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Assessing the influence of refining, bleaching and TEMPO-mediated oxidation on the production of more sustainable cellulose nanofibers and their application as paper additives

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ABSTRACT

Agro-wastes valorization focusses on production of high value-added products, such as cellulose nanofibers (CNF), and contributes to reduce the environmental impact of these residues. CNF have been used successfully as papermaking additives and some previsions maintain that this sector will become the most important, demanding CNF at a reasonable cost. Furthermore, the optimization of the production process of CNF from agricultural residues would contribute to the goals of a circular economy, the development of rural areas and the costs reduction by producing CNF of the minimum quality fit-for-use in recycled paper. In this study, CNF was produced from two agricultural residues; corn (C-CNF) and rape (R-CNF) stalk pulps, pretreated with bleaching, refining and TEMPO-mediated oxidation. Coagulant and cationic polyacrylamide (dual system) and chitosan were the retention systems. Results show the difficulty of predicting the effect of CNF based on their properties, as fibrillation degree or anionic charge, on the improvement of mechanical properties of recycled paper. That is proved by the low differences in tensile index (TI) improvement (~15% by adding 0.5% C-CNF combined with dual system), obtained with CNF with very different properties. The expensive TEMPO pretreatment could be avoid by applying bleaching pretreatment to the corn pulp, increasing the TI up to 15% without affecting drainage and decoupling the simultaneous deterioration of drainage with TI improvement (drainage time decreased nearly 50% and 20% adding bleached R-CNF and C-CNF, respectively, combined with chitosan). Similar improvements on TI can be achieved by replacing the dual retention system by chitosan without addition of CNF, but the combination of CNF and chitosan allows achieving the highest TI values.

1. Introduction

CNF have attracted significant interest in recent years because of their exceptional mechanical properties, large specific surface area, high aspect ratio, barrier properties, low coefficient of thermal expansion and low weight (Eichhorn et al., 2010). These properties make CNF promising for many industrial applications, such as papermaking (Balea et al., 2016a,b; Osong et al., 2016), composites (Oksman et al., 2016; Siro and Plackett, 2010), packaging (Bradley et al., 2011), films (Siro et al., 2011), electronic devices (Torvinen et al., 2012), filtering materials, rheology modifiers, paints and coatings, biomedicine and automotive (Aspler et al., 2013; Zhou et al., 2014).

One of the main concerns of CNF production is energy consumption during the mechanical treatment required to produce the defibrillation of the fibers (Spence et al., 2011). Several researchers have combined mechanical (Stelte and Sanadi, 2009) and chemical (Saito et al., 2007; Wang and Sain, 2007) or biological (Alemdar and Sain, 2008; Pääkkö et al., 2007) pretreatments to reduce energy consumption. For example, bleaching and refining promote disruption of the cell-wall matrix, including the connection between carbohydrates and lignin, as well as de-polymerization and dissolution of lignin and hemicellulose polymers. Pretreatments boost the reactivity of the cellulosic fibers by promoting accessibility of hydroxyl groups, increasing inner surface, altering crystallinity and breaking cellulose hydrogen bonds (Szczesna-Antczak et al., 2012). Nowadays, the CNF market is still very limited (Osong et al., 2016) and, in most cases, CNF are of higher quality than that required for the application. Thus, new approaches are needed to reduce its costs, like the strategy of CNF fit-for-use, establishing relationships between the CNF properties and the needs required for a certain

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industrial application. The combined strategy considered here represents a progress beyond the state of the art and has potential to reduce the costs and increase the probability of implementation of CNF in papermaking at an industrial scale.

Although wood is certainly the most used source of cellulosic fibers for CNF, current studies are also focused on the production of CNF from agro-wastes because of the goal of agro-waste valorization. Due to their large quantity, low cost and environmental benefits, lignocellulosic biomass is used as bioenergy substrate (Hamelinck et al., 2005), however it implies high production costs and relatively low utilization rate (Guo et al., 2008; Hendriks and Zeeman, 2009). Therefore, it is also studied as a promising alternative resource to obtain chemicals, polymeric materials and novel products (Chaker et al., 2014; Garcia et al., 2014) by fractionation through alkali, hydrothermal and organosolv treatments (Agbor et al., 2011; Garcia et al., 2011; Geng et al., 2012; Moral et al., 2016), among others. After fractionation, further treatments can lead to a variety of high value-added products with important applications in industry (Balea et al., 2016b; Corma et al., 2007; Chirayil et al., 2014; Garcia et al., 2015; Theng et al., 2015).

Corn and rape are among the most commonly cultivated plants worldwide. Both have shorter growing cycles and lower lignin contents compared to main woody fibers sources, and can be delignified easily (Boufi and Gandini, 2015). Therefore, the large amounts of wastes generated in corn and rape agriculture, with high cellulose content, are potential good raw materials for the production of high value-added products, such as CNF. Local CNF production from agro-wastes would contribute to the goals of a circular economy and the development of rural areas. Nowadays the economic feasibility of the biorefineries of lignocellulosic agro-wastes is challenged. The products of the chemical treatment of the wastes, for example by steam explosion, are not valuable enough to cover the costs of the process. The use of organosolv cooking will lead to a high quality lignin from which valuable products can be obtained, and a pulp, whose use to obtain CNF could increase its value more than its use as a substrate for fermentation to obtain bioalcohols, which is the use proposed by other authors (Ragauskas et al., 2014; Yang et al., 2011). On the other hand, the production of CNF of the required quality for its use may reduce its costs.

