

Lignocellulosic nanofibers from triticale straw: The influence of hemicelluloses and lignin in their production and properties



Quim Tarrés^a, Nanci Vanesa Ehman^b, María Evangelina Vallejos^b, Maria Cristina Area^b, Marc Delgado-Aguilar^{a,*}, Pere Mutjé^a

^a LEPAMAP Research Group, University of Girona, C/Maria Aurèlia Capmany, 61, 17003, Girona, Spain

^b Programa de Celulosa y Papel, Instituto de Materiales de Misiones, IMAM (UNaM-CONICET), Félix de Azara 1552, Posadas, Misiones, Argentina

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ABSTRACT

The present work aims to determine the influence of hemicellulose and lignin content in the production of lignocellulosic nanofibers (LCNF) from triticale straws. Triticale straws were digested and then gradually delignified, preserving as much hemicelluloses as possible. The obtained LCNF was characterized and used as paper strength additive, observing that hemicellulose and lignin have a key role on the final properties thereof, as well as on their reinforcing potential as paper additive, obtaining LCNF with the same paper reinforcing potential than CNF obtained by TEMPO ((2,2,6,6-Tetramethyl-piperidin-1-yl)oxyl) mediated oxidation.

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1. Introduction

The key parameters involved in the production of cellulose nanofibers (CNF), as well as their potential applications, have become a topic of great interest to the scientific and technological community in recent years (Brodin, Gregersen, & Syverud, 2014; Osong, Norgren, & Engstrand, 2016). This growing interest is reflected in the increase of the amount of patents and scientific publications on the subject (Future Markets Inc, 2015), leading to many different production processes and potential applications thereof (Missoum, Belgacem, & Bras, 2013).

Regarding processes, in general, most of the scientific publications related to nanofibrillated cellulose deal with cellulose nanofibers obtained by chemical pretreatments, being unaffordable at first sight from an economical point of view. While it is true that the purpose of these treatments was to ease the fibrillation step (such as avoiding clogging in homogenizers) and to reduce the energy consumption during this stage, it is worthy to mention that is the use of such chemicals in fact what makes their large scale production completely economically unviable. These high production costs, as reported by many authors, make cellulose nanofibers a non-feasible strength additive for mature industrial sectors such

as papermaking, fact that has encouraged researchers to investigate other production ways through fully mechanical methods (Delgado-Aguilar et al., 2016; Espinosa et al., 2016). These cellulose nanofibers, when added into paper suspensions, have lower effect on drainability than those chemically obtained, while they have almost the same paper reinforcing potential (Delgado-Aguilar et al., 2016; González et al., 2012). The benefits of using cellulose nanofibers in paper production instead of mechanical refining have been extensively discussed by several authors, taking in consideration technical, economic and environmental aspects (Brodin et al., 2014; Delgado-Aguilar et al., 2015a; González et al., 2012; Tarrés et al., 2016; Vallejos et al., 2016).

On the other hand, it is extensively reported that the chemical composition of the raw material used for the production of cellulose nanofibers is also relevant, such as the hemicellulose and lignin content. Previous works have demonstrated that the presence of high percentages of hemicellulose could improve the fibrillation process (Chaker, Alila, Mutje, Vilar, & Boufi, 2013; Ferrer et al., 2012; Iwamoto, Abe, & Yano, 2008), while high amounts of lignin could, in contrast, hinder this process (Spence, 2011). Usually, delignification processes imply both lignin and hemicelluloses removal. This implies that if the maximum amount of hemicelluloses wants to be preserved for the production of CNF, certain lignin content will be present and the final appearance of the CNF will be brown (lignocellulosic nanofibers, LCNF). This brown appearance will limit their use as reinforcing agent in white papers due to the decrease on

* Corresponding author.

E-mail address: m.delgado@udg.edu (M. Delgado-Aguilar).

whiteness and brightness that they would produce when added in bulk. Nonetheless, this is not relevant when they are used in brown packaging papers such as fluting or liner, which is a growing sector. Packaging papers have been the most consumed and produced papers in Europe since many years. For instance, in 1991 the Europe packaging paper consumption was 42.1%, being this consumption the 50.3% in 2015 (CEPI, 2015).

Cereal straws have higher hemicellulose content (even higher than 30%) than wood (Pickering, 2008). Cereal straws are a major by-product of the agroindustry inasmuch as straw represents around 50% of the yield of a cereal crop. Triticale (*X Triticosecale Wittmack*) is an intergeneric hybrid of wheat (*Triticum* sp.) and rye (*Secale cereale* L.). It is a self-fertilization cereal that was artificially obtained by man, which combines the high yield potential of wheat with the biotic and abiotic stress tolerance of rye, making it more suitable for the production in marginal areas (Kavanagh & Hall, 2015). This culture has experienced a large increase in production over the past century due to its adaptability to different climatic conditions. Since the mid-1980s triticale production has increased at an average rate of 150,000 t/year (an approximate 18% increase per year), reaching nearly 11 million tons in 2002. Approximately 88% of triticale was produced in Europe, 9% in Asia (China) and 3% in Oceania. In 2013, the total area planted worldwide was about 4 million ha being Poland, Belarus, Germany, France, and Russia the major producing countries (Randhawa, Bona, & Graf, 2015). Triticale is grown for various purposes: animal feed, human food, pharmaceuticals and production of first-generation bioethanol.

