Suitability of wheat straw semichemical pulp for the fabrication of lignocellulosic nanofibres and their application on papermaking slurries

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Abstract

The present work studies the feasibility of wheat soda pulp as a raw material for the fabrication of cellulose nanofibres and their application as an additive in papermaking. Wheat straws were cooked under alkaline conditions and the resulting pulp was used as a raw material for the production of lignocellulosic nanofibres (LCNF). Nanofibres were fabricated by intense mechanical beating followed by high-pressure homogenization. The produced LCNF were characterized and applied to papermaking slurry based also on wheat straw soda pulp. Paper sheets made thereof were analysed for their physical and mechanical properties. The results indicated that paper strength was improved after addition of lignocellulose nanofibres (CNF), whereas density increased and porosity was reduced. These improvement in properties is significant (except the Tear Index) because they were achieved using LCNF with lower fibrillation degree compared to previous works where chemically pre-treated LCNF were used as reinforcement.

Keywords: *cellulose nanofibres, wheat straw pulp, paper, mechanical and physical properties*

Introduction

Sustainable development is a concept that is gaining more and more importance in our society, put into practice in all social aspects included industrial production. One of the pillars of sustainable development is the sustainable economy, which relies on integral utilization of natural resources. To achieve this goal it is necessary to valorise by-products and wastes produced in different activities such as agricultural or agro-industrial processes. Industrial activity has always relied on manufacturing products that meet the needs of customers within a market, but in recent years the environmental component has been incorporated into production since more and more society is aware and convinced of the necessity to consume products that have been obtained with environmentally friendly processes.

Europe produced over 96.5 million tons of paper and cardboard in the year 2010, where approximately a 17% was from non-wood raw materials (Confederation of European Paper Industries, CEPI). These non-wood raw materials are usually formed by residues from agriculture or agri-food industry; cellulosic fibres found

in this type of residues are useful for the fabrication of papers that have special characteristics due to its fibre morphology, composition and heterogeneity (García Hortal 2007, González - García *et al.* 2010). From all of these alternative raw materials, cereal straws are the most important source; world production of wheat, corn, barley, oats and rapeseed reached 1742 million tons in 2009 (FAO). Considering that a kilogram of grain generates approximately one kilogram of residue in the form of straws (Rodríguez *et al.*, 2010), agriculture generates a huge amount of wastes each year. These residues are used today, in the best of cases and in small quantities, as organic compost and as cattle feed. However, most of this residue is simply burnt in the field causing air pollution and risk of fire. Moreover, if these residues are not removed they can originate pest problems in the fields.

It is also important to consider the environmental aspects of wheat crop; each wheat plant has an annual CO_2 absorption of 10.3 g CO_2 / plant. If a wheat crop field has a density of 125 plants/m^2 (Carvajal 2008) then a hectare of crop would have an absorption capacity of 12875 tons CO_2 / has. From this amount, 3.5 tons of C are assimilated; this C would return to the atmosphere as CO_2 if plants are burnt. Therefore, integral use of this agricultural residue has not only economic advantages by enhancing what so far is a residue, but it has also direct environmental effects.

The use of cellulose nanofibres (CNF) as an additive for papermaking slurries has gathered increasing interest during the last years. Several recent publications confirm the improvement of paper's strength after addition of CNF as a bulk additive (Brodin *et al*. 2014, González *et al*. 2012, Taipale *et al*. 2010, Eriksen *et al*. 2008). The presence of CNF in the papermaking slurries boosts the formation of hydrogen bonds between fibres during paper formation, the main mechanism that dominates the increase of paper's strength. Besides, CNF promote reduction of porosity and increase of density in paper.

Fabrication of CNF consists mainly in disassembling the hierarchical structure of cellulose fibres by means of intense mechanical treatment. Usually, chemical (Saito *et al.* 2007, Wågberg *et al.* 2008, Besbes *et al.* 2011, González *et al.* 2014) or enzymatic (Janardhnan & Sain 2006, Pääkkö *et al.* 2007, Henriksson *et al.* 2007) pre-treatments are applied to cellulose fibres in order to facilitate the mechanical treatment step and reduce energy consumption. However, the fabrication of CNF using only mechanical treatments has also been reported (Nogi *et al.* 2009, Spence *et al.* 2011, Ferrer et al. 2012, Afra *et al.* 2013). In fact, the first attempts to produce cellulose nanofibres were based only on mechanical treatments (Turbak *et al.* 1983). Most of these studies have been performed mainly on bleached chemical pulps from woody plants such as eucalyptus and pine. Other plant fibres have been also successfully used as a source of nanofibres after bleaching (Alila *et al*. 2013, Besbes *et al*. 2011). These authors reported that the properties of cellulose nanofibres from non-woody plants do not differ significantly from CNF of woody plants. Bleaching removes lignin, hemicelluloses and other polymer carbohydrates that naturally accompany cellulose fibres. The effect that these components have on the fabrication and properties of CNF was already studied by other authors (Spence *et al.* 2011, Ferrer *et al.* 2012, Chaker *et al.* 2013). Their results indicated that residual amounts of both lignin and hemicelluloses play a key role on the nanofibrillaton

effectiveness. Basically, small amounts of lignin and high hemicelluloses content (25-30%) seem to have a beneficial effect during cellulose nanofibrillation by allowing obtaining high degrees of fibrillation. This means that cellulose fibres with such characteristics are potential candidates as raw materials for the production of CNF by using only mechanical disintegration.

In the present work, lingocellulosic nanofibres (LCNF) were fabricated from wheat straw soda pulps by applying only mechanical treatments via PFI-beating followed by high pressure homogenization and used as reinforcement for paper sheets fabricated from the same pulp. To our knowledge, this is the first time that LCNF are isolated from wheat residues using only mechanical treatment; the resulting nanofibres were then characterized and applied as a bulk additive in papermaking slurry of wheat pulp. Then papers sheets were fabricated and characterized for their physical and mechanical properties.

Materials and methods

Materials

Wheat straws were provided by Ecopapel S.L. from cooperatives of Écija, Sevilla, Spain. Because of the way in which these raw materials are harvested, it was necessary to first sift and perform a manual screening in order to separate undesirable elements such as stones, plastic bags, seeds, dust, wires, etc. Once these elements were separated, straws were dried at room temperature to constant moisture and stored in plastic bags for conservation. The content of α-cellulose, holocellulose, lignin, ashes and ethanol extractable was determined according to TAPPI standards T-9m 54, T-203os61, T-222, T-211 and T-204, respectively.

