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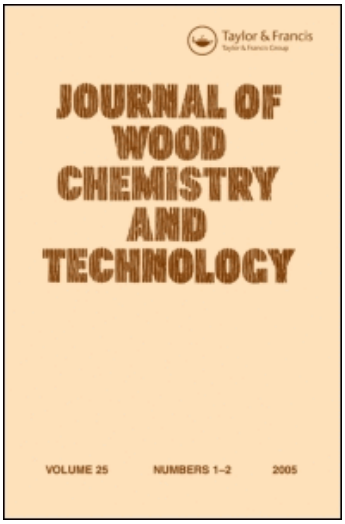

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Surface Characterization of Softwood and Hardwood Kraft Pulp Fibers from Different Stages in a Bleaching Sequence

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Surface Characterization of Softwood and Hardwood Kraft Pulp Fibers from Different Stages in a Bleaching Sequence

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ABSTRACT

Pulp samples from a softwood kraft pulp line and a hardwood kraft pulp line were used to study how the chemical surface composition of different kraft pulp fibers are modified as the fibers are processed in the fiber line. The pulps were bleached according to the following sequence: OQ(OP)(ZQ)(OP). Three different surface analyzing techniques were used and compared to each other in order to determine the content of lignin and extractives on the fiber surfaces. The three techniques studied were electron spectroscopy for chemical analysis (ESCA), ESCA in combination with mercurization of the lignin, and mechanical peeling of the outer part of the fiber surface followed

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by standard chemical analyzing techniques. All analyzing techniques show that the surface coverage by lignin and extractives is higher compared with that of the bulk of the fibers. Standard ESCA, that uses both the theoretical and the measured values of the O/C ratio and C1 carbon content, in most cases gives the highest values on the surface coverage by lignin on both softwood and hardwood kraft pulp fibers, followed by the mercurization and mechanical peeling techniques. More extractives are detected on all kraft pulp fiber surfaces when standard ESCA is used as compared to the mechanical peeling technique. The obtained results indicate that the mercurization technique in combination with ESCA analysis is a good alternative for surface analysis of kraft pulp fibers. However, further investigations are needed to support this recommendation. Standard ESCA indicates that the surface lignin on both unbleached softwood and hardwood kraft pulp fibers has lower reactivity in an oxygen delignification stage as compared to the bulk lignin. In opposite, the mercurization technique and the mechanical peeling technique indicate similar reactivity of bulk and surface lignin towards oxygen. Furthermore, all ESCA techniques show that the decrease in surface coverage by lignin and total lignin content of both softwood and hardwood pulp fibers is low in the last hydrogen peroxide bleaching stage. Oxygen delignification is most efficient in removing surface extractives on both softwood and hardwood pulps and adsorption of surface extractives occurs after the ozone bleaching stage on all pulp samples.

Key Words: ESCA; Mercurization; Mechanical peeling; Softwood kraft pulp; Hardwood kraft pulp; Oxygen delignification; Ozone; Hydrogen peroxide; Bleaching; Extractives.

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INTRODUCTION

Electron spectroscopy for chemical analysis (ESCA), also known as x-ray photoelectron spectroscopy (XPS), has been proved as a useful tool when analyzing chemical composition of fiber surfaces.[1–11] If the O/C ratio or the amount of different carbons is known, the surface coverage by lignin and extractives can be estimated using any of Eqs. (1)–(4). Equations (1) and (2) are taken from Ström and Carlsson,[11] and Eqs. (3) and (4) are taken from Österberg,[7] where 49 in Eq. (3) represents the amount of C1 carbon in pure milled wood lignin and X is the measured value of C1 carbon in pure pulp (5%) or the theoretical value (0%). The O/C ratios and amount of C1 carbons, used for calculations of

the surface coverage by lignin and extractives in this study, can be found in Table 1.

$$\phi_{\text{lignin}} = \frac{\text{O/C}_{\text{after extraction}} - \text{O/C}_{\text{carbohydrates}}}{\text{O/C}_{\text{lignin}} - \text{O/C}_{\text{carbohydrates}}} \quad (1)$$

$$\phi_{\text{extractives}} = \frac{\text{O/C}_{\text{after extraction}} - \text{O/C}_{\text{before extraction}}}{\text{O/C}_{\text{after extraction}} - \text{O/C}_{\text{extractives}}} \quad (2)$$

$$\phi_{\text{lignin}} = \frac{\text{C1}_{\text{after extraction}} - X}{49} \quad (3)$$

$$\phi_{\text{extractives}} = \frac{\text{C1}_{\text{before extraction}} - \text{C1}_{\text{after extraction}}}{\text{C1}_{\text{extractives}} - \text{C1}_{\text{after extraction}}} \quad (4)$$

