Monitoring fibrillation in the mechanical production of lignocellulosic micro/nanofibers from bleached spruce thermomechanical pulp

Ferran Serra-Parareda [1,*], Quim Tarrés [1,2], M. Àngels Pèlach [1], Pere Mutjé [1,2], A. Balea [3], M.C. Monte [3], C. Negro [3], Marc Delgado-Aguilar [1]

1. LEPAMAP Research group, University of Girona, Maria Aurèlia Capmany, 6, 17003 Girona, Spain
2. Chair on Sustainable Industrial Processes, University of Girona, Maria Aurèlia Capmany, 6, 17003 Girona, Spain
3. Department of Chemical Engineering and Materials, University Complutense of Madrid, Avda Complutense s/n, 28040, Madrid, Spain.

[*] Corresponding author: ferran.serrap@udg.edu

Abstract

The present work aims at assessing the main characteristics of lignocellulosic micro/nanofibers (LCMNF) from bleached thermomechanical pulp (BTMP) from spruce while glimpsing the suitability of cationic demand (CD) as effective monitoring parameter of the fibrillation process. For this, BTMP was mechanically refined at different times in a Valley beater, aiming at determining the required refining time and fiber length to be later fibrillated in a high-pressure homogenizer. It was found that 150 min treatment is required to avoid clogging in the pressure chambers of the homogenizer. The mechanically treated BTMP was gradually passed through a high-pressure homogenizer, leading to four LCMNF with different fibrillation degree. The main characteristics of the LCMNF were determined, as well as the effect that high-pressure homogenization may generate onto the LCMNF structure. It was observed that CD is a robust parameter to monitor the fibrillation process, as it is a good indicator of the LCMNF characteristics. In addition, it was found that WRV may not be a good indicator of the extent of fibrillation for LCMNF, as the lignin content varies with the homogenization intensity. Finally, the limitations of CD as monitoring parameter and perspectives on this regard are provided to the reader.

Keywords: Lignocellulosic micro-nanofibers; lignin; Cationic Demand

1 Introduction

Over the past few years, cellulose has gained prominence as a nanostructured material for the development of products with low environmental impact, mainly instigated by the need to reduce the dependence on fossil resources [1–3]. In addition to its sustainable character, cellulose nanofibers (CNF) present high specific surface area and aspect ratio (length/diameter), excellent

mechanical properties, low toxicity, low density and good dimensional stability [4,5]. These properties make CNF a highly attractive material to substitute synthetic materials and to improve the recyclability and biodegradability of products [6].

However, up to date, the production and commercialization of CNF-based products has been limited by several factors [7,8]. A major obstacle to be overcome are the elevated processing costs related to expensive pretreatments involving the use of chemicals and enzymes [9]. For instance, TEMPO catalyst has been reported to be expensive [10] and difficult to recover [11,12]. Besides, chemical pretreatments are also associated with human health effects and environmental issues since they require the employment of toxic reagents [13]. Chemical pretreatments also cause excessive depolymerization of fiber components and contribute to the thermal instability of the fibers, finally dealing with great struggles in both recycling and regeneration processes [14,15]. Besides, the enzymatic pretreatment route is more environmentally friendly than the chemical one, but facing the difficulty in its application owing to the high cost of enzymes and long processing time required for cellulose degradation [16,17].

From a technical viewpoint, the abundance of hydroxyl groups at the CNF's surface highly increases their water uptake and viscosity in aqueous suspensions, which could finally decrease their industrial performance in unit operations like dewatering, pumping and dispersion, among others [18]. Additionally, the development of efficient drying systems allowing their dispersion back into a new solvent avoiding the hornification phenomena is still a challenge nowadays [19].

Such concerns can be avoided or at least mitigated using lignin containing pulps as raw material in substitution to those highly delignified chemical ones [20,21]. So far, the production of lignin containing nanofibers has been based on the use of unbleached chemical pulps with residual lignin content [22–24]. However, high yield pulps with elevated lignin content offer a sustainable low-cost alternative to unbleached chemical pulps. The main advantage of high yield pulping is that it produces much higher yields (> 90 %) than chemical pulping (< 50 %) [25]. These high yield pulps can be produced by means of mechanical defibration methods (mechanical pulp), sometimes combined with elevated temperatures (thermomechanical pulp), and the use of low amounts of chemicals (chemo-thermomechanical pulp) to improve the efficiency of fibers separation. Within these processes, chemo-thermomechanical pulps require the use of chemicals and offer lower yields than mechanical and thermomechanical ones. Besides, thermomechanical pulp fibers offer improved properties in comparison to mechanical pulps, and still retain the high yield and cost effectiveness of mechanical pulps [26]. In this context, spruce wood is widely known to be an interesting resource for thermomechanical pulp production, as they usually present reasonably higher mechanical properties than other softwood pulps. These superior properties, apart from the presumably higher intrinsic properties of spruce fibers compared to the

rest of softwood sources, may come from the low extractives content [27]. The thermomechanical treatment can be followed by a soft bleaching step to increase pulp brightness and remove some surface impurities, leading to a bleached thermomechanical pulp (BTMP).

As mentioned before, thermomechanical pulping offers high processing yields, which means that the chemical composition of the raw material is not significantly affected. Hence, the content of lignin and hemicelluloses is expected to be high in these pulps. It has been reported that lignin and hemicellulose could ease the mechanical fibrillation efficiency of fiber bundles into nanofibers, resulting in a reduction of the energy consumption and better processability [28]. In fact, most delignified pulps are pretreated by means of chemical and enzymatic processes instead of mechanical pretreatment to enable the correct fibrillation of the pulp, whereas the presence of lignin in high yield pulps offer the possibility of replacing those expensive pretreatments by mechanical ones. Amongst possible mechanical pretreatments, the use of the PFI mill and Valley beater has been widely recognized by researchers [29,30]. While PFI mills boost fibers' internal destructuration by replacing the fiber-to-fiber bonds by fiber-to-water bonds, Valley beaters produce larger quantities of fines and are more effective on reducing fibers' length through cutting action. Although in the field of the paper and board such cutting effect has been considered harmful for the paper strength, in the field of nanofibers reducing fibers' length is crucial to enable the correct fibrillation in the homogenizer and reduce the clogging tendency. This idea was supported by Turbak et al., (1983) who claimed that precut fibers at the length range of 600 to 700 µm could ease the fibers destructuring [31]. Hence, the Valley beater route would be a more appropriate choice to pretreat mechanically the fibers prior to homogenization.

Another factor limiting the industrialization of CNF is the lack of fast and robust characterization method to perform an efficient quality control along the production chain. Although progress has been made in this field, there is an absence of process-adapted characterization tools that allow a fast and reliable approach of the suspension quality in a cost-effective way. In addition, the selection of an appropriate process variable is usually difficult. The use of optical methods has been investigated to determine the quality of nanocellulose, though, the observation may not be representative of the whole suspension [32]. In addition, the incorporation of high-resolution microscopy tools in the production chain of nanocellulose can be difficult. Instead, the determination of the nanofibers' quality via a multiparameter analysis has been proposed. Desmaisons et al., (2017) [33] proposed a multi-criteria method that enabled the obtention of a single quantitative grade that allowed the monitorization of the production of nanocellulose. Though, the analysis required the production of nanopapers for the determination of the Young's modulus, generating a critical lag between process and characterization. The WRV has been also proposed to determine the degree of fibrillation, though, still on the way to confirm its validity with high lignin content pulps. Overall, proposing methods to monitor the fibrillation of the

suspensions is required to ease the scale-up production of nanofibers. As a result, in this work the cationic demand (CD) parameter is proposed as a reliable and fast method to monitor the mechanical fibrillation of lignocellulosic micro-nanofibers.

In terms of applicability, nanofibers have been used in sectors such as paper, automotive, paints and coatings, composites, textiles, cement and concrete and pharmaceutical [2,11,34–39]. Nonetheless, the presence of lignin in nanofibers can give rise to the development of novel nanomaterials with chemical, mechanical and physical properties differing from the traditional CNF. The partially hydrophobic character of lignin can give rise to new opportunities in biocomposite materials [40], acting as compatibilizer with hydrophobic matrixes, oil-water stabilization aerogels [41] and medium density fiberboards (MDF) [42]. Lignin can as well act as natural binder in nanopapers, reducing the porosity and providing improved barrier properties [23]. There are also opportunities in the biomedical field as an antioxidant, antidiabetic and antimicrobial material [43,44]. Among these range of applications, the use of nanofibers as strengthening additive in the paper and board sector has been widely recognized. According to a recent report by Future Markets Inc. [45], the paper and board sector currently represents the 74 % of the global demand for cellulose nanofibers with 6,998 tons. The demand of CNF in this sector is far from the second and third most demanded fields, which are the field of composites (12 %) and rheological modifiers (11 %). Furthermore, the use of nanofibers in the paper and board field is expected to increase exponentially in upcoming years, reaching a demand up to 38,643 tons of CNF by the year 2030, which corresponds to an increase by the 452 %. For this reason, along with an increasing market pressure for quality improvements and stricter quality standards, there is a need to instigate the production of nanofibers in this sector making it economically attractive and feasible to implement at large scale.

Overall, the present work aims to produce high lignin content micro-nanofibers using a high yield pulp as raw material and to study the influence of the refining using a Valley beater and homogenization process on the quality of the final suspensions. In addition, the present work also reveals the suitability of cationic demand as robust monitoring parameter of the fibrillation process, while detailing the main limitations and few perspectives on this regard.

2 Experimental

2.1 Materials

Bleached spruce thermomechanical pulp (BTMP) was provided by Norske Skog Saugbrugs (Halden, Norway) and was used for the preparation of lignocellulosic micro-nanofibers. All chemical reagents used for the complete characterization of the micro-nanofibers were supplied by Sigma Aldrich and were used as received.

2.2 Methods

2.2.1 Characterization of the BTMP

The chemical composition of the pulp was evaluated according to TAPPI standard methods. Fibers were dried prior to analysis at 105 ºC for 24h, as required by TAPPI T264. Then, the extractives content was measured by means of ethanol-toluene Soxhlet extraction according to TAPPI T204. Ash and lignin were determined according to TAPPI T211 and TAPPI T22, respectively. The content of cellulose and hemicellulose was determined by high performance anion exchange chromatography (HPAEC). Further details of this methodology were reported by [46].

