Preparation and Characterization of Cellulose Nanofibrils with Varying Chemical Compositions

Chan-Woo Park,[a] Song-Yi Han,[a] Hyun-Woo Namgung,[a] Pureun-narae Seo,[a] Sun-Young Lee,[b,*] and Seung-Hwan Lee [a,*]

Cellulose nanofibrils (CNF) can be divided into lignocellulose nanofibrils (LCNF), holocellulose nanofibrils (HCNF), and pure cellulose nanofibrils (PCNF), dependent upon their chemical composition. The effect of the chemical composition on the defibrillation efficiency and the properties of the CNFs prepared by wet disk-milling was investigated using six different wood species. The defibrillation efficiency was improved when the lignin and hemicellulose was removed, and smaller fibers with diameters in the order of PCNF > HCNF > LCNF were produced. The average diameter of the hardwood LCNF was finer than that of the softwood LCNFs, but there was no noticeable difference in the diameters of the HCNF and the PCNF from the different wood species. The filtration time of CNF suspensions and the tensile properties of nanopaper sheets were longer and higher, respectively, in the order of HCNF > PCNF > LCNF from different wood species.

Keywords: Cellulose nanofibril; Wet disk-milling; Delignification; Alkali treatment; Nanopaper

Contact information: a: Department of Forest Biomaterials and Engineering, Kangwon National University, Chun-Cheon 200-701, Republic of Korea; b: Division of Wood Processing, Department of Forest Products, National institute of Forest Science, Seoul 02455, Republic of Korea;
** Corresponding authors: nararawood@forest.or.kr; lshyhk@kangwon.ac.kr*

INTRODUCTION

On the basis of chemical composition, cellulose nanofibrils (CNF) can be classified as lignocellulose nanofibrils (LCNF) that contain both lignin and hemicellulose, holocellulose nanofibrils (HCNF) that contain only hemicellulose and no lignin, and pure cellulose nanofibrils (PCNF) that contain only the cellulose component (Lee *et al.* 2010; Kumagai *et al.* 2013; Galland *et al.* 2015). The diameter of LCNF generally ranges from the submicron scale up to 15 nm, which is larger than the average diameters of HCNF and PCNF (Jang *et al.* 2013; Park *et al.* 2015). This causes LCNF to have difficulty with defibrillation, along with the structural heterogeneity and complexity of the cell wall constituents of the lignocellulosic biomass, also called biomass recalcitrance. The presence of lignin is known as an important factor to reduce the defibrillation efficiency (Lee *et al.* 2010; Okahisa *et al.* 2011). Barros *et al.* (2013) reported that the defibrillation efficiency from wet disk-milling (WDM) can be improved by partial delignification.

In contrast, holocellulose can be efficiently and evenly defibrillated into HCNF for short periods of time by mechanical treatments; on average, these nanofibrils have a uniform diameter in the range of 15 nm to 30 nm. This may be due to the disruption and loosening of the cell wall structure by delignification (Iwamoto *et al.* 2008; Park *et al.* 2015). The HCNF has a core-shell structure in which the hemicellulose shell surrounds a cellulose core (Wan *et al.* 2010; Galland *et al.* 2015). The presence of hemicellulose is known to improve the mechanical properties of HCNF nanopapers and nanocomposites (Galland *et al.* 2015; Prakobna *et al.* 2015). Iwamoto *et al.* (2008) reported that the

amount of hemicellulose in pulp affects the ease of defibrillation and the properties of the produced paper sheet. They specifically stated that good hemicellulose adhesion among HCNFs improves the mechanical properties of the produced nanopaper sheet.

Regarding PCNF, a large number of investigations on its preparation and characteristics have been reported. Abe *et al.* (2007) introduced the WDM method to prepare even PCNFs with a uniform width of 15 nm from never-dried pure cellulose, after completely removing hemicellulose and lignin. Using a high-pressure homogenizer, Davoudpour *et al.* (2015) prepared PCNF from cellulose extracted from kenaf, with a uniform diameter of 10 nm, by soda-anthraquinone pulping. Zhang *et al.* (2015) reported that PCNF with a diameter less than 100 nm can be obtained by ball-milling bleached softwood pulp.

In this study, three types of cellulose nanofibrils with different chemical compositions were prepared: LCNF, HCNF, and PCNF. The three nanofibrils types were prepared by WDM from 6 different wood species: *Liriodendron tulipifera, Populus tomentiglandulosa, Quercus mongolica, Pinus densiflora, Larix leptolepis,* and *Pinus koraiensis*. These are the main wood species found in Korea. The effects of the chemical composition and wood species on defibrillation efficiency, the morphological properties of the resulting nanofibrils, and the tensile properties of the nanopapers produced were investigated.

EXPERIMENTAL

Materials

Six wood species (*Liriodendron tulipifera, Populus tomentiglandulosa, Quercus mongolica, Pinus densiflora, Larix leptolepis,* and *Pinus koraiensis*) were obtained from the Experimental Forest of Kangwon National University (Chuncheon, Republic of Korea). The wood powder (40-mesh) was prepared by a cutter-mill (KF-20, Korea Medi Co. Ltd., Republic of Korea). Sodium chlorite, acetic acid, and sodium hydroxide were purchased from Daejung Chemicals & Metals Co. Ltd. (Siheung, Republic of Korea) and used without further purification.

Chemical Composition

The compositions of the extractives were analyzed by an alcohol-benzene extraction method with a Soxhlet apparatus. Wood powder (8 g) was stuffed into a thimble filter, and placed in a Soxhlet device. Ethanol (75 mL) and benzene (150 mL) were mixed in a 250-mL round flask. Extraction was performed at 90 °C for 9 h. Next, the thimble filter was taken out from the Soxhlet and kept in a fume hood for 24 h to volatilize the alcohol and benzene. The air-dried residue was vacuum-dried at 35 °C for 3 days, and the content of the extractives was calculated by comparing the solid weight of wood powder before and after the alcohol-benzene treatment.

