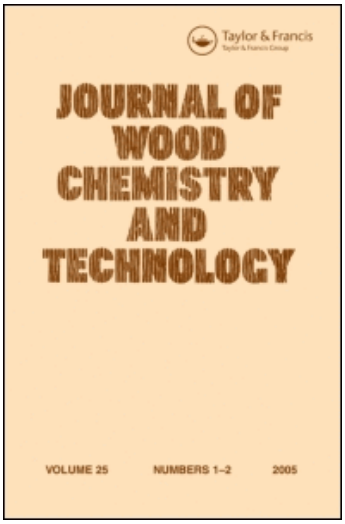

Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

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To cite this Article Francis, R. C. , Wilson, K. L. and Brown, A. F.(1994) 'Concentrations of Phenolic Hydroxyl Groups in Secondary Wall and Middle Lamella of Spruce (Picea abies)', Journal of Wood Chemistry and Technology, 14: 3, 351 — 367
To link to this Article: DOI: 10.1080/02773819408003102
URL: http://dx.doi.org/10.1080/02773819408003102

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 14(3), 351-367 (1994)

CONCENTRATIONS OF PHENOLIC HYDROXYL GROUPS IN SECONDARY WALL AND MIDDLE LAMELLA OF SPRUCE (Picea abies)

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ABSTRACT

A higher concentration of phenolic hydroxyl groups in the lignin of the secondary wall (SW) as compared to the middle lamella (ML) has long been used to explain the topochemical effect observed when spruce is pulped. However, a controversy exists as to whether or not there is a significant difference in phenolic hydroxyl concentration between the two regions. Fractions rich in SW and ML materials were obtained from thermomechanical pulps produced with high specific refining energies. Analysis by periodate oxidation showed that the SW lignin contained approximately 60% more phenolic hydroxyl groups than the ML lignin. However, p-hydroxyphenylpropane units, believed to be concentrated in the ML, were not detected. If a correction factor is applied, then the difference is 37% in favor of the SW lignin. Neutral sulfite treatment generated phenolic hydroxyls at a higher rate in the ML lignin but still sulfonated the SW lignin to a greater extent.

INTRODUCTION

Higher rates of delignification for the secondary wall of spruce wood as compared to the middle lamella have been reported for kraft pulping,[1,2] soda-anthraquinone pulping,[3] neutral sulfite pulping[1,4] acid

sulfite pulping[1-3] and organosolv pulping (alcohol/water) under both acidic[3] and alkaline[5] conditions. Although these topochemical effects have been observed independently by many researchers, there are some convincing results showing that for kraft pulping[6,7] and soda/oxygen pulping[8] of pine wood, the secondary wall (SW) is not more reactive than the middle lamella (ML). It is possible that the topochemical effect observed with spruce is not universal to all wood species.

One theory forwarded by Goring and co-workers to explain the higher reactivity of the secondary wall of black spruce (Picea mariana) was that its lignin contained approximately twice the concentration of phenolic hydroxyl groups as the middle lamella lignin[9-13]. This conclusion was based on phenolic determinations by UV microscopic techniques[9-12] and pyrolytic gas chromatography[13]. This conclusion was supported by Hardell et al.[14] who analyzed Norway spruce (Picea abies) by permanganate oxidation. However, using a UV technique on Picea abies fragments Boutelje and Eriksson[15] concluded that the SW lignin contained only 1.5 times the concentration of phenolic hydroxyl groups as the ML lignin. Sorvari et al.[16] using ionization difference spectra (UV) on thermomechanical pulp (TMP) fractions observed a concentration of phenolic hydroxyl groups in the SW lignin that was only 23% higher than the ML lignin. In a later study Sorvari et al.[17] isolated fractions rich in SW and ML materials and analyzed them for phenolic concentration by proton and ^{13}C NMR, UV, and permanganate oxidation. The highest difference for the SW lignin compared to the ML lignin was 12% obtained by permanganate oxidation.

