

Cellulose Nanomaterials

Tailored and Integrated Production of Carboxylated Cellulose Nanocrystals (CNC) with Nanofibrils (CNF) through Maleic Acid Hydrolysis

Ruibin Wang,^[a, b] Liheng Chen,^[b, c] J.Y. Zhu,^{*, [b]} and Rendang Yang^[a]

Abstract: This study demonstrates the feasibility of tailored and integrated production of carboxylated cellulose nanocrystals (CNC) with nanofibrils (CNF) from bleached pulp fibers through hydrolysis using a recyclable dicarboxylic acid. Hydrolysis experiments were conducted using ranges of 15–75 wt% maleic acid concentrations, 60–120 °C temperatures, and 5–300 min reaction times. Maleic acid esterified cellulose resulted in carboxylated CNC and CNF. Furthermore, the acid-hydrolysis solubilized xylan and depolymerized cellulose, which substantially reduced the energy input for the production of CNF through subsequent mechanical fibrillation. A combined hydrolysis factor (CHF), a measure of

hydrolysis severity, was developed to map xylan dissolution and cellulose depolymerization over the entire reaction space. It was found that CHF can be used to predict the morphological and chemical properties of the resultant CNC and CNF, independent of the individual reaction process variables. This is important for process scale-up design in order to tailor the properties of CNC and CNF for specific applications. With the low temperature hydrolysis and low energy input in mechanical fibrillation, along with the recyclability of maleic acid, the presented process has promise of achieving commercial success in the low-cost and sustainable production of CNC and CNF.

Introduction

Cellulose nanocrystals (CNC) and nanofibrils (CNF), as the primary biogenic nanomaterials, can be sustainably produced from lignocelluloses, which are abundant on earth.^[1,2] CNC and CNF have many potential applications, such as reinforcement in nanocomposites,^[3–6] chiral nematic films,^[7] photoelectric devices,^[8] catalytic scaffolding,^[9] drug delivery,^[10,11] and organic light emitting diodes and flexible electronics.^[12–14] These various applications demand CNC or CNF with tailored properties. For example, a large aspect ratio is important for making films and polymer reinforcements, while transparency is important for optical applications. Unfortunately, limited efforts have

been put into the tailored production of cellulose nanomaterials with desired properties.

CNC are commonly produced using concentrated mineral acid hydrolysis,^[15–19] developed almost 70 years ago.^[20] CNF are often produced through mechanical fibrillation with the assistance of chemical or enzymatic pretreatment to save energy in fibrillation.^[21–27] The main drawbacks of the existing processes for producing cellulose nanomaterials are: (1) difficulties in economic recovery of chemicals which affects environmental sustainability; (2) the requirement of separate production lines for producing CNC and CNF, both of which result in high production cost; (3) high energy input in mechanical fibrillation when chemical pretreatments are not applied. Despite the large amount of reported research, few studies showed promising prospects for achieving economic and sustainable production of cellulose nanomaterials with tailored properties and functionality, all of which are critical to many promising commercial applications.

Previously, we demonstrated the possibility of using concentrated solid di-carboxylic acids for integrated production of thermally stable and carboxylated CNC and CNF.^[28] Although di-carboxylic acids have low strength ($pK_a = 1–3$), effective acid hydrolysis can be achieved at elevated temperatures (around 100 °C without boiling). These acids have low solubility at low temperatures, which allows efficient recovery using commercially proven crystallization technology by cooling spent acid solution down to ambient temperature. The low strength of solid di-carboxylic acids results in a low CNC yield with the majority of feed cellulosic materials remaining as partially hydro-

[a] R. Wang, Prof. R. Yang
State Key Laboratory of Pulp and Paper Engineering
South China University of Technology
Guangzhou, 510640 (China)

[b] R. Wang, Dr. L. Chen, Dr. J. Zhu
Forest Products Laboratory, U.S. Forest Service
U.S. Department of Agriculture
Madison, Wisconsin 53736 (USA)
E-mail: jzhu@fs.fed.us

[c] Dr. L. Chen
Key Laboratory of Biomaterials of Guangdong Higher Education Institutes
Department of Biomedical Engineering
Jinan University
Guangzhou 510632 (China)

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lyzed fibrous cellulosic solid residue (FCSR), which can then be mechanically fibrillated to valuable CNF with low energy consumption.^[28–30] The dissolution of xylan and depolymerization of cellulose by acid hydrolysis facilitates mechanical fibrillation because xylan is a major component that glues cellulose microfibrils together in wood fiber matrix, and cellulose depolymerization is necessary for separating fibrils based on a recent proposed longitudinal wood fiber ultra-structure model.^[27]

The objective of the present study is to conduct a systematic study for integrated production of CNC with CNF from bleached pulp fibers using concentrated maleic acid hydrolysis. The goal of the study is to map the hydrolysis space to achieve tailored production of CNC and CNF with desired properties. Instead of using conventional individual hydrolysis process variables for process optimization, here we use a combined hydrolysis factor (CHF), as a reaction severity measure to map the hydrolysis space. CHF is a combination of hydrolysis temperature and time along with acid concentration and was developed based on xylan dissolution reaction kinetics.^[31] A modified CHF, capable of accurately predicting cellulose depolymerization, was used to correlate the morphological properties of CNC and CNF. The present approach of using acid hydrolysis reaction severity to map the hydrolysis space facilitates process scale-up for commercial applications. As long as the desired hydrolysis severity is achieved, the resultant CNC and CNF properties can be maintained without the need to maintain individual process variables, as might be necessary due to engineering constraints in scaled-up facilities.

