2. The Raw Materials of CA

2.1 Wood as Natural Raw Materials for Cellulose Acetate Production

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Summary: The molecular arrangement of wood cell wall is described in relation to the physical and mechanical properties of wood. The chemical composition of wood is also summarized to illustrate the heterogeneity in distribution of cell wall constituents to use wood plup fibers judiciously as natural raw materials for cellulose acetate production.

Keywords: softwood; hardwood; earlywood; latewood; tracheid; fiber; ray cell; wood cell wall; topochemistry of wood; distribution of chemical constituent; chemical composition; cellulose; hemicellulose; lignin, inorganic constituent

2.1.1 Introduction

Wood is a renewable natural resource with adequate husbandry and long-range planning. The principal sources of commercial timber are trees of angiosperms (hardwoods) and gymnosperms (softwoods). A tree of either hardwoods or softwoods consists of the stem, banches and roots, the stem being a principal source for manufacturing lumber and other woody products. In its structure, wood is composed of natural polymers such as cellulose, hemicelluloses and lignin. These polymers are not uniformly distributed but associated each other within the wood cell wall and their concentration changes from one morphological region to another. In order to use wood pulp fibers judiciously as natural raw materials for cellulose acetate production, it is essential to study the topochemistry of these natural polymers in wood cell wall. This chapter, therefore, deals with the structure of wood and its chemical constituents of hardwood and softwood species.

2.1.2 General Features of Wood Cells

In woody plants, several different types of cell exist in both hardwoods and softwoods, as

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illustrated in Figure 1. However, the anatomy of softwoods is less complex than that of hardwoods. Figure 2 shows a scanning electron micrograph of the typical softwood cells. In hardwoods, the principal types of cell are vessel, tracheid, fiber and parenchyma cell, as shown in Table 1, whereas those in softwoods are tracheid and parenchyma cell (Table 2). Since hardwood fibers and softwood tracheids constitute the majority of wood cells, they contribute in a major way to the physical and chemical properties of wood. In particular, chemical properties of wood is important as wood is pulped and delignified to prepare dissolving pulp which is used for cellulose acetate production.

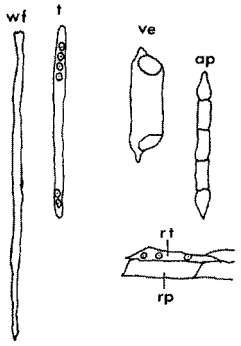

Figure 1. Schematic diagram of the major wood cells. wf, wood fiber; t, tracheid; ve, vessel element; ap, axial parenchyma cell; rt, ray tracheid; rp, ray parenchyma cell.

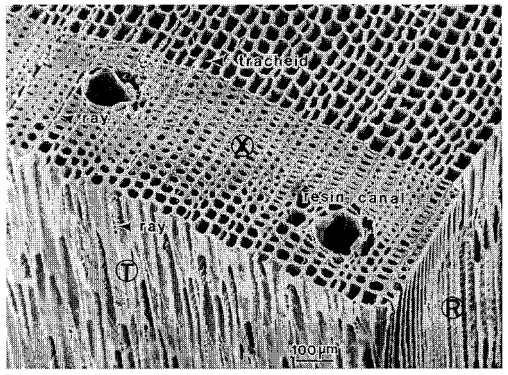

Figure 2. Scanning electron micrograph of a typical softwood (*Pinus densiflora*), showing the radial (R), tangential (T) and transverse (X) surfaces. The tracheids, rays and resin canals typical in softwood are present. (Courtesy of Prof. Emer. H. Saiki, Kyoto University, Kyoto, Japan).

Table 1. Cells in hardwoods.

Transverse	Longitudinal
Ray parenchyma cell	Vessel element
Ray epithelial cell	Tracheid
	Vascular tracheid
	Vasicentric tracheid
	Fiber
	Fiber tracheid
	Libriform fiber
	Axial parenchyma cell
	Epithelial cell

Table 2. Cells in Softwoods.

