Drying Temperature and Hornification of Industrial Never-Dried *Pinus radiata* Pulps. 2. Voith Sulzer Refining

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The results from Voith Sulzer refining, porosity, and morphology studies of bleached *Pinus radiata* fibers showed the main effects described for hornification in dried pulps compared with never-dried pulps. Dried pulps showed higher deformations, measured as an increase in kinks. However, these deformations were shown to be reversible, based on zero-span development after Voith Sulzer refining. It is hypothesized that the observed changes in refining energy, drainability, tensile, zero span, bulk, and optical properties upon drying can be explained based on a combination of mechanisms including delamination and microfibril disarrangement and aggregation in the cell wall. Results suggested that drying-induced deformations and changes in orientation of fiber wall segments were similar to those observed in processing. Solute exclusion and nuclear magnetic resonance results also confirmed expected decreases in pore volume and average pore size for dried pulps (pores under 220 nm in size) and increase in cellulose inner crystallinity upon drying.

Keywords: Hornification; Drying; Cell wall; Porosity

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INTRODUCTION

Jayme (1944) developed the concept of hornification to describe the changes produced in pulps and fibers after drying and rewetting cycles. These changes affect the structure and chemistry of the fibers, modifying their behavior, both alone and in fiber webs, as in the case of paper sheets. The main changes related to hornification are a reduction in strength properties and water-holding ability, and an increase in swelling resistance, drainability, bulk, opacity, flexibility, and conformability (Jayme 1944; Nazhad and Paszner 1994; Weise 1998; Ahrens and Xu 1999; Zhang 2003; Fernandes-Diniz *et al.* 2004; Rebuzzi and Evtuguin 2006). According to Brancato (2008), the most accepted mechanisms of hornification are a combination of irreversible pore closure and microfibril aggregation (Stone and Scallan 1965; De Ruvo and Htun 1983; Laivins and Scallan 1993; Weise 1997; Oksanen *et al.* 1997; Maloney and Paulapuro 1999; Maloney 2000; Welf *et al.* 2005; Rebuzzi and Evtuguin 2006; Hubbe *et al.* 2007).

In the first part of the study (Giacomozzi and Joutsimo 2015), the results of PFI refining showed the expected outcomes of hornification as described by previous authors (loss of tensile and tear indices, tensile stiffness, air resistance, and elongation). Bulk, opacity, and light scattering all increased with drying. The PFI and morphology results showed that the strength reduction was not associated with fiber damage as a primary cause.

The objective of the present work is to confirm the results obtained previously (PFI) by using an industrial-like refining. It is known that Voith Sulzer refining is a better representation of the industrial refining than PFI (Pulkkinen *et al.* 2011; Somboon 2011), giving a more realistic development of properties for papermakers. Besides that, water-holding ability, porosity, and cellulose crystallinity changes in *Pinus radiata* fibers were measured in both never-dried and dried state to determine how the porous structure of the fibers is modified upon different drying conditions.

Due to its heterogeneous chemistry and structure, removal of components during processing creates a porous structure within the cell wall. This porous structure is modified in post-processing stages as beating and/or drying. The changes in the porous structure are studied using techniques such as size exclusion chromatography (Lin *et al.* 1987; Allan *et al.* 1991; Berthold and Salmén 1997), ^{2}H nuclear magnetic resonance (Li *et al.* 1993; Andreasson *et al.* 2005), differential scanning calorimetry (Park *et al.* 2006), Simons' stain (Chandra *et al.* 2008; Meng *et al.* 2013), pressure plate (Stone and Scallan 1967), and mercury intrusion porosimetry (Moura *et al.* 2005; Giesche 2006; Yamauchi 2007). All of these techniques have limitations, and no single method can provide the exact pore size distribution. For this reason, porosity should be analyzed using at least two different techniques.

According to Larsson *et al.* (1997) and Wickholm *et al*. (1998), ^{13}C CP-MAS solid-state NMR is a useful tool to study crystallinity in cellulose. Based on the study of different cellulosic raw materials and the assignation of the signals obtained in the spectrum, the authors presented a model for cellulose fibril aggregates and fibrils. In this model (2x2) when fibril aggregates are formed, some of the accessible cellulose surfaces in the fibrils remain in the inner part of the aggregates in a crystalline state. These surfaces that are not accessible to the solvents are referred to as inner crystalline cellulose. The measurement of the inner crystalline fraction could be related to fibril aggregation, which has been described as one of the main mechanisms for hornification.

EXPERIMENTAL

Laboratory-bleached *Pinus radiata* pulps were produced in a never-dried state and dried in the laboratory (25 and 105 °C) until 92% to 93% final dryness. Both pulps were compared in terms of Voith Sulzer refinability, strength properties, and cell wall porosity.

Materials

The bleached pulps produced in the laboratory from *Pinus radiata* industrial chips (22- to 25-year-old, Arauco Mill, Chile).

Methods

The never-dried and oven-dried pulps were refined in a Voith Sulzer (VTT, Finland), and their strength and optical properties were determined. Pore size distribution (PSD) and crystallinity (^{1}H nuclear magnetic resonance) were also evaluated.

Pulp drying

For the drying studies, 950 g/m^2 sheets were made from the never-dried pulps. The sheets were air-dried at 25 °C and oven-dried at 105 °C in the laboratory under free (no

frame) and restrained (using a metal frame to hold the fibers between two metal wires) conditions until 92% to 93% final dryness was achieved. Five samples were obtained for the refining studies: never-dried, air-dried at 25 °C (free and restrained), and oven-dried at 105 °C (free and restrained).

Voith Sulzer refining

The five samples (each 1.3 kg dry) were refined in a Voith Sulzer mill using conical 3-1.0-60C fillings (SEL of 2.5 Ws/m, 4% consistency). Pulps were obtained at 0, 95, 200, and 300 kWh/t. Strength, optical, and water-holding properties were measured for the never-dried pulps, the pulps dried at 25 °C, and the pulps dried at 105 °C at each energy point (VTT, Finland). Pulp characterization was done based on ISO 5267-1 (Schopper–Riegler drainability), Scan-C 62 (Water retention value), ISO 534:2005 (Bulk), ISO ISO 5270:1998 and ISO 1924-2:1994 (tensile strength properties), ISO 1536:2000 (Zero Span) ISO 1974:1990 (Tear strength) and TAPPI T569 (Scott Bond). Morphology measurements were evaluated with a Kajaani FS-300 device (Metso Automation, Finland).