A novel method to characterize wood fiber surfaces by means of ESCA has been suggested by Westermark.[6] Instead of measuring the O/C ratio or the amount of C1 carbon, specific labeling of the aromatic ring in lignin by mercury acetate is done followed by quantitative determination of mercury by ESCA. Mercury acetate reacts under mildly acidic conditions with the aromatic moiety of the lignin, via an electrophilic substitution reaction, giving a covalent bond between the aromatic ring and the acetoxymercuric group ($-HgOCOCH_3$). An $\sim$1 mol of mercury is incorporated per mole of lignin (C_9-unit) in both spruce and birch wood.[13,14] By using the elemental analysis for softwood lignin, $C_9H_{7.92}O_{2.4}(OCH_3)_{0.92}$[15] and substituting one hydrogen

Table 1. Theoretical and measured values for carbohydrates and theoretical values for lignin and oleic acid (as model for extractable material).

Sample	Atomic ratio (O/C)	C1s total = 100%			
		C1	C2	C3	C4
Carbohydrates (theoretical)[a]	0.83	0	83	17	0
Carbohydrates (measured)	0.81	5	Not measured	Not measured	Not measured
Lignin (theoretical)[b]	0.33	49	49	2	0
Oleic acid (theoretical)[c]	0.11	94	0	0	6

Note: The table shows atomic ratios O/C and chemical shifts in high-resolution carbon spectra (carbon in different functional groups with oxygen).
[a]Mjöberg.[2]
[b]Freudenberg and Neish.[12]
[c]Ström and Carlsson.[11]

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atom per aromatic nucleus with mercury acetate, the theoretical content of mercury in softwood can be calculated from $C_{11}H_{9.92}O_{4.4}(OCH_3)_{0.92}$ Hg. The theoretical mercury content in softwood lignin can then be calculated to 5.48 atomic%. Using the elemental composition of hardwood lignin, $C_9H_{9.03}O_{2.77}(OCH_3)_{1.58}(H_2O)_{0.86}$[16] the theoretical mercury content in hardwood lignin can be calculated to 5.02 atomic%. Using the theoretical value, the surface coverage by lignin can be determined by using the equations as follows:[6]

$$\phi_{\text{softwood lignin}} = 100\left(\frac{\text{atomic\% Hg}}{5.48}\right) \tag{5}$$

$$\phi_{\text{hardwood lignin}} = 100\left(\frac{\text{atomic\% Hg}}{5.02}\right) \tag{6}$$

In addition, there is a method combining enzymatic peeling of hemicelluloses with ESCA to obtain information about the location of different components such as xylan, glucomannan, and lignin on the fiber surfaces.[17]

Beyond ESCA, mechanical peeling techniques combined with fractionation have been used to characterize the chemical composition of pulp fiber surfaces.[18–25] Heijnesson et al.[23] have proposed a procedure for an efficient removal of material from pulp fiber surfaces. According to this procedure, the primary fines (ray-cell enriched fraction) present in the pulp are removed, using a sieve of size 100 μm. The pulp fibers are thereafter mechanical peeled in a disintegrator and the secondary fines (fiber surface material) are removed with the same sieving technique as used for the primary fines. Carbohydrate compositions and the lignin content of pulps, fibers, and fines can then be determined by, e.g., high performance liquid chromatography (HPLC) and the Klason lignin technique, respectively.

Recently performed ESCA studies have reported that the surface concentration by lignin of unbleached softwood kraft pulp fibers is between 5 and 10 times higher in comparison with that of the fiber bulk.[3–10] The surface lignin content was also shown to decrease when cooking was carried out to lower kappa number values and, of course, during lignin-removing bleaching. Furthermore, the surface of kraft pulp fibers, unbleached as well as bleached, have been shown to be rich in extractives, i.e., up to 70 times higher when compared with that of the bulk fiber.[5] In a recently performed study, two techniques, ESCA and ESCA in combination with mercurization, were used for determining the chemical composition of unbleached and oxygen delignified softwood kraft pulp fibers.[10] It was found that the mercurization procedure resulted in much lower values on the surface coverage by lignin in comparison with the standard ESCA method. The results from the mercurization technique showed that the surface lignin content of both unbleached and oxygen delignified softwood kraft pulps was about 2.5 times higher than that

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for the bulk of the fibers. Similar results have been obtained by the mechanical peeling technique, where the lignin content of the fiber surface material, of unbleached pine kraft pulp fibers was about three times higher compared with that of the bulk.[23] Furthermore, Sjöberg et al.[25] concluded, also based on the mechanical peeling technique, that the surface of softwood kraft pulp fibers were rich in lignin, i.e., the lignin content was about 2.5 times higher on the fiber surface than for the corresponding inner layer materials.