Boufi and Gandini (2015) investigated the effects of using different treatments and fibrillation equipment on the final properties of CNF, as well as their morphology and the energy consumption during fibrillation. In that work, authors reported that the degree of nanofibrillation and the energy consumption during fibrillation depended on the previous delignification processes, as well as which oxidative method was used. In addition, the presence of residual hemicelluloses was highlighted, concluding that their presence in fibers was crucial to assure a good fibrillation and lower energy consumption.

For all the above, as an alternative to those chemical-based methodologies and with the aim of preserving as much hemicelluloses as possible to promote fibrillation, a process consisting on appropriately treating triticale was designed. In this sense, triticale was submitted to a soft sodium hydroxide pulping treatment and subsequently bleached in presence of sodium hypochlorite. After this, lignocellulosic nanofibers (LCNF) were produced, characterized and compared with those obtained from wood and chemical methods reported in the bibliography.

2. Materials and methods

Triticale (*Triticale aestivum*) straw was provided by Fundació Mas Badia S.A (Spain). Ence-Celulosas de Asturias S.A. (Spain) supplied the unrefined bleached kraft hardwood pulp (standard pulp). All chemicals used for pulping and bleaching were bought from Sigma-Aldrich (Spain) and were used as received.

2.1. Pulping and delignification

Triticale pulp was obtained by digesting the triticale straws in presence of 7% of NaOH at 160 °C for 90 min, with a liquid/solid ratio of 6. Pulping yield was then determined taking into account the starting raw material and the obtained after the digestion, once dried. After this, digested straws were passed through a Sprout-Waldron refiner to break up fiber bundles until constant diameter was achieved. This diameter was determined using a MorFi equipment (TechPap, France) equipped with a CCD video camera. About

30,000 fibers were analyzed by the software MorFi v9.2. The equipment considered as fines those fibers shorter than 76 μm.

Delignification was carried out in presence of 8% of NaClO₂ for 1, 2 and 3 h, leading to three delignification levels. This process was performed at 10 wt% of consistency at 70 °C under constant stirring.

2.2. Chemical characterization of the raw material and pulps

Both raw material and pulps were prepared for chemical characterization according to TAPPI standard T257. Samples were dried in an oven at 105 °C until constant weight and then, samples were milled and screened (40 mesh) to assure homogeneous particle size.

Once samples were conditioned for chemical characterization, one portion was used for ash content determination (TAPPI standard T211). Briefly, 2-g samples were placed in porcelain crucibles (previously cleaned and dried) and placed in an electric muffle furnace. The initial temperature was 100 °C and temperature was slowly raised until 525 °C to assure sample carbonization without flaming. Crucibles were removed from the furnace when no black particles were observed, indicating that the specimen was completely combusted. Ash content was calculated as follows:

$$\text{Ash, \%} = \frac{W_f}{W_i} \cdot 100 \quad (1)$$

Where W_f is the final weight (ash) and W_i is the initial weight (moisture – free initial sample).

In parallel, samples were submitted to solvent extractives determination (TAPPI standard T204). This determination was carried out by Soxhlet extraction using ethanol-toluene mixture as solvent. This was performed to quantify the extractives of the samples and because the next determinations require extractive-free samples. For the determination, extraction thimbles containing 5-g samples were submitted to Soxhlet extraction for 5 h in presence of 150 mL of ethanol-toluene. Extract was transferred to a tared dish and dried in an oven at 105 °C until constant weight. A blank determination was also carried out with the solvent used in the test. Extractive content was calculated as follows:

$$\text{Extractives, \%} = \frac{W_e - W_b}{W_i} \cdot 100 \quad (2)$$

Where W_e is the oven-dry weight of extract and W_b is the oven-dry weight of blank residue.

Acid-insoluble lignin of the extractive-free samples was determined following the procedure described in TAPPI standard T222. Two samples of 2 g from each extractive-free sample were placed in 100-mL beakers. Then, 40 mL of cold (10 °C) 72% sulfuric acid was added to each beaker. This operation was performed gradually under constant stirring and the beaker was placed in a cold water bath to palliate sample heating. Then the beaker was covered with a watch glass and kept in a bath at 20 °C for 2 h. The material was stirred frequently to ensure complete solution. After this time, the material from the beaker was transferred to a flask containing 400 mL of deionized water, adding more water until achieving a 3% concentration of sulfuric acid and then boiled for 4 h. Extra water was added to maintain the total volume. The flask was left inclined overnight to promote lignin precipitation and then the liquid was filtered by a 0.22 μm of pore size nylon membrane, passing through hot water with to remove free acid. Acid-insoluble lignin was then oven dried at 105 °C until constant weight. Finally, acid-insoluble lignin content of both of raw material and pulps was calculated as follows:

$$\text{Lignin, \%} = \frac{W_l}{W_i} \cdot 100 \quad (3)$$

Where W_l is the oven-dry weight of lignin.

