

# Superposition of Acid Concentration and Temperature at Production of Nanocrystalline Cellulose Particles

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## Abstract

Relationship between concentration of sulfuric acid ( $C$ ) and temperature ( $T$ ) required for the cellulose hydrolysis to prepare nanocrystalline cellulose particles (NCP) has been studied in this paper. The experiments showed that there is a linear  $C$  and  $T$  superposition exists, namely:  $C = C_0 - n T$ . The higher the acid concentration, the lower the hydrolysis temperature should be used, and vice versa. The minimum level of acid concentration that can be used for production of CNP is 40 wt. % at optimal temperature of 80°C. If temperature or acid concentration is lower, there is a tendency to form of microparticles. On the other hand, at higher hydrolysis temperatures, carbonized CNP with decreased yield are obtained. The rod-like crystalline nanoparticles of cellulose produced at optimal hydrolysis conditions ( $C=40$  wt. %,  $T=80^\circ\text{C}$ ) have average sizes of 150 x 15 nm, degree of crystallinity of 75-77% and degree of polymerization of 130-150. The nanoparticles form stable colloidal dispersions in water due to Brownian motion and negative Zeta potential imparting to these particles the mutual electrostatic repulsion. Estimated calculations have also shown that decrease in the concentration of sulfuric acid from 60 to 40 wt. % at production of CNP is economically advantageous despite increase in hydrolysis temperature from 45 to 80°C.

**Keywords:** Cellulose, Crystalline nanoparticles, Acid hydrolysis, C and T superposition

## Introduction

Currently nanocrystalline cellulose is the subject of extensive research due to its unique features such as increased crystallinity, developed specific surface, biodegradability, stability to aggressive medium, increased temperatures and proteolytic enzymes, etc. [1]. Due to these features, nanocrystalline cellulose have diverse potential application in various fields such as papermaking, biodegradable materials, polymer composites, coatings, biotechnology, biomedicine, pharmaceuticals, cosmetics, etc. [2-4].

As is known, cellulose is a semicrystalline natural polysaccharide, which possess unique hierarchical architecture consisting of nano-scale fibrils built from nanocrystallites and non-crystalline (amorphous) nanodomains statistically alternated along the fibril [5,6]. The three-dimensional ordered crystallites are strong and inaccessible constituents. As against, the disordered non-crystalline domains are weak and accessible places of the fibrils. Therefore, cleavage of glycosidic bonds at the hydrolysis occurs mainly in non-crystalline domains of cellulose nanofibrils that facilitates the release of nanocrystalline particles (NCP). Thus to isolate free NCP, the disordered non-crystalline domains of cellulose nanofibrils should be selectively hydrolyzed, whereas the resistant nanocrystallites remained intact and can be isolated as rod-like nanoparticles having

level-off degree of polymerization (LODP) [7].

However, this simple mechanism is not supported by the results of cellulose hydrolysis with dilute (1-3N) acids at elevated temperatures, according to which under such hydrolysis conditions, mainly micro-size particles are formed despite achieving the LODP [8]. To explain the mechanism of NCP isolation from cellulose, it is necessary to take into consideration that in real cellulose fibers the lateral surfaces of nanocrystallites are connected tightly to each other via strong crystalline contacts. These contacts are inaccessible for dilute acid and remain intact after acidic treatment; as a result, large micro-size aggregates instead of free NCP are formed. Only if the concentration of acid is sufficient high, along with non-crystalline domains, also lateral contacts between nanocrystallites are cleaved, thus facilitate the release of free NCP [6, 9].

Practically, NCP are prepared by hydrolysis of cellulose samples with enough concentrated acid solutions at moderate temperatures combined with subsequent mechanical or ultrasound treatment. Among various acids, sulfuric acid (SA) is mainly used for the production of NCP because of its low cost and the ability to form negatively charged sulfonic groups in cellulose, which facilitate the release of nanoparticles and prevent the precipitation of these particles in aqueous dispersions due to the mutual electrostatic repulsion.

NCP can be obtained from celluloses of various origins: cotton, wood pulp, ramie, hemp, flax, sisal, microcrystalline cellulose and some other sources by treatment with 40-70 wt. % SA at temperatures from 20 to 70°C for 30 min to overnight [7,10-12]. Typical hydrolysis conditions are: concentration of SA is 60-65 wt. %, temperature 40-50 and time 1-2 h [13-15]. The nanocrystalline particles prepared from various celluloses have width from 4 to 50 nm and length from 50 to 500 nm. The yield of NCP is 20 to 30% in the case of hydrolysis with 63-65 wt. % SA, but it can be increased if the hydrolysis is carried out at a lower acid concentration.

