Process Scale-Up of Cellulose Nanocrystal Production to 25 kg per Batch at the Forest Products Laboratory

Abstract. *The Fiber and Chemical Sciences Research Work Unit at the Forest Products Laboratory began working out the preparation of cellulose nanocrystals in 2006, using the method of Dong, Revol, and Gray. Initial samples were provided to several scientists within the Forest Service. Continued requests for this material forced scale-up from the initial 20 g scale to kg scale and eventually resulted in an award of $1.7 million dollars to the laboratory to purchase the equipment needed to scale production up to 20 kg per batch. The new pilot facilities started up in July 2012 with batch sizes of 15 kg and a maximum production of about 22 kg per week. Optimization has raised the batch size to 25 kg with a weekly production capability of 50 kg. This summary describes the pilot-plant equipment with current experimental procedure. It also describes scale-up changes from the laboratory procedure and adjustments that have been made in the procedure to correct minor problems.*

Keywords. Cellulose nanocrystals, CNC, nanocrystalline cellulose, NCC, pilot plant.

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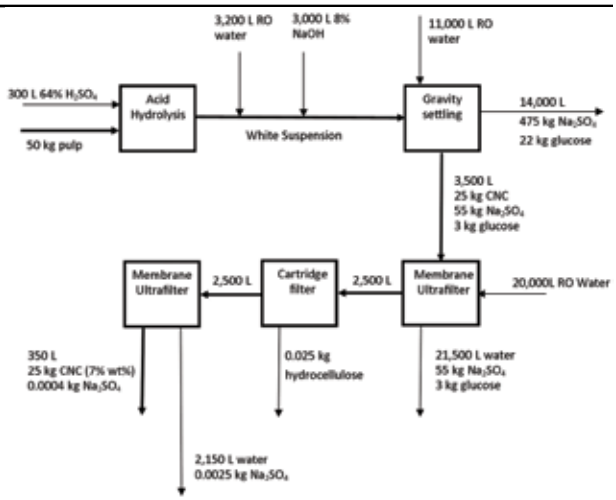

Figure 1. *Experimental processing diagram of the pilot plant method. Acid hydrolysis is carried out in the first 400L glass-lined reactor. Gravity settling is carried out by splitting the sample between the 6000L and 4000L reactors.*

Introduction. A process for isolating cellulose micelles using boiling 2.5 N sulfuric acid was reported by Rånby in 1949 [1], with additional information on characterization provided by Rånby and Ribi one year later [2]. Of critical importance are the dimensions of the rod-like particles: 5–10 nm in diameter and 50–60 nm long. X-ray diffraction demonstrated that the isolated crystals were the same as the crystalline portion of the starting pulp. Mukherjee and Woods subsequently demonstrated that room-temperature treatments with 950–975 gpl (62.3%–63.4%) sulfuric acid provided good-quality cellulose colloid suspensions with little hydrolysis of crystals and no conversion of cellulose I to cellulose II [3]. At 995 gpl (64.3%), the acid completely hydrolyzed the cellulose, and if stopped before complete hydrolysis, they found evidence of cellulose II in the solid residual. Marchessault *et al*. then used 955 gpl sulfuric acid (62.5%) at 40°C for 24 h to prepare samples for extensive characterization of the cellulose crystals produced from textile fibers [4]. In 1996, Dong *et al*. provided a detailed laboratory preparation using 20 g samples of Whatman No. 1 filter paper, 64% sulfuric acid, 45°C, and 1 h. The hydrolysis step was followed by centrifugation to separate the residual cellulose from the acid, dialysis, and ion exchange to remove the residual acid and salt [5]. After an additional effort to optimize the preparation of nanocrystals, Gray *et al*. recommended continued use of the same conditions provided in the earlier paper [6]. A more thorough evaluation of reaction conditions carried out by Bondeson *et al*. in 2005 recommended 63.5% sulfuric acid, 44°C, and 130 minutes [7].

The U.S. Forest Service began working with cellulose nanocrystals in 2006, starting with the methods reported by Gray in 1996 and 1998 [5,6]. Initial laboratory-scale preparations were used to evaluate composite blending with polypropylene [8] and for atomic-force microscopy studies [9]. One year later, experimental samples were requested by James Snyder of the Army Research Laboratory Aberdeen Proving Ground [10]. Faced with the need to supply three research units with ever-increasing requirements for cellulose nanocrystals, the laboratory preparation was scaled up over time from the initial 20 g of wood pulp to 300 g of wood pulp. A request for a full kg of CNC forced an additional scale-up. The 5-L flask used for the acid hydrolysis was the largest round-bottom flask available, but crude product

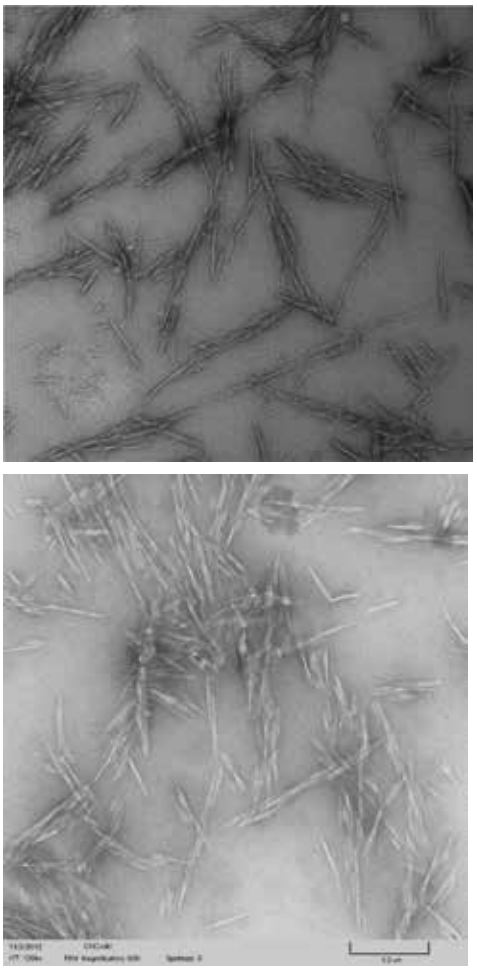

Figure 2. *TEM of cellulose nanocrystals. (Top) produced in the laboratory from a commercial, viscose-grade dissolving pulp. (Bottom) produced in the pilot plant, also from a commercial, viscose-grade dissolving pulp*

from ten reactions was combined for workup. Abandoning the centrifuge and dialysis processes used for laboratory-scale preparations, purification was accomplished by diluting and neutralizing the crude sample and letting it settle to the bottom of a 900 L tank. After decanting the salt solution, the CNC were diluted and the remaining salt removed in a membrane filtration system with a 200,000 Dalton cutoff PVCF membrane. Requests for samples continued, and it became clear that the lack of starting CNC was a severe impediment to research progress. The Forest Service then provided $1.7 million dollars in funding for new pilot equipment to produce CNC at 20 kg scale.

The new pilot plant at the Forest Products Laboratory consists of five reactors set up to produce both cellulose nanocrystals and TEMPO-treated cellulose nanofibrils. The CNC reaction uses a 400 L (100-gallon) De Dietrich glass-lined reactor for the hydrolysis reaction and 6000 L (1500 gallon) and 4000 L (1000 gallon) glass-lined reactors for initial dilution, neutralization, and settling. Any remaining sodium sulfate and glucose are removed in a Membrane Specialists membrane filtration system containing 7.5 m^2 of the 200,000 MW cutoff membrane. The remaining vessels in the new pilot plant are a second 400 L glass-lined reactor, used to dilute sulfuric acid and for the TEMPO-CNF reaction, and a 800 L De Dietrich pressure filter (Nutsche filter), used to collect and wash the TEMPO-treated wood pulp.

Methods. Cellulose nanocrystal (CNC) production: 50 kg machine-dried prehydrolysis kraft rayon-grade dissolving wood pulp is strip-cut (approx. 0.6 × 40 cm) and packed into a 400 L glass-lined reactor. The pulp is placed under a nitrogen atmosphere and the water jacket heated to 45°C. Sulfuric acid (300 L, 64 wt%) is heated to 45°C in a second 400 L reactor and then sprayed over the top of the dry-lap strips. After about 100 L of acid has been transferred, the dry-lap strips are wetted and degraded enough to begin rotating them as a tangled mass under the spray nozzles; after about 200 L has been transferred, the strips begin to turn over and mix. Acid addition requires about 15 minutes, and the mixture is stirred and maintained at 45°C for 90 minutes, when the reaction is quenched by transferring the suspension into a 6000 L reactor containing approximately 1200 L water. The suspension is further diluted to about 3000 L, at which point 2 L of 4 wt% hypochlorite solution (Clorox) is added to remove color. The CNC suspension is then neutralized by slow addition of 5–8 wt% NaOH, split between the 6000 L and 4000 L reactors, and diluted to a total volume of 11,000 L. The CNC suspension is allowed to settle and the salt/sugar solution decanted from the two reactors. On dilution a second time, the sodium sulfate concentration drops to about 1 wt%, at which point the CNC particles begin to disperse in the solution. The aqueous suspension is then transferred to the ultrafiltration system for further purification.

The CNCs are circulated through a tubular ultrafiltration system (Membrane Specialists, A19 modules), where the dilute salt/sugar solution passes through the membrane while CNCs are retained. Reverse osmosis (RO) water is added as needed to maintain the CNC concentrate at 1 wt%. Diafiltration is continued until the residual salt concentration is reduced to about 8 µM, (measured as 40–50 µS/cm^2). This requires about 24 hours of dilution and filtration and 20,000 L RO dilution water. The colloidal CNC suspension is filtered using a 20 µm polypropylene, cartridge-style filter to remove dirt and concentrated to at least 5 wt% solids using the tubular ultrafiltration system. Overall yield is about 50%.

Results. An experimental processing diagram is provided in Figure 1. Major deviations from the laboratory process are the use of gravity settling instead of a centrifuge for the initial separation and of membrane filtration to replace dialysis. The pilot process runs smoothly, providing a CNC suspension that is indistinguishable from laboratory-produced samples. (Fig. 2). The starting pulp contains some cellulose II, and the CNC suspension shows some shorter crystals typical of mercerized pulps [11]. Raman and X-ray analysis confirms a mixture of cellulose I and II. The use of dissolving pulp as a starting material provides a more stable suspension with less color than is obtained using bleached kraft pulp. Mixing is highly critical in the initial stage of the reaction. Experience with the laboratory method has shown that pulp which was contacted by some sulfuric acid, but not mixed into the suspension, formed a gel-like mass that was incompletely hydrolyzed and difficult to disperse in acid. The reactor provides good initial contact with two spray nozzles placed at 180 degrees on the reactor. Once the initial sulfuric acid has been added, the mixer is turned on and rotates the mass of shredded pulp underneath the two spray nozzles. Traditional mixing does not start until about two-thirds of the sulfuric acid has been added.

Initial reactions were run with more dilution water in the quench reactor and using higher-concentration sodium hydroxide to neutralize the acid. This formed a small amount of material (3%–5% of yield) that appeared to be an amorphous cellulose hydrogel. Reducing the initial quench volume to enable neutralization with more dilute caustic has reduced this loss to less than 0.1% of yield. The pilot plant design had to account for the corrosive nature of the materials being used, 64% sulfuric acid for CNC and sodium hypochlorite or sodium chlorite for CNF. Glass-lined reactors were not specified in the request for bids, but the only bids received for the five reactors were as glass-lined equipment. To avoid the need for exotic alloy pumps, the reactors were placed on steel decking with the 400 L reactors suspended high enough to gravity discharge to the 6,000 L and 4,000 L reactors and the Nutsche filter. The larger reactors and the entire deck structure are placed over an epoxy-lined pit for safety in case of an acid spill. The only pumps needed in the pilot plant are lower-pressure Teflon membrane diaphragm pumps used to transfer acid and caustic to the reactors. Acid transfer between the two 400 L reactors is by pressurizing the reactor containing the preheated acid with nitrogen and placing the CNC reactor containing the shredded pulp under partial vacuum. This provides sufficient differential pressure and flow rate for the two spray nozzles. That acid transfer piping is Alloy 20 (20 Cb-3), and the spray nozzles are manufactured from Hastalloy C-276. The remainder of the process piping is either 316 SS or CPVC. The dilution, neutralization, and settling step replaces the centrifuge separation of the laboratory methods [5,6,7]. Most of the settling takes place within 24 h, but it is often carried out for 48 h with a slight increase in separation efficiency. The boundary between clear filtrate and settled CNC can be clearly observed from the top of the large reactors, and a dip tube is inserted to about 3 cm above the CNC suspension. Each batch of CNC requires about 8 h for CNC reaction and neutralization, 24–48 h for settling and initial purification, and 24 h membrane filtration for final salt removal. Current maximum production is 25 kg per batch, with up to two batches per week. If the need continues to increase and no suitable commercial sources of CNC become available, initial consideration has been given to a scale-up to a 4,000 L reactor, which will require inline dilution, neutralization, and initial separation.

The primary product of the pilot plant is the aqueous suspension of CNC at 5–10 wt% concentration. The suspensions are indefinitely stable, and there have been no reports of bacterial growth, with some samples being maintained for a year or more. The FPL can provide a dry powder, using a freeze dryer to reduce aggregation and permanent bonding of the CNC particles. This equipment is not sized for the entire pilot plant capability and can only dry 7% of the maximum CNC production.

Conclusions. The U.S. Forest Service, Research and Development Division, has constructed a small pilot facility at the Forest Products Laboratory in Madison, Wisconsin to produced larger quantities of cellulose nanocrystals and TEMPO-based cellulose nanofibrils. Production from the pilot facility is intended to support research and development on these promising materials. The pilot plant started up in 2012 and is currently running smoothly and is capable of producing up to 50 kg CNC aqueous suspension per week. Freeze drying is available, but capacity is only about 3 kg per week. A second summary in this book will provide information on the status of the cellulose nanofibril portion of the pilot plant.

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Cellulose nanocrystals incorporated within the overcoat varnish of the cover!

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