One of the main reasons for the controversy is the lack of accurate and precise methods for in-situ

determination of phenolic hydroxyl concentrations. The UV methods are hampered by uncertainties about the accuracy of the extinction coefficient or absorptivity. The pyrolytic GC method of Whiting and Goring[13] was criticized by Obst[18] because all of the pyrolysis products were not identified or quantified. The 100% higher yield (on lignin basis) of veratric acid from permanganate oxidation of methylated SW material as compared to methylated ML material reported by Hardell et al.[14] was not reproduced by Sorvari et al.[17]. Actually, if the pyrolytic GC and permanganate oxidation results are not considered, then only the UV results of Goring and co-workers[9-12] show a 100% difference between the phenolic hydroxyl concentrations of the two morphological regions. However, the lignin contents of the ML materials selected by Goring and co-workers were always in the 80% range. This indicates that the cell corners (CC) were analyzed. On the other hand, Boutelje and Eriksson[15] and Sorvari et al.[16,17] selected ML samples with lignin contents of approximately 50%, indicating materials dominated by the compound middle lamella. Since lignin structure varies with morphological region, it is not unreasonable that the phenolic hydroxyl concentration in the cell corner is different from that in the compound middle lamella.

Due to the difficulties and uncertainties involved in separating or differentiating the cell corners from the compound middle lamella, the simplest comparison to be made when studying lignin heterogeneity is between the SW and the rest of the tracheid, i.e. compound middle lamella plus cell corners (ML + CC). However, for phenolic hydroxyl concentrations, there is still a question about the appropriate method to use. Lai et al.[19] surveyed the literature and concluded that the two

methods best suited for in-situ determination are those involving aminolysis and periodate oxidation. They also showed that the two methods gave comparable results for both spruce and aspen wood meals[19]. It was later shown that nearly equivalent results were also obtained for pulps (kraft, TMP, CTMP) from both softwoods and hardwoods[20]. The only drawback of the aminolysis method is that it is time-consuming and tedious[19,20]. For softwoods, the only drawback of the periodate oxidation method is the non-detection of p-hydroxyphenylpropane units[19,20]. However, the concentration of these units is low and can be estimated in the different morphological regions with reasonable accuracy.

The objective of this research was to separate cell wall fragments from Norway spruce into SW-enriched and ML + CC-enriched fractions and analyze them for phenolic hydroxyl concentrations by periodate oxidation.

EXPERIMENTAL

Pulp Samples

Norway spruce was debarked, chipped, and screened just prior to pulping to ensure the use of fresh chips. For the production of TMP, approximately 50 kg (o.d.) of chips were preheated for 3 min at 130°C or 145°C prior to pressurized refining in a Sprout-Bauer Model 418 double disk refiner. The dilution water was replaced by a dilute sodium sulfite solution for the production of in-refiner sulfonated pulps (RCTMP). The primary stage pulps were further refined in a Sprout Bauer Model 401 double disk atmospheric refiner.

CTMP was produced by reacting the chips with a 60 g/L solution of Na_2SO_3 in an M&K digester. A liquor-to-

wood ratio of 6:1 was used. The liquor temperature was increased to 130°C in 30 min and maintained at that temperature for another 15 min. Three stage refining was conducted in a 12-in KRK refiner (Kumagai Riki Kogyo Co. Ltd., Tokyo). The first stage was conducted at 130°C while atmospheric refining was used for the final two stages.

Extractive-free pulp

Pulps were soxhlet-extracted with ethanol-benzene.

Separation of fiber fragments

Fiber-rich material was separated from the fines by Tappi Method T261 cm with the aid of a Dynamic Drainage Jar containing a 200 mesh (76 μm) nickel screen.

Chelation

All pulps and fiber fractions were treated with a chelating agent (0.4% Na_5DTPA) in the presence of $NaHSO_3$ (4% SO_2) at 3% consistency and 90°C for 30 min prior to analyses.

Periodate Oxidation

In general, a sample (~400 mg) of chelated pulp or pulp meal (40 mesh) in a 20-mL glass centrifuge tube was treated with sodium periodate (800 mg) dissolved in 6 mL of distilled water to which 1 mL of distilled water containing 3 mg of acetonitrile was added as an internal standard. Both solutions were cooled to 4°C prior to addition to the sample. The suspension was homogenized and kept in the dark at 4°C in a refrigerator with occasional stirring.

The rate of methanol formation was followed gas chromatographically by periodically injecting a 1-2 μL aliquot of the reaction mixture. The mixture was homogenized and centrifuged to obtain a clear solution prior to sampling and was homogenized again after sampling. Additional information can be obtained in the literature[19,20].

Analytical Methods

Lignin contents (Klason plus acid-soluble lignin) were determined by Tappi Standard Methods. Sulfonate groups were determined by the conductometric method of Katz et al.[21]. A Varian 3700 gas chromatograph, equipped with a flame ionization detector and an electronic integrator, was used for methanol analysis.

