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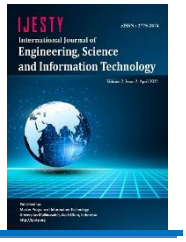

Study of Cellulose Extraction from Robusta Coffee Husk Using NaOH Solution

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Abstract

This study reports on manufacturing cellulose from robusta coffee husks through a solid-liquid extraction process. A high yield of cellulose can be achieved by extraction using 3.5% HNO_3 at a temperature of 100 ºC with a gain of 35.4%. Meanwhile, the extraction process with 4.5% HNO_3 at a temperature of 80 ºC only achieved a yield of 32.8%. From the results of this study, it can be seen that the smaller the concentration of HNO_3 used and the higher the temperature, the greater the yield of cellulose produced. The X-ray diffraction pattern shows high peaks appearing at an angle of 2θ around 22.5º; this area is a typical peak of the cellulose structure. High crystallinity was obtained at a concentration of 3.5% HNO_3 at a temperature of 100 ºC at 82.47%, while the lowest crystallinity was found at a 5.5% HNO_3 concentration at a temperature of 100 ºC at 74.27%. The decrease in crystallinity was caused by the high temperature and concentration of HNO_3, which caused the acid to penetrate quickly into the cellulose tissue layer and hydrolyze the crystalline regions of cellulose. FT-IR analysis showed a high absorption area at 3314 cm^{-1} and a low absorption area at 1028 cm^{-1}, typical of Robusta coffee husk cellulose. The absorption located around the 3314 cm^{-1} bands is a stretch of the –OH group and the absorption in the 1028 cm^{-1} band is related to the -CH_2 group. SEM can show the morphology of cellulose with smaller and uniform crystal dimensions with a scale of 20 µm.

Keywords: *robusta coffee husk,s cellulose, extraction, crystallinity, yield.*

1. Introduction

Coffee husk waste is a material not reused from the processing of coffee cherries to get the seeds. Using coffee husk waste is one alternative to increase the economic value of the waste. Left unchecked, coffee husk waste will hurt the environment, namely, environmental pollution. In contrast, as is known, coffee is one of Indonesia's foreign exchange-earners and plays a vital role in the development of the plantation industry [1].
The availability of coffee husk waste is significant in Aceh because coffee processing will produce 65% of coffee beans and 35% of coffee husk waste. Coffee production in Central Aceh in 2013 reached 26 thousand tons; coffee husk waste has a fiber content of 65.2% [1]. Cellulose from coffee husks can be obtained through the extraction process or the delignification process [2,3]. Delignification is a method of separating components from a material using compounds in the form of alkalis or acids. Delignification using alkali will separate the cellulose and other parts [4,5].
With the delignification process, the cellulose chain will remain intact because cellulose is insoluble in alkali. In contrast, hemicellulose and lignin, which function as adhesives or glue for cellulose, will easily dissolve with alkali. Cellulose from biomass of lignocellulose can be extracted through a solid-liquid extraction process using NaOH [6].

2. Literature Review

Cellulose is a homopolymer of D-anhydroglucose (glucose anhydride) with -1-4-glucoside bonds with the empirical formula $(C_6H_{12}O_5)n$, where n is the number of glucose units bonded or expresses the degree of polymerization ranging from 15 -1400. The structure of cellulose can be seen in Figure 1.
Cellulose is one of the carbohydrates that includes structural polysaccharides, which provide strength to wood and branches for plants. Polysaccharides are easily converted through hydrolysis so cellulose can be converted into monosaccharides. It is estimated that about 1011 tons of cellulose are biosynthesized annually; cellulose accounts for 50% of the free carbon of the earth. Dried leaves contain 10-20% cellulose, 50% wood, and 90% cotton [7].

