Approaching a Low-Cost Production of Cellulose Nanofibers for Papermaking Applications

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The use of cellulose nanofibers (CNF) as an additive in papermaking is an attractive alternative to improve paper's strength. However, the costs of CNF production need to be competitive compared to other approaches aimed at reducing mechanical beating. Five different types of CNFs were prepared following different pretreatments: TEMPO-mediated oxidation at basic and neutral conditions, soft acid hydrolysis, enzymatic treatment, and mechanical beating. All of the pretreated fibers were later passed through a high-pressure homogenizer. The resulting CNFs were each applied to a papermaking pulp to investigate their reinforcing ability. Results indicated that the TEMPO-oxidized CNFs offered the highest increase at the same nanofiber content compared to the other types of CNFs. However, an analysis of the cost of increasing paper's breaking length by 75% indicated that TEMPO-oxidized CNFs were more expensive than the other CNF grades, whereas CNFs from mechanical and acid pre-treatment offered similar increases at lower prices. The results indicated that CNFs of high fibrillation degree were not necessary to induce dramatic increases in paper strength. This finding offers a new possibility for the escalation of CNF production to industrial levels with competitive prices.

Keywords: Cellulose nanofibers; Papermaking; Costs; Mechanical properties

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INTRODUCTION

At times, scientific research has to include in its investigation the costs of the development, production, and application of certain products at an industrial scale. This is the case for the production of cellulose nanofibers (CNFs) for bulk application in papermaking. The term cellulose nanofibres (CNF) is applied to aqueous suspensions in which cellulose fibres (usually from bleached wood pulps) have been disintegrated until the microfibrils are released from the plant cell wall. These microfibrils suspensions already form gel-like substances at very low (0.5 to 2 wt %) concentrations (Klemm *et al.* 2011). Usually, intense mechanical treatments are required to effectively release the microfibrils.

CNFs are becoming a topic of great interest to researchers from many new and well-established scientific and technological fields alike. The amount of publications that deal with the production, characterization, and application of CNFs has been steadily increasing over the last several years. These studies mainly deal with CNFs fabricated from bleached wood fibers pretreated by TEMPO-mediated oxidation at slightly acidic or basic pH before the fibers undergo an intense mechanical treatment in a high-pressure homogenizer or microfluidizer. The conditions of TEMPO-mediated oxidation control the charge density on the fibers' surfaces, which determines several of the final properties of CNFs (Isogai *et*

al. 2011). Pretreatment is aimed at reducing the amount of energy necessary to break down the fibers' structure and at avoiding clogging of the system by fiber entanglement (Spence *et al.* 2011). Energy savings after this chemical pretreatment have been estimated to be up to 98% (Josset *et al.* 2014). Other types of pretreatments include enzymatic hydrolysis with endoglucanases, acid hydrolysis, and mechanical shearing.

The reduction of energy consumption in the papermaking industry has been extensively studied. One of the main methods of energy reduction is to decrease the amount of mechanical beating applied to papermaking pulps. Mechanical beating consumes about 30% of the total electrical energy necessary in papermaking (Lecourt *et al.* 2010). Some of the strategies used to optimize this process include adapting the plate pattern of beaters to modify fiber treatment, varying the pulp consistency, increasing flow through the beater, or redesigning the equipment or beating strategy (Lecourt *et al.* 2010). However, some of these options require modifying existing equipment and making an important investment. The application of dry-strength additives such as cationic polyelectrolytes is extensively used as method to improve strength in paper and drainage rate. The use of enzymes, particularly cellulases, on papermaking pulps has also been studied as a green approach for reducing beating (García *et al.* 2002; Cadena *et al.* 2010) or eliminating it altogether (González *et al.* 2013).

