

Comparison of Conventional and Lignin-Rich Microcrystalline Cellulose

Kari Vanhatalo,^{a,*} Natalia Maximova,^a Anna-Maija Perander,^b Leena-Sisko Johansson,^a Eero Haimi,^a and Olli Dahl^a

Three microcrystalline cellulose (MCC) samples were manufactured from bleached and unbleached softwood kraft pulp, and their properties were compared to those of the commercial MCC, Avicel PH-101. One of the produced samples retained a large portion of lignin (10.3%), while the two others retained only some. The physical, chemical, thermogravimetric, and molecular properties were analyzed. The presence of lignin caused a substantial effect on the thermogravimetric and chemical properties of the MCC, as well as on its surface characteristics. The lignin-containing sample degraded at lower temperatures, and its UV Raman spectra had a high intensity aromatic band (1600 cm^{-1}) arising from the lignin. X-ray photoelectron spectroscopy confirmed a high surface lignin coverage (40%) in this specimen only. Particle size and BET surface area measurement results varied in some limits between MCCs, while the cellulose crystallinity index showed almost equal values between 0.82 and 0.84. This work introduces a new wood-based product, the lignin-containing MCC, comparable in properties to the wide-marketed Avicel.

Keywords: Microcrystalline cellulose; Lignin content; Cellulose characteristics; UV Raman; XPS

Contact information: a: Department of Forest Products Technology, Aalto University School of Chemical Technology, PO Box 16300, Vuorimiehentie 1, Espoo, Finland; b: Kemira Oyj, Espoo R&D Centre, PO Box 44, FI-02271 Espoo, Finland; *Corresponding author: kari.vanhatalo@aalto.fi

INTRODUCTION

More than 50 years ago the development of acid degradation of cellulose by Orlando Battista resulted in commercial forms of microcrystalline cellulose (MCC) (Battista *et al.* 1956, 1961). MCC is widely utilized in various industries and applications, *e.g.*, rheology modifiers, food ingredients (thickeners, emulsion stabilizers, fat mimetics), pharmaceuticals (as a tableting aid), and chromatography (Vasiliu-Oprea and Nicoleanu 1993; BeMiller 2009; Tuason *et al.* 2010).

Different organizations, such as the U.S. Pharmacopeial Convention (USP), the European Commission (EC), and the Joint Food and Agriculture Organization of the United Nations / World Health Organization Expert Committee on Food Additives (JECFA), all define MCC as a partially depolymerized, purified cellulose product, produced from alpha cellulose using mineral acids. Quality requirements include a degree of polymerization (DP) that is typically less than 400, and a maximum of 10% of the material can have a particle size of less than 5 μm . The carbohydrate content of MCC material must be over 97%, calculated as cellulose on an anhydrous basis (JECFA 2000; USP 2005; EC 231 2012).

These organizations also define a similar product, cellulose powder (CP). CP is a fine, white (or almost white), purified, mechanically disintegrated cellulose that does not have a DP level definition. JECFA and EU regulations demand a carbohydrate level of

92% for CP. In the USP regulations, the level is the same as for MCC (97%). Both MCC and CP have E-codes—the food additive numbers given by European Food Safety Authority—which are E460(i) and E460(ii), respectively.

Various materials—such as annual plants, wood, and fruit waste—have been used as raw materials for MCC. Paralikar and Bhatawdekar (1988) used bagasse to produce MCC. Uesu *et al.* (2000) chose soya bean husks, and Das *et al.* (2009) used jute. Myz *et al.* (2007) processed aspen, and Vila *et al.* (2014) used eucalyptus wood to manufacture MCC. Less typical raw materials such as orange mesocarp (Ejikeme 2008) and pine and spruce needles (Leppänen *et al.* 2009) have been used to produce MCC. Softwood kraft pulp is used as a more common raw material for MCC production (Aranguiz *et al.* 1994; Virtanen *et al.* 2012). All of these materials can be used to manufacture CP as well.

After cellulose, the second largest constituent of plant cell walls is lignin, which is unique in that it is the only large-scale biomass source of aromatic functionality. It is composed of up to three different phenyl propane monomers, such as coumaryl alcohol, coniferyl alcohol, and syringyl alcohol. Coniferyl alcohol occurs in all wood species and is the dominant monomer in conifers (softwoods). Beyond structural functions, lignin plays several other important roles in plants. Because it is much less hydrophilic than both cellulose and hemicellulose, it prevents the absorption of water by these polysaccharides in plant cell walls, and it allows the efficient transport of water in the vascular tissues. Its phenolic groups have antibacterial properties that form an effective barrier against attack by insects and fungi (Zemek *et al.* 1979; Jung and Vogel 1986; Sláviková and Košíková 1994; Afrin *et al.* 2012). For humans, lignin acts as a source of insoluble dietary fiber (Dhingra *et al.* 2012).

If whiteness (brightness) as a property requirement of MCC is omitted, the special properties of lignin biopolymers could be utilized for generating MCC/CP, which could create a totally new product category and raise the functionality of MCC/CP particles. The antibacterial properties of lignin could be utilized, and MCC/CP powder could give extra properties to medicine tablets, where MCC is a common excipient (Reier and Shangraw 1966; Thoorens *et al.* 2014). Conventional MCC is used in many plastic composite studies as a filler material (Spoljaric *et al.* 2009; Ashori and Nourbakhsh 2010; Iyer *et al.* 2015). The hydrophobic property of lignin facilitates MCC incorporation into plastics by forming chemical bonds between phenolic groups and plastic polymers giving better mechanical- and thermal properties to composites (Iyer and Torkelson 2015; Iyer *et al.* 2015).

Lignin-based adsorbents have found various applications, *e.g.* in pharmaceutical industry for detoxification of biological fluids (Chopabayeva *et al.* 2014), in water purification (Srivastava *et al.* 1994), and soil remediation (Nikolajeva *et al.* 2005). Preparation of cation-exchange resin from lignin has been reported (Kamel 2006), as well as preparation of ion-exchange celluloses (Burton 1995; Choi *et al.* 2004).

This study introduces a lignin-containing MCC product and compares its properties to commercial MCC. The lignin-containing MCC was manufactured from unbleached softwood kraft pulp with an acid hydrolysis method (Dahl *et al.* 2011; Vanhatalo and Dahl 2014), *i.e.*, AaltoCell™. This paper describes the physical, chemical, thermogravimetric, and molecular level differences of the lignin-containing MCC sample compared to conventional MCCs. Particle size (laser diffraction), specific surface area (Brunauer-Emmett-Teller [BET]), visuality (photography), and micrometer-level appearance (scanning electron microscopy [SEM]) were used to examine physical characteristics. Chemical surface analysis (X-ray photoelectron spectroscopy [XPS]), carbohydrate composition (high-performance anion-exchange chromatography [HPAEC]), and lignin

sensitive characterization (ultraviolet Raman [UV Raman] spectroscopy) revealed the chemical properties of the different MCCs. Thermal degradation studies were made by thermogravimetric analysis (TGA). Molecular size distribution (gel permeation chromatography [GPC]), crystallinity (X-ray diffraction [XRD]), and DP (intrinsic viscosity) revealed molecular level features.

EXPERIMENTAL

Materials

The MCC powder Avicel® PH-101 (Avicel) from Sigma-Aldrich (Steinheim, Germany) was used as a reference material.