Thus, there is a general agreement that the surface of pulp fibers is rich in both lignin and extractives in comparison with the bulk of the fibers. However, the amount of lignin obtained on the fiber surfaces differs from one technique used to another and further investigations are, therefore, needed.

In this study, three different surface analyzing techniques, ESCA, ESCA in combination with mercurization, and mechanical peeling, are used and compared to each other. The study provides information about how the chemical surface composition of softwood and hardwood kraft pulp fibers is modified as the fibers are processed in the fiber line.

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EXPERIMENTAL

Pulps

Pulp samples from a softwood kraft pulp line and a hardwood kraft pulp line were used for the studies in this investigation. The pulps were obtained from svenska cellulosa aktiebolaget (SCA) Östrand in Sundsvall, Sweden. The pulps were oxygen delignified and totally chlorine free (TCF) bleached according to the following sequence: Q(OP)(ZQ)(OP) Table 2 shows a

Table 2. Basic properties of the softwood and hardwood pulps studied.

	Softwood pulp			Hardwood pulp		
Bleaching stage	Kappa-number	Intrinsic viscosity (dm^3/kg)	Brightness (%)	Kappa-number	Intrinsic viscosity (dm^3/kg)	Brightness (%)
Unbleached	30	1,032	26.1	17	1,234	36.4
O	10	878	45.9	11	1,073	53.0
OQ(OP)	6.4	847	62.5	7.2	988	71.4
OQ(OP)(ZQ)	1.7	815	81.7	3.5	835	82.2
OQ(OP)(ZQ)(OP)	1.1	617	89.3	2.8	780	88.6

Note: Data from Ref.[26].

summary of basic pulp properties (data taken from an earlier study made by Risén et al.[26]).

Analysis of the Pulps and Fines

The pulps were extracted with acetone according to the procedure described in SCAN-CM 49 : 93. The content of extractives is given as a percentage of the dry weight of the pulp. The total lignin content, expressed as a percentage of the dry weight of the pulp, was measured as the sum of acid-insoluble (Klason) and acid-soluble lignins.[27] An absorptivity value of 110 L/g cm was used for the determination of acid-soluble lignin.

Preparation of Paper Sheets

Small sheets (diameter: 20 mm, basis weight: $\sim$80 g/m^2) were prepared from the Bauer-McNett fraction R28 (obtained according to SCAN-M 6 : 69). The sheets were formed on filter paper (Munktell analytical filter paper number 5), using a vacuum filtration assembly, and thereafter dried at room temperature before extraction, mercurization, and ESCA measurements.

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Treatment with Mercury Acetate

The mercurization procedure described by Westermark[6] was followed. Generally, a paper sheet ($\sim$25 mg) was placed in a 15 mL glass test tube and 6 mL methanol, 0.25 mL acetic acid, and 0.15 g mercury(II) acetate were added. The test tube was sealed with a Teflon lined screw cap and heated (in an oil bath) for 10 hr at 95°C. The paper sheet was then thoroughly washed with 100 mL boiling acetic acid/methanol (1 : 10) and then dried at room temperature prior to ESCA measurements.

Electron Spectroscopy for Chemical Analysis

The ESCA measurements were carried out at the Institute for Surface Chemistry, Stockholm, Sweden, using a Kratos AXIS HS x-ray photoelectron spectrometer (Kratos Analytical, Manchester, UK). The samples were analyzed in the fixed analyzer transmission (FAT) mode using a monochromatic Al K_α x-ray source operated at 300 W (15 kV/20 mA). The analysis area was less than 1 mm^2. The take-off angle of the photoelectrons was perpendicular to the sample. Detail spectra for C1s, O1s, Hg4f, and Si2s were acquired with

a pass energy of 80 eV. The sensitivity factors used were 0.25 for C1s, 0.66 for O1s, 5.50 for Hg4f, and 0.23 for Si2s (supplied by Kratos). The high-resolution C1s spectra were acquired with a pass energy of 20 eV. Using the curve-fitting program supplied with the spectrometer, Gaussian curves were fitted for de-convolution of the carbon (C1s) peak.

