On the potential of lignin-containing cellulose nanofibrils (LCNFs): a review on properties and applications

Iina Solala[a], Maria Celeste Iglesias[b] and Maria Soledad Peresin*[b]

[a]Department of Bioproducts and Biosystems, Aalto University School of Chemical Engineering, Vuorimiehentie 1, 02150 Espoo, Finland.

[b]Forest Products Development Center, School of Forestry and Wildlife Sciences, Auburn University, 520 Devall Dr. Auburn, AL 36832, Auburn, Alabama, United States.

Email address: soledad.peresin@auburn.edu

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Abstract:

This review outlines the present state and recent progress in the area of lignin-containing cellulose nanofibrils (LCNFs), an emerging family of green cellulose nanomaterials. Different types of LCNF raw materials are described, with main focus on wood-based raw materials, and the properties of the resulting LCNFs are compared. Common problems faced in industrial utilization of CNFs are discussed in the light of potential improvements from LCNFs, covering areas such as chemical and energy consumption, dewatering and redispersibility. Out of the potential applications, barrier films, emulsions and nanocomposites are considered.

Keywords: *lignin-containing nanocellulose, lignin, cellulose nanofibrils, nanofibrillated cellulose*

Introduction

During the last decades, the exponential growth of technology has allowed manipulating materials at scales lower than 100 nm. At this scale, fundamental material properties show different behaviors than those corresponding to the macroscale (Kamel 2007). Simultaneously, the utilization of bio-based products, mainly cellulose, to replace petroleum-based materials has generated an enormous impact, which can be directly seen on the increasing body of research on cellulosic nanomaterials, or nanocellulose, over the years. As is the case with other nanomaterials, also for nanocellulose, the interfacial interactions and chemical composition play a vital role in the properties of the material and on their interactions with other components (Ratner et al. 2013).

Nanocellulose can be obtained from different raw materials utilizing diverse approaches. The two most common man-made types are cellulose nanocrystals (CNCs) – produced by acid hydrolysis – and cellulose nanofibrils (CNFs) – produced by mechanical disintegration of the respective lignocellulosic fibers. Since the production methods are different, the properties of the fibers, as well as their final application, will vary among these nanoparticles (Klemm et al. 2011; Moon et al. 2011; Lavoine et al. 2012). In this review, we focus on CNFs.

Over time, research on CNFs has generally centered on using fully bleached cellulose nanofibrils (BCNFs). Nevertheless, during the last years, efforts have been made to incorporate lignin-containing cellulose nanofibrils (LCNFs) in different applications, like additives in papermaking (Delgado-Aguilar et al. 2016); neat and composite LCNF films (Rojo et al. 2015; Horseman et al.

47 2017); or fillers and reinforcing agents in different matrices (Sun et al. 2014; Wang et al. 2014;

48 Ago et al. 2016; Ballner et al. 2016; Ferrer et al. 2016; Herzele et al. 2016; Visanko et al. 2017a).

49 This review aims to provide a complete overview of the current state of LCNF research; mainly

50 focused on the effect of chemical composition on their processing, properties, and applications.

51 The chemistry involved in pulping and bleaching processes is considered in an attempt to elucidate

52 their impact on the final nanocellulose properties. Additionally, the role of lignin and

53 hemicelluloses in LCNF fibers is carefully described. Finally, a summary of applications such as

54 barrier films, emulsions, and nanocomposites is presented.

55 *Structure and chemistry of wood-based biomass*

56 **In native state.** Wood forms a major part of the plant-based biomass in the world. Structurally,

57 wood can be described as a complex three-dimensional nanocomposite, composed of aligned

58 cellulose microfibrils that are embedded in a matrix of lignin and heteropolysaccharides (mainly

59 hemicelluloses). As a simplification, cellulose microfibrils act as the major load-bearing

60 component in wood, whereas the role of the surrounding matrix is to transfer mechanical stress

61 across the structure, to control the content of water in the wood tissue and to protect the tree against

62 pathogens and insects (Higuchi 1985; Hatfield and Vermerris 2001).

63 Despite ongoing controversies on the exact structure and composition of the native plant cell wall

64 (Keegstra 2010; Crestini et al. 2011; Agarwal et al. 2016), it is commonly accepted that the average

65 cellulose microfibril angle is different at different cell wall layers (primary, secondary and tertiary

66 cell wall layers) and that these microfibrils consist of alternating crystalline and less ordered

67 domains. Cellulose microfibrils are surrounded by a crosslinked lignin matrix (Fengel and

68 Wegener 1984; Kilpeläinen et al. 2007) that is covalently bound to surrounding carbohydrates

69 (Minor 1986; Tenkanen et al. 1999; Lawoko et al. 2005) in the form of the so-called lignin-

70 carbohydrate complexes (LCC). For the purpose of this review, it suffices to say that wood species

71 are generally divided into softwoods (SW) and hardwoods (HW) that have differences both in

72 structural complexity and chemical composition; the latter been summarized in Table 1.

73 **Table 1** Chemical compositions of softwood and hardwood as weight percentages of dry wood.
74 Adapted from Sjöström and Westermark (1999) with permission of Springer Nature.

| Wood type	Cellulose	Hemicelluloses	Lignin	Extractives
Softwood	37-43	20-30	25-33	2-5
Hardwood	39-45	17-35	20-25	2-4

75 Cellulose is the main component in wood tissue (~40% of dry weight). It is a semicrystalline, linear

76 homopolymer that consists of thousands of anhydro-D-glucopyranosyl units linked by β-(1-4)-

77 glycosidic bonds; the degree of polymerization (DP) depending on the source and treatment history

78 of the cellulose, ranging between 15,000 in cotton cellulose and about 10,000 in native wood

79 (Sjöström 1993). A number of different crystalline structures have been identified for cellulose

80 (O'Sullivan 1997), but native celluloses are of crystallinity type I (hydrogen bond structure of

81 cellulose I shown in Fig. 1). Furthermore, for plant-based materials, the dominant crystalline form

82 is cellulose Iβ that consists of two conformationally different chains in a monoclinic unit cell

83 (Atalla and VanderHart 1984). In contrast, its allomorph Iα has one molecular chain in a triclinic

84 unit cell, found in certain algae and bacterial cellulose (Kontturi et al. 2006). In addition to the

85 crystalline parts, cellulose contains a significant portion of less ordered or 'amorphous' regions

86 that are more accessible to water and chemically more reactive than the crystalline domains. As is

87 the case with the DP, also the crystallinity index (CrI) depends heavily on the raw material and its

88 chemical and mechanical processing (O'Sullivan 1997; Liitiä et al. 2003; Ago et al. 2004; Kontturi

89 et al. 2006; Karinkanta et al. 2013).

90
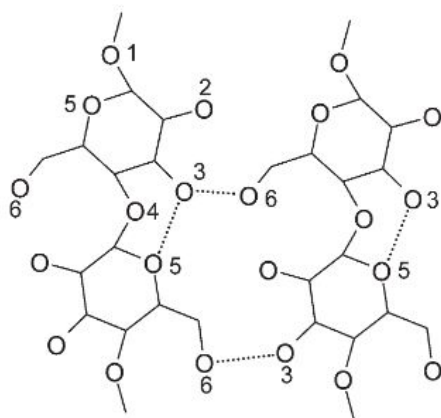
Fig. 1 The supramolecular structure of native cellulose I. Reprinted from Kontturi et al. (2006)
with permission of Royal Society of Chemistry (Note: Hydrogen atoms are not indicated)

93 The next class of wood biopolymers to be discussed are hemicelluloses, amorphous

94 heteropolysaccharides that have structural resemblance to cellulose but have lower molecular

95 weight and often contain side chains (Fig. 2). Some of the hemicelluloses present in the cell wall

96 are covalently linked to lignin (Lawoko et al. 2005; Iversen and Wännström 2009; Brunow and

97 Lundquist 2010), and have a high affinity to cellulose (Eronen et al. 2011; Arola et al. 2013;

98 Villares et al. 2015). These properties enable hemicelluloses to act as compatibilizers between the

99 cellulose microfibrils and the lignin-rich matrix surrounding them. Moreover, hemicelluloses have

100 been proposed to direct the structural development of native plant cell wall during its biosynthesis

101 (Atalla et al. 1993; Martínez-Sanz et al. 2016). Perhaps related to the structural differences in SWs

102 and HW fibers, also their hemicellulose compositions are different. As a generalization, the

103 hemicelluloses in SWs typically consist of galactoglucomannans (15-20%) and

104 arabinoglucuronoxylans (5-10%), whereas HWs are rich in glucuronoxylans (15-30%) and

