Effect of solvent fractionation pretreatment on energy consumption of cellulose nanofabrication from switchgrass

Hang Chen[a,b], Xiaoyu Wang[b,c], Joe Bozell[b], Xinghao Feng[b,d], Jingda Huang[b,e], Qian Li[b.e], Art Ragauskas[b], Siqun Wang[b*], Changtong Mei[a*]

a. College of Materials Science and Engineering, Nanjing Forestry University, Nanjing 210037, China

b. Center for Renewable Carbon, University of Tennessee, Knoxville, Tennessee 37996, United States

c. School of Chemistry and Chemical Engineering, Huaiyin Normal University, Huai'an 223300, China

d. College of Furnishings and Industrial Design, Nanjing Forestry University, Nanjing 210037, China

e. School of Engineering, Zhejiang A&F University, Hangzhou 311300, China

*Corresponding author: Siqun Wang

E-mail: swang@utk.edu

Telephone: +1 (865) 946-1120;

Changtong Mei

E-mail: mei@njfu.edu.cn

Telephone: +86 (25)85427742

Abstract: Lignin-containing cellulose nanofibers (L-CNFs) with various lignin contents were produced by a grinding process from switchgrass, which were pre-treated using organosolv fractionation. The effect of different fractionation conditions (temperature and time) and different number of grinder passes on the energy consumption and morphologies of L-CNFs were investigated. Results showed that nanosized fibers were found in organosolv fractionated samples before grinding. After several grinding passes, L-CNFs with a similar degree of fibrillation as commercial cellulose nanofibers (CNF) were obtained from the fractionated materials. It is beneficial to save energy consumption in the grinding process. The dimensions and dispersion of L-CNFs were significantly influenced by the lignin content in the L-CNFs. Longer and well separated nanofibrils were observed from transmission electron microscopy and fluorescence microscopy with appropriate residual lignin (~13.7 ±1.59%) in the L-CNFs compared to those of L-CNFs with either lower or higher lignin contents. Therefore, microsized and nanosized lignin particles were successfully obtained in a single process, and they not only facilitated L-CNFs dispersion but also help to decrease the energy consumption during the grinding process.

Keywords： solvent fractionation, processing energy, high residual lignin cellulose nanofibers, Supermasscolloider, switchgrass

Introduction

With the increasing consumption of plastic, fuel and non-renewable energy resources annually, there is an essential need to develop green, renewable and environmentally friendly alternatives to petroleum-based plastics as functional materials. In this context, cellulose nanofibers (CNFs) have gained attention as a prime candidate for many materials science applications and have been used to produce acrylonitrile butadiene styrene (ABS)/carbonized cellulose nanofibers (CCNF) nanocomposites [1, 2], ultra-light carbon aerogels [3], superhydrophobic coatings [4], barrier coatings [5] and energy storage devices [6] due to high surface-to-volume ratio, and exceptional mechanical and physical properties [7]. CNFs have diameters at one nanoscale dimension (1-100 nm) [8] conformed by crystalline and amorphous phases at the nanoscale [9] and aspect ratio (length/diameter) is more than 100 [10].

Cellulose nanofibers can be obtained from diverse sources as wood pulps [11], sisal [12], banana leafs [13], waste newspaper [14], wheat straw [15] through mechanical fibrillation. However, significantly high cost demand required by mechanical fibrillation process is the major challenge for their application at industrial level [11, 16, 17]. Only a few studies focus on reduction of cost and energy consumption on CNFs production. Spence et al. (2011) compared different fibrillation processes and reported that grinding required less energy consumption (5580 kJ/kg in total) than homogenization which reached at 78800 kJ/kg and it can avoid clogging issues which raised in homogenization process [18]. But it is challenging to manufacture nanoscale fibers from raw materials because the cellulose is embedded by matrix substances (lignin and hemicellulose), it is imperative to extract hemicellulose and separate lignin. Despite chemical pretreatments such as TEMPO-mediated oxidation [19-21], periodate–chlorite oxidation [20] and enzymatic pre-treatments [7] has been used to decrease the energy requirements of the mechanical process to 2 MWh/t [22], due to low yield (30%-40%) of these pretreatments, more materials are required and increase the cost of manufacturing CNFs drastically [10, 23, 24].

Lignin, as main component of lignocellulosic materials, is the second-most abundant biopolymer and the most resourceful aromatic-containing polymer in nature [13, 25, 26]. It intimately linked wood and non-wood fibers as a random polymer network which is considered to be the material to hold other polysaccharides (hemicellulose and cellulose together)[27, 28] and its strong crosslinking is an obstacle to water absorption in cell walls of plants. In addition, lignin has more stable thermal property and harder to decompose than cellulose and hemicellulose due to its high molecule weight. Most studies of CNFs used lignin-free pulp fibers. However, lignin-residual cellulose fibers represent it is a potential material for producing lignin-containing cellulose nanofibers (L-CNFs). Several studies have reported that lignin improved the thermal, mechanical and hydrophobicity properties of cellulose products[29-32]. Moreover, it was reported that enzymatic pre-treatment to obtain pure CNFs had higher production costs with 13.71 €/kg compared with producing lignin-containing CNFs with a cost of 2.55 €/kg [15]. Microfibrillation up to now is challenging when using wood fibers with a high level of residual lignin (>25%) [16]. By given advantages of residual lignin in cellulose fibers, the subsequent study is needed to investigate the effect of residual lignin in CNFs on the energy consumption of producing L-CNFs and obtain controlled content of residual lignin in cellulose materials via adjusting pre-treatment conditions.