Delignification was performed according to the Wise method (Wise *et al.* 1946). Wood powder (20 g) and distilled water (1200 mL) were poured into a 2-L round flask and kept in a water bath at 80 °C for 20 min while being stirred at 150 rpm. The delignification reaction was initiated by adding sodium chlorite (8 g) and acetic acid (1600 μL) into the suspension, and was continuously stirred for 1 h. The same amount of sodium chlorite and acetic acid was added every hour, and the process was repeated 7 times. The residue was then vacuum-filtrated and washed with distilled water several times until the pH was neutralized. The lignin content was calculated by comparing the solid weight of wood powder to the obtained holocellulose. Pure cellulose was produced from holocellulose by the following method. Holocellulose (30 g) was poured into a

17.5% sodium hydroxide solution (750 mL), and the reaction was performed for 50 min while being stirred at 150 rpm at a temperature between 20 °C and 23 °C. At the end of the reaction time, 10% acetic acid (750 mL) was added to the solution for neutralization. Then, the reactant was vacuum-filtrated and washed with distilled water several times. The hemicellulose and cellulose contents were calculated by subtracting the obtained cellulose's weight from the weight of holocellulose.

Defibrillation by Wet disk-milling

The wood power for LCNF was suspended at 5.0 wt.% concentration (3,000 mL), and holocellulose for HCNF and pure cellulose for PCNF were suspended at 1.0 wt.% concentration (1,500 mL). The suspensions were subjected to WDM (Supermasscolloider, MKCA6-2, Masuko Sangyo Co. Ltd., Kawaguchi, Japan). The rotational speed was set at 1800 rpm, and the clearance between the upper and lower disks was reduced to between 80 μm and 150 μm from the zero point, at which the disks would begin to rub. The operation for LCNF was repeated until the fifteenth pass, and the operations for HCNF and PCNF were repeated until the fifth pass. The duration was recorded for each number of WDM passes, and each WDM time (h/kg) was calculated on the basis of the solid weight. The energy consumption of each number of WDM passes was calculated from the voltage, the current, and the recorded duration.

Methods

Morphology observation

The LCNF, HCNF, and PCNF suspensions, after WDM, were diluted to 0.001 wt.%, and then sonicated using an ultrasonicator (VCX130PB, Sonics & Materials, Inc., Newtown, CT, USA) for 1 min. The suspensions were vacuum-filtrated on a polytetrafluoroethylene (PTFE) membrane filter with a pore size of 0.2 μm (ADVANTEC®, Toyo Roshi Kaisha Ltd., Tokyo, Japan). The filtration time was measured at this stage as a criterion of the degree of fibrillation. The filtrated products, which were stacked on the PTFE filter, were immersed in tert-butyl alcohol for 30 min. This procedure was repeated thrice to completely exchange water with tert-butyl alcohol. The CNFs were freeze-dried using a freeze dryer (FDB-5502, Operon Co. Ltd., Gimpo, Republic of Korea) at -55 °C for 3 h to prevent the aggregation of the CNFs. The freeze-dried samples were coated with osmium tetroxide using an osmium plasma coater (HPC-1SW, Vacuum Device Inc, Mito, Japan). The morphologies of the LCNF, HCNF, and PCNF were observed using a scanning electron microscope (SEM, S-4800, Hitachi, Tokyo, Japan) in the Central Laboratory of Kangwon National University. The diameter of individual fibers was measured at least 800 times on each sample by ImageJ software (Version 1.45, Windows, National Institute of Mental Health (NIMH) of National Institute of Health (NIH), Bethesda, USA)

Nanopaper preparation and tensile testing

The LCNF, HCNF, and PCNF suspensions of 0.2 wt.% (220 mL) were prepared, sonicated for 1 min, and vacuum-filtrated on a silicone-coated filter (Whatman® No. 2200 125, GE Healthcare Ltd., Buckinghamshire, UK). The filtrated CNFs were sandwiched between the silicone-coated filters and pressed at 105 °C at 15 MPa pressure for 5 min using a hot press machine (HK-HP12T, Hankuk S & I Co. Ltd, Hwaseong, Republic of Korea).

For tensile testing, 7 specimens between 5.0 mm × 0.7 mm and 0.8 mm × 70.0 mm (width × thickness × length) were cut from the nanopaper sheet and kept in a thermohygrostat at 25 °C at 65% relative humidity to minimize the effect of relative humidity on the tensile properties of the nanopaper sheets. The tensile test was conducted

using a testing machine (H50K, Hounsfield Test Equipment, Redhill, UK), at a cross-head speed of 5 mm/min with a specimen span length of 50 mm.

RESULTS AND DISCUSSION

Chemical Composition

Table 1 summarizes the chemical composition of the 6 different wood species. The lignin content of softwoods ranged from 34.2 ± 1.3% to 35.8 ± 1.8%, which was higher than the 26.7 ± 1.5% to 29.8 ± 0.7% lignin content of the hardwoods. In contrast, the cellulose content (35.6% ± 1.1 to 38.2 ± 0.7%) of softwoods were lower than those (40.4 ± 0.8% to 42.8 ± 1.0%) of hardwoods. The hemicellulose and extractive content were not prominently different between softwoods and hardwoods.

