Preparation and characterization of cellulose microcrystalline made from palm oil midrib

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Abstract. Palm oil midribs are solid wastes from oil palm (Elaeis guineensis Jacq) plantations which have high cellulose content which has not been utilized in increasing economic value in the palm oil industry. This study aims to produce Microcrystalline Cellulose (MCC) from PKS and characterize MCC. The stages of this research are 1). Lignocellulose delignification from oil palm midribs with HNO₃ 3.5% and NaNO₂ at a temperature of 90˚C for 2 hours, followed by heating in the mixture of NaOH 2% and Na₂SO₃ 2% at a temperature of 50˚C for 2 hours. The second stage of delignification process was using a solution of NaOH 10%. 2). Hydrolysis of α-Cellulose (the results from delignification) with a solution of H₂SO₄ with each concentration of 1 N; 1.5 N; 2N; 2.5N; 3N; 3.5N and simmer at 80°C temperature for 30 minutes. From the hydrolysis results, the optimum yield from MCC is 87.9% using concentration of H₂SO₄ 2.5N. 3). The resulting MCC was then analysed using Fourier Transform Infrared (FT-IR), Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). FTIR uptake from the MCC results showed the existence of wave numbers at 3344.57 cm⁻¹ and 2897.08 cm⁻¹ which indicated the presence of OH and CH groups. The results of the analysis with SEM showed that the MCC produced had a particle diameter of < 10 µm. From the results of the analysis using XRD, it is known that MCC has a crystallinity of 76.47%.

1. Introduction
Sumatera Utara Province recorded having oil palm plantations reaching to 1.2 million hectares [1], hence it has the potential to produce as many as 14.2 million tons of oil palm midribs per hectare in one year. Oil palm midribs so far had only been used as animal feed and compost.

Palm midribs contain 34.89% cellulose, 27.14% Hemicellulose, and 19.87% Lignin[2]. showed that oil palm midribs have the opportunity to be further processed hence they have results that have benefits with high economic value and application. Based on the degree of polymerization and solubility in the 17.5% NaOH compound, cellulose can be divided into three types that are, α-Cellulose, β-Cellulose, and γ-Cellulose. α-Cellulose is the highest quality (pure) cellulose. The α-cellulose content in palm oil midribs is very potential to be processed into further cellulose product derivatives. α-Cellulose of > 92% is eligible to be used as the main raw material (nitrocellulose) for making propellants or explosives. One derivative of α-cellulose is microcrystalline cellulose.

Cellulose microcrystals can be made through chemical reactions that are by hydrolysis of strong acids at controlled temperatures. Controlled acid hydrolysis can damage the amorphous region of cellulose micro fibrils, which will leave the intact crystalline segment leading to the formation of a single crystal [3]. Microcrystalline cellulose is a new type of cellulose material that is characterized by
an increase in crystallinity, aspect ratio, surface area, and increased ability of dispersion and biodegradation. With this capability, cellulose microcrystalline particles can be used as polymer reinforcement fillers, additives for biodegradable products, membrane reinforcement, thickeners for dispersing and drug carrier media and also implants [4]. In addition, cellulose microcrystals can also be applied such as electronic displays, packaging, optical devices, super-absorbents, Nano-composites and bio-composites [5].

Hydrolysis of cellulose in acid can be carried out using dilute strong acids at high temperatures and pressures, and can be carried out using concentrated acids at temperatures and low pressures. Hydrolysis with acid solution usually uses dilute acid, where the reaction speed is proportional to the acid concentration [6].

Microcrystalline Cellulose is a material that can be obtained chemically using the delignification method using a NaOH base solution accompanied by a heating process, which is then hydrolyzed using mineral acids such as HCl and H2SO4 [7].

Research related to the making of OPEFB microcrystalline cellulose, as conducted by [8] with the acid hydrolysis method, namely hydrochloric acid (HCl) using variations in the concentrations of HCl 2N, 2.5 N, and 3 N and the optimum results obtained at 3 N HCl concentrations with the highest crystallinity level of 61.6% [9] stated that cellulose was taken by delignification process then cellulose was hydrolysed with 2.5 N HCl acids finally washed with 5% NH4OH to produce microcrystals with 87% crystallinity.

