



# The key role of lignin in the production of low-cost lignocellulosic nanofibres for papermaking applications



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## ABSTRACT

The use of cellulose nanofibres (CNF) for the enhancement of paper's mechanical properties has been reported by many authors. Concretely, the available literature is mainly focused on TEMPO-oxidized cellulose nanofibres. However, recent industrial research projects, in which LEPAMAP group has been involved, have demonstrated that this type of nanocellulose has unaffordable production costs for the papermaking industry. In this sense, the present work aims to produce low-cost lignocellulosic nanofibres (LCNF), finding some strong alternatives to TEMPO-mediated oxidation. For that, lignocellulosic nanofibres (LCNF) were produced from stone groundwood pulp (SGW) from pine after a chemical pulping process (sodium hydroxide and anthraquinone). The effect of lignin content was studied and controlled through bleaching steps and quantified. It was found that high lignin content makes nanofibrillation difficult. The reinforcing effect of CNF was mechanically characterized by the addition of 3 wt% of CNF into different papermaking pulps. The results showed that it is possible to obtain low-cost LCNF that provide the same increase in mechanical properties than TEMPO-oxidized CNF when they are used for paper reinforcement. It was also found that lignin plays an important role in the obtaining of LCNF by fully mechanical treatments, where lower lignin contents expedite the nanofibrillation.

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## 1. Introduction

The use of cellulose nanofibres (CNF) as an additive for papermaking slurries has been already assessed by several authors (Abola et al., 2008; Brodin et al., 2014; Delgado-Aguilar et al., 2015a; Eriksen et al., 2008; González et al., 2012; Taipale et al., 2010). CNF suspensions are formed by the smallest structural unit of cellulose fibres, the microfibril, also called nanofibril or nanofibre in some literature (Chinga-Carrasco, 2011; Klemm et al., 2011). CNF had diameters between 3 and 5 nm, though CNF suspensions usually contain aggregates thereof whose diameters can reach 100 nm. The addition of CNF into papermaking slurries improves the mechanical strength of papers, reduces porosity and increases paper's density; besides, CNF addition reduces or even eliminates the need of mechanical refining of paper slurries, which reduces considerably the lifespan of fibres (Delgado-Aguilar et al., 2015c). The main mechanism behind the improvement in paper's properties is the boost in specific surface area that CNF provide to papermaking

slurries. Higher specific surface area increases the amount of hydrogen bonds and London-Van der Waals forces between fibres which is the main mechanism of paper strengthening. In this sense, the addition of CNF into paper slurries is supposed to be a promising alternative to those conventional processes due to their interesting properties. However, the overall cost for the fabrication and application of CNF into an industrial papermaking process has not been completely clarified. Fabrication of CNF requires passing the fibre suspensions (usually bleached wood pulps) through high-pressure homogenizers/microfluidizers where the elevated shear forces delaminate the fibres until nanofibres are released (Klemm et al., 2011; Siró et al., 2011). The first attempts to produce CNF performing numerous passes of fibre suspensions through homogenizers, which is translated into high energy consumption (Spence et al., 2011). Different pre-treatment methodologies have been studied with the purpose of reducing the number of passes necessary to effectively produce CNF suspensions and, thus, reducing energy consumption during fibrillation. Pre-treatments can be classified into three different categories: chemical, enzymatic and mechanical. Chemical pre-treatments include carboxymethylation (Wågberg et al., 2008), acid hydrolysis (Dufresne et al., 1997) and TEMPO-mediated oxidation (Saito et al., 2007). Enzymatic

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pre-treatments consist on submitting the cellulose fibres to the action of endoglucanases that hydrolyse the amorphous regions of cellulose chains (Henriksson et al., 2007; Pääkkö et al., 2007) and also cleaving the p-1,4 linkages of cellulose creating new chain ends and, thus, reducing the cellulose chain length (Wang et al., 2015); in mechanical pre-treatment, fibres are subjected to intense refining before passing to the definitive mechanical treatment (Delgado-Aguilar et al., 2015e; Khalil et al., 2014). Chemical pre-treatment, particularly TEMPO-mediated oxidation, has been recognized as the most effective methodology that greatly reduces the amount of mechanical treatment (Besbes et al., 2011). Moreover, since TEMPO-mediated oxidation and carboxymethylation introduce negative charges onto the cellulose surface, the repulsion created among fibres helps to create transparent, well-dispersed suspensions of highly individualized nanofibres (Saito et al., 2007). The main drawback of chemical pre-treatment is that the high costs of some of the chemical used do not allow an industrial up scaling of the processes, today, rendering CNF as unaffordable for the paper-making industry. Under this view, it becomes necessary to find new alternatives to produce CNF with more competitive costs (Delgado-Aguilar et al., 2015e; Espinosa et al., 2016). On the other hand, the beneficial effect that residual lignin and hemicelluloses have on CNF suspensions has been already studied by several works (Ferrer et al., 2012a,b). Results indicate that the presence of residual amounts of lignin and other polysaccharides facilitate the mechanical dismantling of the cellulose fibre structure due to increased swelling caused by hemicelluloses and formation of mechanoradicals stabilized by residual lignin (Ferrer et al., 2012a,b). Improvements of dewatering in fibres suspensions and reduction in hydrophilicity have also been reported as desirable consequences of residual lignin in nanofibres (Rojo et al., 2015). In the present work, we study the fabrication of lignocellulosic nanofibres (LCNF) following an entirely mechanical procedure using stone groundwood pulp (SGW) as raw material with varying amounts of lignin. The reinforcing effect of the LCNF from the present work was studied by addition of LCNF into several different pulps to evaluate the breaking length of paper sheets made thereof.

