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EFFECT OF HIGH-TEMPERATURE FIBERIZATION ON THE CHEMICAL STRUCTURE OF SOFTWOOD

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ABSTRACT

Softwoods fiberized at high temperatures (above 170°C) were subjected to bulk and surface chemical analyses. It was found that the frequency of lignin β-O-4 linkages declined while that of phenolic hydroxyl groups increased with an increase in fiberization temperature. The amount of water extractable aromatic compounds increased with increasing temperature of fiberization, which was associated with cleavage of lignin ether linkages. The water extractable material generated was enriched in hemicelluloses and contained aromatic compounds rich in phenolic hydroxyl groups and

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low in β-O-4 linkages. The amount and hemicellulose content of the water extracts increased with increasing fiberization temperature. Lipophilic extractives covered most of the fiber surfaces while the surface lignin content of extractives-free fibers roughly doubled their bulk lignin content.

INTRODUCTION

Mechanical stress in wood fiberization causes depolymerization of the main components of wood as covalent bonds connecting lignin and carbohydrate molecules are ruptured.[1] Bond cleavage occurs partly homolytically producing mechanoradicals. The chemical and physical properties of fiberized wood depend on the extent of these depolymerization reactions and on the fate of the radicals. Most radicals are decayed rapidly but particularly phenoxy radicals, formed via homolytic cleavage of ether bonds between lignin phenylpropanoid units,[1–3] may be stabilized in the lignin matrix. The chemical structure of wood is also altered as mechanoradicals react by coupling reactions, are converted into phenolic hydroxyl groups or, in the presence of oxygen, generate chromophoric carbonyl and double bond structures. On commercial mechanical pulping of softwood, polar substances including low-molecular weight sugars, lignin fragments, lignin-like oligomers, and lignans are released in the process waters.[4–7] Some of these substances, e.g. lignans, are present as such in the wood raw material, while others are depolymerization products of lignin and carbohydrates.

The relative proportions of cellulose, hemicellulose and lignin differ from each other in the various layers of the wood cell.[8] On wood fiberization, the surface coverage of the fibers therefore reflects the chemical composition of the zone of wood failure rather than the bulk chemical composition of wood. This applies to the part of fiber surface not covered by wood extractives, which tend to migrate to the fiber surface. In commercial pulping processes involving fiberization at temperatures below the glass transition temperature of lignin, the main zone of wood failure is the largest part of the wood cell, the secondary wall.[9] Commercial extractives-free RMP,[10] groundwood,[10] CTMP[11] and TMP[9,10] softwood pulps, fiberized well below 150°C, have similar surface and bulk chemical compositions. However, in high-temperature TMP pulping[10] or mechanical pulping according to the Asplund process,[9] carried out at temperatures exceeding the glass transition temperature of lignin, wood failure mainly takes place in the highly lignified middle lamella. As a result, the lignin/carbohydrate ratio

of fiber surfaces formed on high-temperature fiberization is considerably higher than the bulk lignin/carbohydrate ratio of the fibers.[9,12]

At present, published data on the chemical structure of wood fiberized at temperatures above 170°C where thermal plasticization of lignin occurs is scarce, and is mostly related to the surface chemical composition of the fibers rather than to their bulk composition. There is a lack of systematic study on the type and extent of mechanochemical reactions taking place and the amount and type of water extractable material formed at high fiberization temperatures. Addressing this issue, this paper deals with the effect of high-temperature fiberization on the bulk and surface chemical structure of spruce and pine fibers, the main goal being the elucidation of the effect of temperature variation within the range 171–202°C. In addition, the water extractable material present in the fibers is quantified and characterized.

EXPERIMENTAL

Fiberization

Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*) chips of debarked wood were fiberized at 171–202°C at Sunds Defibrator, Sundsvall, Sweden.

Sample Preparation

The unextracted and water extracted fibers were ground in a Wiley mill (20 mesh screen) before most analyses. The water extracts were used as such.

Determination of Lignin Contents

The fibers were Soxhlet-extracted with dichloromethane according to SCAN-C 7:62 to remove lipophilic extractives. The acid-insoluble lignin content of the fibers was then determined gravimetrically after acid hydrolysis of the polysaccharides.[13] The amount of acid-soluble lignin was estimated from the filtrate by UV-spectroscopy by measuring the absorbance at 205 nm and using an absorptivity value of 110 L $g^{-1}cm^{-1}$ for lignin.[14] The reference solution was 3% sulfuric acid.