105 glucomannans (2-5%) (Sjöström and Westermark 1999).
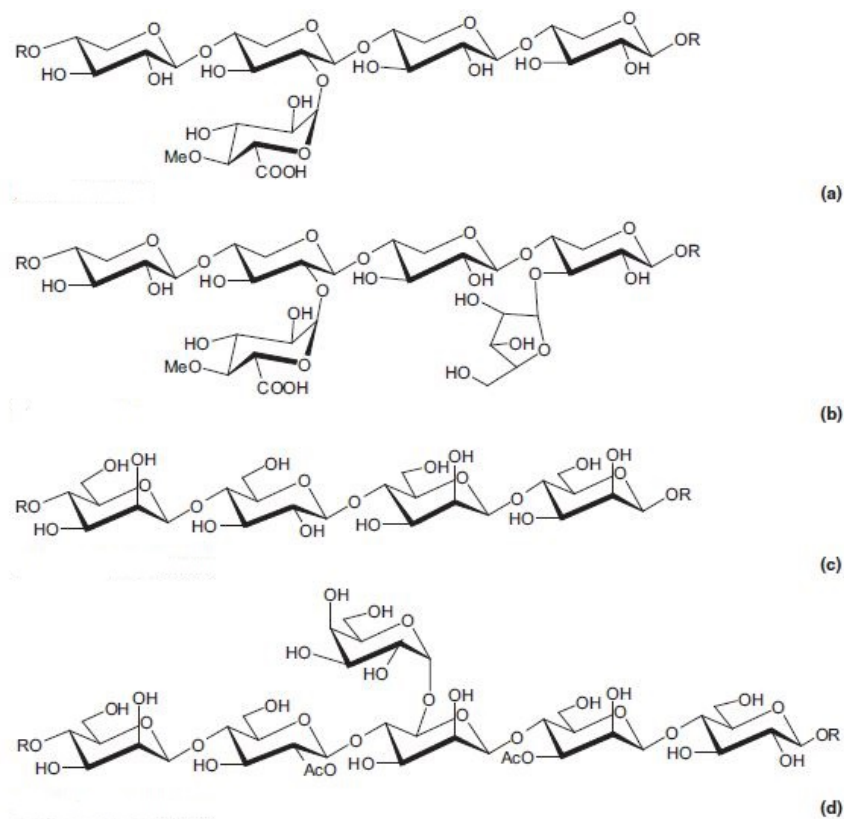
106

107 **Fig 2.** Molecular structures of hemicelluloses on HWs and SWs; a) Harwood xylan, b) Softwood
108 xylan, c) Hardwood glucomannan, and d) Softwood glucomannan. Adapted from Sixta (2006)
109 With permission of John Wiley and Sons.

Whereas cellulose and hemicelluloses are both carbohydrates, lignin is a complex amorphous polymer that consists of phenyl propane units with one, two or three methoxy groups (Fig 3). It is often referred to in plural form to accentuate the enormous variation in its structure, depending on where and how it is isolated (proposed structure of softwood kraft lignin shown in Fig 4). Due to its complex network structure (Brunow et al. 1999; Hatfield and Vermerris 2001; Ralph et al. 2004) and covalent attachment to surrounding carbohydrates (Lawoko et al. 2005; Iversen and Wännström 2009), the precise chemical structure and molecular weight of native lignin remains unknown, despite of the number of extensive studies on the chemical composition of isolated lignins (Froass et al. 1996; Ämmälahti et al. 1998; Capanema et al. 2001, 2004; Brunow 2005; Balakshin et al. 2009; Brunow and Lundquist 2010; Crestini et al. 2011, 2017; Alekhina et al. 2015; Lupoi et al. 2015). In general, it can still be said that lignin is more hydrophobic than the carbohydrates that form the majority of the plant cell wall. For this reason, it has a major role in enabling water transport in living plants, as well as protecting them against microbial and fungal attacks (Ruiz-Dueñas and Martínez 2009).
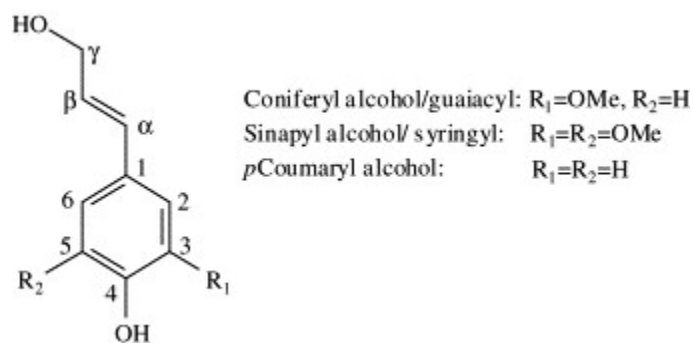
Fig 3. Three lignin precursors. Reprinted from Chakar and Ragauskas (2004) with permission from Elsevier.

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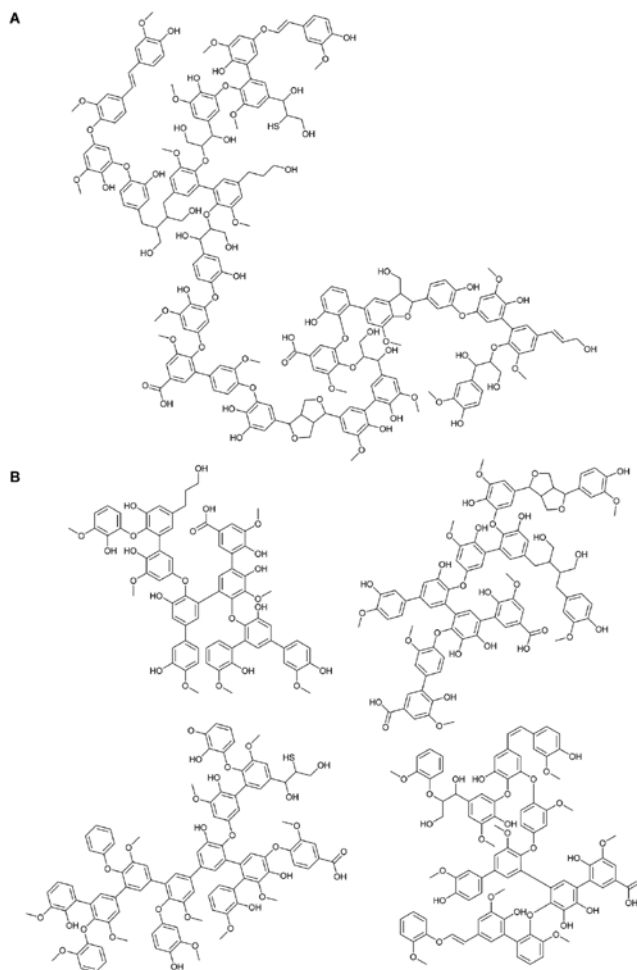
Fig 4. Proposed constitutional structural schemes for softwood kraft lignin. (a) Acetone insoluble fraction (**AIKL**); (b) acetone soluble fraction (**ASKL**). Reprinted from Crestini et al. (2017) with permission of the Royal Chemical Society.

Extractives, the remaining class of wood components, are a chemically diverse class of low-molecular weight components that typically comprise about 2-5% of wood, but their amount greatly varies, depending on the wood species and tissue in question (Fengel and Wegener 1984; Brunow et al. 1999). Their biological role is to provide microbial resistance to the wood tissue. Details of their chemistry and properties are outside the scope of this review. For the purposes of the present paper, it suffices to state that most extractives are lipophilic, and some possess antioxidant or antimicrobial properties. Examples of common wood extractives include components such as fatty and resin acids and lignans (Willför et al. 2003a, b). Despite their low content, extractives have a tendency to enrich on the fiber surfaces (Laine et al. 1994; Fardim and Holmbom 2005), potentially impacting the surface chemistry of especially unbleached pulps.

Chiefly, it is important to bear in mind that as wood biomass is pulped, bleached, and processed into cellulose nanofibrils (CNFs), it undergoes many structural and chemical changes. These will be outlined briefly in the following sections to prepare the reader for the subsequent discussion of lignin-containing pulps and their potential as a raw material for cellulose nanofibrils. For a more thorough overview on the subject of wood chemical composition, the reader is advised to consult more extensive reviews and textbooks on the chemistry of wood and its individual components, such as the ones cited here (Fengel and Wegener 1984; Salmén and Olsson 1998; Sjöström and Westermark 1999; Grabber et al. 2004; Ralph et al. 2004, 2007; Klemm et al. 2005; Glasser et al. 2012; Lupoi et al. 2015).

Mechanical pulping. Generally speaking, mechanical pulps have approximately the same chemical composition as native wood. However, the combination of mechanical shear and elevated temperature (typically about 120 °C) at a high moisture content causes some changes in the structure and chemistry of the material. Notably, part of the heteropolysaccharide fraction is degraded, dissolved and resorbed during mechanical pulping (Thornton et al. 1994). The elevated temperature and high moisture content of the mechanical pulping process cause wood to soften (Salmén 1984; Blechschmidt et al. 1986), enabling the separation of individual fibers. Furthermore, depolymerisation of the cell wall polymers occurs both by thermal and mechanical means, resulting in the formation of reactive free radicals in the course of mechanical pulping (Hon 1979; Widsten et al. 2001). Widsten et al. (2001) reported that high-temperature mechanical pulping causes lignin depolymerisation and formation of phenoxy radicals. However, the presence of phenoxy radicals may be a consequence of their high stability and not necessarily of their role as the primarily formed radicals. The significance of radical formation in CNF manufacturing will be addressed in a later section (*Lignin as an antioxidant*).

