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Effect of High-Temperature Defibration on the Chemical Structure of Hardwood

By P. Widsten[1], J.E. Laine[1], P. Qvintus-Leino[2] and S. Tuominen[3]

[1] Laboratory of Paper Technology, Department of Forest Products Technology, Helsinki University of Technology, Espoo, Finland
[2] VTT Chemical Technology, Process Technology, Espoo, Finland
[3] Orion Pharma, Espoo, Finland

Keywords

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Summary

The present paper aims at elucidating the effect of high-temperature defibration at different temperatures on the bulk and surface chemical properties of defibrated birch, aspen and eucalypt. The results indicate that defibration of these hardwoods results in partial depolymerization of fiber lignin *via* (homolytic) cleavage of interunit alkyl-aryl (β-O-4) ether bonds. This increases the phenolic hydroxyl content and produces relatively stable (phenoxy) radicals. Syringyl-type lignin is more extensively depolymerized than guaiacyl-type lignin. Defibration generates water-extractable material, which is enriched in hemicellulose-derived carbohydrates and has a substantial content of aromatic compounds rich in phenolic hydroxyl groups. The amount of water-extract and the extent of lignin interunit ether bond cleavage increase with an increase in defibration temperature. The differences between various hardwood species in this respect are small. The surface chemical composition of the fibers differs considerably from their bulk composition, but is not significantly influenced by variations in defibration temperature. Lipophilic extractives cover a large portion of the fiber surface, while the lignin content of lipophilic extractives-free fiber surfaces is 2–3 times as high as the bulk lignin content of the fibers.

Introduction

Wood is a composite material whose main constituents are cellulose, hemicellulose and lignin. These are unevenly distributed between the different morphological regions of wood (Fergus and Goring 1970a). Also the syringyl/guaiacyl (S/G) ratio of lignin units in hardwood varies between different layers of the wood cells (Fergus and Goring 1970b). In the secondary walls of white birch (*Betula papyrifera*) xylem, the lignin concentration is low and the lignin is mainly of S-type in fiber and ray cells and of G-type in vessel cells. However, in the primary wall and middle lamella of birch xylem, the lignin concentration is high and a mixed S/G-type lignin is found in fiber cells and a G-type lignin in vessel cells. Under mechanical defibration conditions, the surface chemical composition of the separated fibers therefore depends more on the morphology of the fracture zone than on the bulk chemical composition of wood. The fracture zone is largely determined by the temperature of defibration (Koran 1968; Zavarin 1984). Due to a redistribution of wood extractives after surface formation (Zavarin 1984), the fiber surfaces are typically enriched in lipophilic extractives, whose removal by organic solvent extraction leaves a pure lignocellulosic surface. Solvent-extracted commercial mechanical (Dorris and Gray 1978), CTMP (Börås and Gatenholm 1999) and TMP (Dorris and Gray 1978; Mjöberg 1981) softwood pulps for paper have similar bulk and surface compositions. This is because the fracture zone under the conditions of their production is mainly the largest region of the wood cell, the secondary wall. However, in high-temperature TMP pulping (Dorris and Gray 1978) or mechanical pulping according to the Asplund process (Mjöberg 1981), the fracture zone is shifted to the lignin-rich middle lamella. As a result of the thermal treatment to which wood chips are subjected in the preheater before the defibration, the middle lamella lignin is liquefied as the temperature reaches its glass transition point. As the defibration is performed while the lignin is still soft, fibers are separated along the middle lamella, and on cooling the lignin solidifies forming a crust on the wood fibers (Mjöberg 1981; Kharazipour *et al*. 1997). The surface lignin content of even unextracted fibers from high-temperature defibration is thus considerably higher than their bulk lignin content.

In addition to the surface chemical composition, also the inner fiber domains undergo changes during high-temperature defibration. Hydrolytic cleavage of ether bonds in hemicelluloses and lignin is known to occur during high-pressure refining (Suchsland and Woodson 1991; Sun *et al*. 1999). As a result, water-extractable material is formed, a part of which is released in the process water. The hydrolysis is catalyzed by acetic and formic acids formed from wood carbohydrates. Moreover, mechanical stress causes structural modifications of the wood constituents due to homolytic cleavage of covalent bonds, resulting in their depolymerization and the formation of mechanoradicals (Hon 1983; Lee and Sumimoto 1990). Homolytic cleavage of the β-O-4 ether bonds in fiber lignin generates phenoxy radicals,

which may be stabilized in the lignin matrix, undergo free radical coupling reactions, form stable quinonoid structures, or abstract a hydrogen whereby the frequency of phenolic hydroxyl (PhOH) groups is increased. Such changes in the molecular size distribution and content of functional groups of the fiber constituents affect the chemical and physical properties of the fibers.