CNF have emerged as an alternative additive to improve the mechanical properties of paper with additional advantages, such as their renewable nature, biodegradability and potential high availability (Siro and Plackett, 2010). CNF can be added either to the fiber suspension or as coating (Osong et al., 2016; Taipale et al., 2010). Their use as strength additive for recycled paper is of great interest due to the poor tensile strength of recycled paper in regions of high recycling rates. Addition of CNF obtained from different cellulose sources has resulted in higher tensile strength of recycled paper (Balea et al., 2016b; Delgado-Aguilar et al., 2014). Furthermore, recent studies have proved the viability of using CNF to reduce linting propensity in recycled papers with high load of fillers (Balea et al., 2016a). Beside all these benefits, the use of CNF can also hinder dewatering, altering the papermaking process (Osong et al., 2016). Drainage is a critical parameter in the paper manufacturing process because it limits the speed of the paper machine.

Therefore, the main objective of this research was to produce a fit-for-use CNF of lower cost from agro-wastes to be used in the paper sector to improve paper strength, decoupling the associated negative effects of CNF on drainage. In order to do this, agricultural by-products, corn and rape stalk pulps prepared by organosolv cooking, were used as cellulose source. Refining, bleaching and TEMPO-mediated oxidation pretreatments were applied to the pulps to assess the effects of these processes on CNF quality obtained by homogenization. The behavior of the produced CNF as strength additive for recycled paper was assessed. Moreover, the effect of CNF on drainage was studied and its compatibility with two different retention systems (coagulant and cationic polyacrylamide and chitosan) was established.

Table 1
Pretreatment conditions to produced CNF, before homogenizing through three steps at 600 bar.

	Untreated	Refined	Bleached
	Degree of TEMPO-mediated oxidation (mmol NaClO/g)		
Corn stalk pulp	7.5, 5	5, 7.5, 10, 15	0, 2.5, 5, 7.5, 10
Rape stalk pulp	5	5, 7.5, 10	2.5, 5, 7.5, 1

2. Materials and methods

2.1. Materials

CNF were obtained from two different sources of cellulose: (i) corn stalk pulp (C-CNF), and (ii) rape stalk pulp (R-CNF). Both agricultural pulps were obtained through organosolv treatment of the raw material, cooked with 40% ethanol at 165 °C for 60 min, and washed with distilled water to remove the ethanol and the dissolved lignin. The LEPAMAP research group from Girona University (Girona, Spain) kindly supplied the agricultural pulps. The kappa indexes of corn and rape organosolv pulps were 50 and 46, respectively.

Based on both industrial experience and previous studies (Howard et al., 1977; Hubbe et al., 2009), a dual-component retention and drainage system (DRS), composed of low molecular weight and cationic charge density of 0.041 meq/g coagulant NALKAT® 7655 (polyquaternary ammonium chloride) and high molecular weight and cationic charge density of 1.199 meq/g cationic polyacrylamide (cPAM) NALCO® 62101 supplied by NALCO (Naperville, Illinois), was selected as it is commonly used in the recycled paper industry. The commercial coagulant solution was diluted 100 times before use, and the cPAM solution was prepared by dissolving cPAM powder in ultrapure water to 0.05 wt% followed by magnetic stirring for 2 h.

In addition, chitosan from crab shells (28191) supplied by Sigma-Aldrich (Steinheim, Germany) with a cationic charge density of 4.79 meq/g and low molecular weight, was also studied as an alternative biodegradable single retention system (Fatehi et al., 2010). The chitosan solution was prepared at 1% by dissolving chitosan in a solution of glacial acetic acid in ultrapure water subject to mechanical stirring at 400 rpm for 1 h. The chitosan solution was left to settle for 24 h before use.

Doses of 0.7 mg of coagulant/g of dried pulp, 0.75 mg of cPAM/g of dried pulp and 2 mg of chitosan/g of dried pulp were used for experiments. The doses were selected based on industrial recommendations and previous studies which showed that the fastest drainage was obtained with 2 mg/g of chitosan and that dose of chitosan did not affect the mechanical properties of the sheet. The dose of cPAM was chosen based on a compromise between drainage time and tensile index (TI), as the effect of cPAM on both is opposite.

2.2. Production of CNF

2.2.1. Corn and rape pulps pretreatments

Several pretreatments were applied to the agricultural waste pulps in an effort to obtain different CNF yields and degrees of fibrillation with low mechanical energy consumption (Table 1). Bleaching, which aims to remove all the non-cellulose polymers, such as lignin, was performed on pulp at 10% consistency at alkaline pH (pH = 11) by using NaClO (10%) as a bleaching agent for 60 min and at 70 °C, according to Adel et al. (2011). After bleaching, the pulp was washed to remove the reaction medium. Refining was carried out to favor fibrillation using