Porosity measurements

Changes in the porosity of the pulps were determined based on the fiber saturation point (FSP, solute exclusion method) (VTT, Finland) and ^{2}H T1-NMR (Wood K Plus, Austria) for both the dried (25 °C and 105 °C) and never-dried unrefined pulps. The size exclusion method used dextran of molecular weight 2×10^{6} Daltons to determine the fiber saturation point (FSP) of the pulps. This method has the advantage of maintaining the fibers in a water-swollen state during measurement. This means that the pore closure resulting from the different drying methods could be neglected.

The average pore width was determined based on ^{2}H T1-NMR relaxation time measurements. D_2O and deionized H_2O were added at a 1:1 ratio to 1 g of pulp and allowed to equilibrate for 10 h at room temperature. The wetted pulp was placed into a centrifuge tube fitted with a porous ball bearing at the bottom. After centrifugation at 3000 rpm for 15 min, the pulp sample was transferred to a 10-mm O.D. NMR tube for subsequent ^{2}H T1-NMR analysis.

Analysis was done with a Bruker Advance DPX 300 NMR spectrometer (Bruker Corporation, USA) under a 7.05 T magnetic field strength with a 300 MHz ^{1}H resonance frequency, 10-mm ^{1}H/BB observe liquid-state, and probe ^{2}H T1 inversion recovery NMR 46.07 MHz.

Based on these measurements, experimental average ^{2}H T1 NMR relaxation times of D_2O residing within centrifuged cellulose and a 1:1 mixture of D_2O:H_2O were determined using the NMR software. From deuteron spin-lattice relaxation times the average pore volume was computed at different pore sizes (from 1 to 216 nm).

Cellulose crystallinity

Crystallinity determinations were done at Wood K Plus, Austria, with a Bruker Advance DPX 300 NMR spectrometer, using a 7.05 T magnetic field strength, 300 MHz ^{1}H resonance frequency, 4-mm ^{1}H/BB CP-MAS solid-state probe, and max 15 kHz MAS ^{13}C CP-MAS NMR, 4 kHz MAS, 75 MHz.

RESULTS AND DISCUSSION

Voith Sulzer Refining

Tensile index and zero-span

Figure 1 shows that at a 70 Nm/g tensile index, the refining energy requirement increased 70% from 78 kWh/t (never-dried) to 132 kWh/t (oven-dried at 105 °C). At 25 °SR, the tensile index (Fig. 2) was higher for never-dried and air-dried pulps than oven-dried pulps.

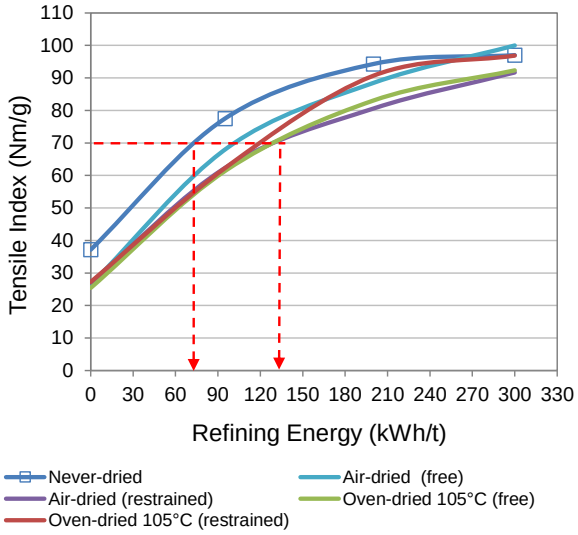

Fig. 1. Tensile index *vs.* specific refining energy for pulps refined in Voith Sulzer

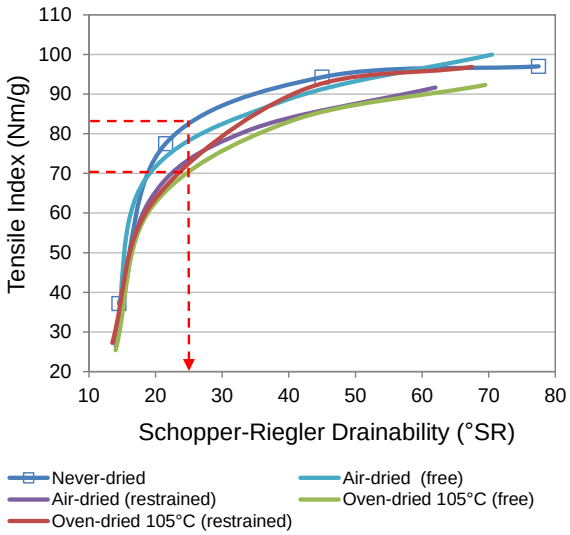

Fig. 2. Tensile index *vs.* Schopper-Riegler drainability for pulps refined in Voith Sulzer

According to authors such as Hakanen and Hartler (1995), Hartler (1995), Terziev *et al.* (2005) and Seth (2001, 2006), the reduction in tensile strength for dried pulps is due to changes in the fiber morphology, such as twists, dislocations, and microcompressions (measured as an increase of kinks and curls). Morphology results confirmed that the dried fibers were more curled and had higher values of kink index than the never-dried pulps (Table 1).

Table 1. Fiber Morphology Results for Dried and Never-Dried *P. radiata* Fibers

RADIATA PINE Fiber distribution, FS-300	**Never-dried**	**Free Drying**		**Restrained Drying (Frame)**	
		Air-drying 25°C	Oven-drying 105°C	Air-drying 25°C	Oven-drying 105°C
Length weighted av. fibre length, mm	**1.93**	1.95	1.91	2.00	1.95
Length < 0,2 mm, %	**2.1**	1.7	2.0	1.5	1.9
Coarseness, mg/m	**0.186**	0.182	0.184	0.177	0.180
Fiber curl, %	**17.9**	17.7	19.0	18.9	18.8
Kink index, 1/m	**910**	1237	1274	1287	1266
Fiber width, µm	**22.7**	22.5	22.7	23.0	22.6

According to Mohlin and Alfredsson (1990 and 1996), fiber defects can be separated in two types: irreversible damage and reversible deformation. Irreversible damage is defined as the difference in zero-span development between damaged and undamaged fibers, while reversible deformation refers to the increase in zero-span tensile index with laboratory refining and fiber straightening. Along the same lines, Salmén and Hornatowska (2014) studied fibre deformations between industrial and laboratory pulps. They separated the effects of these deformations in three types: changes in transverse fibre shape, changes in fibre shape in longitudinal direction, and damaged zones along the fibers. Based on the above, zero span determinations are key to determine the effect of the observed deformations in the in the behavior of the individual fibers and in the fiber network. Results for wet zero-span measurements (never-dried, air-dried, and oven-dried pulps) are presented in Figs. 3 and 4.