Despite abundant investigations, the existing methods for isolation of cellulose nanocrystalline particles are far from the optimal. Since the hydrolysis of cellulose can be carried out in a wide range of acid concentration (C) and temperature (T), the main purpose of this research was to study the C and T superposition in order to find the most profitable conditions for the production of nanocrystalline cellulose particles.

## Materials and Methods

### Materials

Whatman filter paper having 99%  $\alpha$ -cellulose was chosen as an initial feedstock. Besides, the chemical grade 95% sulfuric acid and sodium bicarbonate were used.

### Preparation of CNP

The initial cellulose was mixed with needed amount of water in a lab flask, and then 80 wt. % sulfuric acid was slowly added at cooling in ice bath to obtain the required final concentration of the SA of 40 to 60 wt. % and an acid/cellulose ratio of 10. The flask was placed into a water bath having various temperatures of 40 to 100°C and treated while stirring for 60 min. After acidic treatment, contents of the flask were poured out into a tenfold volume of cold water. Cellulose sediment was separated from the liquid phase by centrifugation at acceleration of 5000 g for 10 min; washed with tap water, 1 wt.% sodium bicarbonate, and finally with distilled water to a pH of about 6, separating it from the water by centrifugation. Then the washed cellulose sediment was diluted with distilled water to a solids concentration of 1 wt. % and disintegrated in an ultrasound disperser at 20 kHz and power of 400 W for 10 min at cooling in ice bath. To study the phase stability of particles in liquid medium, the resulting 1% dispersion of CNP can be diluted 2-4 times and additionally sonicated for 5 min.

### Methods of investigation

The degree of crystallinity of the cellulose samples was determined by method of wide angle X-ray scattering [6]. Concentration of sulfonic groups in the nanoparticles was calculated from a sulfur assay [15]. Size and shape of the nanoparticles were investigated by method of transmission electron microscopy (TEM) [16]. The average degree of polymerization, DP, was measured by the viscosity method using diluted solutions of cellulose in Cadoxen [17].

## Results and Discussion

The results showed that there is a rigorous linear superposition exist between the acid concentration (C) and the temperature (T) for the cellulose hydrolysis process to prepare CNP (Fig. 1). This superposition can be expressed by the following correlation equations:

$$T = 152 - 1.8 C \quad (1)$$

$$C = 85 - 0.56 T \quad (2)$$

The higher the acid concentration, the lower the hydrolysis temperature should be used, and vice versa.

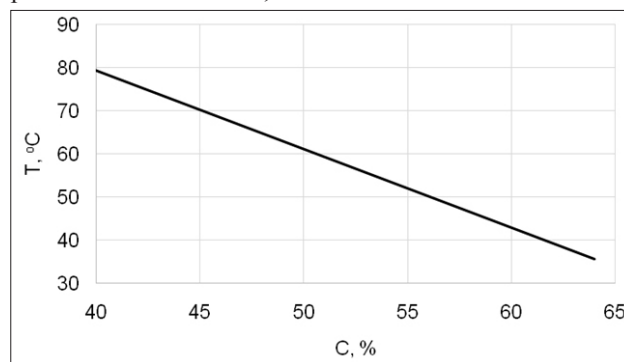


Figure 1: Linear C and T superposition at production of CNP

If the temperature of acid hydrolysis is too high, there is a decrease in yield of CNP (Fig. 2). Furthermore, the high-temperature hydrolysis process is accompanied by darkening of nanoparticles due to the intensification of oxidation, dehydration and carbonization, which is also accompanied by caramelization of dissolved byproducts of cellulose hydrolysis such as oligosaccharides.

