



Nanofibrillated cellulose (CNF) from eucalyptus sawdust as a dry strength agent of unrefined eucalyptus handsheets



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ABSTRACT

Nanofibrillated cellulose has been obtained from the cellulosic fraction of eucalyptus sawdust. The fractionation process involved the partial removal of hemicelluloses and lignin. CNF was obtained using TEMPO oxidation with NaOCl in basic medium followed by mechanical homogenization. The obtained CNF was subsequently used as a dry strength agent on unbleached unrefined eucalyptus pulp. The addition of 3, 6 and 9 wt.% of CNF increased linearly the tensile index of handsheets to about 55 N m g⁻¹ at 35°SR, compatible with papermachine runnability. The other mechanical properties also increased substantially, and porosity decreased moderately. The estimated specific surface and average diameter of these CNF were 60 m² g⁻¹, and of 41.0 nm, respectively. The addition of 9 wt.% of CNF produced an increase in mechanical strength, equivalent to that produced by PFI refining at 1600 revolutions.

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1. Introduction

Biomass is the main biopolymer source for sustainable and renewable uses in chemical, material and fuel bio-products. The demand for bio-based products with equal or better properties than conventional petroleum-based derived products has generated great market opportunities. Nanotechnology is an emerging area of science and technology that has revolutionized the field of materials. The application of nanotechnology will exploit the potential of the forest and pulp and paper industries as a platform for bio-products.

The forest processing industry generates globally around 180 million of cubic metric of lignocellulosic residues (FAOSTAT, 2014) such as sawdust, bark and other wood waste. The excess global sawdust potential after summit raw material demand of the forest industry was estimated of 75 million of cubic metric. More than 67% of global sawdust potential is located in Brazil, Canada and China (Heinimö, Pakarinen, Ojanen, & Kässi, 2007).

Eucalyptus and pine sawdust are important byproducts of the primary processing of wood in Argentina, Brazil and Chile which so far have not found a successful exploitation. In some cases these residues represent a problem and its treatment consumes resources of management, treatment and disposal. In this context, governments have established environmental regulations about its disposal in order to promote their use and evaluate its potential as a renewable resource. Usually, sawdust is used to obtain low value added products as pellets and briquettes (bioenergy), charcoal (adsorbent), filler (composites) and wood panels (furniture and construction materials).

An advantage of sawdust is that it does not require further mechanical treatment for size reduction. Its main disadvantage is the heterogeneity of the material, because sawmills process woods from different origins, which generates a mixture of sawdust in which species and age are difficult to know.

By chemical pulping processes, biomass is fractionated to obtain a pulp rich in cellulose, lignin and other chemical components. This general principle can be used to fractionate sawdust, separating all components by sequential processes, thus producing high value products that can be used in different applications to improve the profit, following the bio-refinery concept. Although sawdust has been tested to make pulp for paper, product quality is not good. However, the possibility of producing CNF with

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this resource appears as an excellent chance of valorization of this waste. In this form, wood can be fully exploited and traditional pulping can be combined with new technologies, conversion infrastructure, and technical knowhow, to develop new bio-based and high value added products.

The autohydrolysis of lignocellulosic materials in aqueous medium at elevated temperature in a pressure reactor is one of the most effective treatments for hemicelluloses solubilization (Garrote, Eugenio, Díaz, Ariza, & López, 2003; Sasaki, Adschiri, & Arai, 2003). The partial solubilization of hemicelluloses (70–90%) to oligosaccharides and monosaccharides takes place, which can be used for different purposes (Teramoto, Tanaka, Lee, & Endo, 2008). Hardwood and grass species are more suitable for the autohydrolysis treatment than conifers, due to their higher content of acetyl groups which provide an increase of catalyst concentration in the reaction medium. On the other hand, lignin can be removed by alternative pulping processes such as kraft, soda-anthraquinone or organosolv pulping to obtain sulfur-free lignin.

