

Effects of Modified Cooking on Fiber Wall Structure of *E. globulus* and *E. nitens*

Rudine Antes* and Olli P. Joutsimo

This work examined the impact of SuperBatch™ (SB), CompactCooking™ (CC), and Lo-Solids™ (LS) modified kraft pulping on the fiber wall structure of unbleached and bleached unrefined pulps of *E. globulus* and *E. nitens*. The kappa number target for all pulps was 17 ± 0.5 . It was found that *E. nitens* had higher water retention values (WRVs) and fiber saturation point (FSP) for both bleached and unbleached pulps versus *E. globulus*. Fibril lateral aggregates width of unbleached pulps increased as WRV increased. After bleaching there was an inverse trend in correlation of WRV versus the lateral fibril aggregate width. The modified cooking methods or wood species did not have an influence on lateral fibril aggregate width. The higher WRV and FSP values for *E. nitens* were not reflected in the cumulative pore volume measurements including pore widths below 216 nm.

Keywords: Modified cooking method; *Eucalyptus globulus*; *Eucalyptus nitens*; Water retention value; Fiber saturation point; Fiber wall structure; Cumulative pore volume; SuperBatch; CompactCooking; Lo-Solids

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INTRODUCTION

Since the invention of kraft pulping, several developments have been tested and implemented in order to improve the production efficiency and quality of the pulp. During the past several decades, the main modifications have been directed toward increasing the pulp yield and improving delignification in order to implement ECF and TCF bleaching sequences (Courchene 1998). In conventional kraft cooking, wood chips and white liquor are charged into a digester at the same time and heated under pressure until the desired degree of delignification is achieved. This means that alkali concentration is very high at the beginning of the cook and low at the end of the cook, which results in severe carbohydrate and yield degradation, and in a low overall delignification rate. Therefore, higher pulping selectivity is needed, minimizing carbohydrate degradation, allowing an extended delignification. Thus, a more selective kraft process was developed by the introduction of several modifications to the conventional kraft process. This concept of a modified kraft process was developed at KTH (Royal Institute of Technology) and STF1 (Swedish Pulp and Paper Research Institute) (Carnö and Hartler 1976; Nordén and Teder 1979; Teder and Olm 1981; Johansson *et al.* 1984). The rules for modified cooking were discovered and can be summarized as: (1) a leveled-out alkali concentration profile throughout pulping; (2) a high concentration of hydrogen sulfide ions, especially at the beginning of the bulk cooking phase; (3) a low concentration of dissolved lignin and sodium ions, especially at the end of the cook; and (4) a lower pulping temperature.

In the last few decades, the pore structure of the fiber walls has received a considerable amount of research attention (Kerr and Goring 1975; Suumaki *et al.* 1997; Alinec and van de Ven 1997; Berthold 1997; Selenius and Lindström 1997; Hubbe *et al.* 2007; Sjöstedt 2014). This is appropriate because the “geometry” of pores in the fiber walls (*i.e.*, size, shape, and arrangement) influences many aspects of fiber behavior. This includes colloidal interactions, fiber shrinkage, and water removal. The method used to characterize a particular porous system will depend on the type of material being characterized, the available analytical techniques, and the information that is most relevant to a given situation (Dullien 1979).

The strength and other properties of softwood kraft pulp fibers are influenced by the porous structure of the fiber wall. The pores in the fiber wall are affected during kraft cooking when the fibers are liberated from the wood by dissolving lignin into the pulping liquors. The macropore void volume of a native softwood cell wall is approximately 0.02 cm³/g, as measured by nitrogen absorption. After kraft pulping to a yield 47%, the macropore volume of a softwood fiber wall will increase to 0.6 cm³/g, as measured by size exclusion or by nitrogen adsorption of solvent-exchanged pulps (Stone and Scallan 1965; Stone and Scallan 1967). The best way to measure cell wall pores is with techniques directly applicable to water-saturated fibers. Four of these methods for quantifying this property are: nuclear magnetic resonance spectroscopy (NMR) (Li 1991), solute exclusion (Campbell 1949; Stone and Scallan 1968a), water retention value (WRV) (Scallan and Carles 1972), and fiber saturation point (FSP). According to Scallan and Carles (1972), WRV directly correlates with the fiber saturation point when the solute exclusion technique is applied. Optionally, the cell wall pore size can also be measured with thermoporosimetry (Maloney 2000; Ksiazczak 2003). According to Zauer *et al.* (2013), the basis of thermoporosimetry to measure pore-size distribution using DSC is the melting point depression of a pore-filling substance or adsorbate in very small pores which occurs by osmotic and capillary effects.

Nuclear magnetic resonance spectroscopy (NMR)

The NMR relaxation method has been shown to be a useful technique to determine the pore size distribution in various materials. The basic idea of this method is that the molecular dynamics of the liquid molecules in the vicinity of a solid surface are perturbed, and thus, the relaxation times for the liquid molecules near the surface are different from that of the bulk liquid. A saturated sample with a discrete pore size distribution should give rise to a distribution of NMR relaxation times. With NMR spectroscopy, the size of the pores that is calculated is directly proportional to the pore volume-to-surface area ratio (Li 1991). One advantage of this method is that measurements can be done over a wide range of moisture contents, which can be used to study the collapse of fiber pores during dewatering.

Water retention value (WRV) and Fiber saturation point (FSP)

A technique that is often used to measure fiber swelling is the water retention value, WRV (Scallan and Carles 1972; Abson 1988; Maloney 2000). With the WRV test, a pulp pad is centrifuged under conditions that are assumed to remove the external water between the fibers. The moisture content of the pad after centrifuging is an indication of the extent of fiber swelling. The WRV is an empirical test whose value depends on specific test conditions (Lebel *et al.* 1979; Abson and Gilbert 1980). Despite this drawback, the WRV