Three grades of MCC (AaltoCell™)—denoted as DP300, DP450, and BrownMCC (the lignin-containing sample)—were manufactured with the following hydrolysis conditions (Vanhatalo and Dahl 2014): 160 °C, 1.5% dosage (Calculated for oven dry cellulose weights) of H₂SO₄, consistency of 10%, and overall hydrolyzing time of 110 min for DP450 and 140 min for DP300 and BrownMCC. The raw material for DP300 and DP450 was bleached softwood kraft pulp and for BrownMCC, unbleached softwood pulp. Hydrolyzed samples were subjected to H₂O₂ bleaching to purify from possible precipitates followed by spray drying. Bleaching was performed with 2.0% of H₂O₂ and 1.4% NaOH, in a consistency of 5.0%, at 70 °C for 10 min. The produced MCCs were spray dried at a 2.0% consistency by using a Büchi Mini Spray Dryer B-290 (Büchi Labortechnik AG, Flawil, Switzerland). The dryer inlet and outlet temperatures were 180 °C and 105 °C, respectively.

Methods

Physical characteristics

Particle size was determined by laser diffraction as described by Vanhatalo and Dahl (2014) using a Mastersizer 2000 (Malvern Instruments Ltd., Worcestershire, UK) equipped with a Hydro 2000MU wet dispersion unit. The measured d₅₀ value was used as a particle size value. The specific surface area was measured using the multi-point BET method (Brunauer *et al.* 1938) with a Micromeritics Tristar II 3020 (Micromeritics, Norcross, USA) using nitrogen gas as an absorbate. Samples were pretreated under nitrogen gas stream before measurement with procedure: first 15 min at 25 °C, then 1 h at 60 °C and finally 15 min at 25 °C. Photographs were taken with a digital camera (Ixus 160, Canon, Tokyo, Japan). The SEM analysis was carried out with a Hitachi S-4700 cold field emission electron gun instrument (Tokyo, Japan) equipped with a semi-in-lens detector. Secondary electron micrographs from the samples were taken using a low voltage (3 kV) charge balance without sample coating. For the secondary electron images, a mixture of semi-in-lens detector and conventional detector signals was utilized.

Chemical analyses

Chemical analysis of the MCC surfaces was evaluated with XPS, using an AXIS Ultra electron spectrometer (Kratos Analytical, Manchester, UK) with monochromatic low power irradiation (100 W) and neutralization. For the experiment, MCC powders were mounted on double-sided tape and pre-evacuated overnight, together with the *in situ* reference (100% pure cellulose) (Johansson and Campbell 2004). Data were acquired from three locations (200 × 800 μm) for each sample. Surface elemental contents were

determined from low-resolution surveys. Cellulose and lignin contents were analyzed from the high-resolution carbon C1s region, and the data were fitted into four Gaussian peaks using CasaXPS software (Casa Software Ltd., Wilmslow, UK), as detailed by Johansson and Campbell (2004). Carbohydrate and lignin contents were analyzed according to a method based on the National Renewable Energy Laboratory procedure (Sluiter *et al.* 2008) using HPAEC-PAD (Dionex ICS-3000, pulsed amperometric detector, CarboPac PA20 column, Dionex, Sunnyvale, USA). Acid-insoluble lignin was measured gravimetrically, whereas acid-soluble lignin was determined from light absorbance at 205 nm on a spectrophotometer (Shimadzu UV-2550, Tokyo, Japan). Extractives were determined gravimetrically, according to the standard SCAN-CM 49:03 (2003), with acetone extraction. The UV-Raman spectra were measured with a Renishaw 1000 UV Raman spectrometer (Gloucestershire, UK) connected to a Leica DM LM microscope (Leica Microsystems, Heerbrugg, Switzerland) and an Innova 300C FreD (Coherent Inc., Santa Clara, USA) frequency-doubled Ar⁺-ion laser. The excitation wavelength of the laser was 244 nm, and the output power was adjusted to 10 mW, with 10% transmittance. The laser beam was directed through a 40x objective onto the sample. The measuring time was 30 s. The Raman spectra were scaled so that the highest peak intensity was set to 1.0 and the baseline to 0.0. Additionally, the baseline was corrected to zero at 800 cm⁻¹ and 2000 cm⁻¹.

Thermal degradation properties

Thermal degradation studies were carried out with a TGA (TGA7, Perkin-Elmer, Waltham, USA). Approximately 5 mg of the sample was placed onto a TGA sample holder; the measurement chamber was closed and purged with nitrogen. The chamber was heated from room temperature to 600 °C at a rate of 5 °C/min.

Molecular level investigations

Molar mass distributions were obtained using a GPC technique. Prior to analysis, samples were prepared according to the procedure described by Testova *et al.* (2014). GPC analysis was carried out with a Dionex Ultimate 3000 system with a guard column (PLgel Mixed-A, 7.5 × 50 mm, Agilent Technologies, Santa Clara, USA), four analytical columns (PLgel Mixed-A, 7.5 × 300 mm), and refractive index detection (Shodex RI-101, Showa Denko K.K, Kawasaki, Japan). The XRD patterns were detected with an X'Pert PRO MPD Alpha-1 (PANalytical, Almelo, Holland) diffractometer using CuK α radiation source (λ = 0.154056 nm) operating at 45 kV and 40 mA. The step size, scanning speed, and 2 θ range were 0.026°, 0.056 °/s, and 5 to 70°, respectively. Crystallinity index (CrI) values were calculated as described by Segal *et al.* (1959). DP values were determined by first measuring viscosities according to the SCAN-CM 15:99 standard (1999) and by calculating DPs using the Mark-Houwink equation, as guided by the SCAN-CM 15:88 standard (1988).



Fig. 1. A photograph of the MCC samples on a marble table

RESULTS AND DISCUSSION

Physical characteristics

All of the samples except BrownMCC were white in color (Fig. 1). The strong brown color of BrownMCC was caused by the high lignin content (confirmed later by chemical analysis). The morphology of the MCC samples on a micro-level was shown in SEM micrographs (Fig. 2).

