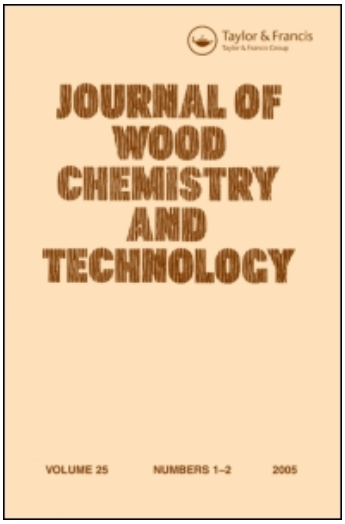

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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Online publication date: 18 March 2003

To cite this Article Hultén, Anette Heijnesson and Paulsson, Magnus(2003) 'Surface Characterization of Unbleached and Oxygen Delignified Kraft Pulp Fibers', Journal of Wood Chemistry and Technology, 23: 1, 31 — 46
To link to this Article: DOI: 10.1081/WCT-120018614
URL: http://dx.doi.org/10.1081/WCT-120018614

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JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY
Vol. 23, No. 1, pp. 31–46, 2003

Surface Characterization of Unbleached and Oxygen Delignified Kraft Pulp Fibers

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ABSTRACT

The chemical and morphological surface properties of different unbleached and oxygen delignified softwood kraft pulp fibers were evaluated by using different ESCA and SEM techniques. The results of the different techniques have revealed that the surface of unbleached and oxygen delignified kraft pulp fibers has a higher content of lignin and in some cases also extractives, in comparison with the bulk of the fibers. However, the amount of lignin obtained on the fiber surfaces differs substantially from one technique to another. The mercurization technique (mercurization followed by the determination of mercury by ESCA) gave about three to five times lower

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DOI: 10.1081/WCT-120018614 0277-3813 (Print); 1532-2319 (Online)

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values on the surface coverage of lignin, in comparison with the normal ESCA procedure. Good correlation between the surface coverage of lignin and the total amount of lignin was obtained for all techniques, however, the best correlation was obtained for the mercurization technique. The results also show that the total and surface charges of the unbleached and oxygen delignified pulp fibers decreased with a decrease in kappa number and that the extent of fibrillation increased with a decrease in kappa number.

Key Words: ESCA; SEM; Mercurization; Bromination; Softwood kraft pulps; Lignin; Extractives; Fiber charge; Fiber surface structure.

INTRODUCTION

The external surface is the part of the fiber that is directly involved in interactions between fibers and between fibers and other components during pulp and paper production. It is obvious that surface properties are of importance to the interactions and that these properties can influence the network strength of pulp fiber suspensions and, thus, also the flow behavior of pulp suspensions.

The external surface of kraft pulp fibers is formed when the fibers separate in the compound middle lamella area during the defibration of wood chips after cooking. The surface properties of pulp fibers differ considerably from one pulp to another. This is due to variations in the raw material, in the pulping process and in the subsequent bleaching process used.

The present article will elucidate the surface properties of unbleached and oxygen delignified kraft pulp fibers and a forthcoming article[1] will provide further information about the mechanisms involved in the fiber suspension's ability to form strong networks. Greater knowledge of how fiber properties influence the behavior of pulp fiber suspensions could facilitate the modification of many kinds of equipments used in the pulp and paper industry in order to optimize their function and efficiency.

The surface characteristics of pulp fibers can be studied with various methods. Several investigators have used mechanical peeling techniques to determine the distribution of lignin and carbohydrates located in the surface layer of softwood fibers.[2–8] It has been reported that the surface of unbleached softwood and hardwood fibers has a high content of lignin relative to the rest of the fibers.[2–8] In recent years, ESCA (Electron Spectroscopy for Chemical Analysis) has been shown to be a powerful technique for analyzing pulp fiber surfaces.[9–12] For example, ESCA analyses have shown that the concentration of lignin on fiber