Determination of Aromatic Substances in Fiber Water Extracts

The aromatic substances in the fiber water extracts were quantified by UV-spectroscopy from a portion of water extract in distilled water (about 0.2 g/L) giving an absorbance reading of 0.3–0.6 at 280 nm. The absorbance at 280 nm can be attributed mainly to dissolved lignins, lignin-like substances and lignans, found also in spruce TMP waters.[5,6,15] The absorptivity value used in the calculations was 17.8 L g^{-1} cm^{-1}. This is based on values reported earlier for spruce[15] and pine dioxane lignin.[16] For lignin-like substances dissolved in spruce TMP water free of lignans, values ranging from 14 to 18 L g^{-1} cm^{-1} have been reported.[5] The reference solution was distilled water.

Because of an apparent contribution of other fiber components to the absorbance at 280 nm of sample S-202, the absorbance at 205 nm (after dilution to an absorbance of 0.6) was related to the aromatic substance content by using the ratio of the absorbances at 205 nm and 280 nm of the water extracts from samples S-188 and S-196, assuming that the ratio would be the same for the water extract from sample S-202, and calculating the 'correct' absorbance at 280 nm.

Carbohydrate Analyses

The carbohydrates were hydrolyzed with sulfuric acid to monosaccharides whose composition was determined by HPLC.[17] The polysaccharide compositions were then calculated from the monosaccharide compositions.[18]

Water Extractions

The fibers (not Wiley-milled) were water-soaked at 2% consistency for 1 h at room temperature. This was followed by vacuum filtration using quantitative filter paper and washing with distilled water until the washings became colorless. The filtrates were freeze-dried and quantified. The water extracted fibers were allowed to air-dry.

Determination of Phenolic Hydroxyl Contents

The phenolic hydroxyl groups were quantified using the periodate oxidation method, which is based on quantification of the methanol

formed from methoxyl groups ortho to a phenolic hydroxyl group.[19] Lignin p-coumaryl units or extractives such as tannins or flavonoids have no methoxyl groups and their phenolic hydroxyl groups (if any) 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 were as follows: GC unit: HP 6890; detector: FID; column: Nordion NB-20 M, 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. Acetonitrile was used as the internal standard.

Surface Characterization of Fibers by ESCA

ESCA spectra were obtained using an AXIS 165 spectrometer (Kratos Analytical). Monochromatic Al 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. Two to four locations per sample were analyzed and the results averaged. The spectra of C1s and O1s 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 according to SCAN-CM 49 : 93. Gaussian line shapes were used for the deconvolution of the C1s signal. The chemical shifts of the C1s component peaks relative to C1 (C-C) were as follows: C2 (C-O): 1.7 ± 0.2 eV, C3 (C=O or O-C-O): 3.1 ± 0.3 eV, C4 (O-C=O): 4.4 ± 0.3 eV. The lipophilic surface extractives of the fibers as well as the surface lignin on acetone extracted fibers were calculated using the following theoretical O/C atomic ratios: lignin: 0.33, carbohydrates: 0.83, and lipophilic extractives: 0.10.[20,21]

ESR Measurements

ESR measurements were carried out on air-dry samples (100 mg) uniformly packed in a quartz tube in a standard volume. The spectra were run at room temperature with a Varian E-line cw ESR spectrometer using a microwave frequency of ~9.5 GHz. The modulation frequency was 100 kHz and the modulation amplitude 0.5 gauss. 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 recorded 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. The cross-polarization contact time was 2 ms, data acquisition time 24 ms and the pulse delay 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 data processing. The peaks were referenced to TMS using hexamethylbenzene (methyl peak at 17.35 ppm) as a secondary reference. The samples were air-dry containing about 5% moisture. The sample amount was ≈200 mg for unextracted or water extracted fibers, and ≈ 50 mg for fiber water extracts.

