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Alkaline Pretreatment on Sugarcane Bagasse for Bioethanol Production

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Abstract

Sugarcane bagasse is a lignocellulosic waste from sugar mills and agricultural processing. The aim of this research was evaluation of alkaline pretreatment on the chemical composition and structure of sugarcane bagasse. Pretreatment was conducted with cooking by sodium hydroxide. It was carried out at 12 L reactor with concentrations variation. Meanwhile, times variations were conducted for 15, 30, 40, and 45 minutes, respectively. Sugarcane bagasse characteristics before and after pretreatment have been analyzed by X-ray Diffraction and Fourier Transform Infra Red Spectrometer. The results showed that the lowest lignin content (7.16%) was the treatment by NaOH 1N for 30 minutes.

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Keywords : sugarcane bagasse; cellulosic ethanol; lignocellulose; alkaline pretreatment; agricultural waste

1. Introduction

Currently, bioethanol research is still continuously expanding. Not only serve as a renewable energy, bioethanol that is believed as most prospective bioenergy, can also be a solution for air pollution problem. While production of first generation ethanol from starchy materials has developed well, production process of second generation ethanol from lignocellulosic materials is still looking for its economical feasibility. Furthermore, first generation ethanol materials are also generally very important food sources that will impair food security issue and their availability are also not sufficient to cover the total required bioethanol production. Therefore, this research aims to elaborate lignocellulosic ethanol production prospective from sugarcane bagasse as an effort to overcome bottleneck of lignocellulosic ethanol.

Waste of wood processing and agricultural are prospective sources of bioethanol. One of them is sugarcane bagasse that abundance available and it has softer structure compare to others that could be easily to break down. Its availability as a waste from agricultural waste and waste from production process of sugar mill could be utilized for bioethanol production. It can be a benefit for both a national energy security program and farmers as well as sugar factory additional profit. In year 2009, there was 2.9 million ton potency of sugarcane bagasse in Indonesia and could yield 614.8 kL of bioethanol from both glucan and xylan [1]. Several sugar factories have also combined sugar mills and first generation bioethanol-plant. The technology for combining sugar mills and bioethanol plant has been in commercial use for the past 30 years and can be considered to be mature as the cost of feedstock accounts for a major part of the production cost [2]. Sugar mills are commonly utilizes molasses as raw material for ethanol production and its derivatives.

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The view of bagasse has changed throughout the years, due to technological breakthroughs, investment opportunities and revenue margin. The integration with first generation production could greatly facilitate this development [3]. Effectively delignification and fermentation are bottleneck in lignocellulosic ethanol production. Besides improving efficiency and cost effective of enzymatic fermentation rate, another problem is to separate lignin from cellulose and hemicelluloses. Cellulose and hemicelluloses need to be converted to sugars and further be fermented to ethanol. Lignocelluloses are resistant to degradation and offer hydrolytic stability and structural robustness, which is mainly due to cross linking between polysaccharides (cellulose and hemicellulose) and lignin via ester and ether linkages. Cellulose and hemicellulose are densely packed by layers of lignin, that offer protect in against enzymatic hydrolysis [4].

There are many methods have been reported to separate cellulose and hemicelluloses from lignin such as acid pretreatment, alkaline pretreatment, steam explosion, wet oxidation and organosolv pretreatment. Extremely low acid treatment has been reported to produce glucose from lignocellulosic material [5]. One of the shortcomings, the acid treatment has known for resulting furfural that could be an inhibitor for further process. Therefore, Alkaline cooking has chosen to be used for pretreatment in this research. The linkage between lignin and cellulose is presented in Figure 1.

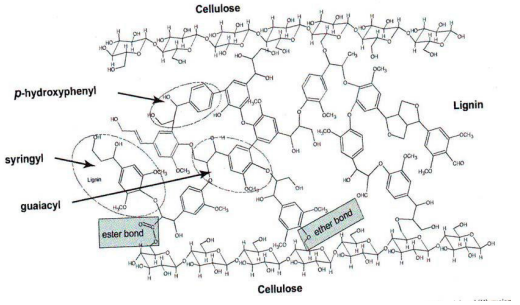

Fig. 1. Chemical linkages between lignin and cellulose [6].