Recently, a relatively innovative organosolv fractionation technology, as a lignocellulose biorefinery process, was demonstrated for separating raw lignocellulosic materials into cellulose, hemicellulose, and lignin for subsequent applications [33-35]. In this process, the lignocellulosic material is obtained using a ternary mixture solution of methyl isobutyl ketone (MIBK)/ethanol/water with an action of an acid promoter, which dissolves lignin and hemicellulose selectively, leaving cellulose as an undissolved solid[36, 37]. This technology is an effective method to produce lignin at high purity (94.6%) [36] and achieve cellulose containing residual lignin which was easier to purify than similar materials produced by other methods. This is significant for the application of cellulose, which requires high-purity starting materials [34].

In this research, cellulose materials with varying content of residual lignin (from 6.28% to 21.0%) were extracted from switchgrass, by organosolv fractionation process under certain conditions. The aims of this study were to produce L-CNFs with lignin nanoparticles through a single process with low energy consumption and to quantify the effect of lignin content on the nanofibrillation. Organosolv fractionation conditions, as pretreatment to control lignin content, was inquired as well. Morphology and water retention values of cellulose materials were determined to estimate the degree of fibrillation of L-CNFs at different numbers of grinding passes. In addition, the features of the lignin on the L-CNFs was analyzed via fluorescence microscopy, Fourier-transform infrared spectroscopy and solid-state ^{13}C NMR spectroscopy.

Materials and methods

Organosolv fractionated materials

Seven never-dried fractionated switchgrass samples (LC20, LC18, LC15, LC13, LC12, LC8 and LC6), treated via organosolv fractionation under different temperature and time conditions, were provided by Prisma Renewable Composites, LLC, USA. Organosolv fractionation process has been reported by Tao et al. (2016). Briefly, switchgrass chips were sealed in a stainless-steel reactor (home made) which operated in flow-through mode, and soaked with the mixture solution (MIBK/ethanol/water at a ratio of 16/34/50 wt.%) with 0.1M sulfuric acid that flowed into reactor. After reactor was heated to target temperature electrically, the solution was pumped through the reactor subsequently. The lignin content of samples was determined by standard procedure (NREL/TP-510-42618) and are listed in Tables 1 and 2. For comparison, a commercial CNF product was purchased from the University of Maine.

Mechanical fibrillation to produce nanofibrils

Each sample was soaked in deionized water (1wt% of solid content) to weight of 1500g for 24 h at room temperature and then blended for 2 min with an Osterizer blender to obtain cellulose slurry. The slurries were then fibrillated using a SuperMassColloider (MKCA6-5JR, DISK model: MKGA46, Masuko Sangyo Co., Ltd., Japan) at 1500 rpm. The slurries were fed continuously into the colloider which consists of two parallel stone grinding disks. The grinding experiments were conducted with the gap between the two disks set to -100 μm for the first pass and then -200 μm for the following twenty passes. The zero gap corresponded to the starting point when the upper disk graze lower disk before slurry was poured. The presence of slurry avoided direct contact between two disks, even in the case of a negative gap.

Preparation of L-CNFs films

The respective L-CNFs suspensions and reference cellulose nanofibers were used to prepare films for the detail characterizations of the nanofibers. Each of suspensions was diluted to 0.33 wt% of solid content and stirred over night at room temperature to ensure the fibers get dispersed evenly. Then suspension was slowly pour into a 50 mm diameter filter funnel which covered with a mixed cellulose filter membrane (pore size is 0.45 μm, Xinya Purification Devices Co. Ltd, China) to obtain gel films with a dry basis weight of ca.80 g/m^2. The gel films were covered between two filter papers and placed with 2 pieces of glasses. The films were oven dried at 100 ˚C for 24 hours and then stored in a conditioned room (25 ˚C and 50 % relative humidity) for future test.

Energy consumption

Each cellulose suspension was passed through the Supermasscolloider twenty-one times while recording the energy consumption with a power meter (EXTECH, 1000 A HVAC True RMS Power Clamp-On Model 380975). The measured power was normalized by the dry weight of the processed material. Samples were collected (*ca.* 70 mL) at 0, 3, 6, 9, 12, 15, 16, 17, 18, 19, 20, and 21 passes for further analysis. Yield was calculated as dry weight of L-CNFs to dry weight of pretreated material expressed as a percentage.

Water retention value

The water retention value (WRV) was used to measure the degree of fibrillation. A 25 mm diameter stainless steel cap with holes of 1 mm diameter was used with Whatman™ grade 5 filter paper placed in the base of the cap to filter the wet masses. Four caps were filled with 8 g of the wet samples (1 wt.% solid content) and placed inside sample holders for centrifugation for 30 min at 4000 rpm using an AccuSpin 400 (Fisher Scientific) with a relative centrifugal force of 900 g to eliminate non-bonded water. Next, the samples were placed onto an aluminum dish (Fisherbrand™), weighed, and then dried at 105 °C for 24 h until they reached a constant mass. The average WRV value was then calculated using the following equation:

$$WRV = \frac{W_{wet} - W_{Dry}}{W_{Dry}} \times 100\%$$

where, W_{Wet} is the weight of the sample after centrifuging and W_{Dry} is the absolute dry weight of the samples.

