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Tailoring the Structure and Morphology of Low-Molecular-Weight Cellulose Produced during Supercritical Water Hydrolysis

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ABSTRACT: This paper discusses the influence of reactor design and initial consistency when partially hydrolyzing microcrystalline cellulose (MCC) in supercritical water. Experiments conducted on two pilot reactors located in Finland and in Spain showed that stopping the reaction using depressurization instead of quenching, combined with a sufficiently high MCC consistency, led to significant change in reaction kinetics. A complete particle size reduction was achieved after 50 ms only due to additional shear-induced degradation, with a low-molecular-weight product yield above 50 wt % and an average DP of 25. In addition, gradually increasing the MCC consistency triggered precipitation under higher apparent temperature, which affected both the morphology and structure of the product. A range of particles from ribbon-like cellulose II to shish-kebab structures to lamellar cellulose IV with different particle shapes and structural properties.

KEYWORDS: Carbohydrates, Cellulose, Hydrolysis, Hydrothermal treatment, Supercritical water, Water chemistry

INTRODUCTION

With a global market estimated to reach around a billion euros by 2020, microcrystalline cellulose (MCC) is one of few cellulosic products whose demand has been steadily increasing since its introduction in the 1960s. Although the scale of MCC production is small compared to that of other cellulose-based materials, a wide range of applications in several distinct industries promise it a prosperous future as a biobased material.

An odorless, tasteless and relatively inert compound, MCC is usually produced from bleached wood-based chemical pulp but can also be obtained from agricultural residues. The pulp undergoes a moderate hydrolysis treatment using mineral acids, such as hydrochloric acid or sulfuric acid. While acidic conditions trigger the complete hydrolysis of hemicelluloses contained in the pulp, the regions of the cellulose fibers with weaker long-range order are also hydrolyzed down to the so-called level-off degree of polymerization (LODP). The final product, a relatively pure and homogeneous form of cellulose composed of aggregated crystallites whose dimensions correlate with the LODP, is then dried to its commercial form by means of a spray dryer. The operating parameters of the drier determine the final characteristics of MCC as a dry powder, usually with an average particle size between 20 and 100 μm.

In addition, numerous applications require redispersing MCC into aqueous suspensions where it serves as thicker, emulsifier, bulking agent, or wet granulation excipient. The crystallite bundles are first defibrillated by mechanical comminution in water using a homogenizer or a high-shear mixer into submicron particles. They are then coated with a water-soluble polymer such as sodium carboxymethylcellulose, alginate, guar gum, xanthan gum or pectin prior to the drying step. The process was commercialized in the late 1970s, creating a new grade of so-called colloidal MCC, MCC gel, or MCC gum that is used extensively in the food, cosmetic, and coating industries today.

New markets for MCC are being researched, such as a reinforcing phase in biocomposites. MCC has also attracted attention for its ability to be further hydrolyzed. As a pure and...
homogeneous form of cellulose with a relatively low degree of polymerization (DP), MCC is an ideal raw material for producing low-molecular-weight cellulose. The objective is to fill the current low-DP gap in commercial cellulosic products, between that of MCC with a typical DP range of 200–400 and water-soluble cello-oligosaccharides with a DP below 10.11 A few methods have been developed for the controlled depolymerization of MCC, such as ball-milling combined with a plasma treatment, enzymatic synthesis, deacetylation of cellulose triacetate, and dissolution in phosphoric acid.12–15 However, these methods are complex and usually slow, which makes their upscaling into continuous industrial processes challenging.

As an alternative, nearcritical and supercritical water treatments, that is mixing MCC with pure water under very high temperatures and pressures near or above its critical point (374 °C and 22.1 MPa), trigger the rapid hydrolysis of cellulose chains.16 This specific reactivity is due to the combination of high reaction temperatures and the unique properties of nearcritical and supercritical water, such as reduced density, polarity and heat conductivity. In addition, the ionic product of water is modified by the high temperature and pressure, reducing the pH of the water.

