Cellulose nanofiber isolation from palm oil Empty Fruit Bunches (EFB) through strong acid hydrolysis

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Abstract. The palm oil industry produces about 25-26% of palm oil empty fruit bunches. The empty fruit bunch of palm oil contains cellulose up to 36.67%. This is a good opportunity for the synthesis of cellulose nanofiber (CNF). Cellulose nanofiber is a nano-sized cellulose material that has unique physical and mechanical properties. The synthesis was performed using a strong acid method with sulfuric acid. Sulfuric acid removes the amorphous region of cellulose so that the crystalline part can be isolated. CNF yield measurement showed that temperature, time, acid concentration, and interaction between each factor were affecting significantly to CNF yield. The result showed that yield of 14.98 grams, was obtained by hydrolysis at 35°C for 6 hours and 55% acid concentration. The crystallinity measurement showed that the temperature, time, acid concentration, and interaction between each factor during hydrolysis were not affected significantly to percent value of CNF crystallinity. The result showed that 31.1% of crystallinity, was obtained by hydrolysis at 45°C for 3 hours and 55% of acid concentration. The size measurement showed that the temperature, time, acid concentration and interaction between each factor were affected significantly. The result showed 894.25 nm as the best result, obtained by hydrolysis with 35°C and 60% acid concentration for 6 hours. CNF color was white with the best dispersion of hydrolysis at 35°C of 55% for 6 hours.

1. Introduction

Isolation of cellulose nanocrystals from palm oil empty fruit bunches becomes an excellent research and industrial opportunity because the palm oil processing industry produces empty fruit bunches of palm oil tree around 25-26% [1]. Cellulose is a carbon-rich material (Cellulose 36.67%, hemicellulose 13.5%, and lignin 31.16%) [2]. The high content of cellulose in palm oil empty fruit bunches that reaches 36.67% making palm oil empty fruit bunches as a potential source of cellulose nanofiber (CNF). The nano size of the CNF provides excellent properties such as high crystalline content, good optical properties, and excellent mechanical properties [3]. CNF can be utilized in various products such as strengthening the tensile strength of plastics, as the filler of nanocomposites to fix the mechanical and barrier properties, aerogel, lithium battery production, as a mechanical strengthening agent for lowthickness polymer electrolytes, improving the physical properties of mechanical adhesive materials, and many other applications [4]. If you don’t wish to use the Word template provided, please use the following page setup measurements.

Cellulose is composed of amorphous and crystalline parts. The cellulose nanocrystals can be isolated by hydrolyzing the amorphous portion. Hydrolysis is carried out on pure cellulose with strong acids under controlled temperature and time. However, the optimum conditions to isolate the crystalline part of cellulose has not been defined. Therefore, this study was conducted to determine the effect of acid concentration, temperature, and hydrolysis time on cellulose nanocrystal (cellulose
nanofiber) isolation, and to characterize the CNF produced. This study was expected to provide information on the conversion of cellulose of palm oil empty fruit bunches into cellulose nanofiber (CNF) using acid hydrolysis.

2. Materials and Methods

The materials used in this study were α-cellulose from empty fruit bunches of palm oil, aquades, and H\textsubscript{2}SO\textsubscript{4} (55%, 60%, 64%). The equipment used in this research was hotplate, magnetic stirrer, glass beaker, measuring cup, erlenmeyer, centrifuge, waterbath, sonicator, oven, refrigerato, tea strainer, vacuum filter, and blender.

Research Procedures

2.1 Preparation of α-cellulose from Palm Oil Empty Fruit Bunches

The dry α-cellulose material was immersed in aquades at a ratio of 1:5 for 24 hours until the cellulose expanded and the texture was smoother. After that, the α-cellulose was crushed so that the size was smaller and smoother and then filtered to remove excess water.

2.2 Isolation of Cellulose Nanofiber from α-cellulose Pulp

Acid hydrolysis was performed by using acid-biomass ratio of 1:10, by adding 30 ml acid into 3 g α-cellulose. A total of 12.77 grams of pulp with a moisture content of 76.5% (3 grams of dry α-cellulose) were dissolved in sulfuric acid with three different concentrations of 55%, 60%, and 64%. Acid hydrolysis was performed with two different time treatments, i.e. 3 hours and 6 hours, and different temperatures used were 35°C and 45°C. Hydrolysis was performed on a hotplate with a stirring speed of 85 rpm. After the hydrolysis process was completed, aquades was added doubled of the amount of acid added. The hydrolysis suspension was washed by centrifugation at 10,000 rpm for 40 minutes, and the washing was performed repeatedly until reaching neutral pH or acid-free. The suspension was then sonicated by an ultra-sonication process for 20 minutes to obtain well dispersed cellulose nanocrystalline and increase the pulp weight after hydrolysis process of CNF.

