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The effect of acid variation on physical and chemical characteristics of cellulose isolated from *Saccharum officinarum* L. Bagasse

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Abstract. *Saccharum officinarum L.* bagasse is waste from sugarcane plants contains lignin, hemicellulose, cellulose and wax compounds. Isolation of cellulose from sugarcane can be done by acid hydrolysis of sugarcane waste and delignification with Sodium Hydroxide (NaOH). The objectives of this research were to study the effect of acid type and concentration on the physical and chemical characteristics of cellulose isolated from sugarcane bagasse. The acid variation that used were nitric acid: sulphuric acid; nitric acid; hydrochloric acid and sulphuric acid: hydrochloric acid in 1:1; 2:1 and 3:1 in the variation of concentration for each combination. Cellulose characteristics observed were color, shape and powder properties such as Hausner Ratio, Carr's index, Angle of Repose and functional group analysis of cellulose using FTIR (Fourier Transform Infrared). The cellulose that isolated from sugarcane bagasse with HNO_3: H_2SO and HNO_3: HCl were matched in white powder form with standard cellulose. Cellulose color that obtained with other acids were cream in fiber form. The results showed that the hydrolysis process of cellulose with nitric acid was more effective than sulfuric acid and hydrochloric acid. Standard cellulose FTIR spectra showed that delignification process was success and cellulose obtained from sugarcane bagasse. Sugarcane bagasse cellulose samples that isolated with nitric acid: hydrochloric acid (2:1) was the largest in percentage of cellulose (44.143%) and showed in line peaks with standard cellulose. Bulk Densities, Tapped Densities, Hausner Ratio, Carr's index and Angle of Repose values of sugarcane bagasse cellulose isolated in sequence were 0.05; 0.07; excellent; 26.6; good.

1. Introduction

Sugar cane (*Saccharum officinarum* L.) is a plant that becomes a source of raw materials for sugar, leaving waste or bagasse. From 1980 to 2013, the sugarcane productivity in the world tends to increase. Even since 2008, the productivity of sugarcane in the world is stable at 6 tons/ha. The highest productivity of sugarcane in the world was achieved in 2006, amounting to 7.35 tons/ha. The amount of sugarcane production at the level of the world, ASEAN and especially in Indonesia represent the amount of sugar production that can be achieved at each level while at the same time illustrating the large amount of potential sugarcane residual waste that may be produced [1].

Sugarcane bagasse is a fibrous residue from sugarcane that obtained after a juice extraction process [2]. Sugarcane bagasse is a waste obtained from the sugar mill and alcohol industry. Commonly, it was used as a fuel for the sugar mill [3]. Other applications of sugarcane bagasse are as animal feeds and sources of fuel in other industries or mill.

On a dry weight basis, sugarcane bagasse contains 43.6% of cellulose; 33.8% of hemicellulose; 18.1% of lignin; 2.3% of ash, and 0.8% of wax [4]. Sugarcane bagasse contains 40-50% cellulose, much of which is in the crystalline structure. Another component in sugarcane bagasse is hemicellulose as much as 25-35% which is an amorphous polymer and mainly composed of xylose, arabinose, galactose, and mannose. The rest is mostly lignin which is about 18-24% [3]. According to that, sugarcane bagasse can be used as an alternative source of cellulose.

Cellulose is a renewable polymer resource which currently has the most abundant of availability. Cellulose is one of the most important natural polymers and is a major source of materials on an industrial scale. Besides, cellulose can be isolated from oil palm of mesocarp fiber [5]; potato skin waste [6]; sugar palm fibre [7]; sago plants [8]; corn husk [9].

Isolation of cellulose can be processed by several methods. First is by using toluene as organic solvent in isolation process [10]. Second is enzymatic hydrolysis [11]. Third is acid-base hydrolysis [3,12]. Toluene was known as toxic solvent in second grade. It means toluene can be the agent of irreversible toxicity disease such as neurotoxicity or teratogenic. Enzymatic hydrolysis process was very difficult and need long time in process for about 72 hours. The method that most widely used is acid hydrolysis.

Acid-base hydrolysis methods commonly used nitric acid, sulphuric acid or hydrochloric acid as single solvent. The first step of acid hydrolysis in converting bagasse to cellulose called delignification. Lignin as the component of bagasse was removed leaving cellulose as end product. The aim of this research was to study the effect of acid combination and concentration. The acid variation that used were nitric acid: sulphuric acid; nitric acid; hydrochloric acid and sulphuric acid: hydrochloric acid in 1:1; 2:1 and 3:1 in the variation of concentration.