In addition to hydrolysis, nearcritical and supercritical water can selectively dissolve the low-molecular-weight cellulose chains formed during the hydrolysis.18,19 And while the short oligomers with a DP below 7–8 essentially remain water-soluble after the treatment, the longer low-molecular-weight chains precipitate into a white solid material exhibiting a cellulose II structure, a typical arrangement for regenerated cellulose.20 The morphology of the precipitate obtained from supercritical water treatment was recently characterized as a simpler, faster and greener alternative for partially depolymerizing MCC and for filling the low-DP cellulose gap.20

In addition to hydrolysis, nearcritical and supercritical water can selectively dissolve the low-molecular-weight cellulose chains formed during the hydrolysis.18,19 And while the short oligomers with a DP below 7–8 essentially remain water-soluble after the treatment, the longer low-molecular-weight chains precipitate into a white solid material exhibiting a cellulose II structure, a typical arrangement for regenerated cellulose.20 The morphology of the precipitate obtained from nearcritical water treatment was recently characterized as composed of nanoscale ribbon-like particles with a DP around 25, suggesting a parallel stacking of the cellulose chains upon precipitation.13,22 However, in this case low conversion yields, the need for an additional filtration step to remove residual MCC-like aggregates, and as well low input MCC consistency suggest that further process investigations are required before any hydrothermal treatment can be considered a viable method for producing low-molecular-weight cellulose.

The high reactivity of cellulose in supercritical water imposes a precise control over the reaction time and especially a rapid mechanism to lower the temperature and stop the reaction after the desired residence time is reached. While most of the continuous reactors in the literature used quenching with cold water as a way to stop the reaction, a group recently proposed a new design where quenching is replaced by a depressurization step using a high-pressure needle valve directly located at the end of the reactor.23 When flowing through the valve, the mixture undergoes an instantaneous decrease in both temperature and pressure without further dilution. In theory, this new design can provide a significantly sharper reaction profile, thus granting superior control over the reaction. To date, this specific reactor was only used with the objective of completely depolymerizing cellulose in a glucose-production scheme, where an exceptional hydrolysis selectivity was reported.24 The effects and potential benefits of using a depressurization design when targeting the production of low-molecular-weight cellulose remain unknown.

The main objective of this work was to determine whether changing the reaction-stopping method, either quenching or depressurization, has an impact on the low-molecular-weight fraction obtained when partially hydrolyzing MCC in supercritical water. Two reactors were used, which shared similar operating principles yet were equipped with different mechanisms for stopping the reaction. In addition to a different design, the two reactors differed in that the depressurization reactor could tolerate high input MCC consistencies, up to levels impossible to reach using the quenching reactor.25 This allowed investigating the combined effect of depressurization and high MCC consistency on the yields, morphology, and structure of the low-molecular-weight materials.

## MATERIALS AND METHODS

### Microcrystalline Cellulose

This work used commercial MCC (Merck, Germany; ref. 102330) with a volume-average particle size of 22 μm as measured using dynamic light scattering (DLS) using a Mastersizer 2000 (Malvern, UK). The material had a number-average DP (DPn) of 70 and a weight-average DP (DPw) of 340, as measured by size-exclusion chromatography. Both the particle size and the molecular weight exhibited narrow distributions, as shown in Figure S1 in the Supporting Information (SI) file.

### Reaction Setups

Two distinct continuous reactor setups were used, whose operating principles are described in separate papers.26,27 The first reactor is located at Aalto University whereas the second reactor is located at the University of Valladolid. Figure S2 in the SI file summarize the operating principles of the two systems as well as the theoretical temperature and pressure reaction profiles.

At Aalto University, the MCC suspension was first pressurized to 25 MPa using a high-pressure metering pump equipped with a Teflon membrane head (LEWA, Germany) that had a maximum tolerated MCC consistency of 1.0 wt %. The suspension was mixed with supercritical water preheated at around 520 °C, which brought the suspension to a temperature around 395 °C into the one end of a 55 mm tubular reactor with an internal diameter of 3.0 mm (reaction volume 390 μL). The mixture was quenched at the other end of the reactor by a perpendicular stream of cold water, which decreased the temperature down to around 270 °C. The product flowed then through a heat exchanger for further cooling down and finally through a relief valve for depressurization to atmospheric pressure. This system is subsequently referred to as the quenching reactor.

At the University of Valladolid, the MCC suspension was pressurized to about 25–26 MPa using a high-pressure LEWA metering pump equipped with a plunger head which accepted stock MCC consistencies up to 15 wt %. The suspension was mixed with a flow of deionized supercritical water by means of a T-shaped junction. The supercritical water stream was preliminarily preheated to about 480 °C, which brought the suspension to a temperature of approximately 395 °C. The reaction took place within a 47 mm tubular pipe, which combined with fittings and connectors amounted to a total length of approximately 350 mm. The reaction took place within a 2.2 mm (reaction volume 440 μL), before being stopped by a sudden decompression through a needle valve (Autoclave Engineers, USA). This instantaneously decreased the temperature and pressure down to around 190 °C and 1.5 MPa, respectively. The product stream was further cooled down upon passing through two successive heat...
exchangers. This system is subsequently referred to as the *depressurization* reactor.