Transmission electron microscopy

Transmission electron microscopy (TEM) images of the morphology of the fibers after different grinding procedures were observed using a Zeiss Auriga SEM/FIB crossbeam workstation (Germany) at 30 kV. For each material, the slurries collected at 0 and 21 passes were diluted to produce ~0.005% w/w suspensions. Drops of these suspensions were deposited onto carbon film (200 mesh) and dried at room temperature. The diameters and lengths of cellulose nanofibers were calculated from TEM images by image editor software (Photoshop CS 4, Adobe Co., Ltd., U.S.A), 300 fibers of each samples were measured and analyzed.

Fourier-transform infrared spectroscopy

Fourier-transform infrared spectrometry (FTIR; Spectrum One, PerkinElmer, UK) with an attenuated total reflectance accessory was used to obtain spectra for the L-CNF samples processes at 21 passes. The spectra were collected on the range from to 500 cm^{-1} to 4000 cm^{-1} with 32 scans. All L-CNF samples were dried at 105 °C for 24 h before analysis.

Solid-state ^{13}C NMR spectroscopy

Solid-state NMR measurements were performed at room temperature using a Bruker Advance III 600 MHz spectrometer equipped with 4 mm probes for magic angle sample spinning and cross polarization tests. The operating frequencies of carbon is 125 MHz and the speed is 7000 Hz. 800 scans were accumulated for each sample.

Fluorescence microscopy

The lignin distribution in the fiber was investigated by fluorescence microscopy using a Zeiss LSM 510 META. Fibers of LC20 samples at 0 and 21 passes were diluted to solid content of 0.1 wt.% by distilled water. Then drops of diluted samples were placed on a microscope glass and covered by a cover glass for observation.

Water contact angle

The water contact angle (WCA) of L-CNF films were measured using an EasyDrop FM40 system (Krüss GmbH, Germany). Water droplets with a volume of 60 μL were carefully dropped on the surface. Four measurements were made for each sample.

Result and discussion

Water retention value and energy consumption

Water retention value is an empirical method to appraise water uptake of cellulose, and the water retention value for cellulose nanofibers increases because of increment on cellulose surface area. Therefore, WRV is a useful reference to evaluate the degree of fibrillation. The energy consumption plays a significate role in assessing the environmental impact of CNF and their applications. As shown in Fig. 1, the WRV of the seven materials tested here significantly increased during the grinding process. The residual lignin eased mechanical fibrillation, and the WRV of LC20, LC18, LC15, LC13, LC12, LC8 and LC6 increased from 289, 285, 249, 205, 217, 227, 257 to 507, 456, 551, 557, 547, 528, 502 or approximately 75.4%, 60.0%, 122%, 172%, 152%, 133% and 95.3% respectively. After three grinding passes, the WRV of LC20 reached 426, higher than of CNF (365), while the energy consumption of LC20 at three passes was 3.36 kWh/kg. In the case of the LC6 sample, the WRV reached 385 with an energy consumption of 2.76 kWh/kg after three passes. Samples LC15, LC13, LC12, and LC8 showed values above the reference values at six passes: 396 (for 1.89 kWh/kg), 369 (for 4.13 kWh/kg), 400 (for 2.54 kWh/kg) and 432 (for 6.47 kWh/kg), respectively, while LC18 consumed 7.90 kWh/kg at twelve passes. After fifteen passes, no further increases in WRV were observed with further processing. This indicated that the average fiber diameter decremented to a minimum within a limited number of passes using this grinding equipment. Fig. 2 shows that after 21 passes, the WRV of LC13 was higher than those of other samples. When the lignin content was within the range of 8.89% to 15.3%, a lower amount of energy was required to reach the target WRV than the samples with higher residual lignin contents. While a limited amount of residual lignin helped the fibers separate and be fibrillated into nanofibers, lignin contents >15.3% required more energy to process because of the existence of strong covalent linkages between cellulose and lignin; breaking the cross-linked lignin barrier to fibrillate L-CNFs from fibers is difficult. The WRV values after 21 grinding passes of both LC20 and LC6, with lignin contents of 21.0% and 6.28%, respectively, were similar, while LC20 required more energy to process than LC6. Above all, the WRV of L-CNFs, which obtained after 21 passes, were LC13>LC15>LC12>LC8>LC6>LC20>LC8, and the energy consumption obtaining those L-CNFs were LC20>LC8>LC13>LC6>LC12>LC15>LC18. Table 3 lists comparison of energy consumption in present study with consumption in previous studies. It showed a large difference in the energy consumption and degree of fibrillation existed upon pretreatment, processing methods, lignin content and raw materials. In this sense, even though the lignin content was similar between LC 20 and LCNFs from banana leaf, energy consumption of LC

20 was slightly higher with better separation. On the other hand, the homogenizer had much slower processing flow rate than grinder which led to higher energy requirement, it's logic that energy consumption of all samples in present study required 2-3 times lower than energy consumption reported in Delgadoaguilar et al. (2016).

Morphology

TEM images of the morphology of the starting materials are shown in Fig. 3. As shown in Fig. 1, the WRV of the original fractionated samples was in the range of 205–289, close to that of CNF (365), but much higher than that reported for similar materials in a previous study [39]. Nanosized fibers were clearly visible for fractionated samples (Fig. 3 a–i), perhaps as a result of cellulose depolymerization by the acid during the solvent fractionation process. A previous study [34] showed that MIBK is a good solvent for lignin and hemicellulose, making cellulose accessible to the acid. It was reported that the concentration of the acid had a strong effect on the amount of cellulose released into glucose, as well as the pumping time and temperature of fractionation pretreatment. In this study, the residual lignin content decreased as the temperature increased from 130 to 150 °C, and then sharply increased at 160 °C (Table 1). The cellulose dissolves very slowly below 150 °C, while the reaction became much more rapid above this temperature. The proportion of soluble lignin increased stably under the temperature conditions used here.