The use of the cellulosic fraction to produce micro and nano-fibrillated cellulose (MFC or CNF, respectively) grew strongly in recent years due to their unique properties, renewable nature and large availability. CNF and MFC are fibrils or aggregates of cellulose with a diameter between 5 and 60 nm and several microns in length. CNF is obtained from the delamination of the cellulosic fibers by mechanical treatment of chemical or enzymatically pretreated fibers (González et al., 2012). The processes used affect the structure, properties, and price of CNFs, therefore the great challenge of research studies is to find a process to produce large amounts of cellulose nanofibers at low-cost (low amount of energy, inexpensive reagents and efficient enzymes). This process should keep the properties of cellulose and generate nanofibers with uniform size distribution (length and diameter). CNF is produced by pumping the pretreated fiber slurry (consistency 1–2%) in a high pressure homogenizer where the fibers are forced to collide with a valve and an impact ring. This procedure generates shear forces and a pressure drop, causing fiber delamination and the release of the microfibrils from the fiber wall layers. The fibrous slurry acquires the appearance and characteristics of a gel after several passes through the homogenizer. Micro-fibrillation may be facilitated by TEMPO oxidation in water (Nakagaito & Yano, 2004), which consists of a selective surface catalytic oxidation of the primary hydroxyls of cellulose at the C6 position to carboxylate groups by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (Saito & Isogai, 2004; Saito, Kimura, Nishiyama, & Isogai, 2007; Saito, Nishiyama, Putaux, Vignon, & Isogai, 2006). This chemical pretreatment is effective in the cellulose oxidation and also reduces the energy consumption in the subsequent mechanical processing for MFC and CNF production. Recently, this methodology has been used to facilitate the mechanical treatment of cellulosic fibers (Isogai, 2013; Isogai, Saito, & Fukuzumi, 2011; Puangsin, Yang, Saito, & Isogai, 2013).

Since the advent of nanotechnology, CNF has been used for nanopaper manufacture and many authors have also studied the effect of nanoparticles (mostly, MFC) on conventional paper. CNF applied directly in the paper sheet showed the enhancement of the mechanical strength and the improvement of the filler retention in the wet-end. This was attributed to the increment of the number of hydrogen bonds fibril-fibers (Kajanto & Kosonen, 2012). Similar to cellulosic fines, CNF increases the network strength due to its high surface area and flexibility. CNF has several advantages as reinforcing element: small diameter, high aspect ratio, biocompatibility, functionalization ability, and high strength and modulus. These characteristics become attractive to CNF as dry strength additive for paper. The use of CNF as reinforcement improves the permeability and tensile index of papers (Eriksen, 2008; González et al., 2012; Mörseburg & Chinga-Carrasco, 2009; Nakagaito & Yano,

2004; Taipale, Österberg, Nykänen, Ruokolainen, & Laine, 2010). The increase of paper strength with CNF addition can be compared with strength gain after a slight refining (González et al., 2012). Also it has been shown that CNF addition increases the strength of canola waste chemithermomechanical pulp in fluting and liner-board manufacture for packing papers (González, Alcalá, Arbat, Vilaseca, & Mutjè, 2013). The addition of CNF to an unrefined pulp produce handsheets with higher tensile strength than standard handsheets (Bardet & Bras, 2014) allowing significant reduction of grammage and energy saving (refining or drying process). Nevertheless, CNF have different chemical natures and morphologies depending on the source and process, so results are variable (Bardet & Bras, 2014). However, the addition of CNF as dry strength additive in the papermaking furnish decreases the drainage capacity of the slurry (González et al., 2012, 2014), limiting the amount of CNF that could be added.

The aim of this study was to evaluate the effect of the addition of CNF obtained from the cellulosic fraction of eucalyptus sawdust on the mechanical properties of paper made from unrefined unbleached eucalyptus pulp.

2. Material and methods

2.1. Materials

CNF was obtained from sawdust generated in a sawmill (Candela Sawmill, Misiones, Argentina) which proceeds from a mixture of eucalyptus species (*E. grandis*, *E. saligna* y *E. rostrata* from).

Unbleached eucalyptus pulps, cationic starch and colloidal silica were provided by Montañanesa Group Torraspapel, Zaragoza, Spain.

2.2. Eucalyptus sawdust fractionation and purification of the cellulosic fraction

Eucalyptus sawdust was fractionated applying biorefinery concept by sequential extraction of hemicelluloses and lignin separately for further applications and cellulosic fraction was purified by oxygen delignification before using it as raw material to obtain CNF (Fig. 1).

The sawdust was classified and the fraction passing 18 mesh and retained on 80 mesh was sequentially fractionated by autohydrolysis to remove the hemicelluloses and delignification treatments. The autohydrolysis stage was accomplished using a 4.5 L digester with a heating jacket and a special agitation system and 450 g of eucalyptus sawdust. The considered factors were: time 20 min, temperature 180 °C, and liquid/solid ratio of 6.

The residual solid of the autohydrolysis was sequentially subjected to two delignifying treatments: (i) alkaline soda-anthraquinone and (ii) oxygen, to extract residual lignin. The soda-AQ stage was carried out using 20% of NaOH, 0.1% of AQ (wt.%, dry basis of residual solid) at 170 °C for 30 min and a liquid/solid ratio of 5.70. Oxygen delignification was conducted in a multipurpose reactor, equipped with a high shear rotor which generates the required agitation conditions in the system, an inlet for oxygen and a heating system. The material was treated with a 3% NaOH charge (o.d.), 0.1% MgSO₄ (o.d.) at 10% consistency. The operational conditions were 100 °C for 60 min and an oxygen pressure of 6 kg cm⁻² (more details in reference (Rodríguez Rivero, Ehman, Area, & Felissia, 2013)).