In periodate oxidation experiments, methanol and the internal standard (acetonitrile) were determined with a 1.8 m x 0.32 cm stainless steel column packed with Tenax GC. The Tenax column (obtained from Alltech Associates, Inc., Deerfield, IL) was operated at 80°C with an injection port temperature of 150°C and a detector temperature of 250°C. A carrier gas (N_2) flow of 30 mL min^{-1} was used in the analyses.

RESULTS AND DISCUSSION

Disk or PFI refining with high specific energy has been shown to produce a fiber fraction enriched with SW material and a fines fraction enriched with ML + CC material[6,14,16]. In this research, disk refining in 2 or 3 stages was used. The lignin and phenolic hydroxyl group contents of the two fractions plus the unfractionated pulp are presented in Table 1 for a

TABLE 1

Concentrations of Lignin and Phenolic Hydroxyl Groups in TMP fractions

	Whole	Fiber-Rich	Fines
Percent of Total	100	75.1	24.9
Lignin Content, %	28.7	24.4	38.7
PhOH, mmoles/kg pulp	188	173	214
PhOH, mmole/g lignin	0.655	0.708	0.554

thermomechanical pulp whose primary stage was conducted at 145°C.

It is widely accepted that the lignin concentration of the secondary wall of spruce tracheids is approximately 23%[15,16,22,23]. Therefore, the fines fraction in Table 1 with a lignin content of 38.7% is obviously enriched with ML + CC material. It can be seen that the lignin in the fines fraction contained less phenolic hydroxyl groups compared to the lignin in the fiber-rich material. However, some mathematical manipulations of the data are required to obtain results in terms of concentrations in SW and ML + CC lignins.

While there is unanimity on the lignin concentration in the secondary wall of spruce fibers there appears to be some difference of opinion on the lignin concentration for the rest of the fiber wall (compound middle lamella plus cell corners). One of the most detailed quantifications of volume fractions and lignin contents for the various cell wall regions of spruce tracheids was conducted with the aid of UV-microscopy by Fergus et al.[22]. Some of the results from that study are tabulated

TABLE 2

Distribution of Lignin in Black Spruce (Picea mariana) Tracheid (Ref. 22)

Wood	Morphological region	Tissue volume (%)	Lignin (% of total)	Lignin concentration (%)
Earlywood	S	87	72	23
	ML	9	16	50
	CC	4	12	85
Latewood	S	94	82	22
	ML	4	10	60
	CC	2	9	100

in Table 2. For simplicity it is important to combine the results for the earlywood and latewood and also to divide the cell wall into only two regions, the secondary wall (SW) and compound middle lamella including the cell corners (ML + CC). A value of 42 weight percent has been reported for the summerwood content of mature Norway spruce[24]. This value will be assumed for black spruce. Fergus et al.[22] analyzed vacuum-dried cell wall material and the void fraction of such material is reported to be <5%[25]. Coupled with the fact that the densities of lignin (1.4 g/cm^3) and carbohydrate (1.5 g/cm^3) are approximately equal[26], it can be concluded that the densities of the various cell wall regions as well as earlywood and latewood are approximately equal.

The lignin concentration of ML + CC can be obtained from Table 2 by summing up the values of volume fraction

times lignin concentration and dividing by total volume fraction for ML and CC as shown below:

$$\text{Lignin Content (ML + CC)} = \frac{0.58\ \Sigma\ V_e C_e + 0.42\ \Sigma\ V_\ell C_\ell}{0.58\ \Sigma\ V_e + 0.42\ \Sigma\ V_\ell} \quad [1]$$

where e = earlywood and ℓ = latewood.

From Equation 1 a lignin concentration of 64.3% is obtained. Whiting et al.[26] used differential sedimentation to separate the different fractions of black spruce and four different methods of measuring lignin content. They obtained a lignin content of 60% for a mixture of ML and CC. Averaging this result with that of Fergus et al.[22], a lignin content of 62% is obtained for ML + CC.

More recent results have indicated a lower lignin concentration for the cell corner of Norway spruce tracheids. Using a lignin content of 49% for the compound middle lamella[15,17], 57% for the cell corner[23] and a 2:1 volume ratio (Table 2), a lignin content of 52% for ML + CC is derived.

With known lignin contents for SW and ML + CC, the proportion of these cell wall materials in the fiber-rich and fines fraction (Table 1) can be calculated. The equations will be written with lignin contents of 23 and 62% for SW and ML + CC respectively. A solution in parentheses will be given for an assumed lignin content of 52% for ML + CC.

$$(1 - a)\ (23) + a\ (62) = 24.4 \quad [2]$$
$$a = 0.04\ (0.05)$$

where a = ML + CC fraction in fiber-rich material.

$$(1 - b)\ 62 + b\ (23) = 38.7 \qquad [3]$$
$$b = 0.60\ (0.46)$$

where b = SW fraction in fines.

