JOURNAL OF ENERGY, MATERIALS, AND INSTRUMENTATION TECHNOLOGY

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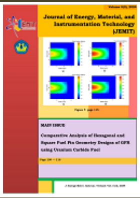

Effect of Variation H_2SO_4 on the Manufacture of Nanocellulose from Corn Cobs

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Article Information

Article history:
Received October 26, 2022
Received in revised form November 27, 2022
Accepted July 25, 2024

Keywords: *acid hydrolysis, cellulose, corn cob, nanocellulose, sulfuric acid*

Abstract

The acid hydrolysis method has been used to manufacture nanocellulose from corn cobs. This study aims to determine the effect of variations in the concentration of H_2SO_4 on the characteristics of nanocellulose produced from corn cobs and their surface morphology. The variations of H_2SO_4 used were 5, 10, 15, and 20%. X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) are characterizations used. The results of XRD characterization showed that the crystallite size obtained followed the nanocellulose crystallite size, which was 1.79-2.59 nm. The SEM characterization showed that the resulting nanocellulose's surface morphology was lumpy and non-porous.

Informasi Artikel

Proses artikel:
Diterima 26 Oktober 2022
Diterima dan direvisi dari 27 November 2022
Accepted 25 Juli 2024

Kata kunci: *hidrolisis asam, selulosa, tongkol jagung, nanoselulosa, asam sulfat*

Abstrak

Pembuatan nanoselulosa dari tongkol jagung telah dilakukan dengan metode hidrolisis asam. Penelitian ini bertujuan untuk mengetahui pengaruh variasi konsentrasi H_2SO_4 terhadap karakteristik nanoselulosa yang dihasilkan dari tongkol jagung dan morfologi permukaannya. Variasi H_2SO_4 yang digunakan adalah 5, 10, 15, dan 20%. Karakterisasi yang digunakan adalah X-Ray Diffraction (XRD) dan Scanning Electron Microscopy (SEM). Hasil karakterisasi XRD menunjukkan bahwa ukuran kristalit yang diperoleh sesuai dengan ukuran kristalit nanoselulosa yang berada dalam kisaran 1,79-2,59 nm. Hasil karakterisasi SEM menunjukkan bahwa morfologi permukaan nanoselulosa yang dihasilkan berbentuk gumpalan dan tidak berpori.

1. Introduction

Research and application of nanotechnology have developed rapidly in the last few decades (Alsaleh, 2021). According to Duncan (2011), nanotechnology involves the characterization, fabrication, and manipulation of a device or material structure with at least one dimension of about 1-100 nm in length. Cellulose is one of the industry's most widely used natural polymers; with the help of nanotechnology, cellulose can be upgraded to produce high-economic value products, namely nanocellulose. Nanocellulose is cellulose with a nano-sized diameter and different properties from natural cellulose (Biao et al., 2011). Cellulose is an organic compound that is the main constituent of cell walls. Cellulose is the most common organic compound on earth (Klemm et al., 1998). The properties of nanocellulose depend on various factors.

Isolating nanocellulose from cellulose uses many methods, including acid hydrolysis. Hydrochloric acid, sulfuric acid, formic acid, and nitric acid are often used in hydrolysis. Sulfuric acid is often used for acid hydrolysis because it produces particles whose surface is negatively charged, leading to a more stable suspension (Xie et al., 2018). The excess of sulfuric acid hydrolysis produces a stable suspension of negatively charged nanocellulose due to sulfate groups (Silvério et al., 2013). Weak acid hydrolysis has advantages such as low environmental impact and low raw material costs (Cheng, 2015).

Corn cobs are a type of plant waste known to contain much cellulose. Plant. Corn cobs contain a chemical composition of 31-39% cellulose (Mendes et al., 2015). According to data from the Ministry of Agriculture of the Republic of Indonesia, maize production in Indonesia continues to increase; in 2018, maize production in Indonesia increased by 24.15% from the previous year (Ministry of Agriculture of the Republic of Indonesia, 2022). Along with the increase in corn production, the waste generated from the corn-based industry will also increase. Corn is generally only taken from the flesh, while the cobs and skin will become waste. Utilization of

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waste is an alternative way to increase the economic value of the waste. Utilization of nanocellulose has been used for the manufacture of antimicrobial wound dressings because it provides a moist effect on the wound that helps better wound healing (Maneerung et al., 2008); this research will make nanocellulose from corn cobs using the acid hydrolysis method with XRD and SEM characterization tests. Sulfuric acid is used, with 5, 10, 15, and 20% concentrations.

