

CHEMISTRY AND SURFACE CHEMISTRY OF VESSELS IN EUCALYPTUS KRAFT PULPS

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ABSTRACT

Vessel picking is a problem that paper professionals are coping with and struggling to find a solution for. The behaviour of vessel elements in pulp and papermaking processes needs to be understood and their chemistry and morphology has to be clarified. This study focused on the vessel chemistry and surface chemistry, morphology and nanostructure of vessel elements. Our efforts have been put in to clarify the effects of cooking and bleaching on the vessel chemistry and ultrastructure. XPS was applied to the surface measurements, and the ultrastructure was investigated by FE-SEM and AFM. Vessel chemical composition was also investigated by Py-GC/MS. The main findings can be summarized as following: 1) Vessel elements of pulps had a similar chemical composition with fibres. The most significant differentiation could be found in the content of cellulose and lignin, i.e. vessel elements were richer in cellulose compared to fibres, and lignin could be found in the vessels even after bleaching stages. 2) FE-SEM images suggested that the cell wall structure of vessel elements was layered and complex, and the different layers were removed layer by layer during the pulping and bleaching processes. The layered wall structure strengthens the vessel elements and due to this unique construction the vessel elements may pass through the whole fibre line, including refining and recycling, undamaged.

Keywords: FE-SEM, kraft pulp, Py-GC/MS, vessel chemistry, vessel element, XPS

INTRODUCTION

Hardwood species differ in their chemical composition and structure. Eucalyptus stands out for its high cellulose content and low lignin content, but also has large vessels in its wood structure. Vessel elements cause serious problems in offset printing, especially today, since the printing speeds are much higher than a few years ago. The vessel elements in the paper surface tend to be picked out or the ink does not adhere on the vessel elements, and this result in a repeating white spot in the print. The large surface area of the vessel element is observed to increase the picking tendency. Also, a poor vessel-to-fibre bonding at the paper surface allows vessel elements to be easily pulled off. In wood, the shape of vessels varies from drum

and barrel-like to rectangle with or without tail-like extensions in one or both ends. In eucalyptus, the thin tails are one of its identifying marks. Many vessel elements are large enough to be seen without magnifying glass or microscope. Their lengths vary from 200 to 600 μm , and width can be up to 500 μm . Width/length (W/L) ratio varies from 1:1 to 1:3 (Alén, 2000; Chen *et al.*, 2005; Ilvessalo-Pfäffi, 1995).

The chemical characteristics of eucalyptus vessel elements are not extensively studied, although each wood fibre gives a unique property to both pulp and paper. Lignin is an important component of all woods and represents what has been called the cementing material. It is an aromatic, amorphous substance, and is generally insoluble in common solvents. It is distinguished from the polysaccharides by its resistance to hydrolysis by acids and by its relatively greater reactivity with oxidizing and other reagents (Browning, 1967). The content and chemical structure of wood components, in particular lignin content and its composition in terms of p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) moieties, are important parameters for predicting pulp properties and pulp production (del Río *et al.*, 2005; Ona *et al.*, 2001). In hardwoods, such as eucalyptus, lignins are made up of S and G units in varying ratios, while softwood lignin is made of G units and small amounts of H units. The lignin content and S/G ratio of cell walls in hardwood differ among cell types and among cell-wall layers. Although high S/G ratios are beneficial for pulping, differences in S/G ratios among hardwoods affect the chemical properties of the wood and the degradation rate of lignin that is required for chemical pulping (del Río *et al.*, 2005; Watanabe *et al.*, 2004). The S/G ratio in HW (hardwood) lignin affects not only the pulping efficiency but also the strength of manufactured pulp and end products. According to del Río *et al.* the lignin composition in terms of S/G ratio can be correlated with the pulp yield – pulp yield increases as the S/G ratio increases. This indicates that the lignin composition is more important parameter influencing pulp yield than the lignin content. The S/G ratios of *Eucalyptus globulus* wood samples determined by Py-GC/MS ranged from 3.5 to 6.4, whereas in the study by Rodrigues *et al.*, the ratio was ranging from 1.5 to 2.6 (del Río *et al.*, 2005; Rodrigues *et al.*, 1999). Fergus and Goring (1970) studied the distribution of lignin in birch wood by ultraviolet microscopy

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and reported that the lignin contents of the fibres and vessels were 0.19-0.22 g/g and 0.24-0.28 g/g respectively. They found that the fibre secondary wall contained mostly syringyl lignin, while the vessel secondary wall contained mostly guaiacyl lignin.

A histochemical study on heterogeneity of lignin in eucalyptus species by Watanabe *et al.*, (2004) correlates with the results from Fergus and Goring (1970). The fibre cell walls of *E. camaldulensis* contain both guaiacyl and syringyl units, vessel walls contain mostly guaiacyl units. Fibres in *E. globulus* contain mainly syringyl units, while vessel walls contain both guaiacyl and syringyl units. There are other authors, as well, showing that the vessel walls in hardwood species contain mostly guaiacyl lignin units (Alves, 2005; Tateishi *et al.*, 2004; Musha *et al.*, 1975). Tateishi *et al.* (2004) add, anyway, that assumption of the real significance of extracted lignin fragments to vessel morphology is difficult, since lignin pyrolysis mechanism is not yet clear.

