

## Oil Palm Frond Waste for the Production of Cellulose Nanocrystals

Noor Afeefah Nordin, Othman Sulaiman,\* Rokiah Hashim  
and Mohamad Haafiz Mohamad Kassim

Division of Bioresource, Paper and Coatings Technology,  
School of Industrial Technology, Universiti Sains Malaysia,  
11800 USM Pulau Pinang, Malaysia

\*Corresponding author: osulaiman@gmail.com

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**ABSTRACT:** *Oil palm frond (OPF) waste is one of the sustainable raw materials obtained after pruning of the OPFs. The objective of this study is to produce cellulose nanocrystals (CNC) from OPFs by chemo-mechanical treatment. The multi-step process started with removal of extractives, wax and pectins by soxhlet extraction, followed by removal of lignin using sodium chlorite and 10% (v/v) acetic acid. The bleached samples were then soaked in potassium hydroxide to remove the hemicellulose and finally underwent acid hydrolysis with 64% (v/v) sulphuric acid hydrolysis for 1 h. The CNC obtained were characterised using transmission electron microscopy (TEM), X-ray diffractions (XRD), Fourier transform infrared spectroscopy (FTIR) and thermal gravimetric analyser (TGA). The TEM images showed that the fibres were well dispersed and the treatment had reduced the size of fibres with average dimensions of 9.88 nm in diameter and 504.12 nm in length. The XRD results showed that the crystallinity index of the extracted cellulose fibres was 52.3% in comparison with the raw OPF, 35%. The results from FTIR analysis showed some differences in the peaks and some were shifted due to removal of some components in the fibres. The TGA confirmed that the CNC had improved its thermal property by having an onset temperature of 258.34°C in comparison with the raw OPF, 197.48°C. This isolated CNC has great properties and can be used in many applications such as in biomedical field, food industry, cosmetics and wood products.*

**Keywords:** Oil palm frond, cellulose nanocrystals, chemo-mechanical, OPF waste, isolated CNC

## 1. INTRODUCTION

Lignocellulosic materials are derived from agricultural waste and in Malaysia, a major contributor of biomass waste is from the oil palm (*Elaeis guineensis*) plantation. Malaysia has the second largest oil palm plantation area in the world which was reported to be 5.4 million hectares as of 2014.<sup>1</sup> Oil palm plantation has generated a huge quantity of lignocellulosic resources consistently throughout the year in the form of oil palm trunk (OPT), empty fruit bunches (EFB), oil palm frond (OPF) and leaves. The OPF was reported to be the largest biomass which is 47% out of the total oil palm waste.<sup>2</sup> Despite being a waste, OPF is abundant, readily available and inexpensive which makes it suitable to be used as a raw material for some value-added products.<sup>3</sup> The current practice for disposal of OPF is by direct decaying and burning on the site while some small amount of OPF is used for composting.<sup>4</sup> These actions are not desirable to the environment as they do not only pollute the environment, but will also cause harm to human beings due to the effect of polluted air. Hence, a proper waste management is needed to overcome the problems and minimise environmental issues.

OPF is spongy and fibrous in nature.<sup>5</sup> Since it is highly fibrous, the OPF is suitable to be used in the production of cellulose nanocrystals (CNC) that has gained much attention in recent years. The main composition of the OPF are vascular bundles and parenchyma that contain extractives, cellulose, hemicellulose and lignin. Therefore, to obtain CNC, the other components have to be removed by chemical, mechanical, chemo-mechanical or enzymatic treatment. Generally, cellulose has a high molecular weight homopolymer of  $\beta$ -D-glucopyranosyl repeating units joined by 1, 4-glycosidic linkages.<sup>6</sup> The mechanical strength of cellulose is comparable to steel thus making it suitable as a reinforcing agent in some applications. In recent years, CNC has gained interest in the production of environmentally friendly and sustainable biocomposite materials for biomedical and industrial applications due to its biodegradability and renewable sources.<sup>7</sup> For instance, it can be used for bone and tissue repair and reconstruction when mixed with suitable matrix.<sup>8</sup> A study by Cherian et al. developed cellulose nanofibres from pineapple leaf and found that its versatility is suitable for the production of cardiovascular implants, repair of articulate cartilage, vascular grafts and artificial skin.<sup>9</sup>