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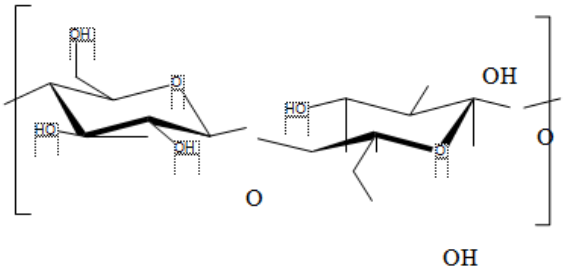

Fig 1. Cellulose structure

In its development, cellulose can be used in various ways; for example, the cellulose in coffee husks has the potential to be used as a renewable energy source in the form of bioethanol. Bioethanol is produced by removing lignin to obtain cellulose, which will later be fermented for bioethanol production. Still, the lignin must be broken down by delignification and sulfonation [8].
Synthesis of polyaniline-cellulose composites using a cellulose matrix derived from coffee husks through the swelling stage [9]. The polyaniline-cellulose obtained is a semi-conductor because it has a higher conductivity value than the synthesized composite without going through the swelling pretreatment [10].
Cellulose from coffee husks can be used as renewable energy in the form of ethanol through simultaneous saccharification-fermentation using cellulase enzymes and yeast *Saccharomyces cerevisiae*. Cellulose can also be combined with ZnO to manufacture bioplastics easily degraded by microbes. [11].
Cellulose can be converted into cellulose acetate through the cleanse process using α-cellulose as the raw material. The reaction steps are activation, acetylation, hydrolysis, neutralization, and drying [12]. Isolation of cellulose nanocrystals from α-cellulose derived from coffee husks by delignification process using HNO_3 [13]. Nanocrystalline cellulose was manufactured through a hydrolysis process using 45% H_2SO_4 [14].
Based on the degree of polymerization (DP) and solubility in 17.5% sodium hydroxide (NaOH)n compounds, cellulose can be divided into three types [15] :

a. Alpha Cellulose (*Alpha Cellulose*) is long-chain cellulose that is resistant and insoluble in 17.5% NaOH or robust alkaline solution with DP (Polymerization Degree) 600 – 15000. – cellulose is used as an estimator or level of cellulose purity.
b. Beta Cellulose (*Betha Cellulose*) is short-chain cellulose soluble in 17.5% NaOH solution or strong base with Polymerization Degree (DP) ranging from 15 – 90. This beta cellulose can precipitate if the extract is neutralized.
c. Gamma Cellulose (*Gamma Cellulose*) is short-chain cellulose soluble in 17.5% NaOH solution or strong base with a Polymerization Degree (DP) less than 15. The main content is hemicellulose.

3. Method

The materials and equipment needed in this research include robusta coffee husks from plantations in the Bener Meriah area. Other materials used were HNO_3 solution (3.5%, 4.5%, and 5.5%), $NaNO_2$, 2% NaOH solution , 2% Na_2SO_3 solution, 1.75% NaOCl solution, and 10 % H_2O_2 solution . The equipment used in this research includes analytical balance, *hot plate*, *beaker glass*, Erlenmeyer, measuring cup, measuring flask, thermometer, funnel, *stirrer*, and frequent paper.
Robusta coffee husk extraction was carried out using a solution of HNO_3 (3.5%, 4.5%, and 5.5%) and $NaNO_2$ 0.03 grams heated at 80ºC, 90ºC, and 100ºC for 2 hours. Then it was delignified using 2% NaOH solution and 2% Na_2SO_3 at a temperature of 50ºC for 1 hour. Then it was bleached with 1.75% NaOCl solution for 30 minutes, followed by bleaching with 10% H_2O_2 for 1 hour in the oven.

