



Study of steam explosion pretreatment and preservation methods of commercial cellulose

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ABSTRACT

Steam explosion (150–200 °C, 5–30 min) was performed on a commercial cellulose presented in two configurations (fiberized and compact sheet) and its effect on their chemical and physical properties was studied, along with the influence of two different preservation methods (acetone drying and freezing) after pretreatment. No degradation compounds were produced during pretreatment, although solid recovery (R_S) decreased with temperature from 90% to 62%. Similar particle size and surface conditions (increased porosity) were found for both types of pretreated samples despite the extremely different initial configuration. Crystallinity diminished for 150 °C samples, but 200 °C pretreatment promoted recrystallization. Pretreatment also reduced polymerization degree, although enzymatic accessibility did not improve. Both acetone and freezing processes extremely affected cellulose properties. Acetone drying counterbalanced crystallinity and enzymatic accessibility variations of pretreated samples, while decreasing polymerization degree. Freezing dramatically decreased enzymatic accessibility of pretreated samples down to 15.8%.

1. Introduction

Fossil sources depletion has increased prices of petrol-derived polymers and natural fibers are starting to be considered a suitable alternative due to their easy processing and eco-friendly advantages. Significant amounts of natural fibers are currently considered a waste, and their disposal creates harmful environmental problems (Oliveira et al., 2013), so they can be a promising renewable raw material due to their abundance and low cost. Among the new alternative uses, polymeric materials based on natural fibers are emerging in the last decades for numerous diary and important purposes, such in biomedical or automotive industries (Thakur & Thakur, 2014).

Natural fibers are a well-known source of cellulose, since it is its principal component ($\geq 60\%$). Usually, chemical methods are used to produce cellulose rich pulp, which is commercialized as roll-sheets of compacted fibers, being transformed back into fibers by mechanical processes such as carding.

A pretreatment like steam explosion could be a useful step in cellulose production processes for both substituting physical processing of cellulose rolls and improving cellulose fibers versatility, opening its structure and increasing its porosity, reactivity and specific surface, with minimum degradation. It is an innovative and effective pretreatment which has provided interesting results for lignocellulosic biomass. It consists in applying high-pressure saturated steam to biomass for

short times, followed by a sudden decompression. Its advantages over chemical methods are low environmental impact and capital investment, energy efficiency, and the possibility of treating larger amounts of biomass (Jacquet et al., 2012). Commonly, steam explosion processes take place at temperatures between 150 °C and 250 °C for times varying from 2 to 60 min. Severity factor (SF) of the process is calculated from these two variables by Eq. (1) (Jacquet et al., 2011):

$$SF = \log_{10}[t_{SE} \times \exp((T - 100)/14.75)] \quad (1)$$

Where t_{SE} is reaction time (min) and T is the steam temperature (°C). The steam breaks and modifies the structure and could even provoke the hydrolysis of the glycosidic bonds, producing organic acids due to shearing forces during decompression (Medina et al., 2016). The global effect of both processes involves modifications on physical and chemical properties of the biomass such as reactivity (related with specific surface area), viscosity or crystallinity among others (Sui & Chen, 2016), which can be beneficial for ulterior industrial uses of cellulose fibers. When applied to lignocellulosic materials, steam explosion treatment lead to opened structures, modification of physicochemical properties such as the specific surface area, depolymerization and solubilization of hemicellulose, and increase of cellulose enzymatic hydrolysis degree, assisting following valorization processes. (Medina et al., 2016; Neves, Pitarello, & Ramos, 2016),

However, scarce information about its effects on commercial

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cellulose fibers could be found. (Jacquet et al., 2011) studied the effect of different conditions during the steam explosion on degradation of pure cellulose, finding degradation products as 5-hydroxymethyl furfural (HMF) for severity factors higher than 4.0. In their subsequent study, (Jacquet et al., 2012) reported no improvement on enzymatic hydrolysis rate after steam explosion. Nevertheless, they observed modification on physicochemical properties of cellulose fibers, such as an increase in water retention and crystallinity index values. Water retention after treatment might play a significant role not only during pretreatment but afterwards as well, even accelerating cellulose degradation (Sui & Chen, 2016).

(Yamashiki et al., 1990) used acetone instead of the traditional oven drying, to avoid drastic structural changes due to temperature. Nevertheless, they did not consider that acetone might also have some other effects. After drying, samples are usually stored in $-20\text{ }^{\circ}\text{C}$ freezers, but the formation of ice crystallites might harm microfibrils structure. To the best of authors' knowledge, no study has been conducted for systematically evaluating the influence of steam explosion in compacted cellulose pulps or the influence of the preservation methods on physical properties.

The aim of this work was to study steam explosion as a pretreatment for commercial cellulose samples presented in two different handlings, to explore the possibilities of this treatment as a substitute for other mechanical pretreatments and its effects on the modification of several physicochemical properties of cellulose fibers regarding a future use. To that end, several analyses were performed such as chemical composition, particle size distribution, crystallinity rate, limiting viscosity number and degree of polymerization. In addition, two different preservation methods of pretreated samples (acetone washing and freezing) were tested to study the effects of preservation methods could have on the stability and quality of pretreated samples.