The aim of this paper is to gain insight into the effect of temperature variation in high-temperature defibration (171–196 °C) on the chemical properties of hardwood fibers. It is also of interest to find out whether different hardwood species are affected in the same way. Hardwood fibers produced at different refining temperatures are characterized with regard to their bulk and surface chemical composition, and the amount and type of water-extractable material formed. Particular emphasis is placed on the determination of the extent and type of lignin modification at each temperature level.

Materials and Methods

Materials

The samples subjected to chemical analyses included both untreated (chips) and defibrated wood, and were obtained from entire freshly cut, debarked birch (mainly *Betula verrucosa*) or aspen (*Populus tremula*) logs of unknown age from Sundsvall, Sweden. In addition, eucalypt (*Eucalyptus* sp.) chips from trees of unknown age were obtained from elsewhere.

Defibration

The wood chips (moisture content 50 %) were defibrated at Sunds Defibrator, Sundsvall, Sweden using a pressurized Asplund defibrator consisting of a chip feeder, a preheater (pressurized) equipped with a temperature sensor, a double-disc refiner (pressurized) and a chamber (pressurized) from which the pulp is discharged to atmospheric pressure. The preheating time was 4 min and the production rate 65–80 kg/h. Approximately 50–100 kg of chips were processed for each fiber batch.

Preparation of fibers for analysis

Unless otherwise indicated, air-dry unfractionated or water-extracted fibers representative of an entire fiber batch or wood chips from the furnish were ground in a Wiley mill to pass a 20 mesh screen before analysis. The lyophilized water-extracts were analyzed as such.

Determination of lignin contents

The acid-insoluble lignin content of the fibers was determined gravimetrically after acid hydrolysis of the carbohydrates (Jayme *et al*. 1967) from fibers Soxhlet-extracted with CH_2Cl_2 for the removal of lipophilic extractives. The amount of acid-soluble lignin was estimated from the filtrate by UV-spectroscopy (Dence 1992) by using 3 % acid as the reference solution and measuring the absorbance at 205 nm. An absorptivity value of 110 l g^{-1} cm^{-1} for lignin (Dence 1992) was used in the calculations.

Determination of aromatic substances in fiber water-extracts

The aromatic substances of lyophilized fiber water-extracts were quantified by UV-spectroscopy from a small portion of water-extract in distilled water by using the absorbance at 280 nm (0.4–0.6) and distilled water as the reference solution. The absorptivity values used for birch (13.1 l g^{-1} cm^{-1}) and aspen (12.2 l g^{-1} cm^{-1}) samples were as reported for the corresponding dioxane lignins (Dence 1992). The value of 13.1 l g^{-1} cm^{-1} was also used for the eucalypt water-extract.

Carbohydrate analyses

The monosaccharide compositions were determined with a HPLC system according to Hausalo (1995) after acid hydrolysis of the carbohydrates to monosaccharides. The polysaccharide compositions were calculated from the monosaccharide compositions according to Janson (1974).

Water-extractions

The fibers were soaked in water at 2 % consistency for 1 h at room temperature. The fibers were not Wiley-milled before treatment. After soaking, the fibers were vacuum filtered using quantitative filter paper and washed with distilled water until the filtrate was colorless. The filtrate was lyophilized and weighed for the determination of water-extractives content while the insoluble fiber fraction was allowed to air-dry.

Organic solvent extractions

The dichloromethane and acetone extractions were carried out according to SCAN-C 7:62 and SCAN-CM 49:93, respectively.

Determination of PhOH contents

The periodate oxidation method based on the formation of methanol from methoxyl groups ortho to a PhOH group (Lai 1992) was used for PhOH group determination. PhOH groups of lignin p-coumaryl units or extractives such as tannins or flavonoids have no methoxyl groups and are therefore not included in the results. Methanol reached its maximum concentration and was quantified after 3 days reaction time. The GC equipment and conditions for the quantification of methanol were as follows: GC unit: HP 6890; detector: FID; column: Nordion NB-20M, 25 m × 0.20 mm i.d., film thickness 0,20 µm; injection volume and type: 1–1.5 µl, split injection (50:1); detector gases: H_2 (0.5 MPa) and air (0.7 MPa); carrier gas: He (1.5 MPa); oven temperature: 80 °C (isothermic), detector temperature: 240 °C; injector temperature: 250 °C. The internal standard was acetonitrile.