2. Research Methods

The tools are used in this research are a beaker, measuring cup, spatula, balance, petri dish, oven, hot plate, magnetic stirrer, mortal, water bath, centrifuge, aluminum foil, plastic wrap, Erlenmeyer flask, and litmus paper for pH measurement. The materials are used are corn cob powder, 10% NaOH, H_2O_2 10%, H_2SO_4 5,10,15 and 20% and equates. as for the sample characterization using X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM).

2.1 Sample Preparation

Sample preparation was carried out by drying the corn cobs in the sun to dry. Then, grind it using a grinder until it becomes corn cob powder.

2.2 Cellulose Insulation

Isolation of cellulose from corn cobs consisted of delignification and bleaching. Step by step are described as follows:

a. Delignification. A total of 5 grams of corncob powder was put into a beaker glass, then 10% NaOH solution was added with a dissolution ratio (1:10). The mixture was stirred using a magnetic stirrer and allowed to stand for 24 hours.

b. bleaching. The designation results left for 24 hours are filtered. The resulting residue is bleached with 10 ml of H_2O_2 10% solution and allowed to stand for 24 hours at room temperature. Then, the mixture is filtered, and the resulting solid is washed using distilled water several times until the smell of H_2O_2 disappears and the pH becomes neutral. The bleaching results were dried at 40°C using an oven and then stored at room temperature.

2.3 Nanocellulose Insulation

Cellulose powder from the previous process was weighed using an analytical balance to determine its weight after treatment. Then, 2 g of cellulose powder was added to a solution of H_2SO_4 40 ml, with variations as in **Table 1**.

Table 1. Variation of acid concentration

Cellulose samples	Sample massa	H_2SO_4
a	2 g	5%
b	2 g	10%
c	2 g	15%
d	2 g	20%

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Hydrolysis is carried out using a *water bath* for 3.5 hours at 50°C. After that, the residue is centrifuged until the pH becomes neutral. Then, the samples are dried in an oven at 40°C until dry. After drying, the sample is crushed using a mortar to make a powder.

2.4 Characterization

At this stage, the obtained nanocellulose powder was characterized using XRD to determine the crystalline index and particle size and SEM to determine the nanocellulose microstructure of corn cobs. The size of the crystallites was calculated using the Scherrer Equation shown in **Equation 1**.

$$D = \frac{K\lambda}{B\cos\theta} \quad (1)$$

where D is the crystal size, K is the form factor of the crystal (0.9), λ is the X-ray wavelength (1.54056Å), B is the value of Full Width at Half Maximum (FWHM) or diffraction peak (rad), θ is the diffraction angle (Scherrer, 1918). The crystallinity index is calculated using the Segal Equation shown in **Equation 2**.

$$Crl = \frac{I_{002} - I_{am}}{I_{002}} x\ 100 \quad (2)$$

where I_{am} is the intensity of amorphous scattering and I_{002} crystalline scattering intensity lies on the [002] lattice and has a diffraction angle of 2θ around 22° (Segal et al., 1959).

3. Results and Discussion

3.1 Results and Analysis of Nanocellulose Production

Corn cobs are used as raw material and are prepared into powder before the cellulose isolation process is carried out. The corn cobs obtained are washed thoroughly and then dried in the sun until they are completely dry. This drying stage aims to reduce the corn cobs' water content. Then, the dried corn cobs are ground using a grinder and sifted to get an excellent powder. Manufacturing nanocellulose consists of three stages: delignification, bleaching, and nanocellulose isolation.