test is simple, fast, and precise; it remains today as a popular technique. It was postulated that the WRV can deviate from the FSP because some water is retained between the fibers, and some water is pressed from the cell wall when the pulp pad is centrifuged. The amount of external water retained between the fibers is largely affected by the capillary structure of the fiber-fiber network. The amount of internal water pressed from the fiber wall depends on the viscoelastic properties of the swollen fibers. For example, mechanical pulps, which are relatively stiff (Scallan and Tigerstrom 1992) and have a high fines content (Luukko 1999), retain a significant amount of water in the inter-fiber spaces; however, they do not have any water pressed from the cell wall. Therefore, their WRV is much higher than the FSP. On the other hand, highly swollen pulps, such as unbleached hardwood kraft, have a significant amount of water pressed internally from the fiber walls. For these pulps, the FSP may even be slightly lower than the WRV. While the conditions used during a WRV test, such as centrifugal force, time, pad basis weight, *etc.*, may be adjusted so that the WRV correlates well with the FSP for a given pulp, it does not seem possible to find a set of test conditions that will accurately measure fiber swelling for a wide range of pulps (Maloney 2000). A FSP test involves mixing relatively high consistency fiber slurry with a solution of high molecular weight dextran (Scallan and Carles 1972; Scallan 1978). The dry mass of fibers, the total amount of water, and the total amount of dextran need to be known precisely. After a period of mixing, a filtrate sample is obtained, and the FSP is determined with a Rayleigh interference refractometer (*i.e.*, polarimeter) (Stone and Scallan 1968b) based on the concentration change of dextran solution, as only the water outside the pores will dilute the sample. The validity of this test relies upon the assumptions that the dextran has no affinity for the fiber surfaces and that its molecular size does not allow it to pass into the pores within the fiber wall (Hubbe *et al.* 2007).

Thermoporosimetry

Water held in the capillaries of porous materials melts at a depressed temperature. This is because of the higher pressure of water in cavities with a curved interface. The relationship between the pore diameter (D) and the melting temperature depression is described by the well-known Gibbs-Thomson Equation (Eq. 1):

$$D = \frac{-4V_m\sigma_{ls}}{\Delta H_m \ln\left(\frac{T}{T_0}\right)} \quad (1)$$

where V_m is the molar volume of ice, T_0 is the melting point of water at normal pressure, T is the melting temperature, σ_{ls} is the surface energy at the ice-water interface (equal to 12.1 mN/m), and ΔH_m is the latent heat of melting. This equation assumes that the pores are spherical (Maloney 1999).

In differential scanning calorimetry (DSC), the heat involved in various thermal transitions can be measured. DSC has been widely used to study the behavior of water in gels and other hydrated polymer systems (Silvy *et al.* 1964; Nakamura *et al.* 1986; Galin and Galin 1992; Yamauchi and Hasegawa 1993; Galin and Calla 1993). This is normally done by studying the melting behavior of water-saturated samples. Different water fractions are detected as separate peaks on the differential power-temperature plot.

Different water fractions are detected as separate peaks on the differential power-temperature plot. One fraction, the nonfreezing water, is not explicitly detected, but its

value is readily calculated from the DSC data. DSC measurements of hydrated systems sometimes have multiple peaks whose origin and meaning are unclear (Hatakeyama *et al.* 1987; Hatakeyama and Liu 1999; Yamauchi and Murkami 1991). For wood pulps, there are three main water fractions (Nakamura *et al.* 1981). While smaller fractions and sub-fractions may be detected under certain conditions, this distinction will not be considered here. Hatakeyama *et al.* (1987) used the terms “nonfreezing water” and “freezing bound water” for the two types of bound water that are measured for cellulose using DSC (Pouchlý *et al.* 1979). The same terminology will be used in this work.

When characterizing fiber wall pore sizes, the measurement technique has to be taken into account. This is because the different techniques yield different results. It is reported that NMR relaxation measurements can be used for determining pore sizes in the range of 6.5 to 10 nm, depending on the pulp and pulp treatment type (Maloney 2000). Size exclusion chromatography (SEC) has been reported to be limited by the availability of the interior of the fiber wall to polymers of different sizes. This means that if the pores near the surfaces of the fiber walls are narrower than pores further within them, then the volume of the fiber wall will be ascribed just to the class of pores as big as the openings in the external fiber wall layer, as pointed out by Lindström (1986). The porous fiber wall structure, which is created during pulping, influences the ability of molecules to move in and out of the fiber wall. The amount of lignin removed, among other factors, will determine the size of the openings in the fiber wall, as discussed by Stone and Scallan (1965). As mentioned earlier, the openings in the fiber wall will determine the movement of molecules into and out of the fiber wall. This has been studied by Alince and van den Ven (1997), who found that the radii of the openings in the fiber walls limiting the adsorption of cationic polyelectrolytes was around 50 nm. This information has been used, for example by Maloney (2000) in solute exclusion studies, together with thermoporosimetry to determine fiber saturation point and pore diameter distribution. According to Maloney and Paulapuro (2001), the pore size diameters can vary between 0.3 to 600 nm. It seems that the estimated pore size distribution varies depending on the method employed (Paavilainen 1993).

The objective of this work was to study the effect of modified cooking, at the laboratory scale, on the fiber wall structure of *E. globulus* and *E. nitens* pulps, which are the most common *Eucalyptus* species used for producing market pulps in Chile. The modified cooking methods examined in this research work were SuperBatch™ (SB), CompactCooking™ (CC), and Lo-Solids™ (LS). The work focused on the cooking results (H-factor, kappa number, yield, and brightness) and amount of bleaching chemicals needed to produce fully bleach pulps. Regarding fiber wall, the effect of cooking method and *Eucalyptus* species on fiber morphology and fiber wall structure (measured as lateral fibril aggregate width, lateral fibril width and pore size distribution) was evaluated. Also, the water retention values and fiber saturation point were measured to determine the water holding capacity of the unrefined and never dried pulps.

EXPERIMENTAL

Raw Material

The brownstock used in this work was produced from fresh chips of *E. globulus* and *E. nitens* from central Chile (Region VIII). The chip classification prior to cooking

followed the standard SCAN CM:40-01 (2001). The wood age was chosen so that the wood basic density would be at very similar levels around $500 \pm 20 \text{ kg/m}^3$; *i.e.*, the *E. globulus* sample was 12 years old and had a basic density of 523 kg/m^3 , and the *E. nitens* sample was 15 years old and had a basic density of 507 kg/m^3 . The standard employed to measure the basic density of wood was TAPPI T 258 om 11 (2011). Details about the raw material are reported by Antes and Joutsimo (2015a).