The proportions of vessel, fibres and parenchyma cells differ among hardwoods species. In most species the fibres contribute approximately 50% or more of the total wood volume, and are the main constituents of the hardwood pulps (Ilvessalo-Pfäffi, 1995). But not only the proportions differ, the morphology of these "building blocks" varies depending on the species or habitat. For example: the mean fibre length of oak species ranges between 1.10 and 1.35 mm and that of Mediterranean shrubs between 0.56 and 0.82 mm. The mean values of vessel dimensions ranges 0.22–0.31 mm (vessel length) and 0.080–0.087 mm (vessel diameter) for oaks and 0.19–0.40 mm (vessel length) and 0.033–0.043 mm (vessel diameter) for Mediterranean shrubs. Within-tree variations in the eucalyptus vessel morphology can be also notable, e.g. the average radial diameter in *E. camaldulensis* is approximately 0.134 mm, while in *E. globulus* the same value is 0.159 mm. In *E. camaldulensis* the vessel frequency is also much higher compared with *E. Globulus*: 13.85 per mm² and 8.65 per mm² respectively (Ohshima, 2004). According to the results from Ona *et al.*, (2004) by Raman spectroscopy the vessel elements in *E. camaldulensis* are shorter than in *E. Globulus*: 0.204 mm and 0.240 mm, respectively.

Ona *et al.*, (2001) performed an investigation of relationships between cell and kraft pulp properties in *Eucalyptus camaldulensis* and *Eucalyptus globulus* by examination of within-tree property variations. They found that the characteristics of the ray and axial parenchyma have a significant influence on pulp properties, but all cell types are important for predicting pulp properties. In *E. camaldulensis* cell length relates to burst factor, breaking length, folding endurance and Kappa number, while in *E. globulus* to sheet density and folding factor. Proportions of ray and axial parenchyma (not vessels) correlate with almost all pulp properties in *E. Camaldulensis*, and in *E. globulus* with pulp yield, kappa number and unbleached brightness (Ona *et al.*, 2001). Wall thickness of fibres, parenchyma cells and vessels are important factors for pulp properties in *E. camaldulensis*. In *E. globulus*

vessel and cell wall thickness are significantly related to tear factor and kappa number. Vessel wall thickness is more important than axial parenchyma wall thickness (Ona *et al.*, 2001). The relationships between diameters of fibres or vessels and pulp properties have a major species divergence. Tear factor relates to fibre radial and average diameters in *E. camaldulensis*, and to vessel radial and average diameters in *E. globulus*. Pulp yield relates to fibre lumen diameter in *E. camaldulensis* and to vessel tangential and average diameters in *E. globulus*. Unbleached brightness and kappa number relates to fibre lumen diameter in *E. camaldulensis*, and to vessel and fibre tangential and average diameters in *E. globulus* (Ona *et al.*, 2001).

Radial/tangential diameter ratio of vessel is related to paper strength in *E. globulus* and the vessels are notably larger in diameter than those of *E. camaldulensis*. Vessel percentage is only 11% (w/w) in *E. Globulus* (15% in *E. Camaldulensis*), thus, the individual cell strength cannot be so important. Bonding between vessels and fibres is considered to be very central because vessels, which have larger radial/tangential ratios, will fold easier and make more contacts with the fibres during pressing and drying (Ona *et al.*, 2001).

The effects of pulping are diverse at fibre chemistry and fibre surface chemistry levels. At the surface chemistry level, pulping can be categorised as a process in which carbohydrates are exposed with concomitant lignin removal, increasing the work of adhesion with water. The extractives play different roles at the fibre chemistry and surface chemistry levels. These low molar mass components are removed during pulping and subsequently redeposited on the surface (Fardim and Duran, 2002, 2004, 2005). When Fergus and Goring (1970) examined the distribution of lignin in birch wood they found that the vessel tori disappeared in the initial stages of kraft pulping. But generally little work has been reported of the effect of kraft cooking on the vessel elements. More attention has been put on the investigations of pulping effects on the fibres and relationships between cell and pulp properties.

In this work, we investigate the effects of cooking and bleaching on chemistry and surface chemistry of eucalyptus vessel elements using advanced methods of chemical and surface chemical analyses.

EXPERIMENTAL

Sampling

The eucalyptus pulp samples, *E. grandis* and *E. dunnii* mixtures, were collected from different points at the fibre line in two Finnish pulp mills. The taken samples were chips, blow line, O₂, ZD₀/D₀ and pulp sheets. Pulps were washed with distilled and deionised water and then centrifuged to dry matter content of approx. 30%.

Vessel separation

The separation method is based on flotation followed by selective separation by size exclusion. 30 g (o.d.) pulp was disintegrated, filtered into a pad and air-dried for three days.

After the drying, a fraction of the pad was put in deionized water at 60°C for 20 min and then allowed to settle. A fraction rich in parenchyma could be collected from the water surface. The pulp fraction containing fibres and vessels was poured into the Åbo Akademi (ÅÅ) separation jar equipped with a screen so that the input consistency was 1% in the 2 litres jar. At first, the fibre bundles were collected from a wire of 15 mesh, and then vessel elements and fibres were separated from each other with a screen with 80 µm net. Deionized water in a closed system was used during the whole separation process. The separation process was monitored by light microscopy.