As a process, the major advantage of mechanical pulping is its high yield, which is typically above 80% of the original wood material. However, the high yield comes at the expense of using significant amounts of electricity and achieving only a limited degree of fiber-fiber bonding – a critical property in end uses such as papermaking. For this reason, different chemical treatments have been developed to ease the separation of wood fibers. These processes can be classified to chemi-mechanical and chemical pulping processes, both of which will be outlined briefly in the following sections.

Chemi-mechanical pulping. In addition to purely mechanical pulps, there is another class of so-called high yield pulps, namely chemi-mechanical pulps, where mechanical treatment is preceded by a sulphite treatment in alkaline or neutral conditions (Annergren and Rydholm 1959; Gellerstedt et al. 1976; Hanhikoski et al. 2016b). The lower energy consumption associated with chemi-mechanical pulping is most often attributed to sulphonation of lignin that allows a more extensive swelling of the fibers by water, accompanied by more extensive softening of the material (Beatson et al. 1984; Konn et al. 2002).

In alkaline conditions, a significant portion of heteropolysaccharides gets dissolved. This effect is much less pronounced in near-neutral sulphite pulping but the degree of delignification remains lower unless the reaction is catalysed with e.g. anthraquinone (Annergren et al. 1961; Gellerstedt et al. 1976; Konn et al. 2002; Hanhikoski et al. 2016b). From the point of view of nanofibrillation, it is important to note that both – a high degree of lignin sulphonation and the preservation of wood heteropolysaccharides – are expected to promote fiber swelling, thus facilitating the production of cellulose nanofibrils. Lahtinen et al. (2014) observed improved nanofibrillation of chemi-mechanical pulps in comparison to the corresponding mechanical pulps. More recently, Hanhikoski et al. (2016a) found that near-neutral sodium sulphite pulps with yields 58-64% can be efficiently fibrillated to LCNFs, which was interpreted as an indication of high hemicellulose content promoting fibrillation, provided that the remaining lignin was sufficiently degraded.

Chemical pulping. A major difference of chemical pulps to mechanical and chemi-mechanical pulps is that their yield is only about 40-50%. Unbleached chemical pulps contain 2-5% residual lignin, and fully bleached chemical pulps contain only trace amounts of it (<0.1%) (Sjöström and Westermark 1999; Chakar and Ragauskas 2004). Furthermore, the DP of their polysaccharides is lower than in native wood – typically 2,000-4,000 for cellulose and 50-100 for hemicelluloses (Sjöström and Westermark 1999). Examples of typical polysaccharide compositions in chemical pulps are given in Table 2.

Table 2 Polysaccharide compositions of common bleached chemical pulps as weight percentages of dry pulp. Adapted from Sjöström and Westermark (1999) with permission of Springer Nature

Pulp type	Cellulose	Glucomannan	Xylan
Pine kraft	81.3	8	10.7

| Birch kraft | 67.5 | 1.9 | 30.6 |
| Spruce sulphite | 82.9 | 8.8 | 8.3 |

Kraft pulping, the most common industrially used chemical pulping method, is chosen as an example to demonstrate the chemical changes that occur in wood upon chemical treatment. During kraft pulping, wood chips are subjected to alkaline conditions (an aqueous solution of NaOH and Na_2S) at an elevated temperature (170 °C), causing lignin to break down into smaller, water-soluble molecules (Chakar and Ragauskas 2004). Towards the end of the cooking, the selectivity of the process decreases, and degradation of carbohydrates, especially hemicelluloses, takes place.

In comparison to the extensively fractured soluble lignin, the residual lignin that remains in the pulp has a much higher molecular weight and contains more carbohydrates, as can be expected from the presence of the aforementioned lignin-carbohydrate complexes. It has been reported for softwood kraft pulps that some of the LCCs are broken by kraft pulping, whereas some remain intact even after oxygen delignification (Tenkanen et al. 1999; Lawoko et al. 2004, 2005). Moreover, studies have shown that the lignin fraction that is attached to glucomannan undergoes condensation and is thus of higher molecular weight than the more extensively degraded lignin fraction that is attached to xylan (Lawoko et al. 2005).

Bleaching. A detailed description of pulp bleaching chemistry is outside the scope of this review, but it is worth mentioning that before commercial use, both mechanical and chemical pulps are typically bleached to reach a higher brightness. This is especially important for kraft pulps that undergo significant colour formation in the alkaline conditions of the process (Falkehag et al. 1966; Ziobro 1990). For the purpose of this review, it is sufficient to say that pulping strategies are generally based on two main principles: either removing lignin or changing the chemical structure of lignin and carbohydrates to remove their colour-causing structures, referred to as chromophores (Agarwal and Atalla 1994; Vuorinen et al. 2004; Rosenau et al. 2007; Jääskeläinen et al. 2009).

For understanding the chemical changes taking place during the bleaching of chemical pulps, let us consider a SW kraft pulp that is bleached by an oxidative chemical, such as ozone, oxygen, or chlorine dioxide. In this situation, the residual lignin undergoes the following changes (Lachenal et al. 1995):

224   •   The content of aliphatic and phenolic hydroxyls decreases slightly;

225   •   The carboxylic acid content increases, except for ozone;

226   •   Methoxy groups are removed;

227   •   Some C=O is formed during oxygen and ClO_2 treatments.

228 It should be stressed that the aforementioned changes only describe the structure of the residual

229 lignin fraction, not the carbohydrates that form nearly 100% of bleached chemical pulps. Upon

230 bleaching, most of the cellulose is retained, but some hemicelluloses are lost together with the

231 residual lignin (Annergren and Rydholm 1959; Annergren et al. 1961; Hanhikoski et al. 2016b).

232 The changes that take place in hemicelluloses during bleaching include degradation and oxidation

233 (formation of carbonyl and carboxylic groups (Jääskeläinen et al. 2000). More detailed information

234 on the chemistry of different bleaching stages is available in the articles and textbooks referenced

235 herein (Lachenal et al. 1995; Dence 1996; Dence and Reeve 1996; Vuorinen et al. 1999; Potthast

236 et al. 2009). Overall, it is important to remember that, depending on the pulping and bleaching

237 processes used, the pulps will have different chemical compositions but also different surface

238 charges and charge densities (the latter are predominantly caused by the presence of sulphonic and

239 carboxylic acid groups), both of which influence the ease of pulp fibrillation. These issues will be

240 addressed in more detail in section *The importance of hemicelluloses*.

241 *Cellulose nanofibrils – state of the art and bottlenecks*

242 The pioneers in the production of cellulose nanofibrils (CNFs) were Turbak et al. (1982) and

243 Herrick et al. (1983) who investigated how to produce microfibrillated cellulose (MFC) by

244 homogenizing cellulose pulp suspensions under pressure during the early 80's. They discovered

245 that after intensive mechanical disintegration, cellulose pulps result in colloidal fibrous

246 suspensions at a very low solid content (typically ~2% wt.). The gel-like structure (Fig 5) and the

247 enhanced hydrogen bonding capability of CNFs confer it great potential for being incorporated in

248 formulations for thickeners and emulsifiers for food, cosmetics, and paints (Turbak et al. 1982;

249 Herrick et al. 1983; Lavoine et al. 2012). Furthermore, CNFs present high aspect ratio, low density

250 and thermal expansion, high strength modulus and stiffness (Hsieh et al. 2008; Eichhorn et al.

251 2010; Siró and Plackett 2010), as well as remarkable film-formability when dried (Spence et al.

252 2011a); properties that make them interesting in terms of producing high-strength composites and
253 barrier materials from renewable resources.
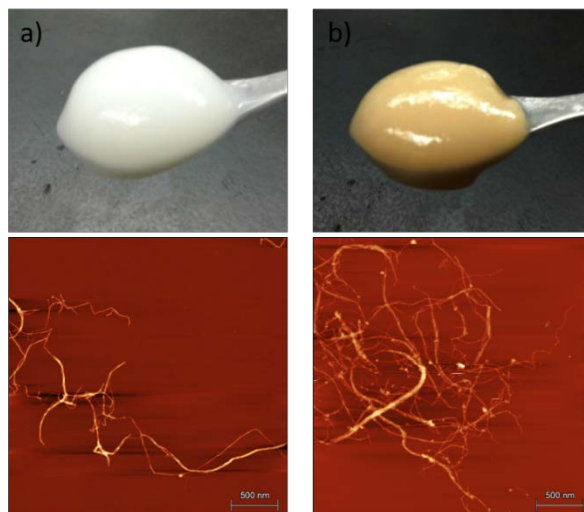
255 **Fig 5.** Gel-like structure and Atomic Force Microscopy image showing the morphology of a)
256 bleached CNFs, and b) unbleached CNFs.