The delignification process was done by mixing 5 g of corn cob powder with 10% NaOH using a magnetic stirrer and then allowed to stand for 24 hours. Process bleaching out using a solution of H_2O_2 10%, which was mixed with the delignification, allowed to stand for 24 hours and then washed until the pH became neutral and dried. The nanocellulose isolation process was carried out by mixing cellulose powder with an H_2SO_4 solution 5, 10, 15, and 20% were then heated for 3.5 hours at 50°C using *a water bath*, then allowed to stand for 24 hours. Then, it is washed until the pH is neutral, dried, and then crushed using a mortar. The results of the manufacture of nanocellulose are shown in **Figure 1**.

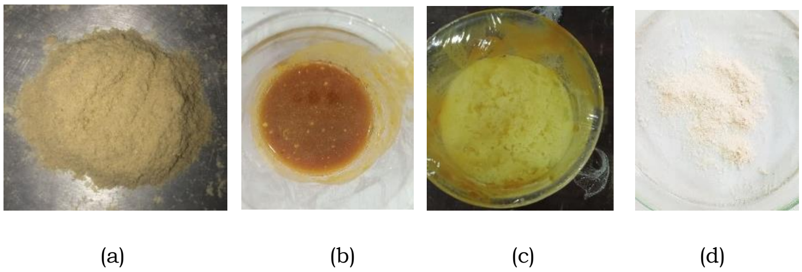


Figure 1. The results of the manufacture of nanocellulose (a) Corn Cobs powder, (b) Delignification results, (c) Results of bleaching, (d) Nanocellulose yield

3.2 Results and Analysis of X-Ray Diffraction (XRD)

3.2.1 Qualitative Analysis

XRD characterization was carried out to determine the crystallinity index and size of the resulting nanocellulose crystallites. The results of the XRD analysis diffractogram are shown in **Figure 2**.

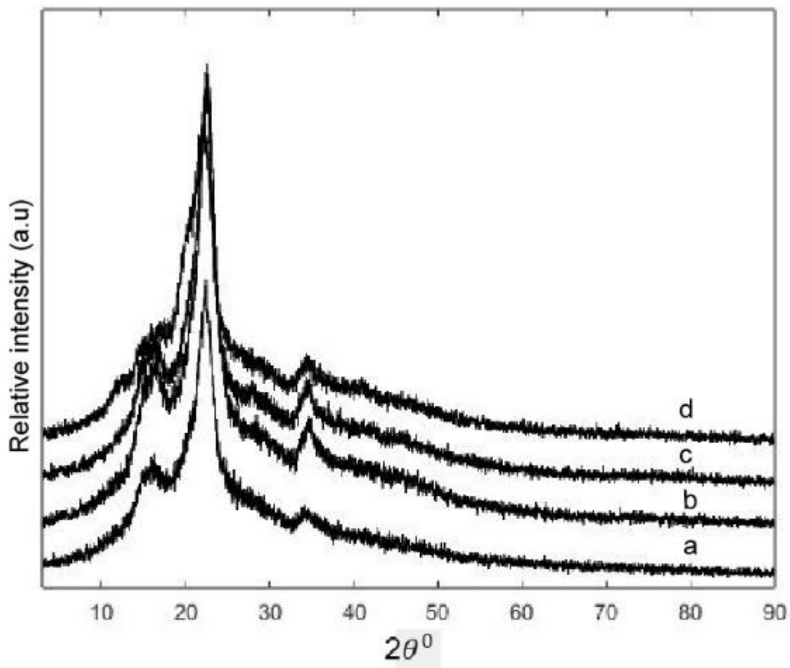


Figure 2. Corn cobs nanocellulose XRD diffractogram with variation H_2SO_4

In **Figure 2**, it can be seen that there are peaks of 2θ 22.44°, 22.66°, 22.48° and 22.28° which are typical peaks for cellulose (D. Klemm et al., 2005). It is similar to the research conducted by Deepa et al. (2015) and

Liu et al. (2016), which isolated nanocellulose and obtained a 2θ peak XRD diffractogram at around 22°. The results of the calculation of the crystallite size are shown in **Table 2**.