2.3. Chemical characterization of the raw material and the solid fraction

The chemical characterization of eucalyptus sawdust before and after fractionation was performed according to laboratory

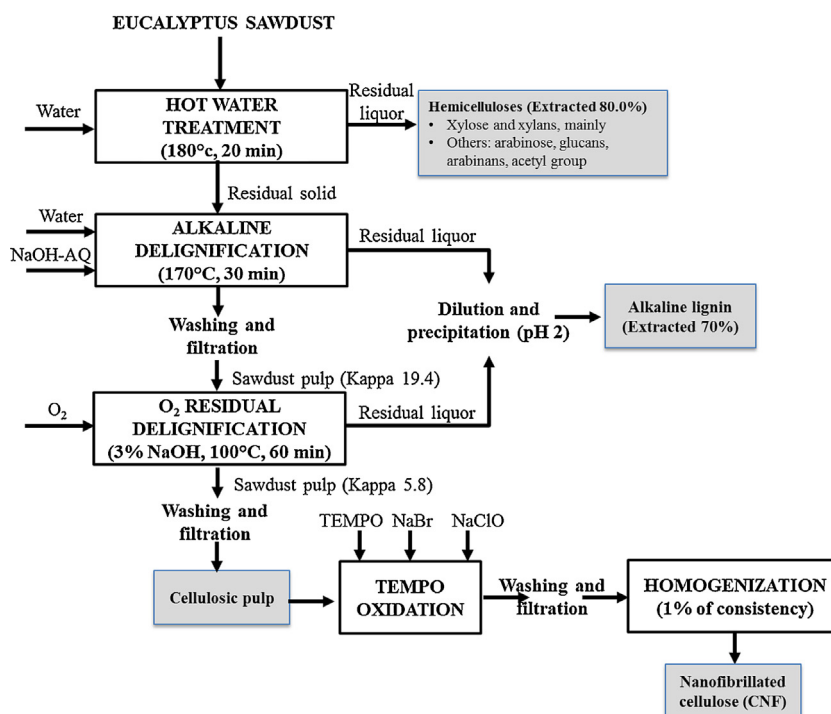


Fig. 1. Schematic process used to obtain nanofibrillated cellulose from eucalyptus sawdust applying the biorefinery concept.

analytical procedures (LAPs) for standard biomass analysis from the National Renewable Energy Laboratory (NREL). Carbohydrates, organic acids and other products (furfural, HMF) were identified by liquid chromatography (HPLC) using an Aminex-HPX87H (Bio-Rad) column with refractive index and diode array detectors. The soluble lignin was determined by UV–visible spectrophotometry at 205 nm according to TAPPI UM 250 “Acid-soluble lignin in wood and pulp”. The polymeric carbohydrates were hydrolyzed to monomers and quantified by HPLC. The monomer concentrations were multiplied by the following conversion factors to be expressed as polymers: glucose to glucans: 0.900, HMF to glucans: 1.286, xylose to xylans: 0.880, furfural to xylans: 1.375, arabinose to arabinans: 0.880 and acetic acid to acetyl: 0.717.

The viscosity of the cellulosic materials was determined according to ISO 5351-1 “Cellulose in dilute solutions – Determination of limiting viscosity number – Part 1: Method in cupri-ethylenediamine (CED) solution”. Carboxyl groups were determined by conductimetric titration. The cellulosic fractions were first washed with 0.1 N HCl for 45 min and after they were washed with distilled water until a conductivity value close to distilled water. The washed materials (1–3 g of dry material) were suspended in a solution of 0.1 M of HCl with stirring. The slurries were titrated with a solution of 0.1 M of NaHCO_3 and the conductivity was recorded in mS cm^{-1} until stabilization and subsequent increase of conductivity.