surfaces is generally several times higher than the amount of lignin in the bulk of the fibers.[11,12] It has also been shown that the surface lignin content decreased when cooking was carried out to a lower total lignin content and, of course, also during lignin-removing bleaching. Furthermore, the content of extractives located in the surface of fibers, unbleached as well as bleached, was found to be very high, in some cases up to 100 times higher than in the bulk of the fibers.[11,12] Buchert et al.[13] have used ESCA in combination with enzymic peeling of unbleached chemical pulps. It was concluded from that study that the surfaces of both unbleached pine and birch kraft fibers were rich in lignin and that relatively more lignin was relocated on the surface of birch kraft fibers than on the surface of pine kraft fibers during cooking. Recently, Westermark[14] developed a technique for the quantitative determination of the content of lignin on pulp surfaces based on the selective labeling of lignin by mercurization followed by the determination of mercury by ESCA, and concluded that the surface of unbleached softwood kraft pulp fibers was enriched in lignin in comparison with the rest of the fibers.

In this article, the morphological and chemical surface properties of well-defined relevant papermaking fibers are evaluated. Different techniques, ESCA, ESCA in combination with mercurization, and SEM (Scanning Electron Microscopy) in combination with bromination, for determining the chemical composition of the pulp fiber surfaces are used and compared with each other. The structure of the fiber surfaces is studied with SEM. The surface characterization of the pulp fibers has been done in order to render a base for being able to describe a fiber network more properly which will be done in the next paper of this series.[1]

EXPERIMENTAL

Materials

Commercially produced unbleached and oxygen delignified softwood kraft pulps, obtained from three Swedish mills (mills A, B, and C), were used for the studies described in this article. The oxygen delignification was performed in two stages. All pulps were then thoroughly washed with deionized water before further analysis. Table 1 summarizes selected pulp properties.

General Analytical Procedures

Standard methods were applied for the determination of brightness (SCAN–CM 11:95), intrinsic viscosity (SCAN–C 15:88), drainage

Table 1. Pulp properties of unbleached and oxygen delignified softwood kraft pulps.

Softwood kraft pulp	Kappa number	Intrinsic viscosity (dm^3/kg)	Brightness (% ISO)	Drainage resistance °SR	Water retention value, WRV (%)[a]
Unbleached					
Pulp A_{Un}	34.6	1330	27.9	18	1.77
Pulp B_{Un}	30.0	1190	28.2	17	1.65
Pulp C_{Un}	21.5	1120	31.9	15	1.50
O_2-Delignified					
Pulp A_{O_2}	19.7	1090	36.3	18	1.76
Pulp B_{O_2}	12.7	1010	41.2	18	1.67
Pulp C_{O_2}	8.8	940	48.1	16	1.50

[a]The procedure followed the SCAN–C 102 XE method with two exceptions; a lower centrifugal force (2000 g) and a longer centrifugal time (30 min).

resistance (SCAN–C 19:65), and kappa number (SCAN–C 1:77). The procedure used for determining the Water Retention Value (WRV) was as described in standard method SCAN–C 102 XE with the exception of a lower centrifugal force (2000 g) and a longer centrifugal time (30 min).

Extraction of Pulps

Acetone extractions of pulps were performed according to the procedure described in standard method SCAN–CM 49:93. The content of extractives was determined as a percentage of the dry weight of the pulp.

Total Lignin Content

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.[15] An absorptivity value of 110 L/g cm was used for calculating acid-soluble lignin.

Fractionation and Classification of Pulps

The pulps were classified in a Bauer–McNett apparatus according to standard method SCAN–M 6:69. The long fiber fraction (R28) of the

screened pulps was collected and used for scanning electron microscopy (SEM) and electron spectroscopy for chemical analysis (ESCA) studies.

Preparation of Paper Sheets

Small sheets (diameter: 20 mm, basis weight: ~80 g/m^2) were prepared from the Bauer–McNett fraction R28. 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 mercurization and/or ESCA measurements.

