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A study of the production of cellulose nanocrystals through subcritical water hydrolysis

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ABSTRACT

Cellulose nanocrystals (CNC) have a wide range of potential applications. For classical CNC production, amorphous cellulose is hydrolyzed using concentrated sulfuric acid; however, subcritical water can also accomplish this objective. Here, for the first time to the best of our knowledge, we study the experimental conditions employed in subcritical water treatment, to investigate the behavior of the technique and the properties of the products in an experimental domain of 120–200 °C temperature and 8.1–20.3 MPa pressure. We observed the CNC formation in all the different reaction conditions tested; however, the yields were lower than the classical production of CNC. The yield of the reaction was directly proportional to the pressure. On the other hand, temperature had a directly proportional effect on the stability of the suspension and an inversely proportional effect on the whiteness of the CNC produced. The most drastic reaction conditions produced CNCs was chemically indistinguishable from raw cellulose, having the same crystalline structure and crystallinity index, albeit with nanometric size.

1. Introduction

Cellulose nanocrystals (CNCs) are produced by cellulose hydrolysis under strong acidic conditions. The most common processes use concentrated sulfuric acid solutions; however, other acids have also been used (Habibi et al., 2010; Mariano et al., 2014; Moon et al., 2011). Different procedures to prepare CNC from several raw materials can be found in the literature and recently reviewed by Jonoobi et al. (2015). With the growing need for greener processes, acid hydrolysis techniques become inadequate because they produce large amounts of effluents and require large amounts of water for the washing steps.

Some greener solutions are also been reported, like the use of enzyme-assisted hydrolysis process (Siqueira et al., 2011), the use of ultrasonic assisted process to improve acid hydrolysis (Guo et al., 2016; Lu et al., 2015, 2013) and the use of ionic liquids to promote the hydrolysis (Mao et al., 2015). In this context, Novo et al. (2015) showed that subcritical water could also promote the hydrolysis of amorphous and semi-crystalline regions of cellulose. This process shows great potential for CNC production because it uses exclusively water as the hydrolyzing agent, and although it demands more energy due to the use of a high pressurized reactor, the overall process would be less expensive, since it does not require many washing steps, as discussed by Novo et al. (2015). However, more studies need to be performed exploring other reaction conditions in order to explain the mechanism of the hydrolysis with subcritical water. Fluids at sub- and supercritical conditions show an increase in the diffusion coefficient and reduction of the dielectric constant (for polar solvents). Both properties could have a positive effect in the disruption of cellulose amorphous domains and thus promoting the accessibility of water to cleave the glycosidic bonds (Adschiri et al., 2011).

This study attempts to elucidate the role of temperature and pressure in the hydrolysis mechanism and their influence on the quality of the produced cellulose nanocrystals.

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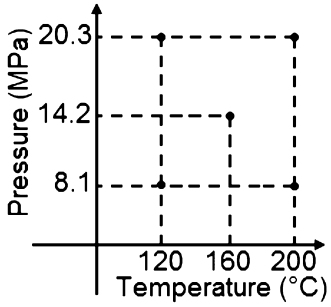

Fig 1. Representation of the experimental design.

2. Material and methods

2.1. Materials

The raw cellulose used for obtaining CNCs was commercial microcrystalline cellulose Avicel® (FMC Corporation, Philadelphia), having nominal particle size of 20 μm. All hydrolysis reactions were performed using distilled water as the sole reagent. Dialysis membranes with molecular weight cut-off of 6–8 kD (Spectra/Por® 1) were purchased from Spectrum Labs.

2.2. Study of the subcritical hydrolysis of cellulose

The reactions were carried out in a 100-mL stainless steel reactor of SFT–250 SFE/SFR System (Supercritical Fluid Technologies, Inc.), operating in batch mode (Novo et al., 2015). The study was performed using a 2^2 experimental design, with temperature (120 and 200 °C) and pressure (8.1 and 20.3 MPa) as the factors and the levels (Fig. 1). For each reaction, the reactor with 1 g of the raw cellulose (dry basis) was completely filled with distilled water and was then heated to the desired reaction temperature. The heating and cooling rates of the reactor were ~6 and ~3 °C min^{-1}, respectively. The reaction was maintained for 60 min at the reaction temperature. The pressure inside the reactor was controlled by injecting small volumes of water with a liquid precision pump or removing water with the restrictor valve. Fig. 2 shows a scheme of the reaction set-up.