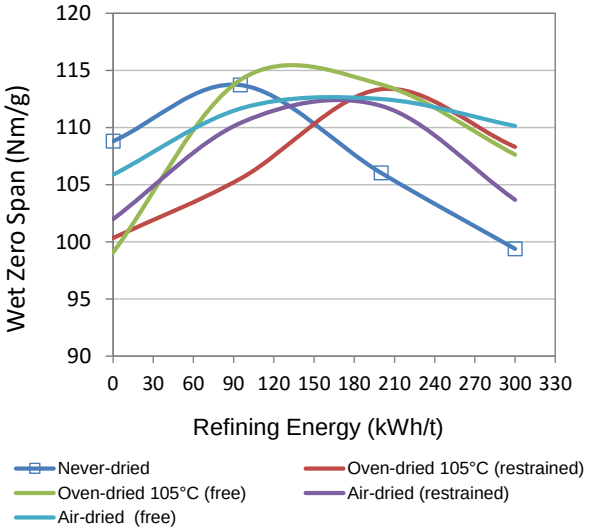

Fig. 3. Zero-span *vs.* refining energy for pulps refined in Voith Sulzer

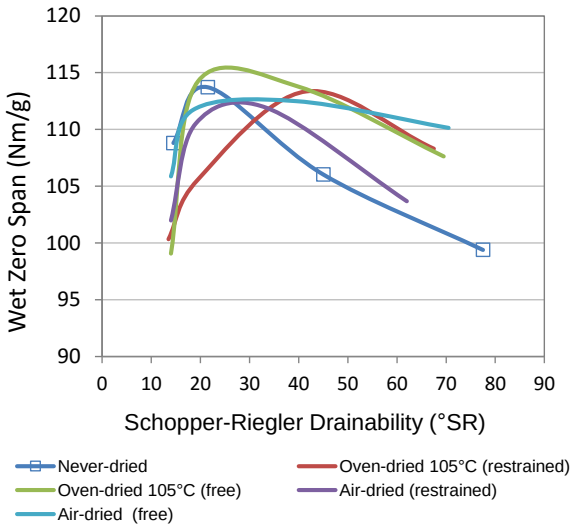

Fig. 4. Zero-span *vs.* Schopper-Riegler drainability for pulps refined in Voith Sulzer

Results showed between 3% (dried at 25 °C) and 9% (dried at 105 °C) lower wet zero-span values for unrefined dried pulps compared with never-dried pulps. Fiber morphology and zero span values confirmed that:

– Dried fibers were more deformed (kinked) and had lower zero span values than never-dried fibers.

– Fibers dried at high temperatures (i.e. 105 °C) were more deformed and had lower zero span values than pulps dried at lower temperatures (i.e. 25 °C).

Joutsimo *et al* (2005) studied the effect of fiber deformations (kinks and curls) on the activation of the fibers in the fiber network, based on the load distribution in the fiber wall. According to the authors, both straight and deformed fibers can carry and distribute load but in different ways. Mechanically deformed or chemically modified fibers distribute load nonuniformly inside the fiber wall meanwhile undamaged fibers have a more even load distribution, leading to higher fiber strength. When deformed or modified fibers are refined, the increase in swelling allows the fibrils to rearrange giving a more uniform load distribution and a restoration in zero span tensile strength.

It is worth noting that, even when the deformations (increase in kinks and curls) are produced upon drying and not during processing, the behavior of zero span values before and after refining for dried and never-dried pulps is consistent with the mechanism presented by Joutsimo *et al* (2005).

Based on the above, it is possible to hypothesize that the changes observed after drying are related mainly to microfibril disarrangement, leading to nonuniform load distribution and reduction in single fiber strength. In addition, results showed that, in all cases, the zero span curves developed to a maximum value that is similar for both dried and never-dried pulps (Fig 3). These results indicate that under the drying conditions applied there was no irreversible damage of the cell wall. After refining, the more curled, kinked dried fibers are straightened and, in addition, at a structural level, fibrils and aggregates in the cell wall are reoriented, restoring the capacity of single fibers to carry load, in the same way than fiber segment activation is produced in the fiber network.

Tear index

For unrefined pulps, the tear index (Figs. 5 and 6) was higher in never-dried pulps than in dried pulps. After Voith Sulzer refining, evaluated at a 70 Nm/g tensile index, the tear index values were similar in never-dried and air-dried pulps (both free and restrain-dried) but lower in oven-dried (105 °C) pulps from both drying conditions.

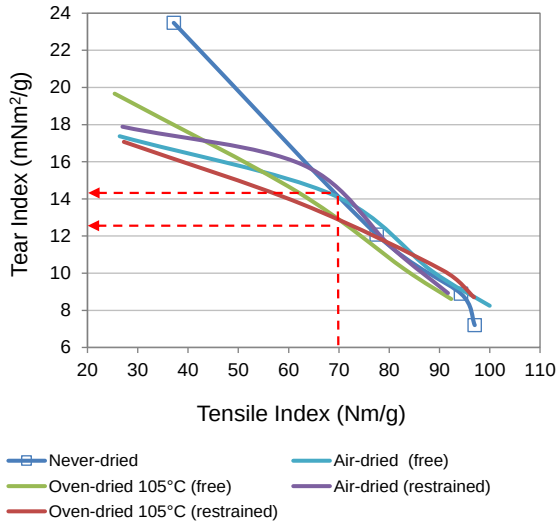

Fig. 5. Tear index *vs.* tensile index for pulps refined in Voith Sulzer

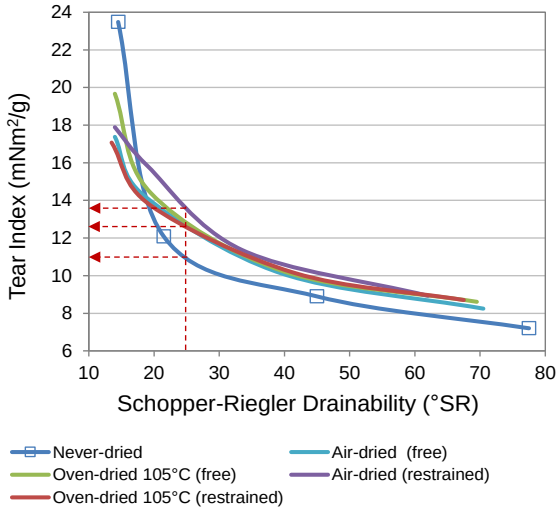

Fig. 6. Tear index *vs.* Schopper-Riegler drainability for pulps refined in Voith Sulzer

According to Mohlin *et al.* (1996), sheets made from deformed fibers required higher energy to tear the papers, primarily because these fibers transferred the load to more fibers in the vicinity compared with straight fibers. Contrary to the expected, however, in the unrefined state, never-dried fibers had higher tear indices than dried fibers (Fig. 6), even though dried fibers had more kinks than the never-dried ones. This result indicates that, as with the tensile and zero-span results, the main reasons for the differences in the tear indices between dried and never-dried fibers were not related to irreversible damages produced during drying.