Treatment with Bromine Gas

An aqueous suspension of fibers was cooled in liquid N_2 (i.e., at −210°C) and thereafter transferred to a Heto Hetosicc CD 2.5 freeze dryer and dried overnight. The dried fibers were then exposed to water-free bromine gas (2.2 mL liquid bromine) in a closed glass reactor (550 mL) for 30 min.[16]

Treatment with Mercury Acetate

The mercurization procedure described by Westermark[14] was followed. Generally, a paper sheet (approximately 25 mg) was placed in a 15 mL glass test tube and 6 mL methanol, 0.25 mL acetic acid, and 0.15 mg mercury(II) acetate were added. The test tube was carefully sealed with a Teflon lined screw cap and heated (in an oil bath) for 10 h at 95°C. The paper sheet was then washed with 100 mL boiling acetic acid/methanol (1:10) and then dried at room temperature prior to ESCA measurements.

Scanning Electron Microscopy (SEM)

The electron micrographs were obtained in a Jeol JSM-5200 scanning electron microscope (SEM) using secondary electron imaging (SEI) or back-scattered electron imaging (BEI) modes, respectively. The BEI mode shows elemental contrast on chemically heterogeneous materials (the gray-scale images are proportional to the average atomic number in the sample). The freeze-dried fibers (R28 fraction) were coated with Au

using a Jeol JFC-1100E ion sputter, and the brominated fibers (R28) were coated with C using an Agar SEM carbon coater prior to examination (SEI and BEI mode, respectively). Observations of fiber surfaces (SEI mode) were made using a 15 kV accelerating voltage in the electron column with the secondary electron detector at a working distance of 10 mm. Back-scattered electron images were obtained using an acceleration voltage of 25 kV and a working distance of 18 mm (magnification of about $\times 200$).

The SEM micrographs (BEI mode) were digitized for determining surface lignin content using a simple image analysis system (NIH Image 1.61/ppc).

Electron Spectroscopy for Chemical Analysis (ESCA)

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.

Polyelectrolyte Adsorption

Polyelectrolyte adsorption and pulp pretreatments were determined essentially according to Wågberg et al.[17] The cationic polymers used were poly(1,5-dimethyl-1,5-diazaundecamethylene)bromide (polybrene, from SIGMA) with a charge density of 5.35×10^{-3} eq/g and poly-(dimethyldiallylammonium)chloride (poly-DMDAAC, from Allied Colloids Ltd) with a charge density of approximately 6.19×10^{-3} eq/g. The molecular weights of the polymers were approximately 8×10^3 and 3.8×10^5, respectively. The excess (non-adsorbed) polyelectrolyte was titrated with anionic potassium polyvinyl sulphate (KPVS from Wako Pure Chemicals Industries, Ltd.) with a charge density of

6.16×10^{-3} eq/g, using a dye indicator, toluidin blue, to detect the end point of titration.

RESULTS AND DISCUSSION

Lignin

The surface lignin content of unbleached and oxygen delignified softwood kraft pulp fibers was analyzed by means of ESCA and SEM. When using the ESCA technique the chemical composition is normally evaluated either using the C1s and O1s peaks by calculating the total O/C ratio, or the relative amounts of different carbons from the intensities of carbons with different chemical shifts of the C1s peak. However, Westermark[14] has recently developed a technique based on selective labeling of lignin by mercurization followed by determining mercury by ESCA. In this study, both techniques were used and compared with each other. Table 2 shows the lignin content and surface coverage of lignin for the different pulp samples, using the different ESCA techniques. As can be seen, the results from the different techniques show that the surfaces of both unbleached and oxygen delignified kraft pulp fibers have a considerably higher lignin concentration compared with the bulk of the fibers. However, with the mercurization procedure, much lower values on the surface coverage are obtained in comparison with the other techniques. The reasons for these differences are not known. A prerequisite for the technique in which the O/C ratio is used for determining the surface lignin content is that the surface only consists of lignin and carbohydrates and that all extractives have been removed. However, Laine et al.[11] have observed an alkyl carbon (C1) in the spectrum of extracted bleached kraft pulp and have assumed that this was due to strongly adsorbed extractives, which are not removable by extraction. Another limitation is that the elementary composition of lignin changes during the pulp and paper making process. Backman et al.[18] have 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 (TCF) and an elementary chlorine free (ECF) bleaching sequence, respectively. An increase in the O/C ratio during oxygen delignification will, however, lead to an under-estimation of the calculated surface coverage of lignin and, thus, the differences between the different ESCA techniques will be even greater. One limitation of the mercurization technique may be that

Table 2. The lignin content and degree of surface coverage of lignin for various unbleached and oxygen-delignified softwood kraft pulps. The content of lignin on the fiber surface was determined with the ESCA method.

