CHEMICAL ENGINEERING TRANSACTIONS

VOL. 73, 2019

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Andrea D'Anna, Paolo Ciambelli, Carmelo Sunseri

ISBN 978-88-95608-70-9; **ISSN** 2283-9216

DOI: 10.3303/CET1973008

Production and Characterization of CNF and LCNF, and Manufacture of LCNF-nanostructured Packaging Papers

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Nanotechnology applied to pulp and paper sector enables production of nanostructured papers with excellent strength properties. The addition of lignocellulose nanofibrils (LCNF) to traditional kraft pulps is an attractive alternative for production of improved packaging papers. In relation to cellulose nanofibrils (CNF), LCNF application in unbleached papers has the advantage of eliminating the costs of bleaching chemicals and potential advantages in drainage. One aim of this study was producing and characterizing LCNF from eucalypt (E) and pine (P) unbleached pulps and comparing the results with the traditional CNF. Another aim of the work was evaluating LCNF as an additive for production of *kraftliner* and *sackraft* nanostructured packaging papers. LCNF proved to be a viable additive for the production of high-strength nanostructured papers while relying on low energy consumption during the refining process. LCNF addition had positive effects on the mechanical properties of the nanostructured papers produced, resulting in significant increases in strength properties.

1. Introduction

The search for sustainability with the purpose of guaranteeing environmental preservation and providing a better quality of the materials developed, encourages investment in renewable resources. Recently, studies on the production and application of cellulose particles at the nanometric scale (nanocelluloses) have been intensified. The use of sustainable raw materials, such as lignocellulosic fibers instead of synthetic fibers, has the advantage of low environmental impact, in addition to generating products of excellent mechanical properties (Abdul Rashid et al., 2018).
The obtention of cellulose nanofibrils and their applications in composites has gained attention because of their unique properties such as high strength, high stiffness, low weight and high aspect ratio (Mariani et al., 2019). Furthermore, nanocelluloses present other advantageous characteristics due to the presence of hydroxyl groups, such as biocompatibility and considerable reactivity (Phanthong et al., 2018).
Most studies with cellulose nanofibrils (CNF) have been carried out with lignin-free cellulosic fibers, notably bleached kraft pulp. However, unbleached fibers containing residual lignin may also be used for the same purpose. In this case, the nanofibrils produced are known to as lignocellulose nanofibrils (LCNF). In addition to the advantages offered by cellulose nanofibrils, LCNF production has the benefits of a large yield, low cost of production, and low environmental impact, as it does not go through the bleaching process (Rojo et al., 2015).
A potential application for these nanocelluloses is in the paper industry, since paper prepared with the addition of nanofibrils may have better mechanical performance. Thus, nanotechnology applied to the pulp and paper mill turns possible the production of nanostructured papers with improved strength properties, by using nanofibrils additives derived from traditional cellulosic pulps produced in-house.
Lignocellulose nanofibrils (LCNF) represent a promising application as additives in the production of packaging papers (Delgado-Aguilar et al., 2016). The research with lignocellulose nanofibrils for the packaging industry is still incipient. Hence, this study focusses on bringing in new insights on the production, characterization an application of LCNF as an additive for production of *kraftliner* and *sackraft* nanostructured packaging papers.

Paper Received: 22 May 2018; Revised: 22 July 2018; Accepted: 04 September 2018

Please cite this article as: Demuner I., Colodette J.L., Gomes F.J., Oliveira R.C.., 2019, Production and Characterization of Cnf and Lcnf, and Manufacture of Lcnf-nanostructured Packaging Papers , Chemical Engineering Transactions, 73, 43-48 DOI:10.3303/CET1973008

