Production of nanocrystalline cellulose from an empty fruit bunches using sulfuric acid hydrolysis: Effect of reaction time on the molecular characteristics.

Ahmed A Al-Dulaimi[1], Rohaizu R[1] and Wanrosli W D[1]

[1]Bioresources, Paper and Coating Division, School of Industrial Technology, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

Corresponding author: ahmedulaimi@gmail.com

Abstract. Nanocrystalline cellulose (NCC) was isolated from OPEFB pulp via sulfuric acid hydrolysis. The influence of reaction time to the molecular weight and surface charge of the NCC was investigated. Characterization of the product was carried out using zeta potential measurement and gel permeation chromatography test. Zeta potential measurement showed that the surface negative charge significantly increases with increasing reaction time. Gel permeation chromatography test indicates that molecular weight of NCC change variably with increasing of hydrolysis time. (Keywords: Nanocrystalline cellulose; acid hydrolysis; sulfate content; molecular weight)

1. Introduction

Nanocrystalline cellulose (NCC) is derived from the crystalline region of cellulose, which is having been isolated by strong acid hydrolysis. Nanocrystalline cellulose has attracted considerable academic interest due to its lack of toxicity, relative abundance, the negative surface charge and high surface area with zero-dimensional nanostructure, and it is applicable potency such as drug delivery [1], improve conductive polymer processability [2] and preparation of optically transparent film [3].

Acid hydrolysis is a diverse method which contains the dispersion of acid into the cellulose amorphous regions, then followed by cleavage of glycosidic bonds [4]. The reaction breaks the long chains into short fractions while the backbone structure leftovers [5]. The isolation of the NCC was first reported by [6], who used sulfuric acid to hydrolyze a lignocellulosic material to obtain a stable suspension of rod-like NCC structures. This method involves the diffusion of acid into the amorphous region of the lignocellulosic material and the subsequent cleavage of the glycosidic bonds [4] by the rapid protonation of glycosidic oxygen or cyclic oxygen, followed by the addition of water to break down the glycosidic bonds [5].

The strong acid hydrolysis, e.g. sulfuric acid and hydrochloric acid, is the common procedure applied for the isolation of nanocrystalline cellulose from pure cellulose at a controlled reaction time and temperature. For the NCC isolated by sulfuric acid hydrolysis, the suspension is generally shown higher acidic compared to the hydrochloric acid hydrolysis because of the sulfate groups attached to the NCC surface [7].

In this hydrolysis reaction, sulfuric acid reacts with the hydroxyl groups on the cellulose by esterification process when sulfuric acid was applied. This esterification process creates acid half-ester or so-called cellulose sulfate, as illustrated in Figure 1. The sulfate group that cloud surrounded the NCC particles induces negative charge and servicing the suspension stability in the aqueous

medium by electrostatic interaction. The repulsive forces of the double layer electric effectively avoid the NCC agglomeration [8].

Production of cellulose from agricultural by-products is becoming an important agenda due to the availability of these materials in huge quantity that can be supplied at reasonable costs. In this regards, oil palm biomass residue has attracted attention for its potential to be utilized as an alternative for wood replacement in producing cellulose [9,10,11]. Previous work, we successfully isolate nanocrystalline cellulose from totally chlorine free (TCF) pulp for oil palm empty fruit bunches (OPEFB) fibers by sulfuric acid hydrolysis [9]. In this work, the varieties of molecular properties accompanied by increasing acid hydrolysis reaction time in terms of the sulfate content and molecular weight for NCC were investigated using zeta potential and gel permeation chromatography, respectively.

2. Material and methods

The OPEFB that used in this report were obtained from a local palm oil mill in Perak, Malaysia. OPEFB pulp was prepared using an environmentally friendly process as described in our previous works [12,13]. This method involves water pre-hydrolysis, soda pulping and then a totally chlorine-free (TCF) bleaching sequence. Nanocrystalline cellulose was prepared from the OPEFB pulp by treating the pulp with 58wt% sulfuric acid concentrations of sulfuric at a four period of time (40, 60, 80 and 100 min), at a fixed temperature of 45°C and at an acid/cellulose ratio of 1:12. Then, followed by centrifuging, washing with water, and re-centrifuging; with the process being repeated until the supernatant became turbid [14]. Then, the samples were sonicated using a rod-type ultrasonic sonifier (Branson Sonifier 450) for 5 min with an 800W constant power output. Dialysis against deionised water is an important step to remove the remaining acid molecules. Solid OPEFB-NCC was obtained by freeze-drying the sample.

