Properties of nanocrystalline cellulose from pineapple crown leaf waste

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Abstract. Nanocrystalline cellulose was extracted from pineapple crown leaf as agricultural waste. Nanocrystalline cellulose was successfully extracted using chemical treatments followed by acid hydrolysis using sulfuric acid. Hydrolysis of pineapple crown leaf was carried out by using different hydrolysis time while maintaining acid concentration and temperature. The properties of nanocrystalline cellulose were obtained such % yield, moisture content, crystallinity index (CrI) and functional group present were studied. The yield shown a comparable result regardless of different reaction time of hydrolysis. While Fourier transform infrared spectroscopy (FT-IR) showed the progressive removal of non-cellulose content and showed the cellulose molecular structure remains unchanged with the reaction time. X-ray diffraction (XRD) analysis revealed that the crystallinity increased linearly with increasing hydrolysis time. The result showed potential of pineapple crown leaf to be used in nanocrystalline cellulose synthesis process and optimum hydrolysis time was determined based on the properties of nanocrystalline cellulose.

1. Introduction

Pineapple is one type of fruit that is widely used as a source of food in the world. Its processing which produces 3 billion tons of by-products each year, namely pineapple leaves has caused environmental pollution and problems in agricultural land. Generally, pineapple crowns leaf (PCL) are made up of 79-83% cellulose, 19% hemicellulose and 5-15% lignin [6]. Pineapple crown leaf (PCL) has recently been used as an ingredient in the production of textiles, paper and as a reinforcement in polymers [5]. However, in large quantities, pineapple crown leaves are dry and burned in an open environment, which causes environmental pollution issues. Then it is necessary to reduce the problem of environmental pollution by utilizing pineapple crown leaf waste as a source of cellulose. Cellulose is a biodegradable and renewable polymer material and can be processed into cellulose microfibrils, microcrystalline cellulose (MCC), nanocrystalline cellulose (NCC) and many more. This material can be obtained from agricultural by-products such as wood fiber, cotton fiber, kenaf bast, corn stalk and rice husk [1,2,4,11].

Nanocrystalline cellulose (NCC) is a new type of material from cellulose which has physical and chemical properties such as biocompatibility, non-toxic, hydrophilic, has a large surface area and is characterized by increased crystallinity, dispersion ability and biodegradation. These properties make cellulose widely used in various fields of research including being used as a polymer reinforcement, additives for biodegradable products, membrane reinforcement and highly relevant for the development of renewable biomaterials in many fields of chemistry, food, pharmacy, and recently...
used as nanocomposites [9,12]. Based on the analysis of Santos, et al [13] the properties possessed by NCC as polysaccharides can be used in liquid media applications and improve mechanical properties in nanocomposite polymers and are used as reinforcement or fillers in thermoplastic polymer matrix and also bionanocomposite films which have uses as food packaging [4]. Synthesis of NCC from biomass can be done by various methods, including mechanical, chemical and biological methods. Chemical methods that are often used in synthesizing NCC are using the hydrolysis, organosolv, alkaline solvent, oxidation, and ionic liquid methods [3]. NCC can be produced in the form of nanocrystals by using acid hydrolysis method where the amorphous region of cellulose component is disintegrated resulting with different degrees of crystallinity index.[7]. The acid concentration and hydrolysis time are two important parameters in acid hydrolysis process. Acid hydrolysis process reduces the degree of polymerization as a function of hydrolysis time. Increasing the hydrolysis time has great effect on the cellulose because of the β-1,4 glycosidic bond to acid [2]. However, the hydrolysis time parameter impact both the efficient removal of non-cellulosic component and properties of acid hydrolyzed of PCL. The results of the literature extraction of NCC from PCL fibers are still little published, so there is a need for research to extract NCC by using acid hydrolysis techniques. Therefore, this study aims to report the extraction of NCC from PCL by acid hydrolysis with different reaction times. The characterization of the NCC produced properties such as yield, functional group, crystallinity index, moisture content and potential applications were analyzed.

2. Experimental

2.1 Materials
Pineapple crown leaf waste were supplied by local markets in Banda Aceh, Indonesia. NaOH and H2O2 were used as mercerization and bleaching agents while H2SO4 were used for hydrolysis. All the chemicals were purchased from CV. Karya Graha Agung, Medan, Indonesia.