Pulp drainability was measured according to ISO 5267/1 and expressed as Schopper – Riegler degree (°SR) and as Canadian Standard Freeness (CSF), which was directly converted from °SR to CSF. The morphological analysis was performed using a MorFi Compact Analyzer (TechPap, Grenoble, France) equipped with a CCD video camera. About 30,000 fibers were analyzed by the software MorFi v9.2 and, among other parameters, the mean fiber length (l_w^F), mean fiber diameter (d^F) and fines content measured in length (f_l) were determined. Those fibers shorter than 76 μm were considered as fines by the software. The fines content in weight (f_w) was determined by passing the pulp suspension several times through a 200-mesh filter and recovering the filtrate, which was then oven-dried at 105 °C until constant weight and referred to the initial dry weight of pulp. The specific surface area of the pulp was determined by means of dye Congo Red adsorption methodology. Such methodology will be later specified during the characterization of the micro-nanofibers.

2.2.2 Production of lignocellulosic micro-nanofibers (LCMNF)

BTMP was previously disintegrated in a 50 L-pulper equipped with a helicoidal rotor at the bottom at 5 wt.% consistency. Then, the pulp was diluted until reaching a consistency of 2 wt% and mechanically refined in a Valley beater using the 500 g weight. Residence times for the refining operations were set at 50, 100 and 150 min. The appropriate refining time was chosen depending on the aptitude of the suspension to be properly treated in the high-pressure homogenizer (HPH).

The pretreated suspension was passed through a high-pressure homogenizer (NS1001L PANDA 2000-GEA, GEA NiroSoavi, Italy) by progressively increasing the number of passes and pressure. Finally, a mix of both micro and nano fibers was obtained and referred to as lignocellulosic micro-nanofibers (LCMNF). Samples were separated at different stages of the fibrillation process, leading to LCMNF 1, LCMNF 2, LCMNF 3 and LCMNF 4, as reflected in Table 1.

[TABLE 1 ABOUT HERE]

The reason behind the suspensions were subjected to progressive fibrillation is that a sudden increase of the shearing forces can negatively affect the properties of the nanofibers due to the degradation of the fibrils and, thus, a progressive increase of the pressure would avoid damaging the nanofibers [47].

2.2.3 Characterization of the lignocellulosic micro-nanofibers (LCMNF)

The yield of nanofibrillation was evaluated by centrifuging 0.1 g (dry weight) of LCMNF from a suspension at 1 wt.% consistency. The nanofibrillated fraction contained in the supernatant was isolated from the non-nanofibrillated, which was assumed to be retained in the sediment. The recovered sediment was then oven-dried until constant weight. The yield of nanofibrillation was then calculated according to equation 1.

$$Yield\ of\ nanofibrillation\ (\%) = \left(1 - \frac{m_{ds}}{m_S}\right) \cdot 100 \quad (1)$$

Where m_{ds} and m_S are the mass of dry sediment and initial dry sample, respectively.

The transmittance of the LCMNF suspensions was measured via a UV-Vis Shimadzu spectrophotometer UV-160A set in the range between 400 and 800 nm. Distilled water was used as reference and background.

The morphology of the obtained LCMNF was assessed by means of Field Emission Scanning Electron Microscopy (FE-SEM) using a Hitachi S-3000 microscope (Hitachi Europe S.A., Barcelona, Spain) operating at 12 kV of accelerating voltage.

The carboxyl content (CC), which may not be significatively affected by the refining treatment, was determined by conductimetric titration, as previously reported [48]. Cationic demand (CD) was determined by back titration in a particle charge detector (Mütek PCD 04, BTG), as it has been extensively described in other works [10]. According to the supplier, the molecular weight (Mw) of polyDADMAC accounted for 107 kDa.

The water retention value (WRV) was measured by means of centrifuging the LCMNF suspensions in bottles equipped with a nitrocellulose membrane (0.22 μm of pore size), which can separate the non-bonded water out of the LCMNF suspension. Suspensions were centrifuged for 30 min at 2400 rpm (452 G-force). The wet cake that was formed on the top of the nitrocellulose membrane was then collected, weighted, and dried at 105 °C until constant weight. The WRV was calculated referring the amount of water in the wet cake per dry gram of sample [49].

The degree of polymerization (DP) was determined by means of intrinsic viscosity measurements for dissolved LCMNF in cupri-ethylenediamine according to UNE-ISO 5351 standard. The correlation between intrinsic viscosity and DP was given by the Mark-Howink-Sakurada equation

and values for K and a, constants from the equation that depend on the polymer-solvent system, were set at 2.28 and 0.76, respectively [29].

Specific surface area (SSA) was determined by means of two different methods. On the one hand, it was estimated from the CC and CD, considering the interactions between CNF and the added cationic polymer (polyDADMAC). Details from this method have been previously published by the authors and it has been reported to provide reliable values of, at least, diameters [46,50]. On the other, SSA was calculated by means of Congo red adsorption isotherms, as described elsewhere [51].

Changes on the lignin content and crystallinity of the LCMNF were assessed by means of Klason lignin method and X-ray diffraction (XRD), respectively. For this, the suspensions were vacuum filtered in a modified sheet former equipped with a 0.22 μm nitrocellulose membrane and then dried for 20 min to remove water. Klason lignin of the LCMNF was measured on grinded and dried samples according to TAPPI T22 om-98. The crystallinity index (C.I.) was calculated from an XRD profile on the small pieces of the substrates. The C.I. was obtained from the height ratio between the intensity of the crystalline peak ($I_c - I_{am}$) and total intensity (I_c), as reported by Segal et al., (1959) (equation 2) [52].

$$C.I.(\%) = \frac{I_c - I_{am}}{I_c} \cdot 100 \quad (2)$$

3 Results and Discussion

3.1 Characterization of the BTMP

Aiming at glimpsing the effect of the thermomechanical and soft bleaching process, the chemical composition of the bleached thermomechanical pulp (BTMP) was determined and compared to an unbleached [53] and bleached [54] kraft spruce pulp (UKSP and BKSP, respectively), as reflected in Table 2.

[TABLE 2 ABOUT HERE]

BTMP exhibited a content of acid insoluble lignin, also known as Klason lignin, a hemicellulose content and a cellulose content of 25.80, 25.40 and 48.35 wt%, respectively. The content of non-structural elements such as extractives and ashes were relatively low for a thermomechanical pulp with values of 0.25 and 0.20 wt%, respectively. Wang et al., (2018) [55] reported a chemical composition for spruce wood (*Picea abies*) of 42.0 wt.% of cellulose, 20.6 wt.% of hemicellulose, 28.2 wt.% of Klason lignin, 6.5 wt.% of acid-soluble lignin, and 1.04 wt.% of extractives. Out of these values, one can see that the pulping and bleaching process removed the extractives by more than half from 1.04 to 0.25 wt.%. Besides, the lignin content experienced a smooth decrease from

28.2 to 25.8 wt.%, mainly due to the impact of the bleaching process. As a result, the relative content of cellulose and hemicellulose increased with respect to the raw wood from 62.6 to 73.75 wt.%. Overall, this indicates that BTMP, although having been submitted to a bleaching step, still presented a relatively high content of lignin and that the whole treatment did not significantly affect the major chemical constituents of wood.

Table 2 also shows the chemical composition of UKSP and BKSP for comparison purposes. It becomes apparent that the kraft process significantly decreases the lignin content, accounting for 2.23 wt% in the case of the pulp reported by Tutus et al. (2010). In addition, when such pulp is submitted to a bleaching stage (BKSP), the resulting pulp exhibited a lignin content below 0.1 wt.%. The degradation of lignin by the kraft and bleaching processes may inevitably lead to the removal of other constituents embedded in the amorphous region of the fibers, mainly hemicellulose and some extractives. The content of hemicellulose in both UKSP and BKSP decreased by less than half in comparison to the BTMP. Finally, the cellulose content increased to values around 90 wt.%.

As reported by Jonoobi et al., (2014) [56] the chemical composition of the pulp has a major influence during pulp fibrillation. Specifically, other authors pointed out that lignin has a significant role inhibiting the formation of fibril bundles, which may be beneficial for the fibrillation process [51]. Besides, the hemicellulose content has been also reported to be crucial to avoid the aggregation of the microfibrils and re-agglomeration of the nanofibrillated parts [20]. Chaker et al., (2013) [57] exposed that hemicellulose content around 25 wt.% in pulps is optimum to reach the maximum fibrillation efficiency, whereas in pulps exhibiting a hemicellulose content close to 12 wt.% may decrease such efficiency by half. Generally, most chemical pulps, either bleached or unbleached, used to produce cellulose nanofibers exhibit a lower hemicellulose content than the BTMP proposed in the present study [58]. In addition, as there is still a lack of understanding on the role of extractives during pulp fibrillation, it is accepted that this fraction should be reduced to a certain extent to enable its proper fibrillation [59]. Thus, at least in terms of chemical composition, BTMP may be a suitable raw material for LCMNF production, as it will presumably be easy to fibrillate.

Although chemical composition has a key role on the fibrillation process, both morphological and physical properties also may be affected during such process. Thus, the main morphological parameters are summarized in Table 3.

[TABLE 3 ABOUT HERE]

BTMP exhibited a mean fiber length and diameter of 1,178 and 29.8 μm, respectively. Both length and diameter are significantly higher than in the case of other pulps used for LCMNF production that may be found in the literature. Indeed, the selected pulp exhibited a higher length to other

pulps such as chemical pulps from wheat, vine stems and bleached eucalyptus, but shorter than *pinus radiata* [60–62]. The obtained diameter was significantly higher than in the case of hardwoods, but of the same order of magnitude than softwoods [63]. The morphological analysis also returned an elevated content of fines, which partially explains the high SSA (2.87 m^2/g). However, such high surface area may be also explained by the aggressive treatment during pulping, where lignin and other constituents are not dissolved and, thus, the mechanical energy randomly breaks the wood structure increasing the surface fibrillation.

3.2 Effect of the refining in a Valley beater on the BTMP characteristics

Aiming to increase fibrillation, BTMP was subjected to mechanical refining in a Valley beater prior homogenization, as described in the previous section. The morphology, the DP and the CD of the refined pulps were determined, as well as their aptitude to high-pressure homogenization (Table 4).

[TABLE 4 ABOUT HERE]

After 50, 100 and 150 min treatment, fiber length (l_w^F) decreased to 1,064, 790 and 682 µm, respectively, representing a reduction of 42 % at 150 min. In fact, fiber length decreased linearly with the pretreatment time with a correlation factor of $R^2 = 0.967$. These results are consistent with those reported by Turbak et al., (1983) [31], where the need of reducing fiber length to a range between 600 and 700 µm can enhance pulp fibrillation during high-pressure homogenization. The decrease on the fiber length was also observed in the DP, which decreased from 3,250 to 2,540 after 150 min treatment. On the contrary, the diameter of the BTMP fibers was not significantly affected, indicating that fiber bundles were not successfully separated, which is something expectable from such kind of mechanical treatments.

