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Maximizing the yield of nanocrystalline cellulose from cotton pulp fiber

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ABSTRACT

Nanocrystalline cellulose (NCC) has attracted a significant interest in recent years as it is made from renewable resources and has many unique characteristics. In this paper, we prepared NCC from cotton pulp fiber by the method of sulfuric acid hydrolysis, with the objective of achieving a maximum yield. The yield and the particle size of NCC were measured as a function of sulfuric acid concentration, reaction temperature and hydrolysis time, and optimized by an orthogonal test. A high NCC yield of more than 60% was found when the sulfuric acid concentration is 64%, reaction temperature is 50 °C and the hydrolysis time is 5 h. The morphology and the size of NCC were characterized by scanning electron microscope (SEM) and particle size analyzer. The finding from this study should provide guidance in maximizing the yield of NCC from cotton pulps using acid hydrolysis.

1. Introduction

Cellulose is one of the most abundant biopolymers on earth, occurring in wood, cotton, hemp and other plant-based materials and serving as the dominant reinforcing phase in plant structures (Siró & Plackett, 2010). Cellulose contains both amorphous and crystalline structures. Nanocrystalline cellulose (NCC), also called cellulose nanocrystals, is typically a rigid rod-shaped monocrystalline cellulose domain (whisker) with 1–100 nm in diameter and tens to hundreds of nanometers in length (Ruiz, Cavaillé, Dufresne, Gérard, & Graillat, 2000). NCC has a high degree of crystal structure (more than 70%), a very big length-diameter ratio (around 70), and a large surface area (ca. 150 m^2/g). NCC can be used for many applications such as regenerative medicine (Fleming, Gray, & Matthews, 2001), optical application (Revol, Godbout, & Gray, 1998), automotive application (Dahlke, Larbig, Scherzer, & Poltrock, 1998), composite materials (Avella et al., 1993; Jiang & Hinrichsen, 1999) and so on.

Using acid hydrolysis, native NCC suspensions have been prepared from a variety of sources, including bacterial cellulose (Roman & Winter, 2004), bagasse (Hassan, Mathew, Hassan, El-Wakil, & Oksman, 2010), rice straw (Hassan et al., 2010), sugar beet primary cell wall cellulose (Dinand, Chanzy, & Vignon, 1999), cotton (Dong, Revol, & Gray, 1998), tunicate cellulose (Favier, Chanzy, & Cavaille, 1995), softwood pulp (Revol, Bradford, Giasson, Marchessault, & Gray, 1992).

Microcrystalline cellulose (MCC) from lignocellulosic materials such as wood is abundant, inexpensive and readily available. Therefore, NCC is commonly produced from the hydrolysis of MCC with a strong acid such as sulfuric acid (Bondeson, Mathew, & Oksman, 2006). However, the typical yield of NCC produced in such a way is about 25–30% although the crystallinity of cellulose is more than 70%.

In this paper, NCC was prepared from cotton pulp fiber by the method of sulfuric acid hydrolysis. Compared with the cotton linter, cotton pulp fiber had been prepared by the processes of alkaline cooking, bleaching and beating. After the above processing, most of impurities were removed, cotton pulp fiber was purified. Meanwhile cotton pulp fiber was more abundant and more cost-effective than MCC, so it could reduce the manufacturing cost for commercial production. Therefore, we chose cotton pulp fiber as a raw material in this study. In our research, we regarded the NCC whose particles size less than 500 nm as the target product, and we studied the effects of different conditions (different sulfuric acid concentrations, reaction times and temperatures) on the yield of NCC whose particles size is less than 500 nm. We also analyzed the morphology and the size of NCC.

2. Experimental

2.1. Materials

Cotton pulp in dry lap form was purchased from Weifang Henglian Pulp & Papermaking Co., Ltd (Weifang, SD, China). Sulfuric acid (95–98 wt%, analytically pure) was purchased from Yantai Sanhe Chemical Reagent Co., Ltd (Yantai, SD, China). The

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deionized water was utilized throughout the experiments. Dialysis bag (MWCO: Nominal: 8000–14,000) was purchased from Beijing Solarbio Science & Technology Co., Ltd (Beijing, China).

2.2. Characterization instruments

Cold field emission scanning electron microscope JSM-6700F (Japanese electronics company) and Malvern Zetasizer Nano ZS90 (Malvern Instruments Ltd, UK) were used to characterize NCC.

