

## Study of Conversion of Cellulose into Micro-and Nano Crystalline Particles during Acidic Hydrolysis

Michael Ioelovich

*Cel designer Energy Ltd, Rehovot, Israel*

*\*Corresponding Author: Michael Ioelovich, Cel designer Energy Ltd, Rehovot, Israel; bd895892@zahav.net.il*

### ABSTRACT

Acid hydrolysis is a common process used for the production of microcrystalline (MCC) and nanocrystalline cellulose (NCC). When the starting cellulose feedstock is treated with dilute mineral acid (1-3 M), a sharp decrease in degree of polymerization (DP) is observed until achieving a minimum constant value called level-off degree of polymerization (LODP), which is associated with DP of elementary nanocrystallites. Despite achieving of LODP, after such chemical treatment the micron-size particles of MCC are formed instead of nanoparticles - a paradox that requires an explanation. It was found that dilute acid causes a selective degradation of non-crystalline domains (NCD), which leads to transverse splitting of relatively long fibers and obtaining of shorter low-molecular fragments of the fibers, namely micron-size particles of MCC. On the other hand, concentrated acids (7-9 M) cause the degradation not only NCD, but also tightly packed lateral surfaces between nanocrystallites of cellulose microfibrils connected via strong inter-crystalline contacts, thus facilitate the release free particles of NCC.

**Keywords:** Cellulose, Acid Hydrolysis, Degree of Polymerization, Degree of Crystallinity, Microcrystalline Particles, Nanocrystalline Particles

### INTRODUCTION

Cellulose is the most abundant biopolymer, which is used as renewable natural source for production of diverse materials, biochemical's and biofuels [1-3]. Supramolecular structure of cellulose consists of ordered nanocrystallites and low ordered non-crystalline nanodomains [4-6]. The crystallites have three-dimensional order are strong structure, while the non-crystalline domains (NCD) are weak and accessible places of the fibrils.

Structural changes of cellulose materials under the action of mineral acids were studied for more than 100 years [7]. It was found that dilute acids (1-3 M) damage the structure of this polymer only at elevated temperatures, and major structural changes are splitting of NCD, reduction in degree of polymerization and formation of micro-scale fragments of cellulose fibers, i.e. particles of MCC [8-11]. On the other hand, treatment of cellulose with concentrated acids (7-9 M) at moderated temperatures leads to deep depolymerization and formation of nano-scale particles of nanocrystalline cellulose (NCC) [12-15].

Despite abundant investigations, structural changes of cellulose during acidic hydrolysis

have been disclosed insufficiently. Therefore, the main purpose of this research was to explain the mechanism of cellulose conversion into MCC and NCC under the action of mineral acids of various concentrations.

### EXPERIMENTAL

#### Materials and Chemicals

Pure cotton cellulose of Hercules Co. (DP=2500, 98.5%  $\alpha$ -cellulose) and bleached Kraft pulp of Weyerhaeuser Co. (DP=1200, 97%  $\alpha$ -cellulose) were used as initial materials. Chemical pure sulfuric acid and other chemicals were supplied from Sigma-Aldrich Co.

#### Treatment

The cellulose samples were treated with dilute (1-3 M) solutions of sulfuric acid (SA) at boiling temperature for 1 h and concentrated (7-9 M) solutions of (SA) at temperatures 40-60°C for 1 h using the liquid to cellulose ratio 10. The treated cellulose was separated from the liquid phase by centrifugation at acceleration of 5000 g for 10 min, washed with water, neutralized with 5 wt. % sodium bicarbonate to a pH 6, and finally washed with distilled water, separating the cellulose particles from the liquid phase by centrifugation. To prepare aqueous dispersions

of cellulose particles, the washed sediment was diluted with distilled water to a solid concentration of 1 wt. % and disintegrated by ultrasound disperser “Branson S450CE” in ice bath at 20 kHz and power of 400 W for 10 min.

**Methods of Investigations**

Size and shape of the cellulose particles were investigated by scanning electron microscopy [14, 15]. The crystalline degree of the samples was determined by method of X-ray diffraction [16]. The average degree of polymerization was measured by the viscosity method using diluted solutions of cellulose in Cadoxen [17].

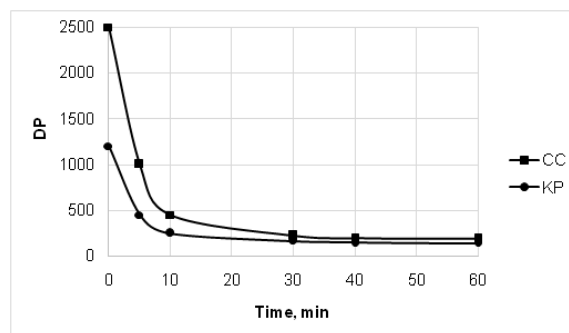
**RESULTS AND DISCUSSION**

The results of cellulose depolymerization under action of boiling dilute acid showed a rapid decrease in degree of polymerization (DP) until achieving the LODP, a minimum constant DP value, DP<sub>m</sub> (Fig. 1). Kinetics of acidic depolymerization of cellulose can be described by the equation of pseudo-first order:

$$(DP - DP_m)/(DP_o - DP_m) = \exp [-k\tau] \quad (1)$$

Where DP<sub>o</sub> is initial degree of polymerization, **k** is kinetic constant, **τ** is time.

The minimum value, DP<sub>m</sub>, obtained after acidic hydrolysis corresponds to DP of intact crystallites [10, 11]. It was found that DP<sub>m</sub>-value of cotton cellulose (CC) was around 180, whereas of Kraft pulp (KP) was around 140. The acidic treatment caused partial removal of non-crystalline domains; as a result, the increase in crystallinity degree of cellulose was observed (Table 1).



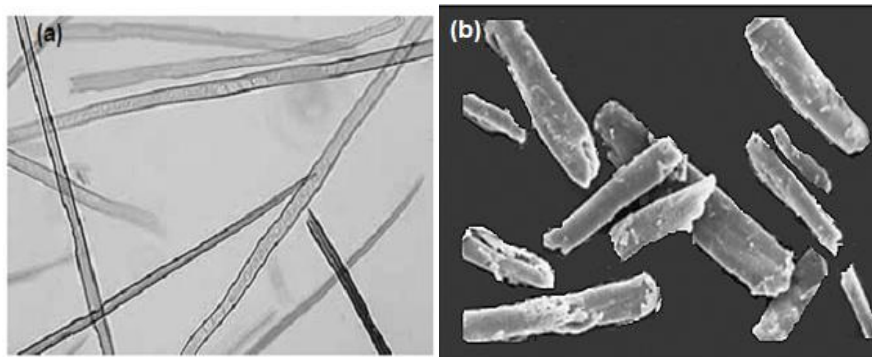
**Fig1.** Depolymerization kinetics of cotton cellulose (CC) and Kraft pulp (KP) during treatment with 3 M solution of SA

**Table1.** Crystallinity degree (X) of cellulose samples

Samples	X
CC initial	0.70-0.71
CC treated with dilute acid	0.74-0.75
KP initial	0.63-0.64
KP treated with dilute acid	0.72-0.73

As is known, cellulose fibers are relatively long and have diameter of 10-30 μm [11, 18]. Furthermore, it is also known that lateral surfaces of crystallites in micro fibrils of cellulose are connected tightly to each other via strong crystalline contacts thus ensuring the integrity of cellulose fibers [5].

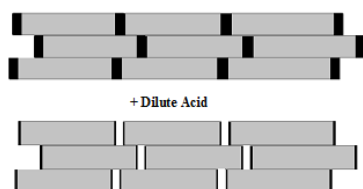
Study of particles forming after cellulose treatment with dilute acid revealed that these particles had length of 50-200 μm, i.e. shorter than of initial fibers, while diameter of the residues was similar to diameter of initial fibers, 10-30 μm (Fig. 2).



**Fig2.** Images of initial cellulose fibers of KP(a) and their fragments (b) isolated after hydrolysis with dilute 3 M solution of SA

Thus, treatment of cellulose samples with dilute acid caused a selective degradation of non-crystalline domains (NCD), which leads to transverse splitting of relatively long fibers and release of shorter low-molecular fragments, namely, micro-scale particles of MCC [8, 9]. Dilute acids cannot penetrate between tightly

packed surfaces of nanocrystallites, and therefore inter-crystallite contacts remain intact after acidic treatment as it is shown in a scheme of MCC formation (Fig. 3). Even the subsequent sonication of MCC aqueous dispersions does not break the strong contacts between crystalline aggregates in MCC particles.



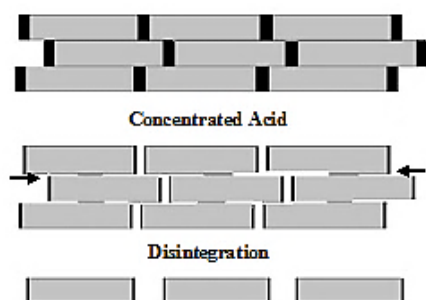
**Fig3.** Scheme of selective degradation of NCD (black areas) of cellulose fibers under action of dilute acid with formation of micro-scale MCC particles

When cellulose fibers are treated with concentrated (7-9 M) solutions of SA, then deeper structural changes of cellulose were observed. Firstly, the degree of polymerization was reduced to a greater extent, to 100-120; and secondly, there was a higher increase in the degree of crystallinity (Table 2).

**Table2.** Characteristics of NCC isolated from CC by treatment with 7 M SA at 60°C and 9 M SA at 45°C

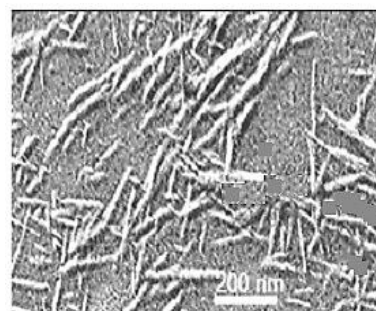
Characteristics	7M SA	9 M SA
Length of CNCs, nm	200-300	100-200
Lateral size of CNCs, nm	20-30	10-20
Degree of crystallinity	0.75-0.77	0.78-0.80
Degree of polymerization	110-120	100-110
Content of SO <sub>3</sub> H-groups, meq/kg	30-40	40-50

Moreover, the particles of NCC obtained by treatment with concentrated SA contain negatively charged sulfonic groups (SG), which impart to nanoparticles high phase stability in aqueous dispersion [19]. The content of SG in NCC after cellulose hydrolysis with 9 M SA was higher than in NCC produced after hydrolysis with 7 M SA (Table 2). Thus, concentrated solutions of SA can degrade not only the non-crystalline domains (black areas), but also strong contacts between nano crystallites, which facilitate the releasing free nanocrystallites after subsequent disintegration of weak aggregates in aqueous medium in accordance with the scheme shown in Fig. 5.



**Fig5.** Scheme of degradation of NCD and inter-crystallite contacts under action of concentrated solutions of SA to isolate the nanoparticles of NCC (arrows denote the corrosion places between nanocrystallites)

Thirdly, after cellulose treatment with concentrated acid and subsequent sonication the nano-scale particles of NCC are formed with a length of 100-300 nm and lateral size of 10-30 nm (Fig. 4).



**Fig4.** SEM image of NCC particles

## CONCLUSIONS

The impact of cellulose treatment with sulfuric acid of various concentrations on the structural transformations of cellulose fibers has been studied. It is known that lateral surfaces of crystallites in microfibrils of cellulose are connected tightly to each other via strong inter-crystalline contacts. When the starting cellulose material is treated with boiling dilute acids (1-3 M), a selective hydrolysis of non-crystalline domains (NCD) to LODP is observed without breaking the strong lateral contacts between crystallites. The subsequent sonication of aqueous dispersions of hydrolyzed cellulose leads to transverse splitting of relatively long fibers and obtaining of shorter low-molecular fragments of the fibers, namely micron-scale particles of MCC. On the other hand, concentrated acids (7-9 M) at moderate temperatures (45-60°C) cause the hydrolysis not only of NCD, but also the destruction of strong lateral contacts between nanocrystallites in cellulose microfibrils, thereby facilitate the release of free nano-scale particles of NCC after subsequent ultrasound disintegration of weak particulate aggregates in the aqueous medium.

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