257 Despite the versatile application potential of CNFs, the original efforts of Turbak and Herrick were
258 initially abandoned due to the inefficiency of the process; large amounts of energy were needed
259 for the refining and beating of the cellulose pulps, resulting in rather low yields of fibril
260 suspensions. To address this issue, a number of different types of mechanical treatments, including
261 homogenization (Nakagaito and Yano 2004; Spence et al. 2011b; Moser et al. 2015), grinding
262 (Taniguchi and Okamura 1998; Iwamoto et al. 2007; Spence et al. 2011a), ultrasonication (Zhao
263 et al. 2007; Cheng et al. 2009; Chen et al. 2011), and cryocrushing (Dufresne et al. 1997;
264 Chakraborty et al. 2005), have since been developed to produce CNFs. The two most common
265 methods are (1) homogenization, also referred to as microfluidization, where the cellulose
266 suspension is forced to pass through a small orifice which causes the fracture of the fibers into
267 smaller fragments (Turbak et al. 1982), and (2) micro-grinding, where the cellulose is beaten
268 between two ceramic disks, defibrillating the fibers and reducing their size (Iwamoto et al. 2005;
269 Stelte and Sanadi 2009). These methods can be used individually or in combination with one
270 another (Iwamoto et al. 2005; Stelte and Sanadi 2009) but both require several passes through the
271 system, contributing to a high energy consumption. Consequently, the main objective of CNF

272 manufacturing has been to reduce the energy consumption with different pre-treatments – these
273 can again be classified as chemical and/or enzymatic pre-treatments.

274 Of the chemical methods, carboxymethylation (Wågberg et al. 1987, 2008) and TEMPO (2,2,6,6-
275 tetramethylpiperidine-1-yl)oxyl radical) mediated oxidation (Saito et al. 2006, 2007) are the most
276 widely used. Both methods increase the fiber electrical charges, thus increasing the repulsion
277 between the individual fibrils and facilitating the fiber disintegration. Moreover, during the last
278 years, alternative chemical pre-treatments have been developed in order to obtain CNFs with
279 improved properties at reduced cost, in an effort to reduce the energy input while avoiding
280 expensive reagents. As an example of such processes, recyclable organic acids, such as oxalic and
281 maleic acid, have been used for simultaneous production of nanofibrillated and nanocrystalline
282 cellulose, while recovering hydrolysed sugars (Chen et al. 2016; Bian et al. 2017a, b, c; Wang et
283 al. 2017).

284 The enzymatic pre-treatments, on the other hand, employ different types of cellulases to weaken
285 the fiber structure, thereby decreasing the amount of mechanical energy required for efficient
286 nanofibrillation (Henriksson et al. 2007; Pääkko et al. 2007). Two main categories have been
287 identified for cellulases: cellobiohydrolases that can cleave highly crystalline cellulose, and
288 endoglucanases that tend to require a certain level of disorder in order to degrade cellulose
289 (Missoum et al. 2013). As a result, these enzyme types have synergistic effects and work best when
290 used together.

291 Despite these efforts, a few factors still limit CNF usage in an industrial scale. Such obstacles
292 include the costs of enzymes and chemical reagents (especially TEMPO), difficulties in CNF
293 dewatering and redispersibility, and the incompatibility of CNFs with commercial polymers that
294 limits the mechanical performance of CNF-reinforced composites. Presently, nearly all CNF
295 grades are produced from fully bleached chemical pulps that contain only trace amounts of residual
296 lignin. The aim of the present review, however, is to discuss the benefits and limitations of utilizing
297 cheaper, less extensively bleached lignin-containing pulp varieties in the production of
298 lignocellulosic nanofibers and assess whether they could solve some of the aforementioned
299 problems related to fully bleached CNFs.

300 *Lignin-containing cellulose nanofibrils (LCNFs)*

In this review, we use the term broadly and refer to any cellulosic fibrils of <100 nm in width and a lignin content of >1% as lignin-containing cellulose nanofibrils (LCNFs). Over the past decade, several efforts have been made to extract LCNFs from different raw materials. Sources like empty palm fruit bunches (Ago et al. 2016), wheat straw (Sánchez et al. 2016; Espinosa et al. 2017), banana, jute, pineapple (Abraham et al. 2011), triticale straw (Tarrés et al. 2017), sunflower stalks (Ewulonu et al. 2019), bamboo chips (Lu et al. 2018) and even bark (Chen et al. 2019) are some of the recently investigated examples. Additionally, many research groups have been working on the isolation, characterization, and application of LCNFs from wood sources. Wang et al. (2012) produced two LCNF samples from kraft wood pulps by using an initial acid hydrolysis following by homogenization at high pressure. Samples containing 5 and 10% of lignin were obtained and characterized. Herrera et al. (2018) successfully isolated LCNFs with 23% lignin content from Eucalyptus pulp through catalysed chemical oxidation followed by high-pressure microfluidization. A method using organic acids followed by mechanical treatment was developed for the integrated production of lignin containing nanocrystals (LCNCs) and LCNFs from unbleached mixed hardwood pulp (mainly birch and maple). This methodology allows for the recovery of the organic acids and reduces the overall energy consumption of the process (Bian et al. 2017b). LCNFs with as high as 18.5% lignin content was obtained via this procedure. More recently, Wen et al. (2019) isolated and characterized LCNFs containing 15.5, 18.6, and 23.15% lignin from a poplar high-yield pulp via TEMPO-mediated oxidation followed by homogenization.

Generally, LCNFs are produced from unbleached cellulose pulps with different lignin contents. However, it has been demonstrated that LCNFs can also be directly isolated from raw wood microparticles. In a recent study, nanofibers were produced using alkali-treated poplar wood powder followed by controlled delignification steps in order to obtain samples with 22.1, 14.1, 8.2, 2.0, 0.4, and 0.2% residual lignin. Subsequent mechanical grinding was utilized to produce nanofibers (Chen et al. 2018). Yousefi et al. (2018), on the other hand, isolated nanofibers containing 30% lignin by mechanical grinding of *Paulownia Fortunei* wood without utilizing any chemical pre-treatment.

Regardless of the raw material, the role of lignin in the nanocellulose suspension needs to be clarified in order to better understand the behaviour of the resulting suspensions in further

330 applications. More details about the properties conferred by the lignin present on LCNFs will be

331 discussed in the following sections.

332 **Lignin – a friend or a foe?**

333 Lignin can have two, seemingly contradictory effects on pulp fibrillation, based on what kind of

334 pulps are utilized as the starting material. On the one hand, it can hinder fibrillation, as has been

335 demonstrated in the case of mechanical pulps (Lahtinen et al. 2014). On the other hand, residual

336 lignin can even significantly lower the energy consumption of fibrillation in the case of chemical

337 pulps (Spence et al. 2011b), serving as an example on how lignin structure affects its function.

338 Moreover, the presence of residual lignin in chemical pulps has been reported to result in the

339 formation of finer CNFs at comparable energy consumption levels (Solala et al. 2012; Rojo et al.

340 2015).

341 Assuming a complex, network-like structure for native lignin, it seems probable that the initial

342 crosslinked structure prevents efficient fibrillation of the highest-lignin pulp grades by 'locking'

343 the individual microfibrils together (Lahtinen et al. 2014; Hanhikoski et al. 2016a). The

344 hydrophobic character of lignin may also play an important role in preventing fiber swelling and

345 fibrillation, as will be discussed in the next section. In contrast, the residual lignin present in

346 chemical pulps is significantly degraded and present in much lower quantities, therefore less able

347 to prevent fiber swelling and fibrillation. We have previously proposed (Ferrer et al. 2012; Solala

348 et al. 2012) that the ease of fibrillation observed in lignin-containing chemical pulps is due to lignin

349 acting as an antioxidant, preventing broken covalent bonds from being formed again. This

350 hypothesis is discussed in more detail in section *Lignin as an antioxidant*.

351 *Lignin hydrophobicity and thermoplasticity*

352 It has been extensively reported on the literature that lignin is covalently linked to cellulose and

353 hemicelluloses within the wood structure (Sjöström 1993; Tenkanen et al. 1999; Lawoko et al.

354 2003, 2005; Balakshin et al. 2009, 2011; Iversen and Wännström 2009). It is also generally

355 accepted that lignin presents more hydrophobic character than carbohydrate polymers (Abe et al.

356 2010; Laurichesse and Avérous 2014). However, different processing methods and chemical

357 compositions of raw material result in different lignin surface free energies and thereby also

358 different hydrophobicities. Understandably, processes that cleave the β-aryl ether linkages or
359 introduce electrical charges in lignin increase its hydrophilicity.