2.3. Preparation of NCC suspension

Cotton pulp in dry lap form was torn into small pieces and soaked in water for several hours, then put into a Hollander beater (type: ZT4-00). Beating was carried out until the degree of beating was about 50°SR. Most of the water was removed with a gauze filter and the pulp sample was centrifuged in a washing machine. The moisture content was about 70%. The cotton pulp after dried was placed in refrigerator for future use.

Three grams of cotton fiber (bone dry) was put into a 100 ml three-neck flask which was fixed on an iron support and in a water bath. A certain concentration of sulfuric acid (64 wt%, 90 g) was then added into the flask and mixed by stirring. After 5 h, the hydrolysis was quenched by adding a large amount of deionized water (about 500 ml) to the reaction mixture. The resulting mixture was sonicated for 30 min, then cooled to room temperature and centrifuged (2383 × *g* or 3000 rpm) for 20 min at room temperature. The supernatant was decanted. Deionized water (about 500 ml) was added to the precipitated material and the mixture was then centrifuged (2383 × *g* or 3000 rpm) for 20 min at room temperature. This centrifugation process was repeated four times. The freshly generated suspension was filtered with a dialysis bag (8000–14,000 molecular weight cut off) until the pH of the suspension reached a constant value. The resultant NCC suspension was stored in a refrigerator at 3.0 °C. There is a certain diffusion pressure (DP) between inside and outside of the dialysis bag because of the presence of sulfuric acid. The pH of the suspension would close to 7 with the continuous replacement of deionized water. However, NCC would stay in the bag because of its relatively large molecular weight. The resultant NCC suspension had a bluish tinge.

2.4. Calculation of the yield of target NCC

The suspension was weighed after dialysis. Then the NCC suspension was placed into a weighing bottle, after that placed in a drying oven (set oven temperature to 105 °C) until constant weight. Finally, the sample was weighed after cooling to room temperature with analytical balance. Yield was calculated as follows:

$$\text{yield}\,(\%) = \frac{m\eta}{M} \times 100\%$$

where M is the mass of bone dry cotton fiber (3 g); m is the mass of the total NCC obtained from hydrolyzed 3 g cotton fiber; η is the percentage of NCC whose particles size is less than 500 nm (obtained by the analysis with nano-particle size analyzer).

3. Results and discussion

First, we studied the effects of beating degree, the reaction temperature, the reaction time, and the sulfuric acid concentration on the yield of NCC. Then, the optimal conditions were obtained through orthogonal test. The morphology and the size of NCC were characterized by the particle size analyzer and SEM.

Table 1
The effect of reaction temperature on η and the yield of NCC.

T (°C)	The mass of NCC in suspension (g)	η (%)	Yield (%)
35	1.40	80.2	37.4 ± 1.0
40	1.47	82.5	40.4 ± 0.9
45	1.66	90.4	50.0 ± 1.1
50	2.17	85.8	62.1 ± 1.2
55	1.61	93.4	50.1 ± 1.2

3.1. The effect of beating degree on the yield of NCC

The level of beating degree could influence hydrolysis of the fiber. On the conditions of sulfuric acid concentration of 64%, reaction temperature of 50 °C, and reaction time of 5 h, the yield of NCC was only 34.5% while the beating degree was 25°SR. The yield of NCC could achieve 62.1% when the beating degree was 50°SR. We inferred that with the increasing of the beating degree, more fibers were cut off, so the surface area of fibers which contact with the sulfuric acid solution would expand. But when the beating degree rose to 60°SR, the yield of NCC decreased to 42.6%. Two reasons might be account for that. First, it was very hard to collect fibers from the beater for that the fibers were too small, which would lead to large quantity lose of fibers during the collection process. Second, excessive beating degree could damage the crystalline region of fiber.

3.2. The effect of reaction temperature on the yield of NCC

We studied the effect of reaction temperature on the yield of NCC when sulfuric acid concentration was 64%, reaction time was 5 h, the results were shown in Table 1. As shown in the table, at lower temperature (below 50 °C), the yield increased with the temperature rising and it reaches the highest value of 62.1% when the reaction temperature is 50 °C. After the peak in 50 °C, the yield begins to fall. The mass of NCC in suspension also increases first and then decreases. Based on this table, the percentages of NCC whose particles size less than 500 nm are more than 80% under different reaction temperatures. Glycosidic bond was broken during the reaction process, so the length and diameter of cotton fiber became shorter and shorter. However, at a higher temperature (>50 °C), cellulose molecule would be further broken down into glucose, which led to decline of the yield. Meanwhile, we could see that the color of the suspension darkened when the temperature rose to 55 °C. This phenomenon might be due to the existence of some coloring matter which generated from glucose by the influence of sulfuric acid and reaction temperature during the reaction process.