Methods

Pulping and characterization of the pulps

Wheat straws were pulped in a 15 L batch reactor at 99 ± 1ºC for 150min containing a 7% NaOH solution and heated by an outer jacket heater. The reactor contents were stirred by rotating the reaction vessel via a motor; the liquid/solid ratio was 10:1. After pulping, cooked material was dispersed in a pulp disintegrator at 1200 rpm for 30 min. The pulp was then passed through Sprout-Bauer beater and separated by sieving through a netting of 0.14 mm mesh size. The beating degree (Schopper-Riegler) of the resulting pulp was determined according to TAPPI T-227. The yield was determined by a gravimetric method after removing uncooked material ~~without cooking~~. Finally the content of α-cellulose, lignin, holocellulose, ashes, ethanol extractable, Kappa number and viscosity were determined according to TAPPI standards T - 9m54, T-203 os61, T-222, T-211, T-204, T - 236cm 85 and T230-om-94, respectively. Morphological analysis and fines content was studied using a MorFI compact analyser (TechPap) controlled with a computer. The equipment analyses 1000 mL of a 1 wt% fibre suspension; about 10000 fibres were analysed by the software MorFI v. 8.2. The pulping and characterization process is resumed in Fig. 1.

FIGURE 1 GOES HERE

LCNF production

Lignocellulosic nanofibres were obtained by mechanical treatment. First, wheat soda pulp was beaten in a PFI beater (NPFI 02 Metrotec SA) according to ISO 5264-2:2002 until achieving a drainage rate of 90 ºSR. Then, ~~a~~ 1.5% aqueous suspension was prepared and passed through a PANDA PLUS 2000 (GEA NIRO) high pressure homogenizer following the next sequence: 4 times at 300 bars, 3 times at 600 bars and 3 at 900 bars. This sequence was chosen to avoid clogging of the equipment in the first passes. During the process the temperature of the suspensions raised to 60-70º C. After this, the suspension was cooled down at room temperature and stored at 4º C. Fig. 2 resumes the fabrication and characterization process of LCNF used for the present study.

FIGURE 2 GOES HERE

LCNF characterization

The degree of polymerization (DP) of wheat soda fibres and LCNF was determined from intrinsic viscosity measurements, according to UNE 57-039-92. The viscosimetric average molecular weight was calculated from the equation: $\eta = K \cdot M^a$, where η is the intrinsic viscosity, K = 2.28 and a = 0.76 (Henriksson *et al*. 2008). The water retention value (WRV) was measured by separating a determined volume of LCNF gel into two equal portions, which were then centrifuged in a Sigma Laborzentrifugen model 6K15 (7 cm of rotation radius) at 2400 rpm for 30 minutes to eliminate non-bonded water. In order to retain the LCNF, a nitrocellulose membrane with a diameter pore of 0.22 μm was used at the bottom of the centrifuge bottles. Once centrifuged, only the LCNF in contact with the membrane was removed, weighed and then dried at 105±2º C for 24 h in containers of previously measured weight. This methodology is partially based on TAPPI UM 256. The average WRV value was then calculated according to the next equation:

$$WRV(\%) = \frac{Ww - Wd}{Wd} x100 \quad (1)$$

W_w is the wet weight (g), W_d the dry weight (g). The carboxyl content (CC) of LCNF was calculated by conductometric titration. A dried sample (50–100 mg) was suspended in 15 ml of 0.01M HCl solution; this exchanges Na cations bound to the COOH group by H ions. After 10 min of magnetic stirring, the suspensions were titrated with 0.01M NaOH, adding 0.1 ml of NaOH to the suspension and then recording the conductivity in mS/cm; this process was repeated until observing a reduction, stabilization and increase in the conductivity. The CC is given by the following equation:

$$CC = 162\,(V_2 - V_1)c\,[(w - 36(V_2 - V_1)c]^{-1} \quad (2)$$

The results indicate the average in mmols of –COOH groups per gram of LCNF. The cationic demand of LCNF was also determined by means of a Mütek PCD 04 particle charge detector, adapting the methodology described by Carrasco *et al.*

(1998). First, 0.04 g of LCNF (dried weight) was diluted in 1 L distilled water and dispersed with a pulp disintegrator for 10 min at 3000 rpm. Afterwards, 10 mL were taken and mixed with 25 mL of cationic polymer polydiallyldimethylammonium chloride (poly-DADMAC) during 5 min with magnetic stirring. After this, the mixture was centrifuged in a Sigma Laborzentrifugen model 6 K 15 for 90 min at 4000 rpm. Then, 10 ml of the supernatant were taken to the Mütek equipment. Anionic polymer (Pes-Na) was then added to the sample drop by drop with a pipette until the equipment reached 0 mV. The volume of anionic polymer consumed was used to calculate the cationic demand though the next equation:

$$CD = \frac{(C_{PolyD} \cdot V_{PolyD}) - (V_{Pes-Na} \cdot C_{Pes-Na})}{W_{sample}} \quad (3)$$

Where CD is the cationic demand (μeq/L), C_{PolyD} = cationic polymer concentration (g/L), V_{PolyD} = used volume of cationic polymer (mL), C_{Pes-Na} = anionic polymer concentration (g/L), V_{Pes-Na} = used volume of anionic polymer (mL) and W_{sample} = sample's dry weight (g). The yield in 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 90ºC until constant weight. The yield of nanofibrillation was then calculated from the next equation:

$$Yield\% = \left(1 - \frac{\text{weight of dried sediment}}{\text{weight of diluted sample x \%Sc}}\right) x100 \quad (4)$$

where %Sc represents the solid content of the diluted gel sample. 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.

In addition, the effect of a 3wt% addition of the LCNF over a standard substrate (bleached kraft hardwood pulp) was also studied. This pulp has 2098m of breaking length and 15ºSR. The methodology followed for this addition was the same of incorporating LCNF into the wheat pulp suspension, as it is described in the following section.

Determination of the energy consumption

The energy consumption of the homogenizer during the production of LCNF was carried out with an energy measuring equipment (Circutor CVM-C10), which gives values of the energy consumption of the equipment or, what is the same, the energy required from the electrical grid.

Incorporation of LCNF into the pulp suspension

In the case of wheat suspensions with LCNF, they were added and mixed into the semichemical wheat pulp slurry by means of a pulp disintegrator operating at 3000 rpm during 60 minutes and 1.5 % consistency using tap water (289 μS/cm) as background. This methodology has been used in previous works (Alcalá *et al.*

2013, González *et al*. 2012, 2013a, Delgado-Aguilar *et al.* 2014) and has proved to be effective in improving the dispersion of CNF in papermaking slurries. After this step, cationic starch and colloidal silica were added at corresponding doses of 0.5 and 0.8 %, respectively, expressed on dry pulp. The application of these retention agents was done at gentle agitation of the suspension at 1% consistency for 20 min. This step becomes necessary in order to avoid the loss of LCNF during the dewatering process since filters at the bottom of the stock container in the Rapid-Köthen equipment are not able to retain nanometric material. The amount of LCNF added was calculated to obtain paper sheets with different percentages of LCNF (from 0 to 4 wt%). Paper sheets with an average basis weight of 75 g/m^2 were fabricated in a sheet former (ISP mod. 786FH) according to ISO standard 5269-2 and conditioned in a weather chamber at 25º C and 50% humidity for 48 h before mechanical tests were performed.