Table 1. Chemical Composition of 6 Wood Species

		Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractives (%)
Hardwoods	*L. tulipifera*	42.8 ± 1.0	24.8 ± 0.4	26.7 ± 1.5	5.7 ± 0.2
	P. tomentiglandulosa	40.4 ± 0.8	24.4 ± 0.7	29.8 ± 0.7	5.4 ± 0.3
	Q. mongolica	41.7 ± 1.8	24.7 ± 0.8	28.4 ± 1.7	5.2 ± 0.3
Softwoods	*P. densiflora*	38.2 ± 0.7	22.7 ± 0.5	34.2 ± 1.3	4.9 ± 0.2
	L. leptolepis	35.9 ± 1.3	23.7 ± 0.6	35.8 ± 1.8	4.6 ± 0.1
	P. koraiensis	35.6 ± 1.1	23.7 ± 1.0	34.4 ± 1.4	6.3 ± 0.5

Wet disk-milling time and power consumption

Figure 1 indicates the WDM time and the power consumption depending on the number of WDM passes. In all species, the WDM time of LCNF was shorter than that of HCNF and PCNF at the same number of WDM passes; the shorter range varied from 1.1 h/kg to 2.1 h/kg in 4 WDM passes as compared to those of HCNF and PCNF. In general, LCNF suspension was relatively low in viscosity compared to HCNF, PCNF suspensions because of the presence of hydrophobic lignin. It is considered that the short WDM time of LCNF suspensions was because the passing speed of the LCNF suspension through the disks during the WDM was fast due to its low viscosity. The WDM time for HCNF was the longest, which may have been due to the increased viscosity by the existence of hygroscopic hemicellulose. Moreover, the difference in the WDM time of HCNF among the species was larger than that of the LCNF and the PCNF. *L. tulipifera* and *P. tomentiglandulosa* had the longest and shortest WDM times among the 6 species, respectively.

In the PCNF samples, the WDM time was shorter than that of the HCNF. The differences in the WDM times of the three CNFs may have been due to their different chemical composition. However, the WDM time tendency of the 6 wood species at the similar chemical composition was not clear. The reason is considered to be that the WDM time may vary within a certain range showing a similar tendency, because of the manual process such as sample input and adjustment of gap between disks. The WDM time was used as a criterion to compare the properties of the CNFs described in the next section. The energy consumption during WDM corresponded well with the WDM time results because it was calculated on the basis of the voltage, the current (torque), and the WDM time.

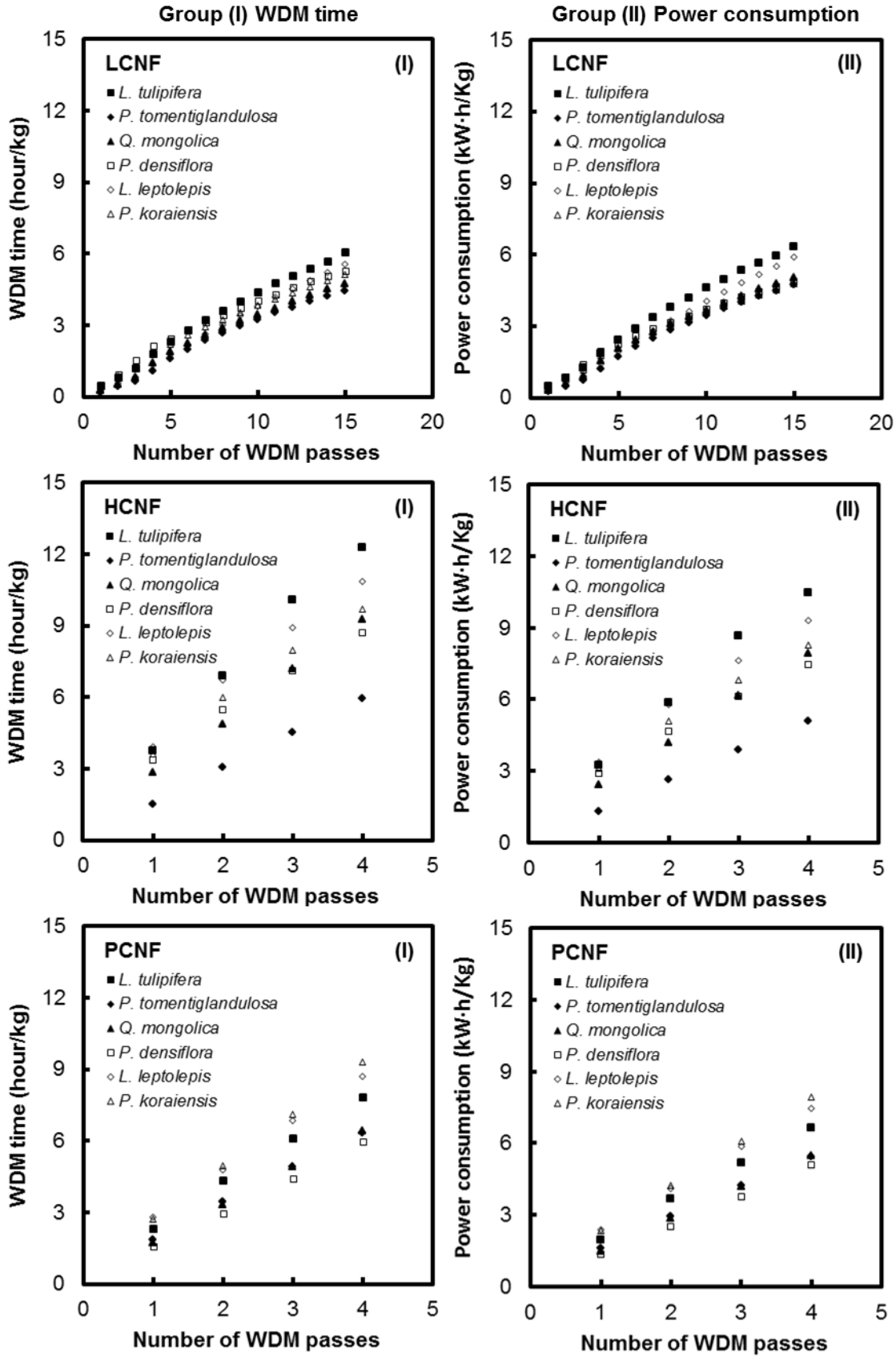

Fig. 1. Relationship between WDM time (Group I) and power consumption (Group II) and the number of WDM passes in LCNF, HCNF, and PCNF

