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Easy production of cellulose nanofibrils from corn stalk by a conventional high speed blender

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ABSTRACT

Agricultural crop residues are an abundant and cheap source of cellulose fibers suitable for uses in composite, textile, pulp and paper manufacture. Besides, field crop fibers might be an attractive source for the production of value-added nanosized cellulose fibrils with a broad potential use. In this study, nanofibrillated cellulose (NFC) from corn stalk crop residues were produced with high yields using a simple high speed blender (HSB). It was shown that a full conversion of cellulose fibers into NFC was successfully achieved by disintegration during 30 min of fibers produced via a $NaClO_2$/acetic acid delignification mode and submitted to a TEMPO-mediated oxidation pre-treatment. The fibrillation yield, transparency degree, colloidal properties and morphological characteristics of the ensuing NFC were analyzed and compared according to the delignification mode and the carboxyl content. The reinforcing potential of the NFC produced with different carboxyl contents was investigated.

1. Introduction

The last two decades have witnessed an increasing interest in the production of nanofibrillated cellulose (NFC) from a wide range of vegetal resources due to the broad possibility of use of this natural nanomaterial in the field of innovative materials (Kalia et al., 2014; Klemm et al., 2011). NFC are fibrils with width in the nanometer scale, typically between 5–50 nm depending on the extent of cell delamination and fibers pre-treatment (Khalil et al., 2012) and length in the range of 1–5 μm. These bio-nanomaterials combine the advantageous properties of cellulose, namely the broad range of chemical modifications, non-toxic character (Vartiainen et al., 2011), biodegradability, renewability, and sustainability with the specific attribute of nanosized materials that expand the spectrum of potential applications.

To produce NFC, the hierarchical structure of macroscopic fibers has to be broken up, by delaminating cellulosic fibers under an intense high mechanical shearing action. Since the advent of NFC in the 1983 by Turbak et al., (1983) high pressure homogenization (HPH) and micro-fluidization have been the main methods used to produce NFC. However, albeit the promising potential usefulness of NFCs in a multitude of applications, their scale-up production is still limited and below expectations. One major obstacle to this development is the high energy consumption involved during the mechanical disintegration of the fibers into nanofibers (Naderi et al., 2015). Another problem is the necessity to call on costly industrial equipment such as the high-pressure homogenizer or the microfluidizer. In both of these disintegration modes, a high pressure is requested to force the diluted suspension of fibers through a tight flow path in the case of the microfluidizer or a narrow nozzle (between 100–200 μm) for the high-pressure homogenizer. This high pressure accounts for the huge energy consumption during the cell wall delamination process. It follows that any mechanical disintegration method operating under atmospheric pressure is likely to contribute to lower the energy input during the disintegration process. The fibers pre-treatment prior to the disintegration process is another approach currently adopted to decrease the energy demand. Chemical pre-treatment has emerged as one of the most efficient and popular pre-treatment strategies to facilitate the break-up of the fibers network by generating ionic or ionisable groups within the internal structure of the fibers. This can be achieved via a TEMPO-mediated oxidation (Saito et al., 2006), (Liimatainen et al., 2012), carboxymethylation (Siró et al., 2011) or via sulfonation with sodium bisulfate (Liimatainen et al., 2013) or quaternization (Chaker and Boufi, 2015, Saini et al., 2016). In general, a critical content in ionic groups is needed to effectively facilitate the release of the cellulose microfibrils and break down the cell wall of the fibers (Besbes et al., 2011). Another merit of the pre-treatment is the reduction of the risk of clogging during the homogenization process, namely when HPH and microfluidization

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were used. In addition to the fibers pre-treatment approach, the delignification mode was recently shown to meaningfully affect the fibrillation efficiency of the bleached cellulose fibers. Leaving the highest content of hemicelluloses in the fibers after the pulping process contributed to make easier the conversion of the fibers into nanosised cellulose fibrils (Chaker et al., 2013, 2014).

The combination of an enzymatic pre-treatment and a mechanical refining has also been extensively used as an eco-friendly approach to facilitate the disintegration of cellulose into nanofibrils and, thus, reduce energy consumption (Pääkkö et al., 2007; Qing et al., 2016). However, enzymatic treatments are known to affect fiber morphology. Enzymatic pre-treatments resulted in CNFs with shorter fibril lengths and higher crystallinity index. The ensuing nanofibrils appeared stiff and had rod-like shape looking quite similar to cellulose nanocrystals prepared through acid hydrolysis.

Field crop residues and/or agricultural by-products such as cereal straw, cornstalks, corn straw, rice husk, bagasse and cereal straw are annually renewable, available in abundance throughout the world and currently of limited values (Reddy and Yang, 2004, 2005). The use of the cereal straw and other agricultural residues or by-products as a source of fibers or cellulosic based materials alleviate the shortage of wood resources and can have the potential to start a natural fiber industry in countries where there are little or no wood resources left, without adversely affecting soil fertility. However, agricultural cropresidues tend to have a high ash from 3% and higher making the pulping process more difficult than woody fibers.