Characterization of paper sheets

Characterization of paper sheets obtained from the different fibrous suspensions was performed by determining first the basis weight (ISO 536) and thickness (ISO 534) of the sheet; density was calculated from the sheet's basis weight and the dimensions; Breaking length was calculated from tensile experiments performed in an Instron universal testing machine provided with 2.5 kN load cell. The testing conditions were set according to ISO standards 1924-1 and 1924-2. Tear index was determined in an Elmendorf Tearing Tester (mod. F53.98401 Frank PTI) and assay conditions were set according to ISO standard 1974. Burst index tests were carried out in a burst tester (IDM mod. EM-50) and test conditions were set according to ISO standard 2758. Gurley porosity was determined in a Gurley porosimeter (Papelquímia) was used and testing conditions were set according to ISO standard 5636/5. Percentage of void volume (%), Scott bond (TAPPI T569). Percentage of void volume was calculated from the next equation:

$$Porosity\ (\%) = 100 \cdot \left(1 - \frac{\rho_{sample}}{\rho_{cellulose}}\right) \quad (5)$$

where ρ_{sample} is the density of the paper sheet (calculated from basis weight, thickness and area) and $\rho_{cellulose}$ is the density of cellulose, assumed to be 1.5 gr/cm^3.

Scanning electron microscopy (SEM)

The microscope was a Hitachi S-3000 variable pressure SEM (Hitachi High-Technologies Corporation, Minatoku, Tokyo, Japan). SEM surface images were acquired at 509 and 1,0009 magnifications, in secondary electron imaging mode. The acceleration voltage and working distance were 5 kV and 12 mm, respectively.

Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) was carried out with a ZEISS EM910 TEM operating at 120 kV. Specimens for inspection by TEM were prepared by slowly evaporating one drop of the LCNF gel, at room temperature on a 400 mesh copper grid, coated by a carbon-supported film.

Results and discussion

Wheat stalks characterization

Wheat stalks presented the next composition: alcohol extractables (5.2%), ashes (7.72%), α-cellulose (39.7%), hemicelluloses (30.6%) and lignin (17.7%). It can be said that the ash content is similar or even lower in comparison to similar agricultural residues such as corn (5.95%), oats (7%), rape (6.38%) and barley (9.49%), (Vargas *et al.* 2012). High values of ashes might give rise to problems of corrosion and fouling in the industrial plants. Lignin is a hydrophobic constituent, which if found in high proportions can hinder the refining process, since it inhibits the absorption of water from the pulp. However, a slight percentage of lignin, as in this case, gives to the pulp relatively high values of specific volume, dimensional stability and rigidity (García-Hortal 2007). Lignin content in wheat straws is very similar to those found in corn (18.2%), oats (16.6%), rape (17.2%) and barley (16.3%) (Vargas *et al.* 2012). The hemicellulose, in contrast to lignin, is very hydrophilic and this fact favors the swelling of fibres, increasing plasticity, flexibility and the ability to bind with other compounds, resulting in improvement of density, strength and physical properties of paper sheets (García-Hortal 2007).

Pulp characterization

Wheat soda pulp was characterized by determining the percentage of alcohol extractables, ashes, α-cellulose, hemicellulose and lignin obtaining following values, respectively; 3.37%, 10.90%, 73.0%, 16.3 and 2.8%. Other characteristics were also determined such as yield, beating degree (ºSR), Kappa number and viscosity (mL/g) as reflected in table 1.

TABLE 1 GOES HERE

The yield obtained with the wheat straw soda pulp is around 70%, a high value within semi-chemical pulp and higher than yields achieved with other raw materials: corn (65.5%), oats (66.9%), rape (63.1%) and barley (65.6%), (Vargas *et al.* 2012). The drainage rate was relatively high compared to that of commercial chemical bleached pulps such as pine and eucalyptus. Higher ºSR is found in some chemithermomechanical pulps from other agricultural residues such as rapeseed (González *et al.*, 2013). An elevated Schopper-Riegler implies high bonding strength between the fibres (González *et al.*, 2012). The Kappa number is a measure of the delignification degree of the raw material. High values for this parameter imply that pulp is not adequate for bleaching process by its high cost. The value obtained for the wheat straw soda pulp (38.6) is the lowest of the different raw materials that have been compared (from 56.7 for the corn until 115.1 for the rape). It must be pointed that the Kappa number found and the lignin content are not in agree. This is probably due to the accuracy in the gravimetric techniques that have been used for the chemical characterization. On the other

hand, the standard ISO 302:2004 provides a correlation between Kappa number and lignin content, in percentage (approximately 6.57). This constant is referred to wood pulps with values of Kappa numbers from 25 to 30. Applying this constant and taking the Kappa number determination as more accurate, the content of lignin would vary from 2.8% to 5.9%, being still a value quite low. The degree of polymerization (*DP*) calculated from intrinsic viscosity measurements was 1381.

TABLE 2 GOES HERE

Table 2 presents the morphology of fibres after pulping. The detection limit for fines was set at 76 and 200 μm in order to indicate the great amount of these particles present in the pulp. The presence of fines accounts for the high breaking length found in paper sheets fabricated from wheat soda pulp and the elevated ºSR of its suspensions. As it is possible to see in table 2, the percentage of fines is higher when the detection limit is set at 200μm. Paper industry usually considers the fine elements those particles with lengths lower than 200μm. Setting the MorFi equipment at 200μm, Moreover, as shown later, the percentage of fines in the pulp plays an important role in the rate of increase of breaking length in LCNF-reinforced papers.

LCNF characterization

Characterization of LCNF is important since it helps to understand the mechanisms that rule the reinforcing effect that they have on papermaking slurries. Table 3 shows the characterization of the nanofibres used in this work. The PFI beating pre-treatment allows a greater capacity of hydration and swelling of fibres, thus facilitating the passing of the pulp suspension through the homogenizer.

TABLE 3 GOES HERE

The LCNF of wheat straw have a nanofibrillation yield of 55.6%. This is a comparatively moderate result in contrast to NFC fabricated after TEMPO-oxidized fibres from bleached chemical pulps reported in the bibliography where nanofibrillation yield reaches over 95% (González *et al.* 2012, Delgado-Aguilar *et al.* 2014). These differences are a direct consequence of the type of pre-treatment applied on the pulp: in CNF fabricated from TEMPO-oxidized fibres, the formation of negatively-charged carboxyl groups in the C6 of the cellulose chain introduces repulsion forces between the fibres which promote water income, fibre swelling and hydration (Saito *et al.* 2007). This facilitates the disassembling of the fibre structure during the mechanical treatment.

Another important factor that determines the suitability of CNF production is the content of lignin and hemicelluloses. In general, the presence of these components

along with other heteropolysaccharides seems to ease the mechanical individualization of microfibrils; it has been inferred that hemicelluloses attached to microfibrils by hydrogen bonds form a physical barrier among them that inhibits the formation of microfibrils aggregates (Chaker *et al.* 2013). The same author concluded that, in the case of non-woody plants, a hemicellulose content of 25% decisively stimulates high fibrillation. In the case of lignin Ferrer *et al.* (2012) reported that residual amounts of lignin promote fibrillation by stabilizing the radicals formed during beating stages. Moreover, the amorphous nature of lignin and hemicelluloses also influences the fibrillation process (Solala *et al.* 2011). Therefore, it is clear that a high hemicellulose content and low amount of residual lignin make the wheat soda pulp a good candidate for LCNF production through solely mechanical treatment.