Now that the quantities of SW and ML + CC fragments present in the fiber-rich and fines fractions have been determined, the phenolic hydroxyl data in Table 1 can be calculated in terms of concentrations in the SW and ML + CC by the following simultaneous equations.

$$0.96\ X_1 + 0.04\ X_2 = 173 \qquad [4]$$
$$0.60\ X_1 + 0.40\ X_2 = 214 \qquad [5]$$

where X_1 = PhOH in SW and X_2 = PhOH in ML + CC.

The results from Equations 4 and 5 are summarized on a lignin basis in Table 3. The results for the extractive-free pulp and the 130°C TMP (Table 4) are in excellent agreement with the results in Table 3. It can be seen that the SW lignin does appear to contain a higher concentration of phenolic hydroxyl groups than the ML + CC lignin. However, the difference (average of 57% for 3 pulps) is likely exaggerated by the non-detection of p-hydroxyphenylpropane units which are present at a higher concentration in the ML + CC lignin. Based on the methoxyl content data of Sorvari et al.[17], 94.7 $OCH_3/100\ C_9$ for SW and 82.6 $OCH_3/100\ C_9$ for ML, approximately 8% and 20% p-coumaryl units can be estimated for SW and ML + CC lignin respectively. Earlier it was speculated that the ML sample used by Sorvari et al.[17] was dominated by compound middle lamella lignin. However, results from an autoradiographic study of mature Pinus thumbergii showed that the p-coumaryl concentration was approximately equal, at approximately 25%, in the ML and CC regions[27]. The data in Tables 3 and 4 can be corrected for the p-coumaryl fractions not detected by dividing the phenolic hydroxyl concentrations of SW and ML + CC by 0·92 and

TABLE 3

Concentrations of Phenolic Hydroxyl Groups in Different Morphological Regions

	SW	ML + CC	SW/(ML+CC)
X_1, mmoles/kg material	168 (168)*	-	-
X_2, " " "	-	282 (253)	-
PhOH, mmole/g lignin	0.732 (0.731)	0.455 (0.487)	1.61 (1.51)
PhOH, per 100 C_9**	13.9 (13.9)	8.6 (9.2)	" "

* Assumed lignin content of 62% for ML + CC, numbers in parentheses obtained by assuming 52% lignin content.
** Assumed a C_9 unit molecular weight of 190[17].

TABLE 4

Phenolic Hydroxyl Groups in the Secondary Wall and Middle Lamella of TMP and CTMP Fibers

Sample	Phenolic Hydroxyls, per 100 C_9		SW/(ML + CC)
	SW	ML + CC	
130°C			
TMP	13.2 (13.3)	8.2 (8.6)	1.61 (1.54)**
RCTMP (30 mmoles SO_2H)	13.6 (13.7)	9.8 (10.2)	1.39 (1.34)***
CTMP (117 mmoles SO_2H)	16.0 (16.1)	11.4 (11.9)	1.40 (1.35)***
145°C			
TMP	13.9 (13.9)	8.6 (9.2)	1.61 (1.51)**
Extractive-free TMP	13.3 (13.4)	8.2 (8.7)	1.62 (1.54)**
RCTMP (31 mmoles SO_2H)	14.7 (14.7)	10.9 (11.4)	1.35 (1.29)***

* per kg whole pulp
** Ratio decreases to ~1.37 if results are corrected for p-coumaryl fractions as described in text
***Ratio decreases to ~1.18 if corrected for p-coumaryl fractions

0·80 respectively. If this is done then the SW lignins in the TMP's contain only ~37% more phenolic hydroxyl groups than the ML + CC lignins. Although this difference is much smaller than that observed by Goring and co-workers[9-13], it is significant and along with a lower concentration of condensed structures[17,27,28] it might help to explain why the SW lignin of spruce appears to be more reactive.

Effect of Sulfonation on the Generation of Phenolic Hydroxyl Groups

The concentrations of phenolic hydroxyl groups in the SW and ML + CC fractions for TMP's and CTMP's are summarized in Table 4. Increasing the primary stage temperature from 130°C to 145°C increased the phenolic hydroxyl concentration of the TMP by only 0.6/100 C_9 units in the SW and 0.5/100 C_9 units in the ML + CC. This result may possibly be explained by the refining pH of approximately 4.5, which is probably not low enough for significant acidolysis of ether bonds.

