellulosic material was gained from ramie processing industry in Wonosobo, Central Java Indonesia. The waste choosen is the fresh waste that is obtained after the decortication process running. The waste is washed with distilled water and dried for 24 hours in 105^0C. Dried ramie decortication waste than mashed and sieved in 18 mesh. The fine grained waste is stored in sealed container in room temperature and called 'sample'. Another materials for processing and analysis are chemical reagents such as sodium hidroxyde, calcium hydroxyde, sulfuric acid and distilled water.

B. Methods

The experiment will focus to examine the effect of the alkaline used in the microwave assisted pretreatment. Two kind of alkaline will be used, sodium hydroxyde and calcium hydroxyde. Ten gr of sample was added in NaOH or $Ca(OH)_2$ solution with concentration of each alkaline were 3%, 4%, 5%, 6% and 7% b/v. Rasio solid liquid is 1: 10. The solution is then pretreated using microwave (power 30% from the maximum power 399W) for 15 minutes. After pretreatment, solution was filtered. The solid part is washed until pH 7 and dried for 4 hours. The sample was analyzed its cellulose and lignin content.

C. Analysis

The original and pretreated samples were analyzed its lignin and cellulose content using Chesson method [10]. One g of dried sample (a) was heated with 150 ml of aquadest at temperature of 100^0C for 1 h. The mixture was filtered and dried until the weight was constant (b). The residue was mixed with 150 ml of 0,5M sulfuric acid and heated at temperature 100^0C for 1 h. The mixture was filtered and the residue was dried (c). The residue was added with 10 ml of 72% H2SO4 at room temperature for 4 h and then heated for 1 h. The solid was dried (d). Finally, the solid was heated until become ash and weighed (e). The cellulose and lignin content was calculated as follows :

$$\% \text{ cellulose} = (c-d)/a \times 100\% \quad (1)$$

$$\% \text{ lignin} = (d-e)/a \times 100\% \quad (2)$$

D. Scanning electron microscopy (SEM) sample preparation

The fresh and pretreated RDW was prepared to imaging with scanning electron microscope (SEM). This analysis will compare the internal structure of ramie decortication waste before and after treatment.

III. RESULT AND DISCUSSION

A. Lignocellulose content of raw material

The composition of ramie decortication waste was analyzed for its cellulose, hemicellulose, lignin and hot water soluble contents. The result is shown in Table 1. From this table we can see that fresh RDW contain high cellulose and lignin. The cellulose composition of fresh RDW is almost same with rice straw (35%) and wheat straw (30%) reported by [4], while the lignin content is higher than them. The result also differ with [6] which reported that RDW can contain cellulose until 63,27% and lignin 30,67%. But the lignin content of fresh RDW is close with the lignin content of softwood stems reported by [3], around 25-35%. The differences of cellulose and lignin content of the biomass is affected by source of the material used in study and different of maturity level. [4] also reported that lignin and lignocellulose content is varying with the age, anatomical structure and plant height. The maturation will increase the lignin and lignocellulose content. The hot water soluble content of RDW is similar with bamboo (13,04%) but the ash content is higher [11].

TABLE I
COMPOSITION OF FRESH RDW

Composition	Percentage (%)
Hot water soluble	17,6
Hemicellulose	9,5
Cellulose	33,1
Lignin	37,2
Ash	2,6

B. Lignin and cellulose content after pretreatment

The lignin content of sample after preteratment in various alkaline solution can be seen in Figure 1, while the cellulose content is shown in Figure 2. From the result above we can conclude that combination of microwave with alkali can be used as pretreatment agent of RDW. The use of alkali can reduce the time, where it is one weakness of conventional alkali pretreatment.

Sodium hydroxide could be the alkaline which was used widely in the pretereatment process [3]-[4]. The use of sodium hydroxide can give great advantage in breaking down the internal sctructure of ligncellulosic material. Sodium hydroxide treatment will cause lignocellulosic materials to swell. Then, cellulose, hemicellulose and lignin bonds will be disrupted and permits cellulose to swell. As result, pore size and intraparticle porosity increased, cristallinity decreased and lignin structure disrupted [2]-[3].

While calcium hydroxide pretreatment (lime pretreatment) will removes amorphous substances e.g. lignin and hemicellulose, therefore increases the crystallinity index. Although the cristallinity index increase, but this condition will affect only on the initial hydrolysis rates and has less effects on sugar yields [3]. Moreover, [3] also reported that effective pretreatment should remove all the acetyl groups and reduce lignin content. Lignin removal will increase enzyme effectiveness by eliminating nonproductive adsorption site and increase access to cellulose.