The Spinsight 3.5.2 program was used for curve fitting in the region of the oxygen-substituted aromatic carbons (160–141 ppm) assigning Gaussian lineshapes for all peaks.[22,23] For deconvolution, two peaks of equal intensity at 152.6 ppm and 148.4 ppm were assigned for C-3 and C-4 of β-O-4 etherified guaiacyl units and two peaks of equal intensity at 148.4 ppm and 145.0 ppm for C-3 and C-4 of phenolic guaiacyl units. The line width was kept equal for all four peaks but varied between samples as in each case the line width that gave the best fit was used. The line widths for different samples were as follows: samples S-Wood – S-202: 298–312 Hz, samples P-Wood – P-188: 288 Hz, water extracts from all samples: 240–250 Hz.

RESULTS AND DISCUSSION

Bulk Composition of Unextracted Fibers and Fiber Water Extracts

The untreated and fiberized samples used in the present study are listed in Table 1 and their lignin and extractive contents in Table 2. The lignin contents of the fiberized samples are similar to those of untreated samples reported elsewhere for the wood species used.[24]

An increase in fiberization temperature causes the amount of water extractives to increase, particularly in going from 171 to 188°C (Table 2). The amount of water extractable aromatic compounds increased significantly only in going from 171 to 188°C while that of water extractable carbohydrates increased with each temperature increase (Table 3). This suggests that at the highest temperatures the carbohydrate-rich secondary wall may contribute more to the water extracts formed. The aromatic compounds may include true lignin as well as oligomeric lignin-like

Table 1. Description of Fiber Samples

Fiber	Species	Treatment
S-Wood	Spruce	Untreated
S-171	Spruce	Fiberization at 171°C
S-188	Spruce	Fiberization at 188°C
S-196	Spruce	Fiberization at 196°C
S-202	Spruce	Fiberization at 202°C
P-Wood	Pine	Untreated
P-171	Pine	Fiberization at 171°C
P-188	Pine	Fiberization at 188°C

Table 2. Lignin and Extractive Contents of Unextracted Fibers

	Lignin, %			Extractives, %	
Fiber	Acid insoluble	Acid soluble	Total	H_2O	CH_2Cl_2
S-Wood	27.0	0.7	27.7	nd	1.6
S-171	28.7	1.2	29.9	6.1	2.7
S-188	27.4	1.3	28.7	11.7	3.0
S-196	27.0	1.5	28.5	13.0	3.5
S-202	26.3	0.9	27.2	15.5	2.5
P-Wood	27.0	0.6	27.6	nd	2.5
P-171	24.5	0.8	25.3	6.3	3.6
P-188	26.2	0.9	27.1	14.3	2.9

compounds and other low-molecular weight aromatic compounds such as lignans and tannins. A water suspension of Norway spruce TMP has been reported[6] to contain a total of 0.6% (dry pulp basis) of low-molecular weight lignin, lignin oligomers, lignans and stilbene glucosides, a value somewhat lower than those found for the samples in the present study.

Using the UV absorbance at 280 nm, similar aromatic substance contents were found for all the water extracts except for that from the sample refined at the highest temperature (S-202), which had a considerably higher absorbance at 280 nm than the other water extracts. The water extracts from samples S-188 and S-196 had nearly equal absorbances both at 280 nm and 205 nm respectively, while that from sample S-202 had a slightly lower absorbance at 205 nm than them but a high absorbance at 280 nm. However, as the ^{13}C NMR spectra of the water extracts (not shown)

indicated that they had similar aromatic substance contents, the absorbance at 280 nm of the water extract from sample S-202 was probably increased by something not present in the other samples, e.g., α-carbonyl groups or carbohydrate degradation products, produced at the very high fiberization temperature of sample S-202. The aromatic substance content of sample S-202 was therefore estimated with the aid of the absorbance at 205 nm as explained in the experimental part.

The water extracts are very low in cellulose, their carbohydrates consisting almost completely of hemicelluloses (Tables 4 and 5). Glucomannan, whose content increases progressively with increasing fiberization temperature, is particularly abundant. The proportion of water extracts not accounted for by lignin or carbohydrate analyses is likely to be made up of mainly degradation products of the principal wood constituents, lipophilic extractives such as fatty acid esters and resin acids, and ash.