360 These effects should be kept in mind when examining literature on the hygroscopicity of LCNF
361 films or nanopapers. In literature, nanopaper water interactions are usually characterized by
362 measuring parameters such as total bound water determined with differential scanning calorimetry
363 (DSC), water retention value (WRV), film water absorption, water vapor transmission rate
364 (WVTR), and water contact angle (WCA) (Spence et al. 2010; Ferrer et al. 2012; Wang et al. 2012;
365 Horseman et al. 2017; Nair et al. 2017; Chen et al. 2018; Herrera et al. 2018; Lê et al. 2018).

366 WCAs are usually higher for LCNF nanopapers than the corresponding CNF nanopapers (Ferrer
367 et al. 2012; Rojo et al. 2015; Chen et al. 2018; Herrera et al. 2018; Lê et al. 2018), but other results
368 are less consistent, showing for example higher water absorption and WVTR for LCNF films
369 (Spence et al. 2010; Ferrer et al. 2012). Ferrer et al. reported water absorption values (g/m^2) of
370 24.6±1.2, 23.1±1.2, and 17.1±1.2 for unbleached, oxygen delignified, and fully bleached CNF
371 samples, respectively. Additionally, for those samples, the WCA results were 60±6, 54±6, and
372 51±4. One might expect that the presence of lignin would automatically make the nanopapers more
373 hydrophobic, but lignin removal tends also to alter the carbohydrate chemistry, so that lignin-
374 containing CNFs often contain more hemicelluloses than the corresponding fully bleached CNFs,
375 which will contribute to their hygroscopicity (Ferrer et al. 2012; Solala et al. 2012). Moreover, the
376 method of film preparation has a significant effect on properties such as porosity, which will in
377 turn affect the WVTR and specific surface area of nanopapers prepared from these nanofibrils.
378 There is a crucial difference in film casting and hot-pressing, for example – the first tends to form
379 more porous films from lignin-containing CNFs (Spence et al. 2010), whereas pressure filtration
380 followed by hot-pressing produces denser films when lignin is present (Rojo et al. 2015). This
381 complex interdependency of film morphology, lignin content, hemicellulose content, and charge
382 density (Ferrer et al. 2012; Solala et al. 2012; Rojo et al. 2015; Herrera et al. 2018) makes direct
383 comparisons between different studies challenging, but when these factors are controlled well,
384 lignin does indeed increase the hydrophobic nature of a cellulosic pulp and the CNFs and
385 nanopapers derived from it (Rojo et al. 2015; Chen et al. 2018; Lê et al. 2018).

In addition to being hydrophobic, lignin softens at elevated temperatures, especially when plasticized by water or some other component (Sakata and Senju 1975; Salmén 1984; Åkerholm and Salmén 2004). It has been reported that at low water contents (<5%), lignin softening temperature is approximately 135 °C, but when the water content increases to 20-40%, the softening temperature decreases to 80-90 °C (Salmén 1982, 1984). Similar behavior has been reported also for hemicelluloses (Olsson and Salmén 2009). This property is well-known from the manufacturing of thermomechanical pulps (Johansson et al. 1998; Gustafsson et al. 2003; Solala et al. 2014), but lignin softening was recently utilized to produce nanofibers from ground wood pulp without applying any chemical pre-treatment (Visanko et al. 2017a). Moreover, this softening behavior has sparked research efforts to develop thermoplastic lignin-based polymers based on these components to replace the presently ubiquitous oil-based polymers (Nägele et al. 2002; Cui et al. 2013; Hilburg et al. 2014). As packaging and barrier films are among the most promising commercial applications for CNFs, the role of lignin hydrophobicity and thermoplasticity may help improving CNF nanopaper moisture barrier properties, as we will discuss in section *Barrier films*.

Lignin as an antioxidant

Mechanically treated polymers typically have a limiting DP, beyond which they will not degrade in the applied conditions (Glynn and van der Hoof 1973; Tomashevskii et al. 1975; Kondo et al. 2004). This levelling off behavior is often attributed to the chain length becoming too small to absorb mechanical energy. On the other hand, the radical content in mechanically stressed polymer samples typically decreases slightly after levelling off, probably due to the occurrence of recombination and disproportionation reactions that quench some of the formed radicals (Kondo et al. 2004).

Following this line of thought, the observed ease of fibrillation of lignin-containing chemical pulps has been hypothesized to be a result of lignin acting as an antioxidant owing to its polyaromatic resonant-stabilized structure (Dizhbite et al. 2004; Solala et al. 2012; Rojo et al. 2015). In other words, as mechanical treatments – be it by grinding, microfluidization or other means – produce free radicals (Sakaguchi and Sohma 1975; Hon 1979, 1983b, a; Solala et al. 2012, 2015), these radicals can get stabilized by the residual lignin present in the fibers due to the resonance

415 stabilization enabled by the phenyl structures and other conjugated double bonds present in lignin.

416 This would lead to less favorable kinetics for the recombination reactions that would otherwise

417 cause a partial reformation of the ruptured covalent bonds and thereby prevent effective

418 nanofibrillation, as is illustrated schematically in Fig 6.
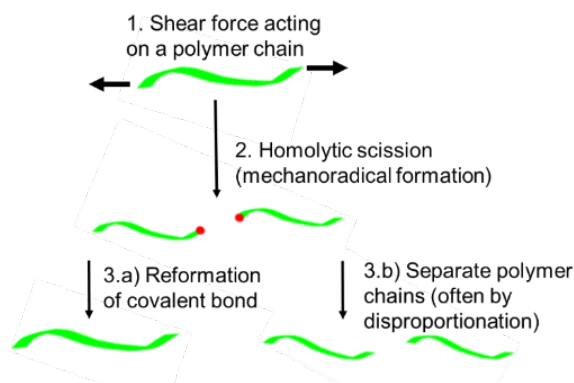
419

420 **Fig. 6** Schematic presentation of mechanoradical formation when a polymer chain is subjected to
421 a shear force (1). After the radicals are formed by homolytic chain scission (2), they typically react
422 fast, either forming new covalent bonds (3.a) or by undergoing other reactions, e.g.
423 disproportionation (3.b), that leave the fractured polymer chains separate. In the presence of
424 antioxidants or radical scavengers, such as lignin, the probability of type (a) reactions decreases,
425 enhancing the formation of separate polymer fragments

426 As mentioned earlier, there is enormous structural variation in different lignins, which inevitably

427 affects their ability to stabilize free radicals (Barclay et al. 1997; Dizhbite et al. 2004; Ugartondo

428 et al. 2008; Vinardell et al. 2008). These differences should be taken into account when evaluating

429 the hypothesis of lignin acting as a radical scavenger. More specifically, the following trends have

430 been found for lignin antioxidant properties (Barclay et al. 1997; Dizhbite et al. 2004; Hage et al.

431 2012; Ponomarenko et al. 2015; Sadeghifar and Argyropoulos 2015):

432 - Phenolic hydroxyls increase but aliphatic hydroxyls decrease antioxidant activity

433 - High molecular weight decreases the antioxidant activity (probably related to the relative
434   number of phenolic hydroxyls)

435 - Conjugated C=C bonds in the propyl side chain increase the antioxidant activity

436 - Carbohydrate structures may decrease the antioxidant activity

437 - Oxygen-containing substituents in the side chains decrease the antioxidant activity

438   Information reported on the effect of methoxy groups is contradictory; some studies have
439   associated especially ortho-positioned methoxy groups with enhanced antioxidant activity, but
440   others have found that controlled methylation of the phenolic OH groups destroyed lignin's
441   antioxidant ability (Barclay et al. 1997; Dizhbite et al. 2004; Sadeghifar and Argyropoulos 2015).

442   Given that the structure of lignin affects its radical scavenging ability significantly, it is important
443   to remember what is known about the structure of the lignin present in the pulps that are to be used
444   for CNF manufacturing. As an example, among the major structural differences between native
445   and kraft lignin is that the number of phenolic hydroxyls increases significantly both in the
446   dissolved and in the residual lignin (Froass et al. 1996; Chakar and Ragauskas 2004), which would
447   be expected to enhance the radical scavenging ability. Another change that occurs is that some
448   methoxy groups are lost during kraft pulping (Froass et al. 1996), but since various research groups
449   agree on the primary importance of phenolic hydroxyls (Barclay et al. 1997; Dizhbite et al. 2004;
450   Ponomarenko et al. 2015; Sadeghifar and Argyropoulos 2015), it seems reasonable to assume that
451   the residual lignin in chemical pulps has radical scavenging properties, despite having
452   carbohydrate structures linked to it.