Fractionated samples were fibrillated into L-CNFs in the form of gels after 21 grinding passes, as shown in Fig. 3. The fibril diameter clearly decreased with decreasing lignin content for the range of 6.28–13.5% (Table 3). When the lignin content was more than 13.5%, the diameter increased with increasing lignin content. As observed from the TEM images and Table 3, the mean fibril diameters were 16.5 nm, 20.1 nm, 14.6 nm, 11.7 nm, 15.2 nm, and 15.3 nm for the LC20, LC18, LC15, LC13, LC8, and LC6 samples, respectively, indicating that the fibril lengths decreased with decreasing lignin content. After 21 grinding passes, slightly longer and well-separated nanofibrils were obtained from LC13 than from other samples. Moreover, the diameter distribution became more uniform and narrower as the lignin content increased to appropriate amount (~13.5%) as lignin acted promotion in fibrillation. However, when lignin content increased over this range, residual lignin protected cellulose during the grinding process to impact fibrillation. More separated and longer fibers were observed for LC20 than LC6. These results suggest that lignin has the ability to scavenge radicals and can prevent crosslinking between cellulose fibrils, also, appropriate residual lignin can lead to easier defibrillation and longer nanofibrils.

Micro- and nano-sized lignin particles were apperceived in the TEM images of both samples and were more prominent in high residual lignin fibrils due to agglomeration during grinding[27, 30]. A color change from dark to light brown was observed in lower lignin content samples (Fig. 4). After 21 grinding passes, the color of the L-CNFs was lighter than the original fibers, and lignin fragments and particles sediments were observed at the bottom of the containers, however, those sediments weren’t observed in samples before grinding.

Fluorescence mapping was used to study the distribution of lignin in switchgrass samples. Fluorescence microscopy is a straightforward and potent method for characterizing the lignin distribution in plant structures as lignin shows auto-fluorescence at 525 nm. The brightness of the fluorescence signal is directly and linearly proportional to the lignin concentration. Comparing Fig. 5a and 5b, showing fluorescence maps of LC20 before grinding and after 21 grinding passes, respectively, indicating that lower fluorescence intensity was observed on the surfaces of fibers which obtained after 21 passes. As shown on Fig. 5b and 5c, lignin was peeled off from the fiber surface, while lignin fragments and micro/nanosized particles formed by friction force in fibers and disks during grinding process and distributed around the cellulose nanofibers or on the surfaces of cellulose nanofibers.

Fourier transform infrared spectroscopy

The FTIR spectra of pretreated samples and L-CNFs samples with various lignin content are shown in Fig. 6a and 6b, where Fig. 6a shows the 4000–500 cm^{-1} region and Fig. 6b shows a magnified view of the 1800–800 cm^{-1} region; the spectrum for commercial CNFs is also included for comparison. FTIR spectra of pretreated samples and L-CNFs help to reveal the structural variation of fibers during fibrillation. Fig. 6a shows a comparison of L-CNFs samples containing different contents of residual lignin, the intensities of peak increased as the lignin contents reduced which appearing at 3330 cm^{-1}. It is generally due to the hydroxyl stretching vibration absorption in the cellulose structure [32]. This peak was more intensity in LC6 than other L-CNFs with higher lignin. Those increases could hint the higher presence of free OH groups in L-CNFs with lower residual lignin. Water uptake capability of fibers is associated with quantity of hydroxyl groups on the fibers' surfaces. The peak at 1640 cm^{-1}, representing the hydrogen bonds formed by absorbed water in L-CNFs, increased with decreasing lignin content of L-CNFs, which means the strongest peak showed in LC6 and weakest peak showed in LC20. This result shows that the residual lignin contributes to the hydrophobic ability of L-CNFs because the lignin coated on the cellulose fiber's surface and restrained the hydrogen bonds [40]. The peaks at 1730 cm^{-1}, 1507 cm^{-1}, 1161 cm^{-1} and 1110 cm^{-1} represent C=O groups, aromatic skeletal, COC stretching in ester group and aromatic C-H deformation of S-units in the residual lignin, respectively. As compared with pretreated samples, the intensity of those peaks reduced in the L-CNFs samples, which suggests that lignin was partly removed from fibers' surfaces after grinding [13]. The peak at 1370 cm^{-1} were related to the C–H group vibration and glycosidic bonds in the cellulose structure. The peak at 1028 cm^{-1} corresponded to the C–O–C pyranose ring stretching vibration and cellulosic glycosidic linkages [41, 42], while the peak at 896 cm^{-1} was related to the typical cellulose structure [43]. The peak at 803 cm^{-1} attributed to the out of plane bending vibration in lignin which appeared in all spectra of L-CNFs, however, it wasn't observed in spectra of samples at 0 pass. It may attribute to the form of lignin particles after grinding. We observed peaks in the L-CNFs spectrum generally attributed to (1028 cm^{-1}), CH_2 scissoring motion in cellulose (1430 cm^{-1}), and CH_2 rocking vibration at the C6 carbon (1314 cm^{-1}) [44]. while the peak appearing at around 1233 cm^{-1} could represent the present of the O–H deformation from the phenolic group (C–OH stretching)[45]. Both of those peaks of cellulose were still observed in all spectrum where they appeared with a lower intensity in L-CNFs samples than materials before grinding.