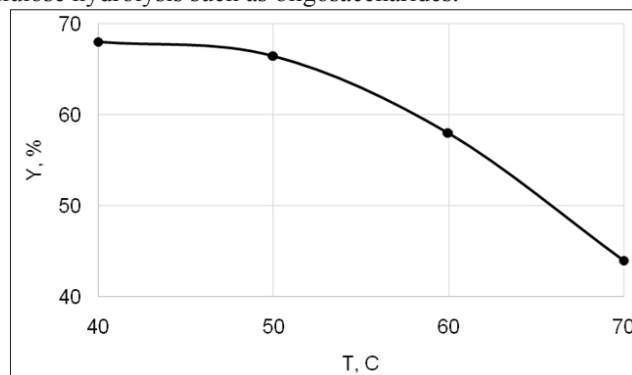


Figure 2: Dependence of yield of CNP on hydrolysis temperature at constant C=55 wt. %

On the other hand, if the hydrolysis temperature is low too, the hydrolysis process remains incomplete, and as a result a heterogeneous mixture is formed containing both nano- and micro-size particles. The cellulose nanoparticles form stable colloidal system in water due to Brownian motion and negative Zeta potential imparting to these particles the mutual electrostatic repulsion (Fig. 3). Besides, these dispersions are translucent.



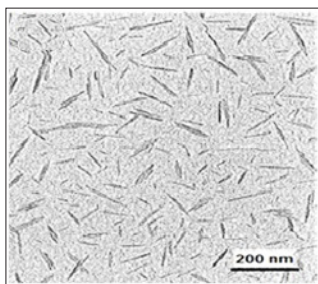
Figure 3: Image of stable translucent 0.5% aqueous dispersion of CNP in test-tube prepared by hydrolysis of cellulose with 40 wt. % SA at 80°C followed by sonication

In contrast to nanoparticles, microparticles (MP) having size  $\geq 3\mu\text{m}$  settle from dilute aqueous dispersions during storage as white precipitate (Fig.4).



**Figure 4:** Image of white sediment of cellulose microparticles on bottom of test-tube precipitated from 0.5% aqueous dispersion containing mixture of CNP and MP prepared by hydrolysis of cellulose with 40 wt. % SA at 60°C followed by sonication.

The results showed that the minimum level of SA concentration that can be used for production of CNP is 40 wt. % at optimal temperature of 80°C. If temperature or concentration of SA is lower, there is a tendency to form of microparticles. On the other hand, at higher hydrolysis temperatures, darkened (carbonized) CNP with decreased yield are obtained. The crystalline nanoparticles of cellulose produced at optimal hydrolysis conditions (C=40 wt. %, T=80°C) are rod-shaped and have average sizes of 150 x 15 nm (Fig. 5). Besides, these particles have degree of crystallinity of 75-77%, degree of polymerization of 130-150 and contain a certain amount of sulfonic (SO<sub>3</sub>H) groups (Table 1).



**Figure 5:** TEM image of CNP

**Table 1:** Characteristics of nanocrystalline cellulose particles

Characteristics	Value
Yield of NCP, %	68-70
Average sizes of NCP, nm	150 x 15 nm
Type of crystalline allomorph	CI $\beta$
Degree of crystallinity, %	75-77
Degree of polymerization	130-150
Content of SO <sub>3</sub> H-groups, meq/kg	36-40

Estimated economic calculations have also shown that reducing the concentration of sulfuric acid from 60 to 40 wt. % can yield a profit of about \$0.23 per kg solids CNP despite increase in hydrolysis temperature from 45 to 80°C.

## Conclusion

The experimental results showed that there is a rigorous superposition exist between the concentration of sulfuric acid (C, wt. %) and the temperature (T, °C) required for the cellulose hydrolysis

to prepare nanocrystalline cellulose particles (CNP), which can be expressed by the following correlation equations:

$$T = 152 - 1.8 C \text{ and } C = 85 - 0.56 T$$

The higher the acid concentration, the lower the hydrolysis temperature should be used, and vice versa.

The minimum level of SA concentration that can be used for production of CNP is 40 wt. % at optimal temperature of 80°C. If temperature or concentration of SA is lower, there is a tendency to form of microparticles. On the other hand, at higher hydrolysis temperatures, carbonized CNP with decreased yield are obtained.

The rod-like crystalline nanoparticles of cellulose produced at optimal hydrolysis conditions (C=40 wt. %, T=80°C) have average sizes of 150 x 15 nm, degree of crystallinity of 75-77% and degree of polymerization of 130-150. The nanoparticles form stable colloidal dispersions in water due to Brownian motion and negative Zeta potential imparting to these particles the mutual electrostatic repulsion.

Estimated calculations have shown that decrease in the concentration of sulfuric acid from 60 to 40 wt. % at production of CNP is economically advantageous despite increase in hydrolysis temperature from 45 to 80°C.

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