3.3. The effect of reaction time on the yield of NCC

Reaction time is one of the most important parameters to consider in the sulfuric acid hydrolysis of cotton pulp. We discussed the effect of reaction time on the yield of NCC when sulfuric acid concentration was 64%, reaction temperature was 50 °C, the results were shown in Table 2. Based on the table, we could see the yield of NCC increases when the reaction time increases from 3 to 5 h, and

Table 2
The effect of reaction time on η and the yield of NCC.

Reaction time (h)	The mass of NCC in suspension (g)	η (%)	Yield (%)
3	1.44	93.8	45.0 ± 1.2
4	1.59	94.3	50.0 ± 1.2
5	2.14	89.5	63.8 ± 1.4
6	2.06	85.6	58.8 ± 1.0
7	1.93	85.2	54.8 ± 1.0
8	1.82	87.8	53.3 ± 0.6
9	1.78	86.6	51.4 ± 0.9

Table 3
The effect of sulfuric acid concentration on η and the yield of NCC.

Sulfuric acid concentration (%)	The mass of NCC in suspension (g)	η (%)	Yield (%)
50	0.97	43.6	14.1 ± 1.3
55	1.76	53.2	31.2 ± 1.3
60	2.31	77.4	57.0 ± 0.7
64	2.20	86.7	63.6 ± 1.0
68	1.11	99.5	36.8 ± 0.8

the highest value of 63.8% is reached at the time of 5 h, however, the yield declines when the time is more than 5 h. It can be seen from this table, from 7 to 9 h, the yield continues to decline, but in a more moderate rate. This may be because the concentration of sulfuric acid was gradually reduced as the reaction proceeds, and the reaction between the fiber and the sulfuric acid then slowed down, when the reaction time was too short (below 4 h), some particles would be clearly found in suspension. We could intuitionally judge that the cotton pulp fiber still continued to be broken down into smaller particles. When the reaction was stopped by adding a large amount of water, this suspension was unstable and showed milky white. When the hydrolysis time extended to 5 h, we could not find any particles with the naked eye from the very stable suspension. Based on this, we could visually see the impact of reaction time to the fiber degradation. With the reaction time increased, sulfuric acid solution would slowly diffuse into fibers, which was a process, so the reaction time couldn't be too short. The mass of NCC in suspension also reached the maximum when the reaction time was 5 h, similar to the yield.

3.4. The effect of sulfuric acid concentration on the yield of NCC

The effect of sulfuric acid concentration on the yield of NCC was investigated when reaction temperature was 50 °C and reaction time was 5 h, the results were shown in Table 3. Table 3 shows that, the yield of NCC increases when the sulfuric acid concentration increases from 50% to 64%, and the maximum yield is 63.6%. The yield declines significantly with the increase in sulfuric acid concentration when the sulfuric acid concentration is more than 64%. During the hydrolysis process, sulfuric acid concentration played a key role and should be optimized. Too high (above 64%) sulfuric acid concentration would degrade the cellulose completely to yield sugar molecules; too low (below 60%) sulfuric acid concentration would yield only large poorly dispersed fibers and aggregates. There existed a fairly narrow range of sulfuric acid concentration (about 60–64 wt%, different materials had different ranges) which would yield the desired suspension of well-dispersed colloidal nanocrystals. When the sulfuric acid concentration was 50%, the mass of NCC in suspension was only 0.97. We could infer that the lower concentration played a negative role in the hydrolysis reaction, so the yield would decrease.

3.5. Orthogonal test

Based on the above experiments, we used the method of orthogonal test in order to optimize the preparation process of NCC. Orthogonal test is a high efficiency, fast and economical method of experimental design, it is used to study the multi-factor, multi-level experiment, and the optimum conditions are obtained by the method of orthogonal test, which selects the representative sample from a comprehensive test based on the orthogonality. Orthogonal test and the results are shown in Table 4. K1, K2, K3 are the mean values of the NCC yields in different factors and different levels, *R* is the difference value between maximum and minimum values of K1, K2, K3. S is the standard deviation. Based on these test results, the optimum reaction conditions were sulfuric acid concentration of 64%, hydrolysis time of 5 h and reaction temperature of 50 °C. The impact level of these three factors was in the following order: sulfuric acid concentration > reaction time > reaction temperature.