The mechanical refining also increased the fines content, both in length and in weight. After 150 min treatment, the amount of fines in length accounted for 79.5 %, while the mass fraction of fines was 40.6 %. The morphological analysis, conducted by the MorFi equipment, does not consider the morphology of fines, thus, the average fiber length and diameter is not considering fines length and diameter. The presence of such fines may be beneficial for the fibrillation process during high-pressure homogenization. Indeed, the 150 min-treated pulp did not exhibit any clogging during fibrillation, contrarily to lower processing times. The changes on fiber morphology, together with the generation of fines, also had a significant effect over the SSA and the CD. SSA increased from 2.87 to 16.01 m^2/g and CD, from 56.3 to 137.6 µeq/g. In previous works, authors already reported that CD can be a good indicator of the SSA [46,64]. In the case of BTMP, this correlation was confirmed, as reflected in Fig. 1.

[FIGURE 1 ABOUT HERE]

For all the above, the treatment time in the Valley beater was set at 150 min, considering that no clogging was observed during high-pressure homogenization and that both SSA and CD, and the morphological characteristics were, in principle, significantly better for LCMNF production than the rest of treated pulps at shorter periods.

3.3 Production and characterization of the LCMNF

The selected pulp was passed through the high-pressure homogenizer at different numbers of passes and pressure, according to the conditions specified in the previous section. Table 5 shows the yield of nanofibrillation, transmittance at 600 nm wavelength (T_{600nm}), WRV, CD and SSA of the different LCMNF. SSA was obtained by means of Congo red (SSA_{CR}) and polyDADMAC adsorption (SSA_{p+}).

[TABLE 5 ABOUT HERE]

As expected, yield of nanofibrillation increased with the number of passes and pressure through the high-pressure homogenizer. LCMNF 1 and LCMNF 2 exhibited a low yield of nanofibrillation, accounting for 4.6 and 11.9 %. These low yields indicate that only a small fraction of nanosized fibers can be obtained by means of passing the suspension through the high-pressure homogenizer at low-moderate pressure (300 – 600 bar). Once the suspension was passed through the pressure chambers at 900 bar, the yield of nanofibrillation increased to 24.1% (LCMNF 3) and, conducting the operation at 900 bar three additional times, this yield was just increased to 28.6 % (LCMNF 4). Indeed, such low yields compared to other suspensions of nanofibrillated cellulose are completely understandable, as neither negatively charged groups are introduced in the cellulose chain (i.e. TEMPO-mediated oxidation) nor specific mechanisms based on enzyme action are occurring (i.e. enzymatic hydrolysis) [65].

It is clear that the raw material also has a direct influence on the yield of nanofibrillation. Indeed, in previous works, lignocellulosic micro/nanofibers obtained from chemical pulps usually lead to higher nanofibrillation yields, such is the case of wheat or alkali-treated mechanical pine pulp, and of the same magnitude than other mechanical pulps such as banana leaf residue or *triticale* straw [46,50,66,67].

The differences in the yield of nanofibrillation were also observed in the transmittance of the suspensions at 600 nm. Transmittance is often used as an indirect indicator of the nanofibrillation yield, as the higher presence of nanosized fibers in the suspension minimizes light scattering [68]. Table 5 reveals that as the intensity in the high-pressure homogenizer was increased, transmittance also experienced an increase. However, the obtained values are far from those that may offer purely nanostructured cellulose, mainly due to a combined phenomenon of low

fibrillation degree and the presence of lignin. Thus, it becomes apparent that the obtained LCMNF suspensions contained both nano- and microsized fibrils, as it can be observed in Fig. 2.

[FIGURE 2 ABOUT HERE]

Fig. 2 evidences the presence of both micro and nano fibers in the suspensions. Fig. 2A shows a microfiber with an approximate diameter of 1 mm, whereas nanofibrils at their surface with diameters in the range of 56.2 to 78.9 nm can be clearly seen. Fig. 2B exhibits a similar scenario, though, as the suspensions has been more intensively fibrillated, the diameter of the nanofibers decreased to a range of 21 to 40 nm. The mix of micro and nanofibers also support the low yield and transmittance values.

As expected, the SSA also increased with the successive passes through the homogenizer. However, the differences between the SSA obtained by means of Congo Red adsorption and the one obtained through the polyDADMAC adsorption are worthy to mention. SSA_{CR} exhibited values in the range of 117.8 (LCMNF 1) and 150.3 m^2/g (LCMNF 4). On the other hand, the SSA_{p+} values were limited from 64.7 (LCMNF 1) to 94.4 m^2/g (LCMNF 4). Several methods have been already reported to determine the SSA of micro and nanostructured cellulose, and all of them are based in different mechanisms. Nonetheless, all the methodologies that can be found in the literature are based on indirect methods, as the estimation of SSA from length and diameter can be misleading due to the presence of surface fibrillation and irregular morphology [50,51,69]. Depending on the method, especially in those involving adsorption mechanisms, the order of magnitude of the SSA can significantly differ, as it is the case of SSA_{CR} and SSA_{p+}. Congo Red molecule has a surface area of 1.73 nm^2/molecule, while in the case of polyDADMAC, surface area accounts for 535.87 nm^2/molecule. The lower surface area of Congo Red may propitiate its penetration into the LCMNF structure, apart from its diffusion onto fibers surface as dimers, providing a higher value during the measurement of SSA [70,71]. In addition, the molecular weight (Mw) of polyDADMAC may also have an effect on the determination of SSA, as it has been previously reported. Briefly, low-Mw polyDADMAC (7.5 – 15 kDa) may result in high detected charge due to polymer penetration into the fiber structure, obtaining the fiber total charge. On the other hand, high-Mw poly-DADMAC (> 100 kDa) leads to lower detected charge, as it is only adsorbed on fiber surface [72].

As in the case of the mechanically refined pulps, as the SSA of LCMNF increased, a noticeable enhancement of the CD was also observed. The CD increased from 179 to 240 μeq/g for LCMNF 1 and LCMNF 4, respectively. Indeed, the increase on the CD evolved linearly with the SSA as in the case of mechanically refined BTMP. This linear evolution can be observed in Fig. 3A.

[FIGURE 3 ABOUT HERE]

WRV also experienced a great enhancement as the mechanically refined BTMP was gradually passed through the high-pressure homogenizer. This increase on the WRV mainly comes from the increase on the SSA and, thus, the extent of fibrillation. However, other effects may be occurring during high-pressure homogenization, such as lignin release from the microfibrils due to the high shear forces [73]. The WRV increased from 1.5 to 3.1 g/g , corresponding to the LCMNF 1 and LCMNF 4, respectively. Several authors have reported the excellent capacity of nanostructured cellulose to bond water, even to form water-based gels at low solid content. The obtained WRV is lower than values reported in the literature, mainly due to a combined effect between the relatively high lignin content and the lower fibrillation degree [49]. The evolution of the WRV with the CD did not respond to a linear regression, as reflected in Fig. 3B. In principle, considering that WRV has been reported to be a reliable measure to characterize the extent of fibrillation of micro and nanofibrils and, in addition, that SSA evolved linearly with CD, one may expect a linear tendency between WRV and CD [74]. Nonetheless, the evolution of WRV responded to a second order polynomial equation, indicating that an additional effect to the enhancement of the fibrillation was occurring. This was corroborated in Figure 3C, where the evolution of WRV as SSA increased is reflected. This additional effect may be a slight increase of the hydrophilicity of the LCMNF as they were passed through the high-pressure homogenizer. Jonoobi et al., (2015) [75] reported that successive passes through the homogenizer could promote the removal of amorphous regions and, thus, increase the crystallinity of the lignocellulosic suspension. In addition, as mentioned above, Qua et al., (2011) [73] already noticed lignin release from the LCMNF suspension due to the shear forces inside the pressure chambers of the equipment. Another plausible explanation is the decomposition of lignin-derived compounds during the high-pressure homogenization process forming low-Mw and water-soluble compounds [76]. Overall, the chemical composition of LCMNF may experience some changes during the high-pressure homogenization process, either due to the release of surface lignin, decomposition of lignin-derived compounds or even the removal of amorphous regions, including hemicellulose.

Aiming at glimpsing the effect of high-pressure homogenization in the chemical structure of LCMNF, the DP, Klason lignin and the crystallinity index was determined for each LCMNF. (Table 6). XRD curves for the determination of the crystallinity index are shown in Fig. 4.

[TABLE 6 ABOUT HERE]

[FIGURE 4 ABOUT HERE]

The determination of Klason lignin revealed that, as previously discussed, there was some lignin removal during high-pressure homogenization. Indeed, a decrease of about 3 wt.% in the lignin content of the LCMNF was observed (comparing LCMNF 1 and LCMNF 4), together with a great reduction of the DP and a slight increase of the crystallinity index. The highest reduction in the

lignin content was observed the first time that suspensions were processed at 900 bar, where shearing was significantly more intensive than at lower processing pressures. This decrease on the lignin content was also observed in the increase on the crystallinity index, where the highest change was also observed when suspensions were processed at the maximum pressure for the first time. This higher crystallinity, thus, can be attributed to the loss of lignin during high-pressure homogenization. The increase on crystallinity may decrease the hydrophilicity of the LCMNF and one could lower WRV. However, the obtained results clearly show that the removal of lignin had a greater effect on WRV than the increase of crystallinity.

As observed before, the CD is highly associated with the nanofibrillation yield and SSA. In addition, the difference between the CD and CC can be used to quantify the number of hydroxyls available at the fiber surface. Such value can be related to the hydrogen bonding ability and thus to the strengthening potential of the nanofibers. The CD can also be useful to attempt different chemical modifications on the nanofibers, including esterification, etherification, oxidation, silylation, polymer grafting, and others, for various end uses [77]. From the obtained results, CD may be used as monitoring parameter for the fibrillation process of LCMNF, though, it presents some limitations that should be considered.