The application of CNFs as an additive for pulp slurries has been recently assessed as an effective alternative to mechanical beating for improving paper strength (Eriksen *et al.* 2008; Taipale *et al.* 2010; González *et al.* 2012; Brodin *et al.* 2014; Delgado-Aguilar *et al.* 2015). Such studies demonstrated that the addition of CNFs into papermaking slurries effectively increased the tensile strength and rigidity of paper by amounts similar to those achieved with mechanical beating. However, in order to consider CNFs as a real alternative to mechanical beating at an industrial scale, it is necessary to assess the final price of CNFs and their effectiveness.

Several attempts have been made to calculate and reduce the price of CNFs by trying to diminish the amount of mechanical treatment. Zimmermann *et al.* (2010) found that the choice of a proper pretreatment was a key factor in reducing the final price of CNF production. Spence *et al.* (2011) studied the energy consumption and physical properties of CNFs produced by different processing methods, finding that the fabrication cost of CNFs could be lower than some plastics typically used in packaging if fiber pretreatment and mechanical processing were optimized.

Extensive chemical pretreatment has also been studied as a way to reduce the energy input necessary to release the nanofibers (Tejado *et al.* 2012). More recently, Josset *et al.* (2014) correlated the amount of energy applied to different cellulose-based materials (using a grinding process) with the mechanical properties and specific surface area of the resulting fibrillated materials. Naderi *et al.* (2015) used carboxymethyl cellulose as an additive for wood pulp in order to aid the microfluidization process and obtain energy-efficient CNFs.

In the present work, CNFs were fabricated after 5 different types of pretreatments: TEMPO-mediated oxidation at basic and neutral pH, enzymatic hydrolysis, soft acid hydrolysis, and mechanical pretreatment. Every pretreatment was then followed by high pressure homogenization. The cost and effectiveness of such CNFs to increase the original breaking length of a commercial hardwood pulp by 75% was then examined to determine the final price and reinforcing potential of each grade of CNF.

EXPERIMENTAL

Materials

Bleached kraft hardwood (BKHW) pulp, kindly supplied by Ence-Celulosas de Asturias S.A. (Spain), was used to produce the different types of CNFs and also to prepare the handsheets. All of the chemicals used in the production of the CNFs were provided by Sigma Aldrich S.A. (Spain) and were used as supplied. Cationic starch and colloidal silica were used as retention agents, as reported previously (Gonzalez *et al*. 2012), and were supplied by Torraspapel S.A (Spain). The enzyme used for enzymatic hydrolysis was a Novozym 476, a monocomponent endo-1,4-b-glucanase with a declared activity of 4500 ECU g^{-1} according to the supplier.

Methods

The experimental procedure followed during the implementation of the present work is shown in Fig. 1.

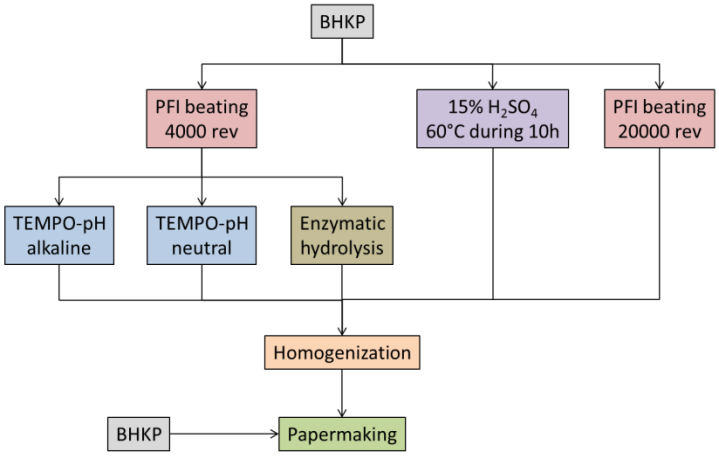

Fig. 1. Flowchart of the experimental procedure.

After pretreatment, each type of pulp was rinsed with water and suspended. Next, a 1-wt% aqueous suspension was formed and passed through a Panda 2K NS1001L high-pressure homogenizer (GEA Niro Soavi, Italy) 3 times at 300 bar and 7 times at 600 bar.