^{13}C-CP/MAS NMR

Solid-state ^{13}C-CP/MAS NMR spectroscopy was used to analyze the lignin-coated cellulose fiber structure. The chemical shifts were assigned following the former research, as shown in Table 4 [46, 47]. Fig. 7 shows the ^{13}C-CP/MAS NMR spectra of LC20 fibers before grinding and after grinding for 21 passes. Peak 1 at 121 ppm was attributed to the carbons of lignin syringyl (aromatic unit with two methoxyl groups) and guaiacyl (aromatic unit with only one methoxyl unit), this signal disappeared after 21 passes. Peak 2 at 107 ppm was attributed to the C-1 carbon of cellulose. Peaks 3 and 4 at 91 and 87 ppm, respectively, were assigned to the resonances of the C4 of crystalline and amorphous cellulose, respectively. Peaks 5 and 6 at 77 and 75 ppm were assigned to C-2, C-3, and C-5 in the cellulose unit. Peak 7 at 67 ppm was due to the C-6 glucopyranosyl repeating units in crystalline cellulose, peak 8 was assigned to Cγ in lignin, and peak 9 was due to the methoxyl groups of lignin. The signal-to-noise ratios of the LC20 sample before grinding (Fig. 7a) and after 21 passes (Fig. 7b) were clearly different. Comparing with other samples, higher intensity signals from cellulose (2–8) were observed for the LC20 original fibers. In addition, the lignin peaks (1, 8, and 9) were weaker for the LC20 L-CNF sample than those of the LC20 before grinding. Although the intensity slightly descended, those characteristic peaks of cellulose were still observed in both spectrums of sample before grinding and after grinding. This result represents that the molecular structures of cellulose weren’t changed during grinding. However, shearing forces and frictional force between fibers generated sufficiently high stresses to form nanoscale fibers, lignin micro-

/nano-sized particles and fragments.

Water contact angle

The average water contact angle (WCA) was measured on the nanofilms with different lignin contents, as summarized in Table 3 and Supplementary Fig. S1. The WCA increased with increasing lignin content; the WCA increased from 62.4° in LC6 (lignin content of 6.28%) to 91.0° in LC20 (lignin content of 21.0%). The comparison shows that the presence of lignin created more hydrophobic surfaces and increased water barrier effect. This is because lignin is some highly complex, condensed macromolecule rich in aromatic groups and is less hydrophilic than cellulose.

Conclusion

Solvent fractionation pre-treatment can remove hemicellulose and partially remove lignin and can also produce some nanosized cellulose fibers, resulting in L-CNFs being obtained from fractioned materials after subsequent multi-step grinding. In particular, in the case of 15.3% lignin content fibers, an energy of only 1.89 kWh/kg was required to obtain L-CNFs; solvent fractionation pre-treatment successfully reduced the energy consumption of subsequent processing. Moreover, the lignin content determined the final length of the L-CNFs; longer separated nanofibrils were obtained from materials with 12.3% residual lignin than from those materials with either lower or higher lignin contents. When the lignin content was over 12.3%, the diameter and length of the L-CNFs increased with increasing lignin content; otherwise, the diameter and length of the L-CNFs decreased with increasing lignin content. Within a limited residual lignin range (13.7 ±1.59%), fine and long L-CNFs were achieved with low energy input. The lignin content determined the water absorption capability, where the water contact angle decreased with decreasing lignin content. Finally, during grinding, lignin delaminated from the fiber surface and micro- and nano-sized lignin particles were obtained with cellulose nanofibers. These findings are expected to contribute to further development and application of L-CNFs.

Acknowledgement

This work was supported by the SDSU Sungrant Regional Program [A18-0659]; the USDA National Institute of Food and Agriculture [Hatch project 1012359]; the Special Fund for Forest Scientific Research in the Public Welfare [201504603]; Priority Academic Program Development [PAPD] of Jiangsu Higher Education Institutions; and Doctorate Fellowship Foundation of Nanjing Forestry University of China.

References

Uncategorized References

[1] Ma L, Zhang Y, Wang S (2016) Modified treatment for carbonized cellulose nanofiber application in composites. Composites Part A: Applied Science and Manufacturing 90:786-793. doi:10.1016/j.compositesa.2016.09.007

[2] Mihranyan A, Razaq A, Alexeichik D, Lindström T (2012) Influence of the nanocellulose raw material characteristics on the electrochemical and mechanical properties of conductive paper electrodes. Journal of Materials Science 47 (10):4463-4472. doi:10.1007/s10853-012-6305-6

[3] Meng Y, Young TM, Liu P, Contescu CI, Huang B, Wang S (2015) Ultralight carbon aerogel from nanocellulose as a highly selective oil absorption material. Cellulose 22 (1):435-447. doi:10.1007/s10570-014-0519-5

[4] Huang J, Wang S, Lyu S (2017) Facile Preparation of a Robust and Durable Superhydrophobic Coating Using Biodegradable Lignin-Coated Cellulose Nanocrystal Particles. Materials 10 (9):1080. doi:10.3390/ma10091080

[5] Motaung TE, Mokhothu TH (2016) The influence of supermasscolloider on the morphology of sugarcane bagasse and bagasse cellulose. Fibers and Polymers 17 (3):343. doi:10.1007/s12221-016-5430-2