Surface characterization of fibers by ESCA

ESCA spectra were obtained using an AXIS 165 spectrometer (Kratos Analytical). Monochromatic A1 Kα radiation from an x-ray source was used to excite the electrons. The fiber surface area analyzed was about 1 mm^2 and the maximum sampling depth 10 nm. 2–4 locations per sample were analyzed and the results averaged. The spectra of C-1s and O-1s were recorded and the total O/C atomic ratio as well as the relative abundances of organic carbons with different degrees of oxidation were calculated for fiber samples before and after acetone-extraction. Gaussian line shapes were used for the deconvolution of the C-1s signal. The chemical shifts of the C-1s component peaks relative to C-1 (C-C) were as follows: C-2 (C-O): 1.7 ± 0.2 eV, C-3 (C = O or O-C-O): 3.1 ± 0.3 eV, C-4 (O-C = O): 4.4 ± 0.3 eV. For samples A1 and A2

Table 1. Description of fiber samples

Fiber	Species	Treatment
A1	Aspen	Defibration at 171 °C
A2	Aspen	Defibration at 188 °C
B1	Birch	Untreated
B2	Birch	Defibration at 171 °C
B3	Birch	Defibration at 188 °C
B4	Birch	Defibration at 196 °C
E1	Eucalypt	Untreated
E2	Eucalypt	Defibration at 171 °C

(Table 1) the spectra of N-1s, Si-2p and S-2p were recorded as well. The surface extractive coverage of the fibers as well as the lignin coverage of acetone-extracted fibers were calculated according to Ström and Carlsson (1992) using the following theoretical O/C atomic ratios: lignin: 0.33, carbohydrates: 0.83, and lipophilic extractives: 0.10.

ESR measurements

ESR measurements were carried out on 100 mg of air-dry fiber samples Wiley-milled to pass a 20 mesh screen, which were uniformly packed in a quartz tube in a standard volume. The ESR spectra were measured at room temperature with a Varian E-line cw ESR spectrometer using a microwave frequency of ~9.5 GHz. A modulation frequency of 100 kHz and modulation amplitude of 0.5 gauss were applied in the measurements. The microwave power was 1 mW. Relative concentrations of radicals were determined by double integration of the baseline corrected first derivative spectra.

Solid-state ^{13}C CP/MAS NMR spectra

The solid-state ^{13}C NMR spectra were run at room temperature using cross polarization and magic angle spinning at 7 kHz on a Chemagnetics CMX Infinity 270 MHz spectrometer operating at 67.9 MHz for carbon. Each cross-polarization contact time was 2 ms and data acquisition time 24 ms. The pulse delay was 2 s. The rf power levels were 60 kHz. The number of transients was ≈20000 for water-extracts and ≈5000 for other samples. A line width of 40 Hz was used for the processing of the spectra. The peaks were referenced to TMS using hexamethylbenzene (methyl peak at 17.35 ppm) as a secondary reference. The samples were air-dry portions of ≈200 mg of Wiley-milled (20 mesh) fiber or ≈50 mg of fiber water-extract and had a moisture content of ≈5 %.

Variations in the frequency of β-O-4 etherified syringyl (S) units of the samples were estimated by monitoring intensity changes of the C-4 of S units across 151 ppm (Leary *et al.* 1986; Leary and Newman 1992). The degree of etherification was expressed as the proportion of etherified C-4 (155–151 ppm) of total C-4 signal strength (155–145 ppm) neglecting signals from guaiacyl (G) carbons. The peak assignments by Leary *et al*. (1986) were based on solution NMR data on beech lignin by Nimz (1974).

Results and Discussion

Bulk chemical composition of fibers and fiber water-extracts

A description of the samples is given in Table 1. The lignin contents of the defibrated samples (Table 2) are close to the values reported for the corresponding untreated samples (Sjöström 1993). This was to be expected since there is no significant loss of raw material during defibration.

The amount of water-extractives tends to increase with increasing defibration temperature (Table 2). This indicates that the extent of breakdown of hemicelluloses and lignin by acid hydrolysis and homolytic bond scission increases with increasing preheater temperature. The results also show an increase in the carbohydrate content of the water-extracts with increasing temperature (Table 3). The aromatic substances may include lignin fragments formed during defibration as well as oligomeric lignin-like compounds, lignans and other aromatic compounds originally present in wood and enriched in the water-extracts (Pranovich *et al.* 1995; Sun *et al.* 1999). Carbohydrate analysis of the water-extracts (Tables 4 and 5) shows that the carbohydrates mainly consist of hemicelluloses, particularly xylan, while the content of cellulose is very low. It is not known to what extent the carbohydrates actually occur as polysaccharides as they may also be present as mono- and oligosaccharides formed from depolymerization of polysaccharides. In high-temperature defibration the fracture zone is mainly the lignin-rich middle lamella, leaving a lignin-rich layer on fiber surfaces (Mjöberg 1981; Kharazipour *et al.* 1997). The proportion of water-extracts not accounted for by lignin or carbohydrate analyses is likely to be mainly made up

Table 2. Lignin and extractive contents of unfractionated fibers

Fiber	Lignin, %			Extractives, %	
	Acid insol.	Acid sol.	Tot.	H_2O	CH_2Cl_2
A1	17.2	4.0	21.3	8.0	3.5
A2	15.1	3.8	18.8	20.0	5.9
B1	16.7	5.1	21.8	–	3.2
B2	18.6	3.7	22.3	8.5	3.6
B3	17.9	3.3	21.2	19.8	5.3
B4	17.8	2.7	20.6	23.2	9.3
E2	17.9	4.5	22.4	5.9	1.1

Table 3. Chemical composition of fiber water-extracts

Fiber	Aromatic substances, %[1]	Carbohydrates, %
A1	27.2	43.2
A2	25.3	47.9
B2	17.5	56.8
B3	15.8	60.4
B4	18.2	68.2
E2	20.7	42.1

[1] Including true lignin, lignin-like oligomers, lignans, tannins etc. aromatic compounds.