TEMPO-oxidized CNFs at alkaline and neutral pH (T10-CNF and T7-CNF)

First, BKHW pulp was beaten in an NPFI-02 PFI mill (Metrotec S.A. Spain) at 4000 revolutions, according to TAPPI method T-248 sp-08. Next, the oxidation was carried out at alkaline (pH 10) and neutral (pH 7) conditions, according to methodologies by Saito *et al.* (2007) and Besbes *et al.* (2011), respectively.

Enzyme-treated CNFs (Enz-CNF)

The enzymatic hydrolysis was performed on the same type of beaten pulp used for the TEMPO-mediated oxidation at a consistency of 5 wt% and a pH of 5. The treatment involved maintaining a temperature of 50 ºC for 3 h, with mechanical stirring, at an enzyme charge of 1.6 wt% (Novozym 476). The process was stopped by heating the suspension to 80 ºC for 30 min.

Acid-treated CNFs (Acid-CNF)

Acid-treated CNFs were obtained from unbeaten pulp. The treatment was carried out at 60 ºC for 10 h on a 5 wt% suspension with 15 wt% of pure sulfuric acid relative to the amount of fiber.

Mechanical CNFs (Mec-CNF)

Mechanical CNFs were prepared from pulp that was beaten at 20000 revolutions in a PFI mill before being passed through the homogenizer.

Characterization and cost evaluation of CNFs

Yield of fibrillation was calculated by a centrifuging a CNF suspension with 0.2% of solid content at 10000 rpm during 20 min in order to isolate the nanofibrillated fraction (contained in the supernatant) from the non-fibrillated one retained in the sediment fraction which is recovered, weighed, and oven-dried until constant weight. Transmittance measurements were performed on CNF suspensions with 0.1% of solid content. The sample was introduced in quartz cuvettes and the transmittance measured with a UV-Vis Shimadzu spectrophotometer UV-160A set in the range between 400 and 800 nm. Distilled water was used as reference. The content of COOH groups was calculated by conductometric titration. A dried sample (50 to 100 mg) was suspended in 15 mL of 0.01 M HCl solution and stirred during 10 min and then taken to a conductivity sensor; N_2 was bubbled into the suspension during the whole experiment. The titration was carried out by adding 0.1 mL of a 0.01 M NaOH solution to the suspension and then recording the conductivity in mS/cm. With these results, a titration curve was plotted, showing the presence of a strong acid that corresponds to the excess of HCl and a weak acid that corresponds to the carboxyl content. The volume of NaOH was finally calculated from the titration curve. The cationic demand was determined with a Mütek PCD 04 Particle Charge Detector streaming current device. First, 0.04 g of CNF (dried weight) were diluted in 1 L distilled water and dispersed with a pulp disintegrator during 10 minutes at 3000 rpm. Next, 10 mL were taken and mixed with 25 mL of cationic polymer (polyDADMAC, 0.001 N). The mixture was then centrifuged during 90 min at 4000 rpm. After that, 10 mL of the supernatant were taken to the Mütek equipment. Anionic polymer (Pes-Na, 0.001 N) was then added to the sample drop by drop until the equipment reaches 0 mV. The volume of anionic polymer consumed was noted and used to calculate the cationic demand. Details for the characterization techniques are presented in González *et al. 2014*. The theoretical specific surface area and diameter of the nanofibers was also estimated, following the methodology reported by Espinosa *et al.* (2015). The production costs were based on the energy consumption of the equipment used during all of the stages of CNF fabrication: pulp disintegration, beating (if needed), and homogenization. The energy consumption was determined using energy measuring equipment: a Circutor CVM-C10 (Spain) and a Socomec Diris A20 (Spain). The cost of the energy was estimated at 0.08 €/kWh. The prices of chemical reactants and enzymes were also considered in the calculation of the final cost.