The differences of lignin content after pretreatment between sodium and calcium hydroxide can be caused by the high lignin content of fresh RDW. Dilute NaOH pretreatment was found to be effective for material with low lignin content, around 10-18%[7]. Therefore when it is used in high lignin content, the effectiveness can decrease. Dilute NaOH also reported have no effect when used for softwoods with lignin content greater than 26% [3].

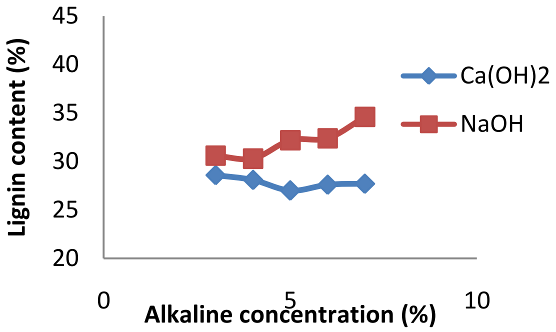

Figure 1. Lignin content of RDW after pretreatment

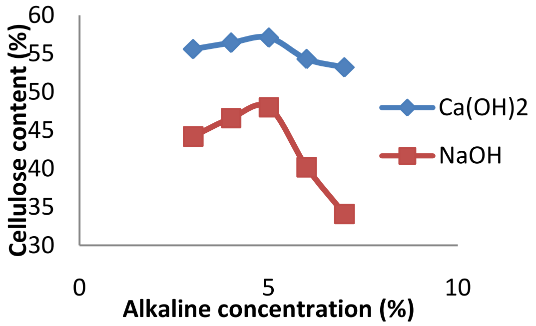

Fig. 1 Cellulose Content of RDW after Pretreatment

IV. SEM ANALYSIS

Scanning electron microscopic (SEM) analysis of the sample before and after treatment is shown in Figure 3. From the imaging, we can see that the microwave assisted pretreatment will change the internal structure of sample. Alkali assisted microwave cause the defibration and fibrilation of the RDW. Defibration is mainly because of alkali action that removed lignin from lignocellulose, while microwave will forke cellulose fibers into fine fibrils. [8] reported that using microwave can cause fragmentation of the fibre. The fragmentation can occur mostly because of high temperature used that can produce chaotic damage on tissue structure. In this experiment, this fragmentation seems less happen since the use of moderate temperature (around 90-91^{0}C). Moreover, [8] also stated that complete tissue collapse can hinder enzymatic hydrolysis due to less space of enzyme action on substrate.

Comparing scanning image between pretreatment using NaOH and $Ca(OH)_2$, it can be seen that both alkali can cause defibration and fibrilation. The use of sodium and calcium hydroxide will give almost the same result. But pretreatment using $Ca(OH)_2$ will produce more destruct fibril that are ready for hydrolysis step.