Results and Discussion

Using combined hydrolysis factor to quantify xylan dissolution

The fraction of xylan retained in water insoluble solids (WIS) after maleic acid hydrolysis, X_R , can be determined from the measured xylan content of WIS, C_{xy} , and WIS yield, Y_{WIS} , as follows in Equation (1):

$$X_R = \frac{C_{xy} Y_{WIS}}{100 C_{xy0}} \quad (1a)$$

where C_{xy0} = 15.5 and is the xylan content of the original bleached eucalyptus pulp fibers (BEP). Previously, we were able to accurately predict xylan dissolution during dilute acid pre-treatment of wood chips^[31] by using a combined hydrolysis factor (CHF_x) as a reaction severity when applying a bi-phasic xylan model.^[31]

$$X_R = (1 - \theta)e^{-CHF_x} + \theta e^{-fCHF_x} \quad (1b)$$

$$CHF_x = \exp\left(\alpha - \frac{E}{RT} + \beta C\right) t \quad (1c)$$

where θ and $(1-\theta)$ in Equation (1b) are the fractions of the slow and fast reaction (hydrolysis) xylan, respectively; f is the ratio of the rate constant between the slow and fast xylan hy-

drolisis reactions. In Equation (1c), α and β are adjustable parameters; E is the apparent activation energy; R is the universal gas constant of $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$; T is the absolute temperature in Kelvin; C is the initial molar concentration of acid; and t is the reaction time.

Although Equations (1b) and (1c) were developed for hydrolyzing wood chips using dilute sulfuric acid solutions, they were successfully applied to predict xylan dissolution during dilute di-carboxylic acid hydrolysis of BEP fibers.^[27] Here, we apply these two equations to the hydrolysis of BEP fibers using a concentrated di-carboxylic acid, namely maleic acid. The experimentally determined xylan dissolution data X_R were fitted to Equations (1b) and (1c) to obtain θ , f , α , β , and E (Table 1). An excellent fitting was obtained as shown in Figure 1a, which suggests that the fraction of xylan dissolved by maleic acid hydrolysis at high concentrations can be well predicted using CHF_x alone.

Table 1. Fitting parameters for xylan dissolution [Eqs. (1b) and (1c)] and cellulose depolymerization [Eq. (2)] by concentrated maleic acid hydrolysis.

	Fitted value	Unit
E	143,000	J mol^{-1}
α	39.43	none
β	0.3725	L mol^{-1}
θ	0.6736	none
f	0.0176	none
ε	0.5	none
F_{DP}	0.467	none
S_{DP}	0.328	none
j	58	none

Predicting cellulose degree of polymerization (DP) reduction using combined hydrolysis factor

For producing cellulose nanomaterials, cellulose depolymerization through pure mechanical or chemical and mechanical actions is essential.^[27,30] Cellulose is an inhomogeneous material, just as xylan is, and can also be modeled using a bi-phasic model to predict cellulose dissolution by acid hydrolysis.^[32–34] Initial data analyses found that the linear contribution of acid concentration to xylan dissolution in Equation (1c) does not accurately apply for cellulose depolymerization. We corrected this nonlinearity of acid concentration on cellulose depolymerization by developing a combined hydrolysis factor for cellulose (CHF_G), as shown in Equation (2a). Then the DP of the hydrolyzed BEP fibers can be expressed by Equation (2b), similar to Equation (1b) as demonstrated previously.^[27]

$$CHF_G = \exp\left(\alpha - \frac{E}{RT} + \beta C^\varepsilon\right) C \quad (2a)$$

$$\frac{DP}{DP_{BEP}} = F_{DP} e^{-jCHF_G} + S_{DP} e^{-CHF_G} + (1 - F_{DP} - S_{DP}) \quad (2b)$$

where ε is an exponential index, DP_{BEP} = 1027 is the DP of feed BEP fibers, F_{DP} and S_{DP} are the respective fraction of cellulose