FIGURE 3 GOES HERE

Transmittance is another method to indirectly measure the fibrillation degree of a LCNF suspension. The presence of cellulose fibres in the aqueous suspension leads to light scattering due to the differences in the refractive index between cellulose and water (1.5 and 1.3 respectively). Since the amount of scattered light is in relation to the particle size when Mie scattering is considered, then high trasmittance values indicate that the suspended material has extensive fibrillation. Transmittance spectra from TEMPO-oxidized CNF are reported to be close to 100% (Saito et al. 2007, Alila *et al.* 2013, Besbes *et al.* 2013, González *et al.* 2014), indicating a very high fibrillation degree. In the case of LCNF from wheat pulp, the transmittance (Fig. 3) can be considered as comparatively moderate since no chemical pre-treatment was applied. Moreover, LCNF contain lignin which also causes light deflection. In the same way, the cationic demand is considerably lower than that obtained by TEMPO-catalyzed oxidation (González *et al.* 2014) as expected. Cationic demand serves also as an indirect indicator of the specific surface area of LCNF. Further mechanical treatment would lead to a slight increase in cationic demand. A possible mechanism of interaction between the cationic polymer (poly-DADMAC) an LCNF surface is reflected in Fig. 4.

FIGURE 4 GOES HERE

This drawing tries to show the two possible mechanisms (Rouger and Mutjé, 1984, Carrasco *et al.* 1996): i) ionic interaction between the cationic polymer and the carboxylic groups on the cellulose surface, and ii) surface interactions due to London-Van Der Waals forces. If both mechanisms are assumed to occur at the same time and that poly-DADMAC forms a single layer, then by estimating the specific surface area of a single poly-DADMAC (σ_{DADMAC}) molecule, it would be then possible to theoretically calculate the specific surface area of LCNF (σ_{LCNF}). Considering the atomic distances and angles between the atoms of a poly-DADMAC monomer and that the molecule adopts an elliptical structure then the

surface of the poly-DADMAC monomer could be calculated through the next equation:

$$\sigma_{DADMAC} = \pi \cdot d \cdot l \quad (1)$$

where, σ_{DADMAC} is the monomer's area, d and l the diameter and length of the monomer's molecule, calculated to be 0.528 nm and 0.488 nm respectively. This makes 0.809 nm^2 for a single monomer molecule. 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 degree of polymerization (*DP*). This yields 535.56 nm^2 for a poly-DADMAC molecule. To calculate the specific surface area of a poly-DADMAC mol, the Avogadro constant is then applied:

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

Then, σ_{dadmac} is converted from nm^2/mol to nm^2/μeq by the next equation:

$$\sigma_{DADMAC} = \frac{3224 \cdot 10^{23} nm^2}{662 \cdot 10^6 \mu eq} = 4.87 \cdot 10^{17}\ nm^2/\mu eq \quad (3)$$

Considering the stoichiometric relationship between hydroxyl and carboxyl groups with poly-DADMAC and applying the next relationship:

$$\sigma_{LCNF} = (CD - CC) \cdot \sigma_{DADMAC} \quad (4)$$

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, then 75.77 m^2/g was obtained. Finally, it is possible to calculate from this value the average diameter of a single LCNF fibre (d_{CNF}), considering a cylindrical geometry:

$$d_{CNF} = \frac{4}{75.77 {}^{m^2}/_{g} \cdot 1600 \cdot 10^3 {}^{g}/_{m^3}} \quad (5)$$

$$d_{CNF} = 32.99nm$$

The diameter calculations based on the poly-DADMAC surface adsorption on the LCNF, show a mean diameter of approximately 33 nm. The actual diameter of LCNF was assessed by TEM microphotography, as reflected in Fig. 5.

FIGURE 5 GOES HERE

The images show a wide distribution of widths with an average diameter of 28 nm. This value is not significantly different from 33 nm calculated by the method described above. Though this theoretical calculation is based on a series of assumptions, it allows having an approximate idea of the evolution of σ_{LCNF} and d_{CNF} in a simple, rapid manner. The TEM microphotography also shows that it is possible to obtain considerably nanofibrillated material by applying only mechanical forces on an unbleached, non-woody pulp.

The carboxyl content is considerably low when compared to values observed in TEMPO-oxidized CNF (Delgado-Aguilar *et al.* 2014) as expected. It is well known that intense fibrillation of cellulose fibres increases carboxylic content

which facilitates their dispersion in water, so it would be expected that further mechanical treatment would boost the carboxylic content. Regarding WRV, a result of 480% means that LCNF from wheat have 4.8 grams of water per gram of LCNF associated chemically. As a comparison, González *et al.*, (2014) obtained CNF of eucalyptus bleached pulp with a WRV of 1700%.

The viscosity of the LCNF suspension allowed calculating the degree of polymerization (1004.8). This indicates a reduction of 31% from the original *DP* of the soda pulp (1381) due to the mechanical forces applied for the preparation of LCNF. One of the main advantages of mechanical treatments for LCNF manufacture is that the loss in *DP* is not as intense as in LCNF prepared from some types of chemically modified fibres. The *DP* is directly linked to the intrinsic mechanical properties of the LCNF, as described in Henriksson *et al.* (2008).

The breaking length increase was assessed over the standard substrate described in the Materials and Methods chapter. This parameter helps to determine the effectiveness or performance that LCNF imparts on breaking length, as well as this parameter allows making reliable comparisons between different CNF. For instance, some published results showed that the addition of a 3wt% of CNF prepared by TEMPO oxidation (from bleached kraft hardwood pulp) at three different oxidation levels (3, 5 and 15mmols of hypochlorite) imparts an increase of about 97, 100 and 112% in breaking length, respectively (González 2014).

Using this parameter as part of the characterization of the produced CNF (or LCNF in the case of the present paper) allows knowing the effectiveness thereof. The main difference between the enhancement achieved between LCNF and CNF (TEMPO) is the diameter. While the average diameter of LCNF is 33nm, TEMPO oxidized cellulose nanofibers present diameters of between 3 and 10nm.

Since the production of LCNF for this study required intense mechanical treatment, an analysis of energy consumption was performed. Additionally, taking into account the amount of chemicals used for the production of TEMPO oxidized CNF and the passes through the homogenizer required to get those (Delgado-Aguilar *et al.* 2015), the production costs of this type of CNF (from bleached kraft hardwood pulp) were also calculated. The results are shown in table 4.

TABLE 4 GOES HERE

Regarding the case of LCNF, it is important to mention that this price does not take into account the energy consumption of soda pulping and the price of the chemicals used for such process. In this sense, in the case of TEMPO oxidized CNF, the price of obtaining the bleached pulp is also not included.