2. Methods

2.1 Materials

Sugarcane bagasse was collected as waste from brown sugar industry located at Kediri, East Java, Indonesia. The other reagents used were: sulphuric acid, hydrochloric acid, nitric acid, sodium hydroxide, hydrogen peroxide. All chemicals were pro analysis grade.

2.2 Methods

a. *Sample preparation*

Sugarcane bagasse was dried under the sunlight and then cut into small pieces. The cut bagasse was then grinded into powder and sifted with a 100 mesh sieve. Sugarcane bagasse powder stored in a closed jar at room temperature. The moisture content of sugarcane bagasse measured with Mettler Toledo HE 53 analyzer.

b. *Isolation of cellulose from sugarcane bagasse*

50 g of sugarcane bagasse was hydrolyzed by using 400 mL acid at 80 °C for 2 h. The acid variation that used were nitric acid: sulphuric acid; nitric acid; hydrochloric acid and sulphuric acid: hydrochloric acid in 1:1; 2:1 and 3:1 in the variation of concentration for each combination. The residue washed with distilled water until neutral pH then added with sodium hydroxide 2 N at 80 °C for 1 h. The residue washed with distilled water and then bleached using 15% hydrogen peroxide at 80 °C for 1 h [12]. The cellulose obtained dried up at 70 °C for 24 h [13].

2.2.1 Physical characterization of sugarcane bagasse cellulose
In this research, cellulose obtained from sugarcane bagasse that was hydrolyzed with acid variation and concentration characterized in both color and form. Each result then compared to standard cellulose. Percentage of cellulose yield counted for each cellulose isolated in acid variation and concentration.

2.2.2 Powder properties of sugarcane bagasse cellulose
Powder properties of cellulose such as bulk densities, tapped densities, hausner ratio, carr's index and angle of repose were calculated in this research. The formula for each properties were:

a. *Bulk Densities*
2 grams of cellulose placed in a sterile 100 mL measuring glass. The bulk volume of the sample was obtained and recorder.

$$\rho\ bulk = \frac{massa\ (g)}{volume\ (mL)} \qquad (1)$$

b. *Tapped Densities*
The measuring glass containing the sample was tapped from a height of 2.5 mm until the analytical balance was read constant. The tapped volume was also recorded.

$$\rho\ tapped = \frac{massa\ (g)}{volume\ (mL)} \qquad (2)$$

c. *Hausner Ratio*

$$Hausner\ Ratio = \frac{\rho\ \text{tapped}}{\rho\ \text{bulk}} \qquad (3)$$

d. *Carr's Index*

$$Compressibility\ Index = 100 \times \frac{\rho\ tapped - \rho\ bulk}{\rho\ tapped} \qquad (4)$$

e. *Angle of Repose*
Through the fixed funnel and free standing cone method, the static angle of repose was obtained. A graphing paper was raised on a horizontal surface with the tip of a funnel, 2 cm away from the paper. The sample powder was put through the funnel until the apex of the one reached the tip of the funnel. The height (h) and radius (r) of the cone were recorded.

$$\theta = \tan^{-1}(\frac{h}{r}) \qquad (5)$$

Angle of Response	Flowability
≤31	Excellent
32-45	Good
46-56	Medium
≥57	Poor

2.2.3 Infrared spectra analysis
The FTIR spectra of sugarcane bagasse and sugarcane bagasse cellulose were recorded on Fourier Transform Infrared (FTIR) Spectrophotometer Shimadzu in the wavelength range from 4000 cm^{-1} to 500 cm^{-1}.

3. Results and Discussion

3.1 Isolation of cellulose from Sugarcane Bagasse
Figure 1 (a) shows the wet sugarcane bagasse and (b) the sugarcane bagasse powder (dried). The moisture content of sugarcane bagasse was 6%. Physically, sugarcane bagasse was in fibre form. The hydrolysis process started with adding acid (in combination and concentration variation). The type of acid variation gave the different characteristics in end product (cellulose), while the concentration

variation didn't. The different type of acid gave the difference hydrolysis effect in linkage breaking between lignin, hemicelluloses, and cellulose of sugarcane bagasse. The adding of sodium hydroxide optimized delignification process and solute. Figure 1 (c) was the cellulose after bleaching process with hydrogen peroxide.