2.3 Characterization of CNF

The isolated cellulose nanofiber (CNF) was characterized by the crystallinity index (User Manual Standard Operational Procedure Measurement Center XRD D8 Advance Brucker), particle size (User Manual Standard Operational Procedure MALVERN Zetasizer), morphology (Standard Operational Procedure Scanning Electron Microscopy Hitachi S-4800), and FTIR (User Manual Standard Operational Procedure Scanning Electron Microscopy Hitachi S-4800).

3. Results and Discussions

3.1 Pulp Weight After Hydrolysis

Hydrolysis at 35°C produced higher pulp weight after hydrolysis compared to hydrolysis occurred at 45°C. The highest weight of pulp after hydrolysis was obtained at the treatment or sample A1B2C1 which was hydrolysis condition at 35°C for 6 hours with 55% acid and A1B1C1 which was hydrolysis condition at 35°C for 3 hours with 55% acid. From the result of variance test (ANOVA α = 0.05) the interaction between temperature factor (A) and time (B) was not significantly different, so that the selected process was treatment A1B1C1 with shorter processing time. Temperature, time, and acid concentration during acid hydrolysis process certainly affected the obtained results. Temperature can affect the energy produced, so the higher the temperature, the more energy that can be used to achieve the activation energy [5]. The temperature of 35°C produced higher pulp weight after hydrolysis, meaning that CNF can be produced at lower temperatures. Higher temperatures will lead to more reactive reactions, so that when the process of destruction of the amorphous portion of cellulose, the crystalline part will also be damaged. Damage of the crystalline portion of cellulose will facilitate
the breakdown of cellulose and convert it into glucose and other compounds [6]. Similar to the time factor, the longer hydrolysis time was used, the more hydrolysis of the material will occur. However, if the time taken was too long, the hydrolyzed material will be converted into other products such as glucose.

Note: A: Temperature (A1 = 35°C and A2 = 45°C)
B: Time (B1 = 3 hours and B2 = 6 hours)
C: Acid concentration (C1 = 55%, C2 = 60%, C3 = 64%)

**Figure 1.** Pulp weight after hydrolysis of CNF at various treatments.

3.2 Crystallinity

The X-ray diffraction pattern (XRD) can be used as a method of identifying and characterizing a substance. In this way, the pattern of crystallinity and amorphous levels contained in cellulose can be determined [7]. The crystallinity index was calculated for SNF obtained from various hydrolysis experiments conducted, so that it is the crystallinity index for each treatment can be compared. The crystallinity index of the starting material used should be known first, given that the hydrolysis treatment of the cellulose was to increase the value of the crystallinity index. The α-cellulose used has a crystallinity index value of 25%. Figure 2 showed no significant difference in the crystallinity index values of the various treatments.

Figure 3 showed that the treatment of A1B1C1 or hydrolysis at temperature 35°C for 3 hours using 55% acid concentration achieved the highest crystalline percentage of 31.1%. Very high acid concentration for a long time can make the crystalline part of cellulose damaged and cellulose will be converted into glucose and other compounds. The crystallinity of the obtained product was still lower when compared to the results of other studies which reported the crystallinity index for CNF was 54-88% [8]. Crystallinity index of cellulose nanocrystalline was 72.5%. The research used bagasse as a material for cellulose nanocrystalline production, and achieved the crystallinity index of bagasse 35.5%, whereas the crystallinity of bagasse waste separated from lignin and its hemi cellulose was 63.5% [9]. Another research uses cotton fiber with crystallinity index of 66.9% with cellulose nanocrystal product of crystallinity index 88% [7]. The previous studies indicated that the removal of lignin and hemicellulose will increase the crystallinity index of the cellulose. The crystallinity index obtained in this study was still very low. This may be because the α-cellulose used still contains lignin and hemicellulose. The presence of high lignin and hemicellulose content in hydrolyzed cellulose will inhibit the hydrolysis process.
Note: A: Temperature (A1 = 35°C and A2 = 45°C)
B: Time (B1 = 3 hours and B2 = 6 hours)
C: Acid concentration (C1 = 55%, C2 = 60%, C3 = 64%)