Scott bond

Results for Scott bond as a function of refining energy and drainability are presented in Figs. 7 and 8.

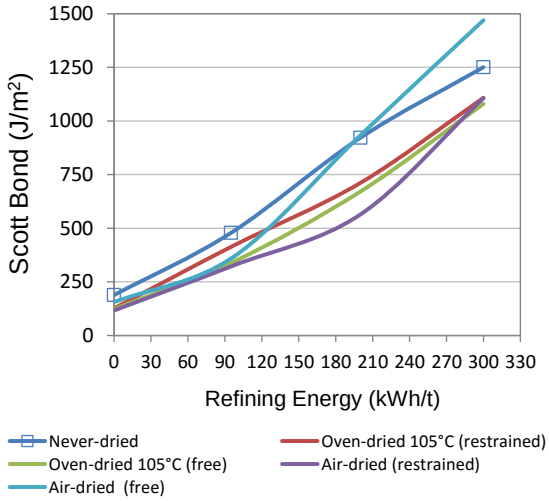

Fig. 7. Scott bond *vs.* refining energy for pulps refined in Voith Sulzer

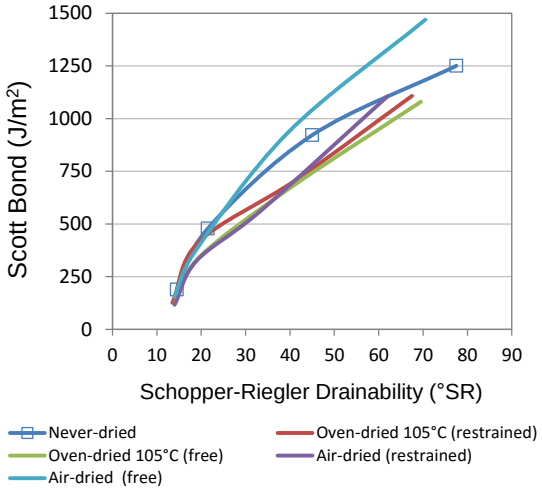

Fig. 8. Scott bond *vs.* Schopper-Riegler drainability for pulps refined in Voith Sulzer

Scott bond values were higher in never-dried fibers compared to dried fibers in all conditions tested (Figs. 7 and 8), for both unrefined and refined (with the exception of the freely air-dried sample). These results are in agreement with previous studies (Seth 2001), which attributed the reduction in Scott bond to lower bonding between dried fibers. However, results also show that fibers are straightened during refining but Scott bond values for dried pulps remain lower than those for never-dried fibers. Therefore, the loss in Scott bond should be attributed to another kind of damage, such as microfibril disarrangement and fiber delamination. This mechanism has been shown to occur during processing (Joutsimo 2004; Joutsimo and Asikainen 2013), were separation of structural elements increase irregularities in the surface of the fibers and reduces bonding ability.

Bulk

As expected, bulk values were lower for never-dried pulps compared to dried pulps (Figs. 9 and 10).

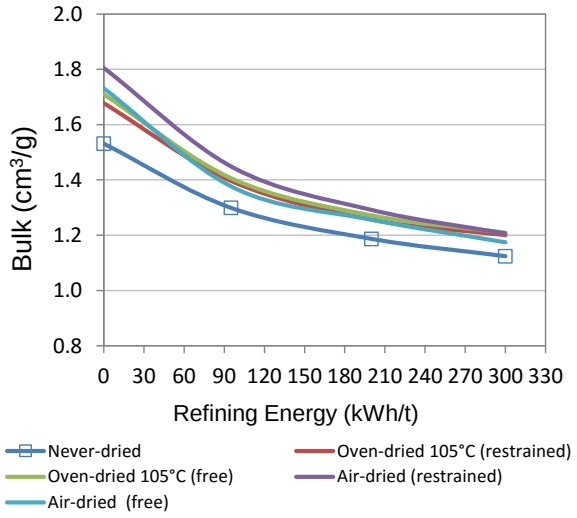

Fig. 9. Bulk *vs.* refining energy for pulps refined in Voith Sulzer

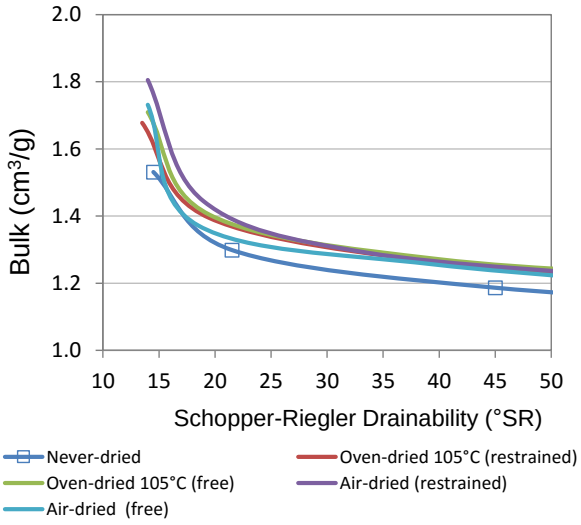

Fig. 10. Bulk *vs.* Schopper-Riegler drainability for pulps refined in Voith Sulzer

The main explanation for the change in bulk has been related to hornification and loss of conformability of the fibers but also can be explained based on the delamination mechanism due to loosening of the cell wall structure upon processing and drying (Joutsimo 2004; Joutsimo and Asikainen 2013; Joutsimo and Giacomozzi 2015).

Water retention value

Water retention values for never-dried and dried samples after Voith Sulzer refinings are presented in Figs. 11 and 12. After drying, WRV values were reduced between 24 and 25% compared to never-dried pulps. The reduction in WRV is one of the main effects described as part of the hornification process.