Mechanical Peeling

Before mechanical peeling, primary fines (ray-cell enriched fraction), was removed from the pulps by fractionation. Surface material (secondary fines) was thereafter released from the pulp fibers by mechanical peeling in a disintegrator at a pulp consistency of 4.5% and at 110.000 numbers of revolutions as recommended previously.[23] Primary and secondary fines (size 100 μm) were removed from the pulp and pulp fibers using the fractionation procedure described by Hardell et al.[28]

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RESULTS AND DISCUSSION

Lignin

Table 3 shows the total lignin content and surface coverage by lignin, calculated using the O/C ratio [Eq. (1)], the amount of C1 carbon [Eq. (3)], the mercurization technique [Eqs. (5) and (6)], and the mechanical peeling technique, for the examined pulps. It can be seen that the surface coverage by lignin is always higher compared with the bulk of the fibers, regardless of which analyzing technique used. This is in agreement with earlier findings.[3–11,13,14,17–26,28] However, the amount of lignin obtained on the fiber surfaces differs substantially from one technique used to another. Standard ESCA, that uses both the theoretical and the measured values of O/C carbohydrates and C1 carbon, in most cases gives the highest values on the surface coverage by lignin, followed by the mercurization and mechanical peeling techniques. When the measured values of O/C carbohydrates and C1 carbon are used instead of the theoretical values, the surface content of lignin decreases. Nonetheless, there is still great difference between the techniques used in this investigation (cf. Table 3).

The differences in obtained results between the different techniques used can be explained by several factors. A different analyzing depth, when compared with ESCA might explain the relatively low surface coverage by lignin, found with the mechanical peeling technique. The amount of material removed from the different pulp fiber surfaces by mechanical peeling was

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Table 3. The lignin content and surface coverage by lignin for the examined pulps.

Pulp	Bleaching stage	Klason lignin (%)	Acid soluble lignin (%)	Total lignin content (%)[a]	Surface coverage by lignin (%)					
					O/C[b] (0.83)	O/C[c] (0.81)	C1[d] (0)	C1[e] (5)	Hg[f]	Peeling[g]
Softwood	Unbleached	4.1	0.4	4.6	36 ± 2	33 ± 2	28 ± 1	18 ± 1	13 ± 0	8.4
	O	1.2	0.4	1.6	29 ± 1	26 ± 1	21 ± 0	11 ± 0	5 ± 0	2.1
	OQ(OP)(ZQ)	0.4	0.2	0.6	27 ± 1	24 ± 1	18 ± 1	7 ± 1	2 ± 0	1.4
	OQ(OP)(ZQ)(OP)	0.3	0.2	0.5	25 ± 1	22 ± 1	18 ± 0	7 ± 0	3 ± 0	0.7
Hardwood	Unbleached	1.9	0.7	2.6	30 ± 0	27 ± 0	22 ± 2	12 ± 2	12 ± 0	4.6
	O	1.0	0.4	1.4	31 ± 1	28 ± 1	20 ± 1	10 ± 1	6 ± 0	2.7
	OQ(OP)(ZQ)	0.6	0.1	0.7	26 ± 2	23 ± 2	16 ± 1	5 ± 1	2 ± 0	1.2
	OQ(OP)(ZQ)(OP)	0.5	0.1	0.6	25 ± 1	22 ± 1	15 ± 0	4 ± 0	2 ± 0	1.0

[a]The total lignin content is the sum of Klason lignin and acid soluble lignin. The experimental error associated with the lignin analysis was maximum ±0.2%.
[b]Equation (1) × 100, where $O/C_{carbohydrates} = 0.83$.
[c]Equation (1) × 100, where $O/C_{carbohydrates} = 0.81$.
[d]Equation (3) × 100, where *X* represents the theoretical value of 0% C1 carbon in pure pulp.
[e]Equation (3) × 100, where *X* represents the measured value of 5% C1 carbon in pure pulp.
[f]Equation (5) for softwood lignin and Eq. (6) for hardwood lignin.
[g]The surface coverage of lignin was determined according to Heijnesson et al.[23]. The experimental error associated with the lignin analysis was maximum ±0.2%.

between 1.0% and 1.4% and even though scanning electron microscopy analysis has shown that the material removed by mechanical peeling consisted of fibrils and thin sheets of material from the fiber surface and that no extensive peeling of the S_2-layers was detected, the analyzing depth was not specified. A deeper analyzing depth will lead to a higher level of carbohydrates in the surface material removed and thus, the lignin content measured will be lower. It is most likely that the analyzing depth of the fibers is deeper for the mechanical peeling technique than for the ESCA techniques, i.e., deeper than 5–10 nm.