Five samples were produced using either of the two reaction setups. Table S1 in the SI file summarizes the main experimental parameters for each of the samples. Under these conditions (pressure 25.0–26.5 MPa, temperature 393–394 °C, reaction time 47–55 s) MCC was only partially hydrolyzed and all samples comprised significant amounts of suspended solids. The solid product, including post-reaction precipitates, was treated as a single fraction. Several papers already described in details the kinetics of cellulose hydrolysis in supercritical water as well as the mechanisms for the formation of water-soluble degradation products through competing dehydration and retro-aldol condensation reactions.\(^{28,29}\) With the production of low-molecular-weight cellulose in mind, the solid material was deliberately the sole focus of this study.

**Product Analysis.** The samples produced with the two reactors were analyzed according to the same procedure, summarized in Figure S3 in the SI file. The samples were allowed to settle for a few days, after which the yield of the solid fraction was measured using gravimetry and 0.45 μm GHP syringe filters (PALL, USA), weighted before and after filtering a known amount of product and drying overnight at 105 °C. The solid and liquid fractions were separated by centrifuge. The yield of glucose and water-soluble cello-oligosaccharides was determined from the liquid fraction using HPLC according to a method described in the literature and further detailed in the SI file.\(^{30}\) The molecular weight distribution, structural characteristics and particle morphology of cellulose were analyzed from the solid fraction.

Size-exclusion chromatography (SEC) used a Dionex Ultimate 3000 system equipped with four identical PLgel Mixed-A columns (Agilent, USA) and a Shodex RI-101 refractive index (RI) detector (Showa Denko K.K., Japan). The samples were first activated and dissolved upon successive solvent exchange steps in water, acetone, DMAC, and DMAC/LiCl (90 g·L\(^{-1}\)) before being diluted with DMAC for a final LiCl concentration of 9.0 g·L\(^{-1}\), the eluent of the columns. The RI signal was calibrated against a series of 11 narrow pullulan standards (Standard Polymer Service and Fluka, Germany), with molecular weights ranging from 342 Da to 2560 kDa.

Scanning electron microscopy (SEM) used a Sigma VP (Zeiss, Germany) setup. One drop of cellulose suspension was placed on a high-purity mica surface and dried on a hot plate at 60 °C. The sample was sputtered using an Emitech K100X Glow Discharge apparatus (Quorum Technologies, UK) equipped with an Au/Pd electrode with a current of 30 mA for 60 s. The micrographs were recorded using a secondary electron detector, an accelerating voltage of 1.0 kV, and a working distance of 5 mm.

Wide-angle X-ray scattering (WAXS) measurements were performed on dried, powdered samples in perpendicular transmission mode using an image plate detector setup. A Montel multilayer monochromator was used to select the Cu Kα energy (8.0 keV). The powders were hand-pressed into metal rings with a thickness of 2.1 mm and sealed with Mylar foils. The WAXS intensities were corrected for the read-out noise of the detector and normalized with the primary beam transmission before Mylar and air background subtraction. After this, polarization, flat panel, and irradiated volume corrections were applied to the intensities.

Solid-state cross-polarization magic-angle-spinning carbon-13 nuclear magnetic resonance (CP/MAS \(^{13}\)C nNMR) spectra were acquired on a Bruker AVANCE III spectrometer operating at 100.61 MHz using a 4.0 mm ZrO\(_2\) rotor. The following parameters were used: a relaxation delay of 5.0 s, a spectral width of 306 ppm, 40k transients of 2k data points, a contact time of 1.0 ms, and a spinning rate of 8.0 kHz. The spectra were then processed using TopSpin 3.0 software.

## RESULTS AND DISCUSSION

This section is divided into three subsections. The first subsection aims at identifying the differences caused by the two reactor designs in terms of yield, particle size, and molecular weight distribution. These results indicate that the mechanical forces generated during *depressurization* at high consistency may induce additional shear-induced degradation. The second subsection further investigates the influence of cellulose consistency and postreaction temperature on the morphology and structure of the low-molecular-weight product. Finally, the third subsection deals with the specific energy demand for the producing the material, stressing the need to work under high MCC consistencies in order to make the process less energy intensive.