3.1 Analysis of coffee husk lignocellulose

Lignocellulosic analysis was carried out using the *Chesson-data method*, first weighing 1 gram of robusta coffee husk as weight (a), then refluxed using 120 ml aqua dest at a temperature of 100ºC for 1 hour, then filtered and dried, then weighed as weight (b). Then the residue was refluxed using 150 ml of 0.5M H_2SO_4 solution for 1 hour; the precipitate was filtered, dried, and weighed as weight (c). The residue was soaked with 10 ml of 72% H_2SO_4 solution for 4 hours, then filtered and dried, then weighed as weight (d), then the residue was ashed and weighed as weight (e). Then the percent chemical content was calculated using the *Chesson-data method*. The percentage of chemical content contained in the biomass was calculated using the *Chesson-data method*, as follows:

a. $\text{Hot water solube } (\%) = \frac{a-b}{a} \times 100\%$
b. $\text{Hemiselulosa}(\%) = \frac{b-c}{a} \times 100\%$
c. $\text{Selulosa } (\%) = \frac{c-d}{a} \times 100\%$
d. $\text{Lignin } (\%) = \frac{d-e}{a} \times 100\%$
e. $\text{Abu } (\%) = \frac{e}{a} \times 100\%$

3.2 Cellulose yield

Cellulose yield is determined from the extraction of cellulose obtained from robusta coffee husks, where yield is the weight of cellulose obtained divided by the weight of the raw material for coffee husks.

3.3 X-ray diffraction (XRD)

It is one of the oldest and most frequently used material characterization methods. This technique identifies the crystalline phase in the material by determining the lattice structure parameters and obtaining the particle size.

3.4 Fourier Transform Infrared (FTIR)

It's a tool used for the analysis of chemical compounds. Infrared spectra of a compound can provide an overview of and molecular structure of the mix.

3.5 Scanning Electron Microscope (SEM) Spectroscopy

A type of electron microscope that uses electron beams to describe the surface shape of the material being analyzed. The function of SEM is to scan a finely focused beam of electrons onto the sample.

4. Results and Discussion

4.1 Analysis of Lignocellulosic Content

The method proposed by *Chesson-Datta* is the method for measuring the commonly used lignocellulosic content. This method is a gravimetric analysis of each component after being hydrolyzed or dissolved. The primary step of this method is to remove the extractive, then hydrolyze hemicellulose with strong acid without heating, followed by hydrolysis using dilute acid at high temperature. The last insoluble part is lignin; the ash content corrects the lignin content.

Table 1. Chemical Composition of Robusta Coffee Husk

No.	Component	Rate (%)
1.	Substance dissolved in water	5.93
2.	Hemicellulose	7.62
3.	Cellulose	59.32
4.	Lignin	3.39
5.	Ash	23.73

From the research data of lignocellulosic analysis using the *Chesson-Datta method*, the chemical components contained in robusta coffee husks are 5.93% solute content, 7.62% hemicellulose content, 59.32% cellulose content, lignin content as much as 3.39%, and ash content of 23.73%.

4.2 Cellulose Yield

I was using the extraction method, the cellulose content contained in the raw material of robusta coffee husk waste. High cellulose content was obtained at a concentration of 3.5% HNO_3 and a temperature of 100°C with a yield of 35.4%. The lowest cellulose content of cellulose is found in HNO_3 concentration of 4.5% and temperature 80°C with a gain of 32.8%. The highest crystallinity was found at a concentration of 3.5% HNO_3 at a temperature of 100°C, which was 82.47%. Meanwhile, the lowest crystallinity was found at a concentration of 5.5% HNO_3 at a temperature of 100°C, which was 74.27%.

Table 2. Cellulose Research Results Data Using the Extraction Process

The concentration of HNO_3 (%)	Temperature (°C)	Cellulose (gr)	Yield (%)	Crystallinity (%)
3.5%	80	8.28	33.12	79.39
	90	8.42	33.68	80.32
	100	8.85	35.4	82.47
4.5%	80	8.20	32.8	81.91
	90	8.32	33.28	79.55
	100	8.45	33.8	75.93
5.5%	80	8.47	33.88	80.63
	90	8.58	34.32	79.20
	100	8.74	34.96	74.27

The relationship between the effect of temperature and concentration of HNO_3 on the yield of cellulose produced can be seen in Figure 1. Figure 1. Shows the percentage increase in *output* at each temperature and concentration of HNO_3. At a concentration of 3.5% HNO_3 at temperatures of 80°C, 90°C, and 100°C, the *results* produced were 33.12%, 33.68%, and 35.4%. At a concentration of 4.5% HNO_3 at temperatures of 80°C, 90°C, and 100°C, the *yields* produced were 32.8%, 33.28%, and 33.8%. At a concentration of 5.5% HNO_3 at temperatures of 80°C, 90°C, and 100°C, the *yields* produced were 33.88%, 34.32%, and 34.96%.