2. Experimental

2.1 Nanofibrils production and characterization

The pine and eucalypt chips were submitted to kraft cooking to obtain the pine (kappa number 30) and eucalypt (kappa number 18) pulps and, from these pulps, the lignocelluloses nanofibrils were produced: LCNF-P (From pine pulp) and LCNF-E (From eucalypt pulp). These pulps (pine and eucalypt) were also bleached at 90 % ISO by the OD(EP)DP and OD(EP)D sequences, respectively. From the bleached pulps, the celluloses nanofibrils were produced (CNF-P and CNF-E) as specified by Demuner (2017). The LCNF and CNF were obtained mechanically through the *Super Masscolloider Masuko Sangyo* mill (MKCA6-3; Masuko Sangyo Co., Ltd.). The pulps were milled under the following conditions of: consistency of 2 % dry mass, 1500 rpm, 6 passes through the mill and distance between disks of 0.1 mm. The procedures used for determination of the chemical composition (acid-soluble lignin, acid-insoluble lignin, sugar composition, ash, uronic acid, hexenuronic acid), crystallinity index, maximum degradation temperature and nanofibrils diameter are described in Demuner (2017).

2.2 Production of nanostructured packaging papers

Pine pulps were used to produce nanostructured packaging papers, with a kappa number of 100 for *kraftliner* papers and of 55 for *sackraft* papers. A grammage of 120 g/m^2 and 60 g/m^2 were adopted for the *kraftliner* and *sackraft* papers, respectively. The refining process was carried out in a PFI refiner, model MARK VI of Hamar Norway, following the Tappi T248 sp-08 standard. The LCNF-P or LCNF-E were added to the already refined pulp slurry, in different percentages (0, 1, 3, and 5 %). The drainage resistance (°SR) was performed following ISO 5267-1: 1999 and the analytical procedures for performing physical-mechanical tests are described in Tappi standard procedures. The interpretation of the properties was done using comparison of non-linear regression equations for each parameter, using F test for model identity at 5 % probability.

3. Results and discussion

3.1 Nanofibrils characterization

The chemical composition of the LCNF-P, CNF-P, LCNF-E, and CNF-E samples is presented in Table 1.

Table 1: Chemical composition of nanofibrils samples

Constituents (%)	Total lignin	Uronic acid	Hexenuronic acid	Ash	Glucan	Xylan	Mannan	Galactan	Arabinan
LCNF-P	4.0	0.4	0.6	0.61	80.0	7.3	6.4	0.2	0.6
CNF-P	0.5	0.2	0.1	0.60	83.7	7.3	6.4	0.4	0.7
LCNF-E	1.8	1.2	1.3	0.81	80.6	13.8	0.2	0.2	0
CNF-E	0.2	0.9	0.1	0.73	83.3	14.2	0.3	0.3	0

The total lignin content observed for the LCNF-P and LCNF-E samples were 4.0 and 1.8 %, respectively. This difference is directly related to the residual lignin content present in the unbleached pulps of pine and eucalypt, that were used to produce these lignocellulose nanofibrils. The nanofibrils residual lignin contents are not proportional to their kappa numbers due to the presence of hexenuronic acid (HexA), which is also quantified in the kappa number test. Li and Gellerstedt (1998) propose the correction of the kappa number of the unbleached pulp without the participation of the HexA and, considering this correction, the residual lignin (4.02 % for pine pulp and 1.74 % for eucalypt pulp) came down to values which are expected. Regarding sugar content, it is known that xylan is the main hemicellulose present in hardwoods, while softwoods exhibit mannan as the most important hemicellulose (Huang et al., 2016). However, the pine pulps presented more xylan than mannan, a result explained by the higher resistance of xylans to alkali during kraft cooking.

The crystallinity index, maximum degradation temperature and diameter of nanofibrils are shown in Table 2. The crystallinity index values were similar to those reported by Silva (2015) and Damasio (2015), which observed values of 85.3% for LCNF of hardwood and 79.5% for CNF of softwood, respectively. The high degree of crystallinity is an important feature because it is usually accompanied by greater tensile strength and higher stiffness (Gharehkhani et al., 2015). The maximum degradation temperatures of the LCNF-P and LCNF-E were higher than of CNF-P and CNF-E, indicating greater thermal stability of the lignocelluloses nanofibrils. The higher thermal stability of LCNF can be explained by the presence of lignin in the chemical composition of these samples, a polymer that is thermally more resistant than carbohydrates. The mean diameter of the fibrils were 18.6 nm, 27.5 nm, 23.7 nm and 38.9 nm for samples LCNF-P, CNF-P, LCNF-E e

CNF-E, respectively. According Spence et al. (2010), the defibrillation of samples containing residual lignin produces fibrils with smaller diameter when compared to the CNF, which are produced from bleached fibers.