In this research, alkaline pretreatment that active alkaline was sodium hydroxide is intended to breakdown the chemical bonds of lignin and cellulose of sugarcane bagasse. Moreover, the optimal conditions will be particularized for scale up purposes. During the research, delignification reactor was carried out at 12 L volume, as preliminary experiment from overall research that will use 120 L reactor which has been installed at our laboratory.

2. Materials and method

2.1 Materials preparation and alkaline treatment

Sugarcane bagasse was provided by PG Madukismo, a sugar mill in Yogyakarta province, Indonesia. The bagasse was washed and dried, then milled to size 40 mesh. 250 g of bagasse was weighted and placed at 12 L reactor. Three litter of NaOH was added to the reactor (solid to liquid ratio was 1:12). Concentration of NaOH was 1N and 2N alternately. The reactor was heated at 100ºC and 1 bar pressure. Cooking time with NaOH 1N was performed by heating the reactor for 15 min., 30min., and 45 min. respectively. Meanwhile cooking time with NaOH 2N was 40 minutes. Before and after cooking, bagasse has been analyzed for its lignin, cellulose and hemicelluloses content by using Chesson method [7]. One g (a) of dry sample was added with 150 ml H_2O. Then, refluxed at 100 °C in water bath for 1 h. The result was filtered, and the residue washed with hot water (300 ml). The residue was then dried in an oven until constant then weighed (b). Residue was added 150 ml of 1 N H_2SO_4 then refluxed in a water bath temperature of 100° C for 1 h. The results are filtered to neutral (300 mL) and dried (c). Dried residue was added with 10 ml of 72% H_2SO_4 and soaked at room temperature for 4 h. Residue then added 150 ml of 1 N H_2SO_4 and refluxed on a water bath for 1 h. Residue was filtered and washed with H_2O to neutral (400 mL) and then heated in an oven with a temperature of 105ºC and the results weighed (d), the residue weighed and ashed in the furnace (e). Hemicellulose content = [(b-c)/a] x 100%; Cellulose content = [(c-d)/a] x 100%; Lignin content = [(d-e)/a]x 100%.

2.2 Sugarcane bagasse characterization

Characterization of bagasse before and after treatment has been conducted by using difractometer X-ray Shimadzu with condition X-ray tube Cu (1.54060A); 40kV; 30mA; and scanning range 3-80º. Furthermore, characterization of functional groups has been performed by Fourier Transform Infra Red (FTIR) spectrometer Shimadzu, wavelengeth 400-4000cm^{-1} at detector with resolution 16 cm^{-1}.

3. Results and discussion

Alkaline pretreatment by cooking with sodium hydroxide is one of essential steps in bioethanol research. Pretreatment cooking was performed and chemical composition of sugarcane bagasse was analyzed before and after the treatment. The result is presented in Table 1.

Table 1. Percentage of chemical compounds of sugarcane bagasse .

Treatment	Cooking time (minutes)	Cellulose	Hemicellulose	Lignin	Water solub. materials
		Mean ± S.D. (n=3)	Mean ± S.D. (n=3)	Mean ± S.D. (n=3)	Mean ± S.D. (n=3)
untreated	0	44.43 ± 0.86	22.9 ± 0.67	17.52 ± 0.65	14.18 ± 0.24
NaOH 1N	15	66.16 ± 0.13	17.06 ± 0.4	8.34 ± 0.35	8.43 ± 0.24
NaOH 1N	30	62.16 ± 0.87	18.62 ± 1.65	7.16 ± 0.32	11.62 ± 0.77
NaOH 1 N	45	61.46 ± 0.79	20.60 ± 0.53	7.54 ± 0.57	10.21 ± 0.29
NaOH 2 N	40	56.33 ± 0.79	20.86 ± 0.90	9.93 ± 0.57	13.03 ± 0.83