Table 2. Crystallite size

Sample	H_2SO_4 Concentration	λ	FWHM (rad)	θ (°)	Crystallite size (nm)
a	5%	0.154	0.06393	11.22	2.21
b	10%	0.154	0.05439	11.33	2.59
c	15%	0.154	0.05530	11.24	2.55
d	20%	0.154	0.07875	11.14	1.79

From **Table 2**, the crystallite size is 3.74 nm to 5.33 nm. The crystallite size obtained is by the crystallite size in general for NCC, which is > 20 nm (D. Klemm et al., 2005). These results are similar to the research conducted by Yu et al. (2013) on crystallite size in nanocellulose samples isolated using the acid hydrolysis method, which obtained crystallite sizes of around 4.6 nm to 5.9 nm. In this study, it was found that the higher the concentration of H_2SO_4 used, the smaller the size obtained. The results of the calculation of the crystallinity index are shown in **Table 3**.

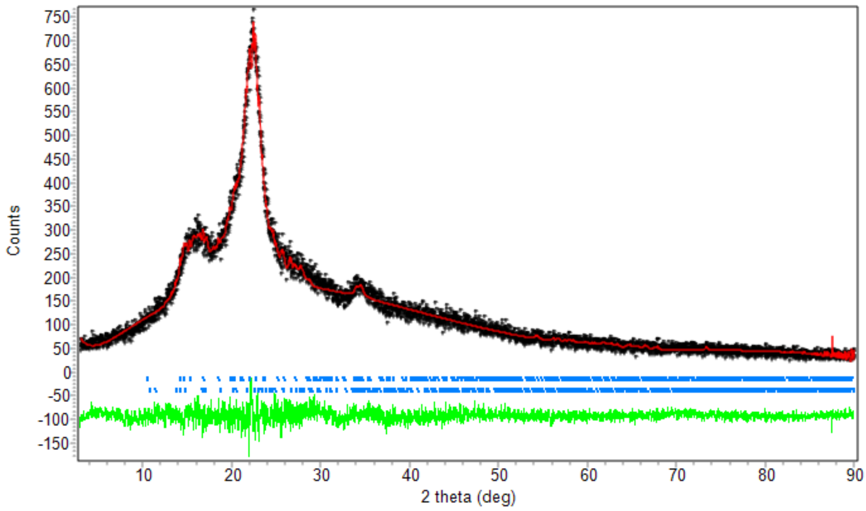
Table 3. Nanocellulose crystallinity index

Sample	H_2SO_4 Concentration (%)	I_{002}	I_{am}	Crystallinity index (%)
a	5	667	281	57.87
b	10	1108	425	61.40
c	15	932	364	60.94
d	20	734	310	57.76

The crystallinity index in samples 3 and 4 decreased compared to sample 2, which indicates that a stronger acid concentration will result in a slight decrease in the crystallinity index, which is considered that a more vital acid can not only remove theamorphous part of cellulose but also can damage the crystals during the hydrolysis process (Yu et al., 2013). Because high acid concentrations can damage cellulose crystals, in this study, the higher the concentration of H_2SO_4, the lower the value of the crystallinity index. The results of the crystallinity index obtained are similar when compared with research conducted by Liu et al. (2016) using the same materials and methods; the results of a crystallinity index of 55% are obtained.

