

FROM PINE SAWDUST TO CELLULOSE NANOFIBRES

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Biorefinery technology is a current alternative to petroleum based industry to produce energy, chemicals and materials. The use of forest and agricultural lignocellulosic residues as raw materials to generate value-added products has become a topic of great interest due to their renewability and availability. Pine sawdust is a promising candidate as raw material for biorefinery. This waste, which comes from the primary industrialization of wood, is available in large quantities, at low cost, and is currently open-airburned.

The aim of this study was to obtain cellulose nanofiber (CNF) from pine sawdust. Delignification methods were applied to pulp until a kappa number lower than 1 was achieved. CNF was produced by the combination of chemical (TEMPO-oxidation) pretreatment and mechanical destructure in a homogenizer. Once CNF was produced at different oxidation degrees, the degree of polymerization, cationic demand, carboxyl rate, and the yield of fibrillation were determined with the purpose of assessing the effect of the oxidation degree on the final properties thereof. Finally, the suitability of using the obtained CNF as paper strength additive was studied through the assessment of the mechanical properties increase of paper.

Keywords: cellulose nanofibres, TEMPO-oxidation, characterization, papermaking, cost production

INTRODUCTION

Biorefinery technology is a real alternative to petroleum based industry to produce energy, chemicals and materials. The use of forest and agricultural lignocellulosic residues as raw material to generate high value-added products has become a relevant topic due to their renewability and high availability. Pine sawdust is a promising candidate as raw material for biorefinery. This waste, which comes from the primary industrialization of wood, is available in large quantities and at low cost, and it is currently open-air burned.¹ Current environmental restrictions, in addition to the need for finding new economic benefits, make this waste an adequate raw material for the production of value-added byproducts in the context of a forest biorefinery. Among these value-added byproducts, nanocellulose deserves special attention.

The interest in nanocellulose research has increased significantly in recent years,² focusing on the development of processes for nanocellulose production, characterization and potential applications. However, it must be mentioned that nanocellulose can be classified as follows:

nanofibrillated cellulose (CNF),³ cellulose nanocrystals or nanowhiskers (CNC),⁴ and bacterial nanocellulose (BNC).⁵

CNF consists of cellulose aggregates with diameters between 5 and 60 nm and several microns in length. CNF can be obtained from different raw materials like softwood, hardwood, annual plants or agricultural waste. However, most publications about nanocellulose production use bleached wood fibres as raw material. The processes to obtain CNF usually include chemical or enzymatic pretreatments followed by a mechanical treatment.⁶ Pretreatments help to reduce the energy consumption during cellulose fibres nanofibrillation, from 20,000-30,000 kWh/ton to about 1000 kWh/ton.⁷ Nevertheless, sometimes the use of chemicals increases significantly the production costs of CNF, which makes it unaffordable for the papermaking industry. In the case of enzymatic hydrolysis, enzymes degrade lignin and hemicelluloses while preserving the cellulose fraction.⁸ On the other hand, chemical pretreatments, such as catalytic oxidation with 2,2,6,6-tetramethylpiperidine-1-

oxyl (TEMPO) in water, is the most promising and efficient chemical pretreatment to produce CNF for high-tech applications. When cellulosic fibres are oxidized using a TEMPO/NaBr/NaClO system in water at room temperature and pH 10 for 2-4 h, C6-carboxyl groups are selectively formed on the crystalline cellulose microfibrils and carboxyl contents up to 1.8 mmol g⁻¹ can be achieved, depending on the oxidation conditions.⁹ The destructuration stage involves passing a pretreated fibre suspension through the destructuration equipment (high pressure homogenizer, microfluidiser, or micro-grinder). Nanofibrils are obtained by shearing forces when the fibres are forced to collide against the elements of the equipment and also between them. The high bonding capacity of nanocellulose prepared by TEMPO-oxidation pretreatment allows the generation of a gel suspension at 1wt%. CNF has a wide variety of potential applications, including its use as dry strength additive for paper and board,^{10,11} barrier material,¹² nanopapers,^{13,14} nanocomposites,^{15,16} thickeners, hydrogels and aerogels.¹⁷