Cooking Experiments

All the cooking experiments were performed at VTT Technical Research Centre of Finland. The laboratory digester for modified cooking was performed in a forced circulation digester with a volume of 30 L. Heating of the digester was carried out with steam jacket heating. The digester used to generate black liquor, which was used as the displacement liquor and wash liquor for the LS modified cooks, was a 15 L rotating batch digester. The batch cooking system was electrically heated by the digester jacket and controlled electronically. The cooks for liquor generation were carried out at $160 \text{ }^\circ\text{C}$ and with a constant alkali charge of 17% EA (expressed as NaOH). For all the modified cooks, the kappa number target was 17 ± 0.5 . The cooking procedure and conditions for all three modified cooking methods are presented in Table 1.

Table 1. Main Features used for Modified Cooking Methods: SB, CC, and LS

Phase/Modified Cooking Type	SB	CC	LS
Impregnation Zone			
Temperature ($^\circ\text{C}$)	90	115	105
Liquor to wood ratio	5:1	6:1	4:1
Alkali charge WL + BL as EA (%)	5	6.3	10.5
Time <i>E. globulus</i> / <i>E. nitens</i> (min)	40/40	60/60	45/45
Cooking Zone I			
Temperature ($^\circ\text{C}$)	148 (HBL fill)	141	135
Liquor to wood ratio	4.25:1 (HBL fill)	6:1	4:1
Alkali charge as EA (%)	5 (HBL fill)	7	7.2
Time <i>E. globulus</i> / <i>E. nitens</i> (min)	60/60	90/100	20/20
Cooking Zone II			
Temperature ($^\circ\text{C}$)	152 (Cooking circulation)	141	148
Liquor to wood ratio	5:1 (Cooking circulation)	3.8:1	4:1
Alkali charge as EA (%)	10.6 (Cooking circulation)	0.0	0.0
Time <i>E. globulus</i> / <i>E. nitens</i> (min)	34/40	90/100	100/100
Washing Zone			
Temperature ($^\circ\text{C}$)	80	NA	90
Washing Liquor to wood ratio	5:1	NA	4:1
Alkali charge as EA (%) or g/L (NaOH)	2.2%	NA	5.0 g/L
Time <i>E. globulus</i> / <i>E. nitens</i> (min)	90/90	60/60	40/40
Total Alkali charge in the cook as EA (NaOH) (%)	22.8	21.0	21.9

*NA = Not applicable

Bleaching Conditions

The unbleached pulps were bleached at VTT (in Finland) using the $\text{D}_0\text{E}_1\text{D}_1\text{E}_2\text{D}_2$ bleach sequence (Antes and Joutsimo 2015b). Every experiment was repeated twice, and the results presented are the average. The following were the bleaching conditions:

D-stages were performed in 18 L air bath electrically heated reactors. Preheated pulp was initially added to the reactor, and then the water with acid or alkali was added for pH adjustment. After mixing, the pH was measured, the chlorine dioxide was charged into the reactor, and the cover was closed immediately. Pulp was first mixed in the reactor for 4.5 min at a speed of 30 rpm. During the reaction time, the reactor was periodically stirred (*i.e.*, the rotor was stopped for 70 s, and then the rotation direction was reversed and mixed for 30 s). After the prescribed reaction time, the final pH of the pulp slurry was measured at the reaction temperature. The residual chlorine dioxide content of the bleaching filtrate was determined iodometrically. The pulp was diluted and washed by a standardized procedure that is described later in this section. Specific reaction conditions of the individual D stages (*i.e.*, D₀, D₁, and D₂) are presented in Table 2. The kappa factor (KF) of the D₀ stage was fixed at 0.20.

The **alkaline extraction stage (E)** was performed in a Teflon-coated 40 L reactor as follows. The pulp and most of the water was heated to the reaction temperature in a microwave oven and placed into the reactor. Alkali with additional water was charged, the pulp slurry was mixed for 1 min at 300 rpm, and the pH was measured. During the reaction time, the pulp slurry was mixed every 20 min for 12 s at 300 rpm. After the reaction time, the final pH of the pulp slurry was measured at the reaction temperature. The pulp was diluted and washed by a standardized procedure that is described later in this section. Specific reaction conditions of the individual E stages (*i.e.*, E₁ and E₂) are presented in Table 2.

Pulp washing between the bleaching stages was performed by a standard laboratory procedure. Pulp was diluted to 5% consistency with deionized water, which was at the same temperature as that of the preceding bleaching stage. After dewatering, the pulp was washed two times with cold deionized water with an amount equivalent to ten times the mass of the oven-dry pulp. Homogenization of pulp was done by hand.

Handsheets (10 g oven-dried pulp) for brightness and kappa number measurements were formed after each bleaching stage in the sequence by adjusting the pH to 4.5 with SO₂ prior to sheet formation.

The following standardized methods were employed for characterizing the pulps: kappa number – ISO 302 (2004); dry solid content of pulp – ISO 638 (2008); intrinsic pulp viscosity – ISO 5351 (2010); and brightness from split sheet surface – ISO 2470-1 (2009). Bleaching conditions and results are presented in more detail in Antes and Joutsimo (2015b).

Fiber Morphology

The morphology of the pulp fibers was measured in VTT (Finland) using a Kaajani FS300 fiber analyzer. Additionally fiber wall thickness and fiber width were measured with a light microscope and semi-automatic image analysis from wet (water/glycerol solution) using VTT internal method. Around 500 fibers were analyzed for each sample.

Cell Wall Porosity Measurements and Drainability

The solute exclusion method, using a dextran probe, with a molecular weight of 2x10⁶ Daltons, was used to determine the fiber saturation point (FSP) of the pulps (Stone and Scallan 1967). The advantage of this method is that the fibers can be maintained in their water-swollen state during the measurements. This means that the pore closure within the fiber walls that results from drying of the never-dried pulps can be avoided. According

to Maloney (2000), the different pore sizes can be detected by differential scanning microcalorimetry (DSC). The author also classes the water in the pores according to detection as non-freezing water (NFW), and freezing bound water (FBW). The FSP is the sum of NFW, FBW, and water detected by solute exclusion method. The water retention value (WRV) was measured according to ISO 23714 (2014) and Schopper-Riegler ($^{\circ}$ SR) method ISO 5267-1 (1999).

