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Optimization of Microcrystalline Cellulose from Bagasse (*Saccharum officinarum*) by Acid Hydrolysis

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ABSTRACT

Microcrystalline cellulose (MCC) is a compound produced from refining alpha cellulose with excessive amounts of acidic minerals that has a white visual color, odorless and biodegradable. MCC is often used as an excipient in the pharmaceutical and food industries. This study aimed to determine the content of alpha cellulose from bagasse with varying concentrations of nitric acid and the highest degree of crystallinity produced from microcrystalline cellulose. The research began with drying and smoothing bagasse. Then, the bagasse was delignified using HNO3 solution with a concentration of 5%, 7.5% and 10%, followed by NaOH solution. The sample obtained was bleached using NaClO solution to obtain alpha cellulose. Then, alpha cellulose was hydrolyzed using HCl solution to obtain microcrystalline cellulose. The purity of alpha cellulose with nitric acid concentrations of 5%, 7.5%, and 10% was 37.63%, 32.48%, and 23.73%, respectively, and the highest crystallinity produced was 67.45% in MCC HNO_3 10%.

Keywords: *Crystallinity, HCl, HNO_3, Microcrystalline Cellulose, NaOH*

1. INTRODUCTION

Indonesia is a country that has an abundance of natural resources. One of them is sugarcane. The agricultural industry can produce abundant and cheap lignocellulosic biomass waste. According to the Indonesian statistical agency, the plantation area in Indonesia is around 418 thousand hectares, with sugar production of 2.1 million tons in 2020. Bagasse is a material that contains a relatively highly complex substrate consisting of cellulose (40-50%), hemicellulose (20-35%), and lignin (10-30%) (Katakojwala et al., 2020). So far, sugarcane waste has not been utilized optimally and efficiently. The waste is only piled up on open land, and in the rainy season, it becomes wet and smelly and pollutes the environment (Edison et al., 2019). Considering the abundant amount of sugarcane waste and the high cellulose content, using sugarcane waste as raw material for cellulose production can be an alternative source of renewable materials, namely microcrystalline cellulose.

Microcrystalline cellulose (MCC) is the result of further processing of alpha cellulose obtained from various sources of both plants or microorganism fermentation by hydrolyzing in acidic solutions at high temperatures, then washed until neutral pH and mechanically dried (Mokhena et al., 2018). MCC is an odorless white crystalline solid with a degree of polymerization of less than 350 (Honyuen et al., 2019), has a length of about 1-100 μm and a degree of crystallinity of 55-85% (Putra et al., 2017). Microcrystalline cellulose is utilized in various industries. In the pharmaceutical sector, MCC is used as a filler in tablets, which aims to increase the compactness of tablets from compression mixtures and the flow properties of tablet printing masses [Pratama et al., 2019). MCC is also used in the food, cosmetics, and plastics industries (Putra et al., 2017).

Commercial microcrystalline cellulose feedstock is generally obtained from woody plants such as conifers and cotton. However, the use of woody plant species can reduce the availability of wood due to the increasing demand for pulp in various Asian, African and Latin American countries (Ridho et al., 2015). In addition, timber is obtained from massive deforestation, which can cause ecological imbalances. So, to reduce the excessive use of woody plants, it is necessary to have an alternative source of raw materials for manufacturing MCC in Indonesia.

Previous studies have conducted several methods of MCC isolation from sugarcane. Katakojwala and Mohan (2019) isolated cellulose from sugarcane using HNO_3, delignification using NAOH, and NaClO for bleaching step. MCC was extracted from cellulose utilising a mixture of H_2O_2 and H_2SO_4 solutions with a yield of 0.28 gr/gr bagasse and a crystallinity value of 79.8%. In another study, isolating MCC from bagasse was only done through delignification using NaOH, followed by hydrolysis using HCl solution to produce a yield of 55% (Thiangnam et al., 2015). In this study, MCC isolation from sugarcane will be performed using HNO_3 solution with various concentrations in the pre-treatment stage of cellulose isolation and HCl solution as a hydrolysis agent to obtain the optimum alpha cellulose content and highest crystallinity value. The results of this study are expected to be an alternative solution to obtain microcrystalline cellulose with the best yield and degree of crystallinity.

2. METHODS

2.1 Isolating of alpha cellulose

This research starts with the raw material preparation procedure bagasse. First, the bagasse was washed using flowing water until it was clean of the dirt that sticks. The cleaned bagasse was then dried in the sun for three days. The dried bagasse is cut into pieces up to 1-2 cm in size, and then, the bagasse is ground into 60 cm. Grind the bagasse into a size that passes 60 mesh.