One limitation of the mercurization technique may be that mercury acetate has different reactivity towards different wood elements, such as fibers and ray cells, or different reactivity towards softwood and hardwood lignins. If not all aromatic nucleuses are substituted with one molecule of mercury acetate, the surface coverage by lignin will be underestimated. However, it has been shown that different wood elements, such as ray cells, middle lamella, and compression wood, all reacted at the same rate as the whole wood; ~1 mol of mercury per mole of softwood and hardwood lignin.[13,14] In a work performed by Ericsson et al.,[14] the stability of organically bound mercury, when subjected to electron beam during the observation in transmission electron microscopy, was examined. They found that mercury organically bound to lignin was stable during electron bombardment. However, when ESCA is used, the samples are subjected to x-ray irradiation, and it is possible that x-ray can lead to degradation of mercury during analysis, and thus leading to an underestimation of surface lignin.

A prerequisite for standard ESCA is that all extractives are removed from the analyzed surface. If not, the surface coverage by lignin will be overestimated [cf. Eqs. (1) and (3)]. Actually, Laine et al.[3] have observed an alkyl carbon (C1) in the spectrum of extracted bleached kraft pulp and assumed that this was due to strongly adsorbed extractives, which are not removable by extraction. Furthermore, a recent study has shown that acetone extraction did not completely remove fatty acids, calcium soaps, and sterols from a birch ECF pulp.[29] Another limitation is that the elementary composition of lignin changes during the pulp and paper making process. In a study carried out by Backman and Gellerstedt,[30] it was shown that the oxidative treatment in the bleaching processes leads to an increase in the O/C ratio of the residual lignin of a softwood kraft pulp. The O/C ratio increased from 0.36 for residual lignin in unbleached pulp to 0.47 and 0.50 for residual lignin in pulp from a totally chlorine free and an elementary chlorine free bleaching sequence, respectively. Thus, this would lead to an underestimation of the surface coverage by lignin. Furthermore, in a recently performed ESCA study, it was shown that the preparative methods of the sample had an important impact on the surface chemical composition of the fibers.[8] Air-drying of the fiber

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samples yielded a higher surface coverage of lignin than freeze drying.[8] This indicates the sensitivity of the standard ESCA technique.

By comparing the surface lignin and total lignin content before and after oxygen delignification (cf. Table 3), the reactivity of surface lignin and bulk lignin towards oxygen can be calculated. When using the values obtained from the C1 carbon (measured value, 5%), it can be calculated that oxygen delignification decreases the lignin on the fiber surface of the softwood pulp by about 39%, whereas the total lignin content is reduced by approximately 65%. The same values for the hardwood pulp are 17% and 46%, respectively. Thus, indicating that the surface lignin of both unbleached softwood and hardwood kraft pulp fibers has lower reactivity in an oxygen delignification stage when compared with the bulk lignin. Similar results have been reported earlier.[5,10] Laine et al.[5] have proposed that the lower reactivity of surface lignin are due to condensed lignin structures and/or to lignin–carbohydrate complexes. On the other hand, Kleen et al.[9] using standard ESCA, reported recently that oxygen delignification removes a high fraction of the surface lignin. They explain the contradictory results with that the reactivity of oxygen towards lignin not only depend on the structure of the lignin, but also on the ability of oxygen to penetrate into the fibers. This penetration depends on the porosity (or swelling) of the fibers, which in turn is affected by the cooking conditions and may also be different for fibers of different origin. When using the values obtained with the mercurization technique, both the surface lignin content and the total lignin content are reduced by about 65% for the softwood fibers and 50% for the hardwood fibers, indicating that the surface lignin and bulk lignin have the same reactivity towards oxygen. The values obtained with the mechanical peeling technique also indicate a similar reactivity of bulk and surface lignin towards oxygen. Furthermore, all ESCA techniques show that the decrease in the surface coverage by lignin of both softwood and hardwood pulp fibers are low in the last bleaching stage with hydrogen peroxide. Those results are in agreement with earlier findings.[5]

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Extractives

Table 4 shows the total content and surface coverage of extractives on the different kraft pulp fibers. All pulp samples show low absolute amounts of the surface extractives in comparison with other studies.[3–5] An explanation for the low values obtained might be that the paper sheets prepared for ESCA analysis were dried at room temperature. In other studies, in which similar softwood pulp fibers have shown a much higher degree of surface coverage by extractives, the paper sheets have been dried at 70°C for 2 hr.[3–5] Migration of extractable material is favored by an increase in temperature

Table 4. The total content and surface coverage by extractives for the examined pulps.