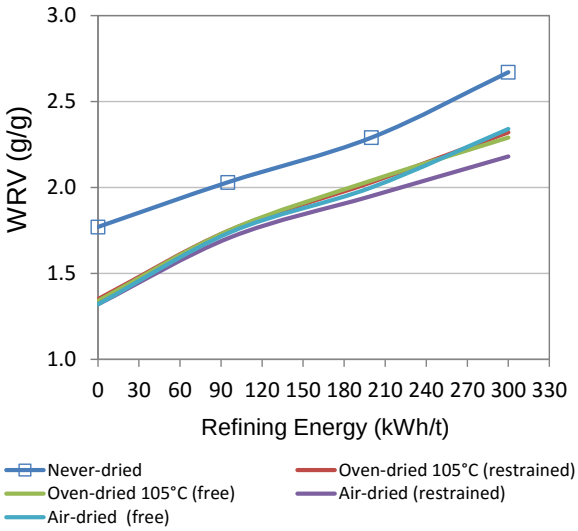

Fig. 11. WRV *vs.* refining energy for pulps refined in Voith Sulzer

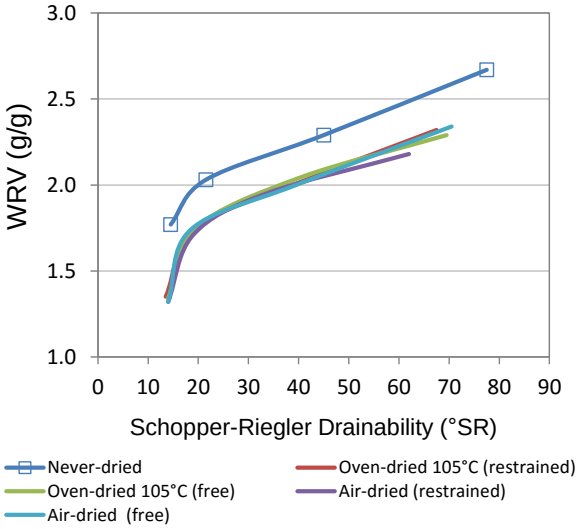

Fig. 12. WRV *vs.* Schopper-Riegler drainability for pulps refined in Voith Sulzer

The changes in WRV after drying and rewetting cycles have been attributed to irreversible pore closure occurring in the cell wall upon drying (Jayme 1944; Stone and Scallan 1965, 1967; Lundberg and De Ruvo 1978; Carlsson and Lindström 1984; Laivins and Scallan 1993; Minor 1994; Weise 1997, 1998; Ahrens 1999; Hubbe *et al.* 2007; Brancato 2008) and to a loss in external fibrillation of the fibers due to rewetting and disintegration. Yamauchi and Yamamoto (2008) studied the treatment of pulps using different amounts of drying-and-rewetting cycles. They found that changes in WRV could be attributed to changes in cell wall porosity and cellulose crystallinity (internal fibrillation) but also to a loss in external fibrillation during disintegration stages.

Another possible explanation is presented in Joutsimo (2004). Characterization of laboratory and industrial pulps using Simons' stain showed that the cell wall becomes delaminated during processing and new big pores are created in the cell wall. These pores are not able to hold water inside them, thus reducing the total WRV value measured. Along the same lines, it can be hypothesized that drying induces changes in the fiber structure that are similar to those presented by Joutsimo (2004).

Fiber saturation point

The results for fiber saturation point measurements are presented in Fig. 13.

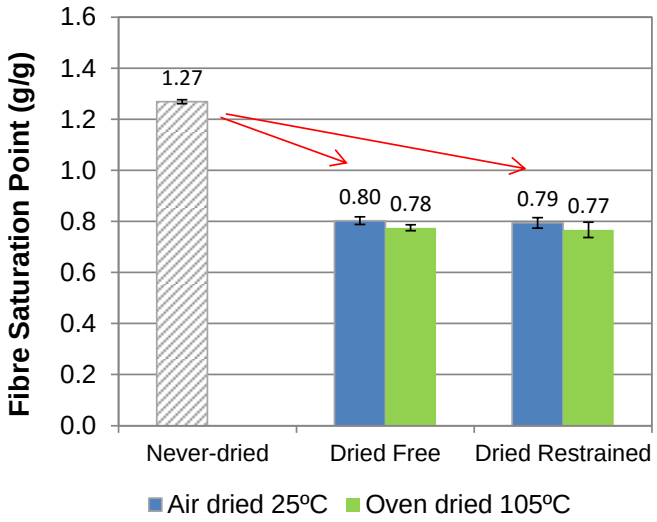

Fig. 13. Fiber saturation point for dried and never-dried *Pinus radiata* pulps, including confidence interval at 95%

The FSP results were similar to those of the water retention values. When the FSP results are compared between air-dried and oven-dried samples, the pulps dried at higher temperature and restrained condition showed the lowest FSP values, indicating that these pulps were less able to hold water inside their pore structure. The causes of this reduction in water-holding ability are typically explained as irreversible pore closure in the cell wall that occurred upon drying of the fibers. Changes in water holding ability are also possible to explain based on the delamination mechanism.

Porosity Measurements

Porosity determinations were based on pore size distribution (PSD, size exclusion method using dextrans), and ^{1}H-nuclear magnetic resonance (^{1}H-NMR). The size of the

pores measured was in the range of 1 to 220 nm (PSD) and 1 to 30 nm in the case of ^{1}H-NMR.

Pore size distribution

Results of the PSD showed a reduction in pores in the range of 0 to 220 nm in size in the dried pulps. Both samples, freely dried and dried under restraint, exhibited a decrease in the total amount of micropores between 0 and 220 nm (between 15 and 25% of the initial value) compared to the never-dried pulps (Fig. 14). The results confirmed that there was a reduction in the cumulative pore volume probably caused by irreversible closure of pores below 220 nm in diameter. It was not possible to determine whether new pores up to 220 nm in diameter were created *via* delamination or *via* disarrangement of the cell wall.

