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Evaluation of high purity cellulose production from pretreated various agricultural biomass wastes

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Abstract. Four kinds of non-wood biomass were studied as raw material for high purity cellulose production. Cajuput (*Melaleuca Leucadendron*) twigs, sugarcane (*Saccharum officinarum*) bagasse, oil palm (*Elaeis guineensis*) empty fruit bunch and rice (*Oryza sativa*) straw were treated by NaOH 1 % at boiling temperature and atmospheric pressure for 2 h. The surface structure of these materials and chemical modification of cellulose, hemicellulose, and lignin during the treatment were analyzed. The result showed that the highest cellulose increasing was from 29.6 to 62.7% for rice straw. Meanwhile, the highest and the lowest cellulose content after treatment were 69.7% for sugarcane bagasse and 48.0% for cajuput, respectively. Scanning electron microscopy (SEM) image showed that the smoother surface for all biomass after pre-treatment.

Keyword: cellulose, cajuput, sugarcane bagasse, oil palm, rice straw

1. Introduction

United Nations Environment Programme (UNEP) reported that in 1950 when the world's population was 2.5 billion, the plastic produced was 1.5 million tonnes. Meanwhile, in 2016 when the population over 7 billion, more than 300 million tonnes of plastic were produced. It is predicted the plastic will reach 33 billion tonnes by 2050 if there are no actions taken [1]. One of possible actions is to use biodegradable plastic or bioplastic. Bioplastics can be produced by using renewable sources such as plant-based raw materials, unlike traditional plastics that are produced from refinery of fossil fuel. In addition, other issues such as biodegradability and other environmental hazards associated with traditional plastics have led to interesting research in the field of bioplastics. Bioplastics currently available on the market are mostly amylose-based such as PLA (Poly Lactic Acid) so that it can affect and compete with food supply. Cellulose plastic is a bioplastic that is produced using cellulose derivatives, which are wood-based both hardwood and softwood. However, because of the deforestation, air pollution, and climate change problems, alternative sources such as biomass from agricultural waste are proposed as promising materials.

Cajuput in Indonesia known as "Kayuputih" is mainly planted in Java, Sulawesi, Moluccas and Nusa Tenggara Timur. Cajuput oil is usually used as herbal remedies such as for baby oil. Indonesia produces

650-ton cajuput oil yearly [2]. If the oil yield is 1-2 %, the biomass potency is about 32.500-65000 ton/year. Regarding sugarcane bagasse (SB), it was reported that in 2014, 2.6 million tons of sugar were produced from 0.48 million ha of planted area [3] and sugar production increased to 2.9 million tons in 2015. Indonesian Ministry of Agriculture estimates that sugar production and harvested area will reach around 3.82 million tons by 2019. During milling, sugar cane is destroyed to extract the juice, producing sugarcane bagasse as a by-product. SB potency was about 9.9–11.2 million tons in 2014 [4].

Indonesia produced 29.3 million tons of crude palm oil (CPO), with production increase to 30.8 million tons in 2015 [Ministry of Agriculture Indonesia, 2015]. In the mill, during milling, fresh fruit bunches (FFB) are separated into fruit (about 70%), empty bunches (about 20 wt.%), and other residues (10%). The potential of oil palm empty bunches (EFB) is around 30-40 million tons per year in Indonesia [5].

Meanwhile, another biomass, rice straw (RS) is also very potential. Rice production in 2015 was 75.36 million tons of milled dry grain (in Bahasa "gabah kering giling") or increased by 4.51 million tons (6.37 percent) compared to 2014 [6]. Previous study reported that there is 18, 9 million ha rice field in Indonesia and if the potency 3 ton of rice straw/ha, 56.7 million ton of rice straw will be produced.

Delignification is commonly known as pulping. The first patent dealing with pulping of wood with aqueous solutions of calcium hydrogen sulfite and sulfur dioxide in pressurized systems was granted in 1886 [7]. Nowadays pulping can be separated to alkaline and acid pulping which is the most common methods. Generally, the lignin reaction during kraft pulping is presented in Figure 1.