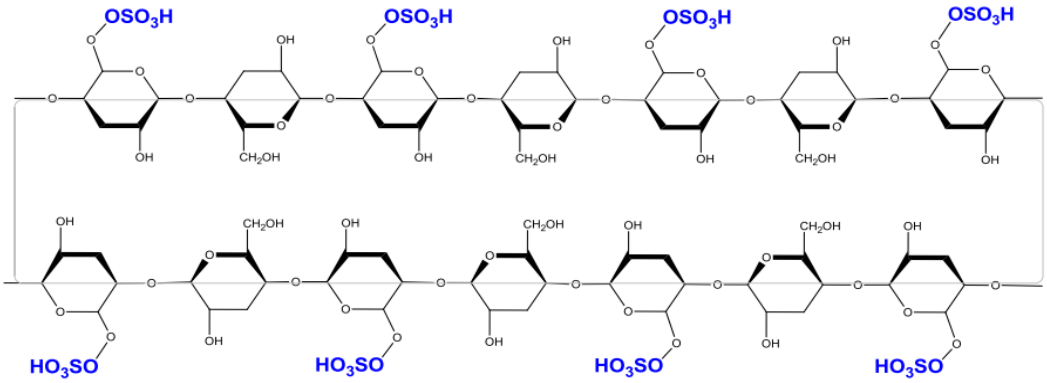

Figure 1. Structure of nanocrystalline cellulose (nanorod particles) isolated by sulphuric acid hydrolysis

2.1 Characterization methods

After having undergone sonication for 5 min, the OPEFB-NCC suspension (0.05wt%) was analyzed for its Zeta potential using a Zetasizer Nano Z model ZEN 2600.

Gel Permeation Chromatography (GPC) measurements were carried out with waters GPC 510 pump equipped with UV and RI detectors using THF as the eluent at a flow rate of 0.7 mL/min at room temperature. Two Ultrastyragel linear columns linked in series (Styragel HR 1 and Styragel HR 5E) were used for the measurements. Standard polystyrenes of narrow disparity with molecular weight ranges from 0.82 to 1860 kg/mol were used for calibration. The number- and weight-average molecular weights were calculated using the Millenium software of Waters.

3. Results and discussion

NCC prepared by hydrochloric acid hydrolysis tends to aggregate; however, NCC prepared by sulfuric acid hydrolysis has higher dispersion stability because of the electrostatic repulsive forces among the crystalline particle effect of the present of sulfate groups on the cellulose surface [16].

Moreover, the influence of sulfuric acid hydrolysis reduces the possibility of the agglomeration of starch nanocrystals and limits their flocculation in aqueous medium has also been observed [17].
In the sulfuric acid hydrolysis, sulfate groups were induced to the surface of the cellulose material effect of the hydrolysis process. The introductions of the sulfate group occur at among of the three hydroxyl groups of cellulose surface, which then the cellulose will possess certain polyelectrolyte properties [5,18,19].

Table 1. Hydrolysis condition and NCC molecular properties

Sample	NCC.40	NCC.60	NCC.80	NCC.100
Hydrolysis condition				
Hydrolysis time (min)	40	60	80	100
H_2SO_4 concentration (wt. %)	58	58	58	58
Cellulose/acid ratio (g/mL)	1:12	1:12	1:12	1:12
Reaction Temperature (°C)	45	45	45	45
NCC molecular properties				
Zeta potential (mV)	-36.2	-38.8	-46.2	-69.8
Molecular weight (M_w)	16049	15198	15288	15403
Molecular weight distribution (M_n)	15997	15155	15238	15348

The examination of the stability of the NCC dispersion in an aqueous medium by zeta potential measurement (Figure 2) is an important parameter to study the polyelectrolyte properties for a sequence of samples prepared under different hydrolysis times. All of four of NCC suspensions showed a negative zeta potential in neutral water (Table 1). Figure 3 illustrates the interaction between the hydrolysis times versus zeta potential measurement. The hydrolysis time of 40 min showed the lowest negative value of -36.2 mV and this value was found to be increased relative with increasing of the hydrolysis time, with 100 min of the NCC isolation was the highest value (-69.8 mV).