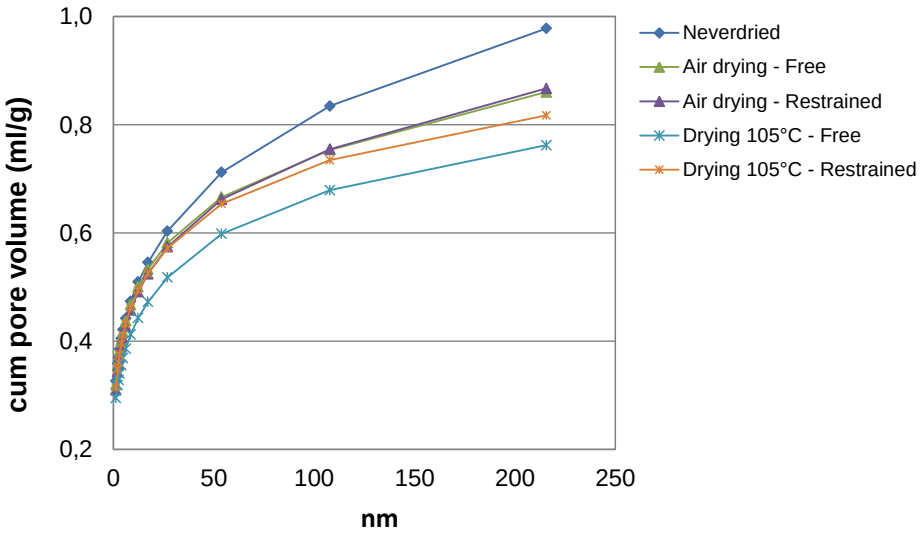

Fig. 14. Pore size distribution for never-dried, air-dried, and oven-dried pulps

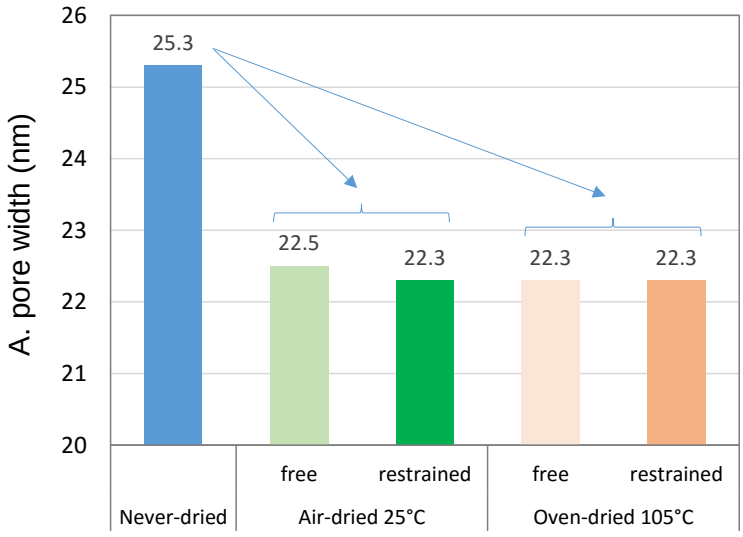

Fig. 15. Average pore size as measured by ^{1}H-NMR for never-dried, air-dried, and oven-dried pulps

Between the dried samples, those dried at lower temperature (25 °C) had higher cumulative pore volume than those dried at higher temperature (105 °C). Drying in free

conditions also affected the cumulative pore volume more at higher drying temperature (105 °C). It is possible to hypothesize that higher temperatures led to higher extent of pore closure, probably due to structural rearrangements in the polymeric constituents favored by the effect of temperature (Lundberg and De Ruvo 1978; De Ruvo and Htun 1983).

Nuclear magnetic resonance (^{1}H-NMR)

Results from the ^{1}H-NMR measurements showed a reduction in the average pore size (1-30 nm) of the dried pulps compared to the never-dried ones (Fig. 15). This result is consistent with the reduction observed in FSP determinations. No clear tendency in average pore size could be determined when drying temperature increased.

Cellulose Crystallinity

Inner crystallinity measurements of the dried and never-dried pulps (Fig. 16) confirmed that the cellulose in the dried pulps was more crystalline (for both free and restrained dried pulps) than the never-dried pulp which is in agreement with previously reported studies (Laivins and Scallan 1993; Fahlén and Salmén 2005; Chen *et al.* 2010, Claramunt *et al.* 2010).

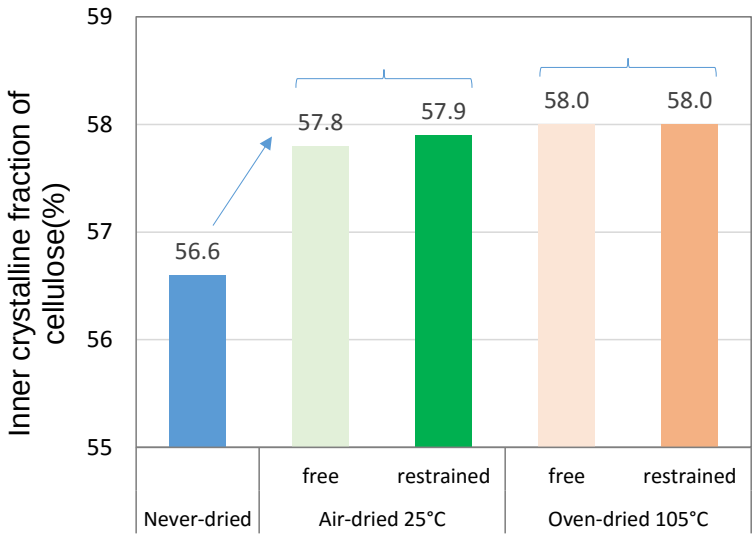

Fig. 16. Crystallinity of cellulose *via* ^{13}CP MAS-NMR for never-dried, air-dried, and oven-dried pulps

Chunilall *et al*. (2010) also observed a similar result for hardwood dissolving pulps, in which higher drying temperatures increased the fibril aggregates' dimensions more than pulps dried at room temperature (air-dried). No clear result was observed for pulps subjected to restrained drying regarding higher crystallinity compared with freely dried pulps.

Based on the results presented, the main mechanisms for hornification process have been confirmed, mainly those related to irreversible pore closure (pores under 220 nm) and microfibril aggregation upon drying. One point that must be further studied is the change of the pores above 220 nm. The reduction in Scott bond and the increase in bulk cannot be explained by changes in cell wall morphology (increase in curls and kinks) after drying, which proved to be reversible if the pulps are refined (Voith Sulzer). A proposed

mechanism to explain these changes is based on delamination of the cell wall and reduction of bonding area upon drying.

CONCLUSIONS

1. The results confirmed most of the changes observed in the hornification phenomenon and previously described by other authors as follows:
   i. A reduction in tensile index and an increase in the refining energy required to reach the same tensile index (70 Nm/g) for dried pulps.
   ii. Dried fibers producing bulkier papers, but with lower Scott bond values than never-dried fibers.
   iii. Morphology showing an increase in kinks after drying. No increase in curl was observed for the pulps.
2. Deformations (measured as an increase in kinks) that occurred in the fibers upon drying were found to be reversible after refining, based on zero-span maximum values achieved during Voith Sulzer refining.
3. Zero Span values and refining behavior for dried and never-dried pulps were found to be consistent with mechanism presented by Joutsimo *et al* (2005), which explained the changes in strength upon processing as the result of deformations in the cell wall (delamination and non uniformities in the orientation of fiber wall segments).
4. Porosity studies confirmed a reduction in pore volume under 220 nm in size. Crystallinity studies also confirmed an increase in cellulose crystallinity of the microfibril aggregates upon drying, which is in line with previous studies.
5. To validate the hypothesis of cell wall disarrangement and delamination, further methods to study pores between 300 and 10,000 nm in size are required.