453   Indirect evidence for the antioxidant activity of residual lignin was also reported by Vänskä et al.
454   (2016), showing improved thermal stability of intensely refined softwood kraft pulp in the
455   presence of residual kraft lignin, as indicated by brightness and viscosity-based DP measurements.
456   High thermal stability has also been reported for high lignin content (20%) nanofibrils derived by
457   sodium chlorite bleached pine bark (Nair and Yan 2015). On the other hand, no difference was
458   seen in the thermogravimetric analysis profile as a function of lignin content in organosolv-treated
459   pulps by Santucci et al. (2016). These inconsistencies highlight the importance of caution when
460   comparing results from different raw materials and processes. It may be speculated that
461   incorporation of a high phenolic OH lignin might be beneficial for the development of new
462   nanocellulose grades with high thermal stability, but more research is needed in this area before
463   definite conclusions can be made.

464   **The importance of hemicelluloses**

465   Depending on the chosen raw material and utilized processing method, the fibers and nanofibrils
466   prepared from them may contain not only cellulose and lignin but also hemicelluloses. Thus, a

467 complete understanding about CNF behavior and its interactions should include the properties
468 conferred not only by lignin but also by hemicelluloses.

469 Regarding CNF preparation and properties, hemicelluloses have been found to impede the
470 agglomeration of the nanofibrils. This effect is partly electrostatic in nature, as many
471 hemicelluloses possess negative charges, generating repulsion between them (Arola et al. 2013).
472 On the other hand, the side chains present in some hemicelluloses contribute to steric repulsion
473 between nanofibrils, thereby also reducing their tendency to aggregate (Hubbe and Rojas 2008;
474 Tenhunen et al. 2014). As a result of these interactions, the presence of hemicelluloses promotes
475 pulp fibrillation (Duchesne et al. 2001; Hult et al. 2001; Iwamoto et al. 2008; Tarrés et al. 2017)
476 and colloidal stability of CNF suspensions (Tenhunen et al. 2014), as will be discussed in the
477 following sections.

478 *Fibrillation*

479 As mentioned before, hemicelluloses enhance pulp fibrillation. This behavior has been attributed
480 to their ability to inhibit fibril coalescence, resulting in an open, porous fiber structure (Duchesne
481 et al. 2001; Hult et al. 2001; Pönni et al. 2012). Both cellulose and hemicelluloses readily swell in
482 moist environments but, due to their lower molecular weight and often higher degree of branching,
483 hemicelluloses have higher accessibility to water than cellulose (Yang et al. 2013). It should be
484 mentioned, however, that it is not only the hemicellulose content that determines the swelling
485 behavior of a fiber material, but also the spatial distribution of cellulose and hemicelluloses within
486 the fibrils is relevant (Tenhunen et al. 2014; Kulasinski et al. 2015). The aforementioned fiber
487 swelling leads to its softening through the breakage of hydrogen bonds, contributing to efficient
488 fibrillation (Åkerholm and Salmén 2004; Kulasinski et al. 2014, 2015). Naturally, after breaking
489 the initial fiber structure into smaller fibrils and fibril bundles, reattachment of these fragments
490 needs to be prevented in order to obtain individual nanosized fibrils. This means that producing
491 high-quality CNFs requires sufficient colloidal stability, which we will address next.

492 *Colloidal stability*

493 Colloidal stability, i.e. the ability of a particle suspension to resist agglomeration and/or
494 sedimentation by remaining in an equilibrium, plays a vital role in determining many of the

495 properties of CNF materials – from specific energy consumption (SEC) during fibrillation to

496 rheological properties and potential redispersibility after drying. As cellulose has strong affinity

497 towards itself, in practice it is necessary to prevent its characteristic tendency for fibril

498 agglomeration. One way to counteract such fibril coalescence is to introduce electrical charges in

499 the pulp material, such as in the case of TEMPO-mediated oxidation (Saito et al. 2007; Isogai et

500 al. 2011a, b) or carboxymethylation (Rácz and Borsa 1997; Wågberg et al. 2008; Siró et al. 2011),

501 in which an increase in negative charge leads to electrostatic repulsion between the fibrils at pHs

502 where the carboxyl groups are in their dissociated state. Importantly, electrostatic repulsion is

503 greatly affected by the ionic strength of the system, meaning that it can be hindered simply by

504 adding salt into the suspension (Fall et al. 2011; Junka et al. 2013). This is not the case for steric

505 stabilization, however, in which bulky molecular chains prevent particle aggregation, regardless

506 of the pH or ionic strength of the system. Nevertheless, if the bulky chains possess electrical

507 charges, such as in the case of xylan, the conformation of the polymers depends on changes in pH

508 and ionic strength (Tenhunen et al. 2014). This will in turn affect the extent of steric repulsion.

509 As mentioned, hemicelluloses can contribute to colloidal stability of CNFs by both electric and

510 steric mechanisms, depending on their structure (Hubbe and Rojas 2008). Xylans, for instance,

511 have carboxyl groups that give them a net negative charge, as well as side chains that contribute

512 to steric repulsion, and both properties influence the colloidal stability of CNFs (Tenhunen et al.

513 2014) (an example of this given in Fig.7). Similarly, galactoglucomannans can sterically stabilize

514 pitch particles in thermomechanical pulping (TMP) process waters (Hannuksela et al. 2003;

515 Tammelin et al. 2007). Recently, a number of researchers have employed the ability of

516 hemicelluloses to adsorb tightly on cellulose (Tammelin et al. 2009; Eronen et al. 2011; Littunen

517 et al. 2015) for producing core-shell structured CNFs, aiming at achieving a better control over

518 their nanostructure (Prakobna et al. 2015; Tanaka et al. 2016).

519
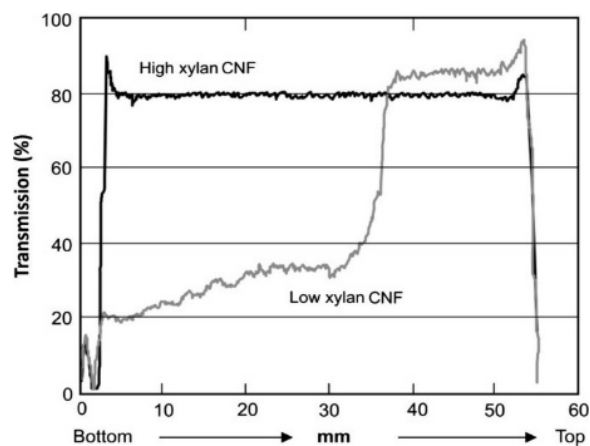
Fig. 7 Light transmission profiles of high xylan content CNFs and low xylan content CNFs. Reprinted from Tenhunen et al. (2014) with permission of Elsevier

It is evident that controlling the hemicellulose type and content by careful selection of raw materials, pulping conditions, and other processing methods is vital for controlling the properties of the resulting CNFs. As an example of this, LCNFs derived from SO_2-ethanol-water (SEW) pulps (Iakovlev et al. 2010; Iakovlev and Heiningen 2012; Yamamoto et al. 2014) and neutral sulphite pulps (Hanhikoski et al. 2016b, a) with comparable lignin contents appear to have very different water retention properties. Although for methodological differences it is not possible to quantitatively compare the water retentions of these LCNFs, the SEW-LCNFs displayed effortless dewatering (Rojo et al. 2015), whereas the NS-LCNFs had markedly high water retention values (in the range of 400 g/g) even after a minimal mechanical treatment (Hanhikoski et al. 2016a). This is most probably due to the difference in their hemicellulose contents (Chakar and Ragauskas 2004; Rojo et al. 2015). One of the challenges in comparing the properties of different CNFs is that there still are no established standardized tests that would allow a clear comparison between different CNF grades. However, reported results indicate that by selecting raw materials with varying (high or low) hemicellulose content for CNFs production, different performance of CNFs will be achieved. We thus recommend a complete lignin and carbohydrate analysis to be run from the fiber material processed to LCNFs to allow meaningful comparisons between LCNF grades.

Practical considerations for LCNFs

Consumption of chemicals and energy

540 As explained before, the required energy consumption in the production of CNFs is rather high: to
541 obtain cellulose nanofibers applying only mechanical treatments, SECs of ~30,000 kWh/ton are
542 necessary (Klemm et al. 2011; Moser et al. 2016). In contrast, by utilizing the TEMPO-mediated
543 oxidation, the SEC can be lowered below 7 MJ/kg, corresponding to 1,900 kWh/ton, while
544 obtaining a uniform transparent gel with fibril width of 3-4 nm and a length of a few micrometers
545 (Isogai et al. 2011a). TEMPO-CNFs are of very high quality but due to chemical costs, still too
546 expensive for bulk industry use (Delgado-Aguilar et al. 2015). As an alternative for TEMPO-
547 mediated oxidation, Tejado et al. (2012) decreased the energy consumption for the preparation of
548 CNFs by periodate oxidation followed by a chlorite oxidation. Their results showed that cellulose
549 nanofibrils can be liberated from the original cellulose fiber structure at a constant yield with a
550 SEC of 1,250 kWh/ton when the carboxylate content is 2.5 mmol/g. They also reported that after
551 increasing the carboxylate content to 3.5 mmol/g, the energy necessary to obtain the same
552 fibrillation level decreased even further, introducing a less energy-intensive alternative for CNF
553 production. As promising as this approach is, it has, to the best of our knowledge, been thus far
554 utilized only for bleached pulps. Other affordable approaches have been sought from enzymatic
555 pre-treatments, but although enzymatically pre-treated CNFs can be prepared from bleached pulp
556 using only 350 kWh/ton (Lindström 2016), the presence of lignin hinders the efficacy of enzymatic
557 hydrolysis (Hoeger et al. 2012, 2013), limiting the use only to bleached pulp varieties. With the
558 interest of producing nanofibrils from fibers with higher yields, efforts have been made to
559 investigate the fibrillation of lignin-containing fibers.