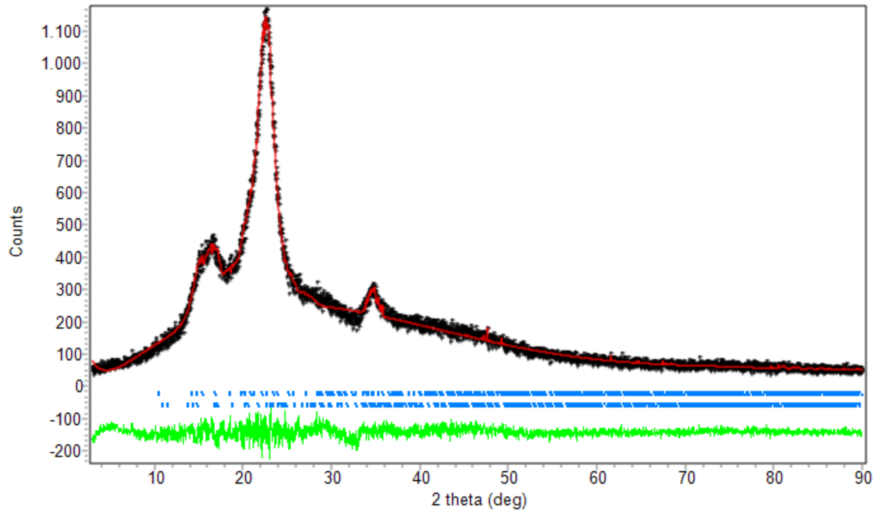
3.2.2 Qualitative Analysis

The refinement process is carried out using Rietica software with the Rietveld method. The refinement begins by opening the data obtained from the XRD test on the Rietica application. Then, the value of B0 is determined by pressing start and then step on refine. Refine several times to get a smoother image result and a lower value for X2. Standard data is needed to compare structured values with standard values in the refinement process. In cellulose I_α value a=6.717Å, b=5.962Å, c=10.400Å, nilai α=118.08Å, β=114.80Å dan nilai γ=80.37Å (Nishiyama et al., 2003). Then on cellulose I_β value a=7.784Å, nilai b=8.201Å, c=10.38Å dan γ=96.5Å (Nishiyama et al., 2002). The refinement results obtained are shown in **Figure 3**.

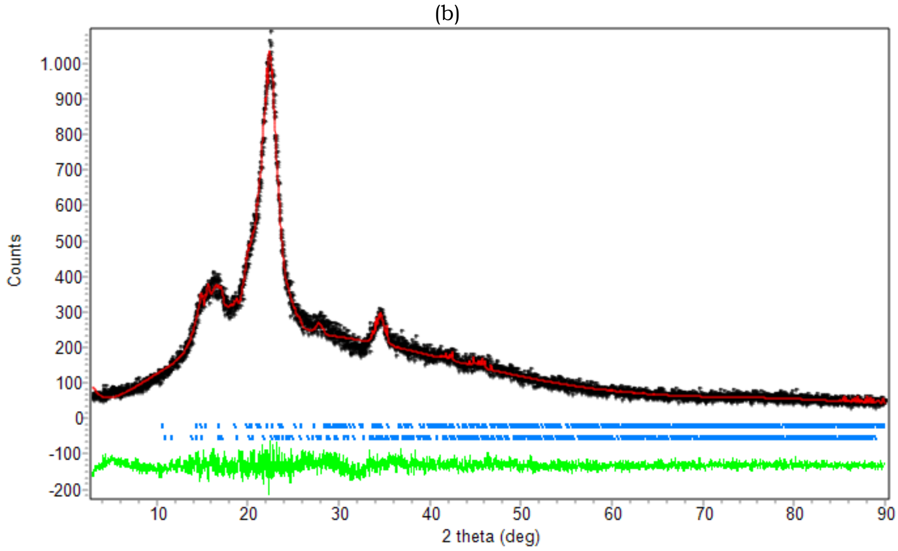


(a)

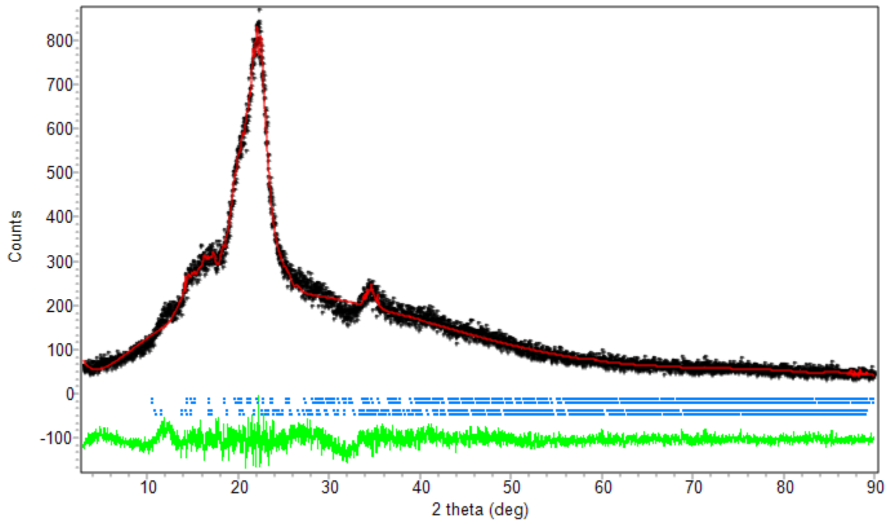
Figure 3. Results *refinement* XRD variation H_2SO_4



(b)



(c)



(d)

Figure 3. (lanjutan)

In general, results of refinement for each sample has provided a match between the data from the XRD research (inblack) and the model (in red). Refinement analysis produced an output that improves the standard crystal pattern based on the calculated diffraction pattern (model). **Table 4** and **5** compare the cell parameters generated by the grinding results against the model.