Based on Table 1, bagasse without pretreatment cooking or untreated bagasse contained 44.43% of cellulose and 17.52% of lignin. It can be seen that after delignification by NaOH 1N for 15 minutes, the cellulose became 66.16% or 48.9% increased and lignin decreased by 40.6%. Meanwhile for 30 minutes of delignification, cellulose shifted to 62.16% or increased 39.9% and lignin content shifted to 7.16% or decreased 59.1%. Moreover, after delignification by NaOH 1 N for 45 minutes, cellulose increased 38.3% and lignin content decreased 57%. While, delignification by NaOH 2N for 40 minutes was the lowest for cellulose content and the highest of lignin content among others. Delignification by using NaOH 2N for 40 minutes has been able to increase cellulose by 26.8% and to decrease the lignin content by 43.3%. From this data, it can be seen that if cellulose content increased higher, the lignin content will also decreased more, except for 15 minutes delignification of NaOH 1N. This anomaly could be caused by chemical linkage between lignin and cellulose are still quite higher compare to other delignification time and cellulose still in cristalline formation. Therefore, during 15 minutes delignification the cellulose content was the highest, but the lignin was also high concentration. The highest of cellulose content probably because cellulose in solid phase is high and only slightly fraction of lignin turn to the liquid phase. After pretreatment, the cellulose could be still in solid phase and small fraction will be in liquid phase. Therefore, it can be concluded that delignification by NaOH 1N for 30 minutes was the most effective for delignification process because of decreased of lignin level was the highest. It can also be seen that the using of NaOH 1N was more effective to reduce lignin content and to increase cellulose content than the using of NaOH 2N for bagasse delignification.

Comparison of the level of lignin, hemicellulose and cellulose content after delignification by NaOH 1N is presented in Figure 2.

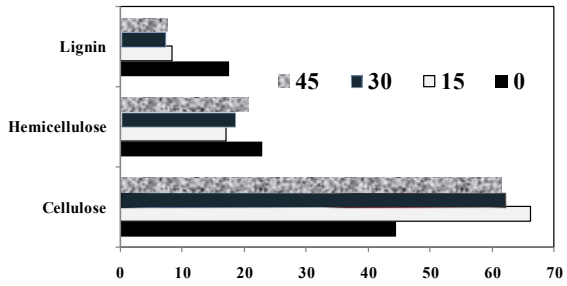

Fig. 2. Comparison of chemical composition in bagasse after delignification by NaOH 1N.

Based on Figure 2, lignin content after cooking 30 minutes was the lowest, 7.16%. Meanwhile ratio of lignin content after cooking times 45 minutes, 15 minutes and untreated bagasse to the lowest percentage were 1.1, 1.2, and 2.5 times respectively.

Characterization of sugarcane bagasse before and after pretreatment cooking has been analyzed by using X-ray Diffraction (XRD). The result is presented in Figure 3.

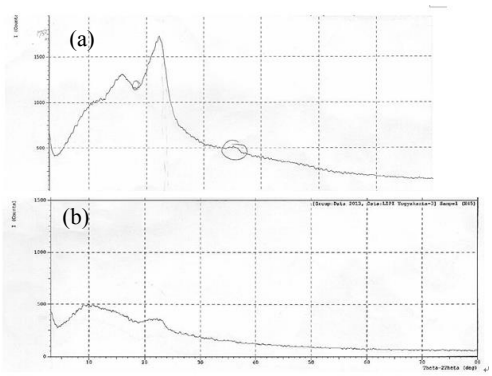

Fig. 3. (a) Diffractogram of fresh bagasse; (b) Diffractogram of bagasse after pretreatment with NaOH 1N 45 minutes.