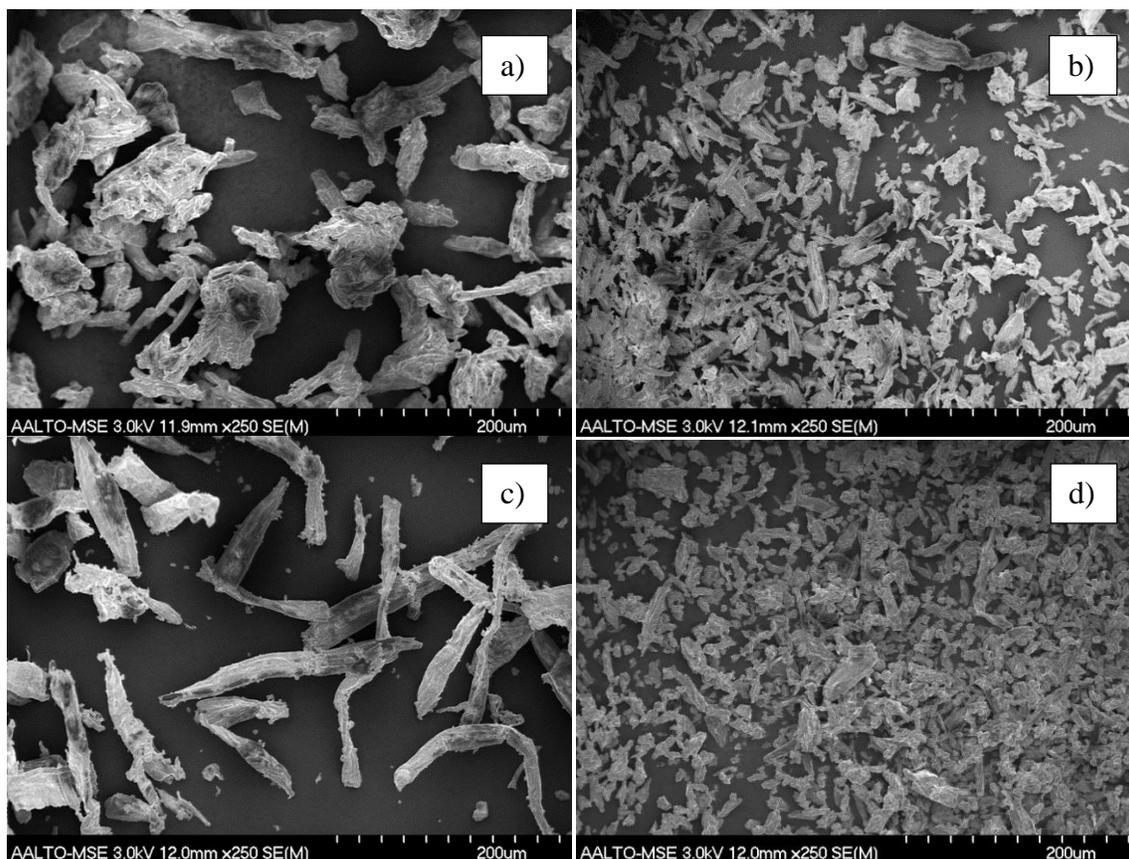


Fig. 2. SEM micrographs of a) Avicel, b) DP300, c) DP450, and d) BrownMCC

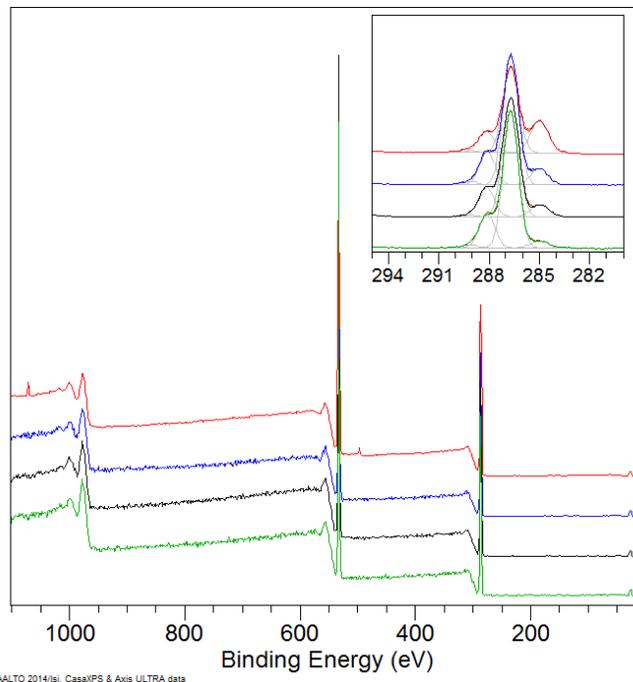
Figure 2 shows that the MCC sample DP450 (Fig. 2c) exhibited clear individual fiber-like architecture, whereas the Avicel sample (Fig. 2a) was dominated by aggregated structures or clusters. Both the DP300 (Fig. 2b) and lignin-containing BrownMCC (Fig. 2d) samples showed noticeably smaller particles than the Avicel and DP450 samples (Figs. 2a and 2c), with the BrownMCC having the finest particles of all four samples. The DP300 and BrownMCC samples were subjected to more extensive hydrolysis than the DP450 sample, which could explain their differences in size and morphology. Table 1 presents the particle size (laser diffraction) and specific surface area (BET) results.

Table 1. Particle Size and Specific Surface Area of MCC Samples

Property	Sample			
	Avicel	DP300	DP450	BrownMCC
Particle Size (μm)	36.2	16.2	51.5	21.7
BET (m^2/g)	0.858	1.358	0.965	0.736

The particle size decreased in the following order: DP450 > Avicel > BrownMCC > DP300. These results together with SEM imaging confirm that prolonged hydrolysis affected MCC physical characteristics as shown by Vanhatalo and Dahl (2014) by using the same manufacturing method. The DP300 sample, which had the smallest particle size, had the largest specific surface area. Somewhat unexpectedly, the BrownMCC sample showed the smallest surface area, having particle size similar to that of DP300. This could be attributed to a heating effect of spray drying at 180 °C, which was above the glass transition temperature (140 °C) for the kraft lignin (Tejado *et al.* 2007).

The analyzed Avicel specific surface area value was somewhat lower than literature data. Steele *et al.* (2008) and Nam-Tran *et al.* (1993) obtained 1.22 m^2/g , and 1.30 m^2/g respectively, for Avicel PH-101. Ardizzone *et al.* (1999) obtained 1.30 m^2/kg for Avicel PH-102, and Zografis *et al.* (1984) obtained from 1.10 m^2/g to 1.44 m^2/g for Avicel PH-101 under varying measuring conditions. The difference in surface area can arise from the following: a difference in sample pretreatment procedures (Ardizzone *et al.* 1999; Steele *et al.* 2008), used gas in BET technique (Zografis *et al.* 1984), and the measurement methods used in different studies.

**Fig. 3.** XPS spectra of Avicel (■), DP300 (■), DP450 (■), and BrownMCC (■)

Chemical analyses

Carbon and oxygen were the major elements in all of the XPS survey spectra (Fig. 3). Their elemental depth distributions were uniform within the XPS analysis depth, *i.e.*, within the topmost 10 nm (Johansson *et al.* 2004). Apart from these two elements, only

trace amounts of sodium were seen in the BrownMCC sample. The most prominent feature in all of the carbon high-resolution spectra was the cellulose signature, consisting of CO and OCO components at 286.7 and 288.1 eV. The non-cellulosic component (carbons without oxygen neighbors) at 285 eV was present in all samples, indicating slight but unavoidable contamination. However, this peak could also be utilized in surface lignin evaluations, and it was markedly elevated in the BrownMCC sample. Using calculations adopted from pulp and paper research (Koljonen *et al.* 2003), the surface lignin coverage after contamination correction was around 40%. The chemical composition of the MCC samples is presented in Table 2.

The Avicel sample exhibited the highest cellulose content, which might be linked to the precursor material, cotton cellulose; the raw materials for the other samples were softwood kraft pulps. The cellulose content of the cotton pulp is high, approximately 95% (Sczostak 2009), whereas bleached and unbleached softwood kraft pulp have around 80% and 70% cellulose, respectively (Shackford 2003; Joutsimo 2004; Spence *et al.* 2010). There was a distinct difference in cellulose content between the DP300 and DP450 samples due to the prolonged acid hydrolysis of DP300, which reduced the hemicellulose fraction.

Table 2. Chemical Composition of the MCC Samples

Component (%)	Samples			
	Avicel	DP300	DP450	BrownMCC
Carbohydrates	99.5	99.5	99.4	89.1
Arabinose	n/a	n/a	n/a	n/a
Rhamnose	n/a	n/a	n/a	n/a
Galactose	n/a	n/a	n/a	n/a
Glucose	97.2	95.0	87.3	87.7
Xylose	1.9	2.0	6.4	0.6
Mannose	0.4	2.5	5.7	0.8
Extractives	0.1	0.1	0.1	0.6
Total Lignin	0.4	0.5	0.5	10.3
Acid-Soluble Lignin	0.3	0.3	0.4	0.3
Acid-Insoluble Lignin	0.1	0.1	0.1	10.0

The BrownMCC sample had a high lignin content, 10.3%, which explained its brown color. BrownMCC prepared from unbleached kraft pulp, which has usually 20 to 25% hemicelluloses (Gullichsen and Fogelholm 1999) and manufactured using acid hydrolysis without any further delignification, had a somewhat lower xylose content than the Avicel sample, and only a small portion of mannose. This result might be due to the lignin-carbohydrate complex structures connected with the ester linkages that were cleaved in acid hydrolysis (Lawoko 2005).

Comparison of the surface lignin coverage (40%, as determined by XPS) and the total lignin content of the BrownMCC sample (10.3%, as analyzed gravimetrically and by using a spectrophotometer) suggested that most of the lignin in the MCC made from unbleached pulp was located on the surface rather than the interior of the particles. A similar phenomenon was observed by Laine *et al.* (1994). In their study, lignin was

concentrated on the thin outer surface of kraft pulp fibers, and it decreased linearly with decreasing total lignin content after alkaline digestion of the pulp.

