The Effect of Acid Hydrolysis Treatment on the Production of Nanocellulose Based on Oil Palm Empty Fruit Bunches

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**Article Info**

Nanocellulose has been known as promising reinforcing material in various polymer based product resulted in remarkable improvement in mechanical and thermal properties. Hence, studies to date have developed and explored various sources of biomass to produce nanocellulose. This study aims to synthesize and fully characterize nanocellulose obtained from abundantly available oil palm empty fruit bunches via two different methods which are strong (H2SO4) and mild acid (H3PO4) hydrolysis at 50 °C for 3.5 hours. Based on the morphological study using Transmission Electron Microscopy, rod-like nanocellulose was obtained using strong acid hydrolysis while mild acid hydrolysis produced long filament shape. X-Ray diffraction analysis showed that the degree crystallinity of nanocellulose produced from strong acid hydrolysis was higher, which is 96% than that of mild acid hydrolysis recorded with 86%. While the sulphuric acid hydrolysis usually produces lower thermal stability than that of other types acid hydrolysis, surprisingly, in this study, the thermal stability of nanocellulose from strong acid hydrolysis was relatively similar to mild acid hydrolysis due to the formation of single crystal structure affording unique characteristic of the obtained nanocellulose.

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**Abstract**

**Keywords:** Oil Palm Empty Fruit Bunches, Nanocellulose, Acid Hydrolysis, Cellulose Nanocrystal, Single Crystal

1. INTRODUCTION

Cellulose constitutes the most abundant resources of biomass production which can be found not only in plant sources (wood, cotton, wheat, and biomass waste) but also in non-plant sources (algae, tunicate (sea animal families) and bacteria) [1, 2]. In the nano-scale, cellulose has been known to exhibit exceptional properties which are outstanding mechanical properties; chemically active surface functionality, easy chemical surface modification; low density; and also biologically renewable and sustainability in addition to their abundance. The remarkable mechanical properties and stability of cellulose nanostructure are due to the formation of the inter-intra hydrogen bonding network of hydroxyl groups at the active surface functionality of individual nanocellulose [1].

Based on their aspect ratio, dimension, and shape, the synthesis of cellulose into nanocellulose can be obtained at different types of morphology in the form of rod-like shaped [3-6]; filament/long like [2, 7, 8]; and sphere-like [9, 10] nanocellulose. Rod-like shape cellulose nanocrystals (CNC) can be synthesized in many ways, such as acid hydrolysis, oxidation process, ionic liquid treatment, mechanical method, and enzymatic hydrolysis [11]. Among these
methods, acid hydrolysis is the most extensive process to produce CNC, in which sulphuric and hydrochloric acids have been the most widely used in CNC production [4].

Sulphuric acid is the most common of CNC production because of some advantages such as producing a more uniform and shorter with a narrow polydispersity of CNC, a higher crystallinity for more than 90%, and better stabilization of solution against flocculation [1, 11-13]. However, the residual sulfate groups (SO₄²⁻) can trigger dehydration reaction leading to lower thermal stability, which limits its application in high-temperature processing polymer production, for example; extrusion, and injection molding. In order to overcome this problem, many studies have been done by using various kinds of acid, for example, hydrochloric acid, and phosphoric acid in order to improve the thermal stability properties of nanocellulose.

Oil palm empty fruit bunches (OPEFB) is one of the most abundant solid biomass wastes in Indonesia. Every year, a massive amount of OPEFB from oil palm industry is generated approximately 43.24 million tonnes/year. Besides, in the aim to convert this excessive amount solid waste into new advance material, it is chemical composition of OPEFB shows the high content of cellulose at about 40 - 43% which is a significant property to be investigated as a potential resource for producing CNC [14].

Thus in this study, nanocellulose will be synthesized from OPEFB as one of the most potential and abundantly available biomass via acid hydrolysis method using two different acid types which are strong (H₂SO₄) and mild acid (H₃PO₄). The properties of the nanocellulose will be studied and investigated to understand the effect of different type of acid hydrolysis in terms of morphology, crystallinity, and thermal stability.

2. EXPERIMENTAL SECTION
2.1. Materials

Oil palm empty fruit bunches (OPEFB) was obtained from PT Perkebunan Nusantara I, Sumatera Utara, Indonesia. Technical grade sodium hydroxide was purchased for alkaline pre-treatment process. Natrium chlorite for bleaching process was purchased from Sigma Aldrich, US, while sulphuric acid 98% and phosphoric Acid 85% were purchased from Merck, US for acid hydrolysis.

2.2. Methods

2.2.1. Pretreatment Process

The pre-treatment process of OPEFB is an important stage prior to acid hydrolysis. This stage consists of several processes, including chopping, grinding, and oven drying to produce fine size dried fiber of OPEFB. This pre-treated OPEFB was then purified from lignin and hemicellulose to produce high content cellulose based OPEFB via simultaneous alkaline and bleaching process using hydrogen peroxide (H₂O₂) [15].

