The Properties of OPEFB Cellulose Nanofibrils Produced by A Different Mode of Ultrafine Grinding

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Abstract. Cellulose Nanofibrils (CNFs) was resulted from deconstruction of the hierarchical structure of cellulose. CNFs are commonly obtained by mechanical fibrillation, such as ultrafine grinding processes and its variation. Nevertheless, the influence of different treatments on the properties of the resulting CNF especially from variety of ultrafine grinding mode has not been reported. This study investigates the properties of cellulose nanofibrils (CNF) produced from bleached pulp oil palm empty fruit bunch (OPEFB) Kraft pulp through an ultrafine grinder with two different treatments in the fibrillation process. These two treatments were: 1) ultrafine grinder with increasing gaps distances; -30, -50, -70, and -90 µm with five cycles in every gap, 2) ultrafine grinder on constant gaps (-30µm) with increasing grinding cycles: 5, 10, 15, 30, and 40 cycles through the grinder. The influence of the treatment was evaluated through particle size distribution, crystallinity index, and morphological properties. The result showed that the increasing gaps treatment efficiently improved the size uniformity of CNFs, length 147-139.5 nm, and scanning electron microscope micrograph confirmed that the diameter of CNF was smaller with the increasing grinding gaps than increasing grinding cycles. However, the increasing cycle’s treatment produced CNF with a higher crystallinity index. The crystallinity index (CrI) of the CNF decreased from 71.27 to 62.25% with increasing gaps, whereas the CrI of the CNF from increasing cycles was 69.35%. This study provides a valuable guideline for determining the appropriate process to produce CNF especially by mechanical grinding using ultrafine grinder from OPEFB according to the desired result.

1. Introduction
Nanoscale cellulose materials, such as cellulose nanofibrils (CNF) derived from renewable lignocellulose, have recently attracted great interest. Cellulose nanofibrils, the material that can replace various materials derived from nonrenewable petroleum, have been used for many applications, including film, membranes, adsorbent, and hybrid composite [1–3]. The diameter of CNFs is about 5–100 nm, and their length is on the order of several or several tens of micrometers depending on starting materials and the processing methods[4]. Mechanical fibrillation was the most common process to produce CNF from lignocelluloses, including high-pressure homogenization, ball milling, micro fluidization, electrospinning, and ultrafine grinding[5–9]. However, the main drawback of mechanical processing is the high energy consumption, and it has been concluded that ultrafine grinding is the most efficient approach in terms of consumed energy for the CNF preparation [10].
The cellulose slurry is transferred between static and rotating grinding stones (disk) during the grinding process. The distance between these disks is called a gap. The cell wall fibers are delaminated, and the CNF is individualized by the shearing force generated between the disks. Moreover, the distance between these disks can be precisely adjusted, giving different fibrillation effects. At a close disk distance, the fed cellulose fibers will be subjected to a more vigorous fibrillation process than the wider disks distance, thus affecting the characteristics of the produced CNF.

The properties such as crystallinity, particle size, and morphology are required for CNF for polymer reinforcement application. In the ultrafine grinding process, increased grinding often results in increased bonding due to the delicate materials produced that substantially increase the surface area of the fibril. On the other hand, increased grinding time might also result in short fibrils because of mechanical actions. Thus, there is a trade-off between increasing bonding and reducing fibril length with extended grinding. Some previous studies have performed cellulose fibrillation with an ultrafine grinder with some experimental conditions. Wang et al. [11] learn the effect of grinder time on properties of CNF. Moreover, using an ultrafine grinder by increasing the number of cycles to 40, Viana et al. [12] succeeded in producing nanocellulose from pine wood.

This study used an ultrafine grinding technique to obtain CNF from bleached OPEFB kraft pulp with two different treatments, i.e., 1) Ultrafine grinder with increasing gaps distances; -30, -50, -70, and -90 µm with five cycles in every gap, 2) Ultrafine grinder on constant gaps distance (-30µm) with increasing grinding cycles: 5, 10, 15, 30, and 40 cycles through the grinder. The observed parameters in this study were the particle size, morphology, and CNF crystallinity index.

2. Experimental
2.1. Material
An unbleached OPEFB kraft pulp was obtained from Biomaterials Research Center-LIPI and stored in a humidity chamber at 25 °C before used. Dried OPEFB was then bleached using alkali hydrogen peroxide 10%. Next, the mixture was stirred and heated to 80 °C. The bleaching process was continued for 1 hour with a temperature maintained at 80 – 85 °C. Finally, the slurry was filtered and neutralized with aquadest, and the bleaching process was conducted three times.

2.2. Method
2.2.1. Cellulose nanofibers preparation. The bleached kraft OPEFB pulp concentration in suspension was adjusted to 1 wt% by adding water, followed by mechanical fibrillation in a Masuko Sangyo Super Masscolloider grinder (MKCA6-3; Masuko Sangyo Co., Ltd.). To obtained nanocellulose, the bleached kraft pulps were subjected to two different methods of grinding (Figure 1), i.e., treatment I Fibrillation with four different distances of gaps through the grinder: -30, -50, -70, and -90 µm with five cycles in each gap, and treatment II Fibrillation with a constant gap distance at four different cycles of 3; 10, 20, 30 and 40. Both samples were without any mechanical treatment before grinding.