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REFERENCES CITED

Ahrens, F. W., and Xu, H. (1999). "Effect of pulp drying history on pressing and drying," in: *Tappi Engineering/Process & Product Quality Conference*, Anaheim, CA, September 12-16, 1999.

Allan, G. G., Ko, Y., and Ritzenthaler, T. (1991). "The microporosity of pulp. The nature of the pore size distribution," *TAPPI Journal* 74(83), 205-212.

Andreasson, B., Forsström, J., and Wågberg, L. (2005). "Determination of fibre pore structure: Influence of salt, pH and conventional wet strength resins," *Cellulose* 12(3), 253-265. DOI: 10.1007/s10570-004-5837-6.

Berthold, J., and Salmén, L. (1997). "Inverse size exclusion chromatography (ISEC) for determining the relative pore size distribution of wood pulps," *Holzforschung* 51(4), 361-368.

Brancato, A. (2008). *Effect of Progressive Recycling on Cellulose Fiber Surface Properties*, PhD Dissertation, School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA. DOI: 10.1.1.562.8354.

Carlsson, G., and Lindström, T. (1984). "Hornification of cellulosic fibers during wet pressing," *Svensk Papperstidning* 87(15), 119-125.

Chandra, R., Ewanick, S., Hsieh, C., and Saddler, J. (2008). "The characterization of pretreated lignocellulosic substrates prior to enzymatic hydrolysis, Part 1: A modified Simons' staining technique," *Biotechnology Progress* 24(5), 1178-1185. DOI: 10.1021/bp.33.

Chen, Y. M., Wang, Y., Wan, J. Q., and Ma, Y. W. (2010). "Crystal and pore structure of wheat straw cellulose fiber during recycling," *Cellulose* 17(2), 329-338. DOI: 10.1007/s10570-009-9368-z.

Chunilall, V., Bush, T., Larsson, P. T., Iversen, T., and Kindness, A. (2010). "A CP/MAS ^{13}C-NMR study of cellulose fibril aggregation in eucalyptus dissolving pulps during drying and the correlation between aggregate dimensions and chemical reactivity," *Holzforschung* 64(6), 693-698. DOI: 10.1515/HF.2010.097.

Claramunt, J., Ardanuy, M., and García-Hortal, J. A. (2010). "Effect of drying and rewetting cycles on the structure and physicochemical characteristics of softwood fibres for reinforcement of cementitious composites," *Carbohydrate Polymers* 79(1), 200-205. DOI: 10.1016/j.carbpol.2009.07.057.

De Ruvo, A., and Htun, M. (1983). "Fundamental and practical aspects of papermaking with recycled fibers," in: *The Role of Fundamental Research in Papermaking*, J. Brander (ed.), Vol. 1, Mechanical Engineering Pub. Ltd., London, UK, pp. 195-225.

Fahlén, J., and Salmén, L. (2005). "Ultrastructural changes in a holocellulose pulp revealed by enzymes, thermoporosimetry and atomic force microscopy," *Holzforschung* 59(6), 589-597, DOI: 10.1515/HF.2005.096.

Fernandes-Diniz, J. M. B., Gil, M. H., and Castro, J. A. A. M. (2004). "Hornification—Its origin and interpretation in wood pulps," *Wood Science and Technology* 37(6), 489-494. DOI 10.1007/s00226-003-0216-2.

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

Giesche, H. (2006). "Mercury porosimetry: A general (practical) overview," *Particle & Particle Systems Characterization* 23(1), 9-19. DOI: 10.1002/ppsc.200601009.

Hakanen, A. and Hartler, N. (1995), "Fiber deformations and strength potential of the kraft pulps," *Paperi ja Puu* 77(5), 339-344.

Hartler, N. (1995). "Aspects on curled and microcompressed fibers," *Nordic Pulp and Paper Research Journal* 10(1), 4-7. DOI: 10.3183/NPPRJ-1995-10-01-p004-007.

Hubbe, M., Venditti, R., and Rojas, O. (2007). "What happens to cellulosic fibers during papermaking and recycling? A review," *BioResources* 2(4), 739-788. DOI: 10.15376/biores.2.4.739-788

ISO 302 (2004). "Pulps — Determination of Kappa number," *International Organization for Standardization (ISO)*, Geneva, Switzerland.

ISO 2470 (2008). "Paper, board and pulps -- Measurement of diffuse blue reflectance factor -- Part 2: Outdoor daylight conditions (D65 brightness)," *International Organization for Standardization (ISO)*, Geneva, Switzerland.

ISO 5267-1 (1999). "Pulps - Determination of drainability - Part 1: Schopper-Riegler method," *International Organization for Standardization (ISO)*, Geneva, Switzerland.

ISO 5351 (2010). "Pulps - Determination of limiting viscosity number in cupri-ethylenediamine (CED) solution," *International Organization for Standardization (ISO)*, Geneva, Switzerland.

Jayme, G. (1944). "Mikro-Quellungsmessungen an Zellstoffen," *Der Papier-Fabrikant/Wochenblatt für Papierfabrikation* 42(6), 187-194.

Joutsimo, O. (2004). *Effect of Mechanical Treatment on Softwood Kraft Fiber Properties*, PhD Dissertation, Department of Forest Products Technology, Helsinki University of Technology, Helsinki, Finland.

Joutsimo, O., Wathén, R., and Tamminen, T. (2005). "Effects of fiber deformations on pulp sheet properties and fiber strength," *Paperi ja Puu* 87(6), 392-397.

Joutsimo, O., and Asikainen, S. (2013). "Effect of fiber wall pore structure on pulp sheet density of softwood kraft pulp fibers," *BioResources* 8(2), 2719-2737. DOI: 10.15376/biores.8.2.2719-2737.

Joutsimo, O., and Giacomozzi, D. (2015). "Changes in cell wall structure during kraft processing of *Pinus radiata*," *BioResources* 10(2), 2461-2478. DOI: 10.15376/biores.10.2.2461-2478

Laivins, G. V., and Scallan, A. M. (1993). "The mechanism of hornification of wood pulps," in: *Transactions of the 10th Fundamental Research Symposium*, Vol. 2, pp. 1235-1260, Oxford, UK, September 1993.

Larsson, P. T., Wickholm, K., and Iversen, T. (1997). "A CP/MAS ^{13}C NMR investigation of molecular ordering in celluloses," *Carbohydrate Research* 302(1-2), 19-25. DOI: 10.1016/S0008-6215(97)00130-4.

Li, T. Q., Henriksson, U., and Odberg, L. U. (1993). "Determination of pore sizes in wood cellulose fibers by ^{2}H and ^{1}H NMR," *Nordic Pulp and Paper Research Journal* 8(3), 326-330. DOI: 10.3183/NPPRJ-1993-08-03-p326-330.