Softwood kraft pulp	Klason lignin (%)	Acid soluble lignin (%)	Total lignin content (%)[a]	Surface coverage of lignin (%)		
				Hg[b]	$C1_{lignin}$[c]	ϕ_{lignin}[d]
Unbleached						
Pulp A_{Un}	5.0	0.4	5.4	14 ± 1	35 ± 0	45 ± 1
Pulp B_{Un}	4.1	0.4	4.5	11 ± 0	27 ± 0	39 ± 1
Pulp C_{Un}	3.0	0.5	3.5	9 ± 0	22 ± 0	28 ± 0
O_2-Delignified						
Pulp A_{O_2}	2.4	0.5	2.9	7 ± 0	24 ± 1	36 ± 0
Pulp B_{O_2}	1.4	0.6	2.0	4 ± 0	20 ± 4	32 ± 4
Pulp C_{O_2}	0.8	0.6	1.4	4 ± 0	15 ± 1	21 ± 1

[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]Determined according to Westermark[14]; 100(atomic% Hg/5.48).
[c]$C1_{lignin} = 100[(C1_{(pulp\ sample)} - X)/Y)]$ where $C1_{(pulp\ sample)}$ is the C1-value of a pulp sample analysis after extraction with acetone, X is the level of contamination (2%), and Y is the proportion of C1 for pure lignin (49%).
[d]$\phi_{lignin} = 100[(O/C_{(pulp\ sample)} - O/C_{(carbohydrates)})/(O/C_{lignin} - O/C_{(carbohydrates)})]$ where $O/C_{(pulp\ sample)}$ is the O/C atomic ratio of a pulp sample analysis after extraction with acetone, $O/C_{(carbohydrates)} = 0.83$, and $O/C_{(lignin)} = 0.33$.

mercury has a different reactivity towards structural differences in lignin. However, in an investigation performed by Westermark et al.[19] it was shown that different wood elements, such as ray cells, middle lamella, and compression wood, all reacted at the same rate as the whole wood; about one mole of mercury per mole of lignin. The results from the mercurization technique show that the lignin content of both unbleached and oxygen delignified kraft pulp fiber surfaces is about 2.5 times higher than that of whole pulps. This should be compared with the results for the unbleached and oxygen delignified pulp, which were 8–15 times higher, respectively, using the O/C technique (ϕ_{lignin} in Table 2). The results obtained with the mercurization technique are in good agreement with earlier findings in which the lignin content of fiber surfaces was studied by using a mechanical peeling technique in combination with chemical analysis.[7] Figure 1 shows the degree of coverage of the surface by lignin vs. the total lignin content. Note that good correlation is

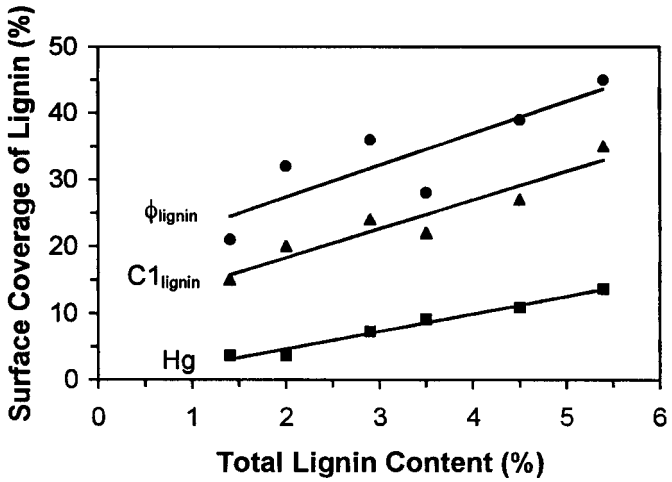

Figure 1. The surface coverage of lignin vs. the total lignin content of unbleached and oxygen delignified kraft pulp fibers (cf. Table 2).