3.4 Limitations of cationic demand as monitoring parameter of fibrillation and perspectives

CD is strongly affected by the surface charge, which may be induced by the introduction of functional groups into cellulose structure. A clear example is the TEMPO-mediated oxidation process, where highly negatively charged groups (COO^-) are introduced by means of the oxidation of the primary alcohol in the C6 of the cellulose chain [11]. Another example could be those cellulose nanofibers obtained by means of cationization processes, which are based on the introduction of quaternary ammonium groups [78,79]. In addition to this, the chemical composition of the starting material may also affect the CD of the micro and nanofibers. Thus, the use of CD as monitoring parameter is restricted to processes where the rest of the conditions are controlled, and the different correlations may apply to such conditions. To the best of our knowledge, the monitoring of the production processes of micro and nanofibers must encompass the combination of different parameters integrated in robust models that allow real-time characterization, which is something that still needs further research, to diminish the uncertainty during production processes. To the authors, such integrative and robust models should integrate variables from the raw material, the pretreatment stage and the fibrillation itself, something that is still missing and that would promote the full deployment of micro and nanocellulose production at large scale.

4 Conclusions

In this work, LCMNF were prepared by means of mechanical methods, combining mechanical refining and high-pressure homogenization. It was found that fiber length plays a critical role on the aptitude of the fibers to be processed by means of high-pressure homogenization, requiring a treatment in the Valley beater of 150 min in order to shorten the fibers from 1,178 to 682 μm, apart from increasing the fines content. From the study at different homogenization intensities, it can be concluded that the high shearing inside the pressure chambers have a positive effect on nanofibrillation, especially at operating pressures above 900 bar, where significant effect can be observed in the different parameters, including nanofibrillation yield, specific surface area, cationic demand and water retention value, among others. It was found that the high-pressure homogenization processes affect the lignin content of the fibers and their crystallinity, as the Klason lignin content decreased from 24.3 to 21.0 wt.% and the crystallinity increased from 70.6 to 75.7%. This was found to have a significant effect over the water retention value of the LCMNF and limiting the use of this parameter to monitor the extent of fibrillation of the samples. Contrarily, it was found that cationic demand is a good indicator of the fibrillation of the LCMNF, as the rest of the parameters evolved linearly at increasing cationic demands. Overall, it can be concluded that high yield pulps can be useful for LCMNF if they are properly treated and, in addition, that cationic demand is a suitable parameter to monitor the fibrillation process, especially in nanostructured cellulose which has not been obtained by means of chemical methods.

Acknowledgements

Authors wish to acknowledge the financial support of the Spanish Economy and Competitiveness Ministry to the Project NANOPROSOST, Reference CTQ2017-85654.

References

[1] A. Isogai, Emerging Nanocellulose Technologies: Recent Developments, Adv. Mater. (2020) 2000630. https://doi.org/10.1002/adma.202000630.

[2] T. Lindström, C. Aulin, A. Naderi, M. Ankerfors, Microfibrillated Cellulose, in: Encycl. Polym. Sci. Technol., John Wiley & Sons, Inc., Hoboken, NJ, USA, 2014: pp. 1–34. https://doi.org/10.1002/0471440264.pst614.

[3] I. Siró, D. Plackett, Microfibrillated cellulose and new nanocomposite materials: A review, Cellulose. 17 (2010) 459–494. https://doi.org/10.1007/s10570-010-9405-y.

[4] J.H. Kim, B.S. Shim, H.S. Kim, Y.J. Lee, S.K. Min, D. Jang, Z. Abas, J. Kim, Review of nanocellulose for sustainable future materials, Int. J. Precis. Eng. Manuf. - Green Technol. 2 (2015) 197–213. https://doi.org/10.1007/s40684-015-0024-9.

[5] C. Ruiz-Palomero, M.L. Soriano, M. Valcárcel, Nanocellulose as analyte and analytical

tool: Opportunities and challenges, TrAC - Trends Anal. Chem. 87 (2017) 1–18. https://doi.org/10.1016/j.trac.2016.11.007.

[6] K. Kępa, C.M. Chaléat, N. Amiralian, W. Batchelor, L. Grøndahl, D.J. Martin, Evaluation of properties and specific energy consumption of spinifex-derived lignocellulose fibers produced using different mechanical processes, Cellulose. 26 (2019) 6555–6569. https://doi.org/10.1007/s10570-019-02567-x.

[7] M. Jawaid, S. Boufi, A. Khalil, Cellulose-reinforced nanofibre composites : production, properties and applications, 2017.

[8] J. Miller, Nanocellulose: Market perspectives, Tappi J. 18 (2019) 313–316.

[9] M. Delgado-Aguilar, I. González, Q. Tarres, M. Alcalà, M.A. Pelach, P. Mutje, Approaching a Low-Cost Production of Cellulose Nanofibers for Papermaking Applications, BioResources. 10 (2015) 5345–5355.

[10] A. Serra, I. González, H. Oliver-Ortega, Q. Tarrès, M. Delgado-Aguilar, P. Mutjé, Reducing the Amount of Catalyst in TEMPO-Oxidized Cellulose Nanofibers: Effect on Properties and Cost, Polymers (Basel). 9 (2017) 557. https://doi.org/10.3390/polym9110557.

[11] A. Isogai, T. Saito, H. Fukuzumi, TEMPO-oxidized cellulose nanofibers, Nanoscale. 3 (2011) 71–85. https://doi.org/10.1039/c0nr00583e.

[12] T. Saito, S. Kimura, Y. Nishiyama, A. Isogai, Cellulose Nanofibers Prepared by TEMPO-Mediated Oxidation of Native Cellulose, Biomacromolecules. 8 (2007) 2485–2491. https://doi.org/10.1021/bm0703970.

[13] R. Singla, A. Guliani, A. Kumari, S.K. Yadav, Nanocellulose and nanocomposites, in: Nanoscale Mater. Target. Drug Deliv. Theragnosis Tissue Regen., Springer Singapore, 2016: pp. 103–125. https://doi.org/10.1007/978-981-10-0818-4_5.

[14] C.I.K. Diop, M. Tajvidi, M.A. Bilodeau, D.W. Bousfield, J.F. Hunt, Isolation of lignocellulose nanofibrils (LCNF) and application as adhesive replacement in wood composites: example of fiberboard, Cellulose. 24 (2017) 3037–3050. https://doi.org/10.1007/s10570-017-1320-z.

[15] L. Kuutti, H. Pajari, S. Rovio, J. Kokkonen, M. Nuopponen, Chemical recovery in TEMPO oxidation, BioResources. 11 (2016) 6050–6061.

[16] M. Pedersen, A.S. Meyer, Lignocellulose pretreatment severity - relating pH to biomatrix opening, N. Biotechnol. 27 (2010) 739–750. https://doi.org/10.1016/j.nbt.2010.05.003.

[17] R.S.A. Ribeiro, B.C. Pohlmann, V. Calado, N. Bojorge, N. Pereira, Production of nanocellulose by enzymatic hydrolysis: Trends and challenges, Eng. Life Sci. 19 (2019) 279–291. https://doi.org/10.1002/elsc.201800158.

[18] A. Balea, E. Fuente, M.C. Monte, N. Merayo, C. Campano, C. Negro, A. Blanco,

Industrial Application of Nanocelluloses in Papermaking: A Review of Challenges, Technical Solutions, and Market Perspectives, Molecules. 25 (2020) 526. https://doi.org/10.3390/molecules25030526.

[19] R.H. Newman, Carbon-13 NMR evidence for cocrystallization of cellulose as a mechanism for hornification of bleached kraft pulp, Cellulose. 11 (2004) 45–52. https://doi.org/10.1023/B:CELL.0000014768.28924.0c.

[20] K.L. Spence, R.A. Venditti, O.J. Rojas, Y. Habibi, J.J. Pawlak, The effect of chemical composition on microfibrillar cellulose films from wood pulps: Water interactions and physical properties for packaging applications, Cellulose. 17 (2010) 835–848. https://doi.org/10.1007/s10570-010-9424-8.

[21] M. Visanko, J.A. Sirviö, P. Piltonen, R. Sliz, H. Liimatainen, M. Illikainen, Mechanical fabrication of high-strength and redispersible wood nanofibers from unbleached groundwood pulp, Cellulose. 24 (2017) 4173–4187. https://doi.org/10.1007/s10570-017-1406-7.

[22] M. El Bakkari, V. Bindiganavile, J. Goncalves, Y. Boluk, Preparation of cellulose nanofibers by TEMPO-oxidation of bleached chemi-thermomechanical pulp for cement applications, Carbohydr. Polym. 203 (2019) 238–245. https://doi.org/10.1016/j.carbpol.2018.09.036.

[23] E. Rojo, M.S. Peresin, W.W. Sampson, I.C. Hoeger, J. Vartiainen, J. Laine, O.J. Rojas, Comprehensive elucidation of the effect of residual lignin on the physical, barrier, mechanical and surface properties of nanocellulose films, Green Chem. 17 (2015) 1853–1866. https://doi.org/10.1039/c4gc02398f.

[24] M. Sánchez-Gutiérrez, E. Espinosa, I. Bascón-Villegas, F. Pérez-Rodríguez, E. Carrasco, A. Rodríguez, Production of Cellulose Nanofibers from Olive Tree Harvest—A Residue with Wide Applications, Agronomy. 10 (2020) 696. https://doi.org/10.3390/agronomy10050696.

[25] S.H. Osong, Mechanical Pulp Based Nano-ligno-cellulose Production, Characterization and their Effect on Paper Properties, (2014) 57.

[26] Y. Wen, Z. Yuan, X. Liu, J. Qu, S. Yang, A. Wang, C. Wang, B. Wei, J. Xu, Y. Ni, Preparation and Characterization of Lignin-Containing Cellulose Nanofibril from Poplar High-Yield Pulp via TEMPO-Mediated Oxidation and Homogenization, ACS Sustain. Chem. Eng. 7 (2019) 6131–6139. https://doi.org/10.1021/acssuschemeng.8b06355.

[27] B. Li, H. Li, Q. Zha, R. Bandekar, A. Alsaggaf, Y. Ni, Review: Effects of wood quality and refining process on TMP pulp and paper quality, BioResources. 6 (2011) 3569–3584.