2.2 Preparation of NCC
Singular pineapple crown leaves were isolated from pineapple crown. Prior to removing non-cellulosic compounds through the mercerization and bleaching treatments, the PCL fibers were washed in running water to remove soluble sugars and impurities. Dried PCL fibers (60°C for 24 h) were cut into small pieces (1 cm) before further treatment. The mercerization and bleaching of PCL fibers was performed by using NaOH and H2O2 1 M at 80°C for 1 h. Upon completion of the mercerization and bleaching process, the samples were rinsed with water. Following the mercerization and bleaching process, the samples was hydrolyzed using 3 M H2SO4 at 45°C for 1, 2, and 3 h. Upon completion of the reaction, the samples were washed and rinsed repeatedly with distilled water until it reached pH 7. The resultant NCC were grounded into fine powder by using blender after the washing and drying process. Finally, the NCC were ultrasonicated and centrifugation for 30 min and were stored until further analysis.

2.3 Characterization of NCC

2.3.1 Percentage yield
Percentage yield was calculated using the following equation:

\[
\text{Yield (\%)} = \frac{\text{weight after hydrolysis}}{\text{weight initial}} \times 100 \%
\] (1)

2.3.2 Functional group analysis. Functional group analysis was carried out using IRAffinity-1S FTIR spectrometer with scanning ranges of 5000 cm⁻¹ to 500 cm⁻¹ at room temperature.
2.3.3 Crystallinity and crystal size. Crystallinity and crystal size were determined using XRD Shimadzu XDR 7000 at an operating voltage 40 kV and applied current was 30 mA. The crystallinity of the samples was calculated with Segal formula using equation:

\[
Crl (\%) = \frac{I_{200} - I_{AM}}{I_{200}} \times 100\%
\]  

(2)

where \(I_{200}\) symbolizes the amorphous and crystalline fractions and \(I_{AM}\) symbolizes the amorphous region [2]. The crystal size of sample was determined based on Scherrer formula using equation:

\[
D_{(hkl)} = \frac{K\lambda}{\beta \cos \theta} \times 100\%
\]  

(3)

where \(D_{(hkl)}\) is the crystal size (nm), \(K\) is the Scherrer constant, \(\lambda\) is the wavelength of XRD \(\beta\) is the full width of reflection and \(\theta\) is the Bragg angle.

2.3.4 Moisture content
The moisture content was determined in triplicate, according to the standard method of AOAC. Sample of 1.4 g each were dried at 80°C and weighted after 30 min of drying. This procedure was repeated until constant mass was reached and calculated using equation:

\[
\text{Yield} (\%) = \frac{m_i - m_d}{m_i} \times 100\%
\]  

(4)

where \(m_i\) symbolizes the initial mass of the sample before drying and \(m_d\) symbolizes the final mass after drying [12].

3. Result and Discussion

3.1 Percentage yield
The yield of NCC sample was determined and the data was summarized in Table 1. Different hydrolysis time (1, 2 and 3 h) were used to extract NCC from PCL while maintaining a constant \(H_2SO_4\) concentration and temperature. The yield for 1, 2 and 3 h hydrolysis time of PCL were found to be 79.36, 78.10 and 76.23% respectively.

| Sample | Yield (%) |
|--------|-----------|
| 1 h    | 79.36     |
| 2 h    | 78.10     |
| 3 h    | 76.23     |

Increasing reaction time of hydrolysis gave a lower NCC yield. This is probably due to the breakdown of the more \(\beta-1,4\) glycosidic bond at higher reaction time and easier removal of short chains during hydrolysis [2]. The percentage yield of NCC varied from sample to sample and depending on the type of raw material, geographical conditions, sample preparation and method of analysis which could be the reason for this variation.

3.2 Fourier Transform Infrared Spectroscopy (FTIR)
Figure 1 shows the FTIR spectra recorded for NCC treated with different hydrolysis time (1, 2, and 3 h) and concentration \(H_2SO_4\) 3 M. All samples display similar spectra, which indicates similarity in chemical compositions and all samples display absorbance regions at 2900-3500 cm\(^{-1}\) and 450-1750 in
The absorption at region 1654 cm\(^{-1}\) in all the sample corresponding to O-H bending vibration of absorbed water [8,12].

It is evident from Figure 1 that by increasing the hydrolysis time, the intensity of the hydrogen bonds increased. This might have been because of the degradation of the amorphous part, which enhanced the crystallinity of the NCC as time progressed. Furthermore, the OH bond shifted to lower wavenumbers with increasing hydrolysis time, which can be described to the increased hydrogen bonding and crystallinity of the NCC. Ahmad et al. [1] reached a similar conclusion by increasing the hydrolysis time, the hydrogen bond of rice husk fibers would shift to a lower wave number because of the increase in the OH bond in the rice husk chains.