Table 1
Characterization of the LCNF-0.

Yield of fibrillation (%)	16.1 ± 0.9
Transmittance at 800 nm (%)	30.8 ± 2.1
Carboxyl groups content (μeq/g)	47.2 ± 1.8
Cationic demand (μeq/g)	162 ± 12
Specific surface (m ² /g)	55.9
Diameter (nm)	47.7
Standard performance (%)	24.9 ± 0.7

Cellulose content was determined by high performance anion exchange chromatography (HPAEC). For this, 200 mg (dry weight) of sample was placed in a 100-mL flask adding 3 mL of 72% sulfuric acid while mixing with a glass rod. Samples were then placed in a vacuum desiccator for 1 h and mixed frequently to assure total hydrolysis. Samples were then diluted by adding 84 mL of deionized water.

Standard solutions of glucose were prepared adding also 3 mL of 72% sulfuric acid and 84 mL of deionized water to the standards. Both samples and standard solutions were placed in an autoclave for 60 min at 125 °C, then filtered under vacuum through a 0.22 μm of pore size nylon membrane, and finally washed twice with deionized water (as explained for acid-insoluble lignin determination). The filtered sample was used for the chromatographic determination. Cellulose was quantified by comparing the peak of the diluted and filtered sample with that of the standard solution of glucose. A differential refractometer (Waters 410) equipped with a system controller (Waters 600E), with an adsorption column ICSEP ICE-ORH-801 was used. Glucose content gave directly the cellulose content. Since the adsorption columns were not able to successfully separate other sugars than glucose, hemicellulose was quantified by difference from 100%. Similar methodology was previously reported by Hausser, Marinkovic, and Estrine (2011).

Kappa number was determined according to ISO 302 in the ranges from 1 to 5 and from 5 to 100.

2.3. High pressure homogenization of the obtained pulps

Fibrillation was performed by passing a 2 wt% consistency fiber suspension through a high pressure homogenizer Panda Plus 2000 (Gea Niro Soavi, Italy) according to the following sequence: 3 times at 300 bar, 3 times at 600 bar and 3 times at 900 bar.

2.4. Characterization of LCNF

Carboxyl content (CC) of LCNF was calculated by conductimetric titration. A dried sample (100 mg) was suspended in 15 mL of 0.01 M HCl solution; this exchanges Na⁺ cations bound to the COO⁻ groups by H⁺ ions. After 10 min of magnetic stirring, suspensions were titrated with a 0.01 M NaOH solution, adding 0.1 mL of NaOH to the suspension and then recording the conductivity in mS/cm. This process was repeated until a U-shaped curve was obtained.

Cationic demand (CD) of LCNF was determined with a Mütex PCD 04 particle charge detector (BTG Instruments, Germany), adapting the methodology reported by Carrasco, Mutjé, and Pelach (1998). First, 0.04 g of LCNF (dry weight) were diluted in 1 L of deionized water and dispersed by means of a pulp disintegrator for 10 min at 30 rpm. Afterwards, 10 mL were taken and mixed with 25 mL of cationic poly(diallyldimethylammonium chloride) (poly-DADMAC) for 5 min. Then, the mixture was centrifuged for 90 min at 4000 rpm. After this, 10 mL of the supernatant were taken and added to the particle charge detector. Anionic polymer (Pes-Na) was then added to the sample drop by drop with a pipette until the equipment reached 0 mV. The yield of nanofibrillation was determined by centrifuging a 0.2 wt% suspension 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. Transmittance measurements were performed on LCNF 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.

Specific surface and diameter were estimated from carboxyl content and cationic demand. For this, it was considered that the interaction between the LCNF surface, which have hydroxyl and carboxyl groups, and the added cationic polymer occurred through two different mechanisms: on the one hand, part of the polymer got retained by ionic interaction between carboxylic groups from LCNF and the polymer thereof. On the other hand, the rest of the consumed poly-DADMAC during cationic demand determination was assumed to be retained by surface adsorption.

Moreover, the calculation of the specific surface was accomplished taking into account two assumptions: 1) the surface adsorption of the poly-DADMAC polymer takes place in the form of a monolayer and 2) the poly-DADMAC polymer has a cylindrical geometry.

The surface of the poly-DADMAC polymer was initially estimated by calculating the surface of the monomer and its polymerization degree, taking into account the bond distances and assuming a cylindrical monomer.

The calculated distances were 5.427 Å for A and 4.849 Å for B, obtaining a surface value of 535.87 nm², equivalent to 4.874 × 10¹⁷ nm²/μeq.

Moreover, using the values obtained for cationic demand and the carboxyl content it was possible to calculate the LCNF's theoretical surface area by the following equations:

$$\sigma_{LCNF} = (CD - CC) \cdot S_{Poly-DADMAC} \text{ nm}^2/\mu\text{eqg} \quad (5)$$

Where CD is cationic demand, CC is carboxyl content (both expressed in μeq-g/g) and $S_{Poly-DADMAC}$ is the specific surface of Poly-DADMAC, in nm²/μeq-g.

