Preparation and characterization of nanocrystalline cellulose using ultrasonic assisted autohydrolysis

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Abstract. Cellulose is a biopolymer whose availability is abundant in nature. In its development, cellulose is widely used in the form of nanocrystalline cellulose because it has better properties than the original material. The method commonly used to produce nanocrystalline cellulose is acid hydrolysis. In this study, nanocrystalline cellulose was produced through a method of modification of acid hydrolysis with hydrothermal treatment by autoclave, then ultrasonic treatment was conducted. The results of nanocrystalline cellulose were analyzed by particle size analyzer (PSA), scanning electron microscope-energy Dispersive X-ray spectroscopy (SEM-EDS), Fourier-transformed infrared spectra (FT-IR), X-ray diffraction (XRD) and thermogravimetric analysis (TGA).

1. Introduction
One important source of cellulose fiber for the industry is wood. Fiber is composed of lignin, cellulose, and hemicellulose \cite{1}. Holocellulose is the total fraction of carbohydrates consisting of cellulose and hemicellulose. Holocellulose is a combination of cellulose (40 - 45\%) and hemicellulose (15 - 25\%), which usually has levels of 65 - 70\% based on the dry weight of wood \cite{2}. When it is viewed from its level of holocellulose, all types of wood studied are excellent as pulp material because the cellulose content is more than 65\%. Cellulose is a major component of building plant cell walls. The cellulose content in plant cell walls is high at around 35 - 50\% of the dry weight of plants. Cellulose is the basic structure of plant cells. According to \cite{3}, cellulose is the most abundant natural polymer on earth with annual biomass production of 50 billion tons. Fiber can be further processed into cellulose microfibrils which have a diameter of less than 100 nm \cite{4, 5}. Nano-sized fibers are new materials that can be used as reinforcing materials in polymers \cite{5}. The application can be added to polymers to make composites for automotive, electronics, building materials and household appliances \cite{5, 6}. The fiber cell wall is a natural composite compound (nanocomposite cellulose), where cellulose is a reinforcement with its matrix is a combination of lignin and hemicellulose \cite{7}.

2. Materials and Methods
The material used in this study was \textit{Eucalyptus pellita} wood fiber obtained from wood harvesting waste at PT. Toba Pulp Sustainable (TPL), dialysis membrane and distillate water. The chemicals used were...
sulfuric acid, ethanol, sodium chloride, potassium hydroxide, and sulfuric acid. Isolation of cellulose fibers was carried out through a pulping process in 25% sodium hydroxide solution at 170 °C and a pressure of 1 bar for approximately 2 hours. After forming a pulp, the fiber was washed with running water until it was clean and reached a neutral pH, then dried in the oven.

Furthermore, nanocellulose isolation was carried out by acid hydrolysis using 45% sulfuric acid solution at 45 °C for 60 minutes with constant rotation (fiber ratio with 1:20 solution). Hydrolysis was stopped by the addition of cold distillate water; then the autohydrolysis process was carried out using 121 °C autoclave pressure 1.5 bar for 60 minutes. Then, centrifuges were repeated with a rotating speed of 7000 rpm until a constant pH was reached. Afterwards, the supernatant was sonicated using 120 w of ultrasound for 60 minutes.

The size and distribution of nanocrystalline cellulose were measured using the NanoPlus-3 tool from Particulate System, USA using the dynamic light scattering method. The morphology of fibers and microfibrils was characterized by scanning electron microscope (SEM) type JEOL-JSM-6510LV. To determine the type and percentage of relative elements in the sample, Energy Dispersive X-ray Spectroscopy (EDS) was used. X-Ray Diffraction (XRD) was used to determine the crystallinity of fibers and cellulose microfibrils, and to know the phase and additives contained in the sludge. The sample was placed into the aluminum holder as a sample handle and analyzed under spatial conditions. Diffractogram XRD was recorded with the Shimadzu XRD-7000 MaximaX series. Radiation penetrated the sample with the microstructure of Fibril Angel (MFA). Scan angle 2θ was 10-40° every 2°/minute. XRD data obtained was used to calculate the crystal size of the sample using the Scherrer equation [8] as follows:

\[ D = \frac{k \cdot \lambda}{B \cdot \cos \theta} \]  

where D is the size of the crystal (nm), k is a constant with a value of 0.9, λ is the wave number 1.54, B is the value of FWHM (Full Wide Half Maximum), and \( \theta \) is the diffraction angle.