Table 3. Chemical Composition of Fiber Water Extracts

	Water extractable aromatic compounds, %[a]		Water extractable carbohydrates, %	
Fiber	of water extract	of unextracted fiber	of water extract	of unextracted fiber
S-171	13.2	0.8	65.9	4.0
S-188	11.7	1.4	66.1	7.7
S-196	11.7	1.5	74.6	9.7
S-202	9.8	1.5	71.7	11.1
P-171	12.0	0.8	66.7	4.2
P-188	10.2	1.5	78.4	11.2

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

Table 4. Polysaccharide Composition of Fiber Water Extract Carbohydrates

	S-171	S-188	S-196	S-202	P-171	P-188
Cellulose %	3.0	0.0	2.4	0.0	0.0	0.0
Xylan %	19.0	24.7	27.7	16.5	15.1	18.1
Glucomannan %	52.2	65.5	60.0	81.7	68.7	75.7
Arabinan %	15.1	5.9	4.8	1.8	15.2	6.2
Galactan %	10.7	3.9	5.1	0.0	1.0	0.0

Dichloromethane extraction (Table 2) removed considerably less material than water extraction, reflecting the polar nature of the water extractable material.

Surface Composition of Unextracted Fibers

The results of fiber surface analysis by ESCA (Table 6) show that the surface lignin content of the extractives-free fibers approximately doubles their bulk lignin content (Table 2). This agrees with the fact that at high fiberization temperatures, lignin is plasticized and the main zone of wood failure is therefore the lignin-rich middle lamella. In the case of spruce, the

Table 5. Monosaccharide Composition of Fiber Water Extract Carbohydrates

	S-171	S-188	S-196	S-202	P-171	P-188
Arabinose %	17.9	8.9	8.1	3.7	18.2	8.8
Galactose %	14.9	9.1	10.0	6.3	6.9	6.5
Glucose %	13.0	12.5	14.1	13.3	10.9	11.9
Xylose %	14.4	18.9	21.3	12.8	11.5	14.1
Mannose %	39.8	50.6	46.5	63.9	52.5	58.7
Rhamnose %	0.0	0.0	0.0	0.0	0.0	0.0

Table 6. Results of Fiber Surface Analysis by ESCA

			Proportions of carbons at different oxidation levels, %								Lignin,	Extractives,
	O/C		C1		C2		C3		C4		%	%
Sample	a	b	a	b	a	b	a	b	a	b	b	a
S-171	0.20	0.53	61	30	26	54	9	13	4	3	59.4	75.6
S-188	0.21	0.53	63	31	27	55	7	12	3	2	57.7	74.5
S-196	0.28	0.57	59	30	31	53	7	14	3	3	49.3	62.7
S-202	0.28	0.59	57	25	33	56	8	17	2	3	46.2	63.0
P-171	0.19	0.56	72	27	23	56	3	15	3	2	52.8	79.6
P-188	0.23	0.56	63	27	29	55	5	16	3	2	52.1	71.9
Average											52.9	71.2

a = unextracted fibers, b = acetone extracted fibers.

surface lignin content seems to somewhat decrease with an increase in fiberization temperature, suggesting that the carbohydrate-rich secondary cell wall of the fibers may become more exposed as the temperature is increased.

Lipophilic surface extractives such as fatty acid esters and resin acids, with a low O/C ratio and containing mainly unoxidized (C1) carbon, cover about 70% of the unextracted fiber surfaces. This is probably due to a migration of extractives from inner fiber domains to the surface. Also the paraffine wax added to the fibers in connection with fiberization to impart water resistance to the final product may add to the amount of surface extractives. The bulk lipophilic extractives, included in the dichloromethane extracts (Table 2), amount to only a few percent. Acetone extraction removed the lipophilic surface extractives, as evidenced by an increased O/C ratio. Figure 1 shows the ESCA C1s signal of fiber surfaces of sample S-196 before and after acetone extraction. The decrease in the proportion of C1 carbon, due to the removal of lipophilic substances, left a fiber surface composed mostly of oxygen, C1 carbon of lignin and C2 carbon of carbohydrates and lignin.

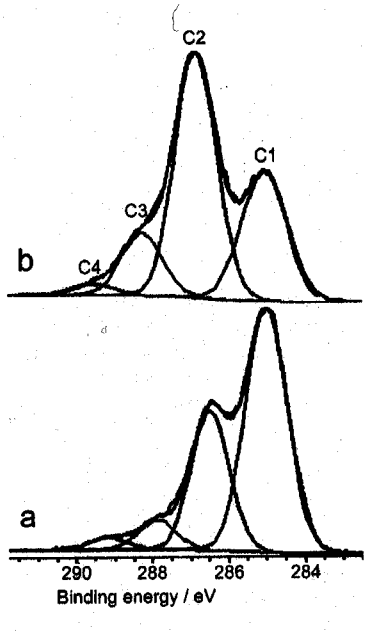

Figure 1. Curve-fitted ESCA C1s signals of a) unextracted and b) acetone extracted sample S-196. C1 = unoxidized carbon (C-C), C2 = carbon with one bond to oxygen (C-O), C3 = carbon with two bonds to oxygen (C=O or O-C-O) and C4 = Carbon with three bonds to oxygen (O-C=O).