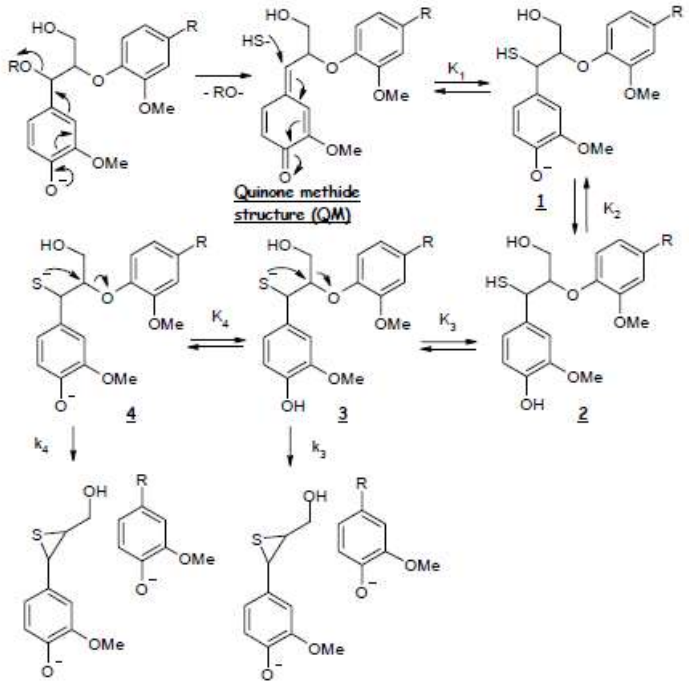


Figure. 1 Cleavage of phenolic b-O-4 linkages during the initial delignification [8].

Cellulose needs to be modified chemically to become bioplastic. Therefore, in this research, isolation, and purification of cellulose from cajuput twigs, sugarcane bagasse, oil palm empty fruit bunch and rice straw as potential cellulose source for bioplastic production, is reported.

2. Materials and Methods

Cajuput twigs (CT) was collected from cajuput oil mill in Gunungkidul region. SB was collected from PG Madukismo, sugar mill in Yogyakarta region. Meanwhile, oil palm EFB was sent from PT Ladang Sawit Mas, Kalimantan Barat and rice straw was collected from rice field in Bantul region, Yogyakarta.

All biomass samples were reduced to 1-2 cm for cooking and further ground to about 40 mesh for chemical analysis. The chemical compositions analysis of raw material and pulp after soda cooking were

determined. The cellulose, hemicelluloses, lignin and water-soluble compound by using Chesson-Datta method [9]. 150 ml of distilled water was added to about 1 g (oven dry) (a) of each biomass and heated in the oil bath for 1 h at boiling temperature. Furthermore, the mixture was filtered and washed with distillation water. Solid residue then subjected to oven and dried to constant weight (b). Solid residue was further reacted with 1 N sulfuric acid 150 ml and heated in the oil bath 100°C for 1 h. The mixture was again filtered and washed with distillation water until neutral and residue dried in the oven (c). The solid residue was again reacted with 72% of sulfuric acid 10 ml at room temperature for 4 h and then 1N sulfuric acid 150 ml was added and refluxed for 1 h in the oil bath. The mixture was filtered and washed again with distillation water until neutral and residue dried in the oven (d). After that, solid residue was heated in the furnace 400°C and weighted (e). The calculation of % hemicellulose = (c – b)/a x 100%; % cellulose = (d – c)/a x 100%; % lignin = (e – d)/a x 100%.

Soda cooking for all ± 15 g (oven dried) biomass were performed at boiling temperature for 2 h with 1% NaOH dosage and solid to liquid ratio was 1: 10.

3. Result and Discussion

In biomass biorefinery, how to separate cellulose, hemicellulose and lignin effectively are very important. In this study, sodium hydroxide 1% was chosen for delignification at boiling temperature. NaOH is widely used in the pulp and paper industry to separate lignin from cellulose because of its effectiveness and its economic process. Solid to liquid ration was 1:10 in order to make sure that all biomass soaked in the alkaline. The previous study was also reported advantages of NaOH compare to other chemicals [10]. The temperature condition was boiling point at atmospheric pressure. This stage is called delignification-1 which is the first step for a further increment of the reaction temperature and pressure. The chemical composition of various biomass before and after delignification is presented in Table 1.

Table 1. Chemical composition of materials after delignification.

Materials		Water soluble compound	Cellulose	Hemicellulose	Lignin
Rice straw	raw material	24.00	29.55	25.35	9.99
	delignification-1	6.68	62.72	15.68	14.51
Oil palm empty fruit bunch	raw material	21.10	42.56	20.27	15.36
	delignification-1	6.68	62.72	15.68	14.51
Sugarcane bagasse	raw material	16.18	42.31	20.74	18.61
	delignification-1	4.12	69.69	14.73	10.77
Cajuput twigs	raw material	22.16	31.94	17.99	27.51
	delignification-1	6.15	47.98	15.34	30.31

Table 1 shows that the highest cellulose content obtained for sugarcane bagasse that is 69.69% while the lowest is cajuput twigs which are 47.98%. While the highest increasing in cellulose content during delignification was obtained by rice straw which was 111.8%, and the lowest was eucalyptus twigs 50.2%. Lignin content of rice straw and cajuput twigs increased after process can be explained by removal process of lignin, cellulose, and other compounds. For instance, the total percentage of chemical composition of rice straw was 88.9% (about 11.1% was other materials) and after delignification increased to 99.6%. Hence, the dividing factor smaller than the raw material. For comparison, total chemical composition of raw material for SB was 97.8% and 99.3% after delignification. Other chemical compounds in the wood and non-wood biomass usually ethanol or other organic solvents soluble compounds; acid-insoluble lignin; organic acids and ash content.