Corn straw is an annually renewable biomass, available in abundant volumes throughout the world that is often left behind after corn grain is harvest. In terms of chemical composition and ultrastructure, corn stalk can serve as a cheap source for NFC.

Although several papers have dealt with the production of NFC from different agricultural products, most of them have used a high energy demanding disintegration process such as high pressure homogenization or microfluidization (Alemdar and Sain 2008; Hassan et al., 2012; Alila et al., 2013). This conventional approach led to a high-energy NFC cost production, making the use of agricultural by-products less attractive and unforeseeable as a resource for the production of NFC. As a result, an important challenge to be tackled is how to develop less energy consumption processes that are likely to make the production of NFC easier. In the present work, we pursue our investigation regarding the production of NFC from agricultural residue using a conventional high-speed blender (Boufi and Gandini 2015). One of the main advantages of the use of a high-speed blender lies in its simplicity and the possibility to scale-up the process for high volume production without any risk of clogging. By using this conventional high speed blender, our main objective is to highlight how the carboxyl content of fibers and the disintegration time affected the yield of fibrillation and the morphology of the ensuing nanofibrils,

2. Experimental section

2.1. Samples

Corn stalk residue was obtained from local sources. The stem of the plants had a length of 0.7–1 m and diameter of 2–3 cm. After further drying at 80 °C for 2 h, the stalk was ground to a coarse powder with about 0.5–2 mm length and crude fibers were Soxhlet extracted for 12 h, using a solvent mixture composed of toluene/ethanol (60/40 v/v). After drying at room temperature, the fibers were kept under mechanical stirring in hot water (70 °C) for 1 h to remove pectin and sand. The fibers were recovered by filtration through Whatman 200 μm filter and then submitted to the pulping process to remove lignin.

The pulping procedure for the crude fibers was carried out as follows:

2.1.1. Delignification processes $NaClO_2$/acetic acid pulping mode

The $NaClO_2$/AA pulping process was carried out as follows: Five grams of dry Soxhlet extracted biomass were added to water and mixed to form suspensions at a solid content 10 wt%. Then, 0.5 g of sodium chlorite ($NaClO_2$) and 0.5 mL of acetic acid per gram of dry biomass were added, and the suspension was kept under mechanical stirring at a temperature of 70 °C for 6 h without the removal of any liquor. Fresh charges of sodium chlorite (0.25 g/g fibers) and acetic acid (0.25 g/g fibers) were added to the reaction every 1.5 h for up to 6 h.

The pulp yield is calculated through Eq. (1):

$$\text{Pulp Yield\%} = \frac{\left[m_w(1 - MC/100\right]}{m_d} \times 100 \quad (1)$$

where, m_w, m_d and MC are the weight of the wet biomass recovered, the weight of the dry sample used and MC the moisture content of the recovered solids, respectively. The ensuing pulp recovered after washing with water was white and no bleaching treatment was implemented.

2.2. NaOH pulping mode

The extracted biomass was added to water (solid content 10 wt%) and then pulped with a 5 wt% NaOH solution for 2 h at 70–80 °C under mechanical stirring. This treatment was repeated three times until the fibers were well individualized. The ensuing fibers were subsequently filtered and rinsed with distilled water and twice bleached with $NaClO_2$ at 70 °C and pH 4–5 to remove the residual lignin.

2.3. Chemical composition

The determination of the basic chemical composition was conducted following TAPPI standard protocols. (TAPPI T 257 cm-02). Samples were first submitted to Soxhlet extraction with ethanol/toluene and water. Then, the chemical contents were determined using the following methods, Ash (Tappi T 211 om-93) extractive (Tappi T264 om-07), Klason lignin (Tappi T222 om-88), and hemicelluloses (Tappi T249-cm-85).

2.4. TEMPO-mediated oxidation

The TEMPO-mediated oxidation was carried out at pH 10, using NaClO as oxidizing agent and TEMPO as a catalyst. Briefly, cellulose fibers (2 g) were suspended in 200 mL water. TEMPO (30 mg) and NaBr (250 mg) were added to the suspension. Then 50 mL of a commercial NaClO solution (12°) was added dropwise to the cellulose suspension at a temperature around 5 °C which was kept constant throughout the oxidation reaction. The pH was maintained around 10 by the continuous addition of a 0.1 M aqueous solution of NaOH. The oxidation was stopped by adding ethanol (20 mL) and the pH was adjusted to 7 by adding 0.1 M HCl.

2.5. Carboxyl content

The carboxyl content of the oxidized cellulose was determined using conductimetric titration, as described elsewhere (Besbes et al., 2011).

2.6. Fibrillation process

using a conventional high speed blender (*HSB*): the fibers in a water suspension at a concentration of 2 wt% were disintegrated