2.4. CNF preparation

The oxidation of the cellulosic fraction was performed with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), sodium bromide and a commercial solution of sodium hypochlorite. TEMPO oxidation was carried out on 15 g of dry cellulosic fraction of sawdust (previously disintegrated). The cellulosic fraction was suspended in 1000 mL of distilled water containing 0.016 g of TEMPO g^{-1} of dry material and 0.1 g of NaBr g^{-1} of dry material. The TEMPO oxidation was performed at room temperature using 6 mmol of NaClO g^{-1} of dry material (solution 15 wt.%). The solution of NaClO was added

dropwise with stirring, so that pH was maintained at 10. After NaClO addition, a solution of 0.5 M of NaOH was added dropwise until pH did not decrease below 10. The TEMPO oxidized cellulosic fraction was washed with distilled water until neutral pH and filtered. CNF was obtained by mechanical treatment of the oxidized cellulosic fraction slurry (1% consistency) in a Panda homogenizer (GEA Niro Soavi). A total of 5 passes at 300 bar and 10 passes at 600 bar through the homogenizer were required to obtain a gel characteristic.

2.5. CNF characterization

To measure cationic demand (Mütek PCD 04), the CNF (0.04 g) was diluted in 1000 mL of distilled water and dispersed in a disintegrator for 10 min at 3000 rpm. This slurry (10 mL) was mixed with 25 mL of the cationic polymer polyDADMAC (polydiallyldimethylammonium chloride) for 5 min with magnetic stirring. The mixture was centrifuged for 90 min at 4000 rpm, and the supernatant (10 mL) was titrated in the particle charge detector with the anionic polymer PES-Na added dropwise until 0 mV. The consumed volume of the anionic polymer was used to calculate the cationic demand of CNF.

To measure conversion yields of fibers to CNF, the homogenized slurry (consistency 0.1%) was centrifuged for 20 min at 10,000 rpm. The supernatant (with the CNF) was separated from the solid fraction (partially fibrillated fibers) and it was dried at 105 °C for 24 h. Yield was determined as the percentage of the dry weight of CNF in the supernatant relative to the dry weight of the fibrous material in the initial slurry.

The polymerization degree (DP) was calculated from intrinsic viscosity by Eqs. (1) and (2) (Marx-Figini, 1987):

$$\text{DP} (< 950) \quad \text{DP} = \left[\frac{\eta_s}{0.42} \right] \quad (1)$$

$$\text{DP} (> 950) \quad \text{DP}^{0.76} = \left[\frac{\eta_s}{2.28} \right] \quad (2)$$

where η_s is the intrinsic viscosity of the cellulosic material, determined by the ISO standard 5351-1: "Determination of limiting viscosity number in cupri-ethylenediamine (CED) solution".

The water retention value (WRV) of the CNF was performed on two fractions of the same weight of CNF gel, centrifuged at 2400 rpm for 30 min to remove unbound water. Nitrocellulose membranes were placed at the bottom of the centrifuge containers (pore diameter of 0.65 μm) to retain the CNF. The samples were dried at 105 °C for 24 h to determine the dry weight. WRV was calculated as the percentage of the weight of retained water respect to the dry weight of CNF (methodology based on TAPPI UM 256).

CNF mean diameter was determined from its specific surface. The specific surface of CNF was calculated from the difference between its cationic demand and the carboxyl group content. This difference corresponds to the cationic polymer unabsorbed by the carboxyl groups (Mutjé, 1989). This value was multiplied by the specific surface generated per 1 micro-equivalent of poly-DADMAC cationic polymer ($1.027 \times 10^{17} \text{ nm}^2$) to obtain the specific surface of 1 g of CNF. Finally, the diameter of CNF was calculated by Eq. (2):

$$\text{m}^2 \text{ g}^{-1} = \frac{4}{\rho \cdot d} \quad (2)$$

where $\text{m}^2 \text{ g}^{-1}$ is the specific surface of CNF, ρ is the density of the cellulose (1.53 g m^{-3}) and d is the diameter of the CNF.

2.6. Addition of sawdust CNF and sheet formation

Unbleached eucalyptus pulp together with CNF was dispersed using a laboratory disintegrator at 3000 rpm for 60 min. The amounts of each component were calculated to obtain handsheets of 75 g m^{-2} , with 0, 3, 6, and 9 wt.% of CNF. Then, cationic starch and colloidal silica (0.5 to 0.8 wt.% on dry basis of pulp, respectively) were added and the slurry was stirred mechanically for 20 min. The handsheets were formed in a Rapid Köthen type laboratory sheet former (ISP mod. 786FH) according to ISO 5269-2. Handsheets drying was carried out at 80 °C in the vacuum dryer equipment incorporated in the sheet former. After recording the weight of the handsheets, they were conditioned in a conditioned chamber at 25 °C and 50% RH. To form handsheets from refined pulps, a slurry of 10% consistency was refined in a PFI laboratory refiner (NPMI 02 Metrotec SA) at 1000, 2000 and 3000 revolutions, and then the above described procedure was followed.