Unhydrolyzed raw cellulose and the CNC produced by hydrolysis were separated from the solution containing hydrolyzed sugars and degradation products using a Pyrex® Buchner funnel with glass-fritted disc ASTM 10–15. The CNCs could be separated by filtration owing to their low stability, which was confirmed by observing the absence of laser diffraction by the filtrate solution.

Soluble sugars and other by-products were removed from the solid sample by dialysis against distilled water for 5 days. The resulting suspension was treated with a 250 Sonifier (Branson) for 3 min at 100 W in pulses for half the time and then filtered through a 1-μm canvas (NITEX 3-1/1—Sefar) to separate the unhydrolyzed cellulose from the CNC suspension.

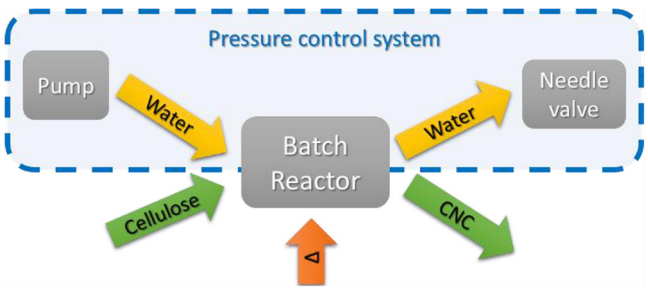

Fig. 2. Scheme of the reaction set-up.

2.3. Characterization of the CNC

The responses to the experimental design were in terms of CNC characterization that was performed by atomic force microscopy (AFM), dynamic light scattering (DLS), colorimetric analysis, X-ray diffraction (XRD), and thermogravimetric analysis (TGA). Other than these, the yield of CNC was also used as a response to the experimental design.

For DLS and AFM analyses, diluted aqueous suspensions of ~0.001% wt of CNC were dispersed with a 250 Sonifier (Branson). The average hydrodynamic diameter (Z_D) of the CNCs were determined in a Vasco® I particle size analyzer (Cordouan Technologies), in which the measurements were performed using the cumulant method, with 10 acquisitions per analysis. AFM images were acquired in a Nanoscope IIIa microscope (Veeco Instruments) working in tapping air mode, with a scanning probe of silicon and a maximum radius of curvature of 10 nm. Information about the morphology of the CNCs was obtained from the AFM images. The average length and width of the CNCs were determined using the open-source software ImageJ, obtained using the dimensions of about 60 particles distributed in different images.

The XRD patterns were recorded in a PW 1720 X-ray generator (Philips) operating at 45 kV and 40 mA with Cu Kα radiation (λ = 0.154 nm) with angle range of 6–56°. The analysis was performed on dried pulverized samples. Using XRD analysis, the crystallinity index of the samples was calculated according to Eq. (1) (Lin and Dufresne, 2014; Novo et al., 2015; Segal et al., 1959), where I_{200} is the height of the peak ~22.5° and I_{am} is the value of the baseline ~18.0°.

$$C_I = \frac{I_{200} - I_{am}}{I_{200}} \times 100 \quad (1)$$

Colorimetric analysis was performed using a spectrophotometer Elrepho (Lorentzen & Wettre) designed for the paper industry. For this purpose, films were prepared using the CNC suspensions and their reflectances at 457 nm were measured against an opaque background, since some of the samples gave translucent films. Thus, the percentage of measured whiteness can be used as an index of comparison between samples.

The thermal stability of the CNCs was evaluated using a TGA-6 (PerkinElmer). The thermal analyses were performed under a constant air flow of 50 mL min^{-1}, with a heating rate of 10 °C min^{-1} up to 700 °C. For these analyses, powdered samples of 10–20 mg were used.

The experimental design results were analyzed using the software Statistica 7.0. The variables used as responses in the experimental design analysis were the yield (Y), length (L), width (W), aspect ratio (L/W), Z_D, whiteness (B), average temperature of degradation (peak on the differential thermal analysis (DTG)) and crystallinity index (C_I) of the CNCs. A model and a statistical analysis of the significance of the experimental design were developed for each response. The polynomial equation that describes the models is given by Eq. (2), where R is the desired response, a_0, a_1, a_2, and a_3 are the regression coefficients for the model, T is the temperature (°C), and P is the pressure (MPa).

$$R = a_0 + a_1 P + a_2 T + a_3 PT \quad (2)$$

2.4. Chemical characterization of the CNC

The chemical characterization of the CNCs involved Fourier-transform infrared (FTIR) spectroscopy, solid-state ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopy, and elemental analysis. These characterization studies were not performed for all the samples in the experimental design and were used to verify