[6] Dutta S, Kim J, Ide Y, Kim JH, Hossain MSA, Bando Y, Yamauchi Y, Wu KC-W (2017) 3D network of cellulose-based energy storage devices and related emerging applications. Materials Horizons 4 (4):522-545. doi:10.1039/C6MH00500D

[7] Nechyporchuk O, Belgacem MN, Bras J (2016) Production of cellulose nanofibrils: a review of recent advances. Industrial Crops and Products 93:2-25. doi:10.1016/j.indcrop.2016.02.016

[8] Habibi Y, Lucia LA, Rojas OJ (2010) Cellulose nanocrystals: chemistry, self-assembly, and applications. Chemical reviews 110 (6):3479-3500. doi:10.1021/cr900339w

[9] Moon RJ, Martini A, Nairn J, Simonsen J, Youngblood J (2011) Cellulose nanomaterials review: structure, properties and nanocomposites. Chemical Society Reviews 40 (7):3941-3994. doi:10.1039/C0CS00108B

[10] Fernandes AN, Thomas LH, Altaner CM, Callow P, Forsyth VT, Apperley DC, Kennedy CJ, Jarvis MC (2011) Nanostructure of cellulose microfibrils in spruce wood. Proceedings of the National Academy of Sciences 108 (47):E1195-E1203. doi:10.1073/pnas.1108942108

[11] Lekha P, Mtibe A, Motaung T, Andrew JE, Sitholè BB, Gibril M (2016) Effect of mechanical treatment on properties of cellulose nanofibrils produced from bleached hardwood

and softwood pulps. Maderas Ciencia y tecnología 18 (3):457-466. doi:10.4067/S0718-221X2016005000041

[12] Morán JI, Alvarez VA, Cyras VP, Vázquez A (2008) Extraction of cellulose and preparation of nanocellulose from sisal fibers. Cellulose 15 (1):149-159. doi:10.1007/s10570-007-9145-9

[13] Tarrés Q, Espinosa E, Domínguez-Robles J, Rodríguez A, Mutjé P, Delgado-Aguilar M (2017) 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. Industrial Crops and Products 99:27-33. doi:10.1016/j.indcrop.2017.01.021

[14] Bistamam MSA, Takagi H, Nakagaito AN, Katoh M, Kusaka K, Pandey JK Development of green nanocomposites reinforced by cellulose nanofibers from waste newspaper. In: Joint Canada-Japan Workshop on Composites, 2012. pp 135-142. doi:10.1142/S0217984915400254

[15] Espinosa E, Tarrés Q, Delgado-Aguilar M, González I, Mutjé P, Rodríguez A (2016) Suitability of wheat straw semichemical pulp for the fabrication of lignocellulosic nanofibres and their application to papermaking slurries. Cellulose 23 (1):837-852. doi:10.1007/s10570-015-0807-8

[16] Hoeger IC, Nair SS, Ragauskas AJ, Deng Y, Rojas OJ, Zhu J (2013) Mechanical deconstruction of lignocellulose cell walls and their enzymatic saccharification. Cellulose 20 (2):807-818. doi:10.1007/s10570-013-9867-9

[17] Iwamoto S, Nakagaito A, Yano H (2007) Nano-fibrillation of pulp fibers for the processing of transparent nanocomposites. Applied Physics A: Materials Science & Processing 89 (2):461-466. doi:10.1007/s00339-007-4175-6

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

[19] Ehman NV, Tarrés Q, Delgado-Aguilar M, Vallejos ME, Felissia F, Area MC, Mutjé P (2016) From Pine Sawdust to Cellulose Nanifibers. Cellulose Chemistry & Technology 50 (3-4):361-367

[20] Liimatainen H, Visanko M, Sirviö JA, Hormi OEO, Niinimaki J (2012) Enhancement of the Nanofibrillation of Wood Cellulose through Sequential Periodate–Chlorite Oxidation. Biomacromolecules 13 (5):1592-1597. doi:10.1021/bm300319m

[21] Ammala, Liimatainen, Henrikki, Niinimaki, Jouko, Burmeister (2013) Effect of tempo and periodate-chlorite oxidized nanofibrils on ground;calcium carbonate flocculation and retention in sheet forming and on the;physical properties of sheets. Cellulose 20 (5):2451-2460. doi:10.1007/s10570-013-0012-6

[22] Ankerfors M, Aulin C, Lindström T Nanocellulose research and developments at Innventia. In: 2011 TAPPI International conference on nanotechnology for renewable materials, Washington DC, USA, 6-8 June 2011, 2011.