Transverse	Longitudinal
Ray tracheid	Tracheid
Ray parenchyma cell	Strand tracheid
Ray epithelial cell	Axial parenchyma cell
	Epithelial cell

2.1.3 Cell Wall Organization

In wood cell walls, cellulose acts as the structural framework in the form of cellulose microfibrils, while hemicellulose is the matrix substance present between these microfibrils. Lignin, on the other hand, is the encrusting substance binding the wood cells together and giving rigidity to the cell wall. Generally, the S_2 layer increases with increasing wall thickness, whereas the S_1 and S_2 layers remain fairly constant. Because of its greater thickness, the S_2 layer is largely responsible for not only the physical and mechanical properties but also the chemical properties of the cell walls.

The cell wall organization of typical hardwood fibers or softwood tracheids [1, 2] is described in Figure 3. Basically, the cell wall consists of the primary (P) and secondary (S) wall layers. The P wall layer is formed during the surface growth of the cell wall, while the S layer is formed during the thickening of the cell wall. This layer is composed of three sublayers termed S_1, S_2 and S_3 based on differences in microfibril orientation. In more detail (Figure 4), cellulose microfibrils are loosely aggregated in the P layer and oriented axially to the cell axis on the outer surface (P_0) and transversely on the inner surface (P_1). In the S layer inside the P wall, the S_1 layer is a flat

helix and crossed fibrillar structure with alternating S- and Z-helices of microfibrillar orientation, whereas the S_2 layer is the thickest within the S wall, comprising a steep Z-helix with a high degree of parallelism in the microfibrils. The S_3 layer is a thin lager with a flat S-helix that is loosely textured. [2, 3] In addition to these cell wall layers, a layer called middle lamella (ML) is located between adjacent cells. For a morphological region of the ML and the two P walls on either side, the term compound middle lamella (CML) is frequently used as shown in Figure 5, which encompasses the ML and the two adjacent P wall layers.

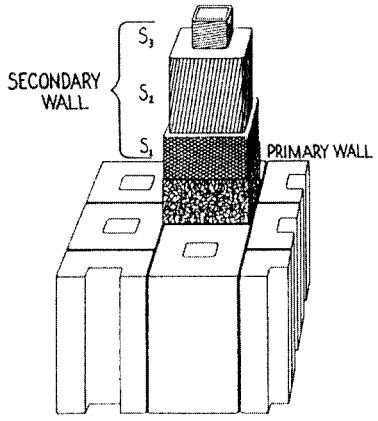

Figure 3. The gross structure of a typical hardwood fiber or softwood tracheid. (Courtesy of Prof. Emer, R. J. Thomas, North Carolina State University, Raleigh, NC).

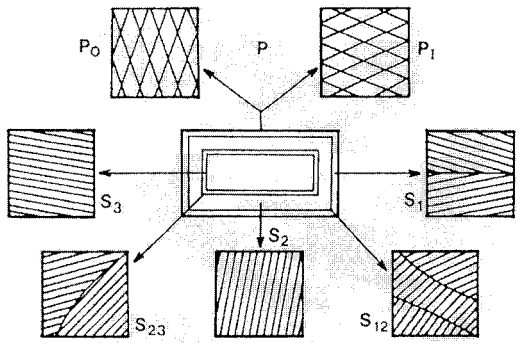

Figure 4. Schematic diagram of the microfibrillar orientation in the wood cell wall in hardwood fibers and softwood tracheids: P_0 and P_1 are the external and internal surfaces of the primary wall: S_{12} and S_{23} are the intermediate layers between S_1 and S_2, and between S_2 and S_3, respectively. [2]

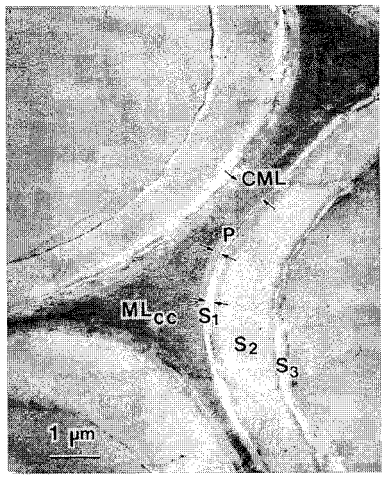

Figure 5. Transmission electron micrograph of the cross section of brominated normal wood tracheids in Douglas fir [*Pseudotsuga menziesii* (Mirb.) Franco]. Dark zones indicate the higher lignin concentration.