Finally, assuming that nanofibers are perfect cylinders and that cellulose density is 1.5 g/cm³, diameter was estimated.

Standard performance can be described as the tensile strength enhancement that a 3% of LCNF impart over a paper made of unrefined bleached kraft hardwood pulp without any retention aid. Thus, the neat reinforcing potential of LCNF can be assessed. For this, with the purpose of avoiding any weight loss, paper sheets were formed over a nitrocellulose membrane with a pore size of 0.22 μm under vacuum.

Standard performance can be calculated as follows:

$$\text{Standard performance, \%} = \left(\frac{BL_{of\ 3\% \text{ reinforced paper}}}{BL_{of\ non - reinforced paper}} - 1 \right) \cdot 100 \quad (6)$$

Where BL refers to breaking length, in meters.

2.5. LCNF incorporation into test-liner pulp and paper sheets production

Dried, test-liner paper was used as primary raw material for paper sheets production. First, papers were teared in small pieces to be dispersed in water in a pulp disintegrator for 90 min at 3000 rpm. In the case of LCNF-reinforced papers, LCNF were added to the slurry during disintegration process. The amount of LCNF was calculated to obtain 3% LCNF-reinforced paper sheets. After disintegration, pulps containing LCNF were stirred for 30 min at 500 rpm in presence of 0.8 and 0.5% of colloidal silica and cationic starch, respectively.

Table 2
Chemical characterization of the unbleached and partially bleached triticale pulps.

Pulp	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Kappa number	Extractives (%)	Ash (%)
LF-0	75.13 ± 3.15	13.93 ± 1.01	8.42 ± 0.68	30.7 ± 2.9	0.71 ± 0.03	1.87 ± 0.12
LF-1	78.77 ± 4.02	12.78 ± 0.91	5.74 ± 0.72	23.4 ± 2.6	0.61 ± 0.05	1.41 ± 0.19
LF-2	85.60 ± 5.91	11.64 ± 0.87	1.23 ± 0.21	6.7 ± 1.2	0.59 ± 0.04	1.16 ± 0.09
LF-3	87.15 ± 4.13	11.03 ± 1.01	0.54 ± 0.09	1.7 ± 0.7	0.44 ± 0.04	0.95 ± 0.08

LF-X: Lignocellulosic Fiber. X refers to the delignification stage.

Afterwards, paper sheets were prepared in a Rapid-Köthen sheet former (ISP mod. 786 FH) according to ISO 5269-2 and conditioned at 23 °C and 50% of relative humidity for 48 h before testing, following ISO 187.

2.6. Test-liner pulps and papers characterization

Regarding pulps characterization, only drainage rate was conducted. In this sense, Schopper-Riegler degree (°SR) was determined in a Schopper – Riegler Tester (mod. 95587 PTI) following ISO 5267-1 standard.

Regarding paper sheets, density, air permeability, breaking length, internal bonding, burst index and tear index were determined. Density was calculated from basis weight (ISO 536) and thickness (ISO 534). Air permeability was obtained with a Gurley Porosimeter (Papelquímia). Testing was performed according to ISO 5636-5. Paper samples, measuring 50 × 100 mm, were cut and marked on both sides for easy identification. Results are expressed in seconds, meaning the required time to pass through the paper 100 cm³ of air.

Breaking length was obtained from tensile testing. Testing experiments were performed in a Hounsfield 42 universal testing machine equipped with 2.5 kN load cell. Testing was performed according to ISO standard 1924-2. The gap between clamping jaws was set to 150 mm and cross head speed was set to 20 mm/min. Preload was set at 0.1 N. Specimens were cut into paper strips 15 mm in width and 200 mm in length. Breaking length was calculated as follows:

$$BL, km = \frac{F}{9.81 \cdot G \cdot w} \quad (7)$$

Where F is force in Newton, G is the basis weight of the paper sheet in g/m² and w is the width of the paper stripe, in meters.

Internal bonding was determined in an internal bond tester (mod. IBT 10A IDM). Testing samples were cut to paper strips with dimensions of 25.4 × 200 mm and conditions were set according to TAPPI standard T569. Burst index was determined in a Burst Tester (mod. EM-50 IDM) and testing experiments were performed according to ISO 2758. Testing specimens were cut unto 100 × 100 mm pieces. Tear index was determined in an Elmendorf Tearing Tester (mod. F53.98401 Frank PTI). Testing samples were cut into 63 × 76 mm pieces and testing conditions were set according to ISO 1974.