[23] Syverud K, Chinga-Carrasco G, Toledo J, Toledo PG (2011) A comparative study of Eucalyptus and Pinus radiata pulp fibres as raw materials for production of cellulose nanofibrils. Carbohydrate Polymers 84 (3):1033-1038. doi:10.1016/j.carbpol.2010.12.066

[24] Abe K, Iwamoto S, Yano H (2007) Obtaining cellulose nanofibers with a uniform width of 15 nm from wood. Biomacromolecules 8 (10):3276-3278. doi:10.1021/bm700624p

[25] Fang W, Yang S, Yuan TQ, Charlton A, Sun RC (2017) Effects of Various Surfactants on Alkali Lignin Electrospinning Ability and Spun Fibers. Industrial & Engineering Chemistry Research 56 (34). doi:10.1021/acs.iecr.7b02494

[26] Wang X, Zhang Y, Wang S, Jiang H, Liu S, Yao Y, Zhang T, Li Q (2018) Synthesis and characterization of amine-modified spherical nanocellulose aerogels. Journal of Materials Science 53 (18):13304-13315. doi:10.1007/s10853-018-2595-7

[27] Rojo E, Peresin MS, Sampson WW, Hoeger IC, Vartiainen J, Laine J, Rojas OJ (2015) Comprehensive elucidation of the effect of residual lignin on the physical, barrier, mechanical and surface properties of nanocellulose films. Green Chemistry 17 (3):1853-1866. doi:10.1039/C4GC02398F

[28] Nechyporchuk O, Pignon F, Belgacem MN (2015) Morphological properties of nanofibrillated cellulose produced using wet grinding as an ultimate fibrillation process. Journal of Materials Science 50 (2):531-541. doi:10.1007/s10853-014-8609-1

[29] Feng X, Yang Z, Chmely S, Wang Q, Wang S, Xie Y (2017) Lignin-coated cellulose nanocrystal filled methacrylate composites prepared via 3D stereolithography printing: Mechanical reinforcement and thermal stabilization. Carbohydrate Polymers 169:272-281. doi:10.1016/j.carbpol.2017.04.001

[30] Nair SS, Yan N (2015) Effect of high residual lignin on the thermal stability of nanofibrils and its enhanced mechanical performance in aqueous environments. Cellulose 22 (5):3137-3150. doi:10.1007/s10570-015-0737-5

[31] Ferrer A, Quintana E, Filpponen I, Solala I, Vidal T, Rodríguez A, Laine J, Rojas OJ (2012) Effect of residual lignin and heteropolysaccharides in nanofibrillar cellulose and nanopaper from wood fibers. Cellulose 19 (6):2179-2193. doi:10.1007/s10570-012-9788-z

[32] Fu J, He C, Wang S, Chen Y (2018) A thermally stable and hydrophobic composite aerogel made from cellulose nanofibril aerogel impregnated with silica particles. Journal of Materials Science 53 (9):7072-7082. doi:10.1007/s10853-018-2034-9

[33] Sammons RJ, Harper DP, Labbé N, Bozell JJ, Elder T, Rials TG (2013) Characterization of organosolv lignins using thermal and FT-IR spectroscopic analysis. BioResources 8 (2):2752-2767. doi:10.15376/biores.8.2.2752-2767

[34] Bozell JJ, Black SK, Myers M, Cahill D, Miller WP, Park S (2011) Solvent fractionation of renewable woody feedstocks: Organosolv generation of biorefinery process streams for the production of biobased chemicals. Biomass and bioenergy 35 (10):4197-4208. doi:10.1016/j.biombioe.2011.07.006

[35] Klamrassamee T, Champreda V, Reunglek V, Laosiripojana N (2013) Comparison of homogeneous and heterogeneous acid promoters in single-step aqueous-organosolv fractionation of eucalyptus wood chips. Bioresource Technology 147 (7):276-284. doi:10.1016/j.biortech.2013.08.015

[36] Tao J, Hosseinaei O, Delbeck L, Kim P, Harper DP, Bozell JJ, Rials TG, Labbé N (2016) Effects of organosolv fractionation time on thermal and chemical properties of lignins. RSC Advances 6 (82):79228-79235. doi:10.1039/C6RA16296G

[37] Baker DA, Rials TG (2013) Recent advances in low - cost carbon fiber manufacture from lignin. Journal of Applied Polymer Science 130 (2):713-728. doi:10.1002/app.39273

[38] Delgadoaguilar M, González I, Tarrés Q, Pèlach MÀ, Alcalà M, Mutjé P (2016) The key role of lignin in the production of low-cost lignocellulosic nanofibres for papermaking applications. Industrial Crops & Products 86:295-300. doi:10.1016/j.indcrop.2016.04.010

[39] Bian H, Chen L, Dai H, Zhu J (2017) Integrated production of lignin containing cellulose nanocrystals (LCNC) and nanofibrils (LCNF) using an easily recyclable di-carboxylic acid. Carbohydrate Polymers 167:167-176. doi:10.1016/j.carbpol.2017.03.050

[40] Pandey K (1999) A study of chemical structure of soft and hardwood and wood polymers by FTIR spectroscopy. Journal of Applied Polymer Science 71 (12):1969-1975. doi:10.1002/(SICI)1097-4628(19990321)71:12<1969::AID-APP6>3.0.CO;2-D

[41] Diop CIK, Lavoie JM (2016) Isolation of Nanocrystalline Cellulose: A Technological Route for Valorizing Recycled Tetra Pak Aseptic Multilayered Food Packaging Wastes. Waste & Biomass Valorization 8 (1):1-16. doi:10.1007/s12649-016-9585-2

[42] Sun H, Wang X, Zhang L (2014) Preparation and Characterization of Poly (lactic acid) Nanocomposites Reinforced with Lignin-containing Cellulose Nanofibrils. Polymer Korea 38 (4):464-470. doi:10.7317/pk.2014.38.4.464

[43] Schwanninger M, Rodrigues J, Pereira H, Hinterstoisser B (2004) Effects of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose. Vibrational Spectroscopy 36 (1):23-40. doi:10.1016/j.vibspec.2004.02.003