There are some methods reported elsewhere to determine the energy consumption of passing a suspension through the homogenizer (Ankerfors 2015, Naderi *et al.* 2015). These methodologies are based on the energy balance between two data collection points (the surface of the inlet tank and after the pressure pump). Inasmuch as the energy losses of the internal and dynamical energy are quite difficult to measure, it has to be assumed that there are no changes, as well as in

the case of the sample heating due to friction in the chambers. Not just that, but the pump efficiency is also neglected, thus forcing to assume an efficiency of 100%.

On the other hand, using the energy measurement equipment (Circutor CVM-C10), it is possible to determine the energy required, which is the same of the energy required from the electrical grid, becoming more reliable energy consumptions since it takes into account all the assumptions listed above. In fact, when assessing production costs, this is the energy that producers will be supposed to pay for.

As it is possible to see, the energy required for LCNF is higher than for CNF (TEMPO oxidized). This is mainly due to the effect of TEMPO oxidation, since the pretreatment is harder than in the case of LCNF and the energy required to nanofibrillate becomes lower.

Looking at the total production costs, it is possible to see that TEMPO CNF is about 70 times more expensive than LCNF. This difference is mainly due to chemicals costs. Nowadays, there is still missing a methodology to recover successfully TEMPO catalyst, which costs about 8,800€/kg. Looking at the costs breakdown of this type of CNF, it is possible to see that TEMPO represents about 80% of the total cost.

Bulk application of LCNF on wheat soda pulp

To evaluate the feasibility of wheat straws in the papermaking industry, paper sheets from wheat soda pulps were fabricated and added with different percentages of LCNF in combination with cationic starch and colloidal silica as retention agents. The first one, cationic starch, is added in order to ensure a good retention of the LCNF on paper. On the other hand, and due to the flocculation effect of cationic starch, colloidal silica is added in order to ensure a good paper formation. The physical properties of the manufactured paper sheets are shown in table 5.

TABLE 5 GOES HERE

The results indicate that, under a constant grammage, paper's thickness decreases with growing contents of LCNF. Probably, nanofibres moving freely in fibres suspensions behave in a way similar to that of fines by reducing the meniscus radius that appears during dewatering of the papermaking suspension; this increases the pressure difference between the aqueous phase and the fibres surroundings, helping thus to draw the fibres closer together, compacting the paper sheet. Besides, nanofibres attached to the larger fibres' surface significantly increase the contact area between fibres which boost the formation of hydrogen bonds and establish permanent bonds among the fibres when they are brought into contact during the dewatering step. This also explains the increase in density higher LCNF contents. Papers with a 4 wt% of LCNF presented the highest density. Porosity calculated as the percentage of empty space is also reduced with the presence of LCNF. The decrease in porosity is also a consequence of the increase in paper's compactness. It is also expected that a part of the nanofibres

occupy the spaces between the larger fibres, forming a nanometer network that occupy the gaps between fibres. As a whole these mechanisms help to reduce the diameter and number of pores of the paper. The same trend is observed in the Gurley porosity, whose test time increases until a 685% versus paper sheets made of pulp without reinforcement. Test times develop linearly in relation to the amount of LCNF. In fact, the evolution of physical properties in paper sheets has a good correlation with the content of the LCNF as shown in Fig. 6.

FIGURE 6 GOES HERE

Table 6 summarizes the Schopper-Riegler and mechanical properties of LCNF-reinforced papers sheets. Neat wheat straw soda pulp has a high Schopper-Riegler in comparison to a typical bleached eucalyptus pulp (González *et al*. 2012).

TABLE 6 GOES HERE

An elevated ºSR is consequence of the high percentage of fines found in wheat straw pulp in comparison to bleached chemical pulps; these fines increase the specific surface of the pulp and block the spaces between fibres where water drains, increasing the ºSR. After addition of LCNF, the ºSR increases due to the high water-holding capacity that LCNF in general show. The large specific surface area of LCNF promotes the formation of hydrogen bonds between the hydroxyl groups of cellulose and water. This causes that the LCNF retain a great quantity of water even at low concentrations, modifying the viscosity of the suspension and hampering dewatering. As the LCNF content rises, ºSR significantly increases. The evolution of ºSR shows a correlation with the amount of LCNF (Fig. 7).

FIGURE 7 GOES HERE

With regard to the mechanical properties of paper sheets made without LCNF, it is important to highlight that this fibre already has a breaking length suitable for the manufacture of certain types of paper. Fig. 7 shows the evolution of the breaking length according to the percentage of LCNF added; the results obtained are from paper sheets made with an isotropic former. It can be observed that breaking length experiences a linear increase up to a 28% with the addition of a 3% of LCNF. Tensile strength of paper mainly depends on three factors: the number of links among fibres, the type of links and the intrinsic resistance of the fibre. The improvement observed in paper reinforced with LCNF is due to the boost in the number of hydrogen bonds between fibres promoted by the greater specific surface area of the LCNF. More than 3 wt% of LCNF did not bring about an improvement in breaking length probably because there is no more linkable area available. The burst index also increased up to 50% after the addition of 4% of LCNF. In contrast to the other physical properties, tear index showed its maximum value with 1% of LCNF, being this increase of a 7.1% versus initial

value. This is because in pulps with low degree of union between the fibres, the tear index increases when the fibre-to-fibre union improves, as it is the case with the addition of LCNF. However, when the degree of union between fibres is already high, as in the case of pulps reinforced with LCNF, tear index is determined by the strength and length of the fibres, so larger amounts of LCNF will not produce significant improvement of the tear index.

Interactions between wheat fibres, fines and LCNF

The rate of increase in breaking length after LCNF addition depends on the tensile strength of fibres and their morphological properties. This means that pulps and fibres with different morphology and tensile strength will increase their breaking length at different rates. Considering that the increase in the number of hydrogen bonds between fibres is the main mechanism of resistance of paper, it is expected that fibres with a low binding capacity show higher rate increase than those that are well linked. Therefore, it can be accepted that mechanical and recycled pulp show a more significant increase than, for example, beaten chemical pulps (Brodin *et al.* 2014). However, when LCNF were used to reinforce papermaking slurries from bleached eucalyptus pulp, breaking length improved from 2098 to 3972 m, an increase of 89% after addition of 3 wt% of LCNF; this rate of increase is far superior than seen in paper sheets from wheat soda pulp with the same nanofibres content, as it has been explained before.

FIGURE 8 GOES HERE

In order to understand this difference in the rate of increase it is important to consider the role that the high content of fines may have in the interaction between wheat soda pulp and LCNF.