Table 4. Parameters of phase *Iα* nanocellulose cells

Sample	*a* (Å)	*b* (Å)	*c* (Å)	*α* (Å)	*β* (Å)	*γ* (Å)
Model	6.717	5.962	10.400	118.08	114.80	80.37
5%	6.667	6.021	10.501	118.28	115.40	79.89
10%	6.725	5.997	10.583	118.14	115.82	79.18
15%	6.721	6.079	10.583	118.33	115.53	79.48
20%	6.697	6.095	10.640	119.06	115.72	79.04

Table 5. Parameters of phase *Iβ* nanocellulose cells

Sample	*a* (Å)	*b* (Å)	*c* (Å)	*α* (Å)	*β* (Å)	*γ* (Å)
Model	7.784	8.201	10.38	90	90	96.5
5%	7.794	8.329	10.48	90	90	96.16
10%	7.803	8.278	10.49	90	90	96.64
15%	7.858	8.328	10.57	90	90	96.74
20%	7.850	8.311	10.52	90	90	96.93

3.3 SEM Analysis Results

SEM characterization test was conducted to determine the morphology of the resulting nanocellulose. Based on the results of the XRD analysis that was carried out, it was found that the best pineapple peel samples studied had a concentration of 10% sulfuric acid. The results of the morphology of nanocellulose from corn cobs with variations in concentration H_2SO_4 10% with a magnification of 10,000 times are shown in **Figure 4**.

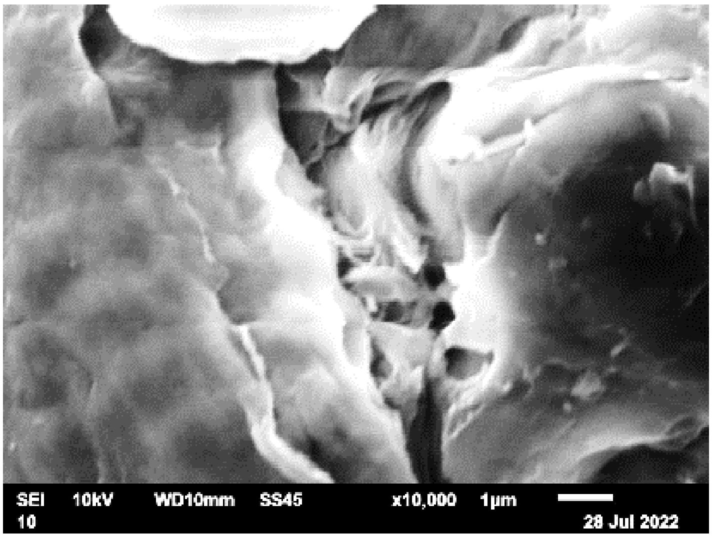


Figure 4. SEM results of corn cobs nanocellulose with variations of concentration H_2SO_4 10%

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Figure 4 shows that the resulting nanocellulose morphology appears to have a clumpy and non-porous surface. This is similar to the results of Winarti et al.'s (2018) research, which made nanocellulose from the same material and different methods; the resulting morphology was slightly lumpy.

4. Conclusions

Based on the research that has been done, variations in the concentration of H_2SO_4 affect the characteristics of the resulting nanocellulose. From the XRD test results obtained, the highest crystallinity index at 10%sulfuric acid concentration variation is 61.4%, and the largest crystallite size at 15% sulfuric acid concentration variation is 5.33 nm. Cell parameters change after administration of variations in H_2SO_4 from the set standard value. The surface morphology SEM results obtained were lumpy and non-porous, and nanocellulose was not visible.

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