3. Results and discussion

3.1. Raw material, unbleached pulp and LCNF-0 characterization

The chemical composition of the native triticale straw, the starting material, for the production of the different LCNF, was determined following the methodology described in the previous section. Comparatively, triticale straw showed similar cellulose content (44.71%) to other straw and stalks, such as sunflower (López et al., 2005), sorghum (Jimenez, Sanchez, & Lopez, 1990), rape-seed (Mazhari Mousavi, Hosseini, Resalati, Mahdavi, & Rasooly Garmaroody, 2013), rice (Rodríguez, Moral, Serrano, Labidi, & Jiménez, 2008) and wheat (Jimenez et al., 1990), as well as to soft-

woods (Mazhari Mousavi et al., 2013). Hemicellulose accounted for 32.71%, being higher than for rice, sunflower, barley, rye and oat straw (Jimenez et al., 1990; López et al., 2005; Rodríguez et al., 2008), but similar to the rest of the abovementioned lignocellulosic fiber sources, except for softwoods. This high hemicellulose content compared both to softwoods and annual and perennial plants makes this sources suitable to be used as raw material for LCNF production, since, as reported by Boufi and Gandini (2015), the presence of the amorphous polysaccharides, that hemicellulose is composed, promotes fibrillation and, thus, LCNF production. Lignin content accounted for 16.27%, being a value of the same magnitude than for the abovementioned straws and lower than for softwoods and hardwoods. The obtained amount of extractives in ethanol-toluene (1.34%) and ash (6.01%) are in consonance with values reported in the bibliography for similar straws (Mazhari Mousavi et al., 2013).

After milling, triticale straws were treated at 160 °C for 90 min in presence of 7 wt% NaOH obtaining a yield of 59%. Then, the treated straws were passed through a Sprout-Waldrone refiner as described above. The obtained fiber length (735 μm) was slightly higher than lengths reported in the bibliography for chemical pulps from straw residues, such as corn (749 μm) and wheat (Espinosa et al., 2016), longer than that of vine stems (590 μm) and *posidonia oceanica* (550 μm) and bleached kraft eucalyptus, and shorter than that of date palm rachis (890 μm), and *pinus radiata* (1.9 mm) (Flandez et al., 2012; Khiari, Mhenni, Belgacem, & Mauret, 2010; Mansouri et al., 2012; Mishra, 2010; Vallejos et al., 2016). Fiber width was medium-narrow (20.6 μm) and in the range of hardwoods (Jahan, Chowdhury, & Islam, 2006). Coarseness (0.105 mg/m) and fines (23.0% in length) were also in the range of pulps usually used for papermaking (Vallejos et al., 2016).

Once LCNF from unbleached triticale pulp (LCNF-0) were prepared, they were characterized in terms of yield, transmittance at 800 nm, carboxyl content, cationic demand and standard performance (Table 1). Yield of fibrillation was significantly lower than those obtained by enzymatic hydrolysis, which are usually between 30 and 40% (Tarrés et al., 2016), and those obtained through TEMPO-mediated oxidation, which reaches over 95% (Delgado-Aguilar et al., 2015b; González et al., 2012; Saito, Kimura, Nishiyama, & Isogai, 2007). These differences are consequence of the methodology used for CNF production: those CNF obtained by TEMPO-mediated oxidation, for instance, present higher yield due to the formation of negatively charged carboxyl groups in the C6 of the cellulose chain, which leads to repulsive forces between fibers, promoting thus water uptake and fiber swelling (Saito et al., 2007). This low yield denotes that the obtained suspension is mostly composed by LCNF with high diameters and also lignocellulosic microfibrils (LCMF). Moreover, this is reflected on the transmittance at 800 nm of the LCNF suspension, which accounted for only 30.8%, while the abovementioned CNF (both enzymatically hydrolyzed and TEMPO-oxidized) present higher values.

The obtained average diameter was high (47.7 nm) and thus the specific surface was low as expected, since no pretreatment was applied to the pulp, apart from a slight PFI-refining to increase fiber swelling, flexibility, and to reduce the particle length, prior to homogenization.

Table 3
Characterization of the delignified LCNF.

	LCNF-1	LCNF-2	LCNF-3
Yield of fibrillation (%)	21.3 ± 1.3	20.8 ± 1.1	19.5 ± 1.8
Transmittance at 800 nm (%)	32.2 ± 2.3	31.8 ± 2.8	31.0 ± 1.9
Carboxyl groups content (μeq/g)	47.2 ± 1.8	47.2 ± 1.8	47.2 ± 1.8
Cationic demand (μeq/g)	198 ± 14	184 ± 16	172 ± 17
Specific surface (m ² /g)	73.4	66.6	60.1
Diameter (nm)	34.0	37.5	41.6
Standard performance (%)	98.7 ± 2.9	82.6 ± 2.0	75.1 ± 3.1

LCNF-X: Lignocellulosic nanofibers. X refers to the delignification stage.

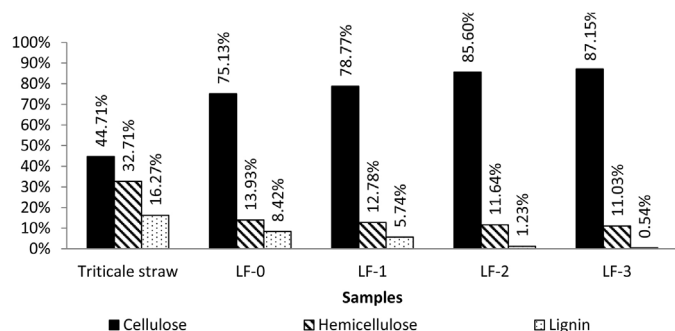


Fig. 1. Evolution of cellulose, hemicellulose and lignin content as fibers were delignified.