Figure 6 shows the relationship for softwood between the lignin content and microfibrillar angle (θ) in the tracheid S_2 layer determined by the X-ray diffractometry. Since the majority of the lignin in softwoods is in the tracheid S_2 layer,[4] the whole lignin content of wood must be closely correlated to the lignin concentration in the S_2 layer of the tracheid. Thus, it is suggested from Figure 6 that the lignin concentration in the S_2 layer increases with increasing microfibrillar angle of the tracheid S_2 layer.[5] It does suggest further that, in order to construct the enforced plywood type of structure shown in Figure 3, the three major chemical constituents of wood, cellulose, hemicellulose and lignin, mutually interact and strengthen each other to make up a natural supercomposite material.

Figure 7 shows such an ultrastructural arrangement of these major cell wall constituents Côté;[6] around the core of cellulose microfibrils, paracrystalline regions of cellulose are thought to exist, which are associated with hemicellulose and lignin. Lignin encases them and binds them into the rigid structure of the wood cell wall. At the molecular level of arrangement of the chemical constituents, the presence of a chemical bond between lignin and hemicellulose has been proved to be a lignin-carbohydrate complex (LCC).[7] The model in Figure 7 suggests the presence of such LCC molecules between hemicellulose and lignin in the wood cell wall.

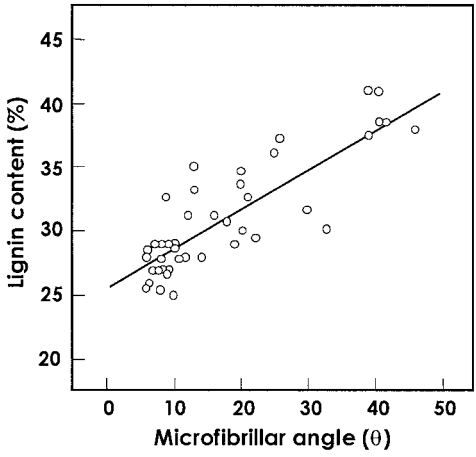

Figure 6. Relationship between the lignin content of wood and the microfibrillar angle (θ) in the tracheid S_2 layer.[5]

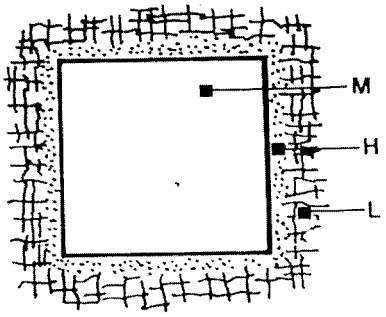

Figure 7. Schematic diagram of the ultrastructural arrangement of a cellulose microfibril (M), hemicellulose (H) and lignin (L) in the wood cell wall.[7]

2.1.4 Chemical Constituents of Wood

The major chemical constituents of wood are well known to be cellulose, hemicellulose and lignin,[8-11] while other polymeric constituents are various kinds of extractives, starch, pectin and inorganic matters present in lesser and often varying quantities.

Tables 3 and 4 show the chemical constituents of the extractive-free wood in five hardwoods and five softwoods, respectively.[12] For these two groups of woods, the cellulose content is more or less the same (43±2%). However, the hardwoods contain less lignin than the softwoods. The lignin content of hardwoods varies between 19% and 24%, whereas that of softwoods is in the range between 27% and 33%. However, tropical hardwoods exceed often the lignin content of many softwoods as estimated by Klason lignin determination. It is not clear whether it is due to the higher content of lignin or the presence of high molecular weight polyphenolic compounds. The chemical structure of lignin is different between these two groups: hardwood lignins consist of syringyl and guaiacyl moieties, whereas softwood lignins are composed mostly of guaiacyl moietiy.[13]

Table 3. Chemical constituents of the extractive-free wood in 5 hardwoods.[12]