2.7. Properties of handsheets

Pulps drainage was measured with a Schopper-Riegler equipment (mod. 95587 PTI) following the ISO 5267/1 standard. The pulp fiber length distribution was determined on a pulp suspension of 0.025% consistency, using a MorFi Compact analyzer (TechPap). The results were acquired and analyzed with the MORFI v.8.3 software.

Tensile index was performed with a universal testing machine equipped with a Hounsfield 42 (load cell of 2.5 kN) following the ISO 1924-1 and 1924-2 standards. Burst index was determined by a IDM mod. EM-50 equipment (ISO 2758 standard).

Density was calculated from the weight and dimensions of handsheets, whereas porosity was calculated using Eq. (3):

$$\text{Porosity}(\%) = 100 \cdot \left(1 - \frac{\rho_{\text{handsheets}}}{\rho_{\text{cellulose}}} \right) \quad (3)$$

where $\rho_{\text{handsheets}}$ is the density of the handsheets and $\rho_{\text{cellulose}}$ is the density of cellulose (1.53 g cm^{-3}).

Table 1
Characterization of the obtained CNF.

Nanofibrillation yield	60% (approximately)
Initial carboxyl groups content	24.3 $\mu\text{eq g}^{-1} \text{ COO}^-$
Pos-oxidation carboxyl groups content	370.6 $\mu\text{eq g}^{-1} \text{ COO}^-$
Cationic demand	495 $\mu\text{eq g}^{-1}$ poly-DADMAC
Water retention value	5.1 $\text{g H}_2\text{O g}^{-1}$
Polymerization degree	203
Specific surface of CNF	60.6 $\text{m}^2 \text{ g}^{-1}$
Diameter of CNF	41 nm

3. Results and discussion

3.1. CNF manufacture and properties

Chemical composition of eucalyptus sawdust (total on od wood) was: 41.8% of glucans, 10.7% of xylans, 1.41% of acetyl groups, 32.3% of lignin, 7.86% of extractives and 0.59% of ashes.

Autohydrolysis yield was 82.2% and the total extracted hemicelluloses respect to initial content was 80.0% (8.53% total on od wood). Carbohydrate content in the residual liquor expressed as percentages of total wood was 9.74% (2.93% of xylose, 0.20% of arabinose, 0.83% of glucans, 5.76% of xylans and 0.02% of arabinans) and acetyl groups content was 0.65%. The main degradation products in residual liquors were acetic acid (0.74%), formic acid (0.18%), furfural (0.12%) and HMF (0.01%).

Kappa number of the cellulosic fraction of sawdust from the hydrothermal-alkaline soda-anthraquinone treatment was 19.4. After the oxygen stage the cellulosic fraction reached 70.1% delignification, Kappa number dropped from 19.4 to 5.8, intrinsic viscosity was 598 mL g^{-1} (degree of polymerization 1513), and hemicelluloses content was lower 3% on over dry cellulosic fraction (global yield: 30.8%).

The characteristics of the CNF are shown in Table 1.

The carboxyl group content of sawdust highly increased after oxidation (from of 24.3 to $370.6 \mu\text{eq g}^{-1} \text{ COO}^-$), which contributed to the next homogenization stage. The obtained cationic demand of $495 \mu\text{eq g}^{-1}$ showed that a portion of poly-DADMAC has been ion exchanged while the remaining has been adsorbed by London–Van der Waals forces, therefore, assuming that the polymer has been adsorbed as a monolayer this amount should be proportional to the surface area of the CNF, which was $60.6 \text{ m}^2 \text{ g}^{-1}$ (Mutjé, 1989). Accordingly, assuming that the CNF particles are ideally cylindrical, the mean diameter would be 41 nm. As the elementary fibril has a diameter of 3 to 5 nm, the obtained value indicates a wide range of diameters, evidencing the presence of elementary CNF as well as bundled CNF. This result is consistent with the homogenization yield (60% approximately). The diameters of CNF were verified by FE-SEM microphotography, as reflected in Fig. 2.

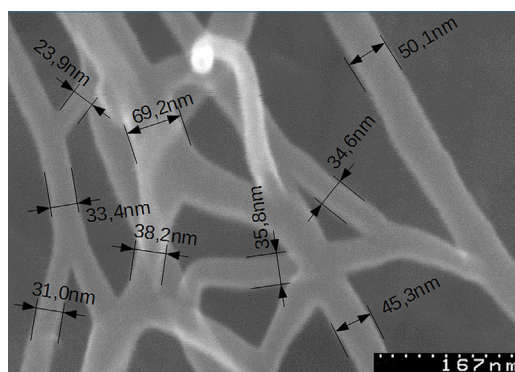


Fig. 2. Diameters of CNFs by FE-SEM microphotography.