FIGURE 9 GOES HERE

During paper formation, the fines that freely float in the water interact with the LCNF in such a way that a part of the nanofibres forms links with the fines and not with the fibres. This would significantly reduce the reinforcing effect of nanofibres while the ºSR would remain at high levels by the combined effect of fines and LCNF. Fig. 8 shows the proposed mechanism of interaction among fines, LCNF and fibres within the suspension. It is expected, therefore, that by removing fines before the addition of LCNF it could be possible to improve the linking ability of LCNF with fibres, which could ultimately lead to more significant increases in paper's strength. According to this reasoning, paper sheets with 3 wt% of LCNF were fabricated from wheat soda pulp without fines. Mechanical tests indicated an improvement in breaking length from originally 5713m (wheat semichemical pulp with 13.9% of fine content) to 7609 m. This result clearly shows that the presence of fines limits the reinforcing effect of

LCNF. The interaction between LCNF and fibres within the paper sheet structure has been observed through FE-SEM (Fig. 9). The images indicate that the LCNF are distributed either filling the gaps between (right picture) fibres or partially covering them (left picture). Both types of distribution increase the amount of hydrogen bonds between fibres, accounting for the significant increase in mechanical properties even at low LCNF content.

Conclusions

In this work, the feasibility of wheat straw as a raw material to produce lignocellulose nanofibres and their application as papermaking additive was studied. This pulp was chosen due to its relatively low residual lignin content and high amount of hemicelluloses. LCNF were prepared using mechanical pre-treatment via PFI beater followed by high-pressure homogenization. The nanofibrillation degree was moderate in comparison to CNF prepared from TEMPO-oxidized fibres and the characterization confirmed the lower content of nanosized material. In addition, it has been demonstrated that TEMPO oxidized CNF are 70 times more expensive than LCNF from wheat semichemical pulp. The use of LCNF on papermaking slurry based on wheat soda pulp induced an improvement in breaking length and burst index in relation to unreinforced paper, whereas tear index remained almost constant. Besides, paper sheets became thinner as more LCNF was added, leading to an increase in density and a reduction in porosity. It was also demonstrated that the presence of fines can sensibly hinder the rate of increase in paper's mechanical properties. By removing fines, the rate of increase was significantly improved in comparison with fine-containing pulps.

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Figure
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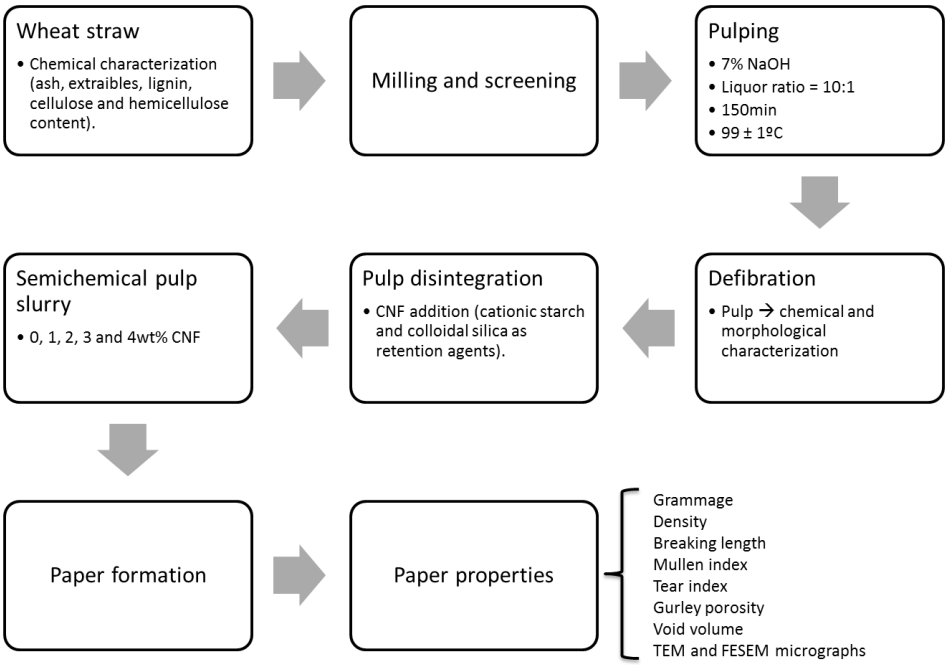

Fig. 1. Flow chart of the whole wheat soda pulp fabrication process and characterization.

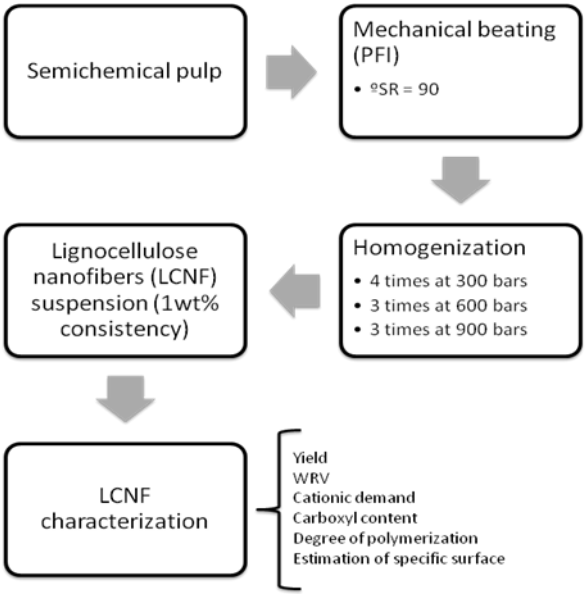

Fig. 2. Flow chart of the fabrication and characterization of LCNF

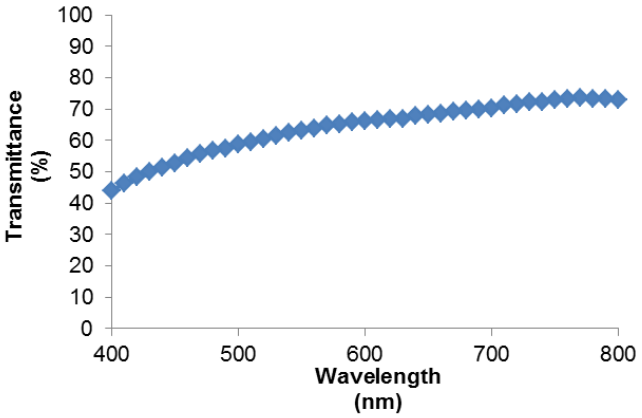

Fig. 3. Transmittance of the suspension of CNF in the range of the visible light spectrum

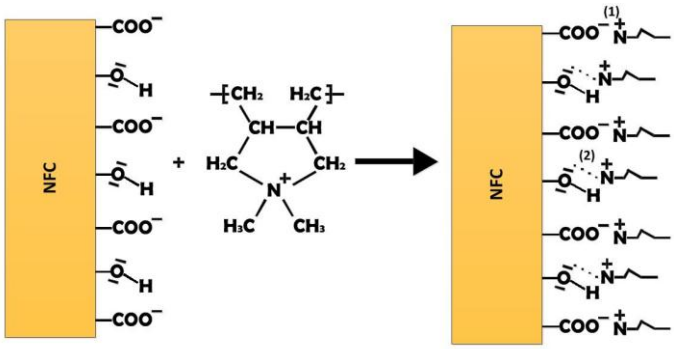

Fig. 4. Proposed mechanisms of interaction between LCNF and poly-DADMAC.