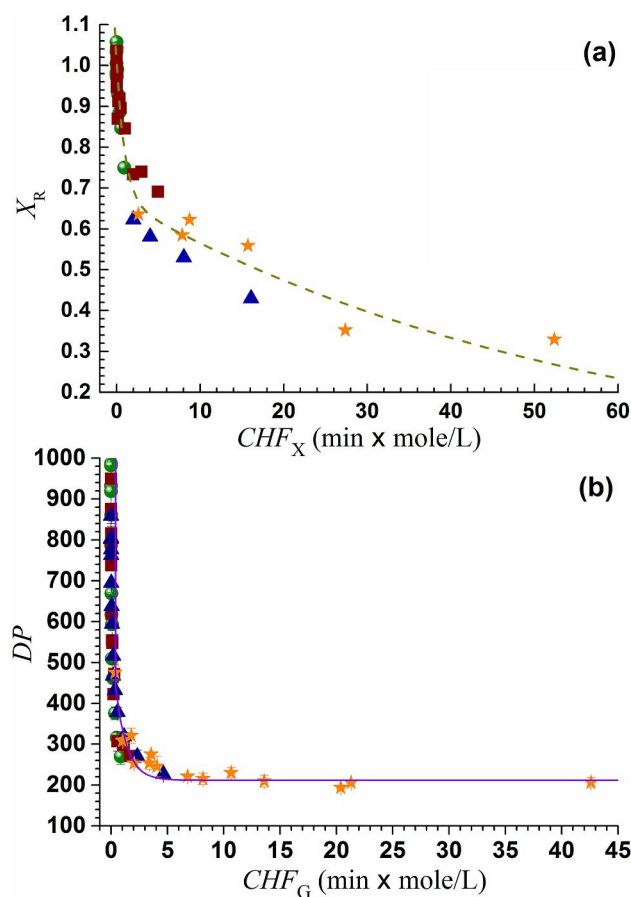


Figure 1. Model predictions of xylan dissolution and cellulose depolymerization under various reaction conditions using combined hydrolysis factors (CHF_X and CHF_G) in comparisons with experimental data. Acid concentrations (wt %): ● 15, ■ 35, ▲ 55, ★ 75; (a) xylan remaining, --- Eq. (1 b); (b) degree of polymerization (DP), — Eq. (2 b).

depolymerization contribution from fast and slow reaction cellulose, j is ratio of the reaction rates between the rapid and slow depolymerizing cellulose. The concept of level of cellulose DP (LODP) is well known.^[35] Here LODP is represented by the balance of depolymerization contributed by the fast and slow cellulose, that is, $LODP = DP_{BEP} (1 - F_{DP} - S_{DP})$. The measured DP data of hydrolyzed BEP samples were fitted using Equations (2a) and (2b) to obtain ε , F_{DP} , S_{DP} , and j (Table 1). An excellent fitting of the data by Equation (2b) was achieved, suggesting cellulose DP can be well predicted by CHF_G , and LODP was obviously reached using concentrated acid hydrolysis as shown in Figure 1 b.

Effects of hydrolysis severity on CNC and CNF morphologies

CNC morphology, revealed by AFM imaging, varies with the severity of hydrolysis represented by CHF_G as shown in Figure 2(a)–2(f). These samples were obtained by centrifuging (at 10000 rpm) the supernatant resulting from dialyzing the hydrolyzed WIS. A high centrifuge speed can remove cellulose crystal bundles as shown by the AFM (Figure S1 in the Supporting Information). It appears, however, that a centrifuge