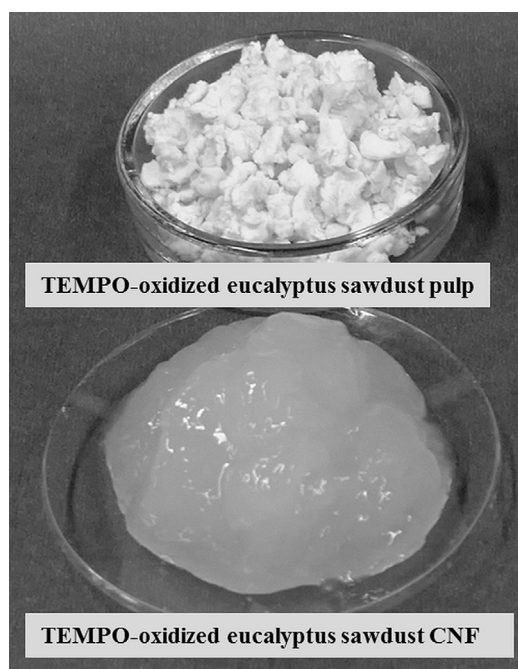


Fig. 3. CNFs from the TEMPO-oxidized cellulosic fraction of eucalyptus sawdust.

Finally, a strong depolymerization of cellulose was evidenced by the polymerization degree, which decreased from 1513 in the fractioned sawdust to 203 in the CNF, affecting its intrinsic properties. As sawdust cellulosic fraction has low hemicellulose content (<3%) is expected that affect its performance as dry strength additive when added in the papermaking furnish. The hemicelluloses are distributed between cellulose microfibrils allowing an easy penetration of TEMPO molecules during oxidation (Isogai, 2013) and facilitating the nanofibrillation of cellulosic fraction (Chaker, Alila, Mutjé, Vilar, & Boufi, 2013). Pulps with the higher hemicellulose content reach higher yields of the nanofibrillated fraction and a better aptitude for microfibrils individualization (Alila, Besbes, Vilar, Mutjé, & Boufi, 2013; Chaker et al., 2013; Galland, Berthold, Prakobna, & Berglund, 2015). By comparison, CNF obtained from bleached eucalyptus fibers has a theoretical specific surface area of $240.1 \text{ m}^2 \text{ g}^{-1}$, an average diameter of 10.4 nm, and a polymerization degree of 352 at the same oxidation level (González et al., 2012, 2013). Bleached kraft pulp generally contain around 5–15% of hemicelluloses which may have favored the nanofibrillation. Fig. 3 shows CNFs obtained from TEMPO-oxidized sawdust cellulosic fraction.

3.2. Unbleached eucalyptus pulp refining

The fiber length distribution of the unrefined unbleached eucalyptus pulp is shown in Fig. 4.

The length weighted in length and fiber diameter of the eucalyptus unrefined unbleached pulp were $557 \mu\text{m}$ and $16.7 \mu\text{m}$, respectively with a fine content of 15.6%. The properties of this pulp were 16°SR (Schopper–Riegler degree), kappa index 14 and

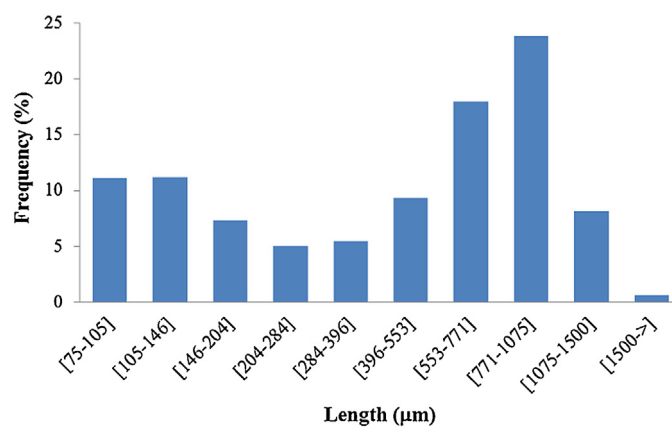


Fig. 4. Fiber length distribution of the unrefined unbleached eucalyptus pulp.

27.3 N m g^{-1} of tensile index. The fraction of particles smaller than $76 \mu\text{m}$ were considered fines, so fiber length weighted in length was smaller than the usual values for this pulps. On the contrary, $^\circ\text{SR}$, Kappa number and tensile index values were the usual for this kind of never-dried pulp (Area et al., 2010). The variation of handsheets properties from this pulp with the refining treatment are shown in Table 2.