Acid hydrolysis

The amount of cellulose was determined by acid hydrolysis (Sundberg *et al.*, 1996). Some modifications were inserted to the method. Approximately 10 mg with 0.01 mg accuracy of extracted, freeze-dried pulp sample was weighted in a test tube. Parallel samples of each vessel fraction and cotton linter for calibration were analysed. In the primary hydrolysis 0.2 mL of 72% sulphuric acid (H₂SO₄) was added, and the test tubes were in a vacuum oven for 2 hours. 0.5 mL of deionised water was added and the sample was kept at room temperature for 4 hours, after which 6.0 mL deionised water was added. The secondary hydrolysis was performed by autoclaving at 125°C for 90 min. 1 mL of internal standard containing 5 mg m⁻¹ sorbitol was added. 1 mL of hydrolysate was evaporated under nitrogen gas flow and silylated with a silylation solution containing 80 µL pyridine, 170 µL hexamethyldisilazane (HMDS) and 70 µL trimethylchlorosilane (TMCS). The silylated sample was analysed with GC the next day.

Py-GC-MS

The identification of lignin components was performed using a HP 6890-5973 GC-MSD instrument (GC-MS) equipped with Pyroly 2000 (foil pulse pyrolyzer). Pyrolysis temperature/time was 650°C/2000 ms, and GC column was HP-1 25 m, 0.20 mm i.d., 0.11 µm film thickness. Helium was used as a carrier gas with constant flow of 0.8 mL/min, split flow was 20 mL/min. Injector temperature was 260°C. Oven temperature program was 50°C (0.5 min) – 300°C, at 8°C/min heating rate. MS ionisation mode was EI at 70 eV electron energy.

FE-SEM

The ultrastructures of vessel elements were analysed by FE-SEM (Field Emission - Secondary Electron Microscopy). FE-SEM analyzes the surfaces of solid samples and produces images of higher resolution than optical microscopy. Secondary electrons are generated by an electron beam, which is scanned across the sample surface. Secondary electron imaging reveals the surface topography and backscattered imaging expose the distribution of compounds or elements in 10 nm depth on the surface. The vessel elements were placed on an aluminium folio and attached to the sample holder, and coated with the Agar scientific coater for 10 seconds with Au/Pd.

AFM

The SPM (Scanning Probe Microscopy) including high spatial resolution AFM (Atomic Force Microscopy) enables to achieve detailed 3-dimensional data about surface topography. The surface images were recorded with a NanoScope IIIa SPM (Digital Instruments, Santa Barbara, Calif., USA) equipped with an extender electronics module, which enables phase imaging in the tapping mode. In the tapping mode, silicon cantilevers (no Al) with a resonance frequency of $f_0 = 327,91$ Hz was used. After engaging, the retrace and trace signals were set to be identical. Scan rate was 1.2-1.8 Hz. All images were measured in air and no filtering was used during scanning. Scan size was 2 µm x 2 µm, and the resonance frequency of the cantilever was 328 Hz (=f₀). The cantilever was of type NSC15/no Al. Three different vessel elements were measured from each sample.

XPS

The vessel fractions were acetone/water (9:1 v/v) extracted. A physical electronics Quantum 2000 instrument using a monochromatic Al K α X-ray source operating at 25 W with take-off angle 45° was used to obtain X-ray photoelectron spectra of surfaces of the vessel elements. Pass energy for low-resolution mode was 187 eV, step 0.8 eV, and measuring time was 10 min. For high resolution mode the pass energy was 23.5 eV, step 0.1 eV, and exposure time was 20 min. C 1s curve fitting C1 reference was 284.8 and Shirley background was used. Low resolution XPS (X-ray photoelectron spectroscopy) was applied to define the elemental surface composition and for calculations of O/C ratios. C 1s spectra were recorded using high-resolution XPS.

Methylene blue sorption

A 60 mM barbital buffer mother solution was prepared by dissolving 2.763 g of pure 5-5 diethylbarbituric acid in about 225 mL of deionised water and adding 5 mL of 2 M NaOH and filled to 250 mL. The methylene blue solution was prepared by dissolving 1.128 g of 3,7-bis-(dimethylamino)phenothiazin-5-ium chloride (C₁₆H₁₈CIN₃S) powder in 200 mL deionised water, adding 10 mL of barbital mother solution, and filling to 1000 mL with deionised water. About 20 mg of each o.d. vessel rich fractions were transferred into two flasks, and different volumes of methylene blue solutions were added. Each mixture, including a blank sample, was allowed to react for 20 min under continuous stirring. The samples were then filtered and the filtrate was analyzed by ultraviolet spectroscopy at 664 nm against a blank barbital buffer solution. A calibration curve was made by diluting different volumes (0.1 mL, 0.2 mL, 0.5 mL, 1 mL and 2 mL) of methylene blue solution to 50 mL and measuring the absorbance. The filtered vessel fractions were air dried and preserved for XPS analyses (Fardim *et al.*, 2005, Orblin *et al.*, 2012).