Table 4. Polysaccharide composition of fiber water-extract carbohydrates

	A1	A2	B2	B3	B4	E2
Cellulose %	1.2	2.8	4.5	0.4	0.0	1.0
Xylan %	51.0	77.3	70.9	81.3	78.0	69.4
Glucomannan %	29.1	10.8	13.0	11.2	16.4	8.3
Arabinan %	13.9	6.4	6.5	3.6	2.5	10.1
Galactan %	4.8	2.7	5.1	3.5	3.1	11.2

Table 5. Monosaccharide composition of fiber water-extract carbohydrates

	A1	A2	B2	B3	B4	E2
Arabinose %	14.8	6.9	7.0	3.8	2.7	10.9
Galactose %	5.0	2.9	5.4	3.7	3.4	11.8
Glucose %	12.9	7.4	10.1	5.0	4.3	4.4
Xylose %	48.7	75.7	69.1	80.1	78.6	67.5
Mannose %	18.6	7.1	8.4	7.4	11.0	5.4
Rhamnose %	0.0	0.0	0.0	0.0	0.0	0.0

Table 6. Results of fiber surface analysis by ESCA. UE = unextracted fibers, AE = acetone-extracted fibers

Sample	O/C		Proportion of carbons at different oxidation levels, %								Lignin, %[1]	Lipophilic extractives, %
			C-1		C-2		C-3		C-4			
	UE	AE	UE	AE	UE	AE	UE	AE	UE	AE	AE	UE
A1	0.20	0.54	74	30	21	55	3	11	2	4	56	78
A2	0.39	0.52	47	30	43	59	7	9	2	2	60	32
B2	0.17	0.53	73	22	22	52	3	17	2	9	59	83
B3	0.13	0.55	79	21	18	59	2	16	1	4	53	93
B4	0.29	0.53	60	29	33	58	5	11	2	2	59	55
E2	0.46	0.60	39	22	47	59	10	16	4	4	43	28
Average	0.27	0.55									55	61

[1] May include other aromatic compounds present on fiber surfaces.

of degradation products of the principal wood constituents, lipophilic extractives such as fatty acid esters, and ash. Dichloromethane extraction (Table 2) removed considerably less material than water extraction, reflecting the polarity of the water-extracted material.

Surface chemical composition of the fibers

The surface composition of the unfractionated fibers was analyzed by ESCA (Table 6). The content of lipophilic surface extractives such as fatty acid esters and terpenoids with a very low oxygen-carbon (O/C) ratio and containing mainly unoxidixed (C-1) carbon is much higher than the bulk content of lipophilic extractives, represented by dichloromethane extractives. In addition to the original lipophilic extractives, the dichloromethane extractives may contain low-molecular weight material of carbohydrate and lignin origin rendered extractable by the defibration process. On the average, about 60 % of the fiber surface is covered by lipophilic extractives, although variations in this regard are very large between the samples. Redistribution of original lipophilic wood extractives by their migration to the surface, a phenomenon known to be associated with fiber surface formation (Zavarin 1984; Laine and Stenius 1994), and the paraffin wax added to the fibers during defibration account for the high surface coverage of lipophilic extractives. The surface extractive content of the fibers decreases with increasing defibration temperature with the exception of sample B3. There is also considerable variance between the different species.

The influence of acetone extraction on the ESCA C-1s signal is seen in the spectra of sample B4 selected as an example (Fig. 1). The removal of the C-1 rich lipophilic extractives reveals a pure lignocellulosic fiber surface composed mostly of oxygen and carbon of types C-2 (carbohydrates and lignin) and C-1 (lignin). The combined proportion of atoms of other elements analyzed (N, Si and S) on the surface of extracted or unextracted samples A1 and B4 was below 1 %. The theoretical O/C ratio is 0.83 for cellulose and hemicellulose (xylan) and 0.33 for lignin (Laine and Stenius 1994). The bulk O/C ratio calculated for an extractive-free fiber sample with lignin and carbohydrate