PFI refining produces internal and external fibrillation and a consequently, the swelling capacity of fibers increases (Carrasco, Mutjé, & Pèlach, 1996). Other consequences are the reduction of fiber length, the increase of fines percentage and the decrease of drainage capacity. As shown in Table 2, this treatment increased density and strength, whereas drainage and porosity decreased. In the studied interval, $^\circ\text{SR}$ increased linearly, certainly due to the increase in specific surface of fibers, and mechanical tensile properties improved correspondingly. The increase of applied energy (number of revolutions) produced an almost linear evolution of tensile index, which correspond to other physical and mechanical properties of the paper as Scott bond and burst index. Refining also increased Young's modulus of the paper (rigidity) and density (reduced bulk) so the percentage of paper voids (porosity) decreases linearly. Industrial refining produces greater effects than laboratory refining in PFI, especially of morphological type, since the industrial disc refiner enhances fiber fibrillation and cutting, increasing fines percentage and decreasing fiber length.

3.3. CNF addition as papermaking additive

Handsheets properties of an unbleached unrefined pulp with different charges of CNF from the cellulosic fraction of eucalyptus sawdust are shown in Table 3.

The addition of 9 wt.% of CNF to this cellulosic fraction of sawdust produced a lineal increase in mechanical strength, equivalent to that produced by 1600 revolutions of PFI refining (53.3 N m g^{-1}). However, the incorporation of the same percentage of CNF produced from eucalyptus bleached pulp to the same furnish generated a tensile index 46% higher, equivalent to 3500 revolutions of PFI refining (González et al., 2012, 2014). Although the improvement

Table 2

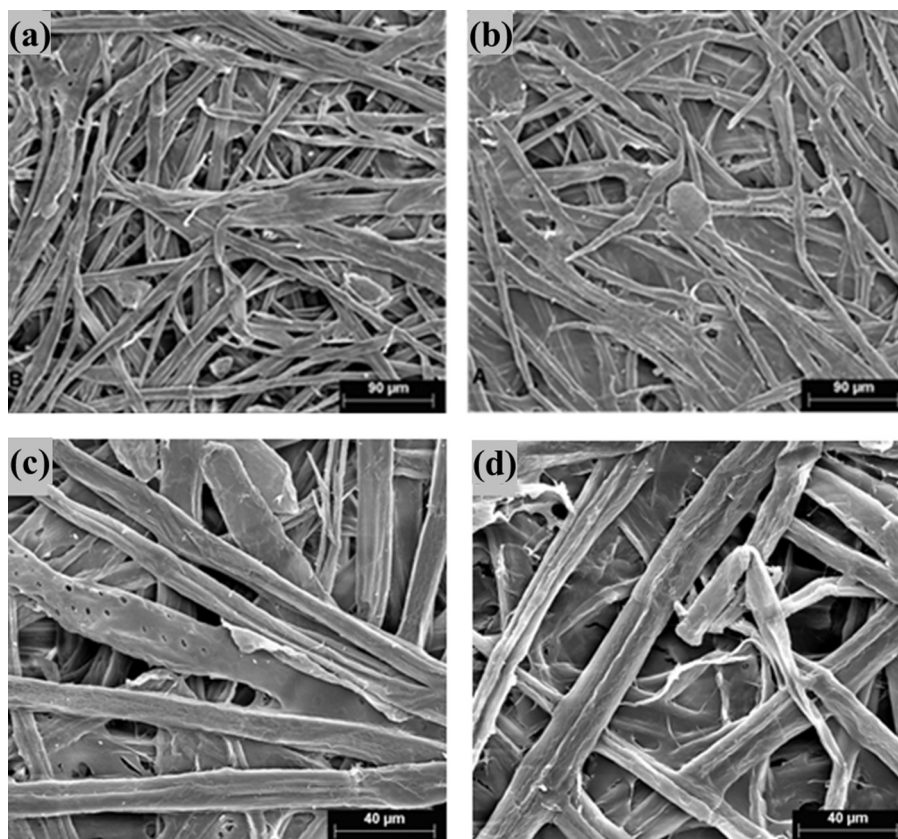
Properties of the refined unbleached eucalyptus pulp (\pm standard deviation).

Rev. PFI	$^\circ\text{SR}$	Tensile index (N m g^{-1})	E (GPa)	Density (g cm^{-3})	Burst index ($\text{kPa m}^2 \text{ g}^{-1}$)	Porosity (%)
0	16	27.3 ± 1.0	3.85 ± 0.05	0.54 ± 0.02	1.35 ± 0.06	63.9 ± 0.6
1000	23	45.2 ± 0.8	4.51 ± 0.10	0.66 ± 0.04	3.20 ± 0.08	56.3 ± 0.4
2000	36	57.3 ± 1.1	5.35 ± 0.07	0.71 ± 0.04	4.90 ± 0.12	53.0 ± 0.7
3000	50	68.1 ± 0.7	5.75 ± 0.11	0.75 ± 0.03	7.15 ± 0.04	50.1 ± 0.3

E: Young's modulus.