The peak intensity obtained in the region of 1427 cm\(^{-1}\) shows the -CH\(_2\) bond which is an aromatic characteristic of polysaccharides. Kumar et al. [11] explain that shifts that occur at peaks of 1488-1455 cm\(^{-1}\) and 997-891 cm\(^{-1}\) indicate vibrational deformation of -CH\(_2\) and C-O-C glycosidic bonds in the synthesis of NCC which indicate crystalline levels in the samples. This shows that the morphological structure of cellulose nanocrystals is intact and the increase in peak intensity is due to increased crystallinity of cellulose. Based on FTIR spectra, lignin and hemicelluloses have been removed via mercerization and bleaching treatments. It is evident in Figure 1, where the peaks at 1500, 1605 and 1700 cm\(^{-1}\) are absent in NCC spectra [8,12]. In addition, no significance difference was observed in all samples at the cellulose region, which indicates the cellulose molecular structure remains unchanged from the treatment.

3.3 X-ray diffraction (XRD)
Cellulose is the important component of PCL contains a crystalline structure resulting from placement of the chain by acid hydrolysis. Figure 2 shows the diffraction patterns obtained for NCC with different hydrolysis time. The peak at 20 = 16°, 22.5° and 36° correspond to cellulose I region for all samples. Additionally, the crystallinity percentage and crystal size are summarized in Table 2.
Figure 2. X-ray diffraction patterns of NCC from pineapple crown leaf waste after 1, 2 and 3 h of hydrolysis.

The crystallinity value of the samples with different hydrolysis time were 78.21, 22.94 and 77.69% respectively. Furthermore, the crystallinity values of NCC with 2 h hydrolysis is higher compared to others. It is due to the removal of amorphous regions of cellulose by acid hydrolysis, which prompts the hydrolytic cleavage of glycosidic bonds, and finally released of more individual crystals [8,10].

Table 2. Crystallinity percentage and crystal size of NCC

| Sample | Crystallinity (%) | Crystal size (nm) |
|--------|------------------|-------------------|
| 1 h    | 78.21            | 16.80             |
| 2 h    | 83.16            | 22.94             |
| 3 h    | 77.69            | 19.38             |

In addition, during the acid hydrolysis process the amorphous part dissolve and single crystals are released and thus can improve the cellulose crystallinity [10]. An increase in crystallinity is related to increases in the rigidity of the cellulose structure, which can lead to higher tensile strength to fibers. This increase would be expected to enhance the mechanical properties of composites. A further increase in hydrolysis time at 3 h caused a reduction in the crystallinity value, probably because of damage to some of NCC crystalline region because of the high of acid concentration. Aprilia et al. [2] reached a similar data by increasing hydrolysis time from 2 h to 3 h, the crystallinity of MCC from kenaf bast decreased from 82.7% to 82%. The crystal size was found to be 16.80, 22.94, and 19.38 nm respectively. By increasing the hydrolysis time, with removal of no-cellulosic components and leaving behind the dense cellulose and leading to increased crystal size [2].

3.4 Moisture content

The moisture content of each sample is listed in Table 3. Cellulose has three hydroxyl groups that can interact with water molecules, which confirm NCC as hydrophilic. Higher moisture content of NCC has influence on potential applications as disperse phase in polymeric composites [12].
Table 3. Moisture content of NCC

| Sample | Moisture content (%) |
|--------|----------------------|
| 1 h    | 10.28                |
| 2 h    | 10.92                |
| 3 h    | 11.42                |

The moisture content of NCC with different hydrolysis time were 10.28, 10.92 and 11.42 % respectively. Higher moisture content can be attributed to the higher surface area of nanoparticles. As seen in FTIR result show band related to O-H bonding, which confers hydrophilic behavior for NCC. This trend is in agreement with previously reported results [12]. By increasing the hydrolysis time, the intensity of the hydrogen bonds increased and might have been because of the degradation of the amorphous part and also the moisture content may depend on several other factors as climatic and storage conditions [14].

4. Conclusions

NCC has been successfully extracted from PCL using chemical treatments involving mercerization, bleaching and acid hydrolysis treatments. The results obtained from FTIR analysis confirmed the removal of the non-cellulosic compounds of PCL. The crystallinity analysis shows that NCC give high crystallinity providing evidence that acid hydrolysis does not change crystal structure from cellulose I of PCL. The proposed of different hydrolysis time gives comparable % yield and % crystallinity making it a potential for condition process hydrolysis. The NCC isolated from PCL show interesting properties that can be used in several applications with high added-value. Their high hydrophilicity allows the use of NCC in liquid media applications and as reinforcement in polymeric nanocomposites. The diverse potential applications of the obtained NCC motivates the use of PCL residues as a source of NCC extraction since they are abundant and inexpensive by-product. Using PCL wastes for NCC extraction arises as an important contribution to solve the agroindustrial disposal problem.

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