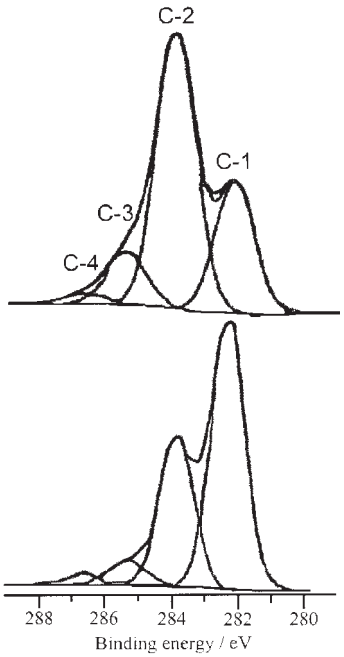

Fig. 1. Curve-fitted ESCA C-1s signals of unextracted (below) and acetone-extracted (top) sample B4. C-1 = carbon with no bond to oxygen (C-C), C-2 = carbon with one bond to oxygen (C-O), C-3 = carbon with two bonds to oxygen (C = O or O-C-O) and C-4 = carbon with three bonds to oxygen (O-C = O).

contents of 21 % and 79 %, respectively, is 0.73, while the O/C ratio for the fiber surfaces analyzed averages 0.55. This means that the surface lignin content of the acetone-extracted fibers is 2–3 times higher than their bulk lignin content (Table 2), which is consistent with the exposure of the carbohydrate-rich middle lamella during defibration. Since the aspen and birch samples have similar surface and bulk lignin contents, it seems that variations in defibration temperature in the range 171–196 °C do not affect the surface lignin content. Judging by the lower surface lignin content of sample E2 as compared to the other samples, the wood species used may have some effect on the amount of surface lignin. Since the bulk lignin content of sample E2 is similar to that of the other samples, it also seems that the amount of surface lignin does not depend on the bulk lignin content.

Table 7. Concentration of mechanoradicals in untreated and defibrated samples

Sample	Radical concentration (relative values)		g-value
	Unfractionated fiber	Extracted fiber	Unfractionated fiber
A1	57	28	2.0037
A2	44	56	2.0037
B1	33	–	2.0039
B2	69	12	2.0035
B3	69	37	2.0035
B4	61	99	2.0035
E1	17	–	2.0043
E2	100	25	2.0036

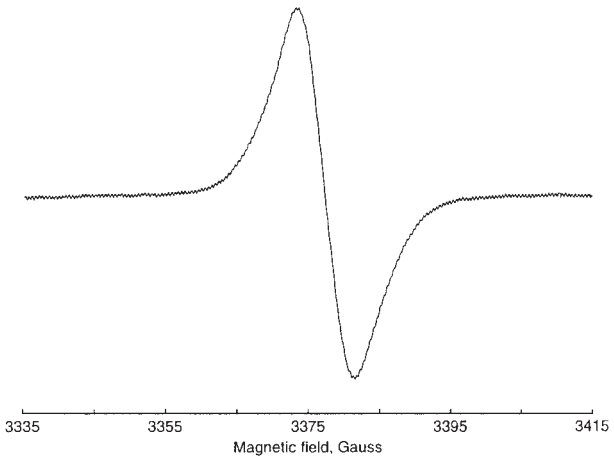

Fig. 2. Solid-state ESR spectrum of sample B4.

Effect of defibration on the chemical structure of fiber lignin

When lignocellulosic material is subjected to mechanical stress, covalent bonds in lignin and carbohydrates are ruptured. Homolytic cleavage results in the formation of mechanoradicals (Hon 1983). In the present study, radicals generated on wood fibers were quantified by means of ESR-spectroscopy (Table 7). A diffuse ESR signal (Fig. 2) indicating the presence of free radicals in defibrated wood is observed for all samples analyzed. Most of the mechanoradicals detectable at ambient conditions are lignin radicals, as their rate of formation and stability are much higher than those of cellulose radicals (Hon 1983). Mechanical energy has been found to produce transient aliphatic and phenoxy radicals in lignin model compounds via homolytic cleavage of the labile α- and β-O-4 ether bonds (Lee and Sumimoto 1990; Lee *et al.* 1990). While part of the lignin radicals are unstable, phenoxy radicals in particular may become entrapped in the lignin matrix (Hon 1983). Their stability is due to the restricted mobility of the lignin polymer and effective delocalization of the unpaired electron. The radicals detected in the fibers of the present study are thus probably mostly phenoxy radicals, as also suggested by their g-values (Hon 1983) given in Table 7.

The results also show that the defibrated samples contain more free radicals than the untreated samples B1 and E1. There is, however, no clear trend regarding the effect of defibration temperature on the radical content. A plausible explanation for this is that both the rate of formation and decay of radicals are likely to increase with increasing temperature. As the temperature increases, the fibers also become darker, indicating an increased frequency of chromophoric groups formed via radical intermediates such as quinonoid structures on fiber surfaces.