Finally, the reinforcing potential of the obtained LCNF was assessed, obtaining a standard performance of 24.9%. This reinforcing potential is considerably low compared to other cellulose nanofibers prepared by mechanical methods, and surely compared to enzymatically hydrolyzed and TEMPO-oxidized (Delgado-Aguilar et al., 2015b; Tarrés et al., 2016).

3.2. Delignified pulps and LCNF characterization

In view of the low properties of the obtained LCNF-0, as well as their low reinforcing potential, pulp was gradually delignified to determine the influence of lignin and hemicelluloses during homogenization. As reported by Chaker et al. (2013), the presence of lignin and hemicelluloses with other polysaccharides should ease mechanical fibrillation, since, as they assumed, hemicellulose form a physical barrier between nanofibers, inhibiting thus the formation of bundles. In any case, some authors have reported previously that the presence of moderate percentages of amorphous constituents in cellulosic pulps should promote mechanical fibrillation, this is, homogenization in the present work. This fact was also previously observed by Iwamoto et al. (2008). Thus, triticale pulp was delignified according to the methodology previously described, and then unbleached and partially bleached pulps were characterized in terms of cellulose, hemicellulose, lignin (and kappa number), ash and ethanol-toluene extractives content.

Table 2 brings to the light that the delignification methodology selected for the development of this work successfully preserved hemicelluloses, while lignin was drastically decreased. In fact, hemicelluloses were considerably decreased after cooking, since the raw material accounted 32.71% of hemicelluloses and the unbleached pulp, 13.93%. Lignin, on the other hand, was reduced from 16.27% to 8.42% after cooking, and almost completely removed at the end of the three-hour delignification treatment. Consequently, while the amorphous constituents (sum of hemicellulose and lignin) were progressively removed, the cellulose content was increased considerably with the first treatment and progressively while bleaching. Fig. 1 shows these tendencies.

The adopted delignification strategy had as main goal to preserve hemicellulose. As it is possible to see in Fig. 3, this objective

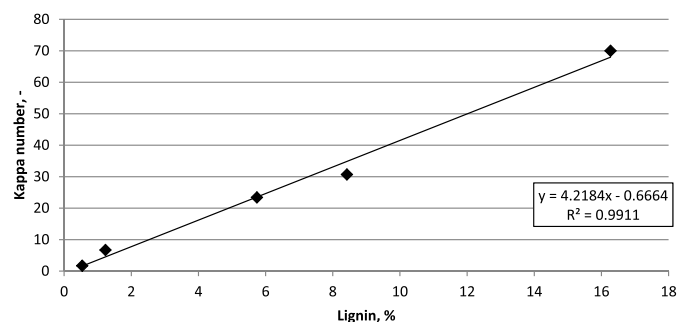


Fig. 2. Correlation between kappa number and lignin content.

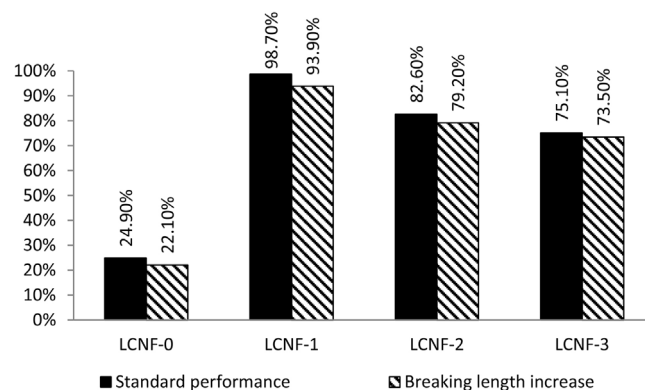


Fig. 3. Comparison between standard performance and breaking length increase.

was achieved, since hemicellulose was almost kept constant between 11 and 13%, while the rest of constituents varied significantly. It must be mentioned that the same lignin content could be achieved by treating further the fibers with NaOH, following the treatment to obtain LF-0. However, hemicellulose would have been also drastically removed, hindering subsequent fibrillation (Boufi & Gandini, 2015). Fiber morphology was also determined for each pulp. However, since delignification has no effect neither over length nor diameter, no significant changes were observed.

By definition, kappa number is an indication of the residual lignin content or bleachability of wood pulp by a standardized analysis method. In fact, kappa number estimates the amount of chemicals required during bleaching, being this amount related to the lignin content of the pulp. In this sense, kappa number can be used to monitor the effectiveness of the lignin extraction phase. The standard also points that kappa number is proportional to the residual lignin, being kappa number 6.57 times higher than lignin content expressed in percentage for wood pulps (ISO 302:2015). This factor cannot be used for straws, such as triticale. However, there is also a correlation (coefficient of 0.9911) between this indicator and the amount of lignin, as it is reflected in Fig. 2. This factor, for the present study, was 4.22 approximately, being valid at least in the range of 0–16% of lignin content.

