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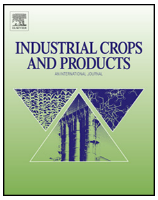

On the nanofibrillation of corn husks and oat hulls fibres

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ABSTRACT

Cellulose nanofibrils (CNF) were isolated from agro-industrial waste (corn husks and oat hulls) and market kraft pulp fibres, and a detailed comparative study was performed. Initially, the raw materials were subjected to a conventional pulping process to remove lignin and hemicelluloses. The chemical pre-treatment was based on 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO)-mediated oxidation and the mechanical treatment was carried out with a high-pressure homogenizer. An extensive characterization of the raw material and of the nanofibrillated celluloses was performed, considering structural and chemical aspects. CNF films were produced for their characterization by optical methods, laser profilometry (LP), scanning electron microscopy (SEM), and atomic force microscopy (AFM). Considering the same pulping and chemical pre-treatment, the analyses indicated that the oxidized corn husks fibres had higher carboxylate content and thus a larger tendency to nanofibrillate compared to the oat hulls fibres. The obtained content of carboxylic acids was directly proportional to the content of cellulose in the assessed samples, confirming the selectivity of the TEMPO-mediated oxidation. The fibrillated corn husks material had a minor fraction of residual fibres (<4%) and homogeneous nanofibril width distribution (<20 nm), which is a major achievement. The homogeneous CNF morphology was confirmed by AFM analysis. Hence, this study demonstrates that the assessed agro-industrial wastes are sustainable resources for production of CNF, which may have a wide range of value-added applications.

1. Introduction

Non-wood sources have been assessed in the last decade as an alternative to wood for production of cellulose fibres. Compared to wood, non-wood sources have lower lignin contents, shorter growing cycles, annual renewability and a high annual yield of cellulose (Alila et al., 2013). Commonly, non-wood waste from agro-industrial activity is mostly burned or used for animal feed. As a relevant example, cereal harvest waste is an important resource. For every ton of cereal production, about 1,5 tons of waste could be obtained. World production of cereals exceeds 1000 million tons per annum, indicating that about 1500 million tons of waste is produced every year (Yuan and Sun, 2010). Hence, agro-industrial waste is considered a promising raw material for the development of high-value products, such as cellulose nanofibrils (CNF).

CNF have been suggested for several applications, including various composite applications (Fukuzumi et al., 2013; Ma et al., 2014; Okahisa et al., 2011; Okubo et al., 2009; Qiu and Netravali, 2012; Abe and Yano, 2011; Josefsson et al., 2014; Lee et al., 2014), emulsion stabilizer (Winuprasith and Suphantharika, 2013; Xhanari et al., 2011; Lif et al., 2010), barrier applications in novel packaging concepts (Aulin et al., 2010; Hult et al., 2010; Syverud et al., 2011; Rodionova et al., 2013), as adsorbents for different contaminants (Gebald et al., 2011; Musyoka et al., 2013; Serrano et al., 2011), encapsulation (Lavoine et al., 2014) and in biomedical applications, where CNF may be applied as scaffolds for tissue or bone (Klemm et al., 2005; Syverud et al., 2015) or as dressings for wound healing

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(Nordli et al., 2016; Powell et al., 2016; Tehrani et al., 2016). For an extensive review of nanocellulose production and application see *e.g.* Nechyporchuk et al. (2016).

TEMPO-mediated oxidation is one of the most applied pre-treatments for the production of CNF. TEMPO-mediated oxidation yields CNF with diameters less than 20 nm and length of several micrometres (Chinga-Carrasco et al., 2011; Lu et al., 2008). The lengths may also depend on the fibrillation process (Fukuzumi et al., 2013). CNF exhibit both amorphous and crystalline parts and present a web-like structure. CNF have large aspect ratio, and large specific surface area. In addition, TEMPO CNF have a good capability to form rigid networks, with high mechanical properties (Lu et al., 2008; Fukuzumi et al., 2013; Lee et al., 2014).

A wide variety of non-wood sources have been studied for the extraction of CNF, including banana rachis (Zuluaga et al., 2009), Kenaf (Jonoobi et al., 2010), Jute (Serrano et al., 2011), corn cobs (Shogren et al., 2011), bamboo (Zhang et al., 2012), corn stover (Chen et al., 2013), mangosteen (Winuprasith and Suphantharika, 2013), non woody plants (Alila et al., 2013), sugar beet pulp (Li et al., 2014), corn stalk (Boufi and Chaker, 2016). Additionally, De Carvalho Mendes et al. (2015) and Paschoala et al. (2015) assessed the production of cellulose nanocrystals (CNC) from corn husk and CNF from oat hulls, respectively. The CNF production reported by Paschoala et al. (2015) was based on acid hydrolysis and yielded a relatively coarse fibrillated material (reported CNF diameters of 70–100 nm). It is important to emphasize that the development of added-value products from agricultural residues, for *e.g.* CO_2 absorbents and drinking water filters, may benefit from producing highly fibrillated and homogeneous CNF with large specific surface area and controlled surface chemistry for additional functionalization purposes. In this respect, TEMPO-mediated oxidation of fibres from agricultural residues seems as a plausible pre-treatment for CNF production and will be explored in this study.