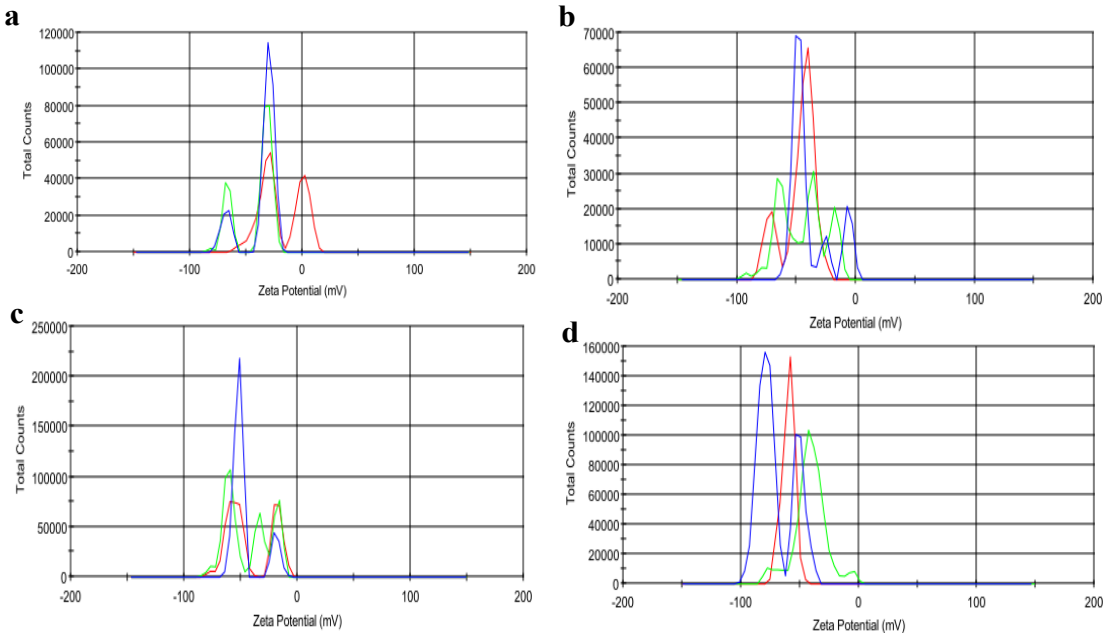

Figure 2. Zeta potential measurement of NCC for (a) 40 min, (b) 60 min, (c) 80 min, and (d) 100 min of sulphuric acid hydrolysis.

The presence of a larger amount of negatively charged of sulfate groups on the surface of the nanocrystalline cellulose effect of reaction time was ascribed in these findings [15]. Thus, the result shows that it is possible to increase the polyelectrolyte properties (surface charges) of nanoparticles by increase the reaction time of the sulphuric acid hydrolysis, which would lead to added electrostatic stabilization of the NCC suspensions against flocculation.

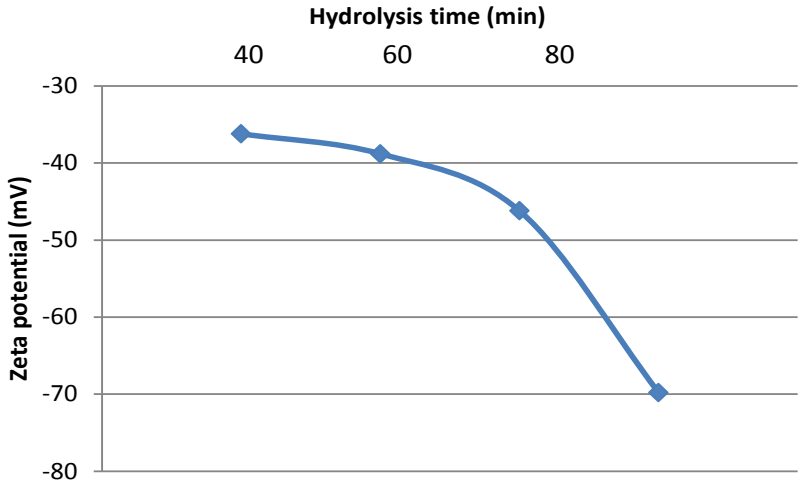

Figure 3. Effect of hydrolysis time to zeta potential of NCC.

The average number of molecular weights (M_w), molecular weight distribution (M_n) and the values of M_w/M_n were determined by gel permeation chromatography (GPC) (Figure 4). The data listed in Table 1 illustrated irregular estimation about NCC molecular weight that accompanied the increasing of hydrolysis time.