Pulp	Bleaching stage	Total extractive content[a] (%)	Surface coverage by extractives (%)		
			O/C[b] (0.11)	C1[c] (94)	Peeling[d]
Softwood	Unbleached	0.25	1.9 ± 0	2.6 ± 1	0.6
	O	0.16	0.9 ± 1	0.8 ± 0	0.6
	OQ(OP)(ZQ)	0.13	4.3 ± 3	3.3 ± 0	0.5
	OQ(OP)(ZQ)(OP)	0.09	3.4 ± 2	1.5 ± 1	0.1
Hardwood	Unbleached	0.56	9.7 ± 0	5.1 ± 0	2.2
	O	0.16	0.9 ± 1	1.3 ± 1	0.9
	OQ(OP)(ZQ)	0.15	2.5 ± 1	2.7 ± 1	1.6
	OQ(OP)(ZQ)(OP)	0.15	5.9 ± 0	3.8 ± 0	1.1

[a]The total extractive content obtained from acetone extraction. The experimental error associated with the analysis of extractives was maximum ±0.1%.
[b]Equation (2) × 100, where 0.11 is the theoretical value for O/C extractives (oleic acid).
[c]Equation (4) × 100, where 94 is the theoretical value for C1 extractives (oleic acid).
[d]Determined according to Heijnesson et al.[23]. The experimental error associated with the analysis of extractives was maximum ±0.1%.

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and may lead to a higher amount of extractives on the fiber surfaces.[31,32] Despite rather low absolute amounts of extractives, the surface coverage by extractives is higher than that of the fiber bulk (cf. Table 4). The ratio lies between 5 and 40, with the standard ESCA technique, and between 1.4 and 11, with the mechanical peeling technique. The lower content of extractives obtained with the mechanical peeling technique is probably due to a deeper analyzing depth and/or that some extractives are lost during the fractionation procedure in which the pulp fibers are thoroughly washed. At the same time, the surface coverage by extractives may have been underestimated with the standard ESCA technique if the extraction was unsatisfactory [cf. Eqs. (2) and (4)].

From Table 4, it can also be noted that oxygen are the bleaching chemical that are most effective in removing extractives from the bulk and the surface of both softwood and hardwood pulp fibers. This is consistent with earlier studies where oxygen treatment of softwood kraft pulps have decreased the surface coverage by extractives considerably.[4,5] It can be expected that the amount of surface extractives should decrease, as the oxygen delignification occurs under alkaline conditions.[33,34] Furthermore, adsorption of surface extractives occurs after the ZQ-bleaching stage, for both softwood and hardwood pulps.

The ozone bleaching stage is acidic which probably cause resorption onto the fibers of already dissolved organic material.[33–35]

Recommended Analyzing Technique for Surface Lignin

The results obtained in this study show the high sensitivity of standard ESCA. Depending on whether theoretical or measured values of the O/C ratio and C1 carbon are used, the surface coverage by lignin varies noticeable. The surface coverage by lignin obtained by the mercurization technique is about the same as achieved for similar pulps in an earlier study.[10] As already mentioned, the mercurization reaction is selective towards both softwood and hardwood lignins and reacts with ~1 mol of mercury per mole of lignin.[13,14] It is, however, possible that x-ray irradiation can lead to degradation of mercury during analysis and thus leading to an underestimation of surface lignin. The mechanical peeling technique most likely underestimates the surface coverage by lignin due to a deeper analyzing depth compared with the ESCA techniques. The obtained results indicate that the mercurization technique in combination with ESCA analysis is a good alternative for surface analysis of kraft pulp fibers. However, further investigations are needed to support this recommendation.

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CONCLUSIONS

The quantities of surface lignin found on the examined softwood and hardwood pulps were always higher than the fiber bulk lignin content, regardless of which analyzing technique was used. However, the standard ESCA technique, that uses both the theoretical and the measured values of O/C carbohydrates and C1 carbon, in most cases gives the highest values on the surface coverage by lignin, followed by the mercurization and mechanical peeling techniques. The obtained results indicate that the mercurization technique in combination with ESCA analysis is a good alternative for surface analysis of kraft pulp fibers. However, further investigations are needed to support this recommendation.