## 2. Materials and methods

### 2.1. Materials

Stone groundwood pulp (SGW) was kindly supplied by Zubialde S.A. (Aizarnazabal, Spain) and it was subjected to a pulping process for 1.5 h, at 180 °C and in presence of a 20 wt% of NaOH with regard to the amount of dry pulp. The liquor ratio was set at 6:1. After the pulping process, the treated SGW pulp was washed with water until constant and neutral pH. Bleached kraft hardwood pulp (BKHW) was kindly supplied by Ence-Celulosas de Asturias S.A. (Spain). Deinked pulp was obtained from a mixing of old newspapers and old magazines supplied by Diari de Girona S.L. (Girona, Spain) and Drim S.A. (Girona, Spain), respectively. Details of the pulping and characteristics of deinked pulp used in the present work can be found in Delgado-Aguilar et al. (2015a). Commercial fluting and liner paper were acquired from Saica S.A. (Zaragoza, Spain). Chemicals used for pulping and bleaching were bought from Sigma-Aldrich Spain and used as received.

### 2.2. SGW bleaching

Bleaching stages were carried out in a digester for one hour at 70 °C and 8 wt% of NaClO with regard to the amount of dry pulp. After bleaching, pulp was washed with distilled water in order to remove any trace of residual NaClO. The different pulps were obtained varying the number of bleaching stages to the treated

SGW pulp (SGW-0, SGW-1, SGW-3 and SGW-4, where the number behind is the number of bleaching stages after cooking).

### 2.3. Determination of the Kappa number

Kappa number was performed according to the standard ISO 302:2004—Determination of the Kappa number.

### 2.4. Preparation and characterization of the cellulose nanofibres

Bleached SGW pulp with different lignin contents were first subjected to a beating process in a PFI refiner (NPF102, IDM) at 20,000 revolutions at 10 wt% of consistency. After that, each pulp was suspended in water (2 wt% of consistency) and passed through a high-pressure homogenizer (PANDA PLUS 2000, GEA Niro Soavi) operating first at 300 bar (three times) and 600 bar (seven times). The obtained LCNF slurry was characterized according to previous works (González et al., 2014). The carboxyl content (CC) of LCNF was calculated by conductometric titration. A dried sample (50–100 mg) was suspended in 15 mL of 0.01 M HCl solution; this exchanges Na cations bound to the COOH group by H ions. After 10 min of magnetic stirring, the suspensions were titrated with 0.01 M NaOH, adding 0.1 mL of NaOH to the suspension and then recording the conductivity in mS/cm; this process was repeated until observing a reduction, stabilization and increase in the conductivity. From the conductometric titration curve the presence of strong and weak acid is observed. The CC is given by the following equation:

$$CC = \frac{162(V_2 - V_1)c}{w - 36(V_2 - V_1)c}$$

where  $V_1$  and  $V_2$  are the equivalent volumes of added NaOH solution (L),  $c$  is the NaOH concentration (mol/L) and  $w$  the weight of oven-dried sample (g). The results indicate the average mmols of  $-COOH$  groups per gram of LCNF. The cationic demand of CNF was also determined by means of a Mütek PCD 04 particle charge detector. First, 0.04 g of CNF (dried weight) was diluted in 1L distilled water and dispersed with a pulp disintegrator for 10 min at 3000 rpm. Afterwards, 10 mL was taken and mixed with 25 mL of cationic polymer polydiallyldimethylammonium chloride (poly-DADMAC) for 5 min with magnetic stirring. After this time the mixture was centrifuged in a Sigma Laborzentrifugen model 6 K 15 for 90 min at 4000 rpm. This allows separating the fibres from the supernatant. Then, 10 mL of the supernatant was taken with the Mütek equipment. Anionic polymer (Pes-Na) was then added to the sample drop by drop with a pipette until the equipment reached 0 mV. The volume of anionic polymer consumed was used to calculate the cationic demand though equation:

$$CD = - \frac{(C_{PolyD} \times V_{PolyD}) - (C_{Pes-Na} \times V_{Pes-Na})}{W_{sample}}$$

where CD is the cationic demand ( $\mu\text{eq/g}$ ),  $C_{PolyD}$  = cationic polymer concentration (1 meq/L),  $V_{PolyD}$  = used volume of cationic polymer (mL),  $C_{Pes-Na}$  = anionic polymer concentration (1 meq/L),  $V_{Pes-Na}$  = used volume of anionic polymer (mL) and  $W_{sample}$  = sample's dry weight (g). The yield of nanofibrillation was also determined; a LCNF suspension with 0.2% of solid content was centrifuged at 4500 rpm for 20 min in order to isolate the nanofibrillated fraction (contained in the supernatant) from the non-fibrillated and partially fibrillated one retained in the sediment fraction, which was recovered, weighed and oven-dried at 90 °C until constant weight. The yield of nanofibrillation was then calculated from the next equation:

$$\text{Yield\%} = \left( 1 - \frac{\text{weight of dried sediment}}{\text{weight of diluted sample} \times \%Sc} \right) \times 100$$

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