[28] S.H. Osong, S. Norgren, P. Engstrand, Paper strength improvement by inclusion of nano-ligno-cellulose to Chemi-thermomechanical pulp, Nord. Pulp Pap. Res. J. 29

(2014) 309–316. https://doi.org/10.3183/npprj-2014-29-02-p309-316.
[29] M. Henriksson, G. Henriksson, L.A. Berglund, T. Lindström, T. Lindstrom, T. Lindstro, An environmentally friendly method for enzyme-assisted preparation of microfibrillated cellulose (MFC) nanofibers, Eur. Polym. J. 43 (2007) 3434–3441.
[30] K.L. Spence, R.A. Venditti, O.J. Rojas, Y. Habibi, J.J. Pawlak, A comparative study of energy consumption and physical properties of microfibrillated cellulose produced by different processing methods, Cellulose. 18 (2011) 1097–1111. https://doi.org/10.1007/s10570-011-9533-z.
[31] A.F. Turbak, F.W. Snyder, K.R. Sandberg, Microfibrillated cellulose, a new cellulose product: properties, uses, and commercial potential, J. Appl. Polym. Sci. 37 (1983).
[32] E. Espinosa, F. Rol, J. Bras, A. Rodríguez, Use of multi-factorial analysis to determine the quality of cellulose nanofibers: effect of nanofibrillation treatment and residual lignin content, Cellulose. (2020) 1–17. https://doi.org/10.1007/s10570-020-03136-3.
[33] J. Desmaisons, E. Boutonnet, M. Rueff, A. Dufresne, J. Bras, A new quality index for benchmarking of different cellulose nanofibrils, Carbohydr. Polym. 174 (2017) 318–329. https://doi.org/10.1016/j.carbpol.2017.06.032.
[34] A. Balea, J.L. Sanchez-Salvador, M.C. Monte, N. Merayo, C. Negro, A. Blanco, In situ production and application of cellulose nanofibers to improve recycled paper production, Molecules. 24 (2019). https://doi.org/10.3390/molecules24091800.
[35] L.A. Berglund, T. Peijs, Cellulose Biocomposites—From Bulk Moldings to Nanostructured Systems, MRS Bull. 35 (2010) 201–207. https://doi.org/10.1557/mrs2010.652.
[36] A. Dufresne, Cellulose nanomaterials as green nanoreinforcements for polymer nanocomposites, Philos. Trans. R. Soc. A Math. Phys. Eng. Sci. 376 (2018). https://doi.org/10.1098/rsta.2017.0040.
[37] D. Klemm, F. Kramer, S. Moritz, T. Lindström, M. Ankerfors, D. Gray, A. Dorris, Nanocelluloses: A New Family of Nature-Based Materials, Angew. Chemie Int. Ed. 50 (2011) 5438–5466. https://doi.org/10.1002/anie.201001273.
[38] R.J. Moon, A. Martini, J. Nairn, J. Simonsen, J. Youngblood, Cellulose nanomaterials review: Structure, properties and nanocomposites, Chem. Soc. Rev. 40 (2011) 3941–3994. https://doi.org/10.1039/c0cs00108b.
[39] Y. Nishiyama, Structure and properties of the cellulose microfibril, J. Wood Sci. 55 (2009) 241–249. https://doi.org/10.1007/s10086-009-1029-1.
[40] A. Winter, L. Andorfer, S. Herzele, T. Zimmermann, B. Saake, M. Edler, T. Griesser, J. Konnerth, W. Gindl-Altmutter, Reduced polarity and improved dispersion of microfibrillated cellulose in poly(lactic-acid) provided by residual lignin and hemicellulose, J. Mater. Sci. 52 (2017) 60–72. https://doi.org/10.1007/s10853-016-0439-

x.

[41] J. Ojala, J.A. Sirviö, H. Liimatainen, Nanoparticle emulsifiers based on bifunctionalized cellulose nanocrystals as marine diesel oil-water emulsion stabilizers, Chem. Eng. J. 288 (2016) 312–320. https://doi.org/10.1016/j.cej.2015.10.113.

[42] D. Theng, G. Arbat, M. Delgado-Aguilar, F. Vilaseca, B. Ngo, P. Mutjé, All-lignocellulosic fiberboard from corn biomass and cellulose nanofibers, Ind. Crops Prod. 76 (2015) 166–173. https://doi.org/10.1016/j.indcrop.2015.06.046.

[43] D. Kai, W. Ren, L. Tian, P.L. Chee, Y. Liu, S. Ramakrishna, X.J. Loh, Engineering Poly(lactide)–Lignin Nanofibers with Antioxidant Activity for Biomedical Application, ACS Sustain. Chem. Eng. 4 (2016) 5268–5276. https://doi.org/10.1021/acssuschemeng.6b00478.

[44] F. Reesi, M. Minaiyan, A. Taheri, A novel lignin-based nanofibrous dressing containing arginine for wound-healing applications, Drug Deliv. Transl. Res. 8 (2018) 111–122. https://doi.org/10.1007/s13346-017-0441-0.

[45] Future Markets Inc., The global market for cellulose nanofibers, 2020. www.futuremarketsinc.com.

[46] Q. Tarrés, N.V. Ehman, M.E. Vallejos, M.C. Area, M. Delgado-Aguilar, P. Mutjé, Lignocellulosic nanofibers from triticale straw: The influence of hemicelluloses and lignin in their production and properties, Carbohydr. Polym. 163 (2017) 20–27. https://doi.org/10.1016/j.carbpol.2017.01.017.

[47] A. Naderi, T. Lindström, J. Sundström, Repeated homogenization, a route for decreasing the energy consumption in the manufacturing process of carboxymethylated nanofibrillated cellulose?, Cellulose. 22 (2015) 1147–1157. https://doi.org/10.1007/s10570-015-0576-4.

[48] D. da Silva Perez, S. Montanari, M.R. Vignon, TEMPO-mediated oxidation of cellulose III, Biomacromolecules. 4 (2003) 1417–1425. https://doi.org/10.1021/bm034144s.

[49] J. Patiño-Masó, F. Serra-Parareda, Q. Tarrés, P. Mutjé, F.X. Espinach, M. Delgado-Aguilar, TEMPO-Oxidized Cellulose Nanofibers: A Potential Bio-Based Superabsorbent for Diaper Production, Nanomaterials. 9 (2019) 1271. https://doi.org/10.3390/nano9091271.

[50] E. Espinosa, Q. Tarrés, M. Delgado-Aguilar, I. González, P. Mutjé, A. Rodríguez, Suitability of wheat straw semichemical pulp for the fabrication of lignocellulosic nanofibres and their application to papermaking slurries, Cellulose. 23 (2016) 837–852. https://doi.org/10.1007/s10570-015-0807-8.

[51] A. Ferrer, E. Quintana, I. Filpponen, I. Solala, T. Vidal, A. Rodríguez, J. Laine, O.J. Rojas, Effect of residual lignin and heteropolysaccharides in nanofibrillar cellulose and nanopaper from wood fibers, Cellulose. 19 (2012) 2179–2193.

https://doi.org/10.1007/s10570-012-9788-z.
[52] L. Segal, J.J. Creely, A.E. Martin, C.M. Conrad, An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using the X-Ray Diffractometer, Text. Res. J. 29 (1959) 786–794. https://doi.org/10.1177/004051755902901003.
[53] A. Tutus, S. Ates, I. Deniz, Pulp and paper production from Spruce wood with kraft and modified kraft methods, African J. Biotechnol. 9 (2010) 1648–1654.
[54] E.L. Hult, P.T. Larsson, T. Iversen, Comparative CP/MAS 13C-NMR study of cellulose structure in spruce wood and kraft pulp, Cellulose. 7 (2000) 35–55. https://doi.org/10.1023/A:1009236932134.
[55] Z. Wang, S. Winestrand, T. Gillgren, L.J. Jönsson, Chemical and structural factors influencing enzymatic saccharification of wood from aspen, birch and spruce, Biomass and Bioenergy. 109 (2018) 125–134. https://doi.org/10.1016/j.biombioe.2017.12.020.
[56] M. Jonoobi, A.P. Mathew, K. Oksman, Natural Resources and Residues for Production of Bionanomaterials, in: 2014: pp. 19–33. https://doi.org/10.1142/9789814566469_0003.
[57] A. Chaker, S. Alila, P. Mutjé, M.R. Vilar, S. Boufi, Key role of the hemicellulose content and the cell morphology on the nanofibrillation effectiveness of cellulose pulps, Cellulose. 20 (2013) 2863–2875. https://doi.org/10.1007/s10570-013-0036-y.
[58] M. Sánchez-Gutiérrez, E. Espinosa, I. Bascón-Villegas, F. Pérez-Rodríguez, E. Carrasco, A. Rodríguez, Production of Cellulose Nanofibers from Olive Tree Harvest—A Residue with Wide Applications, Agronomy. 10 (2020) 696. https://doi.org/10.3390/agronomy10050696.
[59] L. Berglund, M. Noël, Y. Aitomäki, T. Öman, K. Oksman, Production potential of cellulose nanofibers from industrial residues: Efficiency and nanofiber characteristics, Ind. Crops Prod. 92 (2016) 84–92. https://doi.org/10.1016/j.indcrop.2016.08.003.
[60] S. Mansouri, R. Khiari, N. Bendouissa, S. Saadallah, F. Mhenni, E. Mauret, Chemical composition and pulp characterization of Tunisian vine stems, Ind. Crops Prod. 36 (2012) 22–27. https://doi.org/10.1016/j.indcrop.2011.07.036.
[61] S.P. Mishra, Bleaching of cellulosic paper fibres with ozone-effect on the fibre properties, Institut Polytechnique de Grenoble, France, 2010.
[62] M.E. Vallejos, F.E. Felissia, M.C. Area, N.V. Ehman, Q. Tarrés, P. Mutjé, Nanofibrillated cellulose (CNF) from eucalyptus sawdust as a dry strength agent of unrefined eucalyptus handsheets, Carbohydr. Polym. 139 (2016) 99–105. https://doi.org/10.1016/j.carbpol.2015.12.004.
[63] M.A. Arsène, K. Bilba, C. Onésippe, Treatments for viable utilization of vegetable fibers in inorganic-based composites, in: Sustain. Nonconv. Constr. Mater. Using Inorg. Bond. Fiber Compos., Elsevier Inc., 2017: pp. 70–123. https://doi.org/10.1016/B978-0-08-102001-2.00004-8.

[64] I. Filipova, F. Serra, Q. Tarrés, P. Mutjé, M. Delgado-Aguilar, Oxidative treatments for cellulose nanofibers production: a comparative study between TEMPO-mediated and ammonium persulfate oxidation, Cellulose. (2020) 1–18.

[65] Q. Tarrés, S. Boufi, P. Mutjé, M. Delgado-Aguilar, Enzymatically hydrolyzed and TEMPO-oxidized cellulose nanofibers for the production of nanopapers: morphological, optical, thermal and mechanical properties, Cellulose. 24 (2017) 3943–3954. https://doi.org/10.1007/s10570-017-1394-7.