Cell wall constituent	*Ulmus americana*	*Acer rubrum*	*Betula* papyrifera	*Fagus grandifolia*	*Populus tremuloides*
Cellulose	51	45	42	45	48
Lignin	24	24	19	22	21
Glucuronoxylan	19	25	35	26	24
Glucomannan	4	4	3	3	3
Pectin, starch, ash, etc.	2	2	1	4	4

Table 4. Chemical constituents of the extractive-free wood in 5 softwoods.[12]

Cell wall constituent	*Thuja occidentalis*	*Abies balsamea*	*Picea glauca*	*Pinus strobus*	*Tsuga canadensis*
Cellulose	41	42	41	41	41
Lignin	31	29	27	29	33
Glucuronoarabinoxylan	14	9	13	9	7
Galactoglucomannan	12	18	18	18	16
Pectin, starch, ash, etc.	2	2	1	3	3

The hemicelluloses found in these groups vary both in chemical structure and quantity, as shown in Figure 8. The predominant hardwood hemicellulose is *O*-acetyl-4-*O*-methylglucuronoxylan (a partly acetylated glucuronoxylan), accounting for 20-35%, whereas minor hardwood hemicellulose is glucomannan only in a small quantity. Glucomannan in aspen and birch wood is reported to be acetylated at the C-2 or C-3 of some of the mannose residues.[14] On the other hand, in softwoods, *O*-acetylgalactoglucomannan (a partly acetylated galactoglucomannan) makes up as much as 18%, and arabino-4-*O*-methylglucuronoxylan (glucuronoarabinoxylan) is in the range of 10%. These hemicelluloses are present in neighbor with cellulose microfibrils in wood cell wall as described in Figure 7. Therefore, residual hemicelluloses remaining between cellulose microfibrils in dissolving pulps affect the properties of cellulose acetates.

In addition to these major cell wall components, various kinds of extractives, pectic substances and starch are present in much smaller quantities in both hardwoods and softwoods. Extractives of wood vary in quantity in the range of up to 10% that are always more abundant in heartwood than sapwood. Ash from inorganic matters usually makes up between 0.1% and 0.5% of wood, but tropical species often exceed this range.

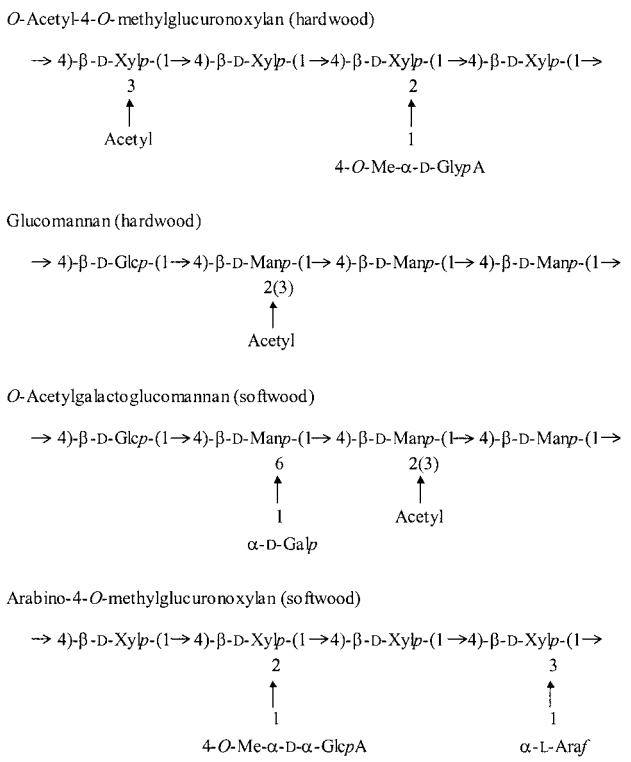

Figure 8. Chemical structures of hemicelluloses commonly found in hardwoods and softwoods.

2.1.4.1 Tracheids and Ray Cells

The fibers in hardwood or tracheids in softwood constitute more than 80% of the cells found in wood. Therefore, the global analyses of wood reflect more or less the chemical constituents of these cells. However, the chemical constituents of ray cells may not be inferred from those of the whole wood.