Table 2: Results of crystallinity index, maximum degradation temperature and diameter of nanofibrils

Parameters	LCNF-P	CNF-P	LCNF-E	CNF-E
Crystallinity index (%)	79.8	81.4	82.2	82.9
Maximum degradation temperature (°C)	365	336	360	330
Diameter (nm)	18.6	27.5	23.7	38.9

3.2 Production of nanostructured packaging paper: *Kraftliner* papers

The effect of the addition of lignocellulose nanofibrils (0, 1, 3 and 5 % on pulp weight) on the physical-mechanical properties of *kraftliner* papers, as a function of the energy consumption in refining process (Wh), are presented in Figure 1 (LCNF-E) and Figure 2 (LCNF-P). *Kraftliner* papers require good resistance against fractures and high compressive strength for their application in cardboard boxes' manufacture.

Drainage resistance (°SR) increased with the addition of LCNF-E (Figure 1A) and LCNF-P (Figure 2A). This increase in drainage resistance is mainly due to the high surface area of the nanofibrils and the high amounts of hydroxyl groups and, in lesser degree, carboxyl groups present on their surface (Delgado-Aguilar et al., 2016).

Interfibrillar connections with the addition of LCNF-E are potentiated in relation to that of LCNF-P since the former has in its chemical composition a higher content of hemicelluloses of the xylan type in relation to the latter (Table 1), resulting in a higher °SR with addition of LCNF-E. The xylans have carboxylic acids groups which increase the amount of negative charges on the nanofibrils, thus increasing the quantity and quality of the hydrogen bonds between them (Winuprasith and Suphantharika, 2013). The low pKa values of the carboxylic acids present in xylans, 3.13 for 4-O-methylglycuronic acid and 3.03 for hexenuronic acids (Teleman et al., 1995), in relation to hydroxyl groups present in the cellulose and hemicelluloses, pKa 13.0-14.0, (Burkinshaw, 2015), greatly favor the hydrogen bonds and water retention by the fibers. In addition, LCNF-P presents higher residual lignin content when compared to LCNF-E, a polymer that exhibits hydrophobic properties and contributes to a lower drainage resistance (Spence et al., 2010).

Industrially, the pulps used for *kraftliner* paper production are refined up to 18°SR. To refine the pulp and reach 18°SR without LCNF addition, 113 Wh of energy is consumed. Upon addition of 5 % of LCNF-E and LCNF-P to the pulp, the energy consumption to reach the same °SR value decreases to 41 and 53 Wh, respectively, due to the effect caused by the addition of these nanofibrils. In this regard, energy savings of 64 % were achieved by adding LCNF-E and 53 % by adding LCNF-P to the pulp. These gains are very significant, especially given the large economic impact of refining process on the total cost of papermaking.

Besides the energy savings, the addition of nanofibrils promoted an increase in the tensile index (Figures 1B and 2B) and in the burst index (Figures 1C and 2C) of *kraftliner* papers. Both indexes are affected mainly by the bonding capacity between the fibers, which justifies the similar trends observed for both indexes. The increase of tensile and burst indexes with LCNF addition is explained by the high surface area of these nanofibrils in contact with the pulp fibers, which reflects in high frequency of intramolecular and intermolecular hydrogen bonds (Kumar et al., 2014). Correlating the tensile and burst indexes of *kraftliner* paper at 18°SR, without LCNF addition and with addition of 5 % of LCNF, an increase of approximately 25 % in the tensile index was observed with the addition of both lignocellulose nanofibrils. In the burst index, an increase of 57 and 42 % was observed with addition of LCNF-E and LCNF-P, respectively.