Previous work has shown some isolation of CNC which is also known as nanowhiskers from various types of biomass such as from oil palm EFB, OPT, bagasse, cotton linters and others due to its potential for various applications. A work done by Saurabh et al. used retting OPF vascular bundles to produce cellulose nanowhiskers but the raw materials and methodology were different compared to this present work.<sup>10</sup> Hence, this study was conducted to characterise the properties

of CNC obtained from the whole fresh OPF and analyse the potential of this material to be used in the production of fibre-based materials.

The process of isolating CNC from the OPF depends on the target cellulose that one desires. Chemical treatment is done by subjecting the raw material with chemicals in order to remove the impurities while mechanical treatment is usually attributed to pulping process to obtain pulp before it is further purified. Chemo-mechanical treatment combines the use of chemicals and mechanical process in order to successfully remove lignin and hemicellulose. The enzymatic treatment uses few types of enzymes and is found to be mild in comparison with chemical and mechanical treatment. It will not cause damage to the fibres. However, the enzymatic treatment alone was reported to be unable to completely remove the lignin and hemicellulose in the samples.<sup>11</sup> Therefore, it is crucial for researchers to find the best treatment for the isolation of CNC before it is being used for further application.

Research by Fahma et al. on the production of cellulose nanofibre from oil palm EFB showed that the optimum condition was obtained by combining chemical and mechanical treatment.<sup>12</sup> Henriksson and Berglund developed an environmentally friendly method for the production of microfibrillated cellulose (MFC) by using pulping and enzyme.<sup>13</sup> It was found that the MFC has a more favourable structure than nanofibres obtained from hydrolysis by strong acid. A work done by Bhattacharya et al. produced cellulose microfibrils from bagasse and proved that 60% (v/v) sulphuric acid hydrolysis managed to almost completely remove the amorphous structure without giving significant damage to the crystal structure.<sup>14</sup>

## **2. EXPERIMENTAL**

### **2.1 Materials**

The OPFs were obtained from oil palm plantation in Kuala Selangor, Selangor, Malaysia. The fronds were debarked and cut into small pieces prior to drying in the oven at a temperature of 50°C for 24 h to avoid fungal attack. After drying, the fronds were ground and sieved using a 70 mesh. The samples that passed through the sieve were used for the isolation of cellulose nanocrystals.

### **2.2 Extraction of Raw Oil Palm Frond**

A total of 24 g of OPF samples were used for the extraction to remove extractives using the soxhlet extractor. The mixture of ethanol and toluene were used as a

solvent with a ratio of 2:1. The extraction was done for 6 h at a temperature of  $60^{\circ}\text{C} \pm 5$  until the colour of the solvent became clear. The extracted samples were washed with distilled water prior to drying. The samples were then dried in the oven of  $50^{\circ}\text{C}$  before being further used.

### **2.3 Isolation of CNC**

Twenty grams of extractive free OPF samples were used for the isolation. They were soaked and shaken in sodium chlorite ( $\text{NaClO}_2$ ) and 10% (v/v) acetic acid alternately for four times, at a temperature of  $70^{\circ}\text{C}$  for 4 h and were subsequently washed with distilled water. This process is also known as bleaching process, which is aimed to eliminate the lignin in the OPF sample. The bleached samples were then soaked in 6% of potassium hydroxide (KOH) solution under  $20^{\circ}\text{C}$  for 24 h to remove hemicellulose. After that, the fibres were washed with distilled water until it reached pH 7. The fibres were then subjected to acid hydrolysis with the ratio of fibre to acid 1:10 by adding 200 ml of 64% (v/v) sulphuric acid at  $45^{\circ}\text{C}$  under strong agitation for 1 h. The hydrolysis was terminated by adding 400 ml of cold distilled water to the solution. The precipitate was resuspended in water and centrifuged at 10000 rpm to remove the excess water. Hydrolysis was done using the dialysis tube to obtain suspension of CNC at pH 7. When the fibres had reached constant pH, they were homogenised, sonicated and freeze dried before they were ready to be used for analysis.<sup>9</sup>

### **2.4 Transmission Electron Microscope Study**

The structure and size of the CNC were observed by transmission electron microscopy using a Philips CM 12 electron microscope. A drop of diluted CNC suspension was deposited on a carbon-coated grid and allowed to dry at room temperature. The diameter of the fibres were measured manually using an image analyser program, XL Docu. A total of 10 single fibres of each sample were measured, and the result was calculated as the mean value of the data from each set of measurements.