The UV-Raman spectroscopy is an extremely sensitive method for aromatic and conjugated structures (Fig. 4). The samples exhibiting an aromatic band around 1600 cm^{-1} were recognized as lignin compounds, and the cellulose band was present at 1100 cm^{-1} (Wiley and Atalla 1987; Halttunen *et al.* 2001; Saariaho 2004). High sensitivity of UV-Raman spectroscopy towards aromatic lignin structures due to UV excitation has been shown previously by Perander *et al.* (2001). For example, a cooked kraft pulp sample that had 4 to 5% lignin showed only lignin bands in the UV Raman spectrum; the cellulose bands were not detected (Perander 2001; Saariaho 2004). Similarly, the lignin band was dominant in the UV Raman spectrum of the BrownMCC sample having 10.3% lignin. No cellulosic bands were observed even though the carbohydrate content of the BrownMCC sample was as high as 89.1% (as determined by HPAEC). The UV Raman spectra of the Avicel, DP300, and DP450 samples revealed a distinct cellulose band intensity at 1100 cm^{-1} and an aromatic band at 1600 cm^{-1} . As the UV Raman spectra of these three MCCs were normalized to the 1100 cm^{-1} cellulose band, the lignin band was used to compare the overall lignin content of the samples. The lignin content decreased in the samples from DP450 to DP300 and finally, Avicel. The intensity of the lignin band of the Avicel sample was the lowest, indicating the high purity of the sample.

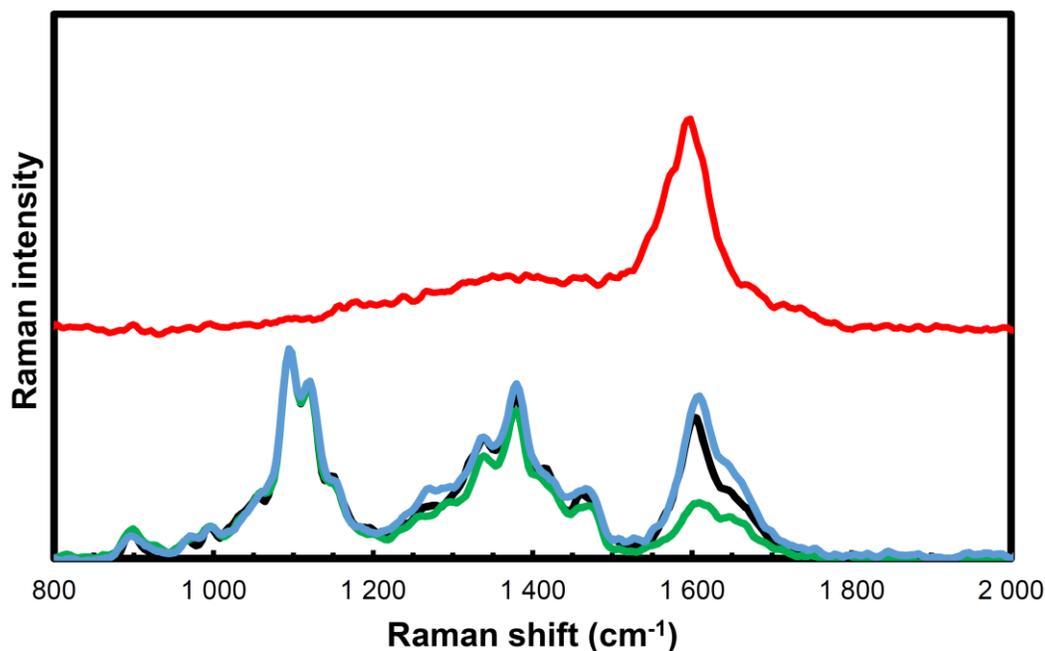


Fig. 4. UV Raman spectra of Avicel (■), DP300 (■), DP450 (■), and BrownMCC (■).

Thermal degradation properties

The MCCs thermal degradation (TGA) and first derivative curves are shown in Fig. 5. The Avicel sample, which had the highest cellulose content, started thermally degrading between 315 °C and 400 °C, which agreed with published data for cellulose degradation (Yang *et al.* 2007; Chuayjuljit *et al.* 2009; Pasangulapati *et al.* 2012).

The DP300 and DP450 samples, which contain cellulose, xylan, and mannose (Table 2), started to decompose around 240 °C, first degrading slowly and then with increased speed. This speed-up point occurred at approximately 350 °C in the DP300 sample, and somewhat earlier, at 340 °C, in the DP450 sample. Degradation continued up to 415 °C and 425 °C in the DP450 and DP300 samples, respectively.

When studying the thermal decomposition of hemicelluloses, Werner *et al.* (2014) and Yang *et al.* (2007) found that most of these five-carbon carbohydrates start to degrade between 200 and 250 °C, which agrees with the data presented in Fig. 5. The decomposition temperatures for xylan, glucomannan, and galactoglucomannan were around 200 °C, 210 °C, and 220 °C, respectively.

The first decomposition point of the BrownMCC sample was observed at 220 °C; in the range 270 °C to 310 °C, degradation slowed down, whereupon it increased again and leveled out at approximately 400 °C. The drop region in the BrownMCC derivative curve was likely due to the combined effect of hemicellulose and lignin degradation. Bartkowiak and Zakrzewski (2004) measured the thermal degradation of kraft lignin isolated from pine, noting that degradation started above 200 °C. Pasangulapati *et al.* (2012) observed similar results with the model compound lignin.

Lignin has a lowering effect on thermal properties of MCC as shown Fig. 5. Beg and Pickering (2008) showed the same thermal weakening effect in the case of unbleached (2.4% lignin content) and bleached softwood kraft fiber. In their study, lignin containing fiber started to decompose at a temperature lower by 30 °C than bleached lignin free cellulose. Fatah *et al.* (2014) and Rayung *et al.* (2014) used empty fruit bunch from oil palm and did TGA for lignin containing and chemically purified materials. They did similar observations, after removing lignin thermal properties developed.