560 A number of studies have demonstrated that unbleached pulps tend to be easier to fibrillate than
561 fully bleached pulps. Spence et al. (2011b) reported SECs in the range of 420 kWh/ton for LCNFs
562 with an estimated specific surface area (SSA) of ~80 m^2/g. Generally, the achieved SSAs were
563 higher for unbleached fibrils than corresponding fully bleached fibrils at comparable specific
564 energy consumptions. Similarly, Lahtinen et al. (2014) reported that unbleached softwood kraft
565 pulp achieved a higher level of fibrillation after utilizing the same specific energy consumption
566 than fully bleached kraft pulps. Also Solala et al. (2012) reported a more thorough fibrillation of
567 unbleached of hardwood kraft pulp in comparison with its fully bleached counterpart. Since
568 unbleached pulps render higher yields of the initial lignocellulosic material and require lower
569 dosages of chemicals to be produced in the first place, LCNFs derived from them might be a viable

570   option for bulk uses where their inherent brown colour does not present problems (Solala et al.
571   2012; Delgado-Aguilar et al. 2016). In terms of particle size, Rojo et al. (2015) reported softwood
572   LCNF fibers containing 0, 2, 4, and 14% lignin with diameters of 44 ± 3, 25 ± 1, 20 ± 2, and $16 \pm$
573   2 nm respectively. Also these results positively correlate with the ease of fibrillation due to
574   increases in lignin and hemicellulose contents.

575   Generally, it should be noted that the comparison of individual studies is complicated because of
576   a lack of consistent, standardized vocabulary in the field; for instance, the exact meaning of the
577   term 'nanocellulose' varies in the literature. Moreover, the reported values are often not
578   comparable to one another, as different analytical techniques are favored by different research
579   groups. Recently, this issue was addressed by Foster et al. (2018) on their review that discusses
580   recommended analytical protocols in this research area.

581   *Dewatering and redispersibility*

582   Typically, CNF suspensions contain 98-99% water and only 1-2% of the cellulosic nanomaterial.
583   Even when higher consistencies can be achieved, they tend to be in the range of 5%, meaning that
584   transportation costs for CNF gels are very high in relation to the transported dry mass. Water
585   removal from CNFs is energy intensive, which is not ideal on itself, but more crucially, it is
586   accompanied by irreversible fibril coalescence, often referred to as hornification by pulp and paper
587   scientists. The extent of coalescence upon drying can be limited by solvent exchanges (Henriksson
588   et al. 2008) or freeze-drying (Lovikka et al. 2016), but these methods are tedious and time-
589   consuming, rendering them impractical in an industrial scale. Alternatively, the surface chemistry
590   of the CNFs may be modified to allow redispersibility after drying by introducing electrostatic
591   repulsion, like in the case of carboxymethylated CNFs (Eyholzer et al. 2010), or by using steric
592   stabilization from pectin or other components (Hietala et al. 2017). Recently, Visanko et al. (2017)
593   reported having made redispersable LCNF nanopapers from spruce ground wood pulp (lignin
594   content 27.4%) when dried from ethanol, which can probably be attributed to the lower density
595   and interfibrillar contact in these nanopapers. Importantly, similar behavior was not seen in fully
596   bleached CNFs (Visanko et al. 2017a), suggesting that at least some lignin-containing nanofibril
597   grades have unique properties that could promote their use in an industrial scale.

598   *Barrier films*

24

599 One of the frequently proposed uses for CNFs has been to use it in barrier applications, for example

600 in food packaging (Lavoine et al. 2012). With a combination of moisture and pressure, CNFs can

601 be turned into dense films, or so-called nanopapers, with porosities in the range of 10-20%

602 (Sehaqui et al. 2010; Österberg et al. 2013). In dry state, the average pore size in such films is

603 typically around 1-10 nm (Henriksson et al. 2008; Lavoine et al. 2012) but the film structure

604 changes in moist conditions, causing a decline in its barrier properties for oxygen and water vapor

605 (Aulin et al. 2010). One working hypothesis has been that lignin-containing films should have

606 better barrier properties, as they are inherently less hygroscopic. However, as discussed earlier,

607 this depends heavily on the method of film formation. If films are produced at temperatures below

608 the softening temperature of lignin, efficient H-bonding between nanofibrils may be compromised,

609 leading to increased pore formation and poor barrier properties (Spence et al. 2010; Santucci et al.

610 2016). On the other hand, if hot-pressed in moist conditions, the lignin in the LCNF films will

611 soften and fill voids as schematically illustrated in Fig. 8. Rojo et al. (2015) demonstrated an

612 improvement on the barrier functionality of the films in terms of oxygen permeability as the lignin

613 content of the samples increases when measuring at 50% relative humidity. At 80% relative

614 humidity, the results showed a slight increase which was not significant when compared with the

615 improvement at 50% relative humidity (Fig 9). Moreover, lignin has been shown to decrease water

616 uptake and increase water contact angle (Wang et al. 2012; Rojo et al. 2015; Herrera et al. 2018),

617 as long as control over the hemicellulose content is maintained (Ferrer et al. 2012).

618

619 **Fig. 8** Proposed model to describe the location of the lignin within LCNF suspension after filtering
620 (left) and LCNF nanopaper after pressing (right) Reprinted and adapted from Rojo et al. (2015)
621 with permission of Royal Society of Chemistry.

622
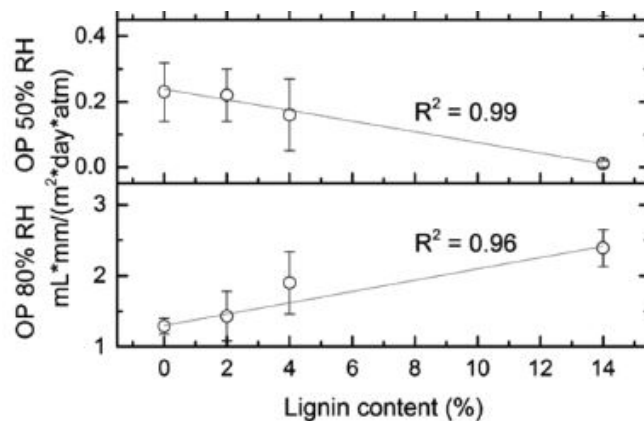
Fig. 9 Oxygen permeability of hot-pressed nanopapers with different lignin contents at 50 and 80% relative humidity. Reprinted and adapted from Rojo et al. (2015) with permission of Royal Society of Chemistry.

In summary, considering just the lignin content of a potential CNF material is not sufficient; it is vital also to control the content of heteropolysaccharides and electrical charges, as both significantly affect the interactions between the material and water. In addition to the chemical composition of LCNF nanopapers, also their morphology in terms of porosity and pore size is of central importance when analysing nanopapers for their barrier properties.

Emulsions

About a decade ago, Andresen and Stenius (2007) reported that hydrophobized microfibrillated cellulose can be used as a stabilizer in Pickering emulsions. Since then, a number of papers have been published on the subject (Xhanari et al. 2011; Cunha et al. 2014; Gestranius et al. 2017). In order to efficiently stabilize emulsions, particles should show a certain extent of amphiphilicity (Kalashnikova et al. 2013). To achieve this, previous studies have commonly utilized synthetic hydrophobization routes (Andresen and Stenius 2007; Xhanari et al. 2011; Cunha et al. 2014), but similar effects can also be reached by utilizing LCNFs (Fig 10) (Ballner et al. 2016; Yan et al. 2016) or lignin particles (Nypelö et al. 2015; Li et al. 2016). Although the exact chemical nature of residual lignin can be difficult to control, there are obvious benefits to avoiding the multistep process of first removing all lignin through sequential bleaching and then derivatizing the nearly pure cellulose with synthetic hydrophobic moieties. We therefore foresee benefits in exploration of lignin-containing nanocelluloses for emulsion stabilization, especially in applications where in-situ polymerization is feasible, as this would solve many of the problems presently associated with

645 CNFs use in composite reinforcement. In fact, Yan et al. (2016), Ballner et al. (2016) and Gindl-
646 Altmutter et al. (2015) have successfully applied this principle to produce composites of LCNFs
647 and synthetic polymers via emulsion polymerization, as discussed in the following section.