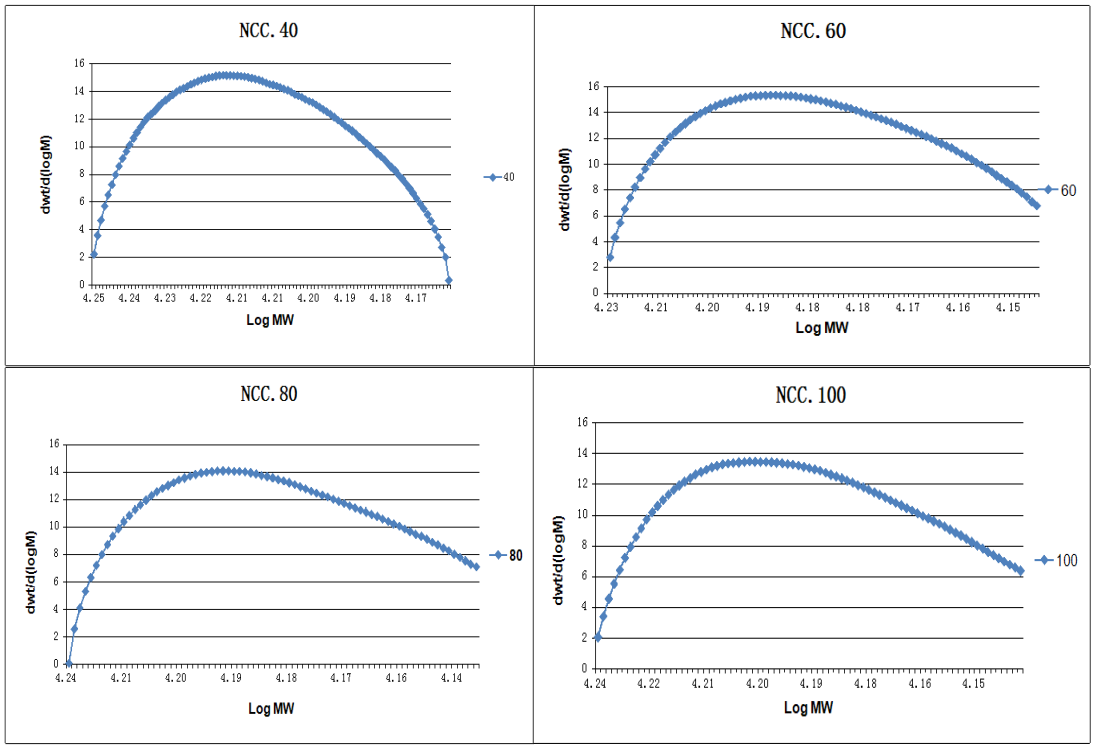

Figure 4. Gel permeation chromatography of NCC for (a) 40 min, (b) 60 min, (c) 80 min, and (d) 100 min of sulphuric acid hydrolysis.

Figure 5 shows that the molecular weight of NCC initially decreases when the reaction time go forward, however, after 60 min of reaction time, the NCC's molecular weight start to increase, which is in contrast to the hydrolysis concept of a cellulose fractioned by strong acid hydrolysis.

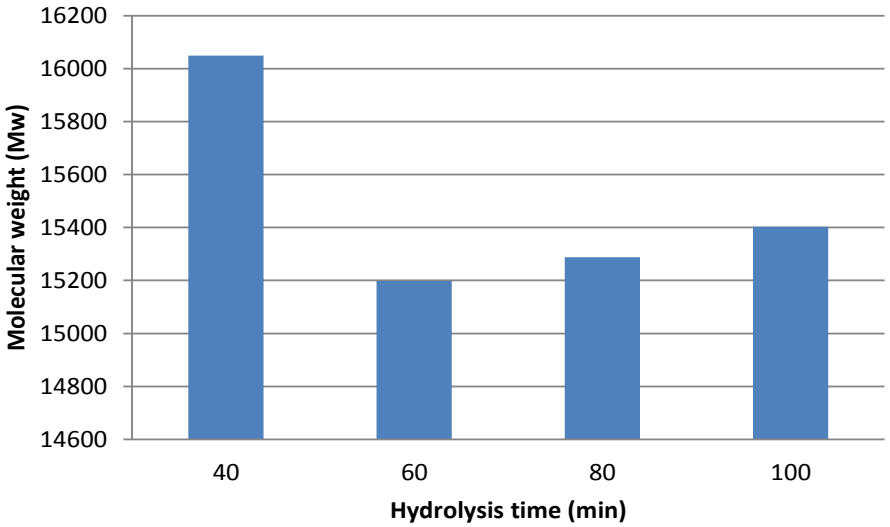

Figure 5. Effect of hydrolysis time to molecular weight of NCC.

These results elucidate that cellulose has to convert into sugars solubilization if further increased in the degradation process occurs, which could be observed by decreasing of the total yield of NCC. Moreover, TEM images support this observation, by did not show any significant changes in the morphological structure of the NCC, in terms of length and diameter distribution, after 60 min of reaction time [9].

However, an observation of increasing of the molecular weight after 60 min of reaction time most probably due to enhancement of the sulfate group on the surface of the NCC particle, which is supported by the zeta potential measurement in the Figure 3.

4. Conclusion

Nanocrystalline cellulose (NCC) was successfully isolated from OPEFB pulp, which is an abundant biomass residue in Malaysia by sulfuric acid hydrolysis. The characterizations of NCC by the zeta potential show that by increase the reaction time of acid hydrolysis, amount of surface charge that induces to the NCC surface was increased. The results of gel permeation chromatography indicate that in the process of cellulose hydrolysis lower molecular weight of the NCC was obtained, however, if further increased in the degradation process occurs, cellulose have to convert into sugars solubilization after reach of a certain amount of molecular weight.

Acknowledgement

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