Lin, J. K., Ladisch, M., Patterson, J. A., and Noller, C. (1987). "Determining pore size distribution in wet cellulose by measuring solute exclusion using a differential refractometer," *Biotechnology and Bioengineering* 29(8), 976-981. DOI: 10.1002/bit.260290809.

Lundberg, R., and De Ruvo, A. (1978). "Influence of drying conditions on recovery of swelling and strength of recycled fibers," *Svensk Papperstidning* 81(11), 355-357.

Maloney, T. (2000). "On the pore structure and dewatering properties of the pulp fiber cell wall," *Acta Polytechnica Scandinavica*: *Chemical Technology Series* N°275, 1-52.

Maloney, T., and Paulapuro, H. (1999). "The formation of pores in the cell wall," *Journal of Pulp and Paper Science* 25(12), 430-436.

Meng, X., Foston, M., Leisen, J., DeMartini, J., Wyman, C., and Ragauskas, A. (2013). "Determination of porosity of lignocellulosic biomass before and after pretreatment by using Simons' stain and NMR techniques," *Bioresource Technology* 144(7), 467-476. DOI: 10.1016/j.biortech.2013.06.091.

Minor, J. L. (1994). "Hornification, its origin and meaning," *Progress in Paper Recycling* 3(2), 93-95. DOI 10.1007/s00226-003-0216-2.

Mohlin, U.-B., and Alfredsson, C. (1990). "Fibre deformation and its implications in pulp characterization," *Nordic Pulp and Paper Research Journal* 5(4), 172-179. DOI 10.3183/NPPRJ-1990-05-04-p172-179.

Mohlin, U. B., Dahlbom, J., and Hornatowska, J. (1996). "Fibre deformation and sheet strength," *TAPPI Journal* 79(6), 105-111.

Moura, M. J., Ferreira, P. J., and Figueiredo, M. M. (2005). "Mercury intrusion porosimetry in pulp and paper technology," *Powder Technology* 160(2), 61-66. DOI: 10.1016/j.powtec.2005.08.033.

Nazhad, M., and Paszner, L. (1994). "Fundamentals of strength loss in recycled paper," *TAPPI Journal* 77(9), 171-179.

Oksanen, T., Buchert, J., and Viikari, L. (1997). "The role of hemicelluloses in the hornification of bleached kraft pulps," *Holzforschung* 51(4), 355-360. DOI: 10.1515/hfsg.1997.51.4.355.

Park, S., Venditti, R., Jameel, H., and Pawlak, J. (2006). "Changes in pore size distribution during the drying of cellulose fibers as measured by differential scanning calorimetry," *Carbohydrate Polymers* 66(1), 97-103. DOI: 10.1016/j.carbpol.2006.02.026.

Pulkkinen, I., Kuitunen, S., and Alopaeus, V. (2011). "The most important eucalypt fiber properties for fiber network strength and structural property development," *5th International Colloquium on Eucalyptus Pulp*, May 9-12, Porto Seguro, Bahia, Brazil.

Rebuzzi, F., and Evtuguin, D. (2006). "Effect of glucuronoxylan on the hornification of *Eucalyptus globulus* bleached pulps," *Macromolecular Symposia* 232(1), 121-128. DOI: 10.1002/masy.200551414.

Salmén, L., and Hornatowska, J. (2014). "A comparison of fibre deformations from mill like and laboratory kraft cooking of softwood," *Nordic Pulp and Paper Research Journal* 29(2), 211-217. DOI: 10.3183/NPPRJ-2014-29-02-p211-217.

Scan-N 33:44 (1994). "Residual alkali (Hydroxide ion content)," *Scandinavian Pulp, Paper and Board Testing Committee*, Stockholm, Sweden.

Seth, R. S. (2001). "The difference between never-dried and dried chemical pulps," in: *Proceedings of the 2001 Pulping Conference*, Seattle, WA, pp. 296-311, 4-7 Nov 2001.

Seth, R. S. (2006). "The importance of fibre straightness for pulp strength," *Pulp and Paper-Canada* 107(1), 34-42. ISSN 0316-4004.

Somboon, P. (2011). "Quality Developments in Pulp Fibers using Conventional Papermaking Laboratory Beaters and an Industrial Pilot Refiner," *Kasetsart Journal – Natural Science* 45, 883-890.

Stone, J. E., and Scallan, A. M. (1965). "Influence of drying on the pore structures of the cell wall. Consolidation of the paper web," in: *Transactions of the 3rd Fundamental Research Symposium*, Cambridge, UK, pp. 145-167, September 1965.

Stone, J. E., and Scallan, A. M. (1967). "The effect of component removal upon the porous structure of the cell wall of wood. Part II. Swelling in water and the fiber saturation point," *TAPPI* 50(10), 496-501.

Terziev, N., Daniel, G., and Marklund, A. (2005). "Dislocations in Norway spruce fibres and their effect on properties of pulp and paper," *Holzforschung* 59(2), 163-169. DOI: 10.1515/HF.2005.025

Weise, U. (1997). "Characterization and mechanisms of change in wood pulp fibres caused by water removal," *Acta Polytechnica Scandinavica*: *Chemical Technology Series* 249, 1-141.

Weise, U. (1998). "Hornification - Mechanisms and terminology," *Paperi ja Puu* 80(2), 110-115.

Welf, E. S., Venditti, R., Hubbe, M., and Pawlak, J. (2005). "The effects of heating without water removal and drying on the swelling as measured by water retention value and degradation as measured by intrinsic viscosity of cellulose papermaking fibers," *Progress in Paper Recycling* 14(3), 1-9.

Wickholm, K., Larsson, P. T., and Iversen, T. (1998). "Assignment of non-crystalline forms in cellulose I by CP/MAS 13C NMR spectroscopy," *Carbohydrate Research* 312(3), 123-129. DOI: 10.1016/S0008-6215(98)00236-5.

Yamauchi, T. (2007). "A method to determine lumen volume and collapse degree of pulp fibers by using bottleneck effect of mercury porosimetry," *Journal of Wood Science* 53(6), 516-519. DOI: 10.1007/s10086-007-0895-7.

Yamauchi, T., and Yamamoto, M. (2008). "Effects of repeated drying-and-rewetting and disintegration cycles on fundamental properties of kraft pulp fibers and paper made from them," *Appita Journal* 61(5), 396-401.

Zhang, M. (2003). *Preventing Strength Loss of Unbleached Kraft Fibers*, Ph.D. Dissertation, Department of Wood and Paper Science, North Carolina State University, Raleigh, NC.

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