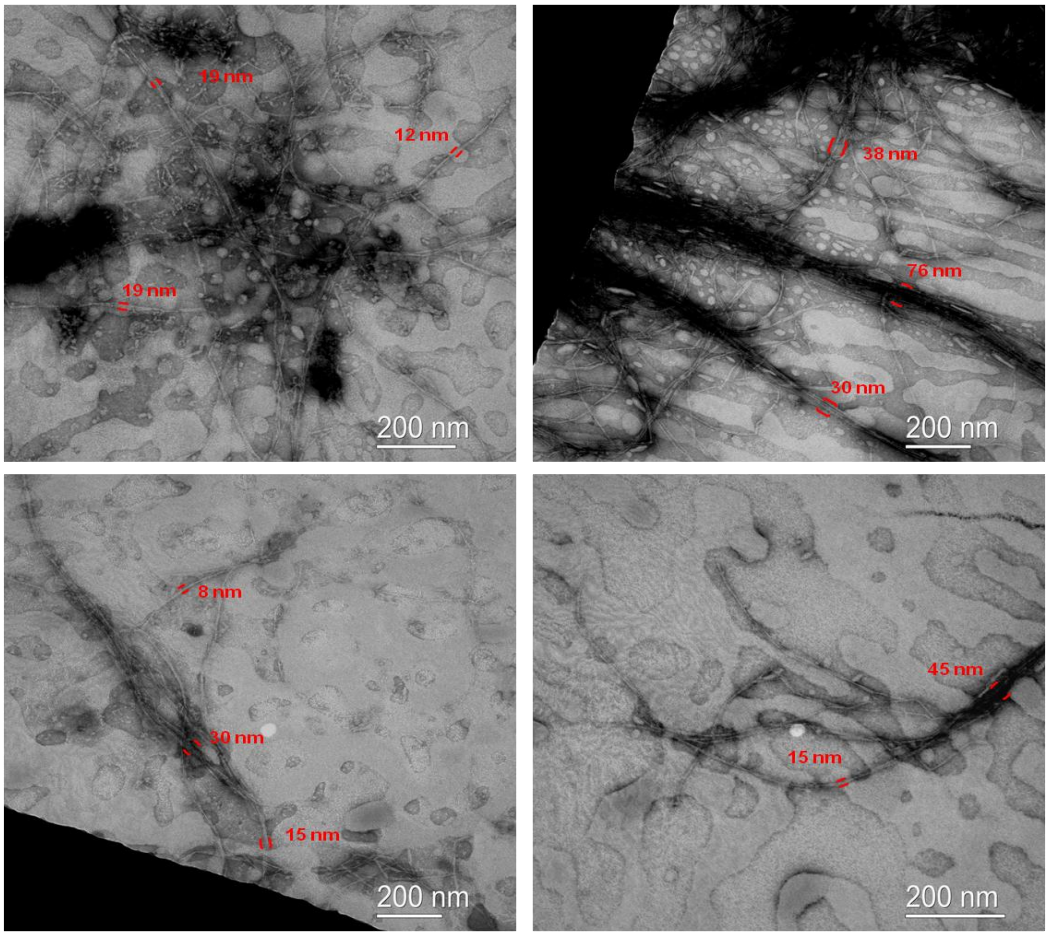

Fig. 5. TEM images of LCNF indicating the diameter of some of the nanofibres**.**

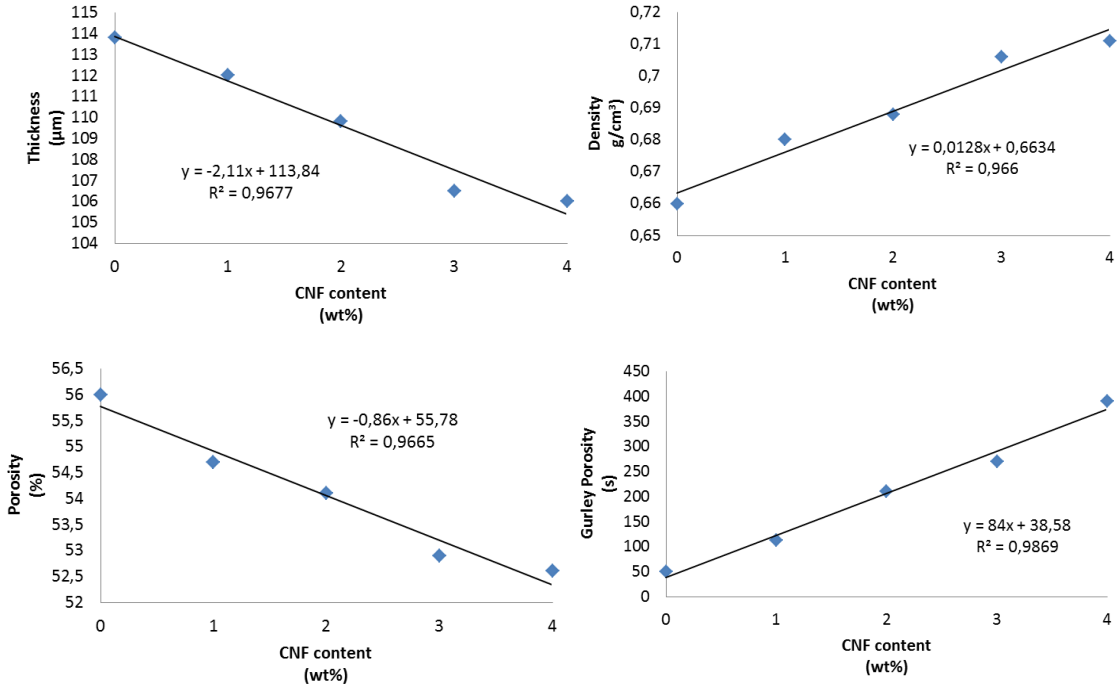

Figure 6. Evolution of the physical properties of papers based on the contents of CNF.

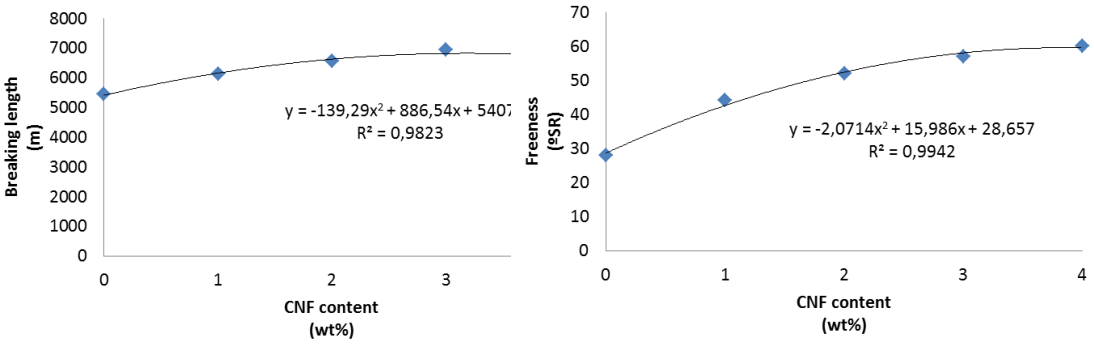

Fig. 7. Evolution of the breaking length (left) and Schopper-Riegler (right) of wheat straw pulps in relation with the CNF content