### **2.5 X-ray Diffraction Analysis**

The X-ray diffraction analysis was performed to check the crystallinity index of the CNC. Structural and phase analyses of the samples were measured by using an X-ray diffractometer, Bruker Advance 8 with  $\text{CuK}\alpha$  radiation (wavelength of  $1.5406 \text{ \AA}$ ) generated at an operating voltage and current of 40 kV and 30 mA, respectively. The  $\text{CuK}\alpha$  radiation was filtered electronically with a Ni-filter. A

$2\theta$  angle range from  $5^\circ$  to  $60^\circ$  in reflection mode was scanned at  $2^\circ/\text{min}$ . The crystallinity index was calculated based on the following Equation 1:

$$\text{CrI (\%)} = (I_{200} - I_{\text{am}}) / I_{200} \times 100 \quad (1)$$

where  $I_{200}$  is the peak intensity corresponding to crystalline and  $I_{\text{am}}$  is the peak intensity of the amorphous fraction.<sup>15</sup>

## 2.6 FTIR Spectrometry

The presence of any changes in functional groups of the samples during the treatment was observed by FTIR spectroscopy. The pellets were prepared by mixing approximately 5 mg of particles samples with 95 mg of finely ground KBr before pressing it into a transparent pellet. Spectra were viewed using a Nicolet infrared spectrophotometer (Avatar 360 FT-IR E.S.P) machine. The spectra produced are transmittance mode between wave numbers of  $4000 \text{ cm}^{-1}$  and  $500 \text{ cm}^{-1}$ .

## 2.7 Thermal Gravimetric Analysis

Thermogravimetric analysis was performed to determine the thermal properties of the OPF fibres for raw and CNC samples. The thermal stability data were collected on a Perkin Elmer TGA 7 thermogravimetric analyser under linear temperature conditions. The temperature was swept from  $50^\circ\text{C}$  to  $800^\circ\text{C}$  for samples of 10–15 mg placed in an aluminium pan at a heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen atmosphere.

# 3. RESULTS AND DISCUSSION

## 3.1 Transmission Electron Microscopy (TEM)

The image from TEM in Figure 1 showed the structure of individual fibre. The dimensions of each fibre were measured and resulted in having the average width of 9.88 nm and 504.12 nm in length. The average aspect ratio of the fibre was 51.02. Based on the dimensions of width and length of the fibre, it is categorised as cellulose nanowhiskers.<sup>16</sup> Since the fibres underwent acid hydrolysis treatment which managed to remove major amounts of its amorphous structure, therefore it is categorised as cellulose nanocrystals.<sup>17</sup> It can be observed that the fibres were in the form of individual fibres and not in a bundle. This is due to the chemo-mechanical treatments subjected to the OPF during the isolation that successfully removed lignin and hemicellulose.

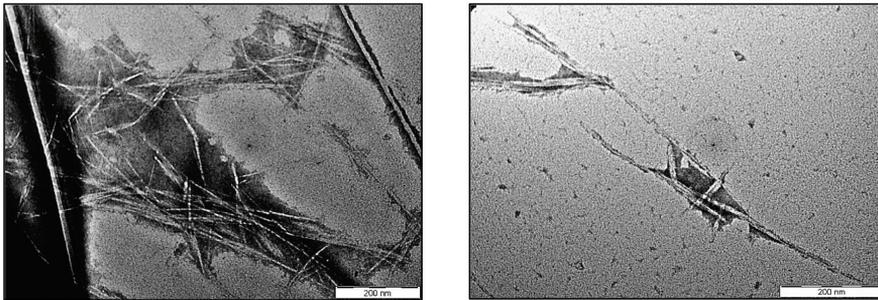


Figure 1: TEM image of CNC at 34000 magnification (left) and 50000 magnification (right).