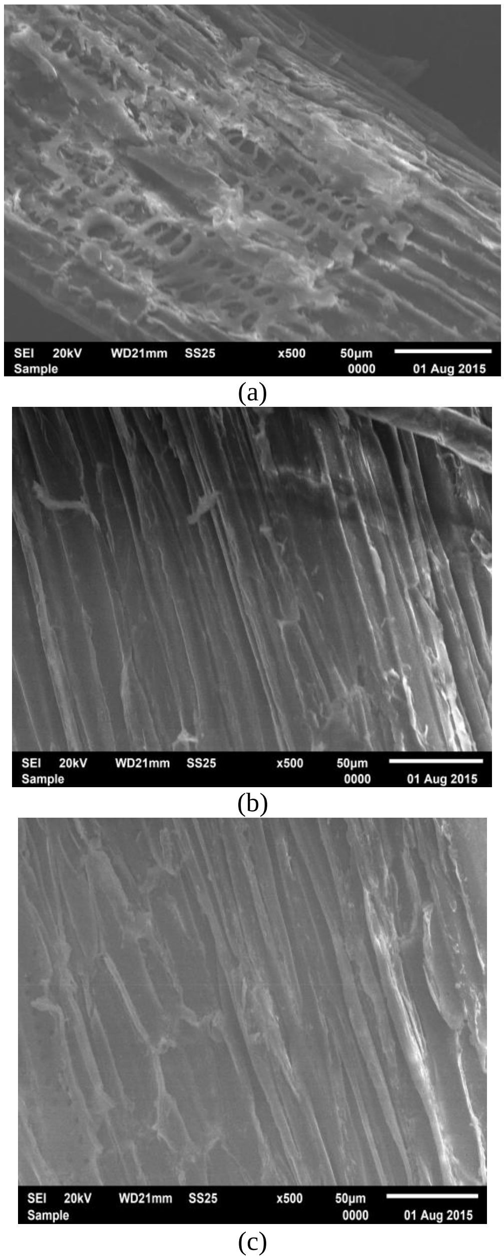

Fig. 2 Scanning Electron Microscopic of (a) untreated RDW (b) microwave-assisted NaOH 5% pretreated (c) microwave-assisted $Ca(OH)_2$ 5% pretreated

V. CONCLUSION

Microwave assisted alkaline pretreatment is one alternative of pretreatment of ramie decortication waste (RDW). Both sodium and calcium hydroxide can be used as the alkaline agent. The use of calcium hydroxide 5% give the best result in reducing lignin content (27,4%). SEM analysis shows that microwave-assisted alkaline pretreatment will cause defibration and fibrilation without chaotic damage on tissue structure

ACKNOWLEDGMENT

The authors greatly acknowledge Directorate General of Higher Education, Ministry of Riset, Technology and Higher Education the Republic of Indonesia for its financial support through Competitive Grant 2015.

REFERENCES

[1] Nomanbhay S M., Hussain, R., Palanisamy, K.., Microwave-Assisted Alkaline Pretreatment of Oil Palm Empty Fruit Bunch Fiber for Enhanced Fermentable Sugar Yield" *J of Sustainable Bioenergy Systems*, Vol. 3, pp. 7-17, 2013.

[2] Leustean, I., Bioethanol from Lignocellulosic Materials, *Journal of Agroalimentary Processes and Technologies*, Vol. 15 (1), pp. 94-101, 2009.

[3] Kumar P., Barrett, DM., Delwiche, MJ, Stroeve, P., Methods for Pretratment of Lignocellulosic Biomass for Efficient Hydrolysis and Biofurl Production, Ind. Eng. Chem. Res, DOI: 10.1021/ie801542g, 2009.

[4] Sukri, SSM., Rahman, RA., Illias, RMD., Yaakob H., Optimization of Alkaline Pretreatment Conditions of Oi Palm Fronds in Improving the Lignocelluloses Contents for Reducing Sugar Production, *Romanian Biotechnological Letters* Vol. 19 (1), 2014.

[5] Gabhane, J., William, SPMP., Gadhe ,A., Rath, R., Vaidya, AN., Wate, S., Pretreatment of Banana Agricultural Waste for Bioethanol Production: Individual and Interactive Effects of Acid and Alkali Pretreatment with Autoclaving, Microwave Heating and Ultrasonication, *Waste Management* Vol. 34, pp. 498-503, 2014.

[6] Purwati, R.D., Strategi Pengembangan Ramie", Perspektif Vol 9 (2), 2010.

[7] Liong, YY., Halis, R., Lai, OM., Mohamed, R., Bioethanol from Grass, *Bioresources* Vol. 7 (4), pp. 5500-5513, 2012.

[8] Gabhane, J., William, SPMP., Vaidya, AN., Anand, D., Wate, S., Pretreatment of Garden Biomass by Alkali-Assisted Ultrasonication: Effects on Enzymatic Hydrolysis and Ultrastructural Changes, *Journal of Environmental Health Science & Engineering*, pp. 12:76, 2014.

[9] Zheng, Y., Pan, Z., Zhang, R., Overview of Biomass Pretreatment for Cellulosic Ethanol Production, *Int J Agric&BiolEng*, Vol. 2 (3), pp. 51-68, 2009.

[10] Mahyati., Patong, AR., Djide, MN., Taba, DP., Biodegradation of Lignin from Corn Cob by Using a Mixture of Phanerochaete Chrysosporium, *Lentinus Edodes and Pleurotus Ostreatus, International Journal of Scientific & Technology Research*, Vol. 2 Issue 11, pp. 79-82, 2013.

[11] Li, Z., Jiang Z., Fei, B., Yu, Y., Cai, Z., Effective of Microwave-KOH Pretreatment on Enzymatic Hydrolysis of Bamboo, *Journal of Sustainable Bioenergy Systems*, Vol. 2, pp. 104-107, 2012.