Focusing on a local level, the production of corn and oat in Chile was 1,538,755 and 421,048 tons, respectively (Instituto Nacional de Estadísticas, 2014). Presently, the residues from corn and oat production are mainly burned to generate energy. Considering the wide variety of waste resources and the corresponding local availability, it is thus important to clarify the potential of local waste biomass for production of high-value cellulose-based products. This is an important aspect for a successful circular bio-economy of the future.

Hence, the purpose of the present work was to compare two waste resources (corn husks and oat hulls) for the production of CNF, considering their chemical composition and ability to nanofibrillate, after TEMPO-mediated oxidation. The characteristics of the obtained CNF were quantified, confirming the potential of agro-industrial waste as a promising resource for the production of CNF.

2. Materials and methods

2.1. Raw materials

The waste generated in Chilean agricultural activities have been considered as renewable raw materials in this study. The corn husks were collected after the harvest of corn (Zea mays L.). The oat hulls were supplied by Gorbea Mill located in Gorbea (Chile). In addition, one never-dried market pulp was utilized for comparison purposes, *i.e.* 100% *P. radiata* kraft pulp, provided by CMPC Celulosa, Chile. It is important to mention that the market *P. radiata* kraft pulp fibres used in this work and the corresponding nanofibrils have been characterized extensively in previous studies (Chinga-Carrasco et al., 2014; Rees et al., 2015; Syverud et al., 2011).

2.2. Agro-industrial waste characterization

The chemical composition of raw materials was determined following standard methods and procedures found in the literature; cellulose and hemicelluloses content (Rowell, 1983), lignin (TAPPI T222 om-98), ashes content (TAPPI T211 om-93), moisture content, (TAPPI T264 cm-97) and extractives with ethanol-toluene (TAPPI T204 cm-97) (Tappi Test Methodos, 1997)

2.3. Cellulose pulp

The method described by Zuluaga et al. (2009), with some modifications, was applied for obtaining cellulose pulp. The corn husks and oat hulls were treated with a solution 0.1 M NaOH under mechanical agitation at 30 °C for 18 h. The residue obtained was treated with 0.1 M HNO_3 at 85 °C for 1 h to remove mineral traces. Subsequently, the insoluble residue was treated with a solution of 3% H_2O_2 at 70 °C for 1 h in order to remove the lignin.

2.4. Characterization of biomass composition

Extractive-free samples (corn husks, oat hulls and kraft pulp) were characterized for glucan and lignin content according to Sluiter et al. (2010). Samples (300 mg) were weighed in a test tube and 3 mL of 72% H_2SO_4 (w/w) was added. Hydrolysis was performed in a water bath at 30 °C for 1 h with stirring every 10 min. Subsequently, the acid was diluted to 4% (w/w) with 79 mL of distilled water; the mixture transferred to a 250-mL Erlenmeyer flask and autoclaved for 1 h at 121 °C. The residual material was cooled and filtered through a porous glass (Gooch filter crucible number 4). Soluble lignin was determined by measuring the solution absorbance at 205 nm (Dence, 1992).

The concentration of glucan (the soluble fraction) was determined by HPLC in a Young lin instrument with an Aminex HPX-87H column at 35 °C, eluted at 0.6 mL/min with 5 mM H_2SO_4 by a refractive index detector. Analyses were performed in triplicate for each sample.

2.5. TEMPO-mediated oxidation

TEMPO-mediated oxidation with 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO) was carried out according to Saito et al. (2006). The never-dried cellulose (5 g) was suspended in water (300 mL) containing TEMPO (0.050 g) and sodium bromide (0.50 g). The TEMPO-mediated oxidation of the cellulose slurry was started with the addition of 30 mL of a commercial NaClO (13%) solution and conducted at room temperature under gentle agitation. The pH was maintained at 10.5 by adding 0.5 M NaOH. The reaction was stopped when the pH reached a stable level, and was adjusted to pH 7 by adding 0.5 M HCl. The TEMPO-oxidized product was thoroughly washed with water by filtration and stored at 4 °C before further treatment and analysis.

2.6. Carboxyl content

The carboxyl content of the oxidized celluloses was determined using conductometric titration, according to the method described by Saito et al. (2006).

2.7. Fibrillation process

The oxidized fibres were dispersed in water with a pulp concentration of 1 wt.% and then homogenized with a high-pressure homogenizer (NS1001L PANDA 2K-GEA). The pulp was passed

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