After the preparation of bagasse material is complete, the next step is to carry out cellulose isolation process. First, 50 grams of bagasse were delignified with a variation of 5% HNO_3, 7.5% HNO_3, and 10% HNO_3 solution of 1000 ml each at 80°C for 2 hours. Then, bagasse sugarcane bagasse was taken from the bath by filtering and washing using distilled water until pH 7. Then, the bagasse was further delignified using a 1000 ml 2N NaOH solution at 80 °C for 2 hours, a yellowish-white sample was obtained. Then, the sample is filtered and washed using distilled water until the pH is neutral. The sample obtained is then bleached or bleached. Bleaching is done by soaking the residue with 1% NaClO + 20 ml CH_3COOH 400 ml at 80 °C for 2 hours. Then, the sample is filtered and washed until the pH is neutral. Next, the sample was dried at 60 °C for 12 hours in the oven, and pulp was obtained in the form of alpha cellulose in the form of white powder. The resulting pulp can be seen in Fig 1.

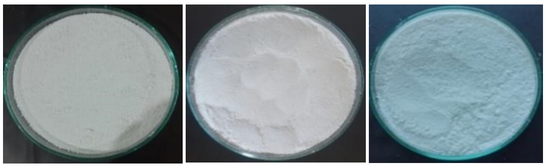

Fig. 1 (A) Pulp 1 (HNO3 5%), (B) Pulp 2 (HNO3 7.5%), (C) Pulp 3 (HNO3 10%)

2.2 Isolating of microcrystalline cellulose

A total of 10 grams of pulp obtained from the previous process was soaked with 200 ml of HCl 3M at 80 °C for 1 hour. Then, the sample was filtered using a vacuum pump until the pH was neutral and dried using an oven overnight at 60°C. The result was obtained as a white crystalline powder, Microcrystal cellulose (MCC).

2.3 Characterization of microcrystalline cellulose

2.3.1 X-ray diffraction

X-ray diffraction (XRD) was carried out to study the crystallinity of the samples using an X'Pert X-ray diffractometer (SIEMENS D5000). Things that are observed are the position of the peak formed in the spectra and the height of the peak. The crystallinity of the samples was calculated using the Zhang method (1993).

2.3.2 Measuring alpha cellulose

Alpha cellulose content testing according to SNI 0444:2009 was carried out on pulp that had been delignified and bleached.

3. RESULT AND DISCUSSION

The isolation of alpha cellulose begins with a pre-treatment process using nitric acid and sulfuric acid solutions that function to damage the lignin structure in bagasse (Anggriani et al., 2022). The destruction occurs because the acid solution will react with water and produce hydronium ions that can damage the lignin structure in the bagasse structure (Putra et al., 2017). Then, the resulting sample will undergo a delignification process with a treatment process with 2N NaOH solution, which separates cellulose and reduces lignin content (Ridho et al., 2019). Lignin dissolves in NaOH quite often, so the color produced in this process is brown pulp. Then the pulp is filtered and washed with distilled water until the pH is neutral and until the filtrate becomes colorless, indicating no solvent is left behind (Anggriani et al., 2022). The reaction that occurs can be seen in Fig 2.

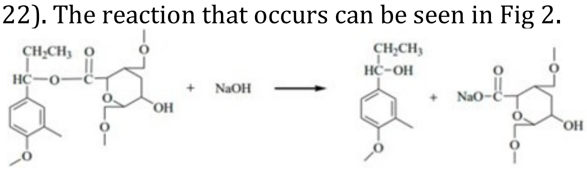

Fig. 2 Delignification reaction using NaOH

Furthermore, the pulp obtained was bleached using 1% NaClO solution by adding a little acetic acid to 20 ml. This bleaching removes the remnants of lignin and hemicellulose and whitens the resulting alpha cellulose sample. The function of adding acetic acid is so that it can react with NaClO and produce hypochlorous acid (HOCl), which is a strong oxidizer and can break lignocellulose bonds and ether bonds in the lignin structure (Supranto et al., 2015). Next is the process of isolating microcrystalline cellulose, which aims to damage the amorphous structure of cellulose. This process will use a strong acid solvent, namely HCl, because the amorphous structure is in the form of fibers, so acidic solutions easily degrade it and will leave the crystalline structure on cellulose (Zhang et al., 1993).

The yield of pulp cellulose produced in this experiment can be seen in Table 1.