RESULTS

Vessel separation

During separation, fibres and parenchyma cells were removed extensively, but long fibres remained in some extent in the vessel-rich fractions (see **Figure 1**). A vessel element to fibre ratio of 2:1 was achieved.

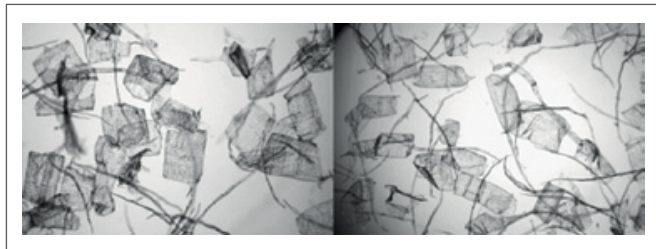


Figure 1. Vessel-rich fractions separated from a pulp sheet sample

Vessel morphology and nanostructure

The ultrastructure of vessel elements was investigated by FE-SEM. Images from a wood cross section and inside the vessel element show the vestures in the region of the pits (see **Figure 2**). The pits were supposedly covered by nutrients: calcium salts, oxalates or extractives that are removed during the pulping processes.

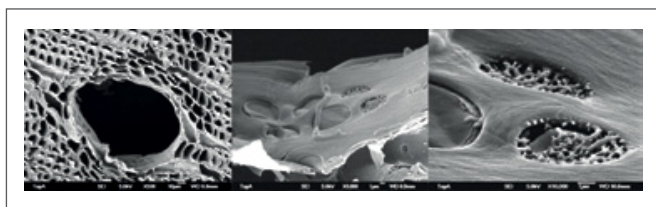


Figure 2. FE-SEM imaging showing the vestures in the pits region

Blow line

In **Figure 3** can be observed that the fibril aggregates in the A sample are not oriented in same extent as in the B sample.

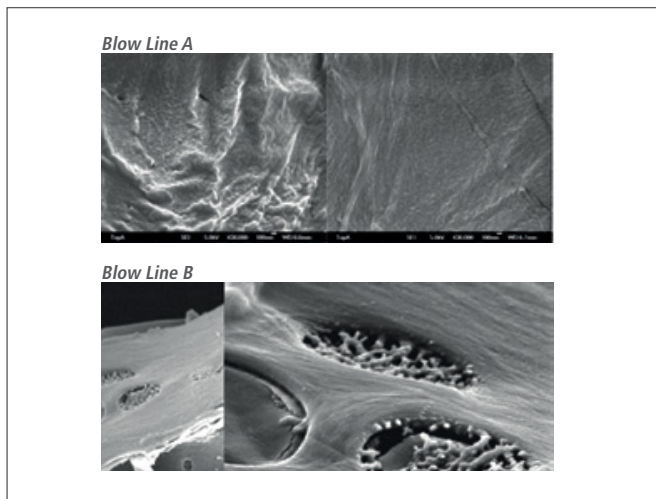


Figure 3. FE-SEM imaging from the surface of two vessel elements after blow line stage. The layering is obvious in both illustrations

The surface of the vessel element is more damaged in the B. The arrangements of the microfibril aggregates are sparser and an oriented layer beneath those is in more evidence.

The AFM images shown in **Figure 4** represent also surface structures of vessel element after blow line stage. The phase images resolve the microfibril aggregates. It can be observed that the surface of a vessel element is composed mainly of cellulose. The microfibril aggregates are oriented in some extent in A. In the B sample can be observed that the surface is more granulated than in the corresponding A surface. The granules are perhaps extractives, which are removed in the subsequent process steps (see **Figure 4**).

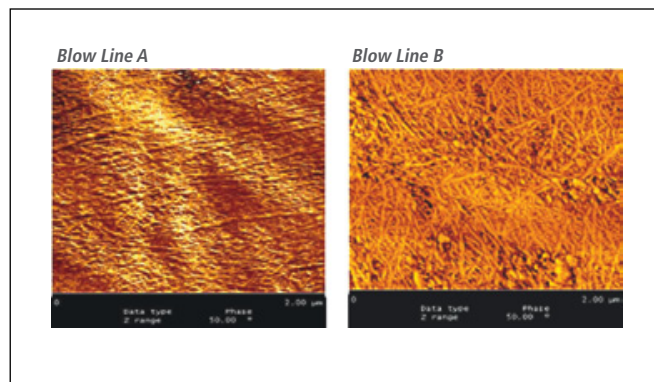


Figure 4. AFM pictures from the surfaces of blow line samples. Scan size 2 µm x 2 µm, resonance frequency of the cantilever = f₀ = 328 Hz, cantilever type NSC15/no Al

Oxygen

Compared to blow line, the structures of fibrils are more open and longer distances between them are observed. Different cell wall layers are apparent.