Based on Figure 3 (a), It can be seen that on bagasse without pretreatment the peak with 2θ=23º and 2θ=15º were peaks of cellulose, the peak height indicates the crystallinity of cellulose levels are still quite high [8]. While on bagasse after preteatment with NaOH 1N for 45 minutes, the peak declined in crystallinity index. This might be due to treatment with NaOH could alter the conformation and morphology of cellulose fibers. During the treatment process, the cellulose chain expands due to diffusion of base into the crystalline cellulose. Furthermore, the cellulose chain will undergo re-arrangements that result in damage to the structure of crystalline cellulose. Damage in the crystalline structure to non-crystalline cellulose led to an increase amorphous cellulose, so that the crystallinity index decreased. Crystallinity of cellulose in this diffractogram was determined by the equation 1 [9].

$$I_c = \left(\frac{I_{200} - I_{am}}{I_{200}} \right) x100 \qquad (1)$$

Where: Ic = Crystallinity, I_{200} = peak at 2θ=23º and I_{am} = peak between 2θ=23º and 2θ=15º
Ic of bagasse without pretreatment was 20.59%. Meanwhile Ic of bagasse after delignification was 13.33%. Therefore, the crystallinity index decreased by 35.3%.

FTIR spectroscopy has been used in this research, since it presents a relatively easy method for obtaining direct information on chemical changes that occur during delignification by NaOH. Infra red spectroscopy is used to determine the functional groups in a compound and to determine the chemical structure changes that occur in the lignocellulosic material. The result obtained is presented in Figure 4.

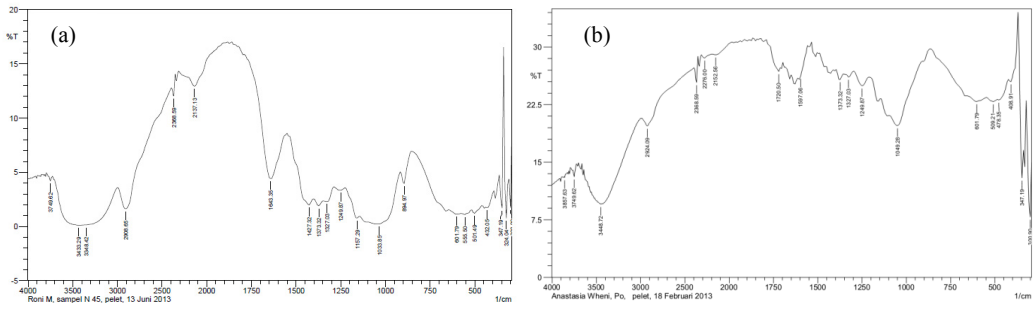

Fig. 4. (a) IR spectra of freshbagasse; (b) IR spectra after pretreatment with NaOH 1N 45 minutes.

Based on Figure 4, there was a significant difference between the spectra of fresh bagasse and the spectra of bagasse after delignification with NaOH. This difference indicated that there are the structural changes because of alkaline treatment. Spectra contained broad peak at a wavelength 3400 to 3500 cm^{-1}, the peaks could be the culmination of a functional group-OH and a peak around 2924 cm^{-1} derived from the CH stretching. Peak appeared around 1033cm^{-1} in the spectra of bagasse after delignification, and the peak around 1049 cm^{-1} at the spectra of fresh bagasse, showing C-O-C stretching of glycoside bond β-(1-4) [10]. At the spectra of fresh bagasse contained peaks at a wavelength of 2924 cm^{-1} derived from the -CH_2 stretching and shifted to 2908 cm^{-1} on bagasse after delignification. Increased peak intensity that occurs at wavelength between 900-1150 cm^{-1} indicated that the presence of elevated levels of cellulose [10]. Therefore, it can be seen that after delignification, cellulose

content increased.

4. Conclusion

Optimal result for delignification of sugarcane bagasse was obtained by pretreatment cooking by using NaOH 1N for 30 minutes. Furthermore, cristallinity of cellulose decreased after pretreatment which is in line with decreasing of lignin level. Meanwhile, increasing of cellulose content can be detected after alkaline pretreatment from the FTIR spectrum result.

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