(a) (b) (c)

Figure 1. Sugarcane bagasse (a), sugarcane bagasse powder (b) and sugarcane bagasse cellulose isolated with HNO_3: H_2SO_4 (2:1) (c).

3.2 Physical characteristics of sugarcane bagasse cellulose

Table 1 shows the effect of acid variations and concentration toward color and form of sugarcane bagasse cellulose. Only sugarcane bagasse cellulose which obtained with sulphuric acid: hydrochloric acid variations that inappropriate with standard cellulose in color and form. The color and form of sugarcane bagasse cellulose of its variations was fibre and more like bagasse before isolation process. Nitric acid optimized the process of sugarcane hydrolysis by changing the shape of the lignin contained in the bagasse into the form of nitro lignin which can be dissolved in the base [14].

The influence of electrons on the nucleus of the guasil group from lignin during the hydrolysis process causes the electrophile to strongly point to the para or orto position to the OH group which causes a breakdown of the bond with the propyl chain side, where the lignin end unit will split from the remaining lignin macromolecule and become a dissolved form [15].

Table 1. The effect of acid variations and concentration toward physical characteristics of sugarcane bagasse cellulose.

No.	Acid variations	Colour	Form	Compare to standard cellulose
1	HNO_3:H_2SO_4 (1:1)	White	Powder	Appropriate
2	HNO_3:HCl (1:1)	White	Powder	Appropriate
3	H_2SO_4:HCl (1:1)	Cream	Fibre	Inappropriate
4	HNO_3:H_2SO_4 (2:1)	White	Powder	Appropriate
5	HNO_3:HCl (2:1)	White	Powder	Appropriate
6	H_2SO_4:HCl (2:1)	Cream	Fibre	Inappropriate
7	HNO_3:H_2SO_4 (3:1)	White	Powder	Appropriate
8	HNO_3:HCl (3:1)	White	Powder	Appropriate
9	H_2SO_4:HCl (3:1)	Cream	Fibre	Inappropriate

The percentage of cellulose yields showed in Table 2. The largest percentage of cellulose (44.143%) obtained from sugarcane bagasse that isolated with nitric acid: sulphuric acid (3:1).

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Table 2. Percentage of cellulose yield in acid variations and concentration.

Acid variations		% Yield	SD
HNO_3:H_2SO_4	1:1	41.128	0.0005
	2:1	44.143	0.0005
	3:1	41.075	0
HNO_3:HCl	1:1	39.145	0.001
	2:1	35.185	0
	3:1	38.125	0.288

3.3 Powder properties of sugarcane bagasse cellulose

Powder properties of sugarcane bagasse cellulose were calculated for cellulose isolated with nitric acid: sulphuric acid (2:1). Using the formula given, the mean bulk densities of cellulose was 0.05 gram and the mean tapped densities was 0.07 gram. Carr's index explores the cellulose indication of compressibility. The result showed that the compressibility index of sugarcane bagasse cellulose was poor to passable (26.6%). The angle of repose tells the property of a granular material or powder to form the steepest angle without slumping [16]. The angle of repose made on the sugarcane bagasse cellulose shows good result. The Hausner Ratio explores the correlation of the flow ability of a powder or granular material. After the tests, the Hausner Ratio of sugarcane bagasse cellulose was excellent.

3.4 Infrared spectra analysis

The aim of infrared spectra analysis was to know the changing peaks of sugarcane bagasse before and after hydrolysis treatment. The difference peaks used to know that the lignin and hemicellulose have been removed during isolation process. Figure 2 shows the infrared spectra of sugarcane bagasse and sugarcane bagasse cellulose. In this figure, we also compared the infrared spectra of sugarcane bagasse cellulose to standard cellulose.

The FTIR spectra of all samples have shown a wide band in the region 3300-3500 cm^{-1} that specifies the free O-H stretching vibration of the -OH groups in cellulose molecules. The increase intensity of peaks (112.64 (a), 128.59 (b) and 141.46 (c)) because of the increase in –OH concentration. The increase of –OH concentration influenced by reduces hydrogen bonding by removal of the hydroxyl groups because of alkali treatment using sodium hydroxide. The infrared spectra of all samples showed the specifies C-H stretching vibration around 2800 cm^{-1} and 2900 cm^{-1} [3,10].