Table 4
The results from orthogonal test.

No.	Temperature (°C)	Time (h)	Acid concentration (%)	Yield (%)
1	45	4	55	30.2 ± 1.3
2	45	5	60	58.8 ± 1.0
3	45	6	64	63.7 ± 0.9
4	50	4	60	59.4 ± 1.0
5	50	5	64	64.1 ± 0.9
6	50	6	55	45.4 ± 1.7
7	55	4	64	46.0 ± 0.9
8	55	5	55	47.4 ± 1.5
9	55	6	60	43.3 ± 1.0
K1	50.9	45.2	41.0	
K2	56.3	56.8	53.8	
K3	45.6	50.8	57.9	
R	10.7	11.6	16.9	
S	5.4	5.8	8.8	

3.6. The appearance of NCC suspension

The appearance of NCC suspension has a bluish tinge, as we can see a bright pathway when shine a light with a flashlight, that's called "Tyndall effect". Because of this phenomenon we can conclude that it is a NCC colloidal suspension. NCC suspension obtained from cotton pulp fiber is very stable and there is no sediment, when it is placed a long time at room temperature.

3.7. Verification of NCC particle size

Fig. 1 shows the results obtained from particle size analyzer. It indicates that the intensity of particle size distribution of NCC produced under the condition of sulfuric acid concentration of 64%, reaction temperature of 50 °C, reaction time of 5 hurs. We can see that the average particles size of NCC is 247.9 nm, the percentage of NCC whose particles size less than 600 nm reaches more than 90%.

The Z-Average of NCC on the conditions of different reaction temperatures, different reaction times and different acid concentrations is shown in Table 5. It can be seen that the different temperature of 35 °C, 40 °C, 45 °C, 55 °C correspond to the average particles size of NCC are 294.0 nm, 288.4 nm, 259.4 nm, 207.5 nm. At the temperature range of 35–55 °C, the particles size of NCC become shorter with the reaction temperature rising. It can be concluded that higher temperature (in the range of 35–55 °C) can promote the acid hydrolysis reaction.

We can also obtain from Table 5 that the average particles size of NCC are 332.4 nm, 302.7 nm, 246.9 nm, 232.0 nm correspond to the reaction time of 3, 4, 6, and 7 h on the conditions of sulfuric acid concentration 64%, and reaction temperature 50 °C. So it indicates that, at a reaction time range of 3–7 h, the particles size of NCC become shorter with the extension of time. It is not hard to understand that the longer of time, the more thorough to the reaction. The average particles size of NCC decreases by 100.4 nm from 3 to 7 h.

The average particles size of NCC are 550.9 nm, 444.8 nm, 320.3 nm, and 173.9 nm correspond to the sulfuric acid concentrations of 50%, 55%, 60%, and 68% under the conditions of reaction temperature 50 °C, and reaction time 5 h. So we can infer that NCC particles size also become shorter with the increase in sulfuric acid concentration within the range of 50–68%. When the sulfuric acid concentration increases from 50–68%, the average particles size of NCC decrease by 377 nm. We can also conclude that the sulfuric acid concentration is the most predominant influence in reaction. Lower concentration of sulfuric acid (below 64 wt%) is not conducive to

		Diam. (nm)	% Intensity	Width (nm)
Z-Average (d.nm): 247.9	Peak 1:	309.2	100.0	135.1
PdI: 0.228	Peak 2:	0.000	0.0	0.000
Intercept: 0.915	Peak 3:	0.000	0.0	0.000
Result quality : Good				