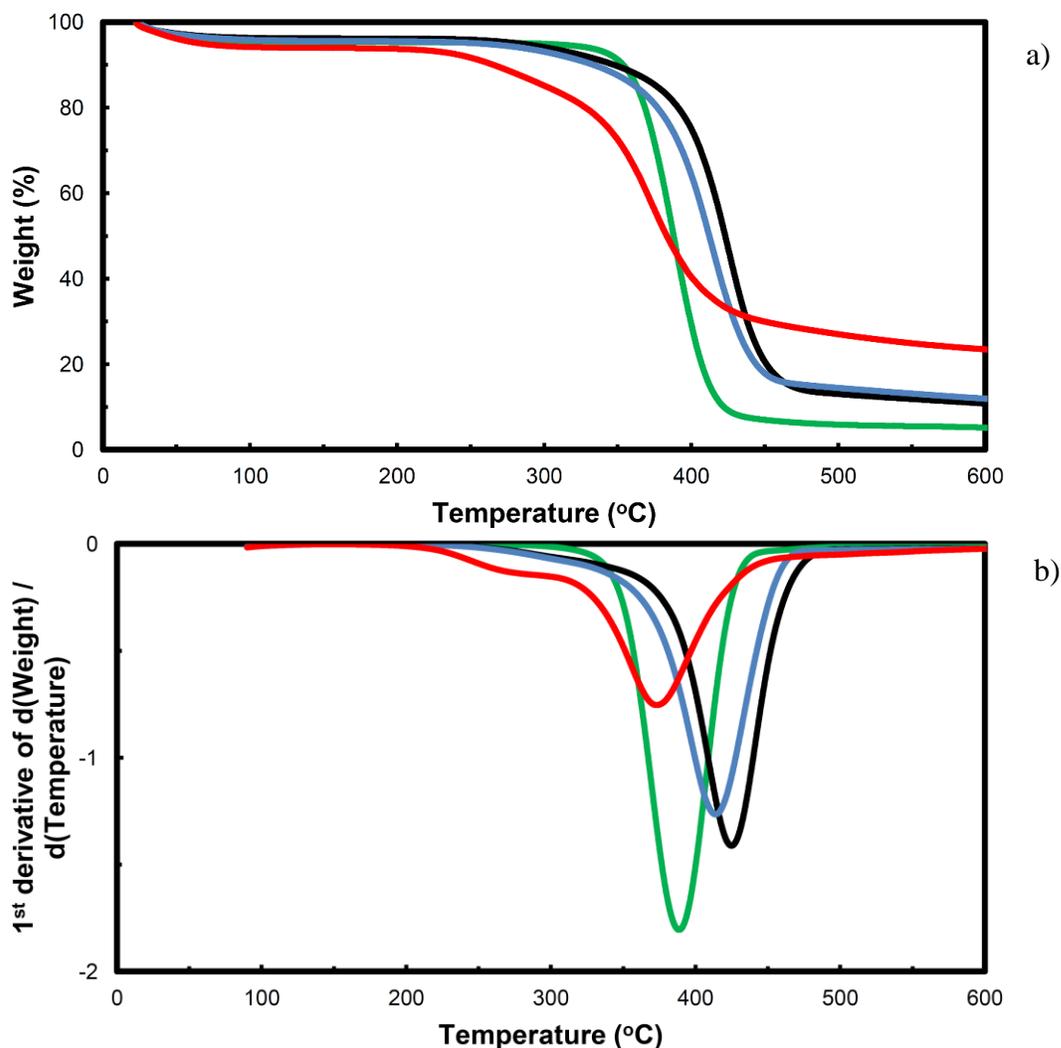


Fig. 5. a) Thermal degradation (TGA) and b) the first derivative curve of Avicel (■), DP300 (■), DP450 (■), and BrownMCC (■)

Molecular level investigations

GPC was used to determine the molecular weight distributions (M_{wD}) of the MCCs (Fig. 6). The Avicel and BrownMCC samples had similar M_{wD} . The DP300 M_{wD} was narrower than that of DP450, which clearly had the widest distribution. The difference in the M_{wD} of the DP300 and DP450 samples could be explained by extended acid hydrolysis and the depolymerizing of cellulose through the cleavage of glucosidic bonds, resulting in shorter molecule chains and narrower M_{wD} . These results agreed with the findings of Cao *et al.* (2012) and Jasiukaitytė-Grojzdek *et al.* (2012), who studied the M_{wD} of cellulose by varying hydrolysis time and biomass sources and found that more intensive hydrolysis gave shorter molecule chains. The CrI values (XRD), average molecular weight (M_w), and DP are presented in Table 3.

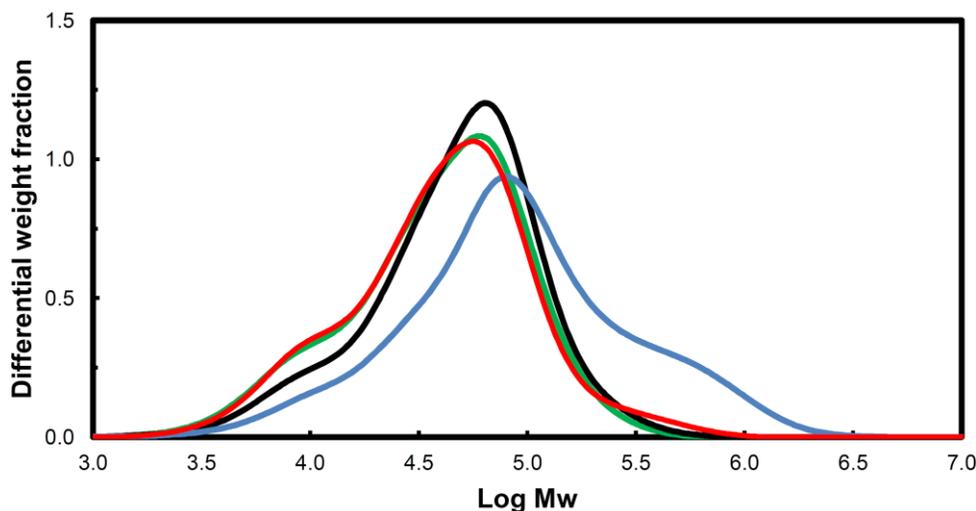


Fig. 6. Molecular weight distributions (GPC) of Avicel (■), DP300 (■), DP450 (■), and BrownMCC (■)

Table 3. The Crystallinity Index, Average Molecular Weight, and Degree of Polymerization of the MCC Samples

Sample	CrI	M _w	DP
	Peak Height	g/mol	
Avicel	0.84	57700	252.7
DP300	0.84	66200	273.3
DP450	0.82	184700	451.2
BrownMCC	0.82	64300	230.2

All MCC samples exhibited similarly high CrI values. In the current study the MCC's have gone through acid hydrolysis manufacturing process which removes some of the hemicelluloses and amorphous part of cellulose. This might influence CrI values, by making content of lignin in BrownMCC less effective. Xiao *et al.* (2011) did severe hot water extractions (at 200 °C) for *Tamarix ramosissima* by removing 90% of the hemicelluloses and raising content of lignin from 23.5% to 41.5%. In spite of high content of lignin, CrI increased from 0.41 to 0.56. Wan *et al.* (2010) manufactured eucalyptus pulps to different hemicelluloses content while keeping the lignin amount almost the same (4.0-4.9%). The pulps exhibited an increase in CrI from 0.73 to 0.83 by lowering the hemicelluloses content from 27.6% to 9.9% and increasing cellulose content from 68.5% to 87.7%. The measured CrI of the Avicel sample was consistent with the literature data (El-Sakhawy and Hassan 2007; Keshk and Haija 2011; Haafiz *et al.* 2013; Trache *et al.* 2014).

The X-ray spectra's (Fig. 7) exhibit typical diffraction peaks for cellulose: such values of 2θ are recognized as the crystallographic planes (Hult *et al.* 2003; Park *et al.* 2010; Jarrett 2011). In the case of BrownMCC, high content of lignin (10.3%) did not changed the form of diffraction pattern.

All samples exhibit similar M_w values, except for the DP450, which is noticeably higher. Measurements with SCAN standard methods (SCAN-CM 15:88 and SCAN-CM 15:99) gave similar DP results. The results of M_w and DP confirmed that prolonged hydrolysis produced cellulose particles with lower molecular weight.

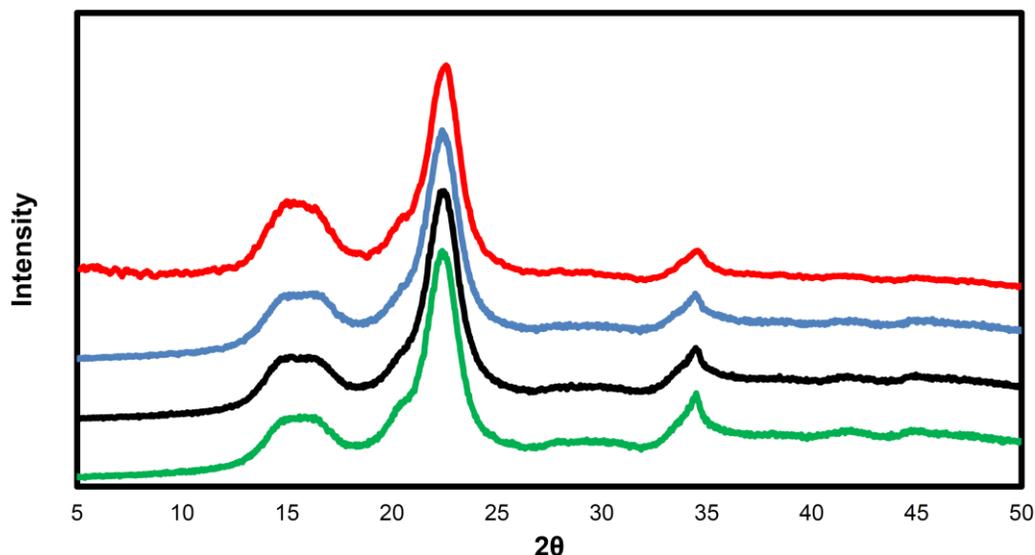


Fig. 7. X-ray diffraction patterns of Avicel (—), DP300 (—), DP450 (—), and BrownMCC (—)