Fabrication and evaluation of CNF-reinforced paper

The CNFs were incorporated into BKHW pulp, and subsequent paper sheet formation was carried out according to González *et al.* (2012). The resulting paper sheets were mechanically characterized for tensile strength following the standards ISO 1924-1

and ISO 1924-2. Schopper-Riegler freeness was determined in a Schopper-Riegler tester (mod. 95587, PTI Austria) following the ISO 5267-1 standard.

RESULTS AND DISCUSSION

Table 1 shows the effect that the addition of 3 wt% of each type of CNF had on the ºSR and breaking length of BKHW pulp. Paper sheets from the original pulp had a breaking length of 2054 m, a tensile index of 20.14 Nm/g and 17 ºSR. Breaking length is the calculated upper limit of length of a uniform paper strip that would support its own weight if it were suspended at one end. Tensile index describes the tensile strength of paper in relation to the amount of material being loaded. The Schopper-Riegler freeness measures the drainage rate of a diluted pulp suspension poured on a fine screen. It is directly related to surface characteristics and swelling of fibres, so it can be used to determine the extent of beating in a pulp.

The first significant change observed after the addition of CNF was the increase in ºSR. The T10-CNF grade induced the highest increase in ºSR, followed by Enz-CNF. Acid-CNF brought about a more discreet increase in this parameter.

Table 1. Drainage and Mechanical Properties of Papers Treated with 3 wt% of Different CNF Grades

CNF Grade	Pretreatment	ºSR	Breaking Length (m)	Tensile Index (Nm/g)	ΔBL (%)
T10-CNF	TEMPO-oxidation at pH 10	29±0.1	4128±112	40.30±1.09	101.0
T7-CNF	TEMPO-oxidation at pH 7	26±0.3	3874±120	37.79±1.17	88.6
Acid-CNF	15% H_2SO_4	21±0.2	3595±105	35.27±1.02	75.0
Enz-CNF	4000 PFI-rev+1'6% enzyme	27±0.2	3891±126	37.96±1.23	89.4
Mec-CNF	20000 PFI-rev	23±0.1	3512±118	34.26±1.15	71.0
Original Pulp		17±0.2	2054±115	20.14±1.13	-

Decreases in pulp drainability after CNF addition had been previously observed by several authors, though this disadvantage can be easily controlled by a proper dosing of retention agents (Brodin *et al*. 2014). The enhancement in breaking length/tensile index also varied depending on the type of CNF utilized. The highest increase was produced by T10-CNF, followed by T7-CNF and Enz-CNF, while Mec-CNF induced the lowest improvement. Overall, Table 1 indicates that T10-CNF had the highest reinforcing potential of the set of CNFs, while Mec-CNF had the lowest. After analyzing these results, experiments were performed to determine the amount of each CNF type necessary to induce an approximately 75% increase in breaking length compared to the original pulp, and the results are presented in Table 2. It can be seen that only 2.2 wt% of T10-CNF was needed to achieve a slightly higher than 75% increase in breaking length, as expected. In comparison, 3 wt% of Acid-CNF and Mec-CNF were required to produce approximately similar increases. Lower amounts of added CNF also brought subtler increases in ºSR compared to non-reinforced pulps. These results helped to establish the degree of effectiveness of the different CNF grades at causing a given enhancement in mechanical properties.

Table 2. Drainage and Mechanical Properties of Papers Treated with Different Grades of CNF

CNF Grade	CNF Content (wt%)	ºSR	Breaking Length (m)	Tensile Index (Nm/g)	%ΔBL
T10-CNF	2.2	26±0.2	3634±124	35.45±1.2	76.9
T7-CNF	2.5	23±0.5	3562±93	34.75±0.9	73.4
Acid-CNF	3	21±0.0	3595±137	35.27±1.3	75.0
Enz-CNF	2.5	25±0.4	3657±150	35.70±1.5	78.0
Mec-CNF	3	23±0.5	3512±117	34.26±1.1	71.0
Original Pulp		17±0.2	2054±115	20.14±1.1	-
The amount added was calculated to induce an increase of 75% in breaking length.					