New PhOH groups can be formed by hydrogen abstraction of phenoxy radicals resulting from the homolytic cleavage of mainly β-O-4 ether bonds or by protonation of anionic PhOH groups from heterolytic ether bond cleavage (Domburg *et al*. 1977). The defibrated samples are considerably richer in PhOH groups than the untreated samples (Fig. 3). The unfractionated samples A1, B2 and E2, from different hardwoods refined at the same temperature, have similar PhOH contents. The same is true for the corresponding water-extracted samples. Moreover, for the unfractionated or water-extracted birch samples B2, B3 and B4, the frequency of PhOH groups increases with increasing defibration temperature. This is also the case for the aspen sam-

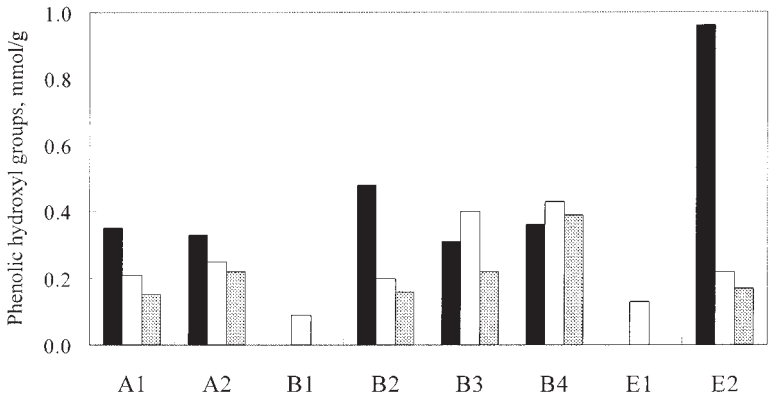

Fig. 3. PhOH content of the fiber water-extracts (black bars), unfractionated fibers (white bars) and water-extracted fibers (gray bars) of untreated and defibrated samples.

ples A1 and A2. These results show that the extent of ether bond cleavage increases with an increase in defibration temperature, which may contribute to the amount of water-extracts formed by generating low-molecular weight lignin fragments.

Representative solid-state ^{13}C CP/MAS NMR spectra of untreated and defibrated samples (unfractionated) and water-extracts from defibrated samples are shown in Figure 4. Selected spectral assignments are given in Table 8. Comparison of the spectra of samples B1 and B4 indicates that the region of oxygen-substituted aromatic carbons (141–160 ppm) is significantly affected by defibration. Another clear change caused by defibration and revealed by these spectra concerns the degree of carbohydrate crystallinity, as evidenced by the increase of the intensity ratio of the crystalline cellulose/hemicellulose peak at 89 ppm to the amorphous cellulose/hemicellulose peak at 84 ppm. Aside from these differences, the spectra are quite similar.

The spectra of the water-extracts differ considerably from those of the unfractionated fibers. An enrichment of hemicelluloses in the water-extracts is evident as the pronounced peaks at about 21, 102 and 173 ppm arise mainly from hemicelluloses, which according to wet chemical analyses (Tables 3 and 4) are the most important component of the water-extracts. The virtual absence of cellulose in the water-extracts, indicated by the wet chemical analyses, is also supported by the absence of signals unambiguously assignable to cellulose. As with the unfractionated fibers, the spectra of different water-extracts are similar except for the region of oxygen-substituted aromatic carbons.

The partial spectra of the defibrated (unfractionated) and untreated wood samples (Fig. 5) show changes in the lignin

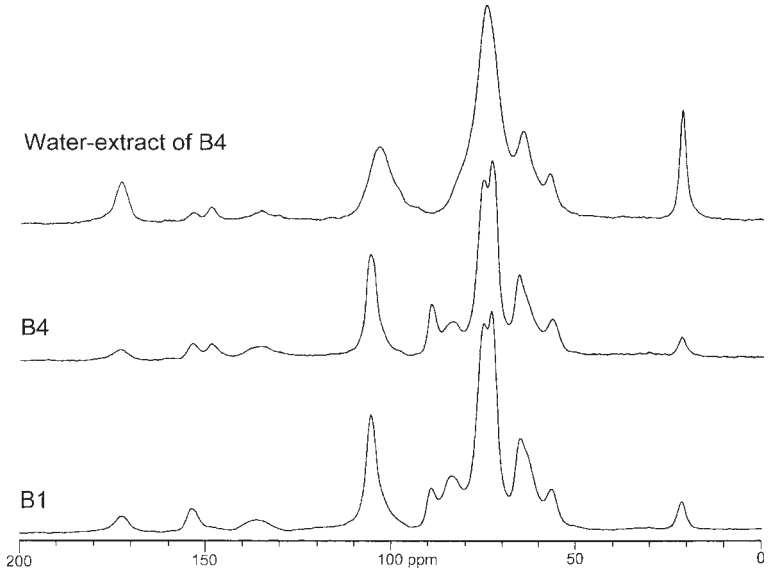

Fig. 4. CP/MAS NMR spectra of untreated sample B1, defibrated sample B4 and water-extract from sample B4.