Morphological Properties

Figure 2 shows the SEM micrographs of LCNF, HCNF, and PCNF prepared from 6 wood species at different WDM times, respectively. In LCNF, 100 nm thick fibers existed alongside 20 nm thick fibers, and lignin-like particles were observed in all species at shorter WDM times (1.9 h/kg to 2.6 h/kg); the morphology became more uniform with increased WDM time. In contrast, HCNF and PCNF were smaller and more uniform at similar WDM times (2.3 h/kg to 3.9 h/kg) in all species, as compared to LCNF. Abe *et al.* (2007) reported a method to prepare cellulose nanofibrils with a uniform width of 15 nm by removing lignin and hemicellulose from radiata pine. Lee *et al.* (2010) reported that the removal of lignin and hemicellulose leads to the formation of nanospaces between microfibrils, resulting in the improvement of the defibrillation efficiency. Chang *et al.* (2012) also reported that the partial removal of hemicellulose and lignin by a hot-compressed water treatment improves defibrillation efficiency by WDM. Park *et al.* (2015) established that an increase in the delignification degree improves the defibrillation efficiency by WDM.

Figure 3 shows the fiber diameter distribution of LCNF, HCNF, and PCNF; their average diameters are summarized in Table 2. The diameter distribution of LCNF was broader than those of HCNF and PCNF. In LCNF, hardwood had a smaller distribution than softwood at a similar WDM time, and the distribution range in both woods decreased with increased WDM time. The average diameter of LCNF from hardwoods and softwoods ranged from 34 nm to 53 nm and from 58 nm to 74 nm, respectively (Table 2). The defibrillation of hardwoods was more efficient compared to softwoods because of the lower lignin content of hardwoods (Table 1). Nair *et al.* (2015) reported that the defibrillation efficiency was higher in lodgepole pine bark fibers with lower lignin content (5.2%) than those with higher lignin content (21.3%).

The range of the diameter distribution of HCNF and PCNF was below 80 nm, and it was narrowest in PCNF, irrespective of the wood species. There was no noticeable difference in the diameter distribution and in the average diameter among the species in HCNF and PCNF. The average diameter of PCNF was smaller than that of HCNF in all species (Table 2).

From these results, it can be said that hemicellulose also affected the defibrillation degree. Nobuta *et al.* (2016) investigated the effect of delignification and hemicellulose removal by the Wise method and alkaline treatment on defibrillation by WDM. They reported that the individual fiber diameter of HCNF and PCNF was 18 nm and 17 nm, respectively. Kumagai *et al.* (2016) reported the effect of the hemicellulose/cellulose ratio in LCNF with similar lignin content on the specific surface area (SSA) of nanofibrillated products by WDM. The hemicellulose content was adjusted by hot-compressed water (HCW) treatment. The decrease in the hemicellulose/cellulose ratio from 0.1 to 0.02 by HCW treatment at 160 °C and 200 °C, respectively, increased the SSA from 196 m^2/g to 262 m^2/g, which indicated the improvement of the defibrillation degree.

Filtration Time

The filtration time of CNF suspensions can be a criterion to indirectly evaluate the defibrillation degree and the surface characteristics. Table 3 summarizes the filtration time of LCNF, HCNF, and PCNF suspensions with different WDM times. The filtration time was longer in the order of HCNF, PCNF, and LCNF in all the species, which may have been due to the different chemical composition and defibrillation degree in the three CNFs. The LCNF contained the highest content of lignin that resulted in hydrophobicity (Table 1) and had fibrils with larger diameters than those of HCNF and PCNF (Table 2), which resulted in a shorter filtration time.