The differences observed in breaking length enhancement in relation to the type of CNF used were a consequence of the quality and properties that resulted from the different pretreatments used prior to homogenization. Figure 2 shows dilutions with 0.1 wt% of the different CNFs prepared for the present study. It can be seen, qualitatively, that the TEMPO-oxidized CNFs were much more transparent than the rest of the samples due to their high fibrillation degree. This fact is a consequence of the formation of carboxylic groups expected in TEMPO-oxidized nanofibers; their presence introduces negative charges onto the cellulose fibers, which increases their repulsion and facilitate their fibrillation when suspended in water. Similarly, in the case of Acid-CNF, pre-treatment with sulfuric acid converts the surface hydroxyl groups into anionic sulfate ester groups that promote a higher fibrillation during high-pressure homogenization. However, in the present work, acid hydrolysis was performed at low sulfuric acid concentration in order to avoid a more extended hydrolysis of amorphous zones in the cellulose chain, which would render cellulose fibers into cellulose nanocrystals instead of nanofibers. This explains the presence of non-nanometric solids in the Acid-CNF suspension. Table 3 presents the results of the quantitative characterization of the CNFs. The first parameter presented is the amount of nanofibrillation, which indicates the fiber fraction of the pulp with sizes in the nanometer scale.

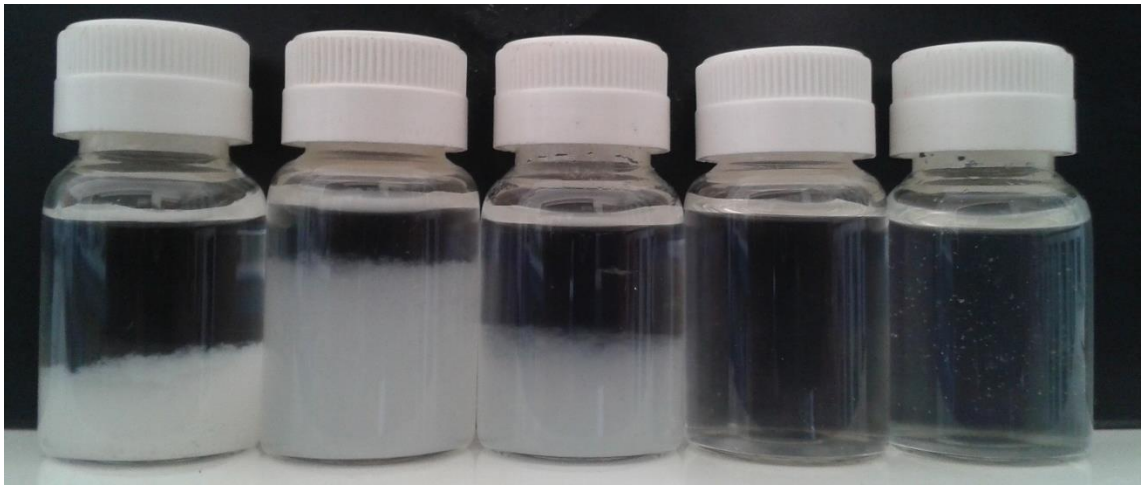

Fig. 2. 0.1 wt% suspensions of the five different CNF samples prepared for the present study. From left to right: Acid-CNF, Mec-CNF, Enz-CNF, T7-CNF, and T10-CNF.

CNFs prepared from TEMPO-oxidized fibers, T10-CNF and T5-CNF, presented the highest amounts of nanofibrillation, followed by Acid-CNF and Enz-CNF. The results are expressed as ">95%" because, after centrifugation, no solid could be recovered from the bottom of the bottles used during the experiments. It is well known that the TEMPO-oxidation pretreatment produces CNFs with a high degree of fibrillation, and this property is dependent on the amount of negatively-charged carboxylic groups formed on the fiber surface (Besbes *et al.* 2011). The presence of such groups produces repulsion between fibers, facilitating the dismantling of the cellulose fibers' structure by shearing forces. The lowest amount of nanofibrillation was observed in Mec-CNF, demonstrating that the sole use of shearing forces was not enough to release a significant amount of nanofibers compared to other pretreatment methods.