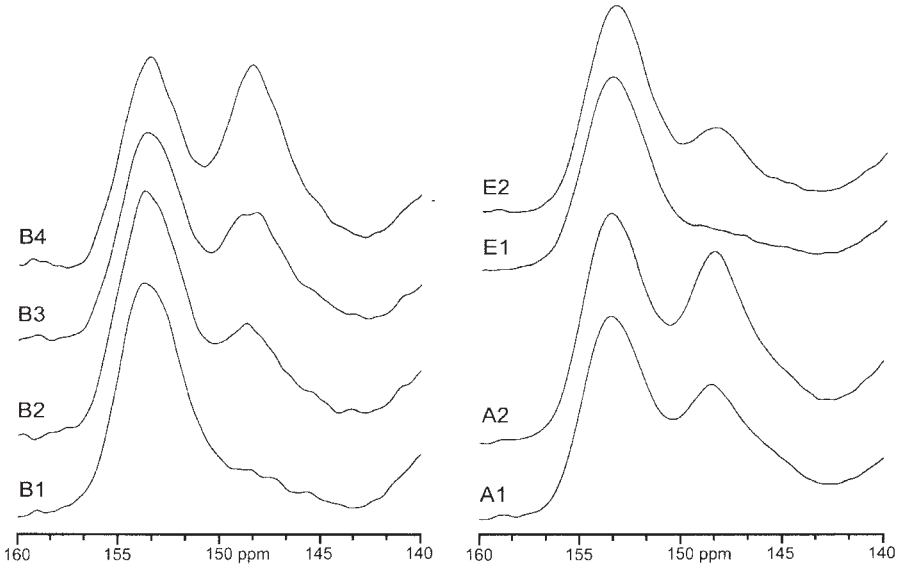

Fig. 5. Partial ^{13}C CP/MAS NMR spectra of defibrated and untreated samples showing that the ratio of β-O-4 etherified S units (153 ppm) to phenolic S units (148 ppm) decreases with an increase in defibration temperature. Birch, aspen and eucalypt behave similarly.

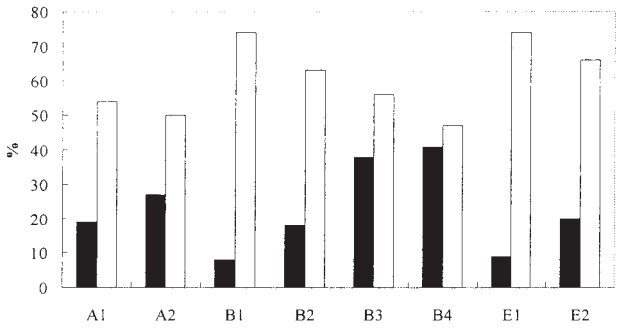

Fig. 6. Proportion of G and S units with a PhOH group (black bars), and degree of β-O-4 etherification of S units (white bars) of the fibers. The PhOH contents are calculated from the lignin contents (Table 2) for an average phenylpropane unit (MW = 200 g/mol).

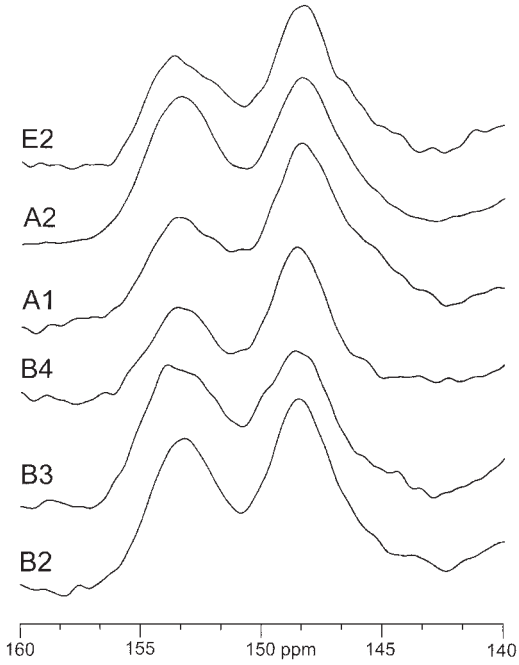

Fig. 7. Partial ^{13}C CP/MAS NMR spectra of fiber water-extracts. The spectra show that the ratio of β-O-4 etherified S units (signal at 153 ppm) to phenolic S units (signal at 148 ppm) is low in these samples.

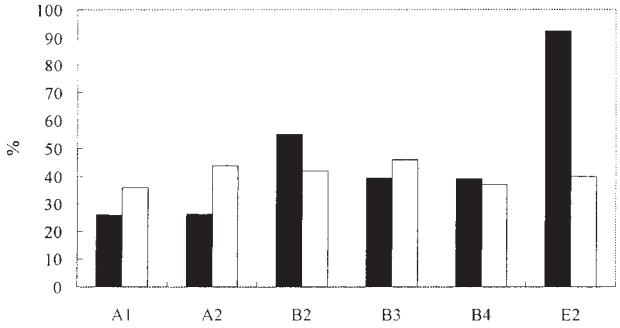

Fig. 8. Proportion of phenolic units of total aromatic units (black bars), and degree of β-O-4 etherification of S units (white bars) of the fiber water-extracts. The PhOH contents are calculated from the aromatic substance contents (Table 3) for an average phenylpropane unit (MW = 200 g/mol).