### 3.2 X-Ray Diffraction

Naturally, celluloses are crystalline unit whereas lignin and hemicellulose are amorphous. The hemicellulose and lignin are categorised as non-celluloses polysaccharides and found surrounding the celluloses. In order to increase the crystallinity index of a sample, lignin and hemicellulose should be removed by chemical, mechanical or enzymatic treatment. Based on Figure 2, it can be observed that the peak of CNC is sharper than raw OPF. This indicates that the CNC possesses higher crystallinity index in comparison with raw OPF. Broader peaks correspond to more amorphous region as raw OPF has high amount of lignin and hemicellulose, meanwhile CNC has sharper peak due to elimination of hemicellulose and lignin after acid hydrolysis treatment.<sup>18</sup>

The diffractogram was presumed to represent typical cellulose I because it showed a single peak at  $2\theta = 22^\circ$  and a shoulder in the region  $2\theta = 19^\circ$ . The crystallinity index were 54.5% and 36% for CNC and raw OPF respectively. The acid hydrolysis treatment managed to improve the crystallinity index of the CNC by 34%. This finding complements a previous study on recovery of nanocellulose from OPF which obtained crystallinity index of 57.7%.<sup>19</sup> Crystallinity index obtained in this study was slightly lower than theirs and this could be attributed to the time of acid hydrolysis. A longer hydrolysis time may have partially degraded the crystalline structure of cellulose nanocrystals hence resulted in a lower crystallinity index in this study. Based on the XRD analysis, it shows that the removal of lignin and hemicellulose could lead to an increment in crystallinity of the samples.