Standard ESCA indicated that the surface lignin of both unbleached softwood and hardwood kraft pulp fibers has lower reactivity towards oxygen in an oxygen delignification stage in comparison with the bulk lignin. In opposite, the mercurization technique and the mechanical peeling technique indicate similar reactivity of bulk and surface lignin towards oxygen. Furthermore, all ESCA techniques showed that the decrease in surface coverage by lignin and total lignin content of both softwood and hardwood pulp fibers is low in the last hydrogen peroxide bleaching stage.

All pulp samples showed low absolute amounts of surface coverage by extractives. Nevertheless, the surface coverage by extractives was found to be higher than that of the fiber bulk with both the standard ESCA technique and the mechanical peeling technique. Oxygen was the bleaching chemical most effective in removing extractives from the bulk and the surface of both softwood and hardwood pulp fibers. Furthermore, adsorption of surface extractives occurred after the ZQ-bleaching stage, for both softwood and hardwood pulps.

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REFERENCES

1. Dorris, G.M.; Gray, D.G. The surface analysis of paper and wood fibres by ESCA. I. Application to cellulose and lignin. Cellul. Chem. Technol. **1978**, *12* (1), 9–23.
2. Mjöberg, P.J. Chemical surface analysis of wood fibers by means of ESCA. Cell. Chem. Technol. **1981**, *15* (5), 481–486.
3. Laine, J.; Stenius, P.; Carlsson, G.; Ström, G. Surface characterization of unbleached kraft pulps by means of ESCA. Cellulose **1994**, *1* (2), 145–160.
4. Laine, J.; Stenius, P. Surface Properties of Bleached Kraft Pulp Fibres and Their Comparison with the Properties of the Final Paper Products. 8th International Symposium on Wood and Pulping Chemistry, Helsinki, Finland, Jun 6–9, 1995; 1, 589–596.
5. Laine, J.; Stenius, P.; Carlsson, G.; Ström, G. The effect of ECF and TCF bleaching on the surface chemical composition of kraft pulp as determined by ESCA. Nord. Pulp Pap. Res. J. **1996**, *11* (3), 201–210.
6. Westermark, U. The Content of Lignin on Pulp Fiber Surfaces. Proceedings of the 10th International Symposium on Wood and Pulping Chemistry, Yokohama, Japan, Jun 7–10, 1999; 1, 40–42.
7. Österberg, M. *On the Interactions in Cellulose Systems: Surface Forces and Adsorption*; The Royal Institute of Technology: Stockholm, Sweden, 2000.
8. Duchesne, I.; Daniel, G.; Van Leerdam, G.C.; Basta, J. Surface chemical composition and morphology of ITC kraft fibres as determined by XPS and FE-SEM. J. Pulp Pap. Sci. **2003**, *29* (3), 71–76.

9. Kleen, M.; Sjöberg, J.; Dahlman, O.; Johansson, L.S.; Koljonen, K.; Stenius, P. The effect of ECF and TCF bleaching on the chemical composition of soda-anthraquinone and kraft pulp surfaces. Nord. Pulp Pap. Res. J. **2002**, *17* (3), 357–363.
10. Heijnesson Hultén, A.; Paulsson, M. Surface characterization of unbleached and oxygen delignified kraft pulp fibers. J. Wood Chem. Technol. **2003**, *23* (1), 29–44.
11. Ström, G.; Carlsson, G. Wettability of kraft pulps—effects of surface composition and oxygen plasma treatment. J. Adhesion Sci. Technol. **1992**, *6*, 745–762.
12. Freudenberg, K., Neish, A.C., Eds. *Constitution and Biosynthesis of Lignin*; Springer-Verlag: Berlin, Germany, 1968.
13. Westermark, U.; Lidbrandt, O.; Eriksson, I. Lignin distribution in spruce (*Picea abies*) determined by mercurization with SEM-EDXA technique. Wood Sci. Technol. **1988**, *22* (3), 243–250.
14. Eriksson, I.; Lidbrandt, O.; Westermark, U. Lignin distribution in birch (*Betula verrucosa*) as determined by mercurization with SEM— and TEM-EDXA. Wood Sci. Technol. **1988**, *22* (3), 251–257.
15. Freudenberg, K.; Sohns, F.; Dürr, W.; Niemann, C. Über lignin coniferylalkohol und saligenin. Cellulosechemie **1931**, *12*, 263–275.
16. Björkman, A.; Person, B. Studies on finely divided wood. Part 2. The properties of lignins exracted with neutral solvents from softwoods and hardwoods. Svensk Papperstidn. **1957**, *60* (5), 158–169.
17. Buchert, J.; Carlsson, G.; Viikari, L.; Ström, G. Surface characterization of unbleached kraft pulps by enzymatic peeling and ESCA. Holzforschung **1996**, *50* (1), 69–74.
18. Kallmes, O. Distribution of constituents across the wall of unbleached spruce sulfite fibers. Tappi **1960**, *13* (2), 143–152.
19. Krause, T. Änderung der morphologischen structur und chemischen zusammensetzung von zellstoff-fasern bei mechanischer abschlägung der äusseren wandschichten. Das Papier **1967**, *21* (7), 385–393.
20. Kibblewhite, R.P.; Brookes, D. Distribution of chemical components in the walls of kraft and bisulphite pulp fibres. Wood Sci. Technol. **1976**, *10* (1), 39–46.
21. Lindström, T.; Glad-Nordmark, G. Chemical characterization of the fines fraction from unbleached kraft pulps. Svensk Papperstidn. **1978**, *81* (15), 489–492.
22. Treimanis, A.P.; Purina, L.T.; Ioelovich, M.J. Localization of Residual Lignin in Pulp Fibre Walls and its Influence upon the Crystallinity Parameters of Different Cell Wall Layers, 1st European Workshop on Lignocellulosics and Pulp, Hamburg, Germany, May 18-20, 1990; 256–265.