Thermoporosimetry Analyses

One gram of the washed brownstock pulp was thoroughly washed with distilled water to remove dissolved substances. The acidic groups in the cell wall were ion exchanged with sodium cations by heating the 1% consistency pulp slurry with 0.1 M sodium acetate for 1 h at 40 $^{\circ}$ C. The pulp was then rewashed several times with distilled water and centrifuged at 3,000 g for 10 min to obtain the moisture content close to the fiber saturation point. After centrifuging, 2 to 2.5 mg of the wet pulp was placed in an aluminum sample pan. The amount of freezing and nonfreezing water was determined using thermoporosimetry. A Mettler 821 differential scanning calorimeter (DSC) from Mettler Toledo (USA) was used for thermoporosimetry measurements. The procedure used was that reported by Maloney *et al.* (1998) and Maloney and Paulapuro (2001). An isothermal step method was used to measure the pore size distribution. In this method, the sample is first frozen, and then the frozen water is melted in steps, which are below the melting point of water. At each step, the temperature is kept constant until melting is completed. The heat absorbed at each temperature is obtained by integrating the endothermic peaks. The latent heat is used to calculate the amount of melted water. The pore size is then related to the melting temperature depression. It is assumed that the pores are cylindrical and that the pore size is the diameter of the cylinder. At the end of the temperature program, the sample is refrozen and then melted completely. This generates the melting peak of the total freezing water. The nonfreezing water is calculated by subtracting the total freezing water from the water content in the sample. The isothermal melting set-points used in this study were -8, -5, -3, -2, -1, -0.6, -0.4, and -0.2 $^{\circ}$ C. The -0.2 $^{\circ}$ C temperature corresponds to a maximum pore diameter of 216 nm. The thermoporosimetry measurements were conducted at Helsinki University of Technology (Aalto, Finland).

NMR Lateral Fibril Aggregate Width and Lateral Fibril Width

All NMR measurements were performed with a digital Bruker Avance DPX300 NMR spectrometer from Bruker (USA). It was equipped with a 4 mm double air-bearing MAS probe head. The 4 mm o.d. ZrO₂ MAS rotors were filled tightly with *ca.* 80 to 90 μ L (*ca.* 80 to 100 mg) of moist sample. ¹³C CP-MAS NMR analyses involved the following acquisition parameters: Resonance frequency used was 75 MHz. The MAS spinning speed was 4 kHz and the temperature: 26 $^{\circ}$ C. The spectral width was 340 ppm, and the acquisition time was 30 ms. The cross-polarization (CP) contact time was 1 ms. The CP-pulse shape was ramped from 70 to 100. ¹H decoupling scheme: SPINAL-64. The repetition interval was 2 s and the number of accumulations used was 3072. The chemical shift reference used was Adamantane. The following processing parameters for ¹³C CP-MAS NMR analyses were used: the size of real spectrum was 4096 points (zero-filling) and no window function was used, only Fourier transform function was used. All the spectra were converted to x-y ASCII files for later lineshape analysis. Spectral deconvolutions of experimental cellulose AGU-C4 line shapes. The technique was

performed according to the procedures of Larsson *et al.* (1997) and Zuckerstätter *et al.* (2009).

RESULTS AND DISCUSSION

Cooking Results

Table 2 presents a summary of the cooking results: H-factor, kappa number, total yield, rejects, screen yield, brightness, and intrinsic viscosity.

Table 2. Summary Results of Different Cooking Methods

Raw Material/ Cooking Results	H factor /SD	Kappa number/SD	Total yield (%)/SD	Rejects (%)/SD	Screened yield (%)/SD	Bright-ness (%)/SD	Intrinsic Viscosity (mL/g)
SB							
<i>E. globulus</i>	300/5.12	16.50/0.46	58.76/0.44	1.62/0.80	57.14/0.70	41.50/0.14	1590
<i>E. nitens</i>	315/3.98	17/0.32	57.89/0.40	1.33/0.40	56.56/0.45	39.36/0.06	1620
CC							
<i>E. globulus</i>	239/4.47	17/0.12	58.59/0.51	1.88/0.33	56.71/0.34	41.57/0.26	1660
<i>E. nitens</i>	262/5.20	16.5/0.10	57.22/0.23	1.13/0.13	56.09/0.22	40.33/0.10	1650
LS							
<i>E. globulus</i>	244/5.23	17/0.51	58.66/0.46	1.71/0.56	56.95/0.40	41.51/0.33	1600
<i>E. nitens</i>	273/4.78	16.5/0.14	56.84/0.37	1.19/0.21	55.65/0.38	39.84/0.17	1625

SB technology requires higher H-factor values to delignify to the same kappa number (17 ± 0.5) when compared to the other processes, which was independent of the *Eucalyptus* species used. *E. nitens* brownstocks presented lower brightness levels when compared to the other cooking methods, whereas *E. globulus* brownstocks presented higher screened rejects and screened yields.

Fiber Morphology

Figures 1A and 1B present the fiber lengths of the unbleached and bleached *E. globulus* and *E. nitens* pulps produced by the three modified cooking methods.

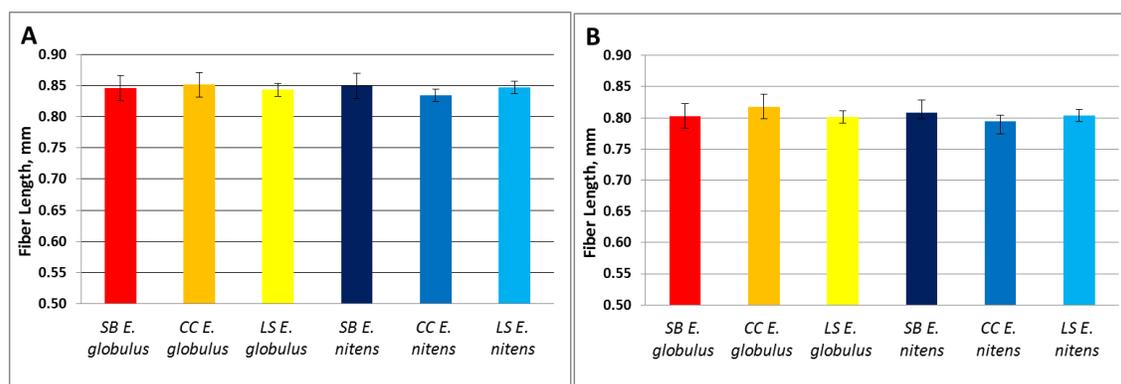


Fig. 1. Fiber length (in mm) of SB, CC, and LS pulps of *E. globulus* and *E. nitens* - (A) unbleached and (B) bleached. The error bars present 95% confidence interval of the mean value

These results are presented as length-weighted average fiber length. This is calculated as the sum of individual fiber lengths squared divided by the sum of the individual fiber lengths (Ring and Bacon 1997).