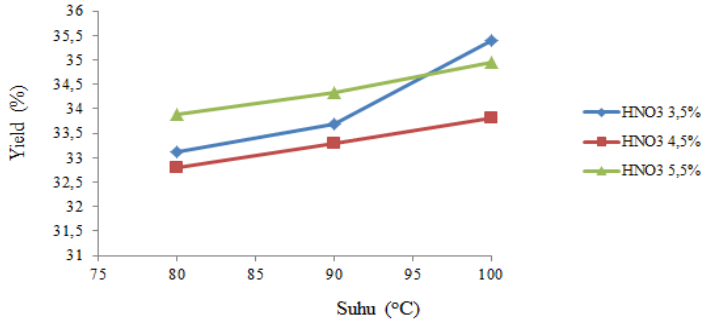

Fig 1. The relationship between temperature and concentration with cellulose *yield*

4.3 Cellulose Crystal Structure Analysis with X-RD. Test

The results of the analysis of the crystal structure of cellulose using the X-RD test, which was hydrolyzed with HNO_3 3.5%, 4.5%, and 5.5% at temperatures of 80ºC, 90ºC, and 100ºC, can be seen in Figure 2 :

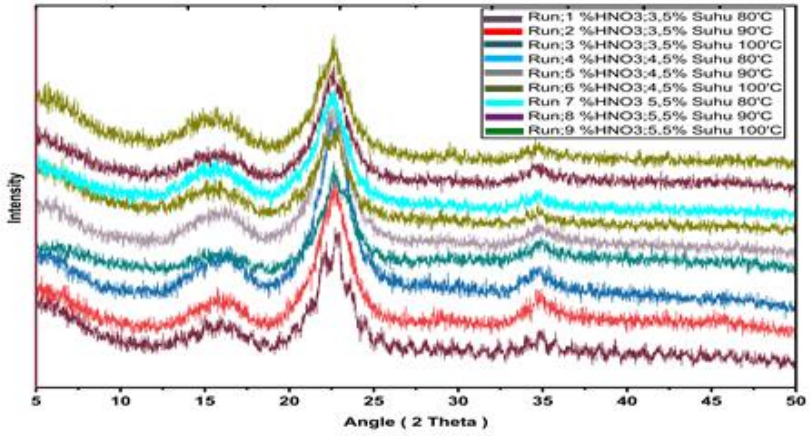

Fig 2 . Cellulose X-RD test results

Figure 2 . shows the X-RD pattern of hydrolyzed cellulose from robusta coffee husks with 3.5 % HNO3, 4.5%, and 5.5% at 80ºC, 90ºC, and 100ºC. All X-RD patterns show a high peak at an angle of 2θ around 22.5º; this area is a typical peak of the cellulose structure. The characteristic height of cellulose appears at an angle of 2θ, around 22.5º [16]

According to Rosli, the characteristic peak of cellulose crystals is at an angle of 22º - 23º [17]. High cellulose crystallinity was obtained by hydrolysis using HNO_3 3.5% at a temperature of 100ºC. The high crystallinity received was due to the deletion of hemicellulose and lignin in the amorphous region leading to the arrangement of cellulose molecules [18].