![Figure 1](image.png)

Figure 1. Schematic different treatments in the grinding process
2.2.2. **Particle size analyzer.** Size distribution of CNF was observed using particle size distribution apparatus Litesizer 500 (Anton Paar, Austria). A low concentration of nanocellulose in water (0.05 mg/mL) was prepared and observed under the following condition: a temperature of 25 °C, automatic angle, water solvent, and refractive index: 1.333. The CNF suspensions were evaluated in triplicate.

2.2.3. **Morphology.** Morphology characterization was observed using Scanning Electron Microscope (SEM) Quatro-S for OPEFB Fiber and Jeol IT2000 for CNF. The sample was prepared by dispersing each sample in water. The suspension was then dropped on a silicon mold and air-dried at room temperature. After that, the sample was placed on a carbon tape attached to an aluminum sample holder.

2.2.4. **Crystallinity Index.** XRD was used to determine the reference values of crystallinity. The diffractograms were recorded using an X-ray diffractometer (XRD 7000 Shimadzu) with Cu Kα radiation 0.15418 nm and voltage of 40 kV with a current of 30 mA. The scanning range was from 2θ = 5° to 50° at a scan speed of 2°/min. The crystallinity index was determined using equation (1)

\[
CI = \frac{I_{002} - I_{AM}}{I_{002}} \quad \ldots \ (1)
\]

CI was calculated from the height ratio between the intensity of the crystalline peak (I_{002} - I_{AM}) and total intensity (I_{002}) after subtraction of the background signal measured without cellulose [13].

3. Result and Discussion

3.1. **Effect of ultrafine grinding condition on particle size reduction**

The particle size analysis (PSA) was used to obtain the particle size of CNFs in suspension. This method is based on Brownian motion generated by thermally induced collisions between the CNF particles and solvent particles. The measured particle size indicates how the CNF diffuses within a fluid, called hydrodynamic diameter[14]. The size distribution of CNFs OPEFB from two different mode in ultrafine grinding process as measured by PSA is shown in Table 1.

| Treatment | Size range distribution (nm) | Treatment | Size range distribution (nm) |
|-----------|-------------------------------|-----------|-------------------------------|
| I         | G3P5 1490-460                 | II        | G3P10 2000-859               |
|           | G5P5 305-281                  |           | G3P20 383-355                |
|           | G7P5 224-166                  |           | G3P30 344-166                |
|           | G9P5 147-139.5                |           | G3P40 363-51                 |

The particle size of CNF from both grinding conditions, either with treatment I or treatment II tends to vary. However, Generally, the CNF particle size was likely to decrease with the different mode that use increasing gap distances or number of cycles. The size range distribution of the CNFs shows the smaller gap distance (treatment I) facilitated a better fibrillation and produce more uniform CNF. Furthermore, the particle size was fluctuated with varying grinding cycle (treatment II).

The particle size found in this study in the end of the treatment, i.e., CNF-G9P5 and, CNF-G3P40, will refer as CNF-TI and CNF-TII respectively, was smaller than that of the OPEFB extracted CNF by Setyaningsih et al. [15]. These authors used hydrolysis treatment and found a particle size of 894.25 nm. Wahyuningsih et al. [16] show the average particle size of pineapple leaf fibers CNF of 284.6 nm procured by ultrafine grinding process. The present finding is better that that found for the kenaf bast fiber CNF obtained by microwave, chemical, and ultrasonic treatments, which had a length in the range
of 400 nm to 1500 [17]. The particle size found in this research was almost in the same range with that obtained with TEMPO [18].

It is essential to understand that in the PSA, the measurement refers to the Stokes-Einstein equation, where the spherical particles and the orientation of the CNF in suspension profoundly influence the particle size value obtained. However, the varied gaps treatment efficiently improved the size uniformity of CNF from OPEFB kraft bleached pulp. Furthermore, both applied grinding treatments were successfully resulting in a stable and homogenous colloidal suspension, which had a gel-like appearance. No phase separation was observed during storage.

3.2. Effect of ultrafine grinding condition on morphology
Morphological studies on OPEFB bleached pulp, CNF-TI, and CNF-TII were carried out using Scanning Electron Microscope (SEM). Figure 2 shows the SEM micrographs and surface morphology of OPEFB bleached pulp before (Fig.2a) and after the ultrafine grinding process (Fig 2b-c). In producing CNF, OPEFB bleached pulp was ground with two different treatments. Ultrafine grinding treatment helps disintegrate the fibers and facilitates defibrillation of the fibers to a nanoscale size.