Figure 1 shows that the fiber lengths were not affected by the modified cooking process employed. These small differences between the cooking processes or *Eucalyptus* species were not statistically significant. The trend in fiber length can be seen for both unbleached and bleached fibers, and for both of the *Eucalyptus* species. Figures 2A and 2B present the fiber widths of the unbleached and bleached pulps produced by the modified cooking processes.

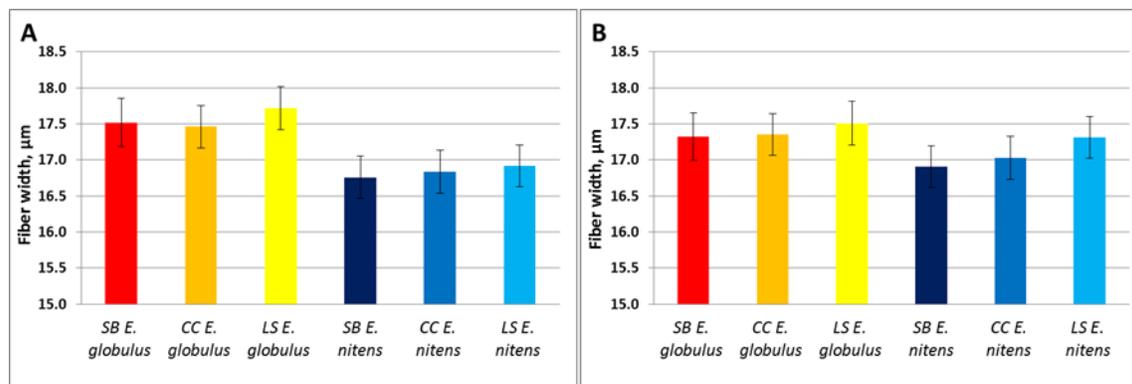


Fig. 2. Fiber width (in μm) of SB, CC, and LS pulps of *E. globulus* and *E. nitens* - (A) unbleached and (B) bleached. The error bars present 95% confidence interval of the mean value.

From Figs. 2A and 2B, it can be observed that the fiber widths from *E. globulus* pulps were slightly wider than those from *E. nitens* in unbleached and bleached pulps, which was independent of the modified cooking process used. This observation can only be attributed to the morphologies of *Eucalyptus* wood species. The fiber walls thicknesses of both unbleached and bleached, for the various pulps, are given in Figs. 3A and 3B.

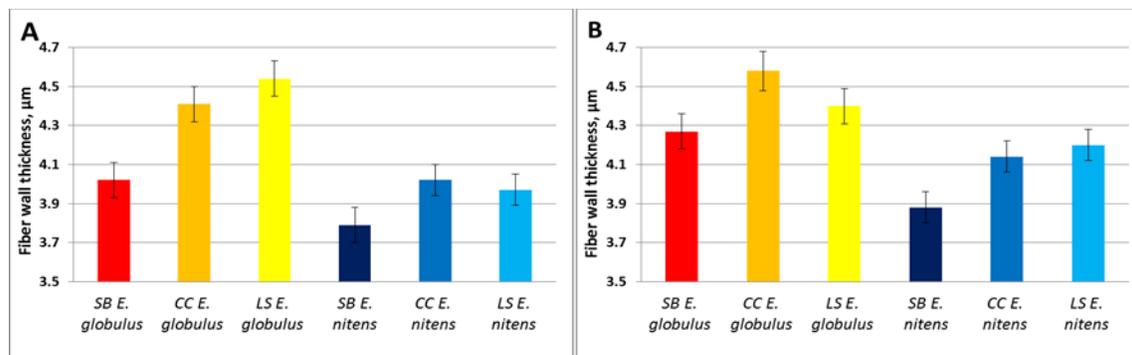


Fig. 3. Fiber wall thickness (in μm) of SB, CC, and LS pulps of *E. globulus* and *E. nitens* - (A) unbleached and (B) bleached. The error bars present 95% confidence interval of the mean value.

From Fig. 3A and 3B it can be observed that the fiber wall thicknesses of *E. nitens* were slightly thinner when compared to those of *E. globulus*. The results of fiber coarseness measured with Kaajani FS-300 of the same samples support these results. Fiber coarseness of unbleached and bleached fibers are presented in Figs. 4A and 4B.

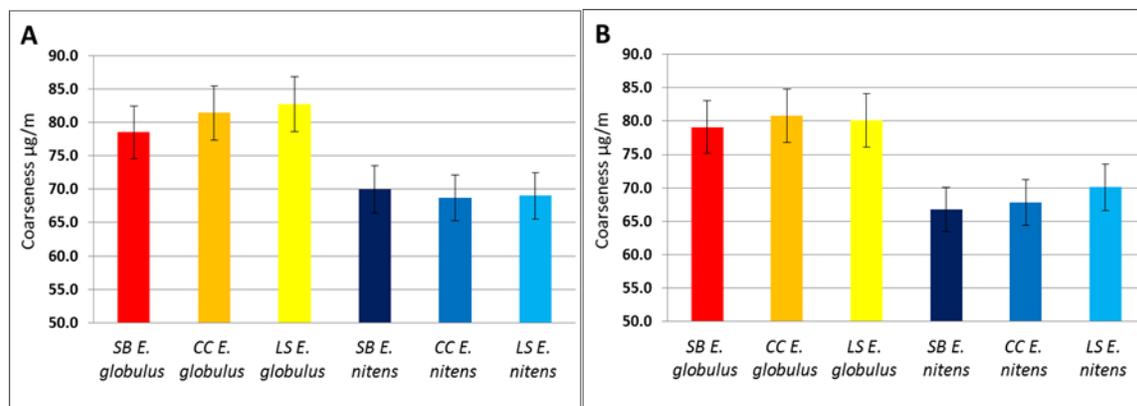


Fig. 4. Fiber coarseness (in µg/m) of SB, CC, and LS pulps of *E. globulus* and *E. nitens* - (A) unbleached and (B) bleached. The error bars present 95% confidence interval of the mean value.

As shown, *E. nitens* presented lower coarseness compared to *E. globulus*. Also, it can be seen that there were no significant differences in the coarseness within the same species independently of the modified cooking method. Figures 5A and 5B present respectively the fines content and °SR of bleached fibers.