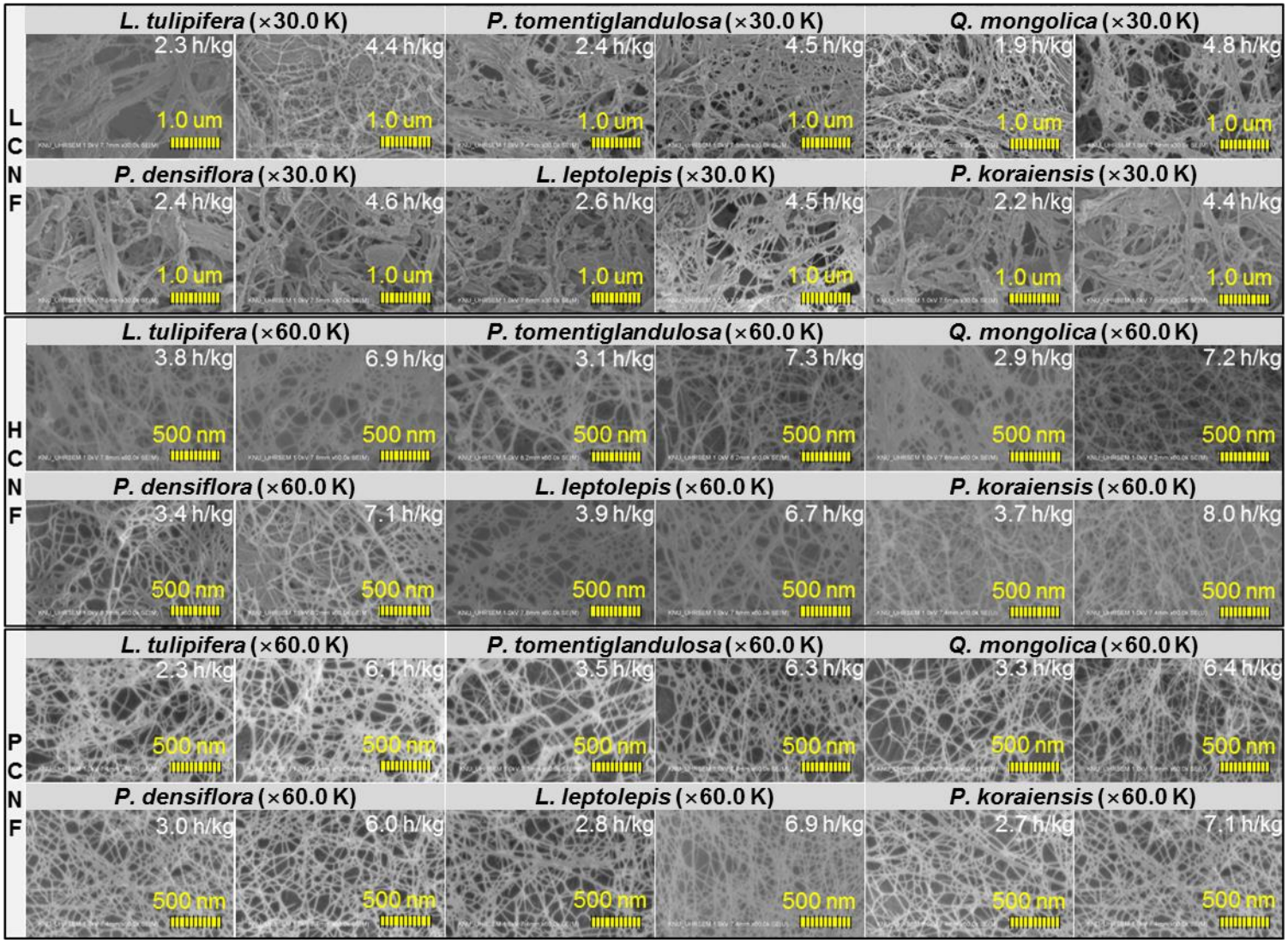

Fig. 2. SEM micrographs of LCNF, HCNF, and PCNF prepared from 6 wood species with different WDM times

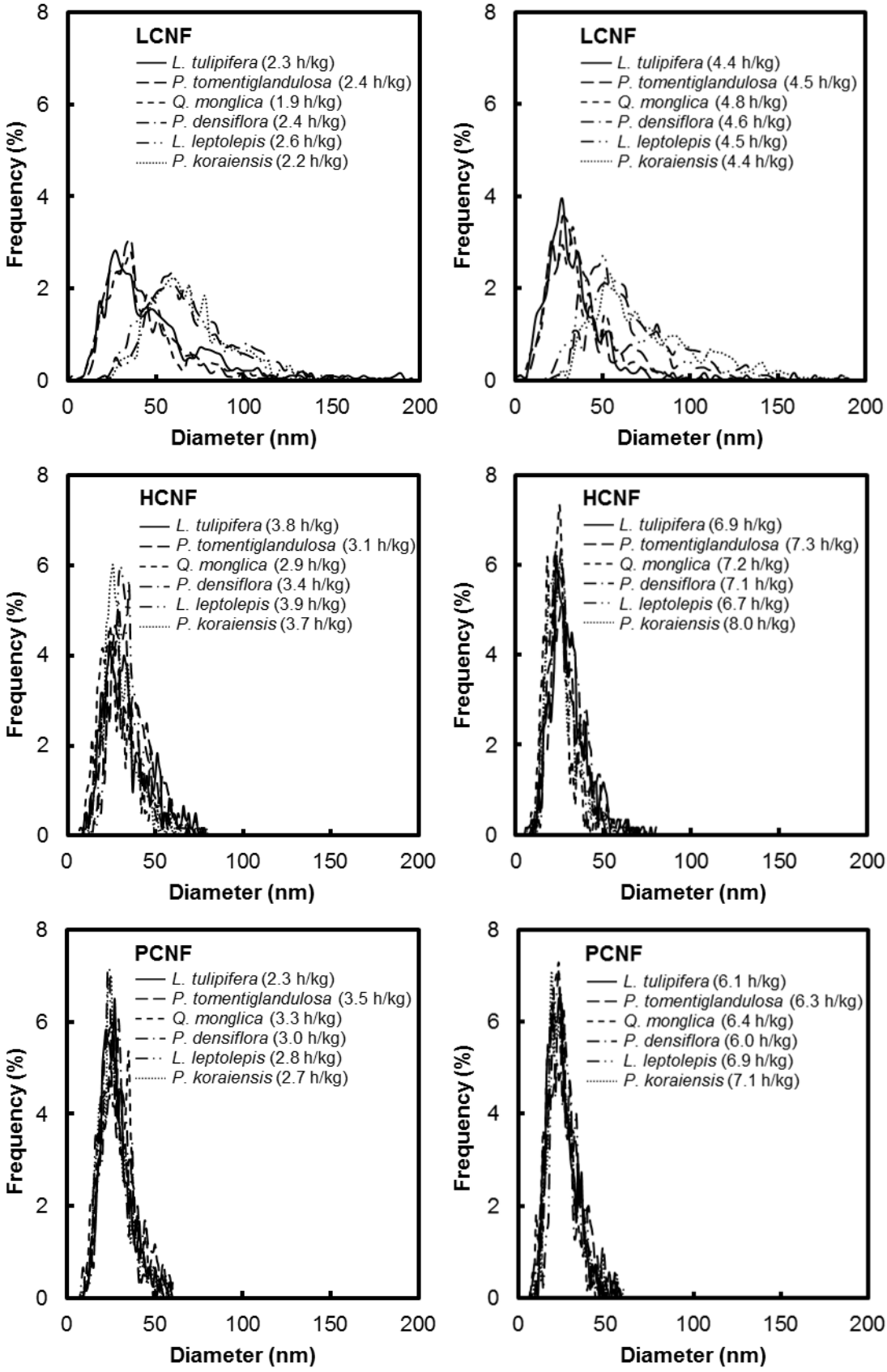

Fig. 3. Diameter distribution of LCNF, HCNF, and PCNF prepared from 6 wood species with different WDM times. Note: the class intervals of the diameter distribution were 1 nm.