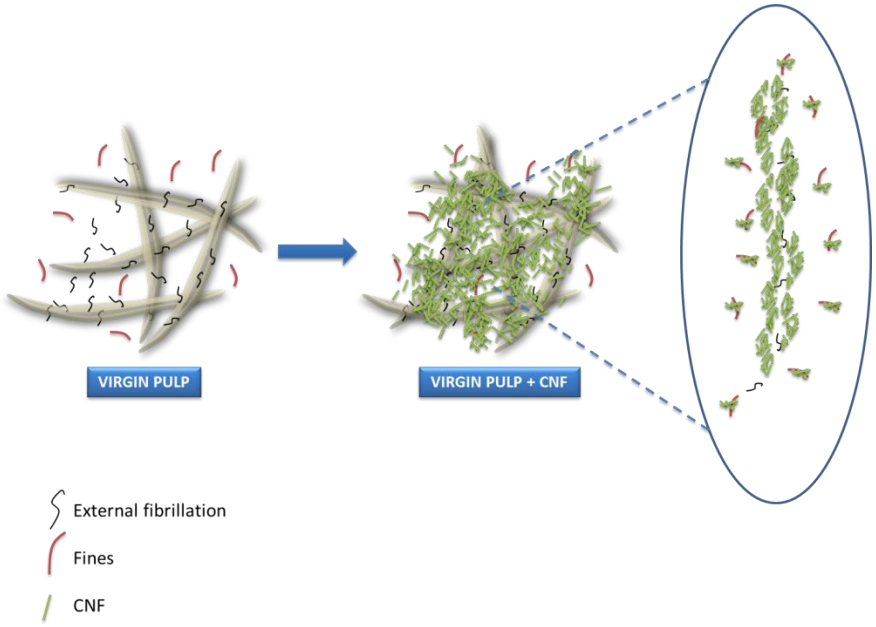

Figure 8. Proposed mechanism of interaction between fines, CNF and fibres.

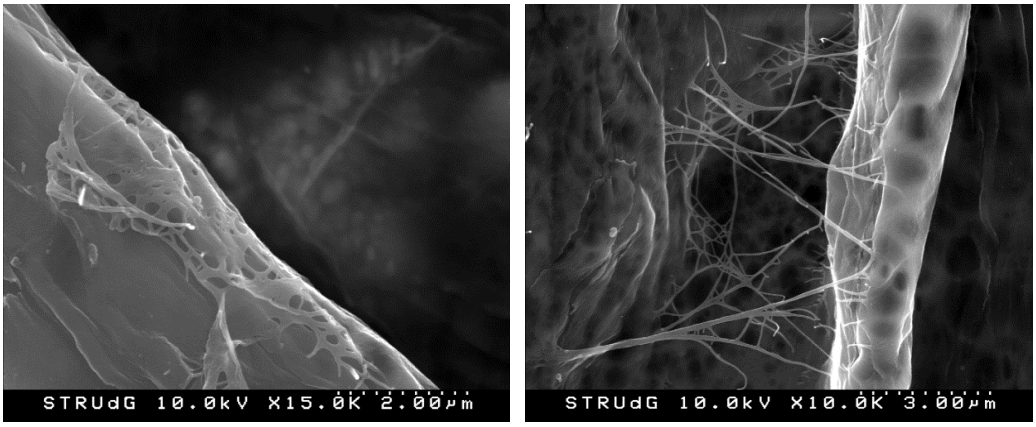

Fig. 9. Interaction between CNF and fibres. Left) LCNF covering the surface of a fibre; right) LCNF occupying the gaps between fibres.

Table
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Table 1. Wheat soda pulp properties.

Yield (%)	**°SR**	**Kappa number**	**Viscosity** (mL/g)	**DP**
70	51	38.6	536	1381

Table 2. Morphology of the wheat soda pulp fibres in relation to the fines detection limit set during the experiment.

Fines detection limit (μm)	**Length arithmetic** (μm)	**Length weighted in length** (μm)	**Width** (μm)	**Fines** (% in length)	**Breaking length** (m)
76	502	730	20.1	26.9	5435
200	510	742	20.1	47.6	5435

Table 3. Characterization of the LCNF

Yield (%)	**Transmittance** (%)	**Cationic demand** (μeq·g/g)	**Carboxyl content** (μeq·g/g)	**WRV** (%)	**Viscosity** (mL/g)	**DP**	**Breaking length increase** (%)
55.6	<75	230	<74.4	480.3	436	1004.8	89.31

Table 4. Energy consumption for the production of cellulose nanofibres.

Type of CNF	Chemicals				Pressure (bar)	Number of passes	Energy consumption (kW·h/kg)	Price* (€/kg)
	TEMPO (€/kg CNF)	**NaBr (€/kg CNF)**	**NaOH (€/kg CNF)**	**NaClO (€/kg CNF)**				
Wheat LCNF					**300**	4	14,22	1,14
					600	3	11,00	0,88
					900	3	6,66	0,53
TEMPO CNF (5mmols)	140,70	10,67	20,13	1,79	**600**	3	29,2	2,34

Wheat LCNF: Total Price* (€/kg) = 2,55

TEMPO CNF: Total Price* (€/kg) = 175,63

* Total price calculated at a price of 0,08€/kW ·h

Table 5. Physical properties of the paper sheets made with different percentages of LCNF.

CNF content (wt%)	**Grammage** (m^2/g)	**Thickness** (μm)	**ρ_{paper}** (g/cm^3)	**Porosity** (%)	**Gurley porosity** (seconds)
Wheat + 0% CNF	75.10±	113.8±0.1	0.660±	56±0.3	49.8±0.2
Wheat + 1% CNF	76.15±	112±0.5	0.680±	54.7±0.6	112.3±0.4
Wheat + 2% CNF	75.50±	109.8±0.6	0.688±	54.1±0.4	209.9±0.4
Wheat + 3% CNF	75.25±	106.5±0.5	0.706±	52.9±0.7	269.9±0.7
Wheat + 4% CNF	75.40±	106±0.4	0.711±	52.6±0.3	391±0.6

Table 6. Drainage and mechanical properties of the paper sheets with different percentages of LCNF.

CNF content (wt%)	**ºSR**	**Breaking length** (m)	**Burst index** (Kpa·m^2/g)	**Tear index** (mN·m^2/g)
Wheat + 0% CNF	28	5435±115	2.38±0.12	4.2±0.01
Wheat + 1% CNF	44	6121±87	2.98±0.05	4.5±0.03
Wheat + 2% CNF	52	6555±102	3.16±0.09	4.4±0.02
Wheat + 3% CNF	57	6937±91	3.39±0.10	3.9±0.07
Wheat + 4% CNF	60	6674±77	3.65±0.11	4.3±0.04