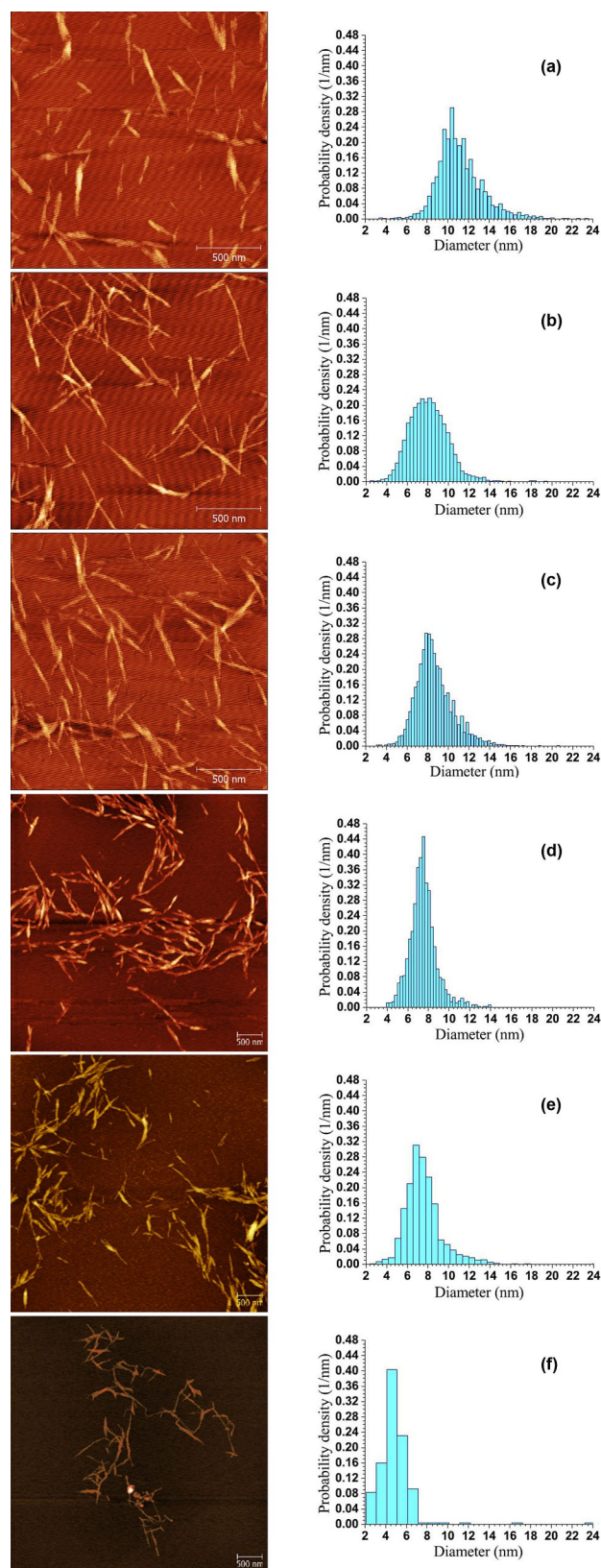


Figure 2. AFM images and AFM-measured height distributions of CNC produced under various hydrolysis conditions. All scale bars = 500 nm. (a) M75T100t30, $CHF_G = 1.02$, mean H = 11.2 nm; (b) M75T100t60, $CHF_G = 2.04$, mean H = 8.1 nm; (c) M75T100t120, $CHF_G = 4.08$, mean H = 8.6 nm; (d) M75T110t60, $CHF_G = 6.80$, mean H = 7.5 nm; (e) M75T100t240, $CHF_G = 8.16$, mean H = 7.6 nm; (f) M75T110t180, $CHF_G = 20.4$, mean H = 4.9 nm.

speed of 4000 rpm is sufficient to result in consistent morphologies without crystal bundles. A severer hydrolysis resulted in thinner and shorter CNC as clearly indicated by the AFM-measured CNC height distribution (right panel of Figure 2). The AFM-measured mean CNC heights (assumed to be equivalent to diameters) and lengths were found to correlate well with CHF_G (Figure 3a and 3b). The mean CNC lengths are in the range of 450–650 nm for the hydrolysis conditions studied (Figure 3b), much longer than those obtained from concentrated sulfuric acid hydrolysis,^[15] and in good agreement with our initial study using oxalic acid.^[28] Typical CNC aspect ratios ranged between 60 and 90, which is high and can be beneficial for applications in polymer reinforcement. Increased hydrolysis severity reduced CNC height (diameter) to result in increased aspect ratio for the hydrolysis conditions examined (Figure 3b).

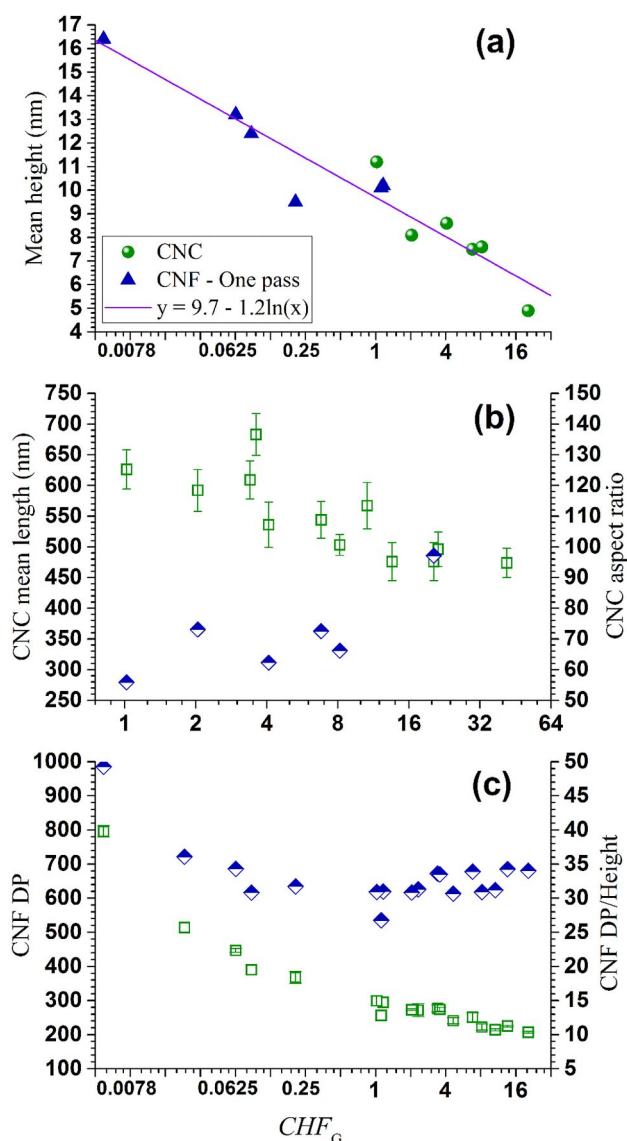


Figure 3. Effects of acid hydrolysis severity, CHF_G , on CNC and CNF morphologies. (a) CNC and CNF mean heights ● CNC, ▲ CNF-one pass, — $y = 9.7 - 1.2 \ln(x)$; (b) CNC mean length by DLS and aspect ratio; (c) CNF DP and ratio of DP over height (an aspect ratio measure).