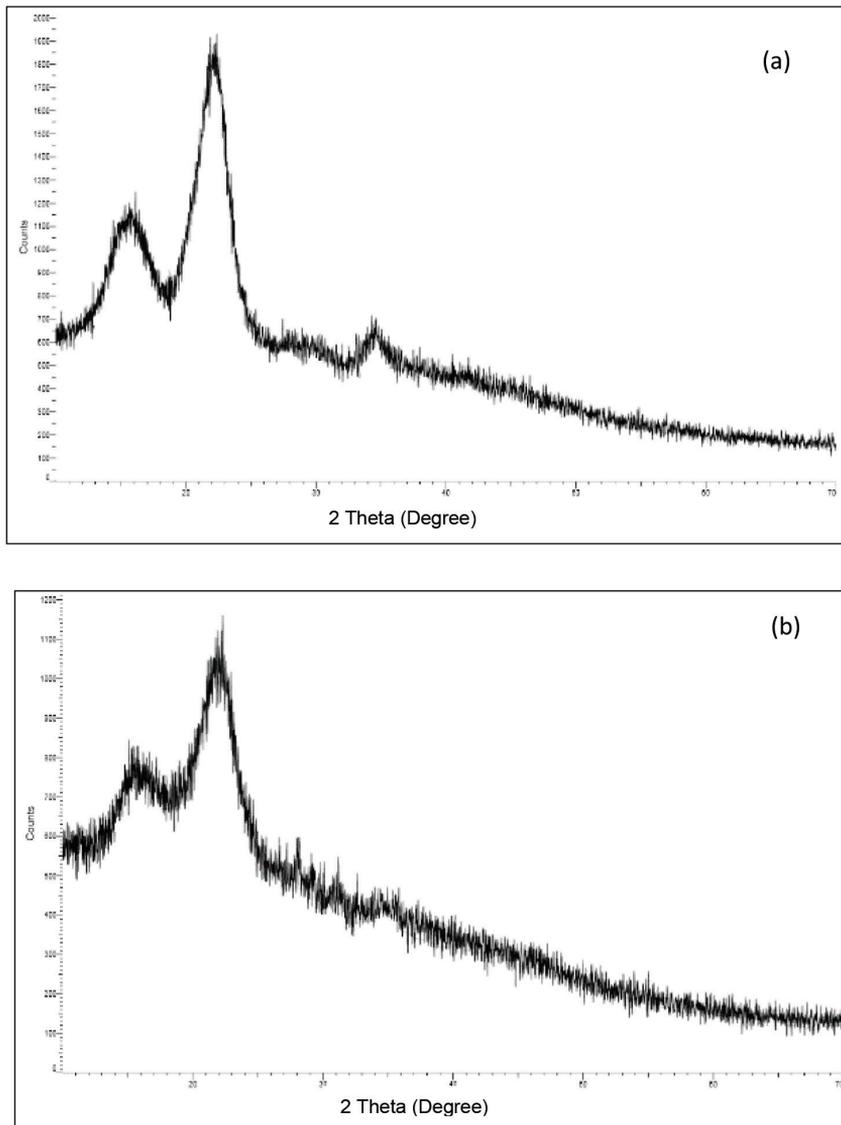


Figure 2: X-ray diffraction of (a) OPF CNC and (b) raw OPF.

### 3.3 FTIR Spectroscopy

The FTIR spectroscopy is a non-destructive method to study the physico-chemical properties of lignocellulosic materials.<sup>20</sup> The spectroscopy was taken between the wavelengths of  $4000\text{ cm}^{-1}$  and  $450\text{ cm}^{-1}$ . It can be observed in Figure 3 that the peaks look almost similar which indicated that both samples have the same chemical

composition. The peaks in the 3,344–3,415 and 1,635–1,645  $\text{cm}^{-1}$  regions were attributed to O–H stretching and bending vibrations, respectively, of hydrogen bonded hydroxyl (OH) groups of absorbed water, aliphatic primary and secondary alcohols found in cellulose, hemicellulose, and carboxylic acids in extractives.<sup>12,21</sup> The peaks at 1,701–1,737  $\text{cm}^{-1}$  in raw OPF corresponded to the C=O stretching of hemicellulose and lignin while in CNC, the peaks were shorter which indicated lesser amount of the chemical components available in the sample. It can also be observed that the peaks at 1,509–1,609  $\text{cm}^{-1}$  which corresponded to C=C aromatic skeletal vibration of lignin only appeared in raw OPF.

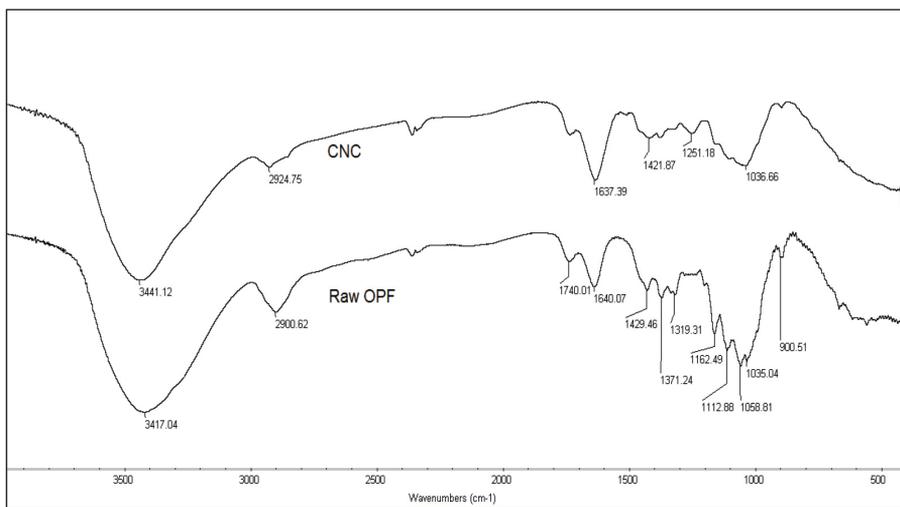


Figure 3: FTIR spectra of raw OPF and CNC.

The peaks at 1,058–1,060 and 896–900  $\text{cm}^{-1}$  were attributed to the C–O stretching and C–H rocking vibrations of cellulose.<sup>22</sup> The peaks indicated that the treatment managed to remove major part of hemicellulose and lignin.<sup>23</sup>

### 3.4 Thermal Gravimetric Analysis

The TGA determined thermal degradation of fibres and weight loss upon heating in order to identify their applicability when it is subjected to high temperature. The summary of thermal degradation data of CNC and raw OPF is tabulated in Table 1, analysed at the temperatures at which 10% weight loss of the samples occurred. The char residue was calculated as percentage from the total amount of sample.