**Reactor Design and Shear-Induced Degradation.** The first sample was produced using the *quenching* setup from a 1.0 wt % MCC suspension. A similar sample was produced with the *depressurization* setup also from a 1.0 wt % suspension for direct comparison. In addition, three additional samples were produced with the *depressurization* setup at higher consistency, from 5.0, 9.0, and 15 wt % suspensions. The amount of precipitated cellulose, water-soluble cello-oligosaccharides with a DP range of 2–10, and glucose in each sample is shown in Figure 1, while corresponding numerical data can be found in Table S2 in the SI file. The remaining mass balance was indistinctly composed of various noncellulosic degradation products, unidentified water-soluble or gaseous compounds, as well as solid buildup in the pipes during reactor operation, which in total accounted for 27–51 wt % of the mass balance; relatively high but common levels for such a process.\(^{20}\)

The *quenched*, diluted sample had the lowest solids yield, slightly below 40 wt %. In contrast, its *depressurized* counterpart contained significantly higher solids amounts, accounting for about 60 wt % of the product. The 1.0 wt % *depressurized* sample also exhibited lower amounts of cello-oligosaccharides and glucose. The lower amounts of solids and higher amounts of water-soluble hydrolysis products obtained using the *quenching* reactor are likely the result of a difference in reaction temperature and pressure profile between the two reactor designs, as depicted in Figure S2 in the SI file. Heat transfer limitations upon mixing the product with cold water, which only decreases the temperature down to 270 °C, inevitably led to further cellulose degradation.

Increasing the cellulose consistency had a visible effect on the product yield. A previous study, in which lower yields and selectivity were obtained at higher consistency, showed that the hydrolysis kinetics are affected when the consistency is
increased. This trend was confirmed in this study: although all  
depressurized samples retained high solid contents, the yield  
slightly decreased from 60 to 54 wt % upon increasing the  
initial cellulose consistency from 1.0 to 15 wt %. In addition,  
increasing the MCC consistency first resulted in significantly  
higher amounts of glucose and cello-oligosaccharides at 5.0 wt  
%, which accounted for over 14 wt % of the sample. Moreover,  
further increasing the consistency resulted in comparatively  
lower amounts of cello-oligosaccharides, yet with an increase in  
both glucose and unidentified products. This indicates that  
above a certain level, further increasing the cellulose  
consistency leads to sensibly higher cellulose depolymerization  
and degradation.

The hydrolysis-enhancing effect of increasing the cellulose  
consistency on the depolymerization in a depressurization  
design was also clearly visible on the molecular weight  
distributions of the products, as shown in Figure 2. As  
expected from the yields, the supercritical water treatment  
triggered severe cellulose depolymerization, clearly visible on  
the molecular weight distribution of the solid products. With  
the depressurization design (Figure 2a) after being in contact  
with supercritical water for only about 50 ms, the weight-
average DP dropped from the initial 340 anhydroglucose units  
down to a $DP_w$ of 120, 50, 27, and 25 with increased MCC  
consistency. The same products had polydispersity indexes of  
2.9, 2.1, 2.2, and 2.3, respectively. The 1.0 wt % sample  
exhibited limited cellulose depolymerization and high amounts  
of residual high-DP cellulose, which concurs with the low  
amounts of water-soluble products observed in Figure 1. In  
contrast, MCC consistencies of 5.0 wt % and above yielded  
significantly more depolymerized samples. The same distribu-
tions were narrowly distributed and unimodal, with no visible  
high-DP shoulder. The hydrothermal depolymerization of  
cellulose in supercritical water was described as following a  
random chain scission model leading to a Flory–Schulz DP  
distribution. Consequently, the molecular weight data clearly  
confirms that the samples produced at higher cellulose  
consistency underwent a larger number of chain scissions, all  
other parameters being equal.

In contrast, the quenching design with a 1.0 wt % MCC gave  
a product with an average $DP_w$ of 80 and a polydispersity of  
4.2 (Figure 2b). The molecular weight distribution also  
exhibited significant amounts of residual high-DP chains,  
although smaller in quantities than for its 1.0 wt %  
depressurized counterpart. A comparison between the two  
reactor designs in terms of molecular weight distribution  
confirms the observation already made from the yields: the  
quenching design cannot provide as sharp a temperature profile  
as the depressurization method. Using the former resulted in  
slightly greater cellulose depolymerization after the same  
reaction time.