[66] M. Delgado-Aguilar, I. González, Q. Tarrés, M.À. Pèlach, M. Alcalà, P. Mutjé, The key role of lignin in the production of low-cost lignocellulosic nanofibres for papermaking applications, Ind. Crops Prod. 86 (2016) 295–300. https://doi.org/10.1016/j.indcrop.2016.04.010.

[67] Q. Tarrés, E. Espinosa, J. Domínguez-Robles, A. Rodríguez, P. Mutjé, M. Delgado-Aguilar, The suitability of banana leaf residue as raw material for the production of high lignin content micro/nano fibers: From residue to value-added products, Ind. Crops Prod. 99 (2017) 27–33. https://doi.org/10.1016/j.indcrop.2017.01.021.

[68] L. Hu, G. Zheng, J. Yao, N. Liu, B. Weil, M. Eskilsson, E. Karabulut, Z. Ruan, S. Fan, J.T. Bloking, M.D. McGehee, L. Wågberg, Y. Cui, Transparent and conductive paper from nanocellulose fibers, Energy Environ. Sci. 6 (2013) 513–518. https://doi.org/10.1039/c2ee23635d.

[69] X. Wang, Y. Zhang, H. Jiang, Y. Song, Z. Zhou, H. Zhao, Fabrication and characterization of nano-cellulose aerogels via supercritical CO2 drying technology, Mater. Lett. 183 (2016) 179–182. https://doi.org/10.1016/j.matlet.2016.07.081.

[70] M.K. Inglesby, S.H. Zeronian, Direct dyes as molecular sensors to characterize cellulose substrates, Cellulose. 9 (2002) 19–29. https://doi.org/10.1023/A:1015840111614.

[71] H. Bian, Y. Gao, R. Wang, Z. Liu, W. Wu, H. Dai, Contribution of lignin to the surface structure and physical performance of cellulose nanofibrils film, Cellulose. 25 (2018) 1309–1318. https://doi.org/10.1007/s10570-018-1658-x.

[72] H. Zhang, C. Zhao, Z. Li, J. Li, The fiber charge measurement depending on the poly-DADMAC accessibility to cellulose fibers, Cellulose. 23 (2016) 163–173.

[73] E.H. Qua, P.R. Hornsby, H.S.S. Sharma, G. Lyons, Preparation and characterisation of cellulose nanofibres, J. Mater. Sci. 46 (2011) 6029–6045. https://doi.org/10.1007/s10853-011-5565-x.

[74] F. Gu, W. Wang, Z. Cai, F. Xue, Y. Jin, J.Y. Zhu, Water retention value for characterizing fibrillation degree of cellulosic fibers at micro and nanometer scales, Cellulose. 25 (2018) 2861–2871. https://doi.org/10.1007/s10570-018-1765-8.

[75] M. Jonoobi, R. Oladi, Y. Davoudpour, K. Oksman, A. Dufresne, Y. Hamzeh, R. Davoodi, Different preparation methods and properties of nanostructured cellulose from

various natural resources and residues: a review, Cellulose. 22 (2015) 935–969.

[76] R. He, X.P. Ye, F. Harte, B. English, Effects of high-pressure homogenization on physicochemical properties and storage stability of switchgrass bio-oil, Fuel Process. Technol. 90 (2009) 415–421. https://doi.org/10.1016/j.fuproc.2008.11.003.

[77] I. Mohammad Tajul, M.M. Alam, M. Zoccola, Review on modification of nanocellulose for application in composites, Int. J. Innov. Res. Sci. Eng. Technol. 2 (2013) 5444–5451.

[78] H. Yang, T.G. van de Ven, Preparation of hairy cationic nanocrystalline cellulose, Cellulose. 23 (2016) 1791–1801.

[79] W. Maatar, S. Boufi, Microporous cationic nanofibrillar cellulose aerogel as promising adsorbent of acid dyes, Cellulose2. 24 (2017) 1001–1015.

Tables

Table 1. Samples and HPH sequence

Sample	Sequence in the HPH nº of passes x pressure (bar)
LCMNF 1	3 x 300
LCMNF 2	3 x 300 + 3 x 600
LCMNF 3	3 x 300 + 3 x 600 + 3 x 900
LCMNF 4	3 x 300 + 3 x 600 + 6 x 900

Table 2. Chemical composition of the BTMP.

	Cellulose (wt.%)	Hemicellulose (wt.%)	Klason lignin (wt.%)	Extractives (wt.%)	Ashes (wt.%)	Reference
BTMP	48.35 ± 0.53	25.40 ± 0.31	25.80 ± 0.21	0.25 ± 0.03	0.20 ± 0.05	Present work
UKSP	86.20	11.30	2.23	0.07	0.20	Tutus et al., 2010
BKSP	93.2	6.9	< 0.1	-	-	Hult et al., 2000

Table 3. Morphology and drainability of BTMP

l_w^F (µm)	1,178 ± 42
d^F (µm)	29.8 ± 0.2
f_{length} (%)	51.9 ± 3.1
f_{weight} (%)	12.0 ± 0.9
SSA (m^2/g)	2.87 ± 0.12
°SR / CSF	21.5 / 578

Abbreviations: mean fiber length weighted in length (l_w^F), mean fiber diameter (d^F), percentage of fines weighted in length (f_{length}), percentage of fines in weight (f_{weight}) and specific surface area (SSA)

Table 4. BTMP characteristics as function of refining time

Valley beater (min)	l_w^F (µm)	d^F (µm)	f_{length} (%)	f_{weight} (%)	DP	SSA (m^2/g)	CD (µeq/g)	Aptitude to homogenization
0	1,178 ± 42	29.8 ± 0.2	51.9 ± 1.1	12.0 ± 0.9	3,250 ± 93	2.87 ± 0.12	56.3 ± 1.6	Clogging
50	1,064 ± 32	28.8 ± 0.1	59.0 ± 0.5	24.6 ± 1.9	3,150 ± 51	6.74 ± 0.09	72.4 ± 2.3	Clogging
100	790 ± 51	28.5 ± 0.2	65.2 ± 1.3	31.8 ± 2.2	2,690 ± 94	12.45 ± 0.18	109.5 ± 2.4	Clogging
150	682 ± 29	28.6 ± 0.3	79.5 ± 0.8	40.6 ± 1.3	2,540 ± 71	16.01 ± 0.10	137.6 ± 3.0	Non-clogging

720 **Table 5.** Characterization of the LCMNF

Sample	Yield (%)	T_{600nm} (%)	WRV (g/g)	CD (μeq·g/g)	SSA_{CR} (m^2/g)	SSA_{p+} (m^2/g)
LCMNF 1	4.6 ± 0.3	3.8	1.5 ± 0.1	179 ± 6	117.8	64.7
LCMNF 2	11.9 ± 0.3	8.1	1.8 ± 0.1	205 ± 4	134.4	77.4
LCMNF 3	24.1 ± 0.2	14.5	2.6 ± 0.2	233 ± 2	145.2	91.0
LCMNF 4	28.6 ± 0.4	17.2	3.1 ± 0.1	240 ± 3	150.3	94.4

721

Table 6. Characterization of lignocellulosic micro-nano fibers (LCMNF)

Sample	DP (-)	Klason lignin (wt.%)	C.I. (%)
LCMNF 1	755	24.3 ± 0.3	70.6
LCMNF 2	561	23.4 ± 0.1	71.9
LCMNF 3	418	22.1 ± 0.2	75.1
LCMNF 4	367	21.0 ± 0.2	75.7

Abbreviations: Degree of polymerization (DP) and crystallinity index (C.I.)

List of Figures

Figures

Figure 1

- Journal: International Journal of Biological Macromolecules
- Author: Ferran Serra-Parareda
- Illustration number: 1

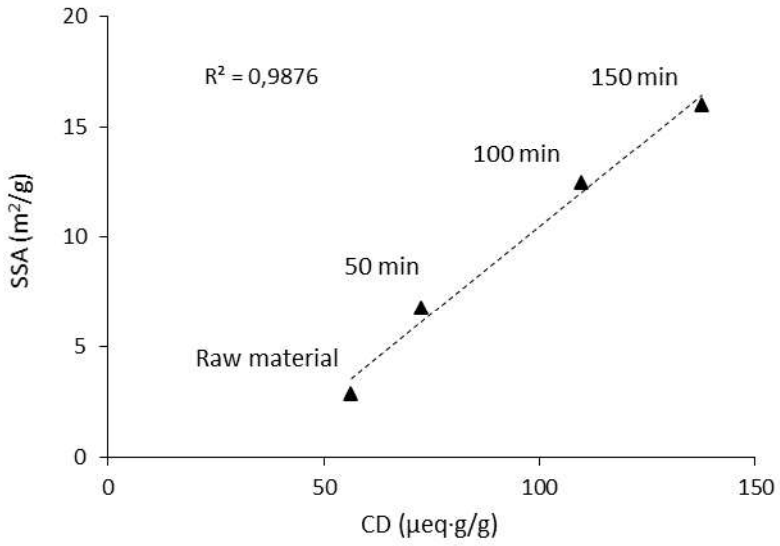


Figure 1. Evolution of SSA and CD at different processing times in the Valley beater.