Table 2. Average Diameter of LCNF, HCNF, and PCNF Prepared from 6 Wood Species with Different WDM Times

		LCNF		HCNF		PCNF	
		WDM Time (h/kg)	Average Diameter (nm)	WDM Time (h/kg)	Average Diameter (nm)	WDM Time (h/kg)	Average Diameter (nm)
Hardwoods	*L. tulipifera*	2.3	53.4 ± 45.8	3.8	33.7 ± 15.8	2.3	24.7 ± 9.4
		4.4	33.4 ± 21.2	6.9	30.2 ± 11.3	6.1	21.0 ± 9.0
	P. tomentiglandulosa	2.4	39.2 ± 18.3	3.1	34.8 ± 14.5	3.5	30.3 ± 11.6
		4.5	33.9 ± 17.6	7.3	29.7 ± 11.4	6.3	26.9 ± 10.3
	Q. mongolica	1.9	45.1 ± 30.7	2.9	35.9 ± 17.0	3.3	31.8 ± 16.5
		4.8	36.2 ± 22.3	7.2	29.6 ± 6.7	6.4	22.6 ± 7.6
Softwoods	*P. densiflora*	2.4	71.3 ± 29.7	3.4	32.6 ± 10.8	3.0	25.5 ± 8.0
		4.6	68.2 ± 27.0	7.1	29.1 ± 8.6	6.0	24.6 ± 8.5
	L. leptolepis	2.6	61.3 ± 21.1	3.9	32.2 ± 8.3	2.8	26.9 ± 8.5
		4.5	58.0 ± 23.3	6.7	26.8 ± 9.5	6.9	26.4 ± 8.2
	P. koraiensis	2.2	73.9 ± 33.8	3.7	29.3 ± 10.1	2.7	26.6 ± 8.8
		4.4	68.9 ± 23.5	8.0	24.9 ± 8.1	7.1	25.5 ± 8.9

Table 3. Filtration Time of LCNF, HCNF, and PCNF Suspensions Prepared from 6 Wood Species with Different WDM Times

		LCNF		HCNF		PCNF	
		WDM Time (h/kg)	Filtration Time (sec)	WDM Time (h/kg)	Filtration Time (sec)	WDM Time (h/kg)	Filtration Time (sec)
Hardwoods	*L. tulipifera*	2.3	53.6	3.8	318.2	2.3	71.0
		4.4	56.8	6.9	387.9	6.1	72.4
	P. tomentiglandulosa	2.4	52.8	3.1	230.7	3.5	65.0
		4.5	57.7	7.3	292.3	6.3	66.8
	Q. mongolica	1.9	52.9	2.9	235.6	3.3	70.5
		4.8	57.6	7.2	292.8	6.4	72.0
Softwoods	*P. densiflora*	2.4	43.2	3.4	301.2	3.0	64.6
		4.6	45.9	7.1	339.8	6.0	67.8
	L. leptolepis	2.6	48.0	3.9	295.4	2.8	71.0
		4.5	49.2	6.7	337.6	6.9	73.4
	P. koraiensis	2.2	43.6	3.7	234.2	2.7	66.9
		4.4	48.2	8.0	243.2	7.1	70.3

The LCNF suspension from hardwoods with lower lignin content needed longer filtration times than those from softwoods, which also corresponded well with the result of morphological analysis; the LCNF from the hardwoods had smaller diameters than those from the softwoods. Jang *et al.* (2013) reported that the LCNF with lower lignin content by an ozone treatment showed 5 to 6 times longer filtration time than non-treated LCNF with a higher lignin content. In contrast, the long filtration time of HCNF compared to LCNF and PCNF, is mainly due to the presence of the hygroscopic hemicellulose (Giacomozzi and Joutsimo 2015). According to Pejic *et al.* (2008), the water retention value of hemp fibers decreased as a result of the removal of hemicellulose. In both HCNF and PCNF, there was no noticeable difference in filtration time among the species. In all CNFs, the filtration time was increased with increased WDM time, which indicated the improvement of the defibrillation degree.

Tensile Properties of Nanopaper

Table 4 shows the density, tensile strength, and elastic modulus of the paper sheets from LCNF, HCNF, and PCNF. The density of the paper sheet from LCNF was smaller than that from HCNF and PCNF, which were similar. This can be attributed to worse packing effect resulting from the low defibrillation efficiency and hydrophilicity of LCNF, and the presence of lignin particle. Jang *et al.* (2013) investigated the effect of ozone treatment on properties of nanopaper sheets produced from CNFs. They explaned that the lignin of lignocellulose was partially removed by the ozone treatment, resulting in improvement of nanodefibrillation efficiency, and the density of the nanopaper sheet produced from ozone treated CNF was higher than that of LCNF sheet. Both of the tensile properties (strength and modulus) followed the order HCNF > PCNF > LCNF, in all species. In the LCNF paper sheet, both the properties in hardwoods were higher than those in softwoods, which may have been mainly due to the lower defibrillation degree of the softwoods. Park *et al.* (2015) also reported that the tensile strength and elastic modulus of the LCNF paper sheets increased with an increased defibrillation degree. The tensile properties of the paper sheets were higher in the HCNF and PCNF than the LCNF due to the absence of lignin, and the higher defibrillation degree. Nobuta *et al.* (2016) also reported that the HCNF and PCNF paper sheets from kenaf bast fiber have better tensile strength and elastic modulus than LCNF paper sheets. This could have been explained by the increase of interfibril hydrogen bonding by increased hydrophilicity on the nanofibril surface due to delignification.

The high tensile strength and elastic modulus in the HCNF paper sheets could have been explained by the existence of hemicellulose. According to Iwamoto *et al.* (2008), hemicellulose can contribute to the improvement of adhesion between cellulose nanofibrils, resulting in the improvement of tensile properties in HCNF paper sheets. Galland *et al.* (2015) also reported that the better packing effect due to a hemicellulose shell around a cellulose core in individual HCNF improves the tensile properties of the HCNF paper sheets. Nobuta *et al.* (2016) also strongly suggested that the existence of hemicellulose imparted high mechanical properties to the cellulose microfiber. In the HCNF and PCNF paper sheets, the tensile strength and elastic modulus in the softwoods was higher than those in the hardwoods. Stelte and Sanadi (2009) and Spence *et al.* (2010) also reported that the tensile properties of nanopapers prepared from softwood pulp were higher than those prepared from hardwood nanopaper. These results are assumed to be due to the greater length and high aspect ratio of the softwood fiber. At higher WDM times, the fiber diameter decreased resulting in an increase in the tensile strength and elastic modulus of all paper sheets.