The data in Table 5 show a comparison in chemical constituents between the ray cells and tracheids from red pine (*Pinus resinosa* Air.).[15] As reported elsewhere,[16] the ray cells contain more lignin, but less cellulose and only half as much galactoglucomannan, with more or less the same amounts of glucuronoarabinoxylan and pectin as in the tracheids. A small amount of a 1, 3-

glucan present in the ray cells appears to be absent in the tracheids. Overall, the results in Table 5 are in good agreement with those in the literature.[17, 18]

Table 5. A comparison in chemical constituents between ray cells and tracheids from red pine.[15]

Cell wall constituent	Ray cells * (%)	Tracheids * (%)
Lignin	40	28
Cellulose	35	42
Galactoglucomannan	9	20
Galactan	Trace	Trace
Glucuronoarabinoxylan	11	8
Pectin	2	1
1,3-Glucan	2	–
Other polysaccharides	1	1

* The defibrated samples after delignification by acid chlorite were subjected to the separation of tracheids and ray cells through screening, followed by subsequent analysis of sugar residues.

2.1.4.2 Earlywood and Latewood

Meier [19] has studied the effect of the cell wall thickness on polysaccharide content of wood by comparing earlywood and latewood from the Scots pine (*Pinus sylvestris* L.). As shown in Table 6, the latewood contains more glucomannan and less glucuronoarabinoxylan than the earlywood. Since the proportion of the latewood tracheid S_2 layer to the whole wood is greater than that of the earlywood, the observed differences are due mainly to the thicker S_2 layer in latewood tracheids. It may therefore be concluded that the tracheid S_2 layer has more glucomannan and less glucuronoarabinoxylan than do other morphologyical regions, which agrees reasonably well with the results of Whiting and Goring [20] for the secondary wall and middle lamella fractions of black spruce (*Picea mariana* Mill.).

Table 6. A comparison in polysaccharide composition between earlywood and latewood from Scots pine.[19]

Polysaccharide	Earlywood (%)	Latewood (%)
Cellulose	56.7	56.2
Galactan	3.4	3.1
Glucomannan	20.3	24.8
Arabinan	1	1.8
Glucuronoarabinoxylan	18.6	14.1

2.1.5 Distribution of Cell Wall Constituents

2.1.5.1 Distribution of Polysaccharides

The distribution of cellulose is rather easy to study at the various morphological regions of wood. Although the orientation of the cellulose microfibrils is quite different in the various cell wall layers, cellulose is quite evenly distributed throughout the secondary wall. However, in the primary wall, microfibrils are rather loosely and randomly arranged (Figures 3 and 4), so the concentration of cellulose in the primary wall may be lower than that of the secondary wall.

Unlike cellulose, the distribution of hemicellulose is difficult to study, because histochemical techniques available are generally nonspecific for hemicellulose and frequently unreliable. In order to overcome these difficulties, the interference microscopy was used with enzymatic treatment.[21] The electron microscopy was also used to study the enzymatic degradation of the cell wall components by xylanases, mannanase and avicellase for delignified spruce [*Picea abies* (L.) Karst.] and beech (*Fagus sylvatica* L.).[22, 23] It was found that xylan concentration is rather high in the S_1 and S_3 layers for both woods. In addition, immunoelectron microscopy has been applied to studying the distribution of glucuronoxylan in buna (*Fagus crenate* Blume).[24] Another attempt was made by Hoffmann and Parameswaran [25] to study the polysaccharide distribution in spruce tracheids through oxidation of polysaccharides with heavy metal. Subsequent electron microscopic observations indicated the highest concentration of hemicelluloses in the S_1 layer.

The distribution of polysaccharides has also been studied by examination of holocellulose skeletons after removal of lignin with acid chlorite,[26] a technique further refined by Fujii et al. [27] by using ultrathin sections. Although the presence of the residual lignin and some removal of polysaccharides may obscure the data, overall the results obtained by this method are in good agreement with the holocellulose distribution inferred from the lignin skeleton.