**Figure 2.** Crystallinity of CNF at various treatments.

**Figure 3.** XRD pattern of α-cellulose and A1B1C1 treatment (hydrolysis at 35°C for 3 hours with 55% sulfuric acid).
3.3 Particle Size

Figure 4 showed that at temperature treatment of 45°C, the higher the acid concentration used and the longer hydrolysis time will lead to smaller particle size produced. The hydrolysis time had a significant effect on the size reduction of cellulose, in which with longer hydrolysis time, the cutting of the cellulose structure by the acid will be occurred more or the cellulose will be more hydrolysed. Acid concentration had no significant effect on the reduction of size of cellulose, but rather had a significant effect on the crystallinity index [10]. The best result obtained based on the average size of the particles was in the treatment of A1B2C2, i.e. it was optimum at 35°C, using 60% acid concentration for 6 hours.

3.4 Functional Groups with FTIR (Fourier Transform Infra-Red)

The α-cellulose and CNF (A1B2C1) showed similar FTIR spectra results (Figure 5). This indicated that the chemical composition of both materials was similar. In general, the sample generated two transmittance percentage groups, i.e. low wavelengths in the range 1000-1633 cm\(^{-1}\) and high wavelengths in the range 2000-3302 cm\(^{-1}\). Absorption peaks at 3302 cm\(^{-1}\) and 1633 cm\(^{-1}\) showed the vibration of the O-H group [11]. The presence of an O-H group was influenced by the presence of water in the tested sample [3]. The absorption peak of 2915 cm\(^{-1}\) indicated the presence of stretching vibration of the C-H group of cellulose, hemicellulose, and lignin [12]. The presence of peak at 1429 cm\(^{-1}\) was due to the presence of various lignin components contained in the cellulose [12]. Peak at 1158-1034 cm\(^{-1}\) indicated that the CNF obtained was formed from cellulose I\(β\) [13]. Cellulose I\(β\) is a cellulose easily soluble in NaOH that has a concentration of 17.5% at 20°C and settled in acid solution [14].
3.5 Physical Characteristics of CNF

The best dispersion was observed in the treatment A1B2C1 (hydrolysis with temperature 35°C for 6 hours with 55% acid concentration) both after cooled for 24 hours and 48 hours, in which the resulting dispersion was stable and not settled. The best dispersion treatment was observed with SEM and compared with α-cellulose. From Figure 7, the structure of cellulose nanocrystal was not observed. The diameter of α-cellulose was 6721 nm and the size of treatment diameter A1B2C1 was 2708 nm. The shape of the stem of CNF had not been seen because the crystallinity index obtained was still low.

Note: A: Temperature (A1 = 35°C and A2 = 45°C)
B: Time (B1 = 3 hours and B2 = 6 hours)
C: Acid concentration (C1 = 55%, C2 = 60%, C3 = 64%)

Figure 5. FTIR spectra of α-cellulose and CNF A1B2C1 (hydrolysis at 35°C for 6 hours with 55% sulfuric acid).

Figure 6. Visualization of sample color and dispersion of various treatments (a) 24 hours (b) 48 hours.
Figure 7. Measurement of SEM (A) treatment A1B2C1 and (B) α-cellulose.

4. Conclusions

The process of synthesis of cellulose nanocrystal by acid hydrolysis method was influenced by several factors, i.e. temperature, time, and acid concentration during hydrolysis process. The results of pulp weight after hydrolysis of CNF showed that temperature, time, acid concentration, interaction between temperature and acid concentration, and interaction between time and acid concentration were significantly affected pulp weight after the hydrolysis of CNF. The highest pulp weight after the optimum hydrolysis was 14.98 g, obtained by hydrolysis at 35°C for 6 hours using 55% acid concentration. The crystallinity test showed that the temperature, time, acid concentration, and interaction between factors during hydrolysis were not significantly affected the crystallinity percentage of CNF. Crystallinity percentage was 31.1%, obtained by hydrolysis at 45°C for 3 hours with acid concentration of 55%. The results of mean size showed that the temperature, time, acid concentration, and interaction between factors were significantly different with the best particle size of 894.25 nm, obtained by hydrolysis at 35°C with 60% acid concentration for 6 hours. The resulting CNF color was white with the best dispersion generated by hydrolysis at 35°C and acid concentration of 55% for 6 hours.

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