After separating CNC, a substantial amount of FCSR remains as partially hydrolyzed fibers since the yield of CNC were low (Table S1) due to the low strength of maleic acid. The FCSR were subsequently mechanically fibrillated to produce CNF as reported previously.^[28,29] The morphology of resultant CNF after one pass through the microfluidizer varied with the severity of acid hydrolysis as shown in Figure 4. Overall, the resultant CNF were entangled networks of fibrils. However, the entanglement decreased as the acid hydrolysis severity CHF_G increased. Low severity hydrolysis also resulted in CNF with greater fibril height or diameter measured by AFM (right panel of Figure 4). The mean heights correlate to hydrolysis severity CHF_G well, as shown in Figure 3a where the data are overlaid with the mean height data of CNC samples. It may be just a coincidence that the mean heights of CNC and CNF can be fitted by the same logarithmic equation using CHF_G . Measurements of CNF length are difficult due to entanglement. However, DP is a measure of cellulose chain length and can be used to represent CNF length. Increased hydrolysis severity produced CNF with reduced mean DP as shown in Figure 3c, clearly indicating that acid hydrolysis cuts cellulose chain length. This acid hydrolysis effect on DP reduction was most obvious at low acid hydrolysis severities. This also can be seen from the reduction in DP of FCSR (Figure 1b). Acid hydrolysis facilitated mechanical fibrillation to result in a reduced fibril height or diameter (Figure 3a) under the same fibrillation intensity. As a result, the ratio of fibril DP over height were not much affected by the severity of acid hydrolysis except in the very low severity conditions considering the sharp decrease in DP as shown in Figure 3c.

Effects of the extent of fibrillation on CNF morphology

The CNF shown in Figure 4 resulted from only one pass of microfluidization through the 200 and 87 μm chambers, suggesting an order of magnitude lower energy input in producing CNF using acid prehydrolysis, than the 40 passes required without any pretreatment or 30 passes with enzymatic pretreatment as reported previously using the same BEP fibers.^[25] This is critical in achieving low-cost CNF production for commercialization. Two FCSR samples, produced using two different hydrolysis severities, and thus with different DP, were separately microfluidized for numerous passes. The first FCSR sample, M55T80t10 with $\text{CHF}_G = 0.014$ and $\text{DP} = 805 \pm 17$, was microfluidized for 3, 5, and 8 passes. The second was from M15T80t180 with $\text{CHF}_G = 0.038$ and $\text{DP} = 617 \pm 5$ and microfluidized for 1, 3, and 5 passes. As expected, additional passes of microfluidization fibrillated the fibers into finer nanofibrils for both samples, as shown by the AFM images in Figure 5 (left panel). The reduction in fibril heights due to more fibrillation was very obvious as shown by AFM-measured fibril height distributions (right panel in Figure 5). Apparently the FCSR sample with lower hydrolysis severity CHF_G (higher DP) required more fibrillation to achieve equivalent fine fibrils (comparing Figures 5(a)–5(c) with 5(d)–5(f)), suggesting that a higher severity hydrolysis can be used to produce CNF with less fibrillation energy input. Furthermore, a higher severity hy-