For the localization of pectin, the hydroxylamineiron method was developed by McCready et al. [28-30] for the quantitative determination of pectin. With this method, Parameswaran and Liese [31] have found a homogeneous distribution of pectin across the secondary wall, with the highest concentration in the middle lamella region. The use of ruthenium red and alcian blue is also proposed for staining pectic substances.[32, 33]

For quantitative determination of the polysaccharide distribution, the microdissesection technique has often been used. This technique was applied for softwood tracheids (*Pinus sylvestris* L. and *Picea abies* Karst.) and hardwood fibers (*Betula verrucosa* Ehrh.) at different stages of development that were microscopically distinguished, isolated and subsequently subjected to microanalysis for sugar residues.[34, 35] Although some doubt exists as to additional deposition of polysaccharides during the later stage of the secondary wall thickening, the contents of polysaccharides at various morphological regions could be calculated.[36]

In 1981, Hardell and Westermark [37] have developed a method for peeling layers of the cell wall from a slightly delignified single tracheid of Norway spruce [*Picea abies* (L.) Karst]. They reported only small differences in the relative amounts of polysaccharides between the secondary wall and the compound middle lamella. A treatment of slight delignification appears to cause a partial dissolution of hemicelluloses and their redistribution. However, the galactose and arabinose contents for the compound middle lamella were found to be 7.6% and 7.3%, values that are considerably lower than those from nonlignified wood.[10]

Whiting et al. [38] have also developed another method of preparing wood tissue fractions from the secondary wall and compound middle lamella of tracheids from black spruce (*Picea mariana* Mill.) by taking advantage of the difference in density (ρ) between lignin ($\rho \cong 1.4$ g/mL) and polysaccharide ($\rho \cong 1.5$ g/mL). The significant finding by this method [20] was that the middle lamella contains less cellulose and glaucomannan but more galactan and arabinan than the secondary wall. However, the concentration of glucuronoarabinoxylan is essentially the same in both morphological regions (Table 7). It is therefore likely that in the tracheid secondary wall the contents of hemicelluloses decrease in the following order: glucomannan, glucuronoarabinoxylan, galactan and arabinan. Compared to the previous methods by Hardell and Westermark,[37] the method by Whiting et al. [38] is more reliable, due to only the physical treatment of the sample without introducing any chemical change.

Table 7. Polysaccharide percentages of the secondary wall and true middle lamella in black spruce. [20]

Polysaccharide	Secondary wall (22% lignin)	Middle lamella (70% lignin)
Cellulose	46.8	0
Glucomannan	18.5	3.8
Glucuronoarabinoxylan	8.4	11.3
Galactan	3.2	8.8
Arabinan	1.2	6.2

2.1.5.2 Distribution of Lignin

Unlike polysaccharides, a number of reliable methods can be used to study the distribution of lignin in wood. One of the oldest procedures is selective staining, followed by study under the light microscope.[39] Although some doubt exists as to this specificity for lignin,[40, 41] potassium permanganate staining[42] has been used extensively to study lignin distribution by electron microscopy.[43-46]

Also reported were studies by electron microscopy of lignin skeletons created by the carbohydrate removal by concentrated hydrofluoric acid[27, 47-49] or brown-rot fungi.[50] Although some alteration of the lignin through condensation may result and the possible presence of residual carbohydrates may obscure the data, overall the results obtained by this method are in reasonable agreement with those from potassium permanganate staining.[49] Although the above methods are useful in elucidating the presence of lignin in the various morphological regions of wood, they can provide only qualitative evaluation of the lignin distribution. For quantitative visualization, ultraviolet (UV) microscopy with thin sections of wood has provided good results on lignin distribution.

Of other methods for the quantitative assay of the lignin distribution, Saka et al.[51-55] developed a new technique for the quantitative determination of the lignin distribution on wood. The method involves a specific bromination for lignin in a nonaqueous system ($CHCl_3$). Bromine concentrations in the various morphological regions of wood are then determined by electron microscopy (TEM or SEM) coupled with energy-dispersive X-ray analysis (EDXA). By knowing the lignin reactivity toward bromination, the distribution of lignin can be determined for various morphological regions of wood. Figure 9 shows the direct comparison made between two

techniques of UV microscopy and EDXA measurement in bromination[55] over the earlywood/ latewood boundary of black spruce (*Picea mariana* Mill.). it is quite apparent that the agreement between the results obtained by the two methods is good.