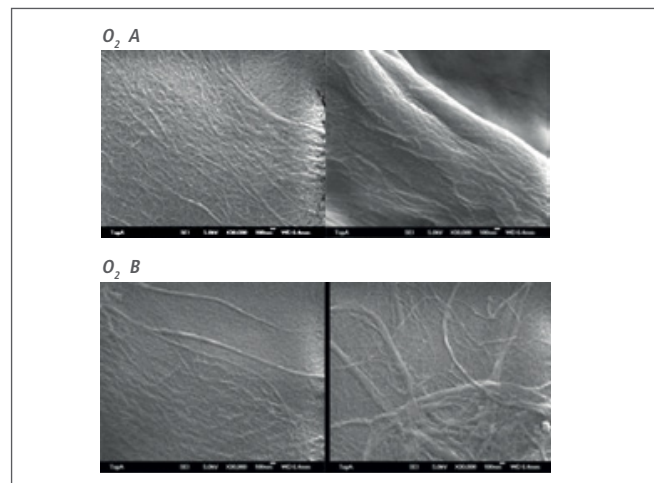


Figure 5. The cell wall of a vessel element after oxygen stage

ZD₀ and D₀

After ozone treatment the surface of a vessel element seems to be very clean. Some unoriented microfibrils can be still observed top

on more oriented layer (see **A in Figure 6**). The pits are surrounded by fibril aggregates (**B in Figure 6**) and an open layer is observed. These fibril aggregates can be also remnants from a preceding wall or formed during cooking.

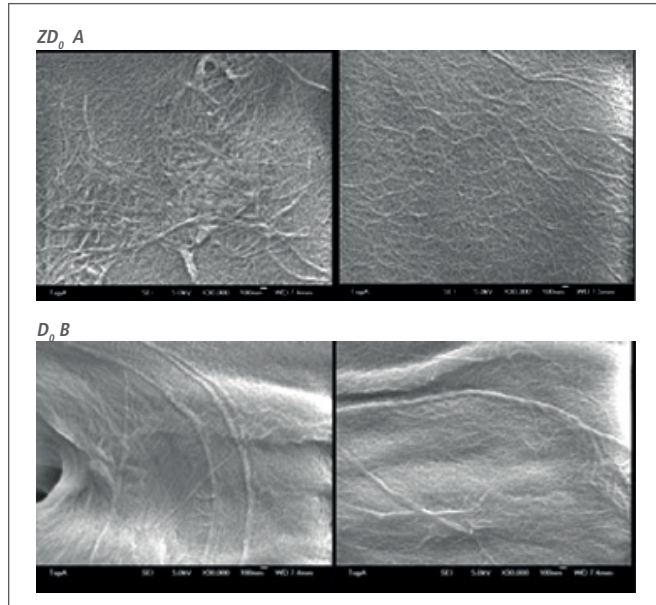


Figure 6. FE-SEM picture showing the orientation of microfibril aggregates

the secondary wall appears to be oriented. Although the vessel elements have passed through the whole fibre line, they are entire and unbroken at the end of the fibre line.

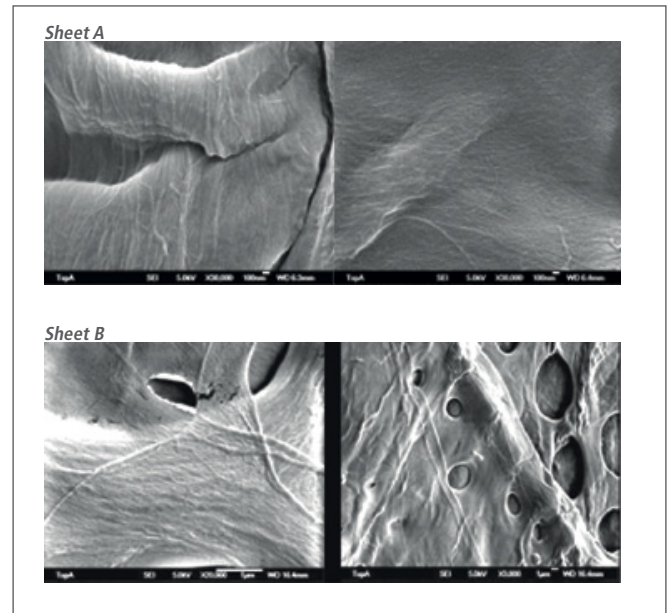


Figure 7. FE-SEM imaging showing the surface of vessel elements that has passed through the whole fibre line

Pulp sheet

The microfibril aggregates of machine dried vessel elements are more oriented compared to surfaces from earlier stages. It can be assumed that the outermost (primary) wall is completely gone and

Cellulose content

The amounts of cellulose for eucalyptus chips and vessel fractions are presented on **Figures 8 and 9**. The cellulose contents for chips are in agreement with the published results (Patt *et al.*, 2006; Neto