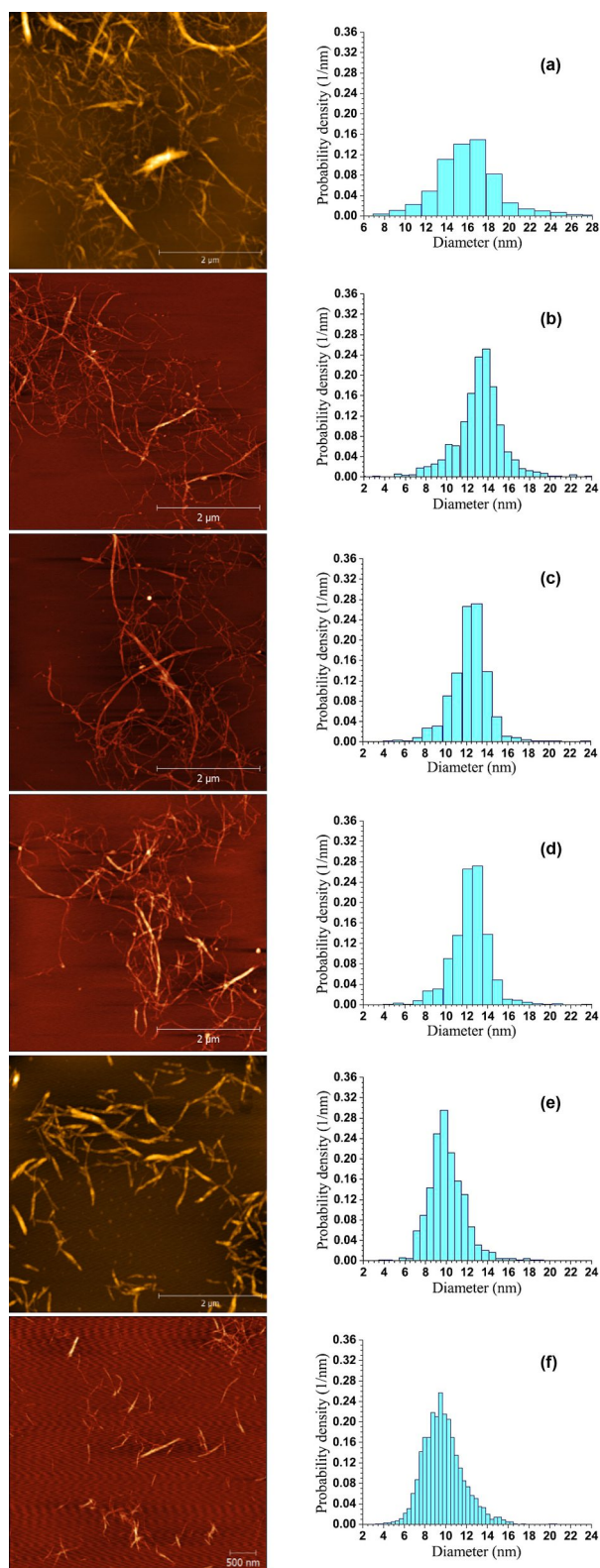


Figure 4. AFM images and AFM-measured height distributions of CNF produced under various hydrolysis conditions with only one pass in microfluidization. Scale bars = 2000 nm for (a)–(e) and = 500 nm for (f). (a) M55T60t60, $\text{CHF}_G = 0.005$, mean, FCSR DP = 796 ± 17 , $H = 16.4$ nm; (b) M15T80t300, $\text{CHF}_G = 0.063$, FCSR DP = 390 ± 0 , mean $H = 13.2$ nm; (c) M15T100t30, $\text{CHF}_G = 0.086$, FCSR DP = 447 ± 6 , mean $H = 12.4$ nm; (d) M35T80t300, $\text{CHF}_G = 0.205$, FCSR DP = 368 ± 18 , mean $H = 9.5$ nm; (e) M35T100t120, $\text{CHF}_G = 1.115$, FCSR DP = 256 ± 0 , mean $H = 10.1$ nm; (f) M75T100t60, $\text{CHF}_G = 2.04$, FCSR DP = 253 ± 8 , mean $H = 9.8$ nm.

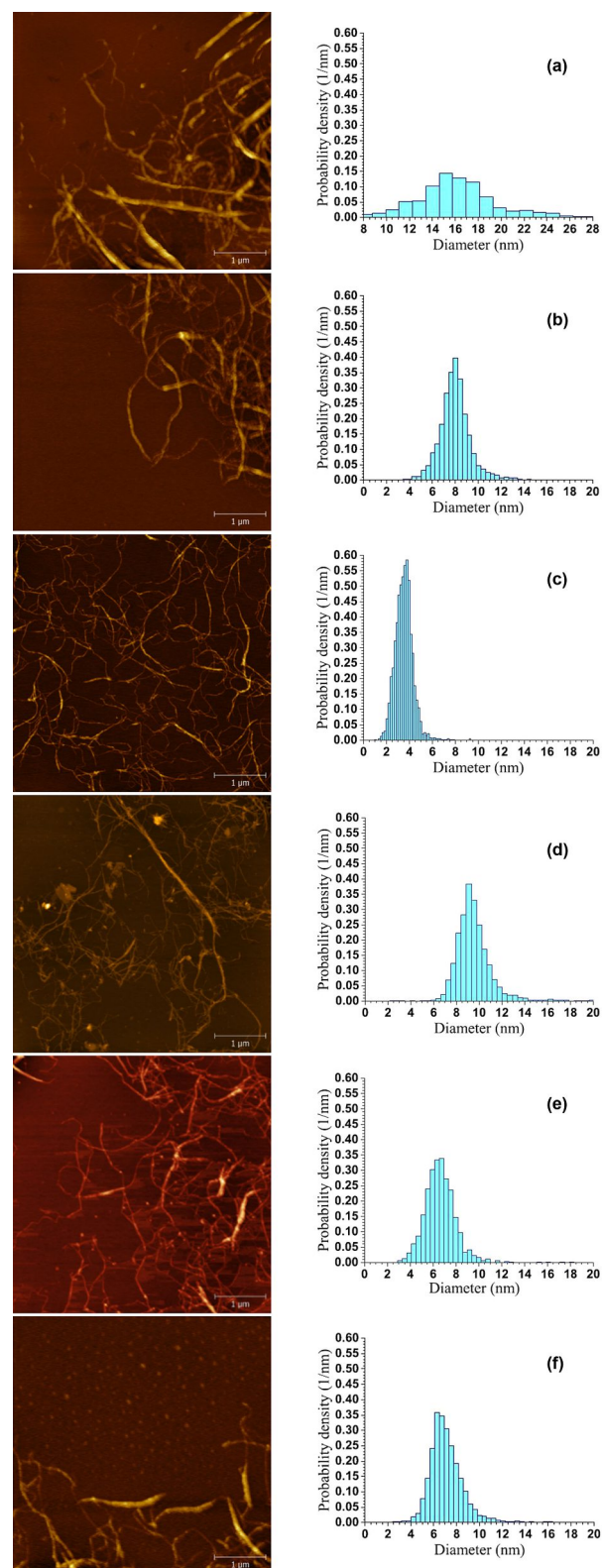


Figure 5. Effects of the extent of microfluidization (passes) on the morphologies of resultant CNF produced from FCSR under two acid hydrolysis severities. All scale bars = 1000 nm. (a)–(c): M55T80t10, $\text{CHF}_G = 0.014$, FCSR DP = 805 ± 17 , 3, 5, and 8 passes for (a), (b) and (c), respectively; (d)–(f): M15T80t180, $\text{CHF}_G = 0.038$, FCSR DP = 617 ± 5 , 1, 3, and 5 passes for (d), (e) and (f), respectively.

hydrolysis can result in less entanglement (Figure S2(a)–S2(c)) or even individually separated fibrils (Figure S2(d)–S2(f)), as we reported previously.^[28–30] FCSR samples obtained from similar severities (CHF_G), and thus with similar DP, resulted in similar morphologies for a given extent of mechanical fibrillation, independent of the individual hydrolysis reaction variables (comparing Figure 5(a)–5(c) with Figure S3(a)–S3(c)).