obtained for all techniques, however, the best correlation is obtained for the mercurization technique. In Table 2, it can also be seen that the surface coverage of lignin decreases as the pulp fibers is subjected to oxygen delignification. When using the values obtained from the O/C ratio, it can be calculated that oxygen delignification decreases the lignin on the fiber surface by about 20%, while the total lignin content is reduced by approximately 50%. Thus, oxygen delignification removes significantly less surface lignin in comparison with the lignin content in the bulk of the fibers, indicating that surface lignin has a lower reactivity to oxygen. The low reactivity of surface lignin has been suggested to be due to condensed lignin structures and/or to lignin-carbohydrates complexes.[20] However, when using the values obtained with the mercurization technique, both the total lignin content and the surface coverage of the different pulp fibers are reduced by about the same values, about 50%, indicating that bulk and surface lignin have the same reactivity to oxygen. Any definite conclusions about the differences in the results obtained with the different ESCA techniques require more detailed analysis, and this is under way.

Another method involving staining lignin with bromine in combination with SEM analysis using the back-scattered electron imaging (BEI) mode (cf. 16) was also carried out in order to evaluate the content of lignin on fiber surfaces. Bromine reacts readily and preferably with

lignin,[21] raising its average atomic number, which makes the lignin appear brighter than carbohydrates in the BEI mode. The results of these studies indicate that there is some lignin on fiber surfaces. However, the concentration gradient between lignin and carbohydrates was not pronounced enough to be able to obtain quantitative values of the degree of surface coverage of lignin.

Extractives

The total amount of acetone-extractable material in the different pulp samples varied between 0.05 and 0.20% (see Table 3), and these values are typical for industrially produced kraft pulps. In order to determine the amount of extractives on fiber surfaces, acetone extraction in combination with ESCA was used. Table 3 shows the total content and surface coverage of extractives on the different commercial kraft pulp fibers. It can be seen that no, or only a small amount of extractives, could be detected on the unbleached and oxygen delignified kraft pulp fiber surfaces. These results are not in agreement with earlier findings, in which the coverage of extractives on the fiber surface of similar pulp fibers have been found to be much higher, in some cases up to 100 times higher in comparison with that of the bulk of the fibers.[10–12,22]

Table 3. Total content of extractives and surface coverage of extractives for various unbleached and oxygen delignified softwood kraft pulps. The content of extractives on the fiber surface was determined with the ESCA method.

Softwood kraft pulp	Total extractive content (%)[a]	Surface coverage of extractives (%)	
		$C1_{extractives}$[b]	$\phi_{extractives}$[c]
Unbleached			
Pulp A_{Un}	0.10	2 ± 0	~ 0
Pulp B_{Un}	0.06	~ 0	~ 0
Pulp C_{Un}	0.20	2 ± 0	4 ± 1
O_2-Delignified			
Pulp A_{O_2}	0.05	~ 0	~ 0
Pulp B_{O_2}	0.05	~ 0	~ 0
Pulp C_{O_2}	0.15	2 ± 0	3 ± 2

[a]The total extractive content obtained with acetone extraction.
[b]$C1_{extractives} = 100(C1_{(before\ extraction)} - C1_{(after\ extraction)})$.
[c]$\phi_{extractives} = 100[(O/C_{(before\ extraction)} - O/C_{(after\ extraction)})/(O/C_{(extractives)} - O/C_{(after\ extraction)})]$, where $O/C_{(extractives)} = 0.12$.

Acetone, which was used as extraction solvent in our study, is known to be very effective, but can, in addition to lipophilic extractives, also dissolve some fragments of carbohydrates. However, Laine et al.[12] have shown that the content of carbohydrates was only about 2% of the total amount of dissolved material during extraction with acetone and, thus, consequently, should not have any significant effect on the estimation of the surface content of extractives. The low values obtained in our study might be due to the fact that the pulp fibers were subjected to thorough washing before extraction. Another explanation for the differences can be that, in our study, the paper sheets prepared for ESCA analysis were dried at room temperature and those used in the study carried out by Laine et al.[11,12] were dried at 70°C for two hours. Migration of extractable material is known to be favored by an increase in temperature and, subsequently, leads to a higher amount of extractives on fiber surfaces.[23]

Fiber Charge

The majority of charged groups in kraft pulp fibers are carboxyl groups, which are mainly present in the 4-*O*-methyl-glucuronic acid units of xylan. However, carboxyl groups are also present in pectic components and, to some extent in the lignin fraction.