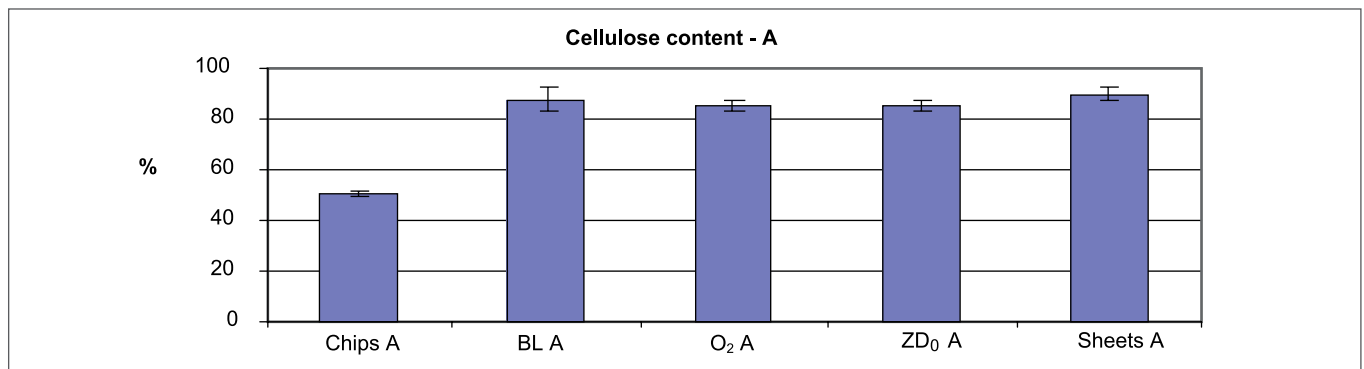


Figure 8. Cellulose content of wood chips and vessel rich fractions in % of o.d. pulp

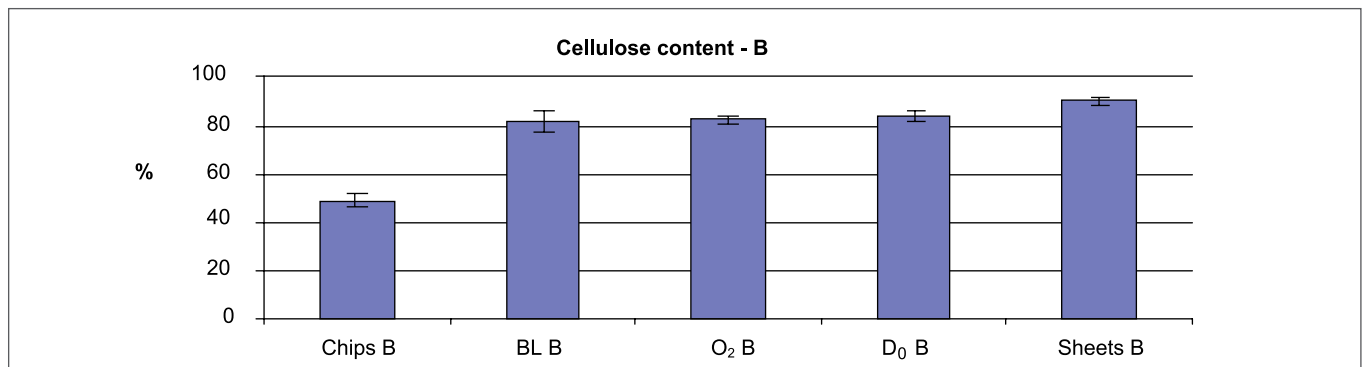


Figure 9. Cellulose content of wood chips and vessel rich fractions in % of o.d. pulp

et al., 2004). The higher amounts of cellulose in the vessel fractions are due to the removal of other wood components during the pulping and bleaching processes. The cellulose content for vessel fractions BL, O₂ and ZD₀/D₀ are similar considering the standard deviations. The vessel fractions for sheets have the highest content of cellulose, and the content is higher when compared with ECF bleached fibre.

Lignin identification by Py-GC/MS

The identification of lignin components in the vessel fractions was determined by Py-GC/MS. The results are shown in **Table 1**. These results indicate that the cell walls of vessel elements contain mostly syringol-type lignin units. From results it can be seen that also vessel elements after bleaching sequences contain lignin. The published results argue that the eucalyptus vessel walls are composed mainly of guaiacyl units (Tateishi *et al.*, 2004; Watanabe *et al.*, 2004). Nevertheless, Tateishi *et al.*, (2004) noted that the thicker vessel wall

relates more cis-propenylsyringol and trans-sinapyl alcohol. It must be mentioned that Tateishi *et al.* (2004) performed the measurements on microtome cross-sections of 15 µm from various parts in the trunk, while here all measurements have been done on individual vessel elements. In addition, we have also been characterizing vessels isolated from chemical pulps that were modified by pulping and bleaching treatments.

Results from the identification of lignin components in the fibres showed no residual lignin in the bleached samples (see **Table 2**)

Surface coverage by lignin and extractives

Results for surface coverage by lignin (**Table 3**) indicate that lignin can be found on the surface from the blow line sample. Approximately one-tenth of surface area was covered by lignin. Although a low amounts of lignin could be detected on the ZD₀A,

Table 1. Identification of lignin components in vessel fractions by Py-GC/MS

| Sample | Syringol | Methylsyringol | Ethylsyringol | Vinylsyringol | Syringylpropene | Syringaldehyde |
|-------------------|----------|----------------|---------------|---------------|-----------------|----------------|
| BL A | X | X | X | X | X | X |
| O ₂ A | X | X | - | X | X | X |
| ZD ₀ A | - | - | - | - | - | X |
| Sheets A | - | - | - | - | - | X |
| BL B | X | X | X | X | X | X |
| O ₂ B | X | X | - | X | X | X |
| D ₀ B | - | - | - | - | - | X |
| Sheets B | - | - | - | - | - | X |