Table 1. Yield of Pulp cellulose

Sample	Initial Mass (gr)	Final Mass (gr)	Yield (%)
Pulp (HNO_3 5%)	50	12.8	25.6
Pulp (HNO_3 7.5%)	50	12.2	24.4
Pulp (HNO_3 10%)	50	11.2	22.4

From Table 1, the highest yield value of pulp cellulose was 25.6% at 5% nitric acid concentration, while the lowest yield was 22.4% at 10% nitric acid. This is because the reaction using nitric acid produces -NO2 groups, which cause the physical and chemical properties of the cellulose produced to change and increase the hydrophilicity of cellulose, which results in cellulose being dissolved by reactants so that the cellulose content decreases (Zhang et al., 1993). This causes the yield produced from the nitric acid process to be less than the yield from the sulfuric acid process, as seen in Table 1. From these results, the concentration of hydrochloric acid used affects the yield value produced. The higher the HCl concentration, the lower the yield produced (Homyuen et al., 2023). With the increase in HCl concentration, more bonds are broken in cellulose so that the amorphous structure in cellulose will be degraded and dissolved in HCl solvent, so that it will reduce the yield of MCC produced (Homyuen et al., 2023).

Table 2 shows the results of alpha cellulose from bagasse using a nitric acid pre-treatment process with a concentration variation of 5%, 7.5%, and 10%.

Table 2. The result of alpha cellulose produced

Parameter	Alpha Cellulose
Pre-treatment HNO_3 5%	37.63%
Pre-treatment HNO_3 7.5%	32.48%
Pre-treatment HNO_3 10%	23.73%

The result of alpha cellulose production decreases with an increase in nitric acid concentration, which can be seen in Table 1. This is because the reaction using nitric acid produces -NO2 groups which cause the physical and chemical properties of the cellulose produced to change and increase the hydrophilicity of cellulose, which results in cellulose being dissolved by reactants so that the cellulose content decreases (Zhang et al., 1993), so that the higher the concentration used, the result of the alpha cellulose produced will decrease.

Crystallinity is one of the parameters that shows how strong the microcrystalline cellulose produced is, which is 55-85% and is used in industry (Supranto et al., 2015). The value of the degree of crystallinity is determined using the XRD (X-ray diffraction) test, which will produce peaks that show the crystalline phase. Then, the calculation is carried out using the method developed by Zhang et al. in 1993. XRD test results can be seen in Fig 3.

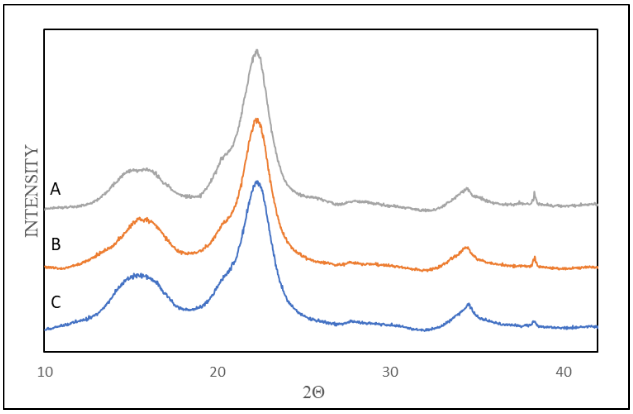

Fig. 3 XRD of MCC (A) 5% HNO3, (B) 7.5% HNO3, (C) 10% HNO3

XRD examination results show the degree of crystallinity of MCC. Microcrystalline cellulose is a powder composed of two phases, namely crystalline phase and amorphous phase (Supranto et al., 2015). The XRD test results of microcrystalline cellulose from bagasse show a sharp peak at 2θ, around 220 (crystalline phase) and a broad peak at 2θ, around 150 (amorphous phase). The degree of crystallinity of MCC indicates the amount of crystalline phase in microcrystalline cellulose. The higher the degree of crystallinity of microcrystalline cellulose, the higher the crystalline phase compared to the amorphous (Katakojwala et al., 2020). Microcrystalline cellulose produced with several variations of HNO3 concentration has different heights and sharpness. The XRD graph peak can be seen in Figure 3. With the difference in peaks, so as to produce different crystallinity degree values, the results of the crystallinity value of microcrystalline cellulose can be seen in Table 3.

Table 3. Sample crystallinity results

Sample	°Kristalinitas
MCC HNO_3 5%	63.94%
MCC HNO_3 7.5%	65.95%
MCC HNO_3 10%	67.45%

Based on Table 3, the high crystallinity value is produced by microcrystalline cellulose with an HNO3 concentration of 10% with a degree of crystallinity of 67.45%, where the value of the degree of crystallinity produced is close to the value of the degree of crystallinity in commercial MCC Avicel PH-101 of 77% (Zhang et al., 1993). The concentration of 10% HNO3 can optimally damage the amorphous structure to produce a high crystallinity value supported by the highest peak produced compared to other sample variations.

4. CONCLUSION

The highest Alpha cellulose purity occurred in pulp with 5% HNO3 concentration, at 37.63%. Microcrystalline cellulose produced under the highest conditions occurred in the 10% HNO3 concentration variation with a degree of crystallinity of 67.45%.

5. ACKNOWLEDGMENTS

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