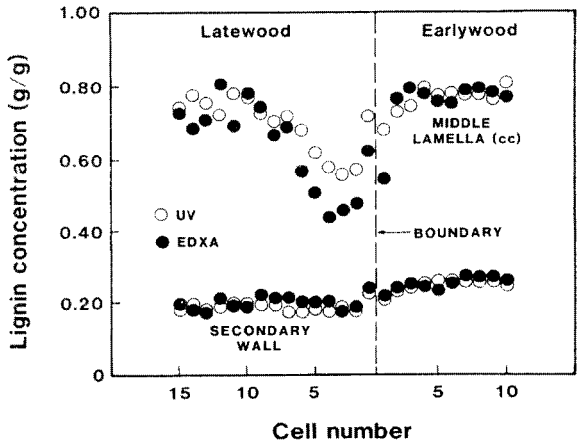

Figure 9. A direct comparison of lignin concentrations across the earlywood/latewood boundary of black spruce determined by UV microscopy (○) and the EDXA technique (●). [55]

(a) Distribution of Lignin in Hardwoods

Hardwood lignins consist of guaiacyl and syringyl residues, and its ratio changes from one morphological region to another. In addition, the syringyl and guaiacyl residues have different UV absorptivities. Thus, its exact ratio has to be known before the lignin concentration in a particular morphological region is computed from the UV microscopy. For this problem, Saka et al. [56, 57] developed a new method to compute the ratio of guaiacyl and syringyl residues at the various morphological regions of hardwoods by combining UV microscopy with bromination-EDXA (UV-EDXA) technique.

Table 8 shows the ratio of guaiacyl/syringyl residues in various morphological region of white birch (*Betula papyrifera* Marsh.) as determined by the UV-EDXA technique.[56] For comparison, the results obtained by UV microscopy alone[58] through UV spectral analysis are included. By both methods, the fiber secondary wall (S_2) is indicated to contain predominantly syringyl residues, whereas the vessel secondary wall (S_2) to consist mostly of guaiacyl residues.

The study by UV-EDXA technique[56] revealed that the ray parenchyma cell contains about equal proportions of guaiacyl and syringyl residues in lignin. However, a predominant amount of syringyl-type lignin was reported by UV spectral analysis,[58] as in the fiber secondary wall.

For the cell corner middle lamella (ML_{cc}), 80-100% of the lignin was found to be guaiacyl residue, with the remaining 0-20% being syringyl residue by the UV-EDXA technique.[56] This results is not in agreement with those by UV spectral analysis[58] that the middle lamella lignin consists entirely of guaiacyl residues. It is, therefore, apparent in Table 8 that the ratio of guaiacyl and syringyl residues in lignin varies in different morphological regions of hardwood.

Shown in Table 9 is the distribution of lignin in white birch as determined by UV-EDXA technique.[56] For comparison, the results obtained by UV microscopy[59] are also included. For the fiber secondary wall, the lignin concentration in the S_3 layer is slightly lower than that in either the S_1 or S_2 layer. However, its difference is so small that the lignin is considered to be distributed uniformly across the secondary wall. The vessel walls also reveal a uniform distribution of lignin, but the concentration is about 1.9 times higher than that of the fiber walls, which in turn is higher than that of ray parenchyma cells. The cell corner middle lamella (ML_{cc}) associated with fibers and vessels has the highest lignin concentration. In spite of sufficient analytical resolution by the EDXA system, the middle lamella between cell corner areas (ML) was 10-30% lower in concentration than the cell corner middle lamella (ML_{cc}).

A comparison of the data made between UV-EDXA and UV microscopy techniques indicates that lignin concentrations in fiber and vessel secondary walls are in agreement with each other. However, lignin concentration in the ray parenchyma cells by UV-EDXA [56] is nearly half as low as the data obtained by UV microscopy alone.[59] Although the middle lamella between two cell corners (ML) of fibers and vessels revealed similar values by these two methods