Fiber Mechanoradicals

When lignocellulosic material is subjected to mechanical stress, carbon-carbon and carbon-oxygen bonds in lignin and carbohydrates are ruptured. Homolytic cleavage results in the formation of mechanoradicals.[1] In the present study, radicals generated on wood fibers were quantified by means of ESR-spectroscopy (Table 7). A diffuse ESR signal (Figure 2) indicating the presence of mechanoradicals in fiberized wood was observed

Table 7. Concentration of Mechanoradicals in Fibers

	Radical concentration (relative values)		g-value
Sample	Unextracted fiber	Water extracted fiber	Unextracted fiber
S-Wood	25	–	2.0042
S-171	10	16	2.0037
S-188	25	21	2.0035
S-196	34	34	2.0034
S-202	31	41	2.0033
P-Wood	35	–	2.0040
P-171	59	23	2.0038
P-188	44	21	2.0037

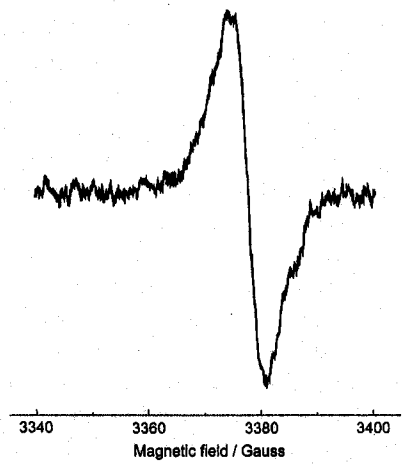

Figure 2. Solid-state ESR spectrum of sample S-196.

for all samples. Most of the mechanoradicals detectable at ambient conditions are probably lignin radicals, whose rate of formation and stability are much higher than those of cellulose radicals.[1] 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.[1–3] While part of the lignin radicals are unstable, many are entrapped in the lignin matrix. Their stability is due to the restricted mobility of the lignin polymer and, in the case of phenoxy radicals, to effective delocalization of the unpaired electron. The stable radicals are thus probably predominantly phenoxy radicals.

The results also show that except for samples S-171 and S-188, the fiberized samples contain more free radicals than the untreated samples. The g-values, which are typical for phenoxy radicals,[1] decrease slightly with increasing fiberization temperature, suggesting changes in the structure of the lignin polymer. Although the radical concentration of the water extracted fibers increases with an increase in fiberization temperature, no such trend is seen for the unextracted fibers. 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 such as free radicals and quinonoid structures (formed via radical intermediates) on fiber surfaces.

Phenolic Hydroxyl Content of Fibers and Fiber Fractions

New phenolic hydroxyl groups can be formed by hydrogen abstraction by phenoxy radicals resulting from the (homolytic) cleavage of mainly β-O-4 ether bonds or by protonation of anionic phenolic hydroxyl groups from heterolytic ether bond cleavage.[25,26] As a result, the fiberized samples (unextracted) are richer in phenolic hydroxyl groups than the wood raw materials (Table 8), although the relationship between fiberization temperature and phenolic hydroxyl content is not straightforward for the unextracted fibers. However, with increasing temperature, the phenolic hydroxyl content of the water extracts decreases while that of the water extracted fibers increases. The cleavage of the lignin ether bonds may also contribute to the amount of water extracts formed by generating water extractable low-molecular weight lignin fragments. It is seen that the water extracts contain more phenolic hydroxyl groups per C_9 unit than the unextracted fibers. This implies that original phenolic wood extractives rich in phenolic hydroxyl groups, e.g. lignans, or lignin fragments formed in the fiberization process are enriched in the water extracts.