The injection of sulfite at both 130°C and 145°C (RCTMP) resulted in a more significant increase in phenolic hydroxyl groups in the ML + CC lignin compared to the SW lignin. At 130°C, sulfonation increased the phenolic content of the SW lignin by 0.4/100 C_9 units while the increase was 1.5/100 C_9 units for the ML + CC lignin. At 145°C, the increases were 0.8 and 2.3/100 C_9, respectively. The higher rate of phenolic hydroxyl generation in ML + CC lignin confirms earlier results[12,29]. It can be seen that mild sulfonations (~ 30 mmoles/kg sulfonate groups in whole pulp) decreased the ratio of phenolic hydroxyl groups in SW to ML + CC from ~ 1.57 to ~ 1.34.

Berry and Bolker[30] concluded from a theoretical study that the ML lignin contained approximately twice as much α-aryl ethers compared to the SW lignin. Phenolic α-aryl ethers will cleave easily under neutral sulfite conditions[31]. Since the ML + CC lignin is highly condensed, some of the phenolic monomers are likely to be attached to the lignin macromolecule by both a C-C and an α-aryl ether bond. In such cases cleavage of the α-aryl ether would result in an increase in the phenolic hydroxyl concentration. Since benzyl aryl ethers are generally more labile than other ethers found in lignin, Sorvari et al. might have significantly cleaved these bonds during their lignin isolation procedures, thus increasing their phenolic hydroxyl concentration in the ML + CC. This possibility was cited by those authors in both of their publications[16,17].

Sulfonation Rates for the Two Morphological Regions

The lignin and sulfonate contents for the unfractionated, fiber-rich and fines fractions of the 145°C RCTMP are presented in Table 5. Utilizing calculations similar to Equations 4 and 5 resulted in sulfonate contents of 0.125 mmole/g lignin for the SW and ~0.091 mmole/g lignin for the ML + CC (Table 6). The results for the CTMP (117 mmoles/kg sulfonate groups in whole pulp) are also presented in Table 6. It can be seen that the SW lignin of the RCTMP contained ~37% more sulfonate groups than the ML + CC lignin while the SW lignin of the CTMP contained ~ 47% more sulfonate groups. These results are consistent with earlier ones[1-4] showing that the SW of spruce wood is more reactive towards nucleophiles. The higher concentration of phenolic hydroxyl groups is a likely contributor to the enhanced reactivity.

TABLE 5

Concentration of Lignin and Sulfonate Groups in CTMP Fractions

	Whole	Fiber-Rich	Fines
Percent of Total	100	75.2	24.8
Lignin Content, %	28.6	24.9	38.1
SO_3H, mmole/kg pulp	31	30	39
SO_3H, mmole/g lignin	0.108	0.120	0.102

TABLE 6

Sulfonate Groups in the Secondary Wall and Middle Lamella of CTMP Fibers

Sample	Sulfonate Groups, mmoles/g lignin		SW/(ML+CC)
	SW	ML+CC	
RCTMP (145°C)	0.125 (0.125)*	0.089 (0.093)	1.40 (1.34)
CTMP	0.438 (0.439)	0.290 (0.306)	1.51 (1.43)

* Values in parentheses obtained by assuming 52% lignin content for ML+CC.

SUMMARY

A controversy has existed as to whether or not the SW lignin of spruce contains a higher concentration of phenolic hydroxyl groups than the ML lignin. Inaccurate and imprecise methods of phenolic analysis coupled with changes in lignin structure during its isolation have contributed to the non-resolution of the controversy.

Fractions rich in SW and ML materials were obtained from thermomechanical pulps produced with high specific refining energies. Analysis by periodate oxidation

showed that the SW lignin contained approximately 60% more phenolic hydroxyl groups than the ML lignin. Application of a correction factor for the non-detection of p-hydroxyphenylpropane units decreases the advantage in favor of the SW lignin to approximately 37%. Neutral sulfite treatment generated phenolic hydroxyls at a higher rate in the ML lignin but still sulfonated the SW lignin to a greater extent.

ACKNOWLEDGEMENTS

The authors thank the staff of the Andritz Sprout-Bauer Pilot Plant and Research and Development Laboratory in Springfield, Ohio, for pulp manufacture. We are most grateful to the Empire State Paper Research Associates (ESPRA) for financial support.

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