The aim of this work was to produce CNF from pine sawdust. The cooking process and delignification treatments have an imperative role on the nanofibrillation of cellulose pulps, according to Chaker *et al.*¹⁸ The raw material, initially delignified with sodium hydroxide was further treated by oxygen bleaching. CNF was produced by varying the oxidation degree and passing the fibres through a homogenizer. Once CNF was produced at different oxidation degrees, the degree of polymerization, cationic demand, carboxyl rate, and the yield of fibrillation were determined with the purpose of determining the effect of the oxidation degree over the final properties thereof. Finally, the suitability of using

the obtained CNF as paper strength additive was studied through the assessment of the mechanical properties increase of paper.

EXPERIMENTAL

Materials

Pine sawdust from a Misiones (Argentina) sawmill was used as raw material. The pine sawdust pulp was prepared with a solid/liquid ratio of 1:5, 20% NaOH and 0.1% AQ during 215 minutes at 170°C. This never-dried pulp was treated as shown in the flow chart of Figure 1 in order to obtain different levels of nanofibrillation.

Further delignification treatments

The pine sawdust pulp was treated in a multipurpose reactor provided with a high shear rotor, a valve for oxygen input and a heating system. The treatment was performed in three steps. Firstly, the pulp was treated with 6 Kg/cm² oxygen, with 2.6 wt% NaOH, 0.086 wt% MgSO₄, 16.1% consistency at 100°C for 60 min. Secondly, the resultant fibres were suspended in a sulphuric acid solution to pH 2.3 for 30 minutes at 2.5% consistency. Finally, the pulp was treated with ozone for 60 minutes.

TEMPO-mediated oxidation

Pine sawdust pulp was subjected to TEMPO-oxidation according to Saito *et al.*¹⁹ The purified pine sawdust pulp (15 g) was suspended in water at 1% consistency (1500 mL) containing TEMPO (0.24 g) and sodium bromide (1.5 g). When all the catalyst was completely dissolved, TEMPO-oxidation was started by adding dropwise a known amount of NaClO to the pulp slurry (5, 10 and 15 mmols per gram of dry pulp) under continuous stirring and at room temperature, so as to maintain a pH of 10. During the reaction time, 0.5 M NaOH was added to maintain the pH at 10 until no decrease in pH was observed. The TEMPO-oxidized pulp was then washed exhaustively using distilled water until reaching a neutral pH.

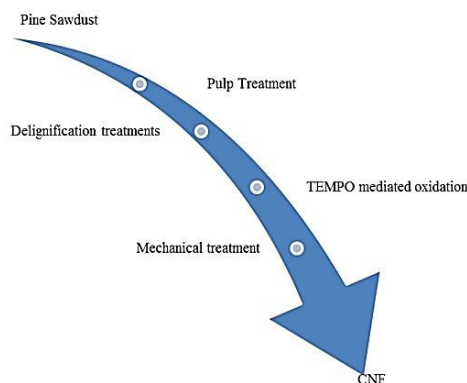


Figure 1: Scheme of CNF production

Mechanical treatment

The nanofibrillation process was performed from the obtained TEMPO-oxidized pulps with different degrees of oxidation. These pulps were repeatedly passed through a Panda homogenizer (GEA NiroSoavi Plus 2000) at 600 bar to break the fibril bundles in fibre walls (nanofibrillation). After nanofibrillation, a transparent gel suspension was obtained.

Characterization of cellulose nanofibres

The carboxyl content was determined by conductimetric titration. A dried sample (50 to 100 mg) was dispersed in hydrochloric acid (15 mL of 0.01 M) solution and stirred for 10 min. The titration was carried out by adding NaOH solution at 0.01 M to the suspension, recording the conductivity in mS/cm. The experiment was performed with constant N₂ bubbling. The titration plotted curve, relating NaOH volume and conductivity, showed the presence of a strong acid (corresponding to the excess of HCl) and a weak acid (corresponding to the carboxyl content).