Table 8. Phenolic Hydroxyl Content of Fibers and Fiber Fractions

Sample	Phenolic hydroxyl groups, mmol/g[a]			Phenolic hydroxyl groups/ 100 lignin C_9 units[b]	
	Unextracted fiber	Water extract	Water extracted fiber	Unextracted fiber	Water extract
S-Wood	0.14	–	–	10	–
S-171	0.20	0.25	0.17	12	34
S-188	0.27	0.17	0.23	18	27
S-196	0.27	0.16	0.25	18	25
S-202	0.31	0.14	0.37	21	26
P-Wood	0.12	–	–	8	–
P-171	0.26	0.25	0.22	19	39
P-188	0.28	0.17	0.25	19	30

[a]Only those phenolic hydroxyl groups with an ortho methoxyl group are included in the figures.
[b]Assuming MW of C_9 unit = 185 g/mol.

CP/MAS NMR Spectral Characterization of Fibers and Their Water Extracts

Representative solid-state ^{13}C CP/MAS NMR spectra of some of the fibers and their water extracts are shown in Figure 3 and selected spectral assignments in Table 9. Comparison of the spectra of the untreated and fiberized samples indicates that the region of oxygen-substituted aromatic carbons (141–160 ppm) is significantly affected by fiberization. Another clear change caused by fiberization 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 reasons of which are discussed below, the spectra of different spruce and pine unextracted fiber samples are very similar.

The spectra of the water extracts differ considerably from those of the unextracted 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 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 supported here by the absence of signals unequivocally assignable to cellulose.

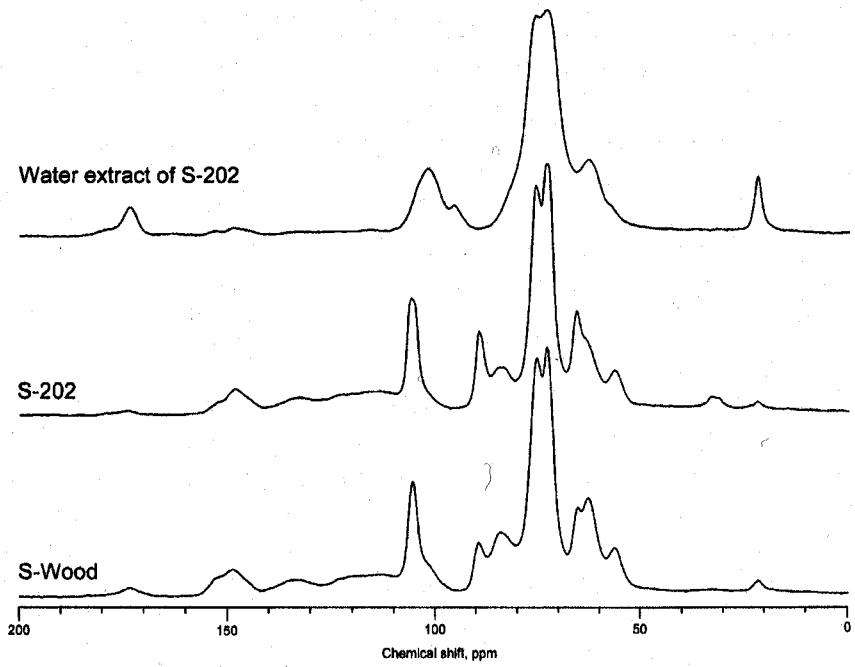

Figure 3. ^{13}C CP/MAS NMR spectra of untreated sample S-Wood, fiberized sample S-202 and the water extract of sample S-202.

Table 9. Assignments of Selected Peaks of CP/MAS NMR Spectra

Chemical shift, ppm	Main assignment
173	COOH(R) in hemicellulose acetate and uronic acid groups and lignin
160–141	Oxygen-substituted aromatic carbons in aromatic compounds
153	C-4 of β-O-4 etherified guaiacyl units
148	C-3 of guaiacyl units
145	C-4 of phenolic guaiacyl units; C-4 of etherified phenylcoumarans
105	C-1 of cellulose
102	C-1 of hemicelluloses
89	C-4 of crystalline cellulose; C-4 of hemicelluloses
84	C-4 of amorphous cellulose; C-4 of hemicelluloses
56	Methoxyl groups in lignin and hemicelluloses
21	CH_3 of hemicellulose (glucomannan) acetate groups

The lower intensity of signals from aromatic and methoxyl carbons relative to those from carbohydrates in the spectra of the water extracts than in the corresponding spectra of the unextracted fibers corroborates the wet chemical analyses in that the water extracts are low in aromatic substances. As with the unextracted fibers, the spectra of spruce and pine water extracts are similar except for the region of oxygen-substituted aromatic carbons.