CONCLUSIONS

1. A new product from chemical pulp, lignin-containing MCC, has been introduced by using unbleached softwood kraft pulp as a raw material in a mild acid hydrolysis process.
2. The surface and thermal properties of MCC were affected by the chemical composition of the precursor pulp; unbleached softwood kraft pulp resulted in MCC with a high surface lignin content (40%) and somewhat lower thermal properties than bleached kraft pulp-based MCC. The crystallinity, hemicellulose content, molecular weight, DP, and BET surface area were comparable to the commercial product Avicel PH-101.
3. Lignin-containing MCC could be used in applications where the brown color is not undesirable – for example, as plastic filler or as medicine-tableting aid.
4. Careful attention should be paid to the analytics of high lignin-content cellulose products. UV Raman spectrometry confirmed the presence of lignin; the cellulose content was overshadowed by lignin. The XPS technique was used to quantify the lignin and cellulose peaks at the same time.

ACKNOWLEDGMENTS

The authors are grateful to the Department of Forest Products Technology, Aalto University, for supporting this work.

REFERENCES CITED

- Afrin, T., Tsuzuki, T., Kanwar, R. K., and Wang, X. (2012). "The origin of the antibacterial property of bamboo," *J. Text. Ind.* 103(8), 844-849. DOI: 10.1080/00405000.2011.614742
- Aranguiz, T. B., Bartulin, J. F., Jaramillo, V. H. M., and Fonseca, L. A. (1994). "Preparation of microcrystalline cellulose from bleached kraft pulp: Comparative evaluation of flow and tableting properties," *Bol. Soc. Chil. Quim.* 39(1), 71-78.
- Ardizzone, S., Dioguardi, F. S., Mussini, T., Mussini, P. R., Rondinini, S., Vercelli, B., and Vertova, A. (1999). "Microcrystalline cellulose powders: structure, surface features and water sorption capability," *Cellulose* 6(1), 57-69. DOI: 10.1023/A:1009204309120
- Ashori, A., and Nourbakhsh, A. (2010). "Performance properties of microcrystalline cellulose as a reinforcing agent in wood plastic composites," *Compos. Part B-Eng.* 41(7), 578-581. DOI:10.1016/j.compositesb.2010.05.004
- Bartkowiak, M., and Zakrzewski, R. (2004). "Thermal degradation of lignins isolated from wood," *J. Therm. Anal. Calorim.* 77(1), 295-304. DOI: 10.1023/B:JTAN.0000033214.95457.fe
- Battista, O. A., Coppick, S., Howsmon, J. A., Morehead, F. F., and Sisson, W. A. (1956). "Level-off degree of polymerization," *Ind. Eng. Chem.* 48(2), 333-335. DOI: 10.1021/ie50554a046
- Battista, O. A., Hill, D., and Smith, P. A. (1961). "Level-off D.P. cellulose products," US Patent No. 2978446.
- Beg, M. D. H., and Pickering, K. L. (2008). "Accelerated weathering of unbleached and bleached Kraft wood fibre reinforced polypropylene composites," *Polym. Degrad. Stab.* 93(10), 1939-1946. DOI: 10.1016/j.polymdegradstab.2008.06.012
- BeMiller, J. N. (2009). "One hundred years of commercial food carbohydrates in the United States," *J. Agric. Food Chem.* 57(18), 8125-8129. DOI: 10.1021/jf8039236
- Brunauer, S., Emmett, P. H., Teller, E. (1938). "Adsorption of Gases in Multimolecular Layers," *J. Am. Chem. Soc.* 60(2), 309-319. DOI:10.1021/ja01269a023
- Burton, S. C. (1995). *Preparation of chemically modified bead cellulose resins and their application to protein purification*, PhD Dissertation, Massey University, Palmerston North, New Zealand, pp. 1-214.
- Cao, S., Pu, Y., Studer, M., Wyman, C., and Ragauskas, A. J. (2012). "Chemical transformations of *Populus trichocarpa* during dilute acid pretreatment," *RSC Adv.* 2(29), 10925-10936. DOI: 10.1039/C2RA22045H
- Choi, Y.-J., Ahn, Y., Kang, M.-S., Jun, H.-K., Kim, I. S., and Moon, S.-H. (2004). "Preparation and characterization of acrylic acid-treated bacterial cellulose cation-exchange membrane," *J. Chem. Technol. Biotechnol.* 79(1), 79-84. DOI: 10.1002/jctb.942
- Chopabayeva, N. N., Mukanov, K. N., and Tasmagambet, A. T. (2014). "Synthesis and application of nano-, meso- and macroporous sorbents based on lignin for detoxication of biological Fluids," in *7th Conference on the Times of Polymers and Composites (TOP): Vol. 1599*, Ischia, Italy, pp. 34-37. DOI: 10.1063/1.4876771
- Chuayjuljit, S., Su-Uthai, S., Tunwattanaseree, C., and Charuchinda, S. (2009). "Preparation of microcrystalline cellulose from waste-cotton fabric for biodegradability enhancement of natural rubber sheets," *J. Reinf. Plast. Compos.* 28(10), 1245-1254. DOI: 10.1177/0731684408089129