Table 4
Physic and mechanical properties of non-reinforced and reinforced liner papers.

	LCNF (%)	°SR	Density (g/cm ³)	Gurley porosity (s)	Breaking length (km)	Internal bonding (J/m ²)	Burst Index (kPa m ² /g)	Tear Index (mN m ² /g)
–	0	31	0.66 ± 0.01	51.2 ± 0.0	3.55 ± 0.15	197.7 ± 7.69	1.69 ± 0.23	8.13 ± 0.69
LCNF-0	3	50	0.80 ± 0.02	202.6 ± 4.1	4.02 ± 0.17	196.8 ± 21.5	2.04 ± 0.12	8.21 ± 0.41
LCNF-1	3	51	0.79 ± 0.03	246.8 ± 5.3	5.47 ± 0.21	600.7 ± 46.8	2.89 ± 0.31	8.30 ± 0.58
LCNF-2	3	51	0.80 ± 0.01	241.7 ± 3.7	4.98 ± 0.12	547.1 ± 31.2	2.78 ± 0.23	8.27 ± 0.21
LCNF-3	3	50	0.81 ± 0.02	253.3 ± 6.1	4.74 ± 0.17	456.8 ± 51.3	2.26 ± 0.11	8.15 ± 0.08

Following with the reasoning that fibrillation could be promoted by the preservation of hemicelluloses, as well as the partial removal of lignin, each pulp was used for LCNF production, maintaining the sequence in the homogenizer described above with the purpose of producing LCNF at a constant energy rate regardless the delignification degree. The obtained LCNF was characterized according to the methodologies described in the previous section.

Table 3 shows that all the partially delignified pulps led to LCNF with slightly higher properties than those obtained from LF-0. Carboxyl groups content remained constant, indicating thus that all the added sodium chlorite was used for bleaching and, thus, there was no oxidation of fibers (Delgado-Aguilar et al., 2016). Cationic demand showed similar behavior than yield of fibrillation. Even the yield of fibrillation was not substantially higher than that obtained for LCNF-0, differences can be observed both in transmittance and cationic demand. Since carboxyl groups content remained constant, specific surface and diameter, thus, varied accordingly. Apparently, the reinforcing potential when added in bulk to paper should not vary significantly. However, as it is reflected in the standard performance, the reinforcing potential of the obtained LCNF was much higher than for LCNF-0. This effect was previously observed by other authors (Delgado-Aguilar et al., 2016; Espinosa et al., 2016). In this sense, it seems that lignin was hindering the reinforcing potential of LCNF when unbleached pulp was used for LCNF production. On the other hand, when partially bleached or delignified pulps were used, the most appropriate (in terms of reinforcing potential) were those submitted to delignification for one hour. This is consistent with Chaker et al. (2013), who reported that an appropriate balance between hemicellulose and other amorphous heteropolysaccharides should promote fibrillation and, consequently, the resulting properties of LCNF (Solala et al., 2012). Moreover, as reported by Ferrer et al. (2012), residual amounts of lignin promote fibrillation by stabilizing the radicals formed during homogenization stages.

Standard performance, which consists on assessing the pure reinforcing potential of a 3 wt% of LCNF addition on a bleached kraft eucalyptus suspension without any retention aid, is indicative of possible reinforcement produced by LCNF. Nevertheless, retention is guaranteed by filtering the suspension on a nitrocellulose membrane with 0.22 μm of pore size. However, retention aids are imperative in papermaking industry, since the pore size of clothes is much bigger than 0.22 μm. As reported in previous works, cationic starch (0.5 wt%) and colloidal silica (0.8 wt%) must be added into the LCNF-containing suspension to assure the retention thereof (Delgado-Aguilar, Tarrés, Pelach, Mutjé, Fullana-i-Palmer, 2015c; Delgado-Aguilar et al., 2015b). In this sense, a 3 wt% of LCNF was added into the abovementioned bleached kraft pulp in presence of the retention aids and then paper sheets were formed over a 200 mesh cloth. The increase on breaking length was assessed and compared to standard performance, leading to the results shown in Fig. 3.

The figure evidences that the increase in breaking length was of the same magnitude both using the standard performance technique (absence of retention aids) and forming the paper sheet in a 200 mesh cloth in presence of cationic starch and colloidal silica. While it is true that in the second case they were slightly lower,

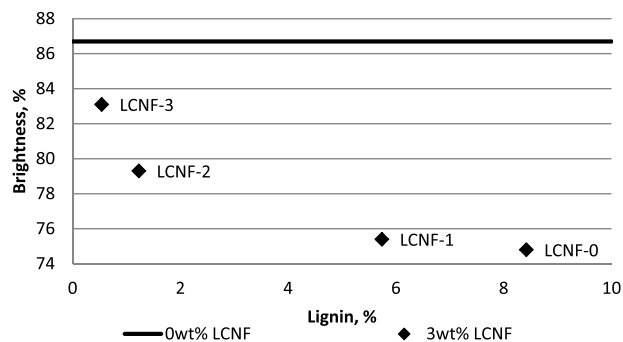


Fig. 4. Brightness of the non-reinforced and reinforced papers with LCNF.

it can be assumed that the used retention system assured almost 100% of LCNF retention, since the ultimate mechanical properties at tensile were almost the same. Thus, LCNF-1 were those that presented the highest reinforcing potential and were considered as the optimum for paper reinforcement.