Fourier transform infrared (FTIR) testing was carried out using an MB 3000 ABB (Reliable FTIR Laboratory Analyzer, Canada) at wavelengths of 500 – 4500 cm\(^{-1}\) with 32 cm\(^{-1}\) resolution and scan 20. KBr 150 mg was added to the samples to facilitate sample formation when the samples were analyzed.

3. Result and discussion

The sample used in the manufacture of nanocrystalline cellulose was E. pellita fiber which has undergone a purification process and where the pulp produced from the chemical process i.e. pulping with NaOH solution is still brownish so that it is necessary to purify (bleaching) to obtain white pulp. The process of purification is also called fiber bleaching process. The sodium hydroxide changed the color of the fiber to white (the bleaching process). The bleaching process aims to eliminate lignin and hemicellulose contained in the fiber. By the statement of [9] that by bleaching fiber with sodium hydroxide will cause hemicellulose to degenerate.

Figure 1. Fiber diffraction x-ray graph experiencing treatment.
The results of x-ray diffraction showed that cellulose which had undergone chemical treatment remained in the form of cellulose type I. Chemical treatment affected the value of crystallinity in the fiber. The crystallinity of the pulp was 58.13%, and it increased to 59.84% in the bleached pulp. This increase is due to the partial decay of lignin and hemicellulose which is an amorphous part. However, there was a decrease in crystallinity in nanocrystalline cellulose to 48.57%. It is possible that during the hydrolysis process, involving strong acids will decay some parts of cellulose, causing a decrease in crystallinity.

The main peaks showing changes in the sample were peaks at 1798 cm\(^{-1}\) and 1420 cm\(^{-1}\). The peak at 1798 cm\(^{-1}\) contained in the fiber was a representation of acetyl and uronic ester groups in the hemicellulose or ester group carboxylic bonds in ferulic acid and p-coumaric acid in lignin. This peak has decreased in samples that have undergone a purification treatment, indicating that there has been a break of ester bonds from non-cellulose components [10, 11]. Meanwhile, the peak at 1420 cm\(^{-1}\) which represents various components of lignin and C-H deformation of cellulose and lignin showed a significant decrease in samples that experienced purification due to bleaching in the purification process [9, 10].

![Figure 2. FTIR graph of bleaching of hydrolysis pulp (a); bleaching pulp that has been autohydrolysis; (c) bleaching of certified pulp which has been autohydrolysis.](image-url)
Figure 3 shows the thermogram of nanocrystalline cellulose TGA. It can be seen from different graphs of the TGA thermogram autohydrolysis with others. The initial heavy changes that showed nanocrystal cellulose began to decompose at a temperature of around 50-160 °C. Weight removal is a function of temperature. Fiber begins to damage at 200 °C. Based on the method of dynamic light scattering, the average size of nanocrystalline cellulose was 325.2 nm with a range of 82.7 - 1294.9 nm.

Figure 3. TGA analysis comparison of (a) nanocrystalline cellulose; (b) bleached-pulp; (c) pulp.

4. Conclusion
Nanocrystalline cellulose was successfully prepared from Eucalyptus pellita by autohydrolysis assisted ultrasonication. Bleaching treatment could increase the crystallinity of cellulose fibers, but the crystallinity of the nanocrystalline cellulose decreased. The average particle sizes of nanocrystalline cellulose by a dynamic light scattering method was 325.2 nm ranging from 82.7 nm and 1294.9 nm.

Acknowledgments
The authors would like to thank the Directorate of Higher Education (DIKTI), Ministry of Research, Technology, and Higher Education of the Republic of Indonesia for its financial support by the Research and Community Service Funding Agreement Fiscal Year 2018.

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