The degree of polymerization of CNF suspensions was estimated from the intrinsic viscosity. Measurements of viscosity for CNF suspensions were carried out according to TAPPI Standard Method T230 om-99, at 1% solid consistency, using 0.5 M cupriethylenediamine as dissolving agent and a capillary viscometer. The degrees of polymerization were then calculated according to the equation: $\eta = K \cdot M^a$, where η is the intrinsic viscosity, $K = 2.28$ and $a = 0.76$ (Henriksson *et al.*).²⁰

The cationic demand of the CNF was performed by the potentiometric titration method with a Mutek PCD 04 Particle Charge Detector. The dried sample (0.04 g) of CNF was diluted in 1 L distilled water and was dispersed during 10 minutes at 3000 rpm in a pulp disintegrator. After that, 10 mL of suspension was mixed with 25 mL of cationic polymer (polyDADMAC, 0.001 N) and was centrifuged (90 minutes at 4000 rpm). Finally, the supernatant (10mL) was titrated on the Mutek equipment with anionic polymer (Pes-Na, 0.001 N).

Nanofibrillation yield was determined as a percentage of the dry weight of CNF in the supernatant relative to the dry weight of the fibrous material in the initial slurry. For this, a CNF suspension was centrifuged with 0.2% solid content at 10000 rpm for 20 minutes. The sediment was recovered and dried until constant weight.

UV-Vis transmittance of the CNF suspensions with 0.1% solid content at 800nm wavelength was determined. Transmittance measurements were performed with a UV-Vis Shimadzu spectrophotometer UV-160A, using quartz cuvettes and distilled water as reference.

Theoretical specific surface area and the diameter of the nanofibres were calculated, according to the possible mechanism of interaction between the cationic

polymer (poly-DADMAC) and the CNF surface, as reflected in Figure 2. Two interactions are possible: ionic interaction between the cationic polymer and the carboxylic groups on the cellulose surface, and surface interactions due to London-Van der Waals forces. If these two interactions occur simultaneously and the cationic polymer forms a single layer, by estimating the specific surface area of a single polymer molecule, it would be possible to theoretically calculate the specific surface area of the CNF:

$$\sigma_{DADMAC} = \pi \cdot d \cdot l$$

where, σ_{DADMAC} is the monomer's area, and d and l are the diameter and length of the monomer's molecule, calculated to be 0.528 nm and 0.488 nm, respectively. The result is 0.809 nm² for a single monomer. Since the average degree of polymerization of poly-DADMAC is 662, the surface area of the polymer is the surface area of the monomer multiplied by the degree of polymerization (DP), 535.56 nm² per mol, and the specific surface of the polymer mol would be:

$$\sigma_{DADMAC} = 535.56 \text{ nm}^2 \cdot 6.02 = 3224 \cdot 10^{23} \text{ nm}^2 / \text{mol}$$

Then, σ_{DADMAC} is converted from nm²/mol to nm²/μeq by the equation:

$$\sigma_{DADMAC} = \frac{3224 \cdot 10^{23} \text{ nm}^2}{662 \cdot 10^6 \mu\text{eq}} = 4.87 \cdot 10^{17} \text{ nm}^2 / \mu\text{eq}$$

Considering the stoichiometric relationship between hydroxyl and carboxyl groups with poly-DADMAC, the following relationship can be applied:

$$\sigma_{LCNF} = (CD - CC) \cdot \sigma_{DADMAC}$$

where σ_{LCNF} is the specific surface area of one gram of LCNF, CD the cationic demand and CC the carboxyl content of the sample. Finally, it is possible to calculate from this value the average diameter of a single CNF fibre (d_{CNF}), considering a cylindrical geometry:

$$d_{CNF} = \frac{4}{\sigma_{CNF} \text{ m}^2 / \text{g} \cdot 1000 \cdot 10^{21} / \text{m}^2}$$