Table 4. Density, Tensile Strength, and Elastic Modulus of the Paper Sheets from LCNF, HCNF, and PCNF Prepared from 6 Wood Species with Different WDM Times

			WDM Time (h/kg)	Density (g/cm^3)	Tensile Strength (MPa)	Elastic Modulus (MPa)
LCNF	Hardwood	*L. tulipifera*	2.3	0.38 ± 0.11	16.9 ± 4.5	1632 ± 496
			4.4	0.48 ± 0.12	32.5 ± 1.4	2466 ± 513
		P. tomentiglandulosa	2.4	0.76 ± 0.14	32.7 ± 4.2	3480 ± 814
			4.5	0.88 ± 0.19	60.2 ± 4.3	4779 ± 765
		Q. mongolica	1.9	0.49 ± 0.11	19.7 ± 3.5	1541 ± 530
			4.8	0.87 ± 0.13	37.9 ± 5.7	3377 ± 762
	Softwood	*P. densiflora*	2.4	0.45 ± 0.09	14.2 ± 1.6	1453 ± 197
			4.6	0.51 ± 0.08	21.1 ± 3.2	2251 ± 262
		L. leptolepis	2.6	0.45 ± 0.13	11.5 ± 1.2	759 ± 363
			4.5	0.49 ± 0.11	17.8 ± 1.6	1769 ± 523
		P. koraiensis	2.2	0.33 ± 0.08	7.32 ± 0.9	1238 ± 315
			4.4	0.40 ± 0.09	15.8 ± 0.8	1439 ± 413
HCNF	Hardwood	*L. tulipifera*	3.8	0.96 ± 0.15	90.7 ± 19.5	1693 ± 426
			6.9	1.08 ± 0.11	121.1 ± 21.4	4329 ± 473
		P. tomentiglandulosa	3.1	1.26 ± 0.21	109.1 ± 17.5	2233 ± 259
			7.3	1.37 ± 0.18	124.7 ± 52.4	4468 ± 239
		Q. mongolica	2.9	1.03 ± 0.18	72.0 ± 6.02	1553 ± 197
			7.2	1.19 ± 0.06	112.2 ± 10.9	3757 ± 368
	Softwood	*P. densiflora*	3.4	1.36 ± 0.20	169.3 ± 27.4	2784 ± 617
			7.1	1.55 ± 0.23	187.2 ± 30.3	4577 ± 407
		L. leptolepis	3.9	1.04 ± 0.14	133.1 ± 37.2	2385 ± 843
			6.7	1.26 ± 0.13	166.6 ± 33.7	4367 ± 393
		P. koraiensis	3.7	1.43 ± 0.22	155.1 ± 34.2	3908 ± 814
			8.0	1.63 ± 0.19	178.8 ± 33.5	4351 ± 713
PCNF	Hardwood	*L. tulipifera*	2.3	1.04 ± 0.11	40.3 ± 2.2	1627 ± 150
			6.1	1.17 ± 0.08	50.1 ± 3.6	2064 ± 140
		P. tomentiglandulosa	3.5	1.20 ± 0.16	47.4 ± 2.6	1999 ± 150
			6.3	1.18 ± 0.07	50.0 ± 3.9	1888 ± 248
		Q. mongolica	3.3	1.20 ± 0.24	43.4 ± 3.3	1671 ± 102
			6.4	1.18 ± 0.11	49.2 ± 4.7	1822 ± 132
	Softwood	*P. densiflora*	3.0	1.12 ± 0.19	60.6 ± 2.6	2503 ± 87
			6.0	1.25 ± 0.14	65.6 ± 2.6	3488 ± 87
		L. leptolepis	2.8	1.13 ± 0.18	69.6 ± 3.2	2527 ± 141
			6.9	1.17 ± 0.14	77.9 ± 4.0	2068 ± 195
		P. koraiensis	2.7	1.22 ± 0.27	59.3 ± 4.1	1847 ± 127
			7.1	1.31 ± 0.12	66.5 ± 3.5	1656 ± 111

CONCLUSIONS

1. The effect of chemical composition and wood species on the defibrillation efficiency and morphological properties of LCNF, HCNF, and PCNF prepared from 6 wood species was investigated.
2. Defibrillation efficiency was improved by the removal of lignin and hemicellulose, producing smaller fibers in the order of PCNF, HCNF, and LCNF.
3. Filtration time of CNF suspensions and tensile properties of paper sheets were longer and higher, respectively, in the order of HCNF, PCNF, and LCNF in all species. The shortest and longest filtration time of LCNF and HCNF were caused by lignin with hydrophobicity and the water holding capacity of hygroscopic hemicellulose, respectively.
4. The hemicellulose in HCNF contributed to the improvement of tensile properties of the paper sheets due to its adhesion effect between cellulose nanofibers.
5. The obtained results are expected to give fundamental data on how and where LCNF, HCNF, and PCNF can be applied, depending on their size and surface characteristics.

ACKNOWLEDGMENTS

This research was supported by the National Institute of Forest Science (FP0400-2016-01) grant. The authors thank the Experimental Forest of Kangwon National University for providing samples of 6 wood species.