Another useful parameter to determine the degree of nanofibrillation of a CNF sample is the transmittance of an aqueous CNF suspension measured by a UV-vis spectrophotometer. The transmittance is wavelength-dependent because light scatters more when the wavelength approaches the diameter of the particles (Saito *et al.* 2007). A transmittance higher than 90% was observed in TEMPO-oxidized CNF, whereas Mec-CNF suspensions had values of only 20%.

Table 3. Characterization of Different CNF Grades

CNF Grade	Yield of Fibrillation (%)	Transmittance at 700 nm (%)	Carboxyl Content (μmol/g)	Cationic Demand (μeq·g/g)	Specific Surface Area (m^2/g)	Diameter (nm)
T10-CNF	>95	92	840.0	1169	160.2	15.6
T7-CNF	>95	97	510.0	859	170.0	14.7
Acid-CNF	72	53	118.7	321	98.5	25.4
Enz-CNF	69	46	78.6	209	63.5	39.4
Mec-CNF	21	20	76.3	233	76.3	32.8

The carboxyl (-COOH) content, calculated by conductometric titration, was higher in TEMPO-oxidized CNFs than the rest of the CNF types. Consequently, the cationic demand was significantly higher in T10-CNF and T7-CNF than the rest of CNFs. Mec-CNF and Enz-CNF showed very similar results. A high cationic demand was expected in the CNFs due to the large amount of fibrillation and the anionic nature of cellulosic materials suspended in water. The quantity of cationic polymer needed to neutralize the surface of a CNF increases in relation to the number of -COOH groups per gram of cellulose. T10-CNF and T7-CNF presented the largest specific surface area of all of the samples studied. This result was also indicative of the high degree of fibrillation that can generally be achieved in TEMPO-oxidized fibers. Acid-CNF was next on this scale. The lowest specific surface area was found in Enz-CNF, which also corresponded to its lower cationic demand. CNF diameter was calculated from the cationic demand, carboxyl content, and specific surface area according to a methodology published previously (Espinosa *et al.* 2015). The CNF diameter from TEMPO-oxidized fibers was very similar, about 15 nm. CNF diameters vary from that of a single microfibril (3 to 5 nm) to thicker microfibril aggregates of up to 100 nm (Isogai *et al.* 2011; Klemm *et al.* 2011; Abdul Khalil *et al.* 2014). Lengths can vary from several hundreds of nm to 1 μm.

The main mechanism that governs the increase in mechanical properties in CNF-reinforced papers is the boost of the relative bonded area (RBA) between fibers due to the

high specific surface area that CNFs add to the papermaking suspension (Brodin *et al*. 2014). Therefore, it is to be expected that CNFs with a high degree of fibrillation and a large specific surface area will produce a greater enhancement in paper strength compared to CNFs with inferior properties. However, the results presented here also show that even CNFs with smaller specific surface areas can produce important enhancements in mechanical properties when added in quantities slightly larger than those required for TEMPO-oxidized CNFs. As a result, the next criterion used to select the type of CNF that best suits industrial requirements should be its price. Table 4 shows the production costs for 1 kg of every type of CNF used in the present study and the equivalent price to increase the breaking length of the reference pulp by 75%. To calculate the cost of CNFs, the prices of chemicals, enzymes, and energy were taken into consideration.