Table 4 shows the total and surface charges of the unbleached and oxygen delignified kraft pulps. A comparison with Table 1 reveals that the total charge of the unbleached samples decreases with the kappa number of the pulps. This can be explained by the fact that cooking to a lower kappa number results in a higher dissolution of lignin and xylan,

Table 4. Total charge and surface charge of various unbleached and oxygen delignified softwood kraft pulps.

Softwood kraft pulp	Total charge (μeq/g)	Surface charge (μeq/g)
Unbleached		
Pulp A_{Un}	121 ± 5	37 ± 0
Pulp B_{Un}	104 ± 3	36 ± 2
Pulp C_{Un}	83 ± 3	34 ± 1
O_2-Delignified		
Pulp A_{O_2}	128 ± 4	38 ± 2
Pulp B_{O_2}	110 ± 2	37 ± 1
Pulp C_{O_2}	99 ± 3	35 ± 1

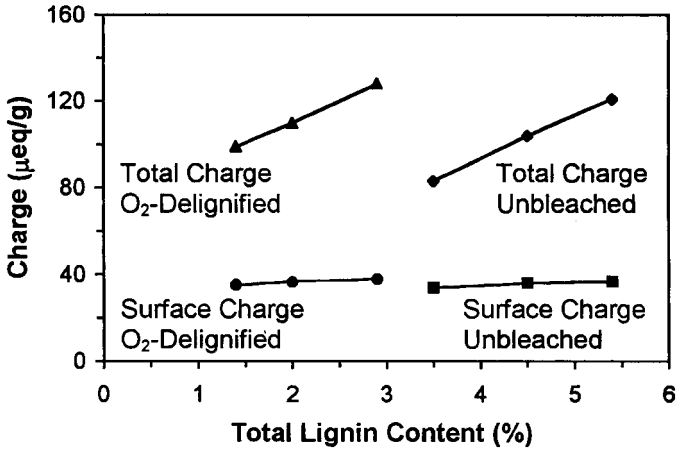

Figure 2. The total charge and surface charge of unbleached and oxygen delignified softwood kraft pulp fibers vs. the total lignin content.

which are known to contain charged groups. When the unbleached pulps are subjected to oxygen delignification, the total charge of the pulps increases somewhat, and this is probably due to oxidation of lignin and/or carbohydrates. The surface charge is between 30–40% of the total charge for both the unbleached and oxygen delignified pulps. This is quite high compared with other investigations.[11,12] However, the ratio of the surface charge to the total charge can vary depending on the raw material, and the cooking and bleaching conditions. As for the total charge, the surface charge of unbleached and oxygen delignified pulps also decreased with a decrease in the kappa number, but this decrease is within experimental errors. Figure 2 shows the total charge and surface vs. the total lignin content for the unbleached and oxygen delignified pulp samples.

Fiber Surface Structure

The appearance of unbleached and oxygen delignified softwood kraft fibers was studied using Scanning Electron Microscopy (SEM). These microscopical investigations revealed that fibers with a different kappa number resulted in fiber surface structures with quite a different appearance.

Figure 3 shows the appearance of unbleached and oxygen delignified kraft fiber samples. It can be seen that unbleached kraft pulp fibers have a