Overall this cellulose yield is still very low compared to the target of above 90%. Therefore, optimization will be carried out by increasing the process temperature, applying pressure and increasing

the NaOH level using will be performed. In addition, bleaching stage will be carried out in the next stage.

The Fourier transform infrared spectra of cajuput twigs before and after treatment with NaOH 1% were shown in Figure 2. The broad peak around 3300-3400 cm^{-1} in all spectra is representative of the stretching of hydroxy (-O-H) groups. The peak around 2800-2900 cm^{-1} and 1970-2200 cm^{-1}, which was observed in all spectra corresponds to the C-H stretching and overtone of aromatic rings of lignin, respectively.

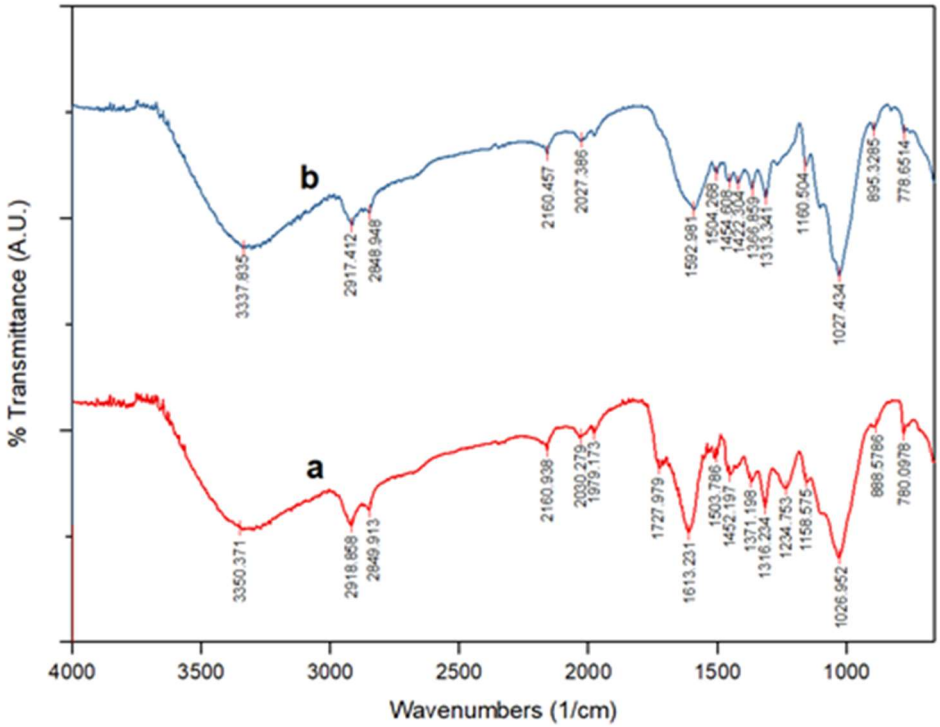
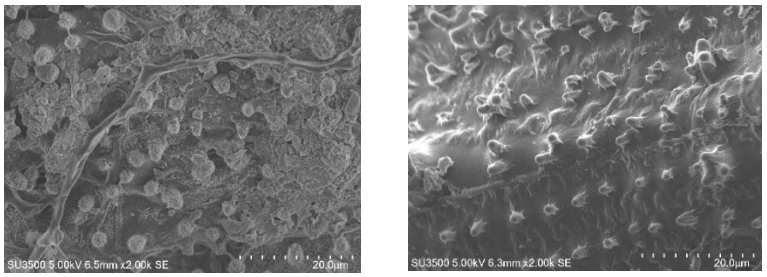


Figure 2. FTIR spectra of raw cajuput twigs (a) and after delignification-1 (b).