Table 2. Identification of lignin components in fibres by Py-GC/MS

| Sample | Vinylguaiacyl | Syringol | Methylsyringol | 3-syringolprop-2-ene | Vinylsyringol | Syringaldehyde |
|----------|---------------|----------|----------------|----------------------|---------------|----------------|
| BL A | X | X | X | X | X | X |
| Sheets B | - | - | - | - | - | - |
| BL B | X | X | X | X | X | X |
| Sheets B | - | - | - | - | - | - |

Table 3. Surface coverage (%) by carbohydrates, lignin and extractives examined by XPS

| Sample | ⊖ (carb.) | ⊖ (lignin) | ⊖ (extr.) |
|-------------------|-----------|------------|------------|
| BL A | 88 ± 8 | 12 ± 6 | 15.3 ± 5.3 |
| O ₂ A | > 96 | < 4 | 6.6 ± 0.8 |
| ZD ₀ A | > 96 | < 4 | 0 |
| Sheet A | 100 | 0 | 0 |
| BL B | > 94 | < 6 | 13.2 ± 3.3 |
| O ₂ B | > 95 | < 5 | 1.0 ± 1.3 |
| D ₀ B | > 96 | < 4 | 0 |
| Sheet B | > 94 | < 6 | 0 |

Table 4. Surface anionic groups on different vessel fractions ($\mu\text{mol/g}$) measured by XPS

| Sample | SAG ($\mu\text{mol/g}$) | SAG/AG ($\mu\text{mol/g}$) x 100 | N/S |
|-------------------|---------------------------|------------------------------------|-----------------|
| BL A | 195 \pm 5 | 1.05 | 3.61 \pm 0.80 |
| O ₂ A | 182 \pm 5 | 1.07 | 2.96 \pm 1.00 |
| ZD ₀ A | 121 \pm 5 | 1.15 | 3.50 \pm 1.40 |
| Sheet A | 200 \pm 4 | 2.25 | 2.79 \pm 0.70 |
| BL B | 171 \pm 5 | 0.88 | 3.50 \pm 0.50 |
| O ₂ B | 170 \pm 5 | 0.99 | 3.00 \pm 0.01 |
| D ₀ B | 146 \pm 1 | 1.68 | 3.33 \pm 0.60 |
| Sheet B | 170 \pm 5 | 2.88 | 2.94 \pm 0.60 |

and on D₀ B. However, surface coverage by lignin decreased while surface coverage by carbohydrates increased with bleaching.

Surface coverage by extractives decreased along fibre line (Table 3). As expected, no extractives were detected on either ZD₀, D₀ or sheet samples.

Surface analysis of methylene blue treated vessel elements by XPS

The surface composition of methylene blue (MB) treated vessel elements were determined by XPS. The results are presented in **Table 4**. The N/S ratio is the proportion of nitrogen and sulphur on the surface of a MB molecule. Considering the standard deviations, samples from A and B showed equal amounts of surface anionic groups. Both sample series are also showing a similar pattern in the contents of SAG. Although the SAGs kept unchanged during pulping processes, the relative content of SAG to AG (data not presented) is clearly increasing.

DISCUSSION AND CONCLUSION

Pulping processes have a similar effect on the chemical composition of a vessel element in comparison to fibres. Pulping and delignification processes remove components from the vessel wall structure and from the surface. The large surface areas of vessel elements are cleaned by bleaching stages, but at the same time the sensitive surfaces are exposed to contamination.

However, vessel elements have a quite similar chemical and surface chemical composition as fibres. The most significant differentiation can be found in cellulose and lignin content – vessel elements are

richer in cellulose when compared to fibres, and lignin can be found in vessels even after the bleaching stages.

Cell wall structure of vessel elements cannot be compared to the structure of a fibre wall due to the FE-SEM pictures that are suggesting the cell wall structure of vessel elements is layered and very complex, and the different layers are removed layer by layer during the pulping processes. The layered wall structure strengthen the vessel elements and due to this unique complicated construction the vessel elements may pass through the whole fibre line almost undamaged.

There still are many questions to be answered: why the vessel wall remains rich in lignin after bleaching? Why the surfaces of vessel elements are so susceptible to contaminants? What would be the best way for eliminating the vessel elements without damaging the fibres and in parallel maintain the pulp yield and pulp strength properties?