In addition to yields and molecular weight distributions,  
SEM images showed the effect of the treatment on the size and  
shape of the particles, as shown in Figure S4 in the SI file. In  
brief, whereas the initial MCC was composed of coarse and  
inhomogeneous particles, mixing MCC in supercritical water  
resulted in a considerable reduction in particle size. All the  
samples contained large amounts of submicrometer particles.  
At the lowest initial MCC consistency of 1.0 wt %, some larger  
partially degraded, MCC-like particles remained visible in both  
the quenched and the depressurized samples. However, large  
particles were no longer observed in the three samples  
produced at higher MCC consistencies.

The decomposition of the particles is generally described  
using a shrinking core model, in which the particle size and the  
reacting core shrink simultaneously. However, this model  
is not universally accepted due to the minor role played by the  
initial particle size in the overall hydrolysis mechanism; instead,  
the degree of cellulose crystallinity was proposed as the  
parameter governing the reactivity of MCC. Here the  
shrinking core model alone could not explain the observed  
reduction in particle size because the three most concentrated  
samples still gave a solid yield over 50 wt % while containing  
no MCC-like residual particle. The initial MCC consistency  
appears as an important additional parameter influencing both  
the final particle size and the hydrolysis kinetics when the  
depressurization setup is used.

One possible explanation for the change in particle size is  
that the increased amounts of cellulose particles create  
additional particle–particle friction forces. Shear forces are  
already known to be able to disintegrate cellulose, and are used  
for instance in high-pressure homogenization to produce  

![Figure 2](image-url)  

*Figure 2.* Molecular weight distribution of the solid fraction obtained after supercritical water hydrolysis (a) using a depressurization design and (b) using a quenching design. Arrows show the weight-average degree of polymerization.
nanocellulose\textsuperscript{22,33} In that case, a sufficiently high cellulose consistency is beneficial in order to enhance the particle size reduction.\textsuperscript{34} In the depressurization setup the suspension undergoes high shear rates upon flowing through the small gap of the needle valve gap under high flow velocity. A simple estimate of the maximum shear rate during the reaction, estimated according to Equation S1 and detailed in Table S3 in the SI file, showed a value of about 2600 s\(^{-1}\) for the quenching reactor, yet slightly above 15 000 s\(^{-1}\) for the depressurization setup. High shear could result in additional mechanical shear-induced degradation that contributes in breaking down the large cellulose bundles and thus enhances the cellulose hydrolysis at the end of the reaction.

**Postreaction Temperature and Product Properties.** Recently, the morphology of low-molecular-weight cellulose precipitated from nearcritical water treatment was characterized as composed of ribbon-like nanoscale particles.\textsuperscript{22} The particles had a shape similar to that of the material precipitated after either acetolysis of cellulose triacetate or hydrolysis in phosphoric acid.\textsuperscript{13,15} The morphology of individual cellulose particles in the five studied samples, as observed with high-resolution SEM images, is shown in Figure 3. The 1.0 wt % quenched sample (Figure 3a,b) was uniformly composed of ribbon-like nanoscale particles that were several micrometers in length and around 50 nm in width, and whose morphology strongly resembled the low-molecular-weight materials obtained from either nearcritical water treatment, deacetylation of cellulose triacetate, or phosphoric acid hydrolysis.\textsuperscript{11,13,22}

In contrast, in the depressurized (Figure 3c,d) sample three types of shapes could be observed: short ribbon-like particles, square-looking lamellar particles with a side dimension up to around 200–300 nm, as well as elongated, so-called “shish-kebab” structures. The same three types of particles composed the depressurized sample from a 5.0 wt % MCC suspension (Figure 3e,f). Both ribbon-like and lamellar shapes could be observed; however, comparatively there was a larger number of lamellar particles. In addition, the lamellar shapes were better formed than in the 1.0 wt % sample and exhibited smoother surfaces. The particles had a lower tendency to aggregate with each other. Further increasing the MCC consistency to 9.0 wt % yielded a mixture of ribbon-like and lamellar particles (Figure 3g,h). However, no shish-kebab structure was found. As for the material obtained from a 15 wt % cellulose suspension (Figure 3i,j), it seemed as nearly entirely constituted from well-defined, square-like lamellar particles. A few ribbon-like particles were still visible but were a minority. No aggregated structures could be observed; instead, the particles stacked horizontally onto the mica substrate.