- Dahl, O. P., Parviainen, K. E., and Vanhatalo, K. M. (2011). "A novel method to produce microcellulose," WO Patent Application 2011154600.
- Das, K., Ray, D., Bandyopadhyay, N. R., Ghosh, T., Mohanty, A. K., and Misra, M. (2009). "A study of the mechanical, thermal and morphological properties of microcrystalline cellulose particles prepared from cotton slivers using different acid concentrations," *Cellulose* 16(5), 783-793. DOI: 10.1007/s10570-009-9280-6
- Dhingra, D., Michael, M., Rajput, H., and Patil, R. T. (2012). "Dietary fibre in foods: a review," *J. Food Sci. Tech.* 49(3), 255-266. DOI: 10.1007/s13197-011-0365-5
- Ejikeme, P. M. (2008). "Investigation of the physicochemical properties of microcrystalline cellulose from agricultural wastes I: orange mesocarp," *Cellulose* 15(1), 141-147. DOI: 10.1007/s10570-007-9147-7
- El-Sakhawy, M., and Hassan, M. L. (2007). "Physical and mechanical properties of microcrystalline cellulose prepared from agricultural residues," *Carbohydr. Polym.* 67(1), 1-10. DOI: 10.1016/j.carbpol.2006.04.009
- European Commission (EC) Regulation 231/2012. (2012). "Commission Regulation (EU) No 231/2012 of 9 March 2012 laying down specifications for food additives listed in Annexes II and III to Regulation (EC) No 1333/2008 of the European Parliament and of the Council," European Union, Brussels, Belgium.
- Fatah, I. Y. A., Khalil, H. P. S. A., Hossain, M. S., Aziz, A. A., Davoudpour, Y., Dungani, R., and Bhat, A. (2014). "Exploration of a chemo-mechanical technique for the isolation of nanofibrillated cellulosic fiber from oil palm empty fruit bunch as a reinforcing agent in composites materials," *Polymers* 6(10), 2611-2624. DOI: 10.3390/polym6102611
- Gullichsen, J., and Fogelholm, C.-J. (eds.) (1999). *Chemical Pulping, Papermaking Science and Technology*, Fapet Oy, Helsinki, Finland.
- Haafiz, M. K. M., Eichhorn, S. J., Hassan, A., and Jawaid, M. (2013). "Isolation and characterization of microcrystalline cellulose from oil palm biomass residue," *Carbohydr. Polym.* 93(2), 628-634. DOI: 10.1016/j.carbpol.2013.01.035
- Hult, E.-L., Iversen, T., and Sugiyama, J. (2003). "Characterization of the supermolecular structure of cellulose in wood pulp fibres," *Cellulose* 10(2), 103-110. DOI: 10.1023/A:1024080700873
- Iyer, K. A., and Torkelson, J. M. (2015). "Sustainable green hybrids of polyolefins and lignin yield major improvements in mechanical properties when prepared via solid-state shear pulverization," *ACS Sustain. Chem. Eng.* 3(5), 959-968. DOI: 10.1021/acssuschemeng.5b00099
- Iyer, K. A., Flores, A. M., and Torkelson, J. M. (2015). "Comparison of polyolefin biocomposites prepared with waste cardboard, microcrystalline cellulose, and cellulose nanocrystals via solid-state shear pulverization," *Polymer* 75, 78-87. DOI: 10.1016/j.polymer.2015.08.029
- Jarrett, K. J. (2011). *X-Ray Scattering Study of Cellulosic Arrangements in Plant Cell Wall Materials*, PhD Dissertation, Curtin University, Perth, Australia, pp. 1-197
- Jasiukaitytė-Grojzdek, E., Kunaver, M., and Poljanšek, I. (2012). "Influence of cellulose polymerization degree and crystallinity on kinetics of cellulose degradation," *BioResources* 7(3), 3008-3027. DOI: 10.15376/biores.7.3.3008.3027
- Johansson, L.-S., and Campbell, J. M. (2004). "Reproducible XPS on biopolymers: cellulose studies," *Surf. Interface Anal.* 36(8), 1018-1022. DOI: 10.1002/sia.1827

- Johansson, L.-S., Campbell, J. M., Koljonen, K., Kleen, M., and Buchert, J. (2004). "On surface distributions in natural cellulosic fibres," *Surf. Interface Anal.* 36(8), 706-710. DOI: 10.1002/sia.1741
- Joint Food and Agriculture Organization of the United Nations / World Health Organization Expert Committee on Food Additives (JECFA). (2000). *Compendium of Food Additive Specifications* (Addendum 8). World Health Organization, Geneva, Switzerland, p. 65-66.
- Joutsimo, O. (2004). *Effect of Mechanical Treatment on Softwood Kraft Fiber Properties*, PhD Dissertation, Teknillinen Korkeakoulu (TKK), Espoo, Finland, pp. 1-57.
- Jung, H. G., and Vogel, K. P. (1986). "Influence of lignin on digestibility of forage cell wall material," *J. Anim. Sci.* 62(6), 1703-1712.
- Kamel, S. (2006). "Preparation of cation-exchange resin from lignin," *Int. J. Polym. Mater.* 55(4), 283-291. DOI: 10.1080/009140390945141
- Keshk, S. M. A. S., and Haija, M. A. (2011). "A new method for producing microcrystalline cellulose from *Gluconacetobacter xylinus* and kenaf," *Carbohydr. Polym.* 84(4), 1301-1305. DOI: 10.1016/j.carbpol.2011.01.024
- Koljonen, K., Österberg, M., Johansson, L.-S., and Stenius, P. (2003). "Surface chemistry and morphology of different mechanical pulps determined by ESCA and AFM," *Colloids Surf. A.* 228(1-3), 143-158. DOI: 10.1016/S0927-7757(03)00305-4
- Laine, J., Stenius, P., Carlsson, G., and Ström, G. (1994). "Surface characterization of unbleached kraft pulps by means of ESCA," *Cellulose* 1(2), 145-160. DOI: 10.1007/BF00819664
- Lawoko, K. (2005). *Lignin Polysaccharide Networks in Softwood and Chemical Pulps: Characterisation, Structure and Reactivity*, PhD Dissertation, Kungliga Tekniska Högskolan (KTH), Stockholm, Sweden, pp. 1-58.
- Leppänen, K., Andersson, S., Torkkeli, M., Knaapila, M., Kotelnikova, N., and Serimaa, R. (2009). "Structure of cellulose and microcrystalline cellulose from various wood species, cotton and flax studied by X-ray scattering," *Cellulose* 16(6), 999-1015. DOI: 10.1007/s10570-009-9298-9
- Myz, S. A., Shakhtshneider, T. P., Medvedeva, A. S., Boldyrev, V. V., Kuznetsova, S. A., Kuznetsov, B. N., Danilov, V. G., and Yatsenkova, O. V. (2007). "Mechanochemical solubilization of piroxicam with the use of microcrystalline cellulose that was produced by means of catalytic delignification of sawdust of aspen wood," *Chem. Sust. Dev.* 15(6), 667-672.
- Nam-Tran, H., Nhuan, V. V., Buchmann, M., Sabra, F., Ruelle, P., and Kesselring, U. W. (1993). "Adsorption isotherms of water on a set of fractosils and on Avicel PH 101^R by frontal analysis chromatography," *Drug Dev. Ind. Pharm.* 19(12), 1413-1445. DOI: 10.3109/03639049309047183
- Nikolajeva, V., Arhipova, N., Telysheva, G., Dizhbite, T., and Lebedeva, G. (2005). "Application of lignocellulosics for long-term stimulation of autochthonous microorganisms and remediation of soil," in *10th International Conference EcoBalt*, Riga, Latvia, p. 154.
- Paralikar, K. M., and Bhatwadekar, S. P. (1988). "Microcrystalline cellulose from bagasse pulp," *Biol. Wastes* 24(1), 75-77. DOI: 10.1016/0269-7483(88)90029-8
- Park, S., Baker, J. O., Himmel, M. E., Parilla, P. A., and Johnson, D. K. (2010). "Research cellulose crystallinity index: Measurement techniques and their impact on