Carboxylation and surface charge

FTIR measurements of CNC and CNF samples verified cellulose esterification through maleic acid hydrolysis as demonstrated previously.^[28] The peak at 1707 cm^{-1} represents the $\text{C}=\text{O}$ bond in carboxylic acid (Figure S4). The peak at 1726 cm^{-1} represents carbonyl bands of the ester groups from cellulose esterification by maleic acid. Conductometric titration was used to determine the carboxyl group contents of the CNC and CNF samples. They in general increased with the increase in hydrolysis severity CHF_G as shown in Figures 6(a) and 6(b), respectively. However specific reaction parameters may have an impact on CNC carboxylation. For CNF production with mild acid hydrolysis severity of $\text{CHF}_G < 1$, such as shown in Figure 4, carboxyl group content is below 0.15 mmol g^{-1} . For typical CNC production of $\text{CHF}_G \approx 4$, CNC carboxyl group content is approximately 0.20 mmol g^{-1} or higher. Surface carboxylation increased sur-

face charge (Figure S5) and facilitated aqueous dispersion as shown by the AFM images in Figures 2, 4, and 5.

Cellulose carboxylation can be enhanced through catalysis or using solvent systems. Carboxylation was quadrupled simply by adding 0.20 mmol L^{-1} sulfuric acid as a catalysts in an aqueous system (Table S3). CNC carboxyl group content as high as 1.5 mmol g^{-1} was achieved when using acetic acid as a solvent together with maleic anhydride and maleic acid.

Conclusions

This study demonstrated integrated production of cellulose nanocrystals (CNC) and nanofibrils (CNF) with tailored properties through hydrolysis of a bleached eucalyptus kraft pulp (BEP) using maleic acid at low temperatures $\leq 120^\circ\text{C}$ and at ambient pressures. A combined hydrolysis factor (CHF) was used to control the hydrolysis severity, and therefore, the extent of xylan dissolution and cellulose depolymerization. Maleic acid hydrolysis produced a small amount of carboxylated CNC with yield of approximately 5% or lower depending on hydrolysis severity. The remaining fibrous cellulosic solid residue (FCSR) as partially hydrolyzed fibers were subsequently fibrillated to carboxylated CNF with an order of magnitude lower energy input than fibrillation without acid hydrolysis. Both the morphological and chemical properties of CNC and CNF can be controlled by CHF, independent of the individual hydrolysis process variables. Using a low solubility di-carboxylic acid, as described, can overcome the problems of un-economical chemical recovery and low strength of mineral acid generated CNF, and would pave the way for low-cost and sustainable commercial production of cellulose nanomaterials.

Experimental Section

Materials

Bleached eucalyptus kraft pulp, BEP, fibers were obtained from a commercial source (Aracruz Cellulose, Brazil). After immersing in distilled water overnight, BEP fibers were disintegrated into a suspension of 5% consistency using a disintegrator (Model 73-06-01, TMI, Ronkonkoma, New York, USA) at 312 rpm for 5000 revolutions. The resultant wet pulp was dewatered and air dried to approximately 8% moisture. The dried fibers had a glucan content of 78.1 wt%, xylan content of 15.5 wt%, and lignin content of 0.1 wt%.

Maleic acid and other chemicals were ACS reagent grade and purchased from Sigma–Aldrich (St. Louis, MO).

CNC and CNF production

The integrated production of CNC and CNF from disintegrated BEP fibers using maleic acid (a solid di-carboxylic acid) hydrolysis follows the procedure described previously.^[28,36] Acid concentration, reaction temperature and time were varied in ranges of 15–75 wt%, $60\text{--}120^\circ\text{C}$, and 5–300 min, respectively. These hydrolysis conditions were abbreviated as MxxTxxTxxx to facilitate discussion. All hydrolysis experiments were conducted at a fiber solid (oven dry weight) to acid solution loading of 1:10 (g mL^{-1}). At the end of hydrolysis, each reaction was thoroughly quenched by adding a 6-