An explanation for such radical changes in morphology can be found in the literature on cellulose crystallization from the mid-1970s and early 1980s. Various crystallization attempts of low-molecular-weight cellulose obtained from the acetolysis of cellulose triacetate provided a theoretical framework entirely relevant to the present supercritical water hydrolysis research. When performed at temperatures below 90 °C, the slow precipitation of low-molecular-weight cellulose with a DP of 15 yielded ribbon-like nanoscale cellulose II particles similar in shape and size to the ones observed in the 1.0 wt % quenched sample.\textsuperscript{13} When seeded with cellulose I microfibrils, the slow precipitation of low-DP cellulose yielded elongated, shish-kebab structures resulting from the growth of cellulose II lamellae perpendicular to the microfibril axis.\textsuperscript{35,36} In addition, lamellar single cellulose IV\(_d\) crystals were obtained when the precipitation was performed at a higher temperature of 150 °C.\textsuperscript{37} However, at a slightly lower precipitation temperature of 120 °C, hybrid cellulose II–cellulose IV\(_d\) crystals were formed.
Moreover, increasing the DPn of cellulose from 22 to 40 resulted in badly formed lamellar crystals.38

At the end of the reaction, the contact between the dissolved low-molecular-weight cellulose chains and water under ambient conditions triggered the precipitation of the former due to a solubility differential. In addition, the higher the cellulose concentration, the more cellulose—cellulose interaction related to cellulose—solvent interactions, and the faster the precipitation occurred. As the low-molecular-weight product underwent a gradual temperature decrease at the end of the reaction due to quenching or depressurization as well as further product cooling, increasing the MCC consistency thus resulted in a precipitation under higher apparent temperature. This in turn affected both the structure and the morphology of the precipitated material. Under low MCC consistency and low precipitation temperature, cellulose I aggregates remained and ribbon-like cellulose II crystals were formed. Upon increasing the consistency, cellulose II and badly formed cellulose IVII crystal mixtures were formed as well as shish-kebab structures seeded from residual cellulose I. When the consistency was further increased, residual cellulose I was no longer available and shish-kebab structures disappeared. The DP also decreased, which resulted in cellulose IVII lamellae with better defined shapes. Finally, the highest precipitation temperatures reached at high MCC consistency favored the formation of pure lamellar cellulose IVII crystals.

A structural analysis of the materials confirmed the predictions from the literature as far as the relationship between supramolecular structure and particle morphology is concerned. The structural changes between MCC, the 1.0 wt % quenched sample, as well as the 15 wt % depressurized sample is presented in Figure 4. WAXS intensities are shown in Figure 4a. The three samples appeared highly crystalline; however, while MCC was composed of pure cellulose I, the depressurized sample contained some cellulose II, visible on the 110 reflection at 12.3°, with an estimated 26% contribution. Previous X-ray studies revealed the formation of cellulose II when using a quenching design and dilute cellulose consistencies.8,20,21 However, here the double peak corresponding to the 110 and 110 reflections of cellulose I was absent; instead, a strong single reflection at 15.5°, typical for the cellulose IVII allomorph, was present.8 Unlike its sibling IVI, whose existence is contested and whose structure has been assimilated to fragmented cellulose I, cellulose IVII, analytically obtained upon heating up cellulose II in water or glycerol, has been confirmed as a genuine cellulose allomorph.39,41 The quenched sample featured similar yet less pronounced cellulose II and cellulose IVII reflections. The sample had a slightly lower cellulose II contribution, estimated at 20%. In addition, its spectrum revealed residual cellulose I-like material, indicated by small peaks corresponding to the 110, 110, and 004 reflections of cellulose I.

The 13C ssNMR spectra of the same three materials, shown in Figure 4b, supported the observation that the two solid samples were composed of cellulosic materials yet with significantly different structures. The exact shifts as well as deconvoluted C4 domain in Table S4 and Table S5 in the SI file, respectively, Minor differences could be observed in the C6 domain between the quenched and the depressurized sample, confirming the presence of different allomorphs within the samples as the shape of the C6 region did not match the deconvolution expected for high-DP cellulose II.42 The overall NMR spectra of the two products did, however, match fairly well the expected shape of the peaks for low-DP cellulose.39 In addition, the presence of higher peak density in the 82–84 ppm region, revealed by a deconvolution of the C4 domain presented in Figure S5 in the SI file, was characteristic of the presence of cellulose IVII allomorph in the depressurized sample.39 The deconvolution also revealed a simultaneous decrease in crystalline domains and increase in inaccessible fibril surfaces, confirming a major rearranging of the cellulose chains during the treatment. This data shows that the entire cellulosic material underwent structural changes during the treatment, including the higher DP regions and not only the precipitated low-molecular-weight fraction. 