- interpreting cellulosa performance," *Biotechnol. Biofuels* 3(10). DOI: 10.1186/1754-6834-3-10
- Pasangulapati, V., Ramachandriya, K. D., Kuma, A., Wilkins, M. R., Jones, C. L., and Huhnke, R. L. (2012). "Effects of cellulose, hemicellulose and lignin on thermochemical conversion characteristics of the selected biomass," *Bioresour. Technol.* 114, 663-669. DOI: 10.1016/j.biortech.2012.03.036
- Perander, A.-M., Halttunen, M., Jääskeläinen, A.-S., Vyörykkä, J., and Vuorinen T. (2001). "Determination of residual lignin from pulp samples with UV resonance Raman spectroscopy," in *11th International Symposium on Wood and Pulping Chemistry: Vol. 1*, Nice, France, pp. 331-334.
- Saariaho, A.-M. (2004). *Resonance Raman Spectroscopy in the Analysis of Residual Lignin and Other Unsaturated Structures in Chemical Pulps*, Ph.D. Dissertation, Teknillinen Korkeakoulu (TKK), Espoo, Finland, pp. 1-54.
- Rayung, M., Ibrahim, N. A., Zainuddin, N., Saad, W. Z., Razak, N. I. A., and Chieng B. W. (2014). "The effect of fiber bleaching treatment on the properties of poly(lactic acid)/oil palm empty fruit bunch fiber composites," *Int. J. Mol. Sci.* 15(8), 14728-14742. DOI: 10.3390/ijms150814728
- Reier, G. E, and Shangraw, R. F. (1966). "Microcrystalline cellulose in tableting" *J. Pharm. Sci.* 55(5), 510-514. DOI: 10.1002/jps.2600550513
- SCAN-CM 15:88. (1988). "Viscosity in cupri-ethylenediamine solution," Scandinavian Pulp, Paper, and Board Testing Committee, Stockholm, Sweden.
- SCAN-CM 15:99. (1999). "Viscosity in cupriethylenediamine solution," Scandinavian Pulp, Paper, and Board Testing Committee, Stockholm, Sweden.
- SCAN-CM 49:03. (2003). "Content of acetone-soluble matter," Scandinavian Pulp, Paper, and Board Testing Committee, Stockholm, Sweden.
- Sczostak, A. (2009). "Cotton linters: An alternative cellulosic raw material," *Macromol. Symp.* 280(1), 45-53. DOI: 10.1002/masy.200950606
- Segal, L., Creely, J. J., Martin, A. E., and Conrad, C. M. (1959). "An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer," *Text. Res. J.* 29(10), 786-794. DOI: 10.1177/004051755902901003
- Shackford, L. D. (2003). "A comparison of pulping and bleaching of kraft softwood and eucalyptus pulps," in: *36th International Pulp and Paper Congress and Exhibition*, São Paulo, Brazil.
- Sláviková, E., and Košíková, B. (1994). "Inhibitory effect of lignin by-products of pulping on yeast growth," *Folia Microbiol.* 39(3), 241-243. DOI: 10.1007/BF02814656
- Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D, and Crocker, D. (2008). "Determination of structural carbohydrates and lignin in biomass: Laboratory analytical procedure (LAP)," *Technical report NREL/TP-510-42619*, National Renewable Energy Laboratory, Golden, CO, USA.
- 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," *Bioresour. Technol.* 101(15), 5961-5968. DOI: 10.1016/j.biortech.2010.02.104
- Spoljaric, S., Genovese, A., and Shanks, R. A. (2009). "Polypropylene–microcrystalline cellulose composites with enhanced compatibility and properties," *Compos. Part A–Appl. S.* 40(6-7), 791-799. DOI: 10.1016/j.compositesa.2009.03.011

- Srivastava, S. K., Singh, A. K., and Sharma, A. (1994). "Studies on the uptake of lead and zinc by lignin obtained from black liquor – a paper industry waste material," *Environ. Technol.* 15(4), 353-361. DOI: 10.1080/09593339409385438
- Steele, D. F., Moreton, R. C., Staniforth, J. N., Young, P. M., Toby, M. J., and Edge, S. (2008). "Surface energy of microcrystalline cellulose determined by capillary intrusion and inverse gas chromatography," *The AAPS Journal* 10(3), 494-503. DOI: 10.1208/s12248-008-9057-0
- Tejado, A., Peña, C., Labidi, J., Echeverria, J. M., and Mondragon, I. (2007). "Physico-chemical characterization of lignins from different sources for use in phenol-formaldehyde resin synthesis," *Bioresour. Technol.* 98(8), 1655-1663. DOI: 10.1016/j.biortech.2006.05.042
- Testova, L., Borrega, M., Tolonen, L. K., Penttilä, P. P., Serimaa, R., Larsson, P. T., and Sixta, H. (2014). "Dissolving-grade birch pulps produced under various prehydrolysis intensities: quality, structure and applications," *Cellulose* 21(3), 2007-2021. DOI: 10.1007/s10570-014-0182-x
- Thoorens, G., Krier, F., Leclercq, B., Carlin, B., and Evrard, B. (2014). "Microcrystalline cellulose, a direct compression binder in a quality by design environment — A review," *Int. J. Pharm.* 473(1-2), 64-72. DOI: 10.1016/j.ijpharm.2014.06.055
- Trache, D., Donnot, A., Khimeche, K., Benelmir, R., and Brosse, N. (2014). "Physico-chemical properties and thermal stability of microcrystalline cellulose isolated from Alfa fibres," *Carbohydr. Polym.* 104, 223-230. DOI: 10.1016/j.carbpol.2014.01.058
- Tuason, D. C., Krawczyk, G. R., and Buliga G. (2010). "Microcrystalline cellulose," in: *Food Stabilizers, Thickeners and Gelling Agents*, A. Imeson (ed.), Wiley-Blackwell, Chichester, United Kingdom.
- U.S. Pharmacopeial Convention (USP). (2005). "Microcrystalline cellulose," *Pharmacopeial Forum* 31(5), pg. 1421.
- Uesu, N. Y., Pineda, E. A. G., and Hechenleitner, A. A. W. (2000). "Microcrystalline cellulose from soybean husk: effects of solvent treatments on its properties as acetylsalicylic acid carrier," *Int. J. Pharm.* 206(1-2), 85-96. DOI: 10.1016/S0378-5173(00)00532-9
- Vanhatalo, K. M., and Dahl, O. P. (2014). "Effect of mild acid hydrolysis parameters on properties of microcrystalline cellulose," *BioResources* 9(3), 4729-4740. DOI: 10.15376/biores.9.3.4729-4740
- Vasiliu-Oprea, C., and Nicolescu, J. (1993). "Micronized (and microcrystalline) celluloses," *Polym.-Plast. Technol. Eng.* 32(3), 181-214. DOI: 10.1080/03602559308019227
- Vila, C., Santos, V., and Parajo, J. C. (2014). "Manufacture of microcrystalline cellulose from *Eucalyptus globulus* wood using an environmentally friendly biorefinery method," *J. Wood Chem. Technol.* 34(1), 8-19. DOI: 10.1080/02773813.2013.804090
- Virtanen, T., Svedström, K., Andersson, S., Tervala, L., Torkkeli, M., Knaapila, M., Kotelnikova, N., Maunu, S. L., and Serimaa, R. (2012). "A physico-chemical characterisation of new raw materials for microcrystalline cellulose manufacturing," *Cellulose* 19(1), 219-235. DOI: 10.1007/s10570-011-9636-6
- Wan, J., Wang, Y., and Xiao Q. (2010). "Effects of hemicellulose removal on cellulose fiber structure and recycling characteristics of eucalyptus pulp," *Bioresour. Technol.* 101(12), 4577-4583. DOI: 10.1016/j.biortech.2010.01.026

- Werner, K., Pommer, L., and Broström, M. (2014). "Thermal decomposition of hemicelluloses," *J. Anal. Appl. Pyrolysis* 110, 130-137. DOI: 10.1016/j.jaap.2014.08.013
- Wiley, J. H., and Atalla, R. H. (1987). "Band assignment in the Raman spectra of celluloses," *Carbohydr. Res.* 160, 113-129. DOI: 10.1016/0008-6215(87)80306-3
- Xiao, L.-P., Sun, Z.-J., Shi, Z.-J., Xu, F., and Sun, R.-C. (2011). "Impact of hot compressed water pretreatment on the structural changes of woody biomass for bioethanol production," *BioResources* 6(2), 1576-1598
- Yang, H., Yan, R., Chen, H., Lee, D. H., and Zheng, C. (2007). "Characteristics of hemicellulose, cellulose and lignin pyrolysis," *Fuel* 86(12-13), 1781-1788. DOI: 10.1016/j.fuel.2006.12.013
- Zemek, J., Košíková, B., Augustín, J., and Joniak, D. (1979). "Antibiotic properties of lignin components," *Folia Microbiol.* 24(6), 483-486. DOI: 10.1007/BF02927180
- Zografí, G., Kontny, M. J., Yang, A. Y. S., and Brenner, G. S. (1984). "Surface area and water vapor sorption of macrocrystalline cellulose," *Int. J. Pharm.* 18(1-2), 99-166. DOI: 10.1016/0378-5173(84)90111-X

Article submitted: November 16, 2015; Peer review completed: January 22, 2016;

Revisions accepted: March 10, 2016; Published: March 17, 2016.

DOI: 10.15376/biores.11.2.4037-4054