Figure 2

- Journal: International Journal of Biological Macromolecules
- Author: Ferran Serra-Parareda
- Illustration number: 2

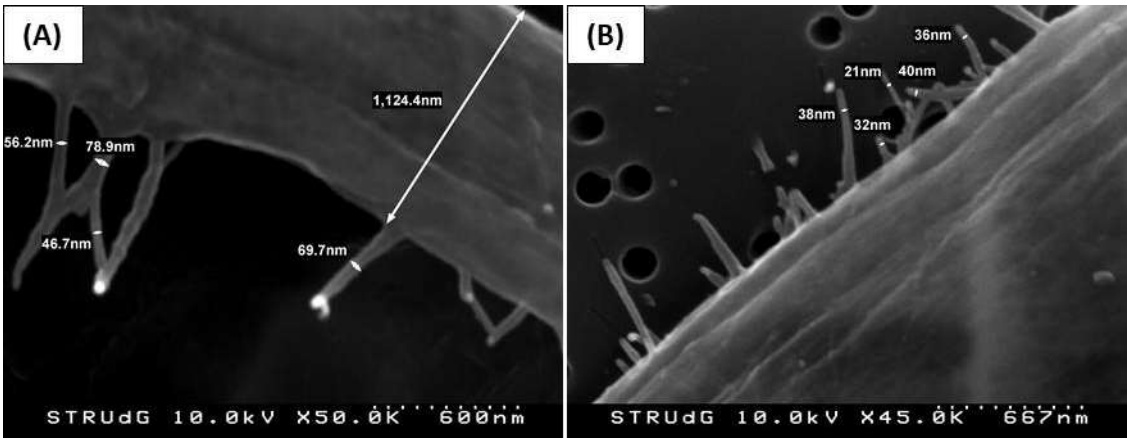


Figure 2. FE-SEM observation of LCMNF 1 (A) and LCMNF 4 (B)

Figure 3

- Journal: International Journal of Biological Macromolecules
- Author: Ferran Serra-Parareda
- Illustration number: 3

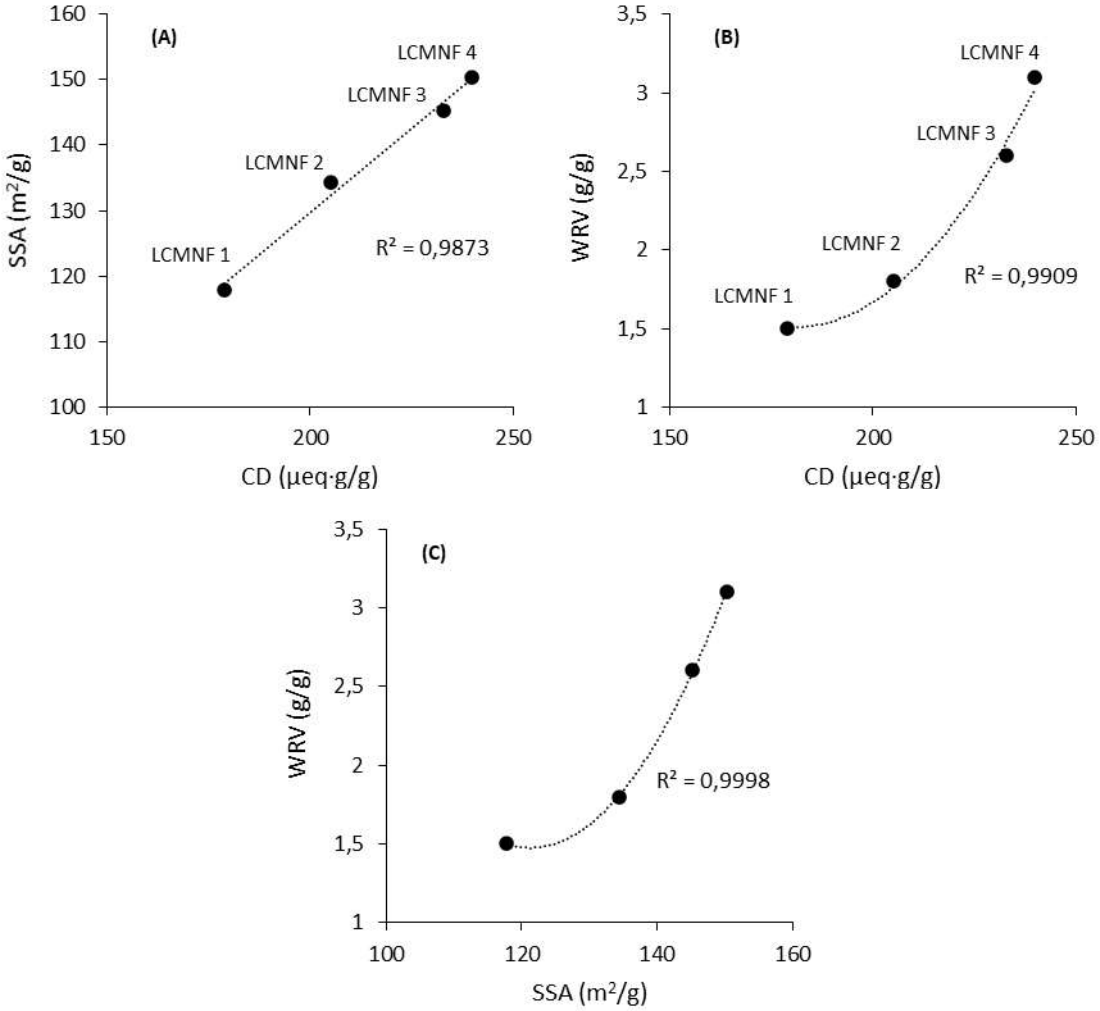


Figure 3. Evolution of the SSA_{CR} (A) and WRV (B) with the CD, and WRV with the SSA_{CR} of the LCMNF (C).

Figure 4

- Journal: International Journal of Biological Macromolecules
- Author: Ferran Serra-Parareda
- Illustration number: 4

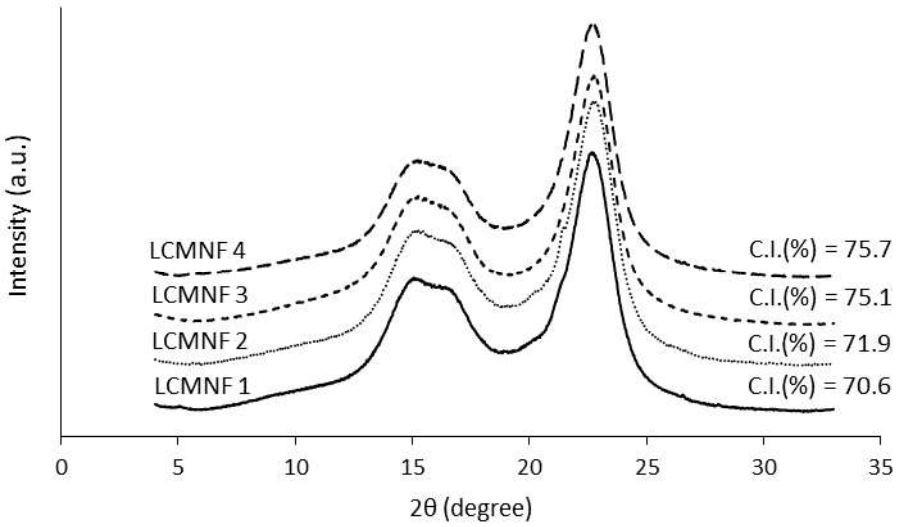
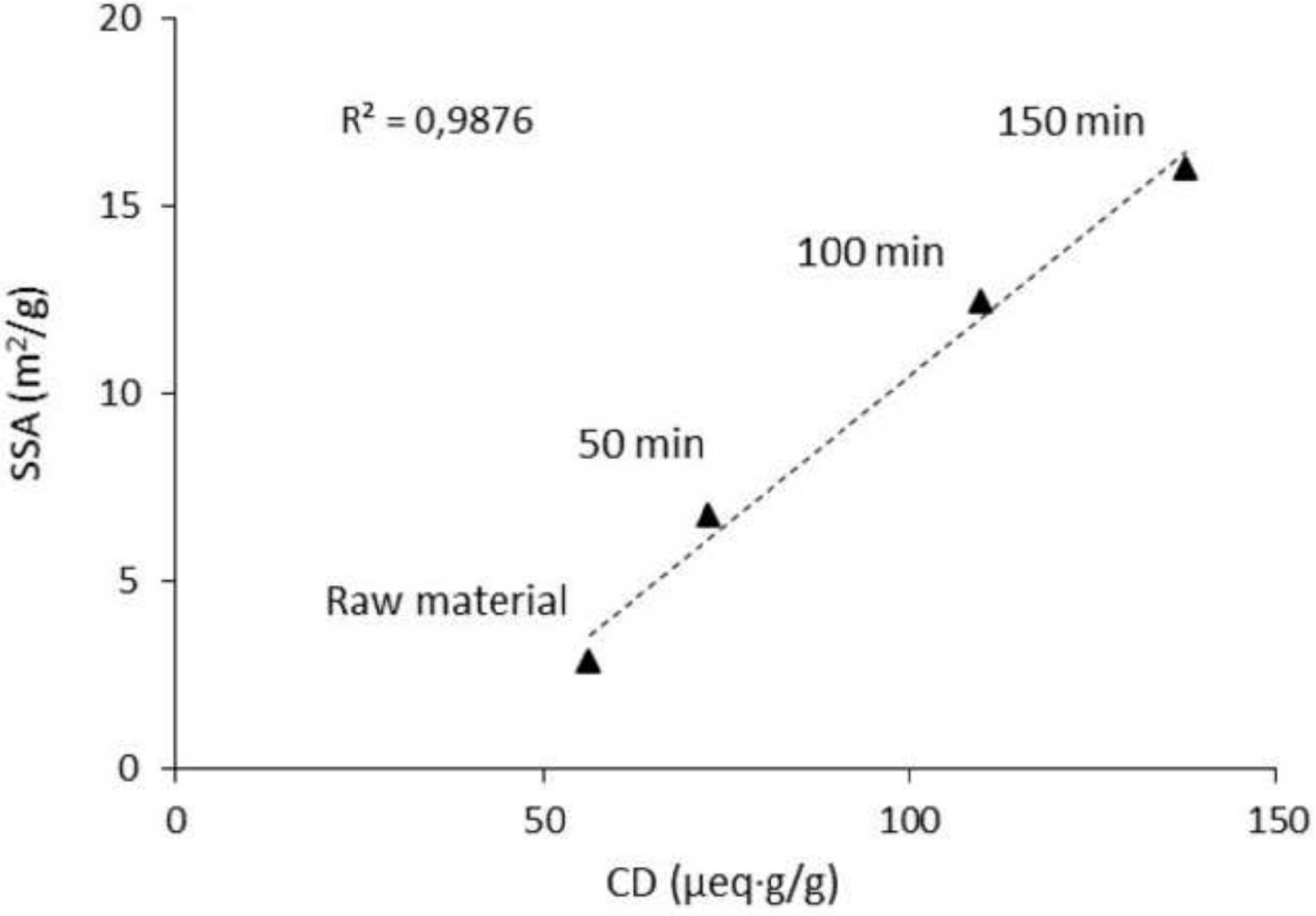