Figure 3 . shows the percentage of crystallinity of cellulose hydrolyzed with HNO_3 acid solution with concentrations of 3.5%, 4.5%, and 5.5% at heating temperatures of 80ºC, 90ºC, and 100ºC:

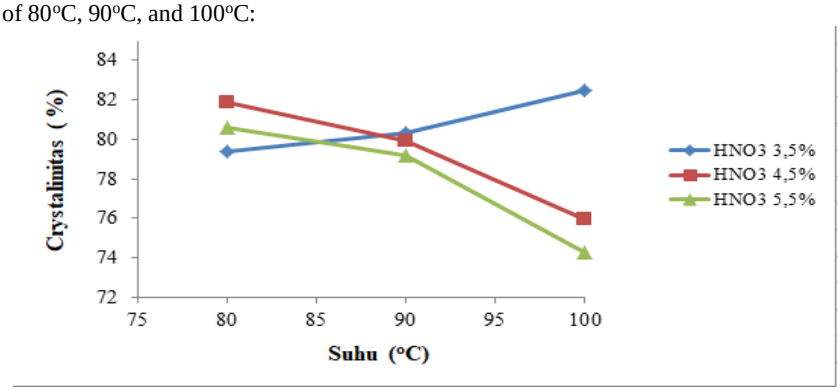

Fig 3 . Cellulose Crystallinity Percentage

Based on Figure 3. it can be seen the percentage of crystallinity of cellulose hydrolyzed with HNO_3 from each temperature. At a concentration of 3.5% HNO_3 at temperatures of 80ºC, 90ºC, and 100ºC, the crystallinity percentages were 79.39%, 80.32% and 82.47%, respectively. Then at 4,5% HNO_3 concentration at 80ºC, 90ºC, and 100ºC, the crystallinity percentages were 81.91%, 79.55%, and 75.93%. At a concentration of 5.5% HNO_3 at temperatures of 80ºC, 90ºC, and 100ºC, the crystallinity percentages were 80.63%, 79.20%, and 74.27%. The highest percentage of crystallinity gain was obtained at 3.5% HNO_3 concentration at 100ºC at 82.47%, while the lowest crystallinity gain was found at 5.5% HNO_3 attention at 100ºC at 74.27%. The higher heating temperature causes a decrease in the percentage of crystallinity and the concentration of HNO_3 used; this causes the acid solution to penetrate quickly into the cellulose tissue layer and participate in hydrolyzing the crystalline cellulose region. This is by research conducted by Zulnazri [16].

4.4 Cellulose Functional Group Analysis with FT-IR

The characteristics of the FT-IR spectrum of cellulose are shown in Figure 4. showing two central absorption regions, namely the high wave number and low wavenumber region. High, namely in the band area of 3314 cm^{-1} and quiet in the band area of 1028 cm^{-1}. The spectrum shows a broad absorption peak located around the 3314 cm^{-1} bands, a stretch of the –OH group. The absorption peak in the 1028 cm^{-1} band region is related to the -CH_2 group; this is to a study conducted by Jahan [19]. The absorption peak of 2896 cm $^{-1}$ is the overlap of the -CH_2 band.

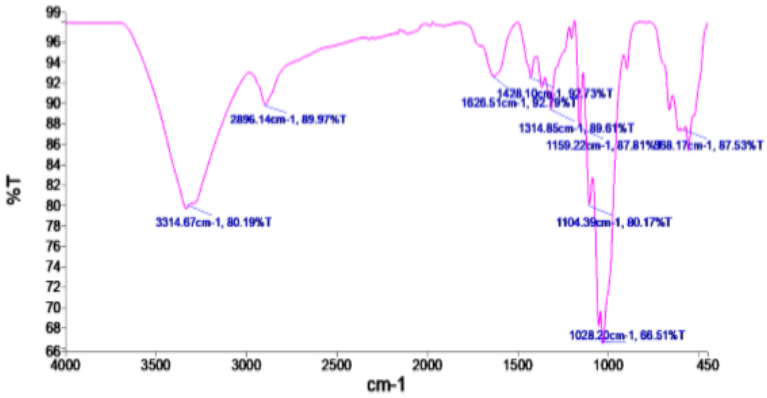

Fig 4. FT-IR spectrum of cellulose

Peak absorption in the region of 1300-1400 cm^{-1} **is the** vibration band of C-H indicated from the ring polysaccharide group. In figure 4, there was an increase in intensity in the 1050 cm^{-1} band, indicating stretching of the C-O-C pyranose ring, which showed an increase in the crystalline value of cellulose. According to Corrˆea, Absorption peaks at 1050 cm^{-1} indicate the pyranose C-O-C from lignocellulose [20]. The absorption peak in the 500 cm^{-1} band area is the lowest CH vibration of cellulose and band area pinger print.