[44] Horseman T, Tajvidi M, Diop CI, Gardner DJ (2017) Preparation and property assessment of neat lignocellulose nanofibrils (LCNF) and their composite films. Cellulose 24 (6):2455-2468. doi:10.1007/s10570-017-1266-1
[45] Diop A, Mijiyawa F, Koffi D, Kokta BV, Montplaisir D (2015) Study of lignin dispersion in low-density polyethylene. Journal of Thermoplastic Composite Materials 28 (12):1662-1674. doi:10.1177/0892705714556829
[46] Bastone S, Spinella A, Martino DFC, Tusa S, Caponetti E (2016) More insight into characterization of the waterlogged wooden part of Acqualadroni Roman Rostrum by solid-state NMR. Microchemical Journal 124:831-836. doi:10.1016/j.microc.2015.10.036
[47] Samuel R, Pu Y, Foston M, Ragauskas AJ (2010) Solid-state NMR characterization of switchgrass cellulose after dilute acid pretreatment. Biofuels 1 (1):85-90. doi:10.4155/bfs.09.17
[48] Josset S, Orsolini P, Siqueira G, Tejado A, Tingaut P, Zimmermann T (2010) Energy consumption of the nanofibrillation of bleached pulp, wheat straw and recycled newspaper through a grinding process. Nordic Pulp & Paper Research Journal 29 (1):167-175. doi:10.3183/NPPRJ-2014-29-01-p167-175

Figure Legends

Fig. 1 Water retention value (WRV) as a function grinding passes for samples processed under different **a** fractionation times and **b** fractionation temperatures

Fig. 2 Energy consumption of different samples during the grinding process **a** under different fractionation time **b** under different fractionation temperature **c** WRV vs Energy consumption of different samples after 21 passes

Fig. 3 TEM images of different fractionated fibers before grinding *(left column)* and after 21 grinding passes *(middle column)*. Distribution of the fiber diameters of the samples after 21 grinding passes *(right column)*. **a** LC20 (before grinding), **b** LC20 (after 21 passes), **c** diameter distribution of LC20 after 21 passes, **d** LC13 (before grinding), **e** LC13 (after 21 passes), **f** diameter distribution of LC13 after 21 passes, **g** LC6 (before grinding), **h** LC6 (after 21 passes), **i** diameter distribution of LC6 after 21 passes

Fig. 4 Photographs of different samples before grinding (0 passes; denoted by -0) and 21passes (denoted by -21)

Fig. 5 Fluorescence microscopy images of LC20 at **a** 0 pass, **b** 21 passes and **c** 3D Fluorescence microscopy images of LC20 at 21 passes

Fig. 6 **a** FTIR spectra of different samples after 21 grinding passes. **b** Magnified FTIR spectra of the 1800 to 800 cm^{-1} region

Fig. 7 ^{13}C CP/MAS NMR spectra of LC20 at **a** before grinding and **b** after 21 grinding passes

Table 1. Lignin content of the materials prepared using different fractionation times

Sample ID	Temperature [°C]	Acid [M]	Runtime [min]	Lignin content [%]
LC20	150	0.1	15	21.0
LC18	150	0.1	30	18.3
LC15	150	0.1	45	15.3
LC6	150	0.1	120	6.28

Table 2. Lignin content of materials prepared at different fractionation temperatures

Sample ID	Temperature [°C]	Acid [M]	Runtime [min]	Lignin content [%]
LC13	130	0.1	120	13.5
LC8	140	0.1	120	8.89
LC6	150	0.1	120	6.28
LC12	160	0.1	120	12.3

Table 3. Parameters of yield, morphological, water contact angle of L-CNFs samples after 21 passes and from different literatures

Sample ID	Lignin content (%)	Feedstocks	Processing method	Energy consumption (kWh/kg)	Yield (%)	WRV (%)	Average length (nm)	Average diameter (nm)	Contact angle (°)	Reference
LC20	21.0	switchgrass	OF + grinding	21.3	83.9	507	789.4	16.5	91.0	Present study
LC18	18.3	switchgrass	OF + grinding	11.4	87.0	456	668.3	20.1	79.1	Present study
LC15	15.3	switchgrass	OF + grinding	11.5	79.2	551	898.2	14.6	76.8	Present study
LC13	13.5	switchgrass	OF + grinding	18.8	77.4	557	926.2	11.7	73.9	Present study
LC8	8.89	switchgrass	OF + grinding	19.9	80.8	528	508.3	15.2	63.3	Present study
LC6	6.28	switchgrass	OF + grinding	15.1	79.1	502	414.4	15.3	62.4	Present study
-	22.4	Banana leaf	NaOH + PFI mill	17.3	82.44	-	-	36.31	-	[13]
-	17.8	Recycling newspaper	Grinding	6.75	-	-	-	-	-	[48]
-	3.09	Stone groundwood pulp	bleach Homogenizer	37.33	37.19	-	-	33.7	-	[38]
-	2.80	Wheat straws	Homogenizer	14.22	55.6	-	-	40.3	-	[15]

Table 4. Assignments of chemical shifts of ^{13}C CP/MAS NMR spectra of LC20

No.	ppm	assignment	nucleus
1	121	lignin	S1, S4, G1
2	107	cellulose	C1
3	91	cellulose	C4 (crystalline)
4	87	cellulose	C4 (amorphous)
5	77	cellulose	C2, C3, C5
6	75	cellulose	C2, C3, C5
7	67	cellulose	C6
8	65	lignin	C_{γ}
9	58	lignin	$O–CH_3$