The increase in breaking length produced by the addition of 3% LCNF to a bleached hardwood kraft pulp (BHKP) was evaluated to verify nanofibres as reinforcement in papermaking. A suspension of 30 dry grams of fibre was disintegrated in a pulper at 3000 rpm at 1.5% consistency for 30 minutes. The amount of nanofibres needed for obtain a 3% LCNF on pulp was then added. These nanofibres were dispersed for 60 minutes at 3000 rpm.

The suspension was then transferred to a plastic jar and it was adjusted to a known volume with water. This suspension was constantly stirred to avoid precipitation of the fibres and aggregation of the nanofibres. Immediately after that, 0.5% cationic starch and 0.8% of colloidal silica (on fibre dry weight in both cases) were added. The suspension was kept under stirring for at least 20 minutes before making the sheets.

The cost of production was calculated on the basis of the chemical reagents used and energy costs. The cost of the chemical reagents was calculated at laboratory scale and the energy cost was measured by the energy consumption of the equipment used during CNF production (Circutor CVM-C10 and SocomecDiris A20, both from Spain). The price of energy was estimated at 0.08 €/kWh.

RESULTS AND DISCUSSION

A raw pulp with a yield of 49.3% and 44.9 kappa number was obtained from unbleached pine sawdust. The yield of the bleaching process was 97.7% and the kappa number was below 1.

The characterization of the CNF obtained at three different levels of TEMPO-oxidation and different levels of destructuretion is presented in Table 1.

Oxidation time increased exponentially with the increase of the oxidation level, which is a typical kinetic behaviour of the oxidative reaction (Table 1).

The sodium carboxylate content of TEMPO-oxidized cellulose is controllable by the amount of NaClO added during the oxidation. The amount of carboxylate groups formed from the primary hydroxyl groups of cellulose increased with the amount of NaClO added, as expected (Figure 1).

The carboxyl content increased markedly using 5 and 10 mmols of NaClO, but it reached a plateau between 10 and 15 mmols. This behaviour is probably the consequence of the difficulty of further oxidizing the fibres, once most hydroxyl groups have reacted. Moreover, the reaction time required for raising the carboxyl content from 940 to 1038 µeq was three times higher than that for raising it from 543 to 940 µeq. This is mainly due to the accessibility of the fibre, as it becomes lower at higher oxidation levels, because the fibre surface is close to reaching saturation and thus the acceptance of more carboxyl groups on fibre surface is hindered (Figure 3).

Table 1
Results of the characterization of CNF from sawdust pulp

Experimental	CNF-1	CNF-2	CNF-3
NaClO added in TEMPO-oxidation (mmol g ⁻¹)	5	10	15
Oxidation time (min)	90	150	330
Destructuration	6p 600bar	3p 600bar	2p 600bar
Applied energy (kWh/kg)	28.8	14.4	9.6
Carboxylate content (µmol g ⁻¹)	543	940	1038
Nanofibrillation yield (%)	88.8	89.7	94.4
Transmittance (%)	85.7	92.5	96.2
Polymerization degree	139	132	150
Cationic demand (µeq g ⁻¹)	1142	1657	1838
Specific surface (m ² g ⁻¹)	291.7	349.2	389.6
Diameter (nm)	8.57	7.15	6.42

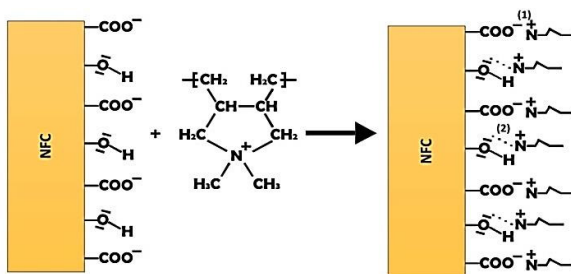


Figure 2: Scheme of CNF interactions

The level of destructuration was determined qualitatively according to the appearance of the obtained hydrogel, which presented differences in