Table 1: Thermal properties of CNC and raw OPF.

Samples	Degradation temp (°C) $T_{10\%}$	Residual weight (%)	DTG peak temp (°C) $T_{max}$
OPF CNC	258.34	14.05	345.37
Raw OPF	197.48	24.91	328.26

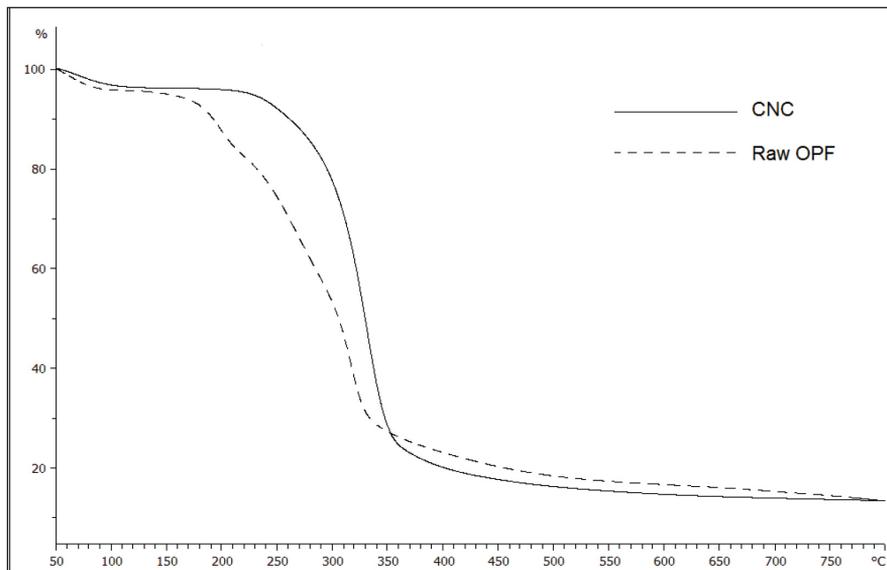


Figure 4: Thermal gravimetric curves of CNC and raw OPF.

Based on Figure 4, it was observed that there was an initial weight loss from 50°C to 150°C for both samples due to evaporation of water in cellulose fibre and nanocrystals while the temperature range between 150°C and 250°C showed depolymerisation of non-celluloses such as hemicellulose and lignin. Degradation of the  $\alpha$ -celluloses took place at temperature range between 300°C and 350°C.<sup>24</sup> It can be observed that the major decomposition peak temperature of CNC occurred at 274.91°C while for raw OPF, it occurred at 227.59°C. These temperatures indicated where cellulose degradation takes place. The degradation of cellulosic materials starts from low to moderate temperatures.<sup>25</sup> The degradation temperature of CNC was higher compared to raw OPF, ascribed to the removal of hemicellulose and lignin in the CNC thus improved its thermal property. According to Ouajai and Shanks, and Haafiz, a greater crystalline of cellulose nanowhiskers structure requires a higher degradation temperature.<sup>26,27</sup>

#### 4. CONCLUSION

This study showed that the properties of OPF CNC had improved compared to its original raw material. The images from TEM showed good dispersion of individual fibres resulted from the chemo-mechanical treatment. The XRD analysis showed increment of crystallinity index of CNC and was supported by the results from TGA. Improvement in thermal properties were attributed to the removal of hemicellulose and lignin in the OPF samples. The FTIR spectra confirmed the removal of non-cellulosic polysaccharides by some shifting and change in intensities of the peaks. Based on the results obtained, CNC is suitable to be used for various applications in biomedical field such as tissue engineering, medical implants, drug delivery, wound dressing and cardiac devices due to their excellent properties. This study has shown that despite being a biomass waste, OPF could be used as a starting material for the production of biocomposites for high performance applications. The substitution of natural fibres to petroleum based materials would reduce the dependency on imported oil thus contributing to cost effectiveness.

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