2. Materials and methods

2.1. Raw material

One bleached commercial cellulose was used in this work, obtained 100% from softwoods pulp, purified from lignin and hemicellulose and presented in two different handlings: Compacted Cellulose (CC) was provided as a compacted sheet and cut in small squared pieces ($10 \times 30\text{ mm}$ approx.) for better manipulation. Fiberized Cellulose (FC) was obtained by mechanical fiberization of the sheet.

Chemical composition (moisture, cellulose, hemicellulose, lignin, extractives and ash content), particle size distribution, enzymatic hydrolysis kinetics, optical and electronic scanning microscopy analysis, soluble impurities (short-chain organic acids, HMF, furfural, and phenols), crystallinity index and limiting viscosity number were analyzed.

2.2. Steam explosion experiments

Steam explosion experiments were conducted in a 5 L stainless-steel reactor, connected on top to a steam generator. Reactor bottom discharged through an electro-valve to a flash vessel partially open to the atmosphere. The reactor was loaded with 50.0 g of cellulose, tightly closed and filled with saturated steam at the desired temperature and pressure. After reaching experimental conditions (this period was called "demand time", t_d), a countdown for the defined "reaction time" (t_{SE}) started. Once it finished, the bottom electrovalve automatically opened, discharging the reactor content into the flash vessel. A set of four experiments was conducted for each sample, combination of two reaction temperatures (150 or $200\text{ }^{\circ}\text{C}$) and two reaction times (5 or 30 min).

Resulting pretreated cellulose was vacuum-filtrated in a Buchner funnel to eliminate excess water, weighed and stored in plastic flasks at $4\text{ }^{\circ}\text{C}$ before analysis. Samples of pretreatment liquid fraction were also stored for chemical analysis to determine possible solubilization and degradation due to pretreatment.

The term "Severity Factor" (SF), calculated by Eq. (1), defined the intensity of the pretreatment, and the term "Solids recovery" (R_s) provided the mass losses due to treatment or manipulation, referred to the initial amount of raw material. Due to the configuration of the steam explosion system, t_d never exceeded 100 s , and it has not been considered for SF calculations. Solids recovery (w/w%) was calculated through the ratio of the recovered and initially loaded mass, both in dry-matter base.

Pretreated samples were analyzed for chemical composition, particle size distribution, enzymatic hydrolysis kinetics, optical microscopy, crystallinity index, limiting viscosity number, and Scanning electron microscopy (SEM).

2.3. Preservation methods assays

Two different preservation methods were evaluated: (1) acetone-drying step and (2) freezing at $-20\text{ }^{\circ}\text{C}$.

For (1), samples were profusely washed with acetone after filtration. Then, acetone-washed cellulose was dried for 48 h at room temperature and stored in plastic flasks. Chemical composition, enzymatic hydrolysis kinetics, optical microscopy, crystallinity index and limiting viscosity number analysis were conducted to evaluate composition and structural changes caused by acetone wash.

For (2), pretreated samples were frozen at $-20\text{ }^{\circ}\text{C}$ for 24 h after water removal by filtration. After that time, they were defrosted and analyzed (chemical composition, enzymatic hydrolysis kinetics, optical microscopy and crystallinity index).

2.4. Physicochemical characterization

2.4.1. Chemical characterization

The chemical composition analysis followed NREL (National Renewable Energy Laboratory – USA) analytical procedures (TP-510-42618). Total and volatile solids (TS/VS), moisture, water extractives and ashes content were determined by gravimetric analysis. Cellulose and hemicellulose content were determined by HPLC analysis of acid hydrolysis liquid phase of samples. A Bio-Rad HPX-87H ion-exclusion column installed in a Waters e2695 separation module equipped with Waters 2414 refractive index detector was used to quantify the concentration of glucose. The mobile phase of $0.025\text{ M H}_2\text{SO}_4$ was eluted at a flow ratio of 0.6 mL/min and $50\text{ }^{\circ}\text{C}$. CC samples needed three successive acid hydrolysis for their correct characterization. Acid Soluble Lignin (ASL) was determined by spectrophotometric method and Acid Insoluble Lignin (AIL) gravimetrically after acid hydrolysis of the samples. All results correspond to the mean value of two measures (Travaini, Barrado, & Bolado-Rodríguez, 2016a).

Solubilized sugars and soluble impurities (HMF, furfural and short-chain organic acids) were determined by HPLC analysis of the liquid fraction of a cellulose-in-water suspension (at 1 g/L under continuous stirring for 24 h), using the same conditions as previously indicated. Results correspond to the mean of two measures. Total phenolic content (TPC) were determined by spectrophotometric method at a wavelength of 765 nm according to an internal protocol of the Laboratory of Instrumental Analysis of University of Valladolid, based on the Folin reaction (Toquero & Bolado, 2014).

2.4.2. Physical characterization

Particle size distribution was determined in triplicate on cellulose-in-water suspensions by Dynamic Laser Scattering (DLS) using a Mastersizer 2000 (Malvern Instruments Ltd), with an initial obscuration of 5%. This instrument reports particle size as a volume equivalent sphere diameter. While this is not an absolute measure, given that the fiber thickness can be considered uniform, it gives a relative value about the effect of the pre-treatment on the fiber length. Percentiles dp_{10} (equal to the value below which 10% of the observations may be found) and dp_{90} (equal to the value below which 90% of the

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