2.2.2 Isolation of Nanocellulose from OPEFB

Pre-treated OPEFB based cellulose was hydrolyzed using two types of acid; sulphuric acid and phosphoric acid according to the existing protocols [5, 6] at temperature 50 °C for 3.5 hours to obtain nanocellulose. Subsequently, centrifugation at 10000 rpm for 15 minutes, followed by dialysis for three days was conducted to neutralize the obtained nanocellulose.

2.2.3 Characterization

Morphological structure of nanocellulose from OPEFB was analyzed by using Transmission Electron Microscopy (TEM) at Eijkman Research Institute while TEM combined with Selected Area X-Ray Diffraction (SAED) was done in the Research Centre for Physics, LIPI using FEI Tecnai G2 20S-Twin at 200kV facility for material phase determination. Aspect ratio (length/width) of nanoparticle was determined based on TEM images using ImageJ software analysis. Crystallinity percentages were characterized by using X-Ray Diffraction (XRD) Rogalu/SMART Lab at 40kV and 30 mA within 2θ - 60°. Crystallinity (%) was calculated using Segal’s method 12 as :

\[
% \text{CC} = \frac{I(200) - I(\text{amorphous})}{I(200)} \times 100\% \quad eq \ (1)
\]
Where $I_{(200)}$ is the (height) intensity of crystallinity peak at the maximum 20 between 22°-23°, and $I_{(amorphous)}$ is the minimum peak (height) intensity at 20 between 18°-19° (of the amorphous region).

Thermal stability was determined by using Thermal Gravimetric Analysis by Licenses from 30° - 1000° C with heating rate 10 °C/min and then hold isothermally for 5 minutes followed by further heating up to 500 °C.

3. RESULTS AND DISCUSSIONS

Prior to acid hydrolysis process, OPEFB was pre-treated simultaneously via alkaline treatment and bleaching process. These processes are important to remove the lignin and hemicellulose content and thus increase the purity of cellulose. Table 1 shows the elemental analysis of a main lignocellulosic component of cellulose, hemicellulose, and lignin. The cellulose content after simultaneous pre-treatment process increased significantly (79.9 ± 0.3 %) compared to the raw material of oil palm empty fruit bunches (37.6 ± 0.3 %) [15]. In addition, the value also comparable to cellulose standard, which recorded 80.8% of cellulose content.

Table 1. Elemental analysis of main lignocellulosic component before and after treatment

<table>
<thead>
<tr>
<th>OPEFB</th>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
<th>Lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>37.6 ± 0.3</td>
<td>23.9 ± 0.3</td>
<td>38.5 ± 0.0</td>
</tr>
<tr>
<td>Delignified</td>
<td>63.2 ± 0.2</td>
<td>14.9 ± 0.2</td>
<td>12.1 ± 0.5</td>
</tr>
<tr>
<td>Bleached</td>
<td>79.9 ± 0.3</td>
<td>8.4 ± 0.1</td>
<td>0.98 ± 0.2</td>
</tr>
<tr>
<td>Cellulose</td>
<td>80.8</td>
<td>16.6</td>
<td>2.6</td>
</tr>
<tr>
<td>Standard</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.1. The Morphology of Obtained Nanocellulose

Morphology of the obtained nanocellulose from two different types of acid was investigated by using TEM equipped with Selected Area X-Ray Diffraction (SAED), and so the crystal structure can also be determined. Figure 1 shows the TEM images of nanocellulose obtained from strong acid hydrolysis (H$_2$SO$_4$), while nanocellulose produced from mild acid hydrolysis (H$_3$PO$_4$) as shown in Figure 2. As can be seen from the Figure 1(a), rod-like nanocellulose from oil palm empty fruit bunches (OPEFB) was obtained via strong acid hydrolysis while the mild acid hydrolysis produced longer fibrillated nanocellulose (Figure 2(a)).

Based on the Image J software, the dimension of nanocellulose from the strong acid hydrolysis produced rod-like nanocellulose low aspect ratio of 13 with 10.7 ± 1.8 nm in width and 128.4 ± 17.2 nm in length. For the nanocellulose obtained from mild acid hydrolysis, the width was almost similar to the nanocellulose sulphuric acid hydrolysis at 10.5 ± 2.1 nm, but the length was much longer above 500 nm, meaning that high aspect ratio at more than 50 was obtained.