Table 8. Assignments of selected peaks of CP/MAS NMR spectra (Nimz 1974; Kolodziejski *et al.* 1982; Leary *et al.* 1986; Leary and Newman 1992)

Chemical shift, ppm	Main assignment
173	COOH(R) in hemicellulose acetate and carboxyl groups; carboxyl groups in lignin
160–141	Oxygen-substituted aromatic carbons in lignin, lignin-like compounds, lignans etc.
153	C-4 of β-O-4 etherified G units; C-3, C-4 and C-5 of etherified S units
148	C-3 of G units; C-3 and C-5 of phenolic S units
146	C-4 of phenolic G units; C-4 of etherified phenylcoumaran structures
105	C-1 of cellulose
102	C-1 of hemicellulose
89	C-4 of crystalline cellulose; C-4 of hemicellulose
84	C-4 of amorphous cellulose; C-4 of hemicellulose
56	Methoxyl groups in lignin and hemicellulose
21	CH_3 of hemicellulose acetate groups

polymer resulting from defibration which are in accord with their PhOH contents. Relative changes with defibration temperature in the degree of β-O-4 etherification of S units were estimated from these spectra (Leary *et al.* 1986; Leary and Newman 1992). As the signals from S and G units overlap partially, the results should be considered as semi-quantitative. Only weak signals from phenolic S and G units are seen at 151–146 ppm in the spectra of the untreated samples B1 and E1. However, a prominent peak centered at 148 ppm from C-3 and C-5 of phenolic S units appears in the spectra of the defibrated samples and grows gradually relative to the region 155–151 ppm containing peaks from etherified lignin units. The results are presented in Figure 6 together with the PhOH content of the samples per phenylpropane unit. It can be seen that the number of β-O-4 etherified S units declines as a result of defibration and with increasing defibration temperature, while a concurrent but opposite effect is observed on the PhOH content. This shows that the extent of β-O-4 ether bond cleavage of at least S units increases with an increase in defibration temperature. Shear deformation at very high pressure (6 GPa) has been found to have the same effect on birch (Gravitis *et al.* 1991; Teeäär *et al.* 1994). Judging by the spectra, the β-O-4 etherified G units are less affected by defibration than S units as no clear signal from C-4 of phenolic G units is seen at 145 ppm. The reason for this may be the higher thermolability of ether bonds of S units as compared to those of G units (Domburg *et al.* 1977). The agreement between increasing PhOH content and decreasing degree of etherification is expected, since the homolytic rupture of alkyl-aryl ether bonds produces phenoxy radicals, which may be converted into PhOH groups by hydrogen abstraction.

The partial spectra of fiber water-extracts (Fig. 7) show that the ratio of phenolic to β-O-4 etherified S units is high for these samples, as is also the proportion of G and S units bearing a PhOH group (Fig. 8). Unlike the unfractionated fibers, no trend regarding the effect of defibration tempera-

ture variations on the degree of etherification is seen for the water-extracts.

Conclusion

The results of the present study allow the following conclusions to be drawn:

- High-temperature defibration of hardwood depolymerizes fiber lignin, resulting in the formation of free (phenoxy) radicals and PhOH groups. S-type lignin is depolymerized to a greater extent than G-type lignin.
- High-temperature defibration of hardwood generates water-extractable material, which is enriched in hemicelluloses and contains aromatic substances with a low degree of β-O-4 etherification.
- The extent of lignin depolymerization and the amount of water-extract increase with increasing defibration temperature.
- The surface chemical composition of the fibers differs considerably from their bulk chemical composition. Lipophilic extractives cover a large portion of the surface of unextracted fibers. There is no clear relationship between their amount and defibration temperature. The main component of acetone-extracted fiber surfaces is lignin (may include other aromatic compounds), whose amount does not correlate with the defibration temperature or the bulk lignin content.
- Birch and aspen are similarly affected by variations in defibration temperature. The surface properties of defibrated eucalypt differ somewhat from those of birch and aspen, but the bulk properties of all the samples refined at the same temperature are similar.

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Petri Widsten
Jaakko E. Laine
Laboratory of Paper Technology
Department of Forest Products Technology
Helsinki University of Technology
P.O. Box 6300
02015 HUT
Finland

Pia Qvintus-Leino
Department of Process Technology
VTT Chemical Technology
P.O. Box 1401
02044 VTT
Finland

Simo Tuominen
Orion Pharma
P.O. Box 65
02101 Espoo
Finland