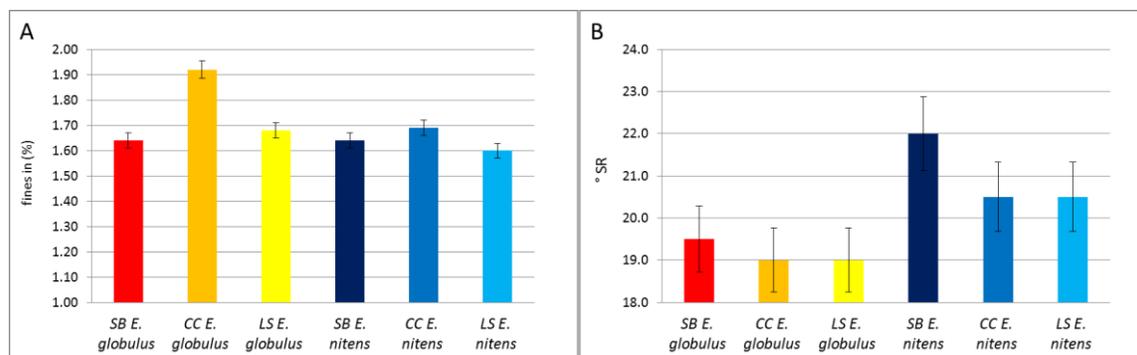


Fig. 5. A) Fines values (in %) and B) °SR (in °SR) of SB, CC, and LS modified cooking methods. The error bars present 95% confidence interval of the mean value.

Figure 5A shows that there was no significant difference among the fines content that could explain differences in °SR shown in Fig. 5B, with the possible exception of CC *E. globulus*. Figure 5B clearly shows that *E. nitens* had a higher initial unrefined °SR.

Cell Wall Porosity Measurements and Drainability

The WRV data (Figs. 6A and 6B) clearly showed that the *E. nitens* pulps had significantly higher values than those from *E. globulus* pulps. However these differences cannot be explained by differences in fines content (Fig. 5A). Antes and Joutsimo (2015) reported that *E. nitens* had higher hemicellulose content when compared to *E. globulus*, which could explain the WRV differences; higher amounts of hemicelluloses absorb and retain more water within the fiber wall.

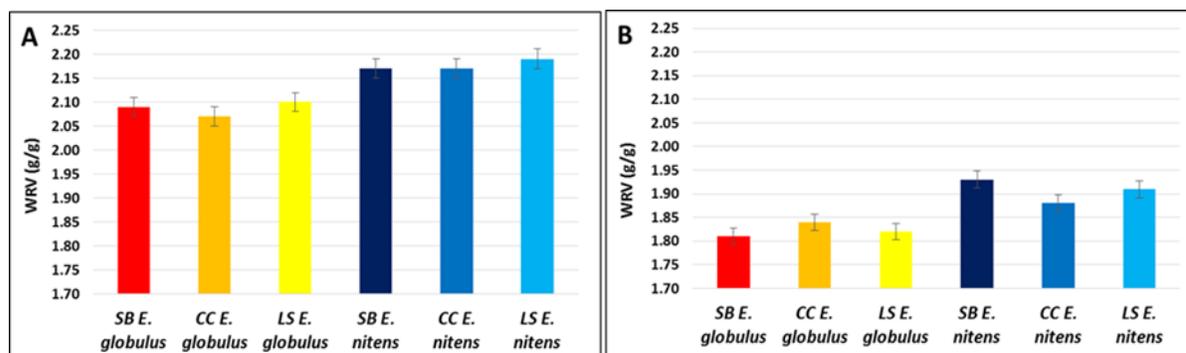


Fig. 6. The water retention values (in g/g) of SB, CC, and LS cooked (A) unbleached and (B) bleached of *E. globulus*, and *E. nitens* pulps. The error bars present the standard deviation of the measurements. Antes and Joutsimo (2015c)

An alternative explanation for the lower WRV could be related to the wall porosity of thicker fibers, which are more porous and cannot retain water by capillary action during the WRV measurement (Joutsimo 2004). Pulkkinen (2010) reported that larger fiber wall thickness resulted in lower water retention value (WRV). The fiber wall porosities were quantified by FSP measurements as illustrated in Figs. 7A and 7B.

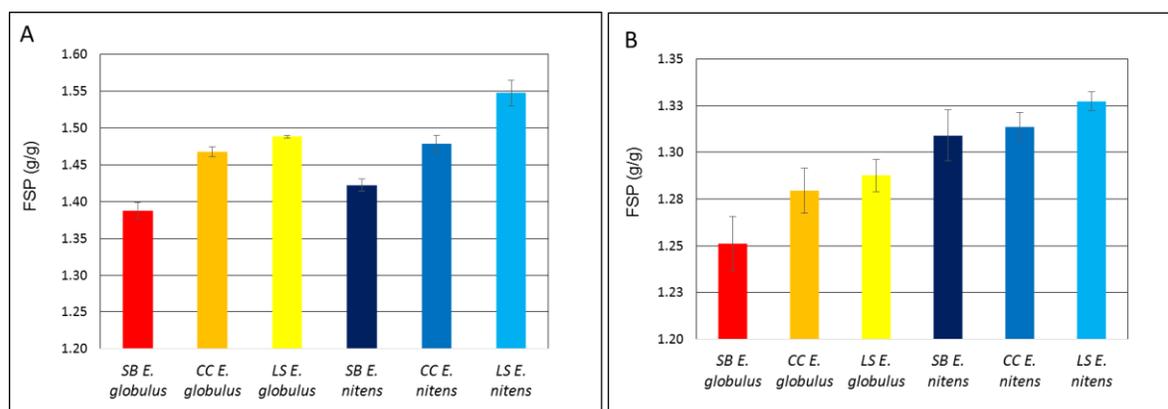


Fig. 7. FSP values (in g/g) of SB, CC, and LS cooked (A) unbleached and (B) bleached of *E. globulus*, and *E. nitens* pulps. The error bars present the standard deviation of the measurements.

It was observed that unrefined *E. nitens* fibers, both unbleached and bleached, presented higher FSP values versus *E. globulus* fibers. The tendency observed is that LS and CC cooked pulp fibers had the highest FSP values; thus, these fibers seemed to be more swollen than those produced from SB modified cooking. WRV and FSP trend value were similar and inversely followed the fiber wall thickness trends (Fig. 3), which indicated that the fiber wall capillary pressure of *E. nitens* (*i.e.*, mean fiber wall porosity) was higher than that of *E. globulus*. According to Joutsimo (2004), the lower FSP values can be explained by higher pore size diameter of unbleached pulps which allows dextrans to migrate from free liquor to inside the fiber walls.