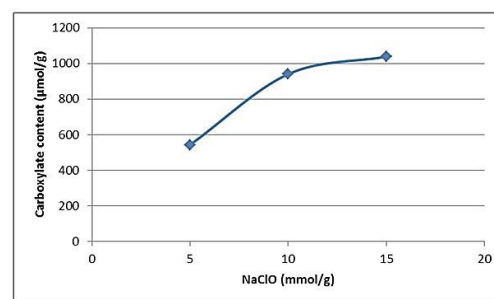


Figure 3: Carboxylate content of TEMPO-oxidized pulp with different amounts of NaClO

the nanofibrillation yield. When the nanofibrillation yield increased with TEMPO-oxidation, the transmittance tended to 100%

(Figure 2). Nanofibrillation yield with regard to carboxyl content has shown the same behaviour. The evolution of the nanofibrillation yield depends mainly on the oxidation level and the energy applied during the destructure process (number of passes). As NaClO charge increased, the required energy decreased (Table 1). A good inverse correlation between the carboxyl content and the nanofibrillation yield was verified under these conditions. On the other hand, the transmittance at 800nm increased with the nanofibrillation yield. TEMPO-oxidations at 10 and 15 mmol NaClO resulted in high nanofibrillation yields (>85%) at low levels of destructure energy applied, proving that the oxidation level prevails over the energy to separate nanofibre bundles.

The polymerization degree is often used to evaluate the effect of the treatment with TEMPO-oxidation on the properties of the produced CNF. As the severity of TEMPO-oxidation increased, the degree of polymerization tended to decrease until certain levels and then remained practically constant. The polymerization degree decreased by 75% for the TEMPO-oxidized pulp, in comparison with the bleached pulp. These results are in agreement with those of Shinoda *et al.*,²¹ and Isogai *et al.*²²

As the carboxyl content increased (as a consequence of the increase in oxidation level), the cationic demand also increased, mainly due to the increase of the CNF specific surface, involving a higher density of negative charges on the nanofibre surface. However, the obtained values allow remarking that the amount of standard cationic polymer far outweighs the stoichiometric 1:1. This might be due to the existence of two interaction mechanisms: ionic

exchange (probably stoichiometric) and surface adsorption by Van der Waals forces (Figure 4).

While the carboxyl content refers only to the ionic interaction, the cationic demand involves ionic interaction and surface adsorption. The difference between these values allows estimating the specific surface and the diameter of the CNF, taking into account the specific surface of a standard cationic polymer, such as polyDADMAC, which is used for colloidal titration. At higher oxidation levels, higher specific surface values and lower diameter values are appreciated. This is mainly due to the increase of carboxylic groups at high oxidation levels.

In order to calculate the specific surface and the diameter of CNF, the polymerization degree of polyDADMAC (P^+) was considered as 662. Taking into account the diameter and length of the monomer, the specific surface of P^+ was estimated as $4.87 \cdot 10^{17} \text{ nm}^2/\mu\text{eq-g/g}$. Moreover, the specific surface of CNF (σ^{CNF}) was calculated from the equation:

$$\sigma^{\text{CNF}} = CD(\text{ad}) \sigma^{P^+}$$

Finally, the diameter of the CNF was obtained applying the geometrical rules corresponding to a cylinder:

$$d^{\text{CNF}} = 4 / (\rho_{\text{cellulose}} \sigma^{\text{CNF}})$$

In all cases, the CNF diameters were about 10 nanometres, which is in agreement with those reported by Gamelas *et al.*²³ A comparison among CNF-1, CNF-2 and CNF-3 evidences that TEMPO-oxidation has a major effect on the resulting diameter of the nanofibrils.