Table 3Effect of CNF from fractionated eucalyptus sawdust addition on the properties of unbleached unrefined pulp (\pm standard deviation).

CNF (%)	$^{\circ}$ SR	Tensile index (N m g^{-1})	E (GPa)	Density (g cm^{-3})	Burst index ($\text{kPa m}^2 \text{g}^{-1}$)	Porosity (%)
0	16	27.3 ± 1.0	3.85 ± 0.05	0.54 ± 0.02	1.35 ± 0.06	63.9 ± 0.6
3	22	37.0 ± 0.7	4.25 ± 0.12	0.57 ± 0.01	2.95 ± 0.11	61.8 ± 0.3
6	26	41.3 ± 0.9	5.95 ± 0.08	0.64 ± 0.01	4.70 ± 0.12	57.1 ± 0.7
9	34	53.3 ± 1.1	5.95 ± 0.05	0.66 ± 0.03	6.10 ± 0.09	55.9 ± 0.5

 E : Young's modulus.**Fig. 5.** SEM images of a 60 g m^{-2} handsheets of (a and c) an unbleached unrefined pulp, (b and d) the same pulp with 6 wt.% of CNF.

in properties produced by adding CNF from the cellulosic fraction of sawdust was a bit inferior, its effect on Young Module was in the same order to those obtained when unbleached eucalyptus pulp was refined at different revolutions. The Young Module of handsheets with 9 wt.% of CNF from eucalyptus bleached pulp was equivalent to Young Module of handsheets refined at 3000 revolutions. Similarly, $^{\circ}$ SR increase was low when sawdust CNF was added (34° SR vs. 68° SR with the addition of 9 wt.% CNF from eucalyptus bleached pulp). WRV showed analogous behavior ($5.1 \text{ g H}_2\text{O g}^{-1}$ vs. $8.3 \text{ g H}_2\text{O g}^{-1}$). Density, burst index and porosity also reflected the lower bonding capacity of CNF from the cellulosic fraction of sawdust. On the contrary, Young's modulus (stiffness) showed the similar values than those obtained by refining at 3000 revolutions. Tensile strength of the paper is controlled by the tensile strength of fibers and by the strength of interfiber bonding. As well, the strength of interfiber bonding depends on the relative bonded area "RBA" between fibers, and of the bond strength per unit of bonded area "b" (Page, 1969). For the same fiber strength, CNF addition would act as an adhesive increasing "RBA" and "b", thus increasing the tensile strength of the sheet. The same behavior is usually verified for burst strength. This is also reflected by density, which increased to 0.695 g cm^{-3} (5%) and porosity, which decreased up to 53.65%. This can be interpreted as a positive effect on barrier

properties. Fig. 5 shows SEM images of handsheets (60 g m^{-2}) of unbleached unrefined pulp (Fig. 5a and c) and of the unbleached unrefined pulp with 6 wt.% of CNF from the cellulosic fraction of eucalyptus sawdust (Fig. 5b and d).

Other groups reported similar results using comparable systems. Addition of 10% CNF (prepared from bleached softwood sulphite pulp) to unrefined softwood sulphite pulp without retention aid, produced similar improvement on tensile strength and density of handsheets than pulp refining (Sehaqui, Zhou, & Berglund, 2013). Increased density and strength are reported in studies where CNF was added to sheets (Ahola, Österberg, & Laine, 2008; Eriksen, 2008; Sehaqui et al., 2013). Possible reasons are: (i) CNF is fine material which helps to consolidate the sheet, and (ii) CNF is attached to fiber surfaces as a layer, thus increasing the number of hydrogen bonds (Brodin, Gregersen, & Syverud, 2014).

4. Conclusions

CNF (virtually free of hemicelluloses and lignin) was obtained from an eucalyptus sawdust cellulosic fraction using a sequential processes into a biorefinery concept. The production of CNF from sawdust cellulosic fraction achieved 60% yield. The lower yield of

the nanofibrillated fraction can be attributed to low hemicelluloses content in the cellulosic fraction. The estimated specific surface and average diameter of these CNF were $60\text{ m}^2\text{ g}^{-1}$, and 41.0 nm, respectively.

The addition of 9% of CNF to an unbleached unrefined pulp produced a lineal increase in mechanical strength, equivalent to that produced by 1600 revolutions PFI refining.

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