In this research the preparation and characterization of cellulose microcrystals from oil palm midribs (PKS) were done by hydrolysing using H2SO4 with various concentrations of 1 N; 1.5 N; 2 N; 2.5 N; 3 N.

2. Method

2.1. Material

The main material used in this study is α-cellulose from dried palm oil midribs, H2SO4, HNO3 3.5%, NaNO2 and Na2SO3 2% and also NaOH 2%. While the tools used in this research are Oven, Thermometer 100°C, Drop Pipette, Measuring Cup, Hot Plate, Stirring Rod, Analytical Balance Sheet, Beaker Glass, Whatman Filter No.1, Porcelain Cup, Funnel, pH Meter, FTIR (Fourier Transform Infrared), SEM (Scanning Electron Microscopy), and XRD (X-Ray Diffraction).

2.2. Experiment Method

Making MCC from PKS is carried out in several stages. In the initial stage; the PKS sample is cleaned and reduced in size, dried in the sun to dry, then crushed and sieved to produce a powder-shaped. Then the PKS delignification process is carried out to remove the lignin content. The PKS is done by heating the PKS dry powder that has been extracted using a mixture of 3.5% HNO3 and NaNO2 at a temperature of 90°C for 2 hours, hence it will eliminate lignin into nitro lignin as well as to remove hemicellulose (HNO3) [10]. Furthermore, reheating is done by using a mixture of 2% NaOH and 2% Na2SO3 at a temperature of 500C for 2 hours. The next step is the process of making MCC by hydrolysing α-cellulose using H2SO4 solution with each concentration of 1 N; 1.5 N; 2N; 2.5N; 3N; 3.5N and simmer at 80°C for 30 minutes. Furthermore, the resulting cellulose microcrystals are washed using distilled water to neutral pH. After neutral, microcrystalline cellulose is filtered and dried in an oven at a temperature of 56-60°C for 3-4 hours. The last stage of the study was in the form of determining the yield and characteristics of the MCC obtained using Infrared Transmitter (FTIR), Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD).

2.3. Observation

2.3.1. Yield Calculation. The yield of microcrystalline cellulose is calculated as a percentage ratio between the weights of microcrystalline cellulose from hydrolysis to the weight of the material used in the form of α-cellulose, in which the calculation of microcrystalline cellulose yield is based on the dry weight of the material. The calculation formula for microcrystalline cellulose yield is as follows:

\[
\text{Yield} = \frac{\text{weight of microcrystalline cellulose}}{\text{dry weight of α-cellulose}} \times 100\%
\]
2.3.2. Cellulose Microcrystals Characteristics. Sample characterization with Fourier Transform Infrared (FTIR) and the characterization of samples with Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) were carried out at the Mineral and Material Maju of FMIPA, University of Malang.

3. Result and discussion

The yield of MMC is the MCC extraction process from the oil palm midribs after a number of delignification stages. The amount of MCC yield from oil palm midribs extraction using H2SO4 hydrolysis solution is presented in the following figure:

In Figure 1, it can be seen that yields ranged from 69.9% - 87.9%. From these results, it can be seen that the highest yield is obtained at Variations of 2.5 N with a result of 87.9%, while the lowest value is obtained at 1.5 N with a result of 69.9%. Based on Figure 1, it can also be seen that the higher the H2SO4 variation, the higher the yield value. Also seen in the H2SO4 variation of 3 N the yield decreases again, the cause of the decrease in the yield in this variation can be caused by the α-cellulose samples used which still contain a lot of lignin and hemicellulose.