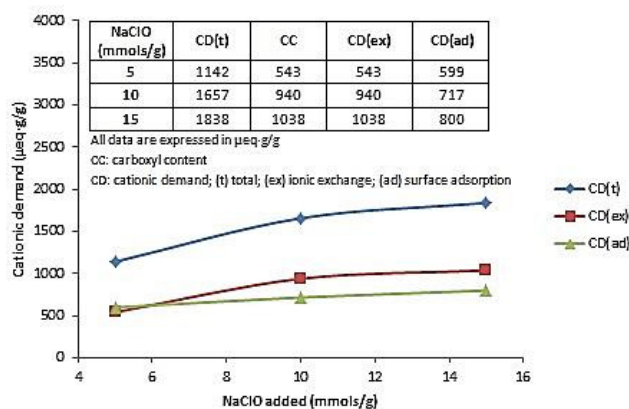


Figure 4: Cationic demand (total, ionic exchange and surface adsorption) of CNF

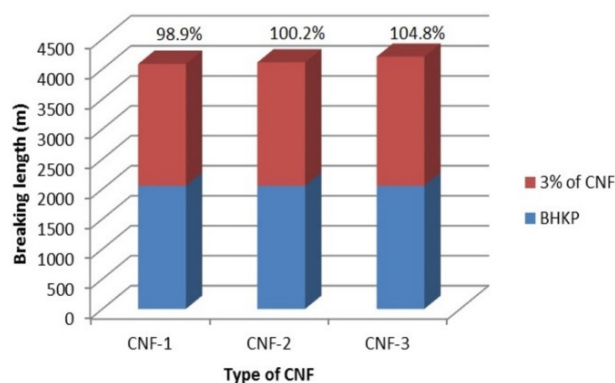


Figure 5: CNF performance as dry strength agent

Table 2
Cost production of different CNFs

Cost (€/kg)	CNF-1	CNF-2	CNF-3
Energy	1.86	2.22	2.45
Chemicals	203.65	253.49	303.06
Total cost	205.51	255.71	305.51

The evaluation of the reinforcement capacity of CNF in papermaking was assessed through the increase in breaking length, when 3% of each kind of CNF was added on a bleached kraft hardwood substrate. The results are shown in Figure 5.

The addition of 3% of CNF increased the breaking length of the sheets in all cases. The tensile strength of paper mainly depends on three factors (Delgado-Aguilar *et al.*):²⁴ the number of bonds per volume unit, the quality of the bonds, and the intrinsic tensile strength of the fibres. At similar intrinsic tensile strength of fibres and quality of bonds, the obtained increase would be associated to the number of bonds per volume unit. Consequently, this effect could be attributed to the CNF addition, being common to all CNFs, even to that obtained under the mildest conditions.

The cost of production of different CNFs is shown in Table 2. An increase in sodium hypochlorite pretreatment produced a decrease of the energy cost. These results demonstrate that TEMPO-mediated oxidation pretreatment facilitates nanofibrillation. Nevertheless, this reduction in energy cost is lower than the increase in the cost of chemical reagents. In conclusion, the intensification of TEMPO-oxidation pretreatment increased the production cost of CNF, without significant difference on the paper reinforcement potential.

CONCLUSION

The suitability of nanofibrillating a pine sawdust pulp for LCNF production has been demonstrated.

Higher levels of NaClO in TEMPO-oxidation pretreatment lead to an increase in the carboxyl content of the obtained CNF, improving the nanofibrillation yield. TEMPO-oxidation pretreatment produces fibre depolymerisation until a practically constant value. An increase in sodium hypochlorite increases the specific surface area and decreases the diameter of the CNF. The mildest pretreatment was demonstrated as sufficient to obtain efficient CNF for papermaking use. Severe TEMPO-oxidation pretreatment conditions reduced the energy necessary in the deconstruction stage, but increased the production cost of CNF.

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