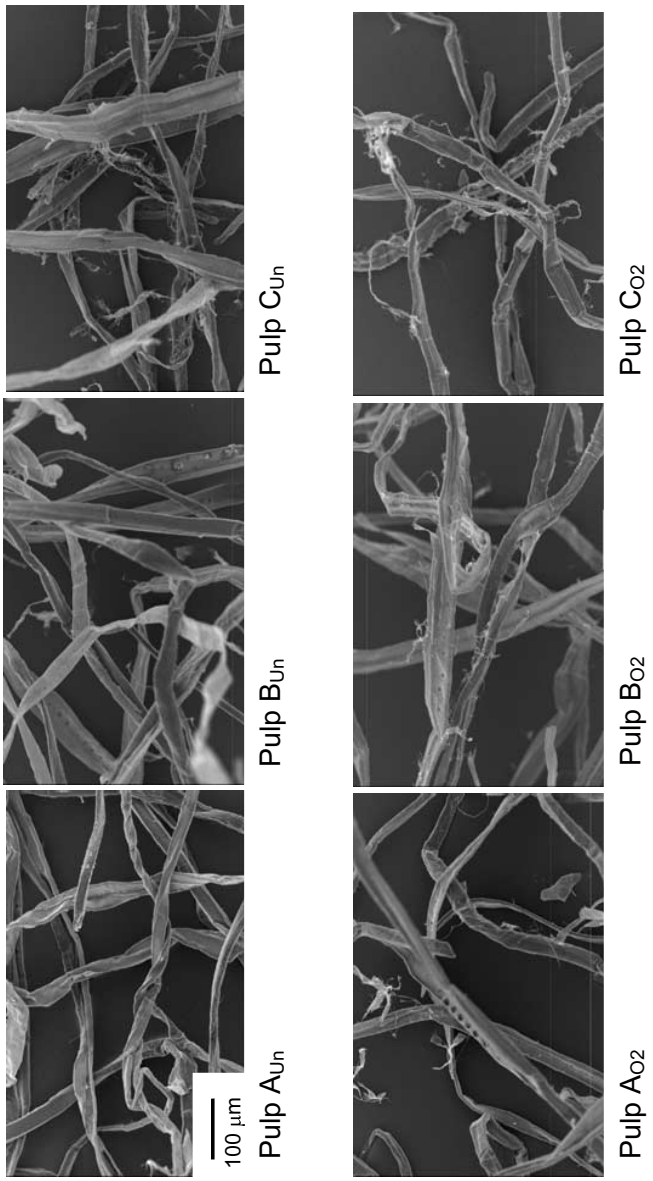

Figure 3. Fibers from unbleached and oxygen delignified kraft pulps.

typical rectangular shape and that the middle lamella remains intact, especially in cell corners. It can also be seen that there are only few fragments of thin layers of surface material loosely attached to the unbleached fibers. However, it can be noted that the extent of fibrillation increases with a decrease in kappa number. This is probably due to the fact that a higher dissolution of lignin will lead to a more porous fiber wall, and this will lead to fiber surfaces being more easily fibrillated by the process equipment used.

The appearance of the oxygen delignified kraft pulp fibers is also illustrated in Figure 3. It can be seen that the fibers have a rectangular shape even after a double oxygen delignification treatment. However, the surface of the oxygen delignified pulp fibers is more fibrillated in comparison with unbleached fibers. As for the unbleached pulp fibers, the extent of fibrillation is highest for the oxygen delignified pulp fibers with the lowest kappa number.

CONCLUSIONS

The results from the different ESCA and SEM techniques presented in this article clearly shows that the surface of unbleached and oxygen delignified softwood kraft pulp fibers are highly enriched in lignin, and in some cases also enriched in extractives. However, the amount of lignin obtained on the fiber surfaces differs substantially from one technique to another. The mercurization technique (mercurization followed by the determination of mercury by ESCA) gave about three to five times lower values on the surface coverage of lignin in comparison with the normal ESCA procedure. Good correlation between the surface coverage of lignin and the total amount of lignin was obtained for all techniques, however, the best correlation was obtained with the mercurization technique. Furthermore, the total and surface charges of unbleached and oxygen delignified pulp fibers decreased with a decrease in kappa number and the extent of fibrillation increased with a decrease in kappa number.

ACKNOWLEDGMENTS

Financial support from the Swedish research foundation, Adlerbertska Forskningsfonden, is gratefully acknowledged. The authors wish to thank Brita Ohlsson, Department of Forest Products and Chemical Engineering, Chalmers University of Technology, and Kaija Matikainen, Department of Chemical Engineering Design, Chalmers University of Technology, for their skilful technical assistance.

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