REFERENCES CITED

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

Barros, R. R. O., Paredes, R. S., Endo, T., Bon, E. P. S., and Lee, S. H. (2013). "Association of wet disk milling and ozonolysis as pretreatment for enzymatic saccharification of sugarcane bagasse and straw," *Bioresource Technology* 136, 288-294. DOI: 10.1016/j.biortech.2013.03.009

Chang, F., Lee, S. H., Toba, K., Nagatani, A., and Endo, T. (2012). "Bamboo nanofiber preparation by HCW and grinding treatment and its application for nanocomposite," *Wood Science and Technology* 46(1), 393-403. DOI: 10.1007/s00226-011-0416-0

Davoudpour, Y., Hossain, S., Khalil, H. P. S. A., Haafiz, M. K. M., Ishak, Z. A. M., Hassan, A., and Sarker, Z. I. (2015). "Optimization of high pressure homogenization parameters for the isolation of cellulosic nanofibers using response surface methodology," *Industrial Crops and Products* 74, 381-387. DOI: 10.1016/j.indcrop.2015.05.029

Galland, S., Berthold, F., Prakobna, K., and Berglund, L. A. (2015). "Holocellulose nanofibers of high molar mass and small diameter for high-strength nanopaper," *Biomacromolecules* 16, 2427-2435. DOI: 10.1021/acs.biomac.5b00678

Giacomozzi, D. E., and Joutsimo, O. (2015). "Drying temperature and hornification of industrial never-dried *Pinus radiata* pulp. 1. Strength, optical, and water holding properties," *BioResources* 10(3), 5791-5808. DOI: 10.15376/biores.10.3.5791-5808

Iwamoto, S., Abe, K., and Yano, H. (2008). "The effect of hemicellulose on wood pulp nanofibrillation and nanofiber network characteristics," *Biomacromolecules* 9(3), 1022-1026. DOI: 10.1021/bm701157n

Jang, J. H., Lee, S. H., Endo, T., and Kim, N. H. (2013). "Characteristics of microfibrillated cellulosic fibers and paper sheets from Korean white pine," *Wood Science and Technology* 47(5), 925-937. DOI: 10.1007/s00226-013-0543-x

Kumagai, A., Lee, S. H., and Endo, T. (2016). "Evaluation of the effect of hot-compressed water treatment on enzymatic hydrolysis of lignocellulosic nanofibrils with different lignin content using a quartz crystal microbalance," *Biotechnology and Bioengineering* 113(7), 1441-1447. DOI: 10.1002/bit.25911

Kumagai, A., Lee, S. H., and Endo, T. (2013). "Thin film of lignocellulosic nanofibrils with different chemical composition for QCM-D study," *Biomacromolecules* 14(7), 2420-2426. DOI: 10.1021/bm400553s

Lee, S. H., Chang, F., Inoue, S., and Endo, T. (2010). "Increase in enzyme accessibility by generation of nanospace in cell wall supramolecular structure," *Bioresource Technology* 101(19), 7218-7223. DOI: 10.1016/j.biortech.2010.04.069

Nobuta, K., Teramura, H., Ito, H., Hongo, C., Kawaguchi, H., Ogino, C., Kondo, A., and Nishino, T. (2016). "Characterization of cellulose nanofiber sheets from different refining processes," *Cellulose* 23(1), 403-414. DOI: 10.1007/s10570-015-0792-y

Okahisa, Y., Abe, K., Nogi, M., Nakagaito, A. N., Nakatani, T., and Yano, H. (2011). "Effects of delignification in the production of plant-based cellulose nanofibers for optically transparent nanocomposites," *Composites Science and Technology* 71(10), 1342-1347. DOI: 10.1016/j.compscitech.2011.05.006

Park, C. W., Lee, S. H., Han, S. Y., Kim, B. Y., Jang, J. H., Kim, N. H., and Lee, S. H. (2015). "Effect of different delignification degrees of Korean white pine wood on fibrillation efficiency and tensile properties of nanopaper," *Journal of Korean Wood Science and Technology* 43(1), 17-24. DOI: 10.5658/WOOD.2015.43.1.17

Prakobna, K., Terenzi, C., Zhou, Q., Furo, I., and Berglund, L. A. (2015). "Core-shell cellulose nanofibers for biocomposites-nanostructural effects in hydrated state," *Carbohydrate Polymers* 125, 92-102. DOI: 10.1016/j.carbpol.2015.02.059

Pejic, B. M., Kostic, M. M., Skundric, P. D., and Praskalo, J. Z. (2008). "The effects of hemicelluloses and lignin removal on water uptake behavior of hemp fibers," *Bioresource Technology* 99(15), 7152-7159. DOI: 10.1016/j.biortech.2007.12.073

Spence, K. L., Venditti, R. A., Habibi, Y., Rojas, O. J., and Pawlak, J. J. (2010). "The effect of chemical composition on microfibrillar cellulose films from wood pulps: Mechanical processing and physical properties," *Bioresource Technology* 101(15), 5961-5968. DOI: 10.1016/j.biortech.2010.02.104

Stelte, W., and Sanadi, A. R. (2009). "Preparation and characterization of cellulose nanofibers from two commercial hardwood and softwood pulps," *Industrial & Engineering Chemistry Research* 48(24), 11211-11219. DOI: 10.1021/ie9011672

Wan, J., Wang, Y., and Xiao, Q. (2010). "Effects of hemicellulose removal on cellulose fiber structure characteristics of eucalyptus pulp," *Bioresource Technology* 101(12), 4577-4583. DOI: 10.1016/j.biortech.2010.01.026

Wise, L. E., Murphy, M., and Daddieco, A. A. (1946). "Chlorite holocellulose, its fractionation and bearing on summative wood analysis and on studies on the hemicellulose," *Technical Association Papers* 29, 210-218.

Zhang, L., Tsuzuki, T., and Wang, X. (2015). "Preparation of cellulose nanofiber from softwood pulp by ball milling," *Cellulose* 22(3), 1729-1741. DOI: 10.1007/s10570-015-0582-6

Article submitted: February 9, 2017; Peer review completed: May 11, 2017; Revised article accepted: May 16, 2017; Published: May 24, 2017.
DOI: 10.15376/biores.12.3.5031-5044