For the production of *kraftliner* papers it is also important to evaluate the compressive strength and two tests were performed: Ring crush test (Figures 1D and 2D) and corrugated medium test (Figures 1E and 2E). The ring crush test (RCT) is indispensable to evaluate the paper quality for the manufacture of corrugated cardboard sheets, usually used in the manufacture of containerboard packaging. The addition of LCNF-E and LCNF-P increased the property of RCT because nanoparticles have good bonding properties (Kiaei et al., 2016), by providing a quantitative increase of interfiber bonds. This number of bonds, along with fiber wall strength, increase stability under the compression column.

Regarding the effect of the nanofibrils addition on the compressive strength of the corrugated board through the corrugated medium test (CMT), it was observed that the addition of LCNF-E and the LCNF-P improved CMT compared with the non-reinforced pulp (Figures 1E and 2E). Silva (2015) also reported this increment with the addition of 5 % of short fiber LCNF and justified the result considering the increase in the quantity of hydrogen bonds and better formation of the fiber network provided by the introduction of the smaller structures. The CMT was 135.7 N at 18 °SR without LCNF addition. An addition of 5 % of LCNF-E and LCNF-P, increased this index to 196.8 and 191.9 N, respectively, evidencing an increment of 45 and 41 % in the CMT property.

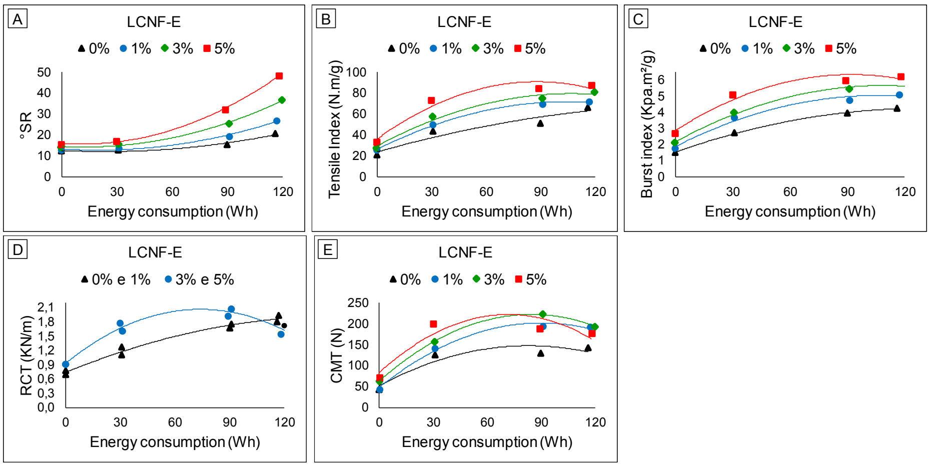

Figure 1 – Properties of kraftliner pulps with addition of LCNF-E, as a function of refining energy consumption: A) Drainage resistance (ºSR); B) Tensile index; C) Burst index; D) Ring crush test; E) Corrugated medium test.

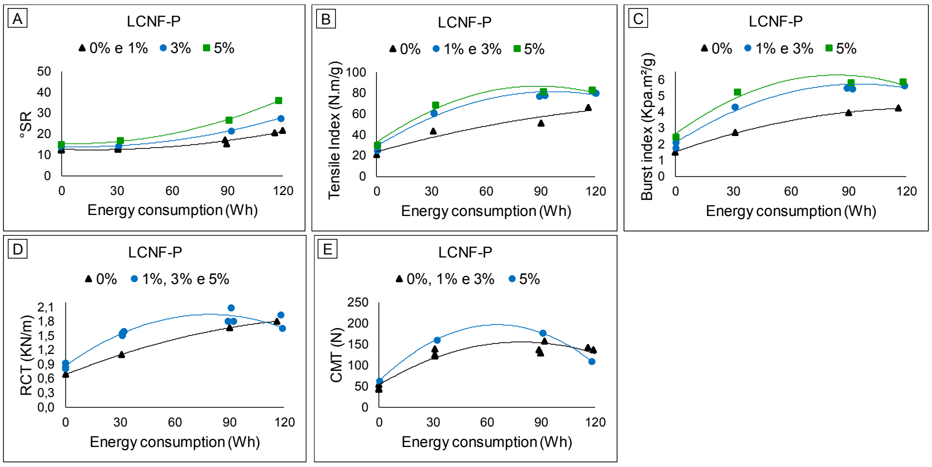

Figure 2 – Properties of kraftliner pulps with addition of LCNF-P, as a function of refining energy consumption: A) Drainage resistance (ºSR); B) Tensile index; C) Burst index; D) Ring crush test; E) Corrugated medium test.