After delignification process, one of the samples, namely the Cajuput twigs, analyzed for its spectrum using FTIR to see the effect of the treatment with NaOH. The Fourier transform infrared spectra of eucalyptus trunk before and after treatment with NaOH 1% were shown in Figure 1. The broad peak around 3300-3400 cm^{-1} in all spectra is representative of the stretching of hydroxy (-O-H) groups. The peak around 2800-2900 cm^{-1} and 1970-2200 cm^{-1}, which was observed in all spectra corresponds to the C-H stretching and overtone of aromatic rings of lignin, respectively. A shoulder at 1727 cm^{-1} of the raw eucalyptus trunk exhibit the spectrum of (C=O st) acetyl and ester groups in hemicellulose or carboxylic acid groups in pectin and p-coumaric components of lignin [1]. Alkaline treatment with NaOH 1% could eliminate non-cellulosic materials. Both sets of peaks are assigned the absorption of water (-O-H bend)around 1590-1620 cm^{-1}. The shifting from 1613 to 1592 cm^{-1}represents the weaker bond of -OH bend of water in the product of NaOH treatment. The existing of a peak around 1500 cm^{-1} (C=C aromatic st) in all peaks indicate that alkaline treatment cannot completely eliminate all of the lignin compounds from the eucalyptus trunk. The appearance of a peak around 1422 cm^{-1} is representative of the absorption of $-CH_2-$ symmetric bending of alkaline treatment product. The absorption around 1300-1400 cm^{-1} of both spectra refers to the bending frequency of in-the-plane CH_2 bending. Both peaks around 1160 and 1027 cm^{-1} refer to C-O-C asymmetric and C-C, C-OH, C-H ring, and side vibrations; while and peak at 895 cm^{-1} is representative of COC, CCO, and CCH deformation and stretching [2]. Furthermore, based on the calculation of spectral ratio (3300/1500 cm^{-1}), the ratio of cellulose and hemicellulose to lignin were significantly increased due to alkaline treatment.

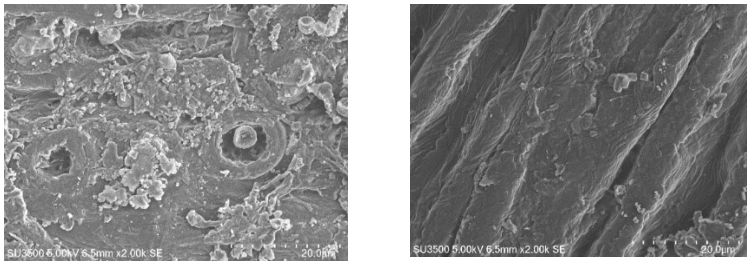
Morphology of surface was analyzed by using scanning electron microscopy (SEM). The SEM is SU-3500 Hitachi, Tokyo, Japan with a magnification of 2000x and the SE 5 kV. Figure 3 shows the SEM image of the biomass surface before and after treatment with NaOH. The SEM profile shows that

the surface of the material at magnification is 2000 times cleaner than the material. It is suggested that the hemicellulose, some lignin, and other impurities dissolved into black liquor.



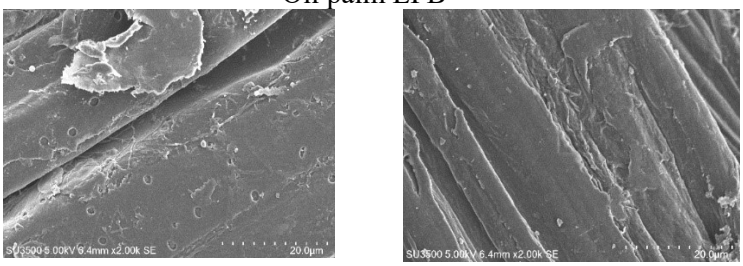
(a) (b)

Rice straw



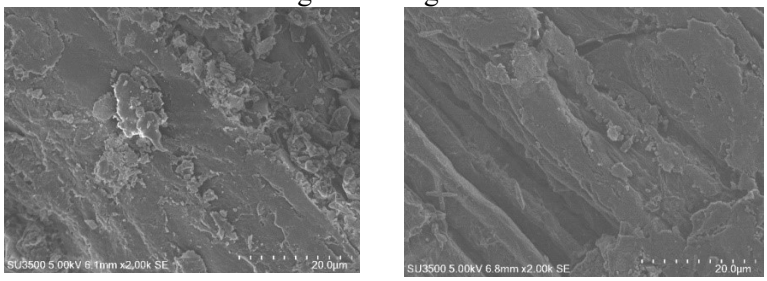
(a) (b)

Oil palm EFB



(a) (b)

Sugarcane bagasse



(a) (b)

Cajuput twigs

Figure. 3 Scanning Electron Microscopy profile of the materials
(a) raw material, (b) after delignification-1

4. Conclusion

The condition of 1% NaOH at boiling temperature and atmospheric pressure for 2 h increased cellulose content 111.8% for the rice straw, the highest among other biomass. In addition, in this condition, the highest cellulose content was 69.7% for sugarcane bagasse.

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