MCC produced in this research was characterized by FTIR. Characterization using FTIR aims to determine the functional groups in the MCC. Figure 2 showed the FTIR spectrum generated from the MCC sample. The FTIR spectrum of the MCC sample showed a peak at the wavenumber of 3344.57 cm⁻¹ (O-H), 2897.08 cm⁻¹ (C-H Alkene), 1635.64 cm⁻¹ (C=C Alkene), 1056.99 cm⁻¹ (C-O), and 1732.08 cm⁻¹ (C=O).
The peaks in figure 1 indicated the presence of O-H, C-H, C = O, C-O-C and C-O stretching groups, and CH2 and C-H bending. Then at a peak of 894.97 cm⁻¹ indicated the presence of β-glycosides. FTIR spectrum analysis showed that the MCC from PKS produced is cellulose compound. The FTIR spectrum showed a decrease in absorbance values at wavenumbers of 3344.57 cm⁻¹ and 2897.08 cm⁻¹, which showed a decrease in strong bonds in the CH and OH stretching groups indicating an increasing number of crystalline regions at MCC [12].

The results of the characterization with SEM are shown in Figure 3. The results of SEM characterization showed that the MCC in this research had an MCC particle size < 10 µm which was the result of an acid hydrolysis process with 2 N H2SO4 solution for 30 minutes. From the literature, it is known that a good MCC will have a diameter ranging from 1-100 µm [13].

Figure 3 (a) showed the particle fibre size which is still rough and irregular, whereas in Figure (b) there is a change in the structure of the particles which were originally coarse and irregular to become finer and regular particles. This is due to the dissolution of the amorphous part after being hydrolysed using Sulphuric Acid (H2SO4) and leaving the Crystal part.

Cellulose molecules are micro fibrils of glucose which are bound to one another to form very long polymer chains. The presence of lignin and hemicellulose around cellulose is a major obstacle to hydrolysing cellulose [14]. The results of MCC characterization using XRD to determine the MCC crystallinity level can be seen in Figures 4 and 5.
In Figure 4 and Figure 5, it is clear that the difference in the peak of crystallinity is seen from the maximum intensity of 2θ (22 °), where in Figure 5 the peak of crystallinity has been seen, the crystal phase changes are not too sharp. This proves that there is still an Amorphous Phase caused by acids that hydrolyse the Amorphous Cellulose portion only partially and not too strongly. Whereas in Figure 6 after being hydrolysed using Sulphuric Acid (H2SO4) the peak of crystallinity was clear and sharp upwards proving that there was a change from the Amorphous to Crystal phase due to hydrolysis that used high Acid. Strong acids can remove the amorphous part of a cellulose chain hence isolation on the crystalline portion of cellulose can be carried out [15].

Index of Cellulose Microcrystalline Crystallinity can be seen in Figure 6 below:

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**Figure 4.** Results of α-Cellulose XRD Analysis

**Figure 5.** Microcrystalline Cellulose XRD Concentration of Sulphuric Acid (H2SO4) 2N

**Figure 6.** Microcrystalline Index of Cellulose Microcrystals from α-Cellulose of Oil Palm Midribs
The index of crystallinity is the crystallinity degree percentage in a material. The Cellulose Microcrystalline Index in Figure 4-6 ranges from 73.07% - 78.48%. This value is not much different from previous research conducted by [12] with a crystallinity percentage of 55% - 85%. Based on these results, the hydrolysis of microcrystalline cellulose from α-Cellulose palm oil midribs with variations in the concentration of Sulphuric Acid (H2SO4) has met the requirements of cellulose microcrystalline crystallinity index.

4. Conclusion

The optimum yield of MCC is 87.9% hydrolysed with H2SO4 2.5 N heating for 30 minutes. The characteristics of the resulting MCC are pure cellulose compounds which can be seen from the results of the FTIR spectrum analysis produced after being compared with the functional groups on cellulose. The MCC obtained had a diameter of < 10 µm using SEM and the results of characterization with XRD showed the best crystallinity level using H2SO4 1.5 N which is a crystallinity level of 76.47%. Based on this research results, the next stage needs to be improved, namely by varying the time, temperature and other reagents in the process of delignification and hydrolysis of PKS waste to find alternative processes that are simpler and more economical.

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