Fig. 1. Nanocellulose based on OPEFB obtained from sulphuric acid hydrolysis[16]

Moreover, the size of CNC from sulphuric acid hydrolysis is more uniform and shorter than those of CNC obtained phosphoric hydrolysis. It
is observed that individual nanocellulose can uniformly be dispersed in the matrix, and no agglomeration nanocellulose was observed (Figure 1a). It was due to residual sulfate groups (SO$_4^{2-}$) gives the CNC a negative surface charge, which makes the CNC dispersible in water [1, 12, 17]. In contrast, entangled and longer nanocellulose were observed in the TEM images from the samples obtained via phosphoric acid hydrolysis. It was also observed by another study showing flocculation on the obtained nanocellulose via mild acid hydrolysis [11].

![100 nm](image1)

**Fig. 1.** TEM images of nanocellulose obtained from (a) sulphuric acid hydrolysis and (b) phosphoric acid hydrolysis

Selected Area X-Ray Diffraction (SAED) respectively. It can be seen that two distinguish diffraction rings using these two hydrolysis methods were observed. Bright spots scattering and surrounding the diffraction ring was only observed on the nanocellulose produced from sulphuric acid hydrolysis. In contrast, no such white spots observed in the nanocellulose obtained from mild acid hydrolysis. The brighter spots were reflected in the single crystallinity structure of the obtained material [18]. The single crystal represents a minimum defect of the crystals structure makes them an promising candidate to offer unique and outstanding monocrystal exhibiting unprecedented mechanical, optical, thermal, and electrical properties.

![X-ray diffraction](image2)

**Fig. 3.** X-Ray Diffraction Method of Nanocellulose

The degree of crystallinity of nanocellulose was determined using the XRD analysis (Figure 3). The apparent intensity peak from the x-ray diffractogram in is at a 2θ value of 22° which represents the crystalline structure of cellulose I, whereas a peak characterized the amorphous background at a 20 value of 18°[19]. The increasing of a degree of crystallinity calculated using Eq (1) by means the acid hydrolysis treatments as follows; pre-treated OPEFB < nanocellulose based H$_2$SO$_4$ < nanocellulose based H$_3$PO$_4$ which are 80%, 86% and 96% respectively.

It has been known that the degree crystallinity of CNC produced from sulphuric acid can exceed 90% as sulphuric acid is more aggressive in attacking amorphous regions than other acids.
like phosphoric acid [12, 13] resulting in a significant increasing crystallinity up to 96%. This XRD analysis confirmed and supported the formation of a single crystal structure as reflected by unprecedented crystallinity of the nanocellulose using sulphuric acid hydrolysis.

Moreover, compared to a similar study, the crystallinity index of sulphuric acid based nanocellulose recorded a much higher value than the other counterparts. For example, Lani et al. [20] and Chieng et al. [21] isolated EFB by using 64%-65% sulfuric acid and the obtained crystallinity index were only 73% and 77.8% respectively. By using a mechanical method like high-pressure homogenization, it also produces nanocellulose, but the crystallinity index was only 69% [22]. The unprecedented index crystallinity obtained in this study was postulated due to a simultaneously pre-treated process that can achieve high purity of cellulose content and thus higher crystallinity index of resulted cellulose before hydrolysis treatments.

3.3 The Thermal Properties of Nanocellulose

Thermal properties of nanocelluloses were investigated by Thermal Gravimetry Analysis (TGA). In the most study, the thermal stability of the nanocellulose from sulphuric acid hydrolysis is relatively lower than other methods which are attributed to the presence of residual sulfate groups (SO$_4^{2-}$) [13] causing dehydration process and lead to decomposition. Surprisingly, Figure 4 shows that phosphoric acid exhibited a slightly higher thermal stability as reflected by the lower onset decomposition temperature compared to sulphuric acid based nanocellulose, which are 260 °C and 250 °C respectively.

The relatively similar thermal stability was possibility achieved due to unprecedented crystallinity of the obtained sulphuric nanocellulose and thus lead to the thermal stability of the single crystal structure. The formation of single crystallinity means that crystal lattice of the entire sample is continuous and unbroken to the entire boundary of the sample with the arbitrary absence of the defect. This unique property enables unique characteristic, including thermal stability.

![Fig. 4. Thermal analysis of the cellulose and nanocellulose](image)

4. CONCLUSION

Two types of acid hydrolysis to produce nanocellulose were successfully conducted via strong acid hydrolysis (using H$_2$SO$_4$) and mild acid hydrolysis (H$_3$PO$_4$). These two types of acid produced unique characteristic of obtained nanocellulose. Strong acid hydrolysis produced a rod-like shape and lower aspect ratio with unprecedented crystallinity index. Meanwhile, long-entangled nanofibrils were produced from mild acid hydrolysis. Surprisingly, while most studies show lower thermal stability of sulphuric based nanocellulose compared to mild acid based nanocellulose, in this study the thermal stability of the sulphuric acid hydrolysis was relatively similar to its counterpart at the temperature of 260 °C. It was postulated due to the formation of a single crystal structure of the prepared sulphuric based nanocellulose.

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