Figure 2. SEM images and diameter size distribution graph of a) OPEFB Pulp b) CNF-TI, c) CNF-TII
The SEM image indicates the OPEFB fibers were curled and having a smooth boundary shape. The surface was rough with some pits. The width of the original OPEFB kraft pulp was around 9-25 µm, which is composed of several microfibrils with various diameters. The diameter of CNFs was measured by image analysis using ImageJ processing of 300 sampling spots. The smallest and the average of the most diameter of CNF-TI and CNF-TII were 41.25 nm and 76-101 nm, respectively. Figure 2 shows the morphological appearance of CNF-TII still has some nanofibrils bundles, where the CNF-TI is more uniform according to the measurement of particle size analysis.

The diameter of CNFs observed from SEM images in this study was larger than CNF from bleached eucalyptus pulp which was observed by TEM where the diameter size approximately 20 nm [19]. Trifol et.al., 2017 [20] extracted CNF from Sisal by chemically treatment using Nitric acid and acetic acid obtained estimated diameter of 27 +/- 13 nm measured by TEM which was shorter that CNFs in this research. The accurate diameter size of nanofibrils could be slightly more apparent in transmission electron microscopy (TEM). SEM has been used for imaging the surface of the nanoparticle on a sub-microscopic scale. In contrast, the use of TEM is to image the internal structure of the nanoparticle on a nanometer scale. However, from SEM images, the CNFs that we found in this research is known that their diameters were displaying nanometric dimension (under 100nm). Both treatments appear to aid in separating the bundle of fibers into individual fibers, thus leading to a significant reduction in their diameter size.

3.3. Effect of ultrafine grinding condition on crystallinity

The XRD was used to determine the crystallinity of the CNF. Figure 3 shows the XRD diffraction patterns of Bleached OPEFB kraft pulp fibers and the fibrils prepared by Ultrafine grinding with two different treatments, CNF-TI and CNF-TII. All the diffractograms pattern showed cellulose-I structure with peaks at 2θ of 16°, 22°, 23°, and 34°, which belong to diffraction from the 101, 021, 002, and 040 planes, respectively [21,22]. The similarities of the pattern between both fibers and nanofibrils after mechanical process indicating the cellulose structure of the fiber were maintained after the nano grinding.

![Figure 3. X-ray diffraction pattern of Cellulose OPEFB, CNF-TI and CNF-TII](image-url)
The crystallinity index (CrI) refers to the relative quantity of cellulose in the crystalline region where the fiber presence higher resistance to stretching, solvation, and tensile force [12]. According to the adopted method, the intensity difference between the highest and lowest peaks originating from the intensities of the I_{002} and I_{am} peaks in diffractograms was used to measure the crystallinity index. The resulted CrI average value can be seen in Table 2.

| Sample       | CrI (%) |
|--------------|---------|
| OPEFB Pulp   | 71.27   |
| CNF-T1       | 62.25   |
| CNF-T11      | 69.35   |

Mechanical treatments decreased the cellulose crystallinity, as shown by Table 2, in which the OPEFB kraft pulp fiber retained the highest crystallinity index (71.27%) and the lowest was CNF-T1 (62.25%). 40 cycles grinding of OPEFB pulp resulted in a similar CrI to that of OPEFB pulp fiber, as shown in Table 2. Fibrillation process decreased the crystallinity. The fibers were well dispersed in the shortest distance of the ultrafine grinder disks, leading to a better defibrillation, and therefore a decreasing cellulose crystallinity. The results also showed that gaps variation was more influential than cycle variation to cellulose crystallinity.

The cellulose crystallinity is determined by the raw material sources, purification time of the sample, and mechanical treatment conditions. The crystallinity of the presently produced CNF (by ultrafine grinding) was higher than that produced by strong acid hydrolysis [15], however it was lower than that of mechanically produced CNF from empty fruit bunch (EFB), which was in the range of 82.93-85.09% [23]. When comparing to other studies, the present study provides a greater degree of crystallinity than those obtained by CNF from Pinus sp Kraft Pulp (66.4%) with a similar 40 cycles ultrafine grinding [12] and Sugarcane Bagasse (46-60%) via endoglucanase assisted mechanical grinding [24]. The higher degree of crystallinity leads to higher tensile strength, thus enhancing the mechanical properties of nanofiber. Therefore, the durability of the CNF from OPEFB is an advantage.

4. Conclusion
This work evaluated the properties of CNF produced from bleached OPEFB pulp using two different grinding treatments. The mode of ultrafine grinding affected the morphology and physical properties (such as particle size and crystallinity). Variation disk distances and grinding cycles and of the ultrafine grinder resulted in a different distribution of particle size and fiber quality. It was noticed that varying the disk gaps at a constant cycle led to a smaller and more uniform particle size, however with a lower crystallinity. The lower obtained crystallinity with varying disk gaps at a constant cycle was thought due to a severer fiber defibrillation. Ultrafine grinding method can be a valuable alternative for the production of CNF from OPEFB.

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