3.3 Production of nanostructured packaging paper: *Sackraft* papers

The effect of addition of lignocellulose nanofibrils (0, 1, 3, and 5 %) on the physical-mechanical properties of *sackraft* papers, as a function of refining energy consumption (Wh), are presented in Figure 3 (LCNF-E) and Figure 4 (LCNF-P). These *sackraft* papers require high tear, burst, and tensile indexes.
An increase in drainage resistance in pulps made with the addition of LCNF-E (Figure 3A) and LCNF-P (Figure 4A) was observed in *sackraft* papers, due to increased hydrogen bonds following the addition of nanofibrils. This was the same trend found for *kraftliner* papers. Industrially, the pulps used for *sackraft* paper manufacture are refined up to 17°SR. To refine the pulp and reach 17 °SR without LCNF addition, 58 Wh of energy was consumed. Adding 5 % of LCNF-E and LCNF-P to the pulp, resulted in a decrease of energy consumption to 10 and 13 Wh to reach the same °SR value, for LCNF-E and LCNF-P, respectively. As a result, energy savings of 82% were achieved by adding LCNF-E and 77 % by adding LCNF-P to the pulp.
An increase in the tensile (Figure 3B and 4B) and burst indexes (Figures 3C and 4C), was observed with the incorporation of the LCNF-E and LCNF-P to the pulp furnish. The combination of a refining process and LCNF addition also provided increase in the tensile and burst indexes of the *sackraft* papers. The refining process, as well as the addition of nanofibrils, enhances the paper interfibrillar bonds due to the hydrogen bonds between the hydroxyl groups of the cellulose chains (Schönberg et al, 2001), conferring improvements in the mechanical properties. Thus, refining is an important operation in the evaluation of the tensile and burst indexes. The energy consumption needed to reach the 17°SR with 5 % addition was unusually low (10 Wh for

LCNF-E and 13 Wh for LCNF-P), when compared to the addition of 0% (58 Wh), and this caused a reduction of tensile and burst indexes for this °SR due to insufficient refining rather than the effect of the nanofibrils. However, improvements in these properties may be achieved with the addition of smaller amounts of LCNF, which results in lower energy savings. Consequentially, since reaching a 17 °SR requires a larger consumption of energy, the combination of the refining process with the addition of LCNF provides an increase in tensile and burst indexes.
An increase of the modulus of elasticity was observed following the addition of LCNF-E (Figure 3D) and LCNF-P (Figure 4D). In the absence of refining, with 5 % addition of nanofibrils, the MOE presented a gain of 17 % with LCNF-E and 28 % with LCNF-P, in relation to 0% addition. There were also significant increases in the MOE values due to nanofibrils addition the pulps that went through refining.

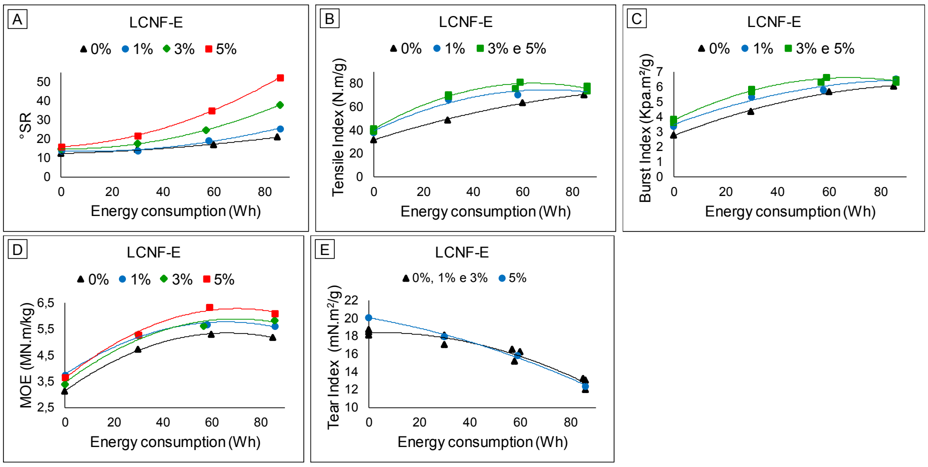

Figure 3 – Properties of sackraft pulps with addition of LCNF-E, as a function of refining energy consumption: A) Drainage resistance (ºSR); B) Tensile index; C) Burst index; D) Modulus of elasticity (MOE); E) Tear index.

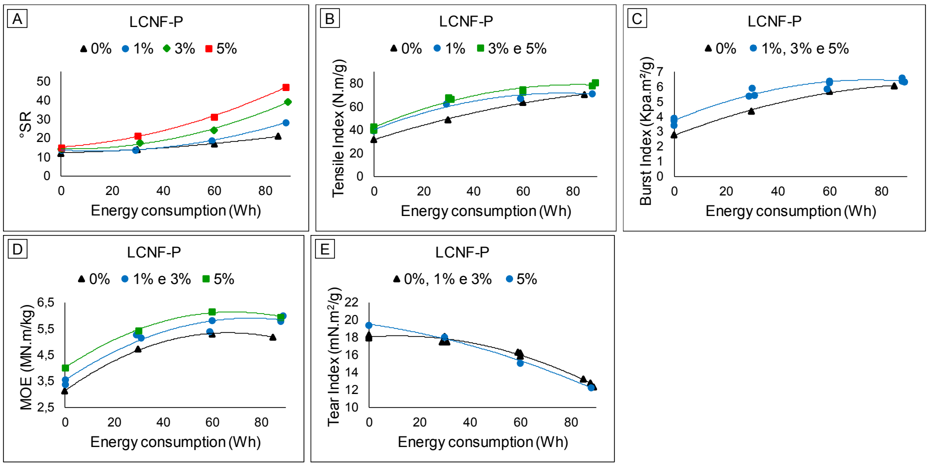

Figure 4 – Properties of sackraft pulps with addition of LCNF-P, as a function of refining energy consumption: A) Drainage resistance (ºSR); B) Tensile index; C) Burst index; D) Modulus of elasticity (MOE); E) Tear index.

Unlike other properties, the tear index presented a significant reduction when high-intensity refining and addition of LCNF-E (Figure 3E) and LCNF-P (Figure 4E) were combined in the production of *sackraft* papers. This occurs due to refining process, which reduces the average length of the fibers. This, in turn reflects on the tear resistance, which is directly related to the length of the fibers. Furthermore, nanofibrils also contribute to reduction in tear index because they have a shorter length than the cellulosic fibers and rupturing this nanofibrils is much easier because of the small diameter (Hassan et al, 2011). However, by evaluating the tear index at 17SR° for *sackraft* papers, since the energy consumption needed to reach the 17 °SR with 5 % addition was very low, a 21 % and 18 % increase in this index was observed with the addition of LCNF-E and LCNF-P, respectively, evidencing that at lower degree of refining the use of nanofibrils favors tear strength.

4. Conclusions

When compared to CNF, the LCNF exhibited a higher lignin content, higher thermal stability and smaller diameter. LCNF-E presented higher content of xylan than LCNF-P. The application of LCNF-E and LCNF-P to produce *kraftliner* and *sackraft* papers resulted in a significant reduction of energy consumption in the refining process and demonstrated positive effects on the mechanical properties of the nanostructured packaging papers produced. There was an energy saving of 64 and 53% on the refining process by adding 5 % LCNF-E and LCNF-P, respectively, in the *kraftliner* paper production (18 °SR), and 82 % and 77 % by adding 5 % LCNF-E and LCNF-P, respectively, in the *sackraft* paper production (17 °SR). Properties such as tensile index and burst index of the papers were substantially increased with the addition of LCNF-E and LCNF-P.

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