Additionally, NMR method was used to measure lateral fibril aggregate width and the lateral fibril width from unbleached and bleached pulps in order to characterize the changes to the fiber wall structure before and after bleaching. The results are displayed in Figs. 8(A and B) and 9(A and B).

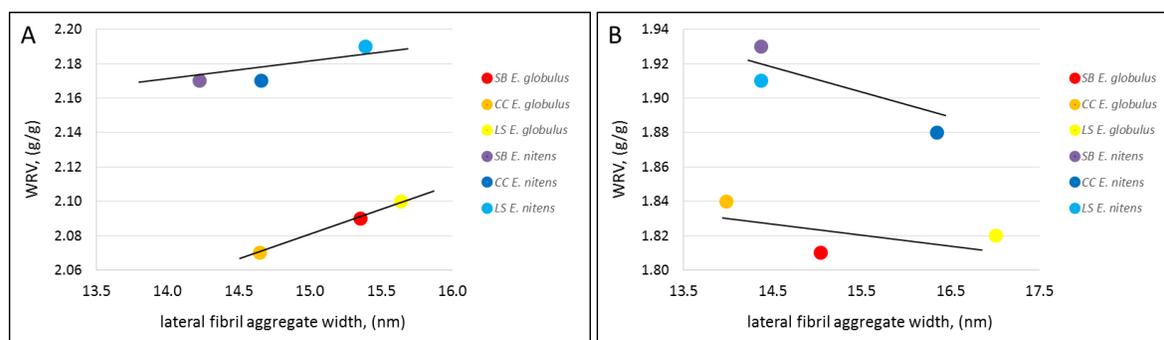


Fig. 8. The lateral fibril aggregate width (in nm) as a function of WRV (g/g) of SB, CC, and LS pulps (A) unbleached and (B) bleached of *E. globulus*, and *E. nitens* pulps. The lines in the graphics were added just to help the reader to see the tendency of the results.

Figure 8A illustrates that for unbleached pulps it seems that when fibril lateral aggregates width increased, the WRV also increased. However after bleaching there was an inverse trend in correlation of WRV versus the lateral fibril aggregate width. That is, as the bleached pulp WRV increased (Fig. 8B), lateral fibril aggregate widths seem to decrease. The modified cooking methods or wood species did not affect lateral fibril aggregate width. Lateral fibril width of the fibers are presented in Figs. 9A and 9B.

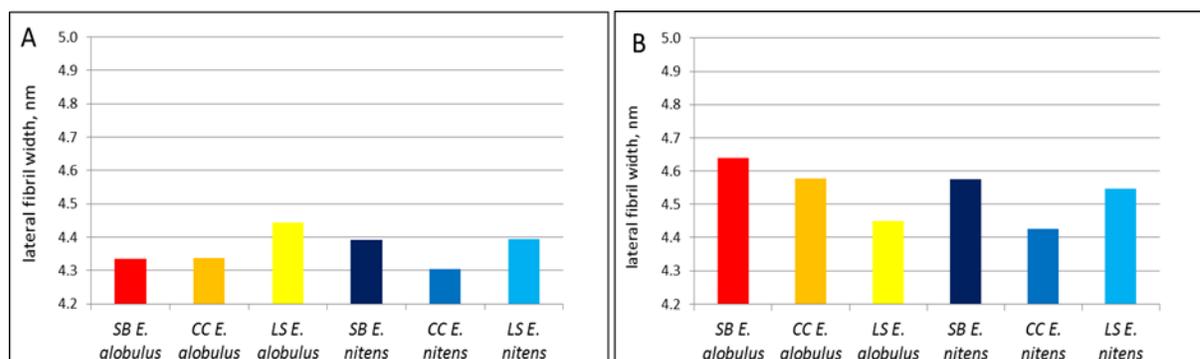


Fig. 9. The lateral fibril width values (in nm) of SB, CC, and LS cooked (A) unbleached and (B) bleached of *E. globulus*, and *E. nitens* pulps

Figures 9A and 9B indicated that the modified cooking method employed or the wood species used did not seem to have an influence on the lateral fibril width values. However, one can observe that lateral fibril width increased when the pulps were bleached. The porosity of the fiber walls was further analyzed, and the freezing bound water (FBW) amounts were extracted from the DSC measurements. Figures 10A and 10B show the nonfreezing water (NFW) values in the fibers from the DSC measurements.

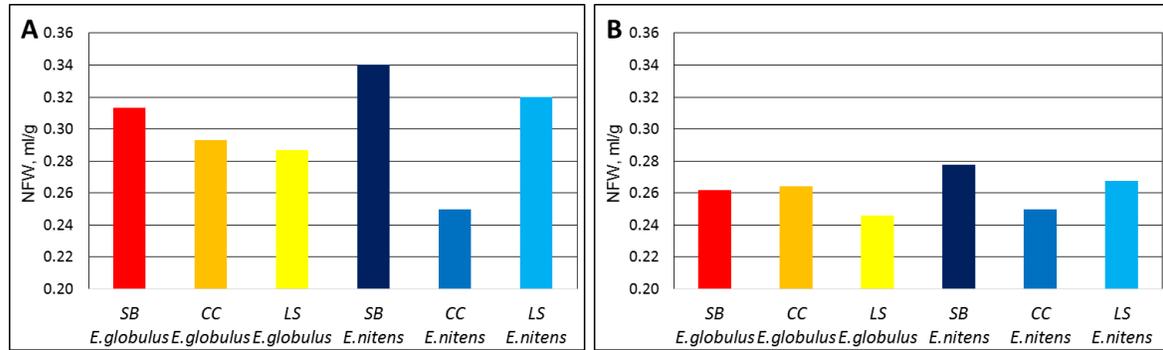


Fig. 10. NFW values (in mL/g) of SB, CC, and LS cooked (A) unbleached and (B) bleached of *E. globulus*, and *E. nitens* pulps

Figures 10A and 10B exemplified that there were no differences in NFW in the unbleached and bleached fibers. *E. nitens* showed only a small tendency of higher values except for the pulps produced from CC pulping. This could be caused by a calibration shift in the DSC thermoporosimetry. However one can observe that there was a general decrease in the amount of NFW when pulps are bleached. One explanation for this could be that when lateral fibril width increased (Fig. 9B), small pores within fibrils/aggregates were closed irreversibly, causing the amount of NFW in the fiber wall to decrease. Figures 11(A and B) and 12 (A and B) present the NFW and freezing water (FW) as a function of fiber pore diameter for the various pulps.