Based on FTIR spectrum, there are several peaks in sugarcane bagasse which is not found in the spectrum of cellulose. The peaks are around 1240.22 cm^{-1}, 1512.19 cm^{-1}, 1602.54 cm^{-1}, and 1734 cm^{-1} and 1738 cm-1. The absorption peak of 1240.22 cm^{-1} is derived from C-O stretching vibration of aryl group in lignin. The peak at 1512.19 cm^{-1} is attributed to the C=C stretching vibration of the aromatic ring in lignin. The peak at 1602.54 cm^{-1} and 1734 cm^{-1} is attribute to the C=O stretching vibration of carboxylic groups of hemicellulose and lignin. These bands were no longer present in the FTIR spectra of cellulose standard and sugarcane bagasse cellulose. The disappearance of these bands could have been caused by the removal of hemicellulose and lignin from bagasse fibres during the chemical extraction [10,17,18].

In addition, the vibration peak detected at 1369.45 cm^{-1} in standard cellulose and sugarcane bagasse cellulose is related to the bending vibration of the C– H and C–O bonds in the polysaccharide aromatic rings. The peak at 1651.06 in standard cellulose and sugarcane bagasse cellulose to show –OH bending of adsorbed water. The slightly higher moisture content may be attributed to the absorption of moisture in the spaces left vacant from the removal of hemicellulose and lignin. The open surfaces created in the alkali treated cellulose helps absorb moisture. The most important absorption band that continually increases from sugarcane bagasse to sugarcane bagasse cellulose is at 867.97 cm^{-1} in sugarcane bagasse, 896.89 in standard cellulose and sugarcane bagasse cellulose. This peak show about associated with the glycosidic linkages between glucose units in cellulose. Finally, the peak observed in the spectra of all samples between the 1053.12 cm^{-1} and 1112.9 cm^{-1} in sugarcane bagasse, 1041.56 cm^{-1} and 1159.21 cm^{-1} in standard cellulose, and 1053.13 cm^{-1} and 1110.99 cm^{-1} in sugarcane bagasse cellulose range is due to the C–O–C pyranose ring (antisymmetric in phase ring) stretching vibration.

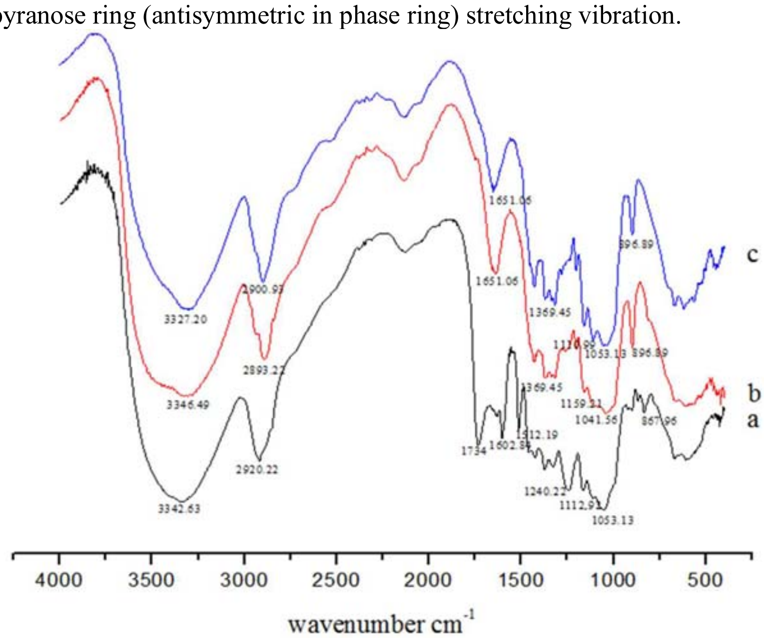

Figure 2. FT-IR spectra of sugarcane bagasse (a); standard cellulose (b) and sugarcane bagasse cellulose (c).

4. Conclusion

The acid type which produces cellulose that appropriate with standard cellulose were nitric acid; sulphuric acid and nitric acid: hydrochloric acid. Physically, cellulose was white powder form. The largest percentage of yields obtained with nitric acid; sulphuric acid in 2:1 combination. FTIR spectra showed that delignification process was success and cellulose obtained from sugarcane bagasse. Sugarcane bagasse cellulose samples that isolated with nitric acid: hydrochloric acid (2:1) was the largest in the percentage of cellulose (44.143%) and showed in line peaks with standard cellulose. Bulk Densities, Tapped Densities, Hausner Ratio, Carr's index and Angle of Repose values of sugarcane bagasse cellulose isolated in sequence were 0.05; 0.07; excellent; 26.6; good.

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