The degree of β-O-4 etherification of the lignin component of the fibers (Table 10) was estimated from their CP/MAS NMR spectra (Figure 4) after curve-fitting by comparing the peak area corresponding to C-3 and C-4 of

Table 10. Frequency of β-O-4 Linkages/100 Lignin C_9 Units in Unextracted Fibers and Fiber Water Extracts as Estimated from the CP/MAS NMR Spectra

Sample	S-Wood	S-171	S-188	S-196	S-202	P-Wood	P-171	P-188
Unextracted fiber	64	59	53	48	46	61	58	48
Water extract	–	36	34	35	52	–	36	40

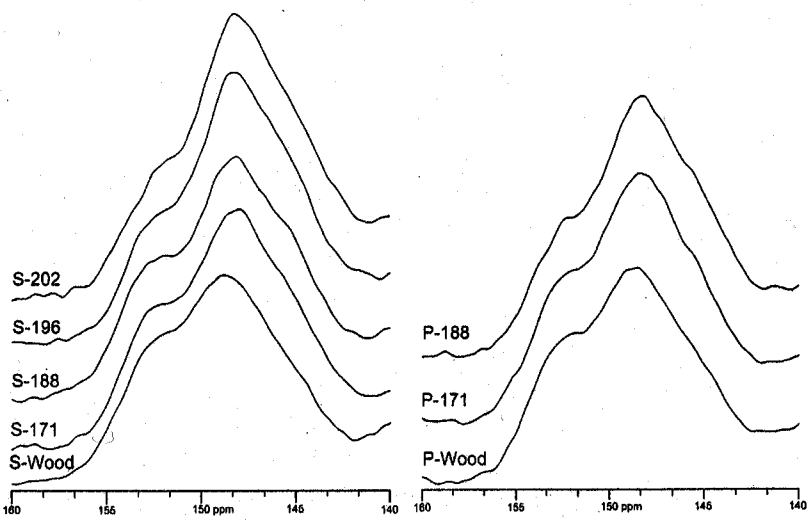

Figure 4. Partial ^{13}C CP/MAS NMR spectra of untreated and fiberized samples (unextracted fibers) showing that for both spruce (S-Wood – S-202) and pine (P-Wood – P188), the ratio of β-O-4 etherified guaiacyl units (153 and 148 ppm) to phenolic guaiacyl units (148 and 145 ppm) decreases with an increase in fiberization temperature.

β-O-4 etherified guaiacyl units at 153 and 148 ppm to the peak area of C-3 and C-4 of the corresponding non-etherified (phenolic) units at 148 and 146 ppm.[17] The latter area also includes signals from C-4 of etherified phenylcoumaran units, which may be present in minor numbers. The partial CP/MAS spectrum of sample S-Wood (Figure 5) provides an example of a curve-fitted spectrum. The spectra in Figure 4 show that untreated spruce and pine have a similar degree of β-O-4 etherification while the fiberized samples are less etherified as the frequency of β-O-4 linkages declines with an increase in fiberization temperature. The increase in phenolic hydroxyl content resulting from fiberization discussed above can therefore be attributed to a cleavage of interunit (mainly β-O-4) ether bonds. However, as the decline in the concentration of β-O-4 linkages seems to be greater than the corresponding increase in phenolic hydroxyl content, part of the phenoxy radicals formed via homolytic rupture of β-O-4 linkages probably decayed