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23. Heijnesson, A.; Westermark, U.; Simonson, R. Removal of lignin-rich surface material from unbleached kraft fibres. Holzforschung **1995**, *49* (4), 313–318.
24. Suurnäkki, A.; Heijnesson, A.; Buchert, J.; Viikari, L.; Westermark, U. Chemical characterization of the surface layers of unbleached pine and birch kraft pulp fibres. J. Pulp Pap. Sci. **1996**, *22* (2), 43–47.
25. Sjöberg, J.; Kleen, M.; Dahlman, O.; Agnemo, R.; Sundvall, H. Analyses of carbohydrates and lignin in the surface and inner layers of softwood pulp fibers obtained employing various alkaline cooking processes. Nord. Pulp Pap. Res. J. **2002**, *17* (3), 295–301.
26. Risén, J.; Heijnesson Hultén, A.; Paulsson, M. The influence of fiber properties on the network strength on hardwood and softwood kraft pulp fibers from different stages of a bleaching sequence. J. Wood Chem. Technol. **2003**, Submitted for publication.
27. Dence, C.W. The determination of lignin. In *Methods in Lignin Chemistry*; Lin, S.Y., Dence, C.W., Eds.; Springer-Verlag: Berlin, Germany, 1992; 33–61.
28. Hardell, H.L.; Leary, G.J.; Stoll, M.; Westermark, U. Variations in lignin structure in defined morphological parts of spruce. Svensk Papperstidn. **1980**, *83* (2), 44–49.
29. Fardim, P.; Gustafsson, J.; von Schoultz, S.; Peltonen, J.; Holmbom, B. Extractives on Fibre Surfaces Studied by XPS, ToF-SIMS and Different Extraction Methods, 7th European Workshop on Lignocellulosics and Pulp, Turku, Finland, Aug 26-29, 2002; 451–454.
30. Backman, L.; Gellerstedt, G. Reaction of Kraft Pulp Lignin with Alkaline Hydrogen Peroxide, 7th International Symposium on Wood and Pulping Chemistry, Beijing, China, May 25–28, 1993, 1; 223–229.
31. Swanson, J.W.; Cordingly, S. Surface chemical studies on pitch. II. The mechanism of the loss of absorbency and development of self-sizing in papers made from wood pulps. Tappi J. **1959**, *42* (19), 812–819.
32. Aberson, G.M. *In The Physics and Chemistry of Wood Pulp Fibers*; Page, D.H., Ed.; TAPPI STAP: New York, 1970; 282(8).
33. Allen, L.H.; Lapointe, C.L. Physical distribution of resin in bleached kraft pulp mills. Pulp Pap. Can. **1987**, *88* (12), 231, 232 and 234–239.
34. Ström, G.; Lindström, M.; Stenius, P.; Ödberg, L. Surface chemical aspects of the behavior of soaps in pulp washing. Nord. Pulp Pap. Res. J. **1990**, *5* (1), 44–51.
35. Lindholm, C.A.; Malkov, S. Resorption of dissolved organic material in acid TCF bleaching stages. Nord. Pulp Pap. Res. J. **1997**, *12* (1), 4–8.

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