Table 4. Production Prices of Different CNF Grades and the Cost to Obtain a 75% Increase in Breaking Length over the Reference Pulp

CNF Grade	Production Cost (€/kg CNF)					Cost to Obtain a 75% increase (€/kg paper)
	Pretreatment Cost			Homogenization Cost	Total Cost	
	Chemical	Enzyme	Energy***			
T10-CNF*	203.6538 €	-	0.5439 €	1.5351€	205.7328 €	4.5260 €
T7-CNF**	173.5312 €	-	0.3248 €		175.3911 €	4.3847 €
Acid-CNF	0.9216 €	-	4.8727 €		7.3294 €	0.2198 €
Enz-CNF	11.1135 €	0.6432 €	0.3643 €		13.6561 €	0.3414 €
Mec-CNF	-	-	0.7121 €		2.2472 €	0.0674 €
Price of the original pulp: 0.5512€/kg						
*TEMPO catalyst cost was estimated at 140.8€/kg CNF						
**TEMPO catalyst cost was estimated at 44€/kg CNF						
***Production cost was calculated assuming an energy cost of 0.08€/kWh						

The results show that, even though T10-CNF and T7-CNF had the highest effectiveness of all of the sets of samples, their estimated costs were also the highest. The main reason behind this result was the market prices of the chemicals used in the oxidation process, mainly the catalyst, TEMPO. Another drawback of the TEMPO-mediated oxidation is that nowadays there is no successful methodology reported to recover the TEMPO catalyst at an industrial scale. Thus, the cost to achieve a 75% increase in breaking length by the addition of TEMPO-oxidized CNF was 4.5260 € per kg of paper. In comparison, CNFs obtained from the other pretreatments were much more affordable and could produce similar increases in breaking length. The cheapest CNFs were those obtained from mechanical pretreatment, followed by Acid-CNF. A point of contention could be that, in the present study, all of the CNF grades received the same number of passes through the homogenizer, even though TEMPO-oxidized fibers usually require much fewer passes than other types of pretreatments. However, a large fraction of the price still corresponded to chemicals; consequently, a reduction in the number of passes would only slightly decrease the overall production costs. It is important to remark that the prices presented in this study are for laboratory-level production and are not intended to be taken directly as a reference for industry application. Besides, price of workforce and treatment of residual waters were not considered in the final price since their cost changes from place to place.

The overall results indicate that, at least in papermaking, CNFs with a high degree of fibrillation and subsequent large specific surface area are not strictly necessary to induce major improvements in paper strength. This conclusion allows for cheaper pretreatment techniques to be explored for scaling up CNF production to industrial levels without reaching unaffordable prices that would render CNFs an uncompetitive alternative to other existing strategies to reduce the energy consumption in the papermaking industry.

CONCLUSIONS

1. CNFs were fabricated from bleached kraft hardwood pulp following 5 different pretreatments, then high-pressure homogenization. The resulting CNFs were characterized and used as a reinforcing additive in papermaking slurry to improve the breaking length of the resulting paper sheets.
2. The addition of 3 wt% of CNFs from different pretreatments increased the breaking length/tensile index of paper by a different proportion depending on the type of CNF used. The increase in mechanical properties was accompanied by a moderate increase in ºSR.
3. Experiments were performed to determine the amount of CNF necessary to increase breaking length by approximately 75%. The results indicated that CNF grades prepared after TEMPO-mediated oxidation produced the best results at the smallest amounts of all of the sets of CNFs.
4. Characterization of the five CNF grades indicated that the CNFs produced by TEMPO-mediated oxidation presented the largest specific surface area, which explains why their addition produced slightly superior increases in the paper's breaking length compared to other CNFs.
5. A study of the fabrication costs of the different CNF grades indicated that TEMPO-mediated oxidation pretreatment was much more expensive than the other methodologies studied, which resulted in higher prices to produce a 75% increase in breaking length. CNFs obtained from solely mechanical pretreatment had the lowest price for the same increase.
6. In general it was possible to conclude that, in papermaking, CNFs with a high degree of fibrillation were not necessary to produce significant increases in the paper's mechanical properties, which would allow for a reduction in the production costs of CNFs by using less expensive methodologies.

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