Energy Aspects. Despite the simplicity, absence of chemical use, as well as low environmental impact of using supercritical water hydrolysis the downside of the process is clearly the high heating requirements because it is necessary to heat up pressurized water up to almost 500 °C prior to mixing it with cellulose suspension. A previous paper reported a minimum value of 3250 kJ·g−1 for a pure fraction of low-molecular-weight cellulose precipitated from nearcritical water treatment.26 For comparison, other energy-intensive mechan-
Consistency is logical considering that the mass quenching step. This lower energy requirement with increasing relatively low yield, as well as the extra dilution created by the applications such as Pickering emulsion stabilization. In characteristic for nanocellulose and highly sought-after in intensive. It should also be noted that in addition to increasing for this process to become economically viable and less energy requirements. The energy cost of production decreased contrast, all depressurized samples showed significantly lower energy requirements. The energy cost of production decreased considerably with increased MCC consistency, with a value of 66 kJ g⁻¹ for the most concentrated depressurized sample. The difference is due to a combination of low MCC consistency, relatively low yield, as well as the extra dilution created by the quenching step. This lower energy requirement with increasing consistency is logical considering that the mass flows were the same throughout the four depressurized samples and because the energy demand for heating up the supercritical water stream remained essentially the same whether the initial consistency was 1.0 or 15 wt %.

Importantly, the decrease in energy requirement as well as change in structure and morphology did not significantly alter the rheological properties of the materials. All samples showed high viscosity, a weak gel-like behavior with clear shear-thinning properties, as shown in Figure S6 in the SI file, as well as exceptional colloidal stability at high consistency. Only the quenched sample exhibited slightly higher viscosity, likely due to the higher aspect ratio of its particles. These properties are characteristic for nanocellulose and highly sought-after in applications such as Pickering emulsion stabilization. In addition, the high level of colloidal stability indicates that these products could also serve as a chemical-free replacement for colloidal MCC.

Therefore, working under high MCC consistency is critical for this process to become economically viable and less energy intensive. It should also be noted that in addition to increasing the consistency of the feedstock, two ways have recently been devised in order to improve the economic efficiency of the process. The first solution is to further concentrate the product using a flash separator. The second solution is to use a so-called desuperheater instead of a needle valve to stop the reaction, which can in theory lower the temperature while keeping the pressure high, thus limiting the energy loss during depressurization.

**CONCLUSIONS**

The results highlighted the importance of choosing the right method to stop the reaction when performing the partial hydrolysis of MCC as this had a considerable impact on the structure, the morphology, and the DP of the samples. Evidence of additional shear-induced degradation was observed, triggered by the combination of a depressurization valve and sufficiently high cellulose consistency were used, which further decreased the molecular weight of the product down to an average DP of 25. The higher the cellulose consistency, the more visible the effect, only at the cost of a few percent which remained over 50 wt % even at the highest consistency.

In addition, the data showed that increasing the cellulose consistency also affected the apparent precipitation temperature. The higher the consistency, the faster the precipitation and the higher the precipitation temperature. This significantly affected the morphology and structure of the low-molecular-weight product. Structural analyses confirmed that cellulose IVα lamellae were formed under high precipitation temperature in a depressurization design, while cellulose II ribbons were obtained at lower precipitation temperatures in a quenching design. All products showed high colloidal stability as well as a shear-thinning rheological behavior that is typical for nanocellulose.

Therefore, these results show that supercritical water hydrolysis is relevant for the environmentally friendly production of low-molecular-weight cellulose. This process becomes all the more pertinent within a biorefinery scheme, in which the properties of the cellulosic products can be tailored according to specific uses. With a theoretical energy cost of production as low as one tenth of that of the quenching design under low MCC consistency, future research on supercritical water hydrolysis must consider the potential combined benefits of depressurization and high input cellulose consistency for partially hydrolyzing MCC.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b04296.

Characterization of the MCC material; thorough description of the experimental setup, product analysis scheme, and sample composition; ssNMR peak analysis and deconvolution; details about the flow regime, shear rate, and energy calculations; rheological measurements (PDF)

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Notes

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