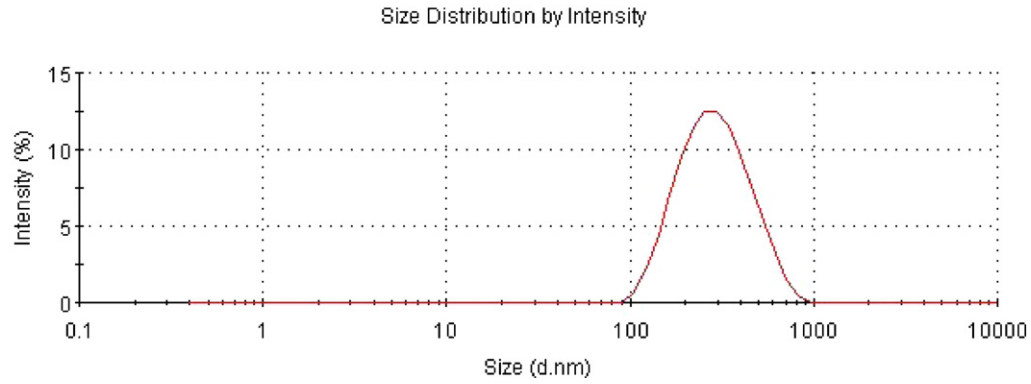

Fig. 1. The intensity of particle size distribution.

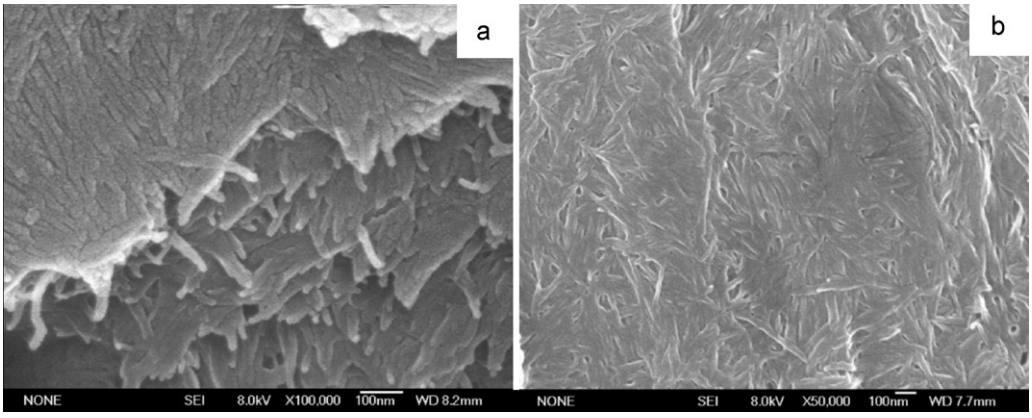

Fig. 2. SEM images of NCC (a) after drying under ambient condition; (b) with addition of surfactant in suspension then dried under ambient conditions.

Table 5
Z-average of NCC on the conditions of different reaction temperatures, different reaction times and different acid concentrations.

Temperature (°C)	*Z*-average (nm)	Time (h)	Z-average (nm)	Acid concentration (%)	Z-average (nm)
35	294.0	3	332.4	50	550.9
40	288.4	4	302.7	55	444.8
45	259.4	6	246.9	60	320.3
55	207.5	7	232.0	68	173.9

the reaction, if the sulfuric acid concentration is too high (more than 64 wt%), the crystal structure of fibers will be destroyed as the high sulfuric acid concentration, and even lead to carbonize the fiber.

Fig. 2 shows the SEM images of NCC. Fig. 2a shows SEM image of NCC after drying under ambient condition, while Fig. 2b shows the image of NCC which added surfactant (lauryl sodium sulfate) into suspension before drying under ambient condition. By comparing these two images, we can see that Fig. 2a shows an orderly arrangement of NCC, which is rod-like. Fig. 2b shows that NCC can be better dispersed under the action of surfactant, meanwhile film formed after drying more easily stripped from the glass plate. NCC prepared from cotton pulp fiber by sulfuric acid hydrolysis is rod-like, about 30 nm in diameter and several hundred nanometers in length.

4. Conclusions

NCC suspension could be successfully prepared from cotton pulp fiber. The resultant NCC suspension was very stable and there was no phase separation or sedimentation, when it was placed at room temperature for long periods of time.

Sulfuric acid concentration was found to have the crucial impact on the yield of NCC prepared from cotton pulp fiber, followed by the reaction time, then reaction temperature. Within an appropriate range of conditions, higher sulfuric acid concentration, longer reaction time and higher reaction temperature all could promote the acid hydrolysis, and the particle size of NCC was found to become smaller.

The optimum conditions were as follows: sulfuric acid concentration of 64%, reaction temperature of 50 °C, hydrolysis time of 5 h.

NCC prepared under the above conditions had a narrow size distribution, with the average particle size of 247.9 nm, and the yield was more than 60%.

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