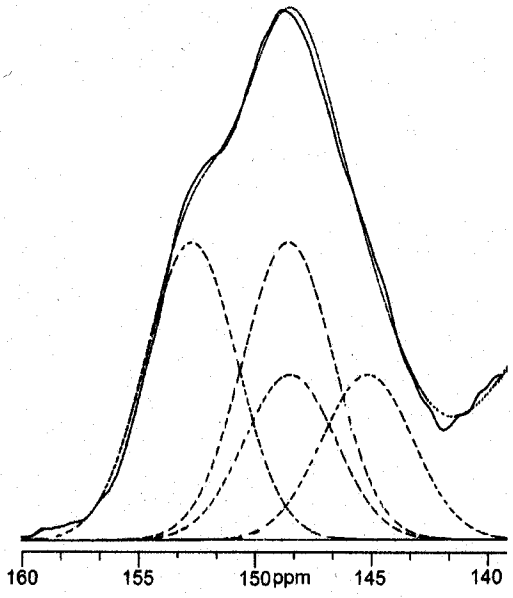

Figure 5. Curve-fitted ^{13}C CP/MAS NMR spectrum of the oxygen-substituted aromatic carbon region of sample S-Wood showing four simulated peaks (dashed lines) with Gaussian lineshapes and a line-width of 312 Hz. Two peaks of equal intensity at 152.6 and 148.4 ppm are due to C-3 and C-4 of β-O-4 etherified guaiacyl units and two peaks of equal intensity at 148.4 and 145.0 ppm to C-3 and C-4 of phenolic guaiacyl units. The solid and dotted lines show the observed and calculated spectra, respectively.

by being converted to e.g. coupling products or quinonoid structures. The increase in quinonoid and other chromophoric structures is also supported by a progressive darkening of the fibers with increasing fiberization temperature.

Figure 6 shows the CP/MAS spectra of the oxygen-substituted carbon region of fiber water extracts. Estimation of the degree of β-O-4 etherification of the aromatic substances in the water extracts in the same manner than for the unextracted fibers reveals that in comparison to the unextracted fibers, they possess a lower degree of β-O-4 etherification (Table 2) than the lignin of the unextracted fibers. This is coupled with a higher phenolic hydroxyl content (Table 8). As discussed above, lignin-related substances characterized by low molecular weight and high phenolic hydroxyl content, either originally present in the wood raw material or rendered extractable as a result of lignin depolymerization during fiberization, are obviously

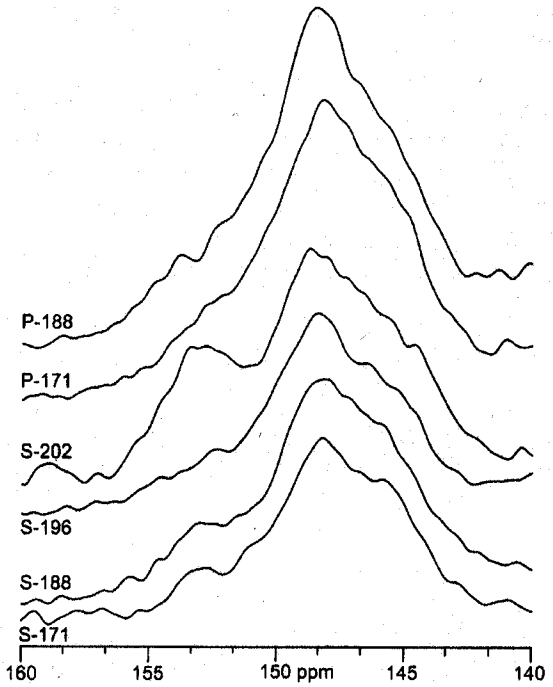

Figure 6. Partial ^{13}C CP/MAS NMR spectra of fiber water extracts containing peaks due to β-O-4 etherified guaiacyl units (153 and 148 ppm) and phenolic guaiacyl units (148 and 145 ppm).

enriched in the water extracts. The aromatic components of the water extracts resemble each other with regard to both phenolic hydroxyl content and degree of β-O-4 etherification. An exception to this is the somewhat higher proportion of β-O-4 linked C_9 units in the water extract from sample S-202, which presently defies explanation.

CONCLUSIONS

The results of the present study allow the following conclusions to be drawn about the effect of high-temperature fiberization on spruce and pine:

- Fiber lignin is depolymerized via cleavage of lignin β-O-4 ether linkages, resulting in the formation of free (phenoxy) radicals and phenolic hydroxyl groups.
- Water extractable material is generated which is enriched in hemicelluloses and contains aromatic substances of lower degree of etherification and richer in phenolic hydroxyl groups than the unextracted fibers.
- The extent of lignin depolymerization and the amount of water extract increase with an increase in fiberization temperature.
- The surface chemical composition of the fibers differs from that of the bulk fibers. Unextracted fibers are largely covered by lipophilic extractives while the lignin on fiber surfaces free of lipophilic extractives amounts to about 50%.
- Spruce and pine undergo rather similar changes.

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