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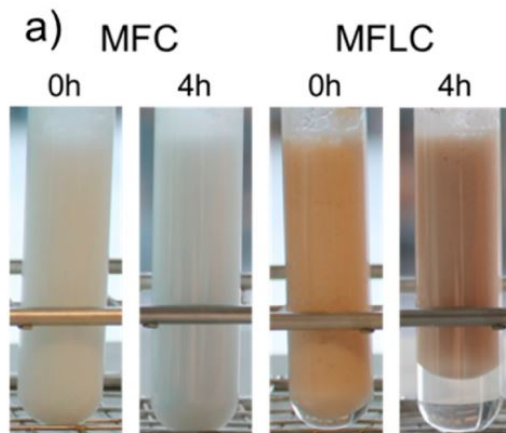
Fig. 10 Styrene-in-water emulsions stabilized using nanofibrillated cellulose (MFC) and lignin-
containing nanofibrillated cellulose (MFLC), at 0 and 4 hours after after mixing. Readapted and
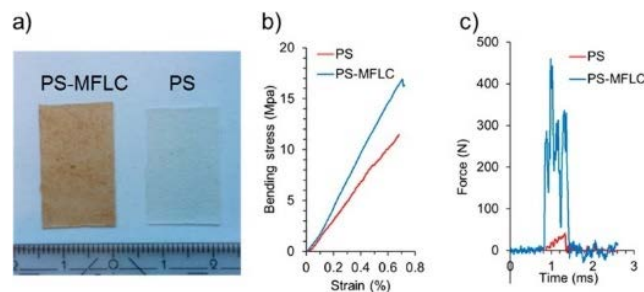reprinted from Ballner et al. (2016) with permission of the American Chemical Society.

652 *Nanocomposites*

653 The utilization of cellulose nanofibrils from bleached fibers has been widely studied as a
654 reinforcing agent in composite materials, prepared by techniques such as solvent casting (Wågberg
655 et al. 1987; Leitner et al. 2007) or emulsion polymerization (Nikfarjam et al. 2015). Due to the
656 high aspect ratio and moderately low thermal stability of CNFs, melt extrusion is usually not a
657 practical method to produce such composites.

658 It is well known that the reinforcing capacity of cellulose nanoparticles combined with different
659 matrices occurs due to strong interactions between the fibrils, allowing to improve the mechanical
660 performance of the composites made thereof (Siqueira et al. 2010; Kargarzadeh et al. 2018). This
661 strong network of nanofibers can be considered the result of a percolation mechanism which
662 assumes that above certain concentration of the fibers, the mechanical properties of the composites
663 will be improved (Boufi et al. 2014) due to increased hydrogen bonding between them (Dubief et
664 al. 1999).

665 In addition to CNFs, the incorporation of LCNFs to different composite materials has become
666 more common, employing a number of matrix materials, such as polylactic acid (Sun et al. 2014;

667 Wang et al. 2014), starch (Ago et al. 2016), polypropylene (Ferrer et al. 2016), polycaprolactone

668 (Herzele et al. 2016), polystyrene (Ballner et al. 2016), and polyurethane (Visanko et al. 2017b).

669 Ballner et al. (2016) utilized in-situ polymerization of styrene in water stabilized by LCNFs,

670 followed by hot-pressing, and obtained composites with increased bending stress and Charpy

671 impact bending strength in comparison to pure PS (Fig. 11). These results are an indication of the

672 potential of LCNFs to be used in composite reinforcement.

673

674 **Fig. 11** The visual appearance of hot-pressed PS and PS-MFLC films (a) and results of mechanical
675 characterization by static three-point bending (b) and Charpy impact bending (c). Reprinted from
676 Ballner et al. (2016) with permission of Royal Society of Chemistry

677 Similarly, Nair et al. (2017) reported that the tensile strength of LCNF/epoxy composites, with

678 23% of lignin content, increased from 65 ±6 MPa to 134 ±10 MPa. This increment was attributed

679 to the increased compatibility between the fibrils and the epoxy matrix caused by the presence of

680 residual lignin. Following this trend, Chen et al. (2019) incorporated LCNFs as a reinforcement

681 material in polymeric diphenylmethane diisocyanate (pMDI) resins, commonly used for wood

682 composite manufacturing. Their results showed positive effects due to the increase in bond line

683 between wood and adhesive at different LCNF loadings. On the other hand, Diop et al. (2017)

684 utilized LCNFs as an adhesive in fiberboards, reporting that by adding 20% LCNFs, the modulus

685 of elasticity (MOE) was 300 MPa higher than the standard requirement of 1241 MPa. Regarding

686 the required modulus of rupture (MOR), by incorporating 20% LCNFs, they reached a MOR value

687 of 12.1 MPa which was close to the target value for commercial panels of 12.4 MPa. Moreover,

688 even if the vast majority of studies have utilized oil-based, non-biodegradable polymers, there are

689 indications that LCNFs can be successfully combined with biobased, compostable polymer

690 matrices. As an example of this, the addition of LCNFs to polylactic acid was studied by Wang et

691 al. (2014) and Sun et al. (2014) who analysed the mechanical properties of films made thereof,

692 agreeing that the addition of LCNFs improved the mechanicals properties, such as tensile strength

693 and elongation at break, when compared with pure PLA films.

694 Despite these promising findings, the reports on LCNF-reinforced composites are scattered,

695 occasionally showing moderate if any improvement in mechanical performance, often reporting

696 increases only in Young's modulus (Iwamoto et al. 2014; Ferrer et al. 2016; Horseman et al. 2017;

697 Kim et al. 2017). This highlights the complexity of the interplay between properties such as fibril

698 size and shape, their distribution in the matrix, adhesion between different components, matrix

699 crystallinity, etc. that influence the performance of composite materials.

700 Regarding the present state of the art, the use of LCNF composite materials holds great potential,

701 as the LCNFs are inherently more compatible with hydrophobic matrices than the analogous

702 bleached CNF, allowing facile mixing of the fibrils and the matrix. Combined with the potential

703 of cost and environmental impact savings through lower SEC and need of chemical processing in

704 comparison to bleached CNFs, we believe it is an area worth exploring even further to develop

705 bio-based alternatives for oil-derived synthetic polymer materials.

706 **Conclusions**

707 Pulp and paper industry has traditionally viewed lignin as something that needs to be removed in

708 order to produce high-quality paper. Although there are many similarities between pulping and

709 papermaking and the production of cellulose nanofibrils, the end uses and therefore also the desired

710 functionalities are partly different. For this reason, we promote a change of paradigm in which

711 lignin is seen as a tool that can be used to tailor the properties of CNFs rather than a problematic

712 component that is always detrimental for high-quality products.

713 For this to happen, it is of uttermost importance to consider the amount and structure of the lignin

714 in question as this will affect the ease of fibrillation, the development of interfibrillar H-bonding

715 as well as the water interactions of the material. Presently, the body of literature on LCNFs remains

716 rather scattered, including a wide range of raw materials and mechanical, chemical or enzymatic

717 processing methods. For this reason, comparisons between individual studies are not always

718 straightforward. In general it can be stated that taking into account the high yield, low chemical

719 consumption and manageable mechanical energy consumption of LCNFs, they can be viewed as

720 an economically and ecologically viable family of materials with a number of potential
721 applications.

722 In order to produce extensively fibrillated LCNFs, it is necessary to first break the network
723 structure of native lignin. In practise, this means including a moderate pre-delignification step prior
724 to fibrillation. Additionally, the presence of hemicelluloses is often linked to the presence of lignin;
725 and both can facilitate fibrillation.

726 While lignin is believed to possess antioxidant properties, stabilizing mechanically or thermally
727 formed free radicals, conclusive evidence of how this mechanism affects the fibrillation process is
728 still needed.

729 Interactions between water and LCNFs are complex and depend on a number of factors, including
730 lignin and hemicellulose contents, electrical charge density, and sample morphology. Lignin may
731 be used as a natural hydrophobizing agent in CNFs, which could be beneficial for example in
732 composite reinforcement and Pickering emulsions.

733 **Main nomenclature**

734 LCNFs: lignin-containing cellulose nanofibrils

735 BCNFs: bleached cellulose nanofibrils

736 CNFs: cellulose nanofibrils

737 CNCs: cellulose nanocrystals

738 MFC: microfibrillated cellulose

739 SW: softwood

740 HW: hardwood

741 LCCs: lignin-carbohydrate complexes

742 DP: degree of polymerization

743 CrI: crystallinity index

744   DSC: differential scanning calorimetry

745   WRV: water retention value

746   WVTR: water vapour transmission rate

747   WCA: water contact angle

748   MOE: modulus of elasticity

749   MOR: modulus of rupture

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