Figure 4. XRD analysis of the LCMNF

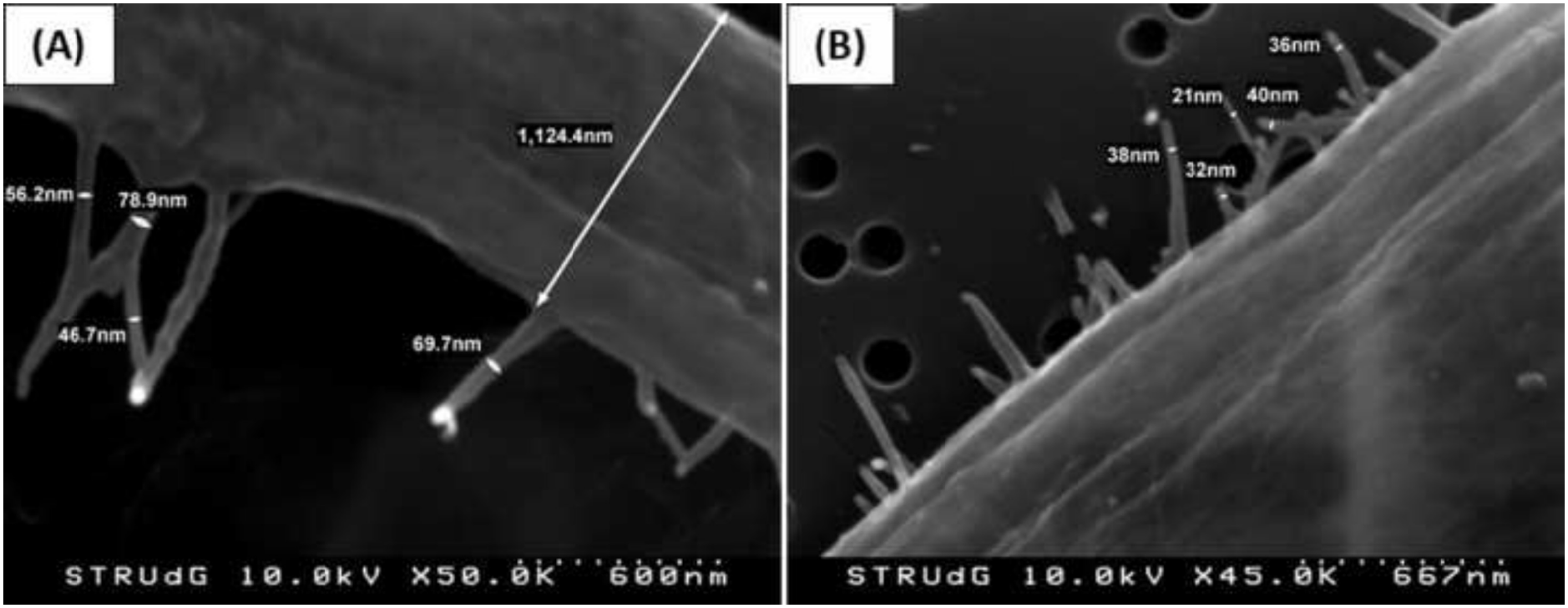
Figure

Click here to access/download;Figure;Figure 1.tiff



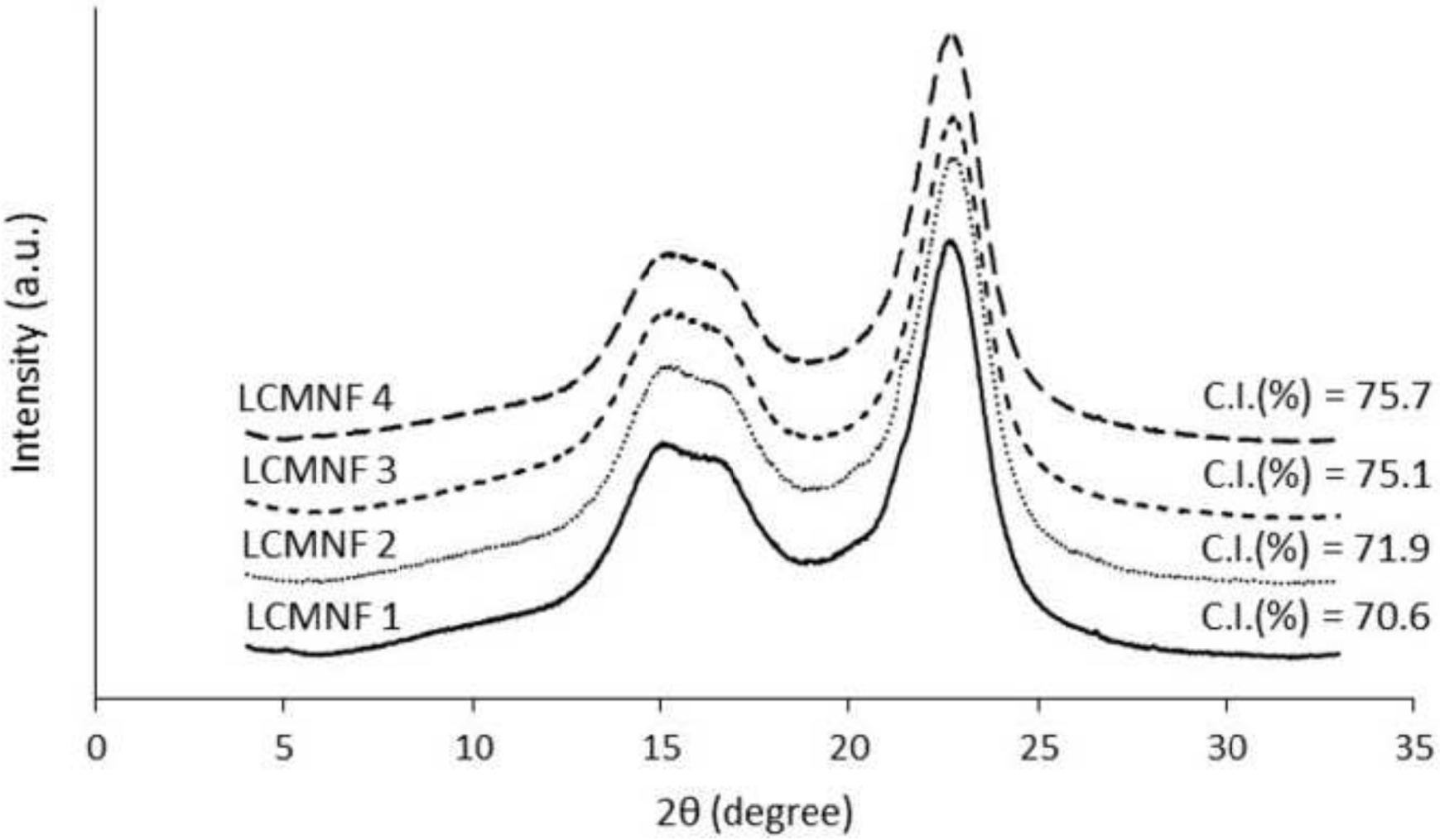
Figure

Click here to access/download;Figure;Figure 2.tiff



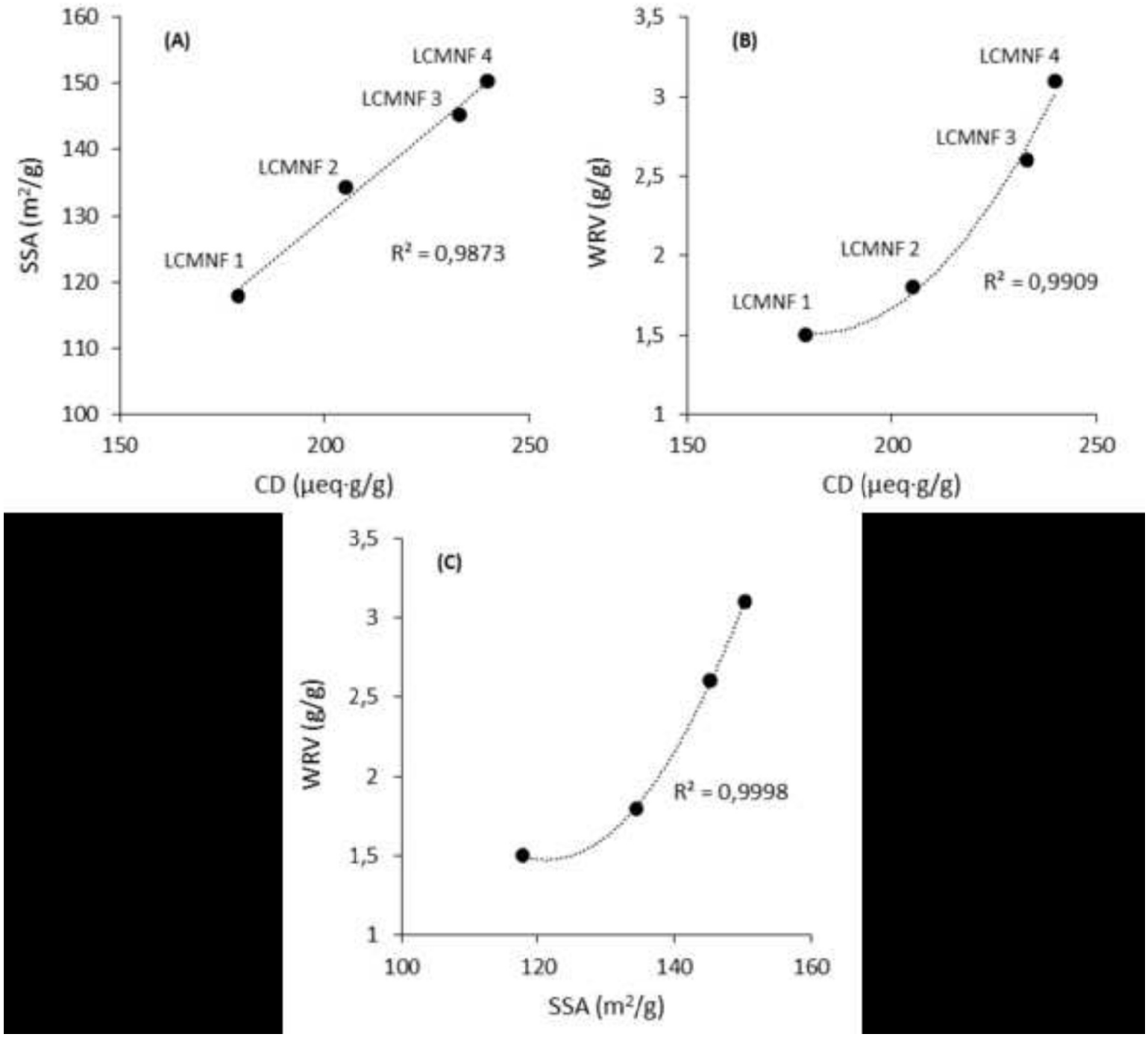
Figure

Click here to access/download;Figure;Figure 4.tiff



Figure

Click here to access/download;Figure;Figure 3.tiff



Author Statement

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: