CHEMICAL ENGINEERING TRANSACTIONS
VOL. 45, 2015
A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet
Guest Editors: Petar Sabev Varbanov, Jiří Jaromír Klemeš, Sharifah Rafidah Wan Alwi, Jun Yow Yong, Xia Liu

ISBN 978-88-95608-36-5; **ISSN** 2283-9216 DOI:10.3303/CET1545285

Isolation of NanoCrystalline Cellulose (NCC) from Palm Oil Empty Fruit Bunch (EFB): Preliminary Result on FTIR and DLS Analysis

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Recent research interest has been focused on the successful synthesis of Nanocrystalline Cellulose (NCC). NCC which can be isolated from natural fibre possesses exclusive properties such as large surface area, high aspect ratio, biocompatibility and exceptional mechanical properties for various industry applications. In this study, NCC was isolated from palm oil biomass waste, i.e. empty fruit bunch (EFB) through various stages of chemical treatments. This multistep process embrace a bleaching and alkali treatment to efficiently remove impurities, waxy substances, hemicellulose and lignin from EFB fibre, and the remaining cellulose product was acid hydrolysed into nanocellulose material. Hence, as an evidence the products obtained from each stage were characterized by using Fourier Transform Infrared Spectroscopy (FTIR) to identify the presence of functional groups in cellulose. Additionally, Dynamic Light Scattering (DLS) technique showed NCC with an average particle size of 499.2 nm was obtained.

1. Introduction

Cellulose is the most abundant biomass found on earth. It is a linear syndiotactic homopolymer of β-(1→4)-glycosidic bonds linked D-anhydroglucopyranose (Lu and Hsieh, 2010). Cellulose materials have been widely used for years due to their renewability, biodegradability and sustainability (Habibi et al., 2010). For the recent development, cellulose was researched to produce bioethanol (Karapatsia et al., 2014) and manufacture of paper-based battery (Lorenzo et al., 2014). Cellulose is naturally produced in higher plants, marine animals, invertebrates and amoeba (Brinchi et al., 2013). Native plants in particular, cellulose resides in microfibrils along with hemicellulose and lignin, which play a significant role in contributing to the strength of plant cell walls (Lu and Hsieh, 2012). These microfibrils consist of highly ordered crystalline regions which are interrupted by amorphous regions before extraction (Moon et al., 2011).

Various isolation methods such as steam explosion (Cherian et al., 2010), enzymatic (Zhang et al., 2012) and acid hydrolysis (Wang et al., 2012) had been used to isolate crystalline particles (Durán et al., 2012). Among the aforementioned, acid hydrolysis is the most well-known and always being the primary approach (Jiang and Hsieh, 2013). This approach adopts acid to break down the disordered and amorphous parts of the cellulose, leaving the crystalline domains intact. The obtained nano size crystalline cellulose is always referred as NanoCrystalline Cellulose (NCC), or Cellulose NanoCrystals (CNC) (Coccia et al., 2014).

NCC having a rod-like shape structure and exhibits unique properties such as large surface area (150-250 m^2/g), low axial thermal expansion coefficient (10-7 K-1), low density (1.566 g/cm^3) and high aspect ratio (10 - 85) (Mondragon et al., 2014). Due to these intriguing properties, NCC has gained significant attention as additives for coatings and paints (Coccia et al., 2014) as well as a reinforcing nanofiller in nanocomposites (Lu and Hsieh, 2012). Over the years, studies have shown that NCC can be isolated from

Please cite this article as: Shanmugarajah B., Kiew P.L., Chew I.M.L., Choong T.S.Y., Tan K.W., 2015, Isolation of nanocrystalline cellulose (NCC) from palm oil empty fruit bunch (EFB): preliminary result on ftir and dls analysis, Chemical Engineering Transactions, 45, 1705-1710 DOI:10.3303/CET1545285

various of natural fibre sources, such as maize straw (Rehman et al., 2014), cotton linter (Morais et al., 2013), corncob (Silvério et al., 2013), garlic skin (Prasad Reddy and Rhim, 2014) and mengkuang leaves (Sheltami et al., 2012). A recent study reported a successful isolation of nanocellulose fibers from EFB (Lani et al., 2014), nevertheless, FTIR study was limited to raw EFB and extracted cellulose nanofibers. Moreover, the approach can be improved to obtain NCC. In this study, conversion of EFB into higher value NCC was attempted, FTIR was conducted on samples received throughout the multistep process, and a preliminary size estimation was determined using Dynamic Light Scattering (DLS) technique.

2. Materials and methods

2.1 Materials

The EFB was received as gift from University Malaya. Sodium chlorite, acetic acid glacial (CH_3COOH, 99.7 %), sodium hydroxide (NaOH, beads, Merck) and sulphuric acid (H_2SO_4, 95-98 %) were used as received without any purification. Purified water was prepared using ELGA MICROMEG water purifier.

2.2 Isolation of NanoCrystalline Cellulose (NCC)

The EFB was milled and then passed through a 63-mesh sieve. The filtered EFB powder was first washed with distilled water to remove soluble extractives and waxy substances covering the surface of fibre. Following that, the EFB powder was treated with a sodium hydroxide aqueous solution of 2 % (w/w) for 3 h at 70 °C under magnetic stirring. The sample was then washed with distilled water until the alkali residual on the surface was completely removed. The fibres were then bleached with acetate buffer and aqueous sodium chlorite. This bleaching treatment was performed at 80 °C for 2 h and subsequently washed with distilled water to obtain pH 7. These alkali pretreatments were to remove hemicellulose and lignin content. Hydrolysis was performed by using 64 % (w/w) H_2SO_4 at 40 °C under vigorous mechanical stirring for 45 min. The reaction was stopped by diluting with 10-fold of purified water. The excess sulfuric acid was removed from the suspension by centrifugation at 7,000 rpm for 10 min. The suspension was then dialyzed against water until a constant pH was reached. Figure 1 shows the scheme of cellulose isolation from EFB.

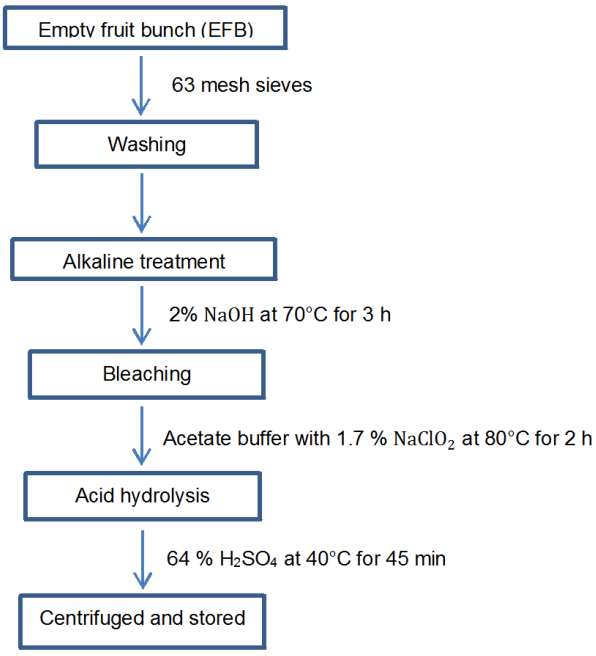

Figure 1: Scheme of NCC isolation from empty fruit bunch (EFB)

2.3 Particle size measurement

Measurements were made to determine mean z-average (z-Avg) and polydispersity (PdI) using Stoke-Einstein relationship by employing Malvern Zetasizer Nano-ZS. Three measurements were conducted for all samples.

2.4 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of the samples were determined at various stages of chemical treatment. Infrared spectra were obtained in the range between 4,000 and 500 cm^{-1} using an infrared spectrophotometer (Shimadzu Scientific Instruments' IR-Prestige-21, Thermo Fisher Scientific, Malaysia).

3. Results and discussion

3.1 FTIR analysis

The main components of EFB are lignin, hemicellulose and cellulose. These substances are usually composed of alkane, esters, aromatics, ketones and alcohols with different oxygen containing functional groups (Abraham et al., 2011). The absorption bands detected from samples at different stages, i.e. raw EFB upon washing, alkali treated fibre, bleached fibre and NCC are shown in Figure 2, while specific infrared absorption peaks (cm^{-1}) of each were presented in Table 1.

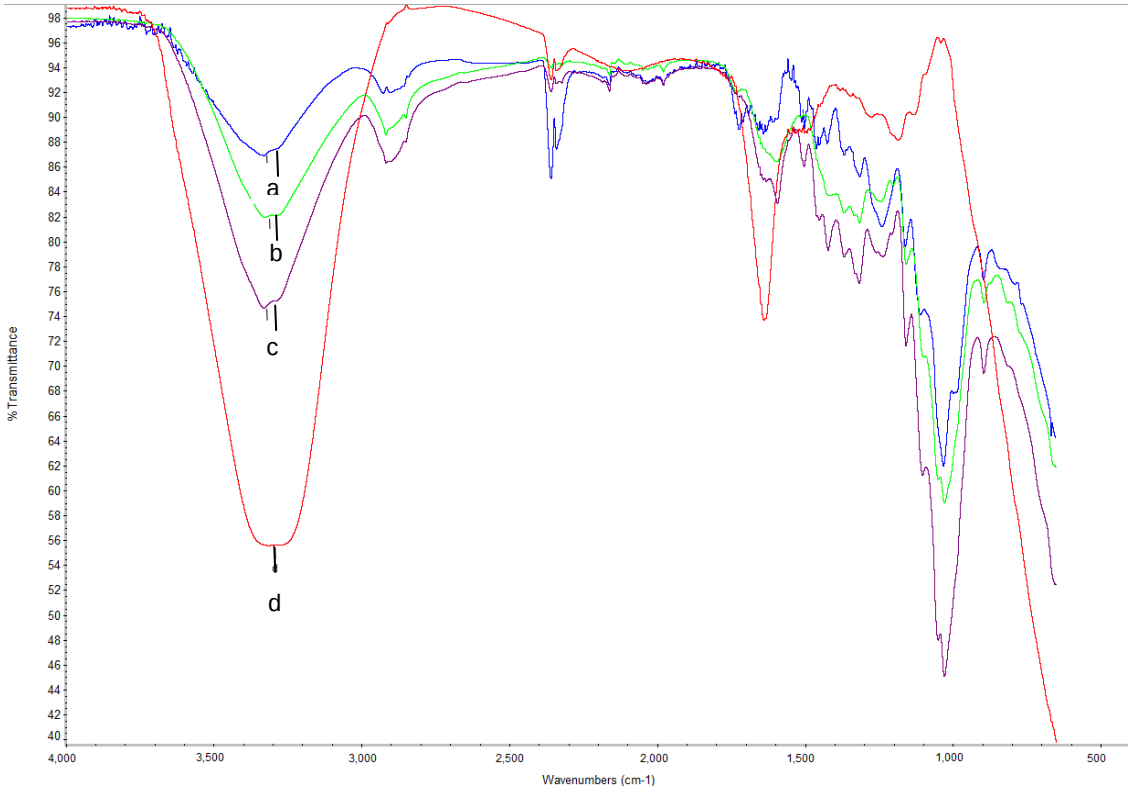

Figure 2: FTIR spectra of EFB from various stages of isolation: (a) raw EFB upon washing, (b) alkali treated fibre, (c) bleached fibre and (d) NCC

It was observed from Figure 2, the characteristics peaks in the range of 1,200 - 1,300 cm^{-1} are related to aromatic skeletal vibrations, indicating the presence of lignin in raw EFB and alkali treated EFB that can be confirmed by the absorption at peak 1,240 cm^{-1} and 1,235 cm^{-1}, suggesting C-O-C stretching of aromatic ether linkages. The absorption peaks around 3,300 cm^{-1} and 2,900 cm^{-1} are probably due to the hydroxyl group and aliphatic saturated C-H stretching of lignin and cellulose, which is generally aligned with a recent study conducted by Alves et al. (2014) for cellulose derivatives. Likewise, the absorbance at 1,422 cm^{-1} and 1,426 cm^{-1} is associated to C-H bending present in cellulose. Meanwhile, the C-O stretching of hemicellulose or aryl-alkyl ether in lignin is represented by the peak 1,029 cm^{-1}.The β-glucosidic linkages between sugar units are reflected by the peak at 896 cm^{-1}. Interestingly, that is water content detected at peak 1,641 cm^{-1} which corresponds to the absorption of water by cellulose molecules (Mondragon et al., 2014). Even though fibres were dried after each stage of treatments, the water adsorbed by cellulose molecules can hardly be removed due to the strong molecules interaction among them. The cellulose-water interaction can be again confirmed by a previous study (Lani et al., 2014) from the appearance of peak presented at 1,641 cm^{-1} after the acid hydrolysis.

As from the FTIR analysis, it can be concluded that almost all the hemicellulose and lignin content were removed after acid hydrolysis. This was proven by the absence of peak 1,724 cm^{-1} and absorption bands between 1,500 and 1,550 cm^{-1} which relates to hemicellulose and lignin content. The NCC obtained from this study contains very small amounts of lignin, hemicellulose and other impurities.

Table 1: Infrared absorption peaks (cm^{-1}) of EFB at different stages

Wavenumber (cm^{-1})				
Raw EFB	Alkali treated fibre	Bleached fibre	NCC	Peak Assignment
3,332.02	3,330.99	3,328.42	3,316.09	O-H stretching
2,927.48	2,917.18	2,917.94	-	C-H stretching
1,724.42	-	-	-	C=O of ketone and carboxyl
1,641.75	-	-	1,639.75	O-H bending of absorbed water
1,426.15	1,422.56	-	-	C-H bending
1,240.85	1,235.98	-	-	C=C stretching vibration of aromatic ring
1,032.44	1,029.67	1,029.43	-	C-O stretching
896.75	896.21	896.02	-	B-glucosidic linkages between the sugar units

3.2 Particle size analysis

DLS is an effective tool to approximate particle size distribution of nano sized materials. Figure 3 shows the particle size distribution of NCC upon acid hydrolysis and indicating an average particle size of 499.2 nm. The measurement was conducted three time therefore three peaks were observed, i.e. measurement 1, 2 and 3, respectively. It was observed that two peak were recorded for measurement 3, where the major peak was recorded with average particle size of 547.8 (95.8 % intensity) and a minor peak with average particle size of 4,793 nm (4.2 % intensity). This occurrence of the two peaks might due to the orientation of rod-shape NCC across the scattering light during measurement, or simply because of dirt. Particle size distribution of nanoparticles was obtained using DLS technique by monitoring particles diffusion moving under Brownian motion. It is governed by Stokes-Einstein relationship Eq(1).

$$D = \frac{k_B T}{6\pi\eta\alpha} \quad (1)$$

Where D is the diffusion coefficient, α is the radius of the beads, k_B is the Boltzmann constant, T is the temperature in Kelvin and η is the viscosity. According to Stoke-Einstein theory, large particles diffuse slower compared to small particle. For instance, when NCC diffuses across the aqueous medium in horizontal orientation against the light source, it stands a chance to be interpreted as smaller particle due to the relatively fast moving rate. Similarly, if NCC diffuses across the aqueous medium in the vertical orientation against the light source, the size defined by DLS will be larger (Sharma and Yashonath, 2007). Based on the previous studies, NCC isolated from maize straw show average length of 388 ± 43 nm (Rehman et al., 2014), hemp and flax with 580 nm and 400 nm respectively (Mondragon et al., 2014), hence, the current obtained readings fit within the defined range.

4. Conclusions

NCC was successfully isolated from EFB through acid hydrolysis evidenced by the characterization results. FTIR spectra of the treated EFB confirmed the removal of non-cellulosic components after each chemical treatment. Moreover, dimensions of NCC estimated using light scattering techniques was also satisfying. As for the future work, optimization of the hydrolysis conditions will be studied in detail to maximize the yield of NCC.

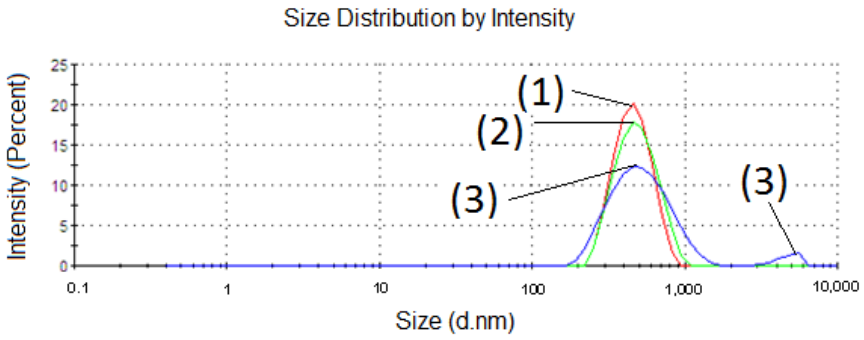

Figure 3: The intensity of particle size distribution

Acknowledgement

The authors are thankful to Ministry of Higher Education (MOHE) for the financial support through ERGS (ERGS/1/2013/TK07/UCSI/03/1) and Centre of Excellence for Research, Value Innovation & Entrepreneurship (CERVIE) for RGS (PROJ-IN-FETBE-015).

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