After all, it would be ideal to manufacture eucalyptus pulp free from vessel picking problem. Elimination of vessel elements by chemical modification during pulping could be a solution, but, then again, reduced pulp yield is also a financial loss. More profitable would be to break the vessels to fines during low-consistency (LC) refining, and keep them in the pulp. The pulp yield would remain unchanged, and the amount of fines, which e. g. improves paper opacity, would increase. Other possibility would be to promote the binding of vessels and fibres in papermaking by addition of polysaccharides. The selection of the best approach depends on process economics and end product requirements. ■

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REFERENCES

1. Alén, R. (2000); *Structure and chemical composition of wood*. In: Papermaking Science and Technology. Book 3: Forest Products Chemistry. Eds. Stenius, P., Pakarinen, H. FapetOy. Helsinki. pp. 20–21.
2. Alves, E.F. (2005); *Interação de fibras e elementos de vasos de polpa kraft de eucalipto com tintas de impressão offset*. Master's Thesis. Universidade Federal de Viçosa. 117 pp.
3. Browling, B. L.; *Methods of wood chemistry*. Volume 1. Interscience Publishers. New York. 1967. pp. 7. 9.
4. Chen, F., Evans, R. (2005); *A robust approach for vessel identification and quantification in eucalypt pulps woods*. Appita 58(6): 442–447.
5. Fardim, P., Duran, N. (2002); *Surface Chemistry of Eucalyptus Wood Pulp Fibres: Effects of Chemical Pulping*. Holzforschung 56(6): 615–622.
6. Fardim, P., Duran, N. (2004); *Modification of fibre surfaces during pulping and refining as analysed by SEM, XPS and ToF-SIMS*. Colloids Surf. A 223: 263–276.
7. Fardim, P., Duran, N. (2005); *Effects of Kraft Pulping on the Interfacial Properties of Eucalyptus Pulp Fibres*. J. Braz. Chem. Soc., 16(5) 915–921.
8. Fardim, P., Moreno, T., Holmbom, B. (2005); *Anionic groups on cellulosic fiber surfaces investigated by XPS, FTIR-ATR, and different sorption methods*. Colloid Interface Sci. 290: 383–391.
9. Fergus, B. J., Goring, D.A. (1970); *The Distribution of Lignin in Birch as Determined by Ultraviolet Microscopy*. Holzforschung 24(4):118–124.
10. Ilvessalo-Pfäffli, M.-S. (1995); *Fiber Atlas - Identification of Papermaking Fibers*. Springer-Verlag. Berlin. pp. 22. 254.
11. Musha, Y., Goring, D. A. I. (1975); *Distribution of Syringyl and Guaiacyl Moieties in Hardwoods as Indicated by Ultraviolet Microscopy*. Wood Sci. Technol. 9: 45–58.
12. Ohshima, J., Yokota, S., Yoshizawa, N., Toshihiro, O. (2004); *Within-tree variation of vessel morphology and frequency, and representative heights for estimating whole-tree values in Eucalyptus camaldulensis and E. Globulus*. Appita 57(1): 64–69.
13. Ona, T., Sonoda, T., Ito, K., Shibata, M., Tamai, Y., Kojima, Y., Ohshima, J., Yokota, S., Yoshizawa, N. (2001); *Investigation of relationships between cell and pulp properties in Eucalyptus by examination of within-tree property variations*. Wood Sci. Technol. 35: 229–243.
14. Ona, T., Ohshima, J., Adachi, K., Yokota, S., Yoshizawa, N. (2004); *Length determination of vessel elements in tree trunks used for water and nutrient transport by Fourier transform Raman spectroscopy*. Anal Bioanal Chem 380: 958–963.
15. Orblin, E., Lindström, N., Fardim, P. (2012); *Probing the chemical and surface chemical modification of vessel cell walls during bleaching of eucalyptus pulp*. Holzforschung 66: DOI: 10.1515/hf-2011-0117, June 2012
16. PascoalNeto, C., Silvestre, A., Evtuguin, D., Freire, C., Pinto, P., Santiago, A., Fardim, P., Holmbom, B. (2004); *Bulk and surface composition of ECF bleached hardwood kraft pulp fibres*. Nord. Pulp Pap. Res. J. 19(4): 513–520.
17. Patt, R., Kordsachia, O., Fehr, J. (2006); *European hardwoods versus Eucalyptus globulus as a raw material for pulping*. Wood Sci Technol 40: 39–48.
18. del Río, J.C., Gutiérrez, A., Hernando, M. Landín, P., Romero, J., Martínez, À.T. (2005); *Determining the influence of eucalypt lignin composition in paper pulp yield using Py-GC/MS*. J. Anal. Appl. Pyrolysis 74: 110–115.
19. Rodrigues, J. Meier, D., Faix, O., Pereira, H. (1999); *Determination of tree to tree variation in syringyl:guaiacyl ratio of Eucalyptus globulus wood lignin by analytical pyrolysis*. J. Anal. Appl. Pyrolysis 48:121–128.
20. Sundberg, A., Sundberg, K., Lillandt, C., Holmbom, B. (1996); *Determination of hemicelluloses and pectins in wood and pulp fibres by acid methanolysis and gas chromatography*. Nord. Pulp Pap. Res. J. 4: 216–219.
21. Tateishi, M., Seino, T. Ona, T., Ohshima, J., Adachi, K., Yokota, S., Yoshizawa, N., (2004); *Rapid assessment of vessel anatomical features by pyrolysis-gas chromatography*. In: Proceedings of IUFRO Conference on Eucalyptus in a Changing World. Aveiro. Portugal. 3 pp.
22. Watanabe, Y., Kojima, Y., Ona, T., Asada, T., Sano, S., Fukazawa, K., Funada, R., (2004); *Histochemical study on heterogeneity of lignin in Eucalyptus species II. The distribution of lignin and polyphenols in the walls of various cell types*. IAWA Journal 25(3): 283–295.