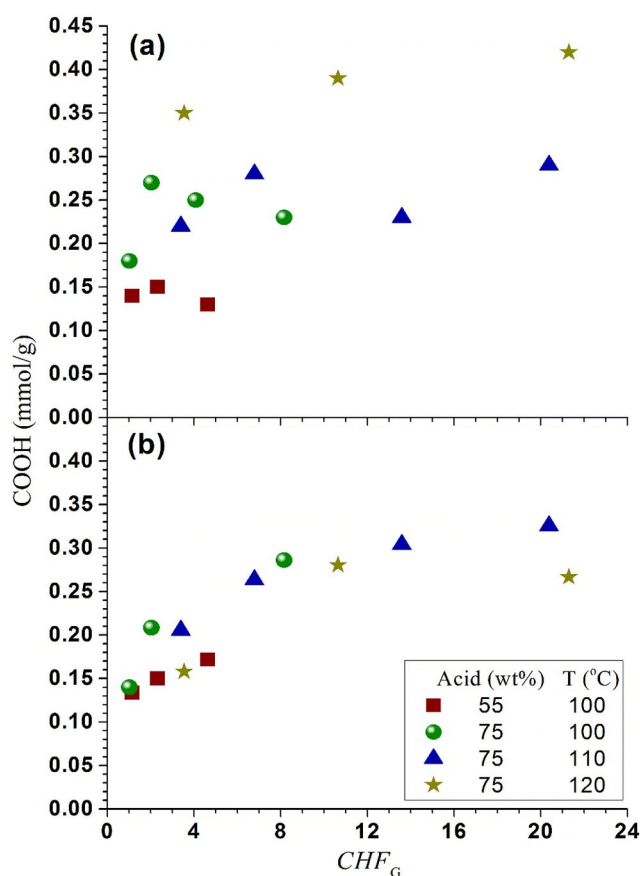


Figure 6. Effects of acid hydrolysis severity, CHF_G , on carboxyl group contents of (a) CNC and (b) CNF. Hydrolysis acid concentration (wt%) and temperature ($^\circ\text{C}$): $\blacksquare$ 55, 100, $\bullet$ 75, 100, $\blacktriangle$ 75, 110, $\star$ 75, 120.

fold volume of de-ionized (DI) water. The slurry was then centrifuged and the precipitated solids at approximately 5 g L^{-1} were dialyzed using a dialysis bag (MEMBRA-CEL MD77 14 kDa, Viskase, Lombard, IL) in DI water until neutral pH was reached with conductivity of approximately $1\text{--}2 \mu\text{S cm}^{-1}$. Finally, the dialyzed suspension was centrifuged at 10000 rpm with CNC remaining in the supernatant (as a colloid). The precipitated FCSR was homogenized using a microfluidizer through a $200 \mu\text{m}$ and an $87 \mu\text{m}$ chamber in series to produce CNF. The feeding FCSR consistency was approximately 0.5 to 1%.

Degree of polymerization (DP)

Cellulose DP was measured using a capillary viscometer after dissolved in a cupriethylenediamine solution. Moisture-equilibrated cellulosic sample (oven dry weight of 0.1 g) was weighed into a conical flask with eight 6-mm glass beads to prepare a 1 wt% cellulosic suspension using DI water. The cellulose was solubilized by adding 10 mL cupriethylenediamine solution of 1 mol L^{-1} . The viscosity of the cellulose solution was determined using a capillary viscometer (150 T447-T450, Cannon Instrument Company, State College, PA) at room temperature after thermal equilibration in a water bath of $25.0 \pm 0.1^\circ\text{C}$. The cellulose DP was determined from the measured intrinsic viscosity of the solution^[37] as expressed by Equation (3):

$$(\text{DP})^{0.905} = \frac{[\eta]}{c} \times k \quad (3)$$

where $[\eta]$ is the intrinsic viscosity of cellulosic solution (g mL^{-1}); c is the concentration of solution (g mL^{-1}); and k is an empirical constant of 0.75. Duplicate measurements were conducted and the averages were reported.

Carboxyl group content

Conductometric titration was used to measure the carboxyl group content. Approximately 0.1 g of cellulosic material was dispersed into 100 mL DI water with agitation. Concurrently, a 10 mmol L^{-1} NaCl solution was added to stabilize the conductance between $100\text{--}200 \mu\text{S m}^{-1}$ as was measured using a conductance meter (Model 35, YSI Incorporated, Yellow Springs, Ohio). The conductance was continually recorded while adding a NaOH solution of 10 mmol L^{-1} dropwise, until the second inflection was observed. The NaOH volume recorded at the second inflection point was used to calculate the carboxyl group content via the following expression [Eq. (4)]:

$$\text{Carboxyl group} = \frac{C_n V_n}{m} \quad (4)$$

where C_n and V_n are the molarity (mol L^{-1}) and consumed volume (mL) of the NaOH solution, respectively; m is the mass (g) of cellulosic sample.

Hydrodynamic diameter and zeta potentials

Dynamic light scattering (DLS) was performed to determine both the hydrodynamic diameter and zeta potential of CNC suspensions using a zeta potential analyzer (Nanobrook Omni, Brookhaven Instruments, Holtsville, NY). CNC sol was diluted to 1 g L^{-1} in advance. Each sample was circulated 5 times for a total of 10 min to obtain averaged hydrodynamic diameter. The mean zeta potentials were averages of 5 measurements.

Morphology

Atomic force microscopy, AFM, was used to exam the CNC and CNF morphology (AFM Workshop, Signal Hill, CA). Briefly, a drop of diluted CNC sol (0.1 g L^{-1}) was deposited onto a clean mica surface and air dried overnight at ambient environment. The heights of CNC and CNF particles were analyzed from the AFM images using Gwyddion imaging analysis software (Dept. of Nanometrology, Czech Metrology Institute, Czech Republic, 64-bit) provided with the AFM system. CNC particles were manually picked from the AFM images to measure their length using Image-pro Plus (Media Cybernetics, Inc., Rockville, MD).

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Keywords: acid hydrolysis severity • carboxylation • cellulose depolymerization • cellulose nanocrystals and nanofibrils • cellulose nanomaterials • xylan dissolution

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