4.5 Morphological Analysis with SEM

The morphology and dimensions of the crystal particles were analyzed by scanning electron micrographs (SEM). Cellulose has a smaller and more regular particle size compared to cellulose which looks more random. This explains that nitric acid hydrolysis can break the cellulose chains into individual crystals. The crystalline regions can resist acid attack and break off amorphous components, resulting in small crystalline dimensions. Reaction time and reaction temperature greatly determine the yield and particle size distribution. As for Figure 5. The following shows the morphology of cellulose hydrolyzed at a temperature of 100ºC using 3.5 % HNO3:

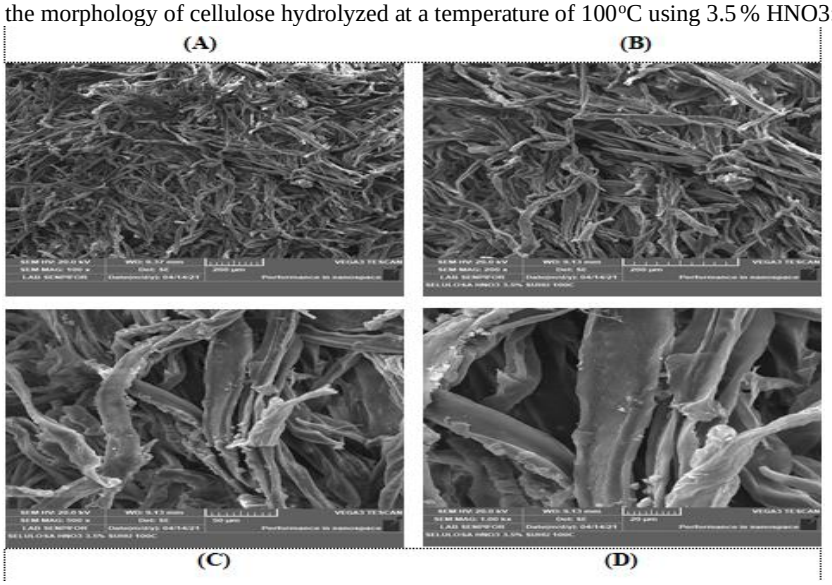

Fig 5. Cellulose SEM test results (a) 200µm scale (100 times), (b) 200µm scale (200 times), (c) 50µm scale (500 times, (d) 20 m scale (1000 times).

Figure 5 (a) shows the morphology of cellulose with a scale of 200µm and a magnification of 100 times. Figure 6 (b) shows the morphology of cellulose with a scale of 200µm and a magnification of 200 times. Figure 6(c) shows the morphology of cellulose with a scale of 50 m and magnification of 500 times, and Figure 6(d) shows the morphology of cellulose with a smaller scale of 20 m and magnification of 100 times. Based on Figure 6, the cellulose surface offers the same morphology as a regular sandwich shape.

5. Conclusion

From the results of the X-RD test, the highest percentage of crystallization was found in the cellulose sample hydrolyzed with HNO_3 3.5% at 100ºC at 82.47%. The lowest percentage of crystallinity was found in the cellulose sample hydrolyzed with HNO_3 5.5% at a temperature of 100ºC of 74.27%. Yield *rate* The highest yield was obtained in samples of cellulose hydrolyzed with HNO_3 3.5% at a temperature of 100ºC as much as 35.4%, while the lowest *result* was found in samples hydrolyzed with HNO_3 4.5% at a temperature of 80ºC as much as

32.8%. The higher the crystallinity of the cellulose obtained indicates that the cellulose obtained has a better quality. This research can be developed into cellulose nanocrystals used as medicinal- biomedical raw materials.

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