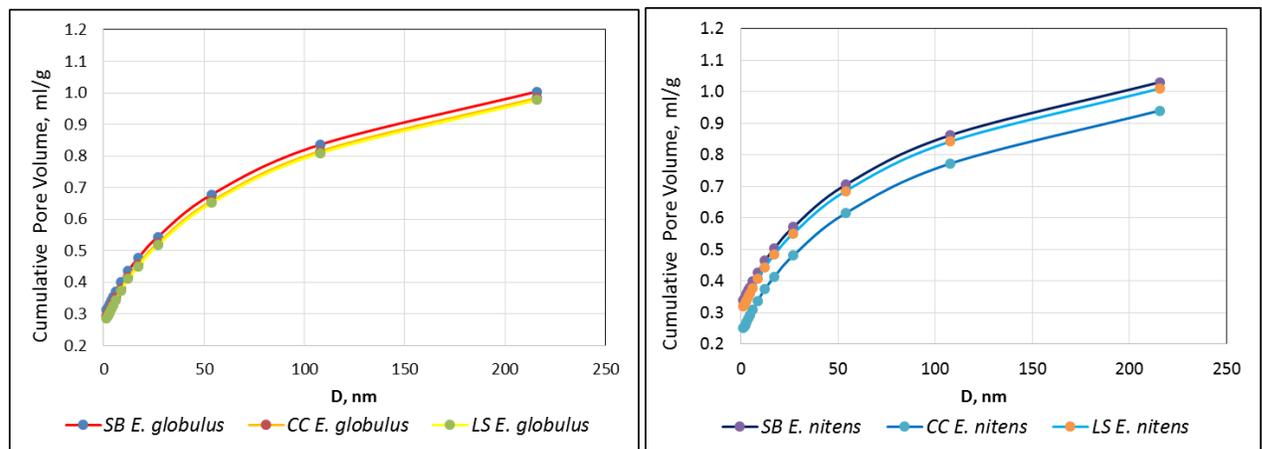


Fig. 11. NFW and FW values, as function of fiber wall diameters, of unbleached SB, CC, and LS pulps of: (A) *E. globulus* and (B) *E. nitens*

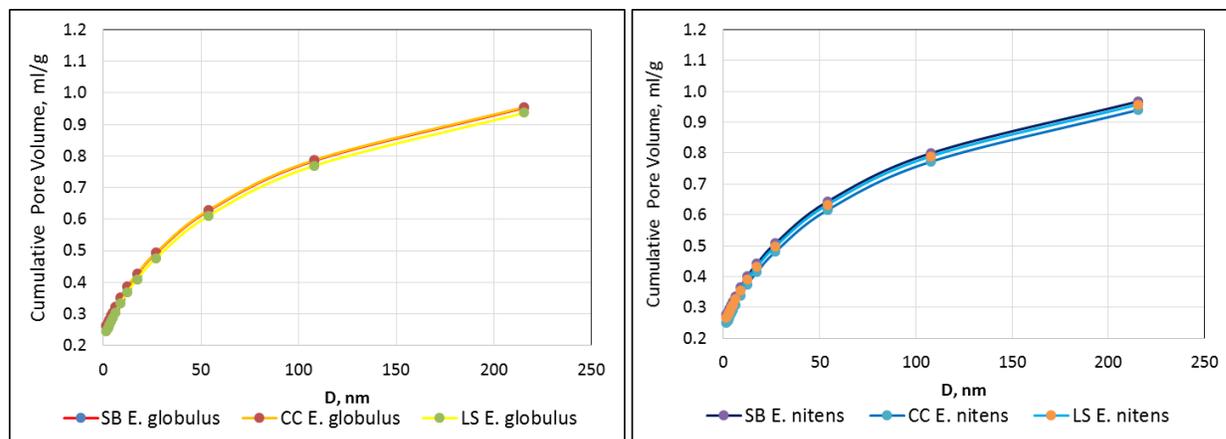


Fig. 12. NFW and FW values, as function of fiber wall pore diameters, of bleached SB, CC, and LS pulps of: (A) *E. globulus* and (B) *E. nitens*

From these graphs (Fig. 11A, 11B, 12A, and 12B), it can be seen that *E. globulus* pulps had similar values of fiber pore volumes for pore diameters up to 216 nm than *E. nitens*. Also, one can obtain from the figures that modified cooking method did not influence pore diameter up to diameters of 216 nm. Therefore, the reason why WRV and FSP did not correlate with the measured pore size distribution done with DSC was most likely that the difference lies outside of measured pore size distribution. A similar conclusion was reached in the work of Joutsimo and Asikainen (2013). According to them, WRV was shown to correlate with the amount of water in the pores with a diameter of at least 200 nm. The WRV and FSP results indicated that the pore structures of these wood species were different, *i.e.*, *E. globulus* had higher average fiber pore diameters, which will release water easier during the WRV determination and will allow the dextran probes to more easily penetrate the fiber wall during the FSP measurements (Joutsimo and Asikainen 2013). The results are also in line with the wall thickness measurements, *i.e.*, *E. globulus* had higher fiber wall thickness.

CONCLUSIONS

1. Fiber morphology was not affected by the modified cooking method employed other than the pulp's fiber wall thickness. SB pulp fibers had the smallest fiber wall thickness for *E. globulus* and *E. nitens* pulps; the highest fiber wall thickness was observed with the LS modified cooking method.
2. Water retention values (WRVs) were not affected by the modified cooking method used for both unbleached and bleached pulps; however, the *E. nitens* pulps had higher WRVs for both bleached and unbleached pulps than *E. globulus* pulps. Fiber saturation point (FSP) was higher for *E. nitens* pulps than for *E. globulus*, which is in accordance with WRV values.
3. For unbleached pulps, when fibril lateral aggregates width increased, the WRV also increased. After bleaching, there was an inverse trend in correlation of WRV versus the lateral fibril aggregate width. The modified cooking methods or wood species did not have an influence on lateral fibril aggregate width.

4. The differences shown by WRV and FSP measurements in fiber wall swelling cannot be observed with cumulative pore volume measurements including pore widths below 216 nm.

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