3.3. Triticale LCNF as paper strength additive

Something disturbing of lignin-containing cellulose nanofibers is their effect on paper brightness when used on white papers. The use of LCNF for white paper manufacturing may entail negative effects on both paper whiteness and brightness. To bear out the effect that the addition of such LCNF imparts on the final brightness of paper, 3 wt% of each LCNF was added into a bleached kraft eucalyptus pulp and brightness at 457 nm of wavelength was measured, as reflected in Fig. 4.

As expected, paper brightness was gradually reduced as the lignin content of the added LCNF was increased. The non-reinforced paper presented a brightness of 86.7%, which was decreased until 74.8% with the addition of 3 wt% of LCNF-0. It must be mentioned that brightness in white paper is usually an imperative requirement, fact that limits the use of these LCNF for many applications.

For all the above, lignin-containing CNF may have market projection for brown-line papers, such as flutting, liner or unbleached kraft. Hence, test-liner papers were disintegrated in water and the obtained LCNF were added in presence of cationic starch and colloidal silica. Next, paper sheets were prepared and characterized, as it is reflected in Table 4.

The non-reinforced test-liner paper properties are shown in the first row of Table 4. The obtained papers presented a density of 0.66 g/cm³ and breaking length accounted for 3.55 km. When 3 wt% of LCNF-0 was added, as expected, breaking length did not increase significantly (13%) and the rest of the properties strongly related with tensile did not too (internal bonding and burst index). However, when 3 wt% of LCNF-1 was added, 5.47 km of breaking length were achieved (54% increase) and the rest of the properties were enhanced accordingly. LCNF-2 and LCNF-3 had similar behavior than when bleached kraft eucalyptus pulp was used. Surprisingly, in all cases the Schopper – Riegler degree was the same, regardless the mechanical properties enhancement. Moreover, no differences were observed between the added LCNF on paper density, since

all they increased it from 0.66 to 0.80 g/cm³ in average. This density increase or, what is the same, porosity decrease comes from the shrinkage forces that LCNF impart between fibers, compacting them and reducing the paper pore size (Delgado-Aguilar et al., 2015a).

In general, the addition of the obtained LCNF into the test-liner slurries resulted in less paper properties enhancement than were added into the bleached kraft eucalyptus pulp. This effect was previously observed by several authors (Delgado-Aguilar et al., 2015a; Espinosa et al., 2016) and it is related to the relative bonded area (RBA), described by Page (1969). Briefly, when RBA increases, the number of bonds per volume unit also increases. Moreover, as the quality of these bonds is higher, mechanical properties are enhanced too. When the maximum number of bonds and their quality are achieved, paper's breaking length approaches the intrinsic tensile strength of fibers. Taking into account this hypothesis based on Page's equation (Page, 1969), the differences on the properties enhancement between test-liner, which is mainly recycled paper, and bleached kraft eucalyptus pulp, which is composed by virgin fibers, are understandable (Delgado-Aguilar, Tarrés, Puig, Boufi, Blanco, Mutjé, 2015d). On the other hand, test-liner pulps contain much more fines than bleached kraft pulps. This higher presence of fines can sensibly hinder the rate of increase in paper's mechanical properties, as well as external fibrillation of fibers (Espinosa et al., 2016).

Therefore, the use of LCNF from triticale residue has many advantages. On the one hand, the substantial mechanical properties enhancement without damaging the structure of fibers increases lifespan of paper products (Delgado-Aguilar et al., 2015d) and, on the other hand, this substantial properties enhancement leads to implement concurrent strategies such as reducing paper basis weights or increasing the mineral filler amount in paper products, reducing thus production costs and saving fresh natural resources in papermaking industry.

4. Conclusions

In this work, LCNF from triticale straws were produced, characterized and applied in test-liner grade paper. It has been found that there is an optimum lignin content of 5.74 (kappa number of 23.4). The adopted delignification strategy decreased considerably the lignin content of pulps preserving 11–14% hemicelluloses. This hemicellulose preservation has been found as beneficial for LCNF production, since LCNF-1 presented the same reinforcing potential than CNF produced from chemically treated bleached wood pulps, even the fibrillation degree was significantly lower. However, lignin limits their use in white papers, since it was found that a 3 wt% addition of such LCNF reduced considerably paper brightness and, in consequence paper whiteness. In this sense, the obtained LCNF have potential application in brown-line papers such as test-liner grades, where brightness is not a fundamental property. LCNF-1 presented the higher mechanical properties enhancement capacity, increasing the breaking length of test-liner paper in 54%. The rest of the produced LCNF did not achieve such tensile strength, but they also imparted significant strength to paper. Overall, triticale straws are a strong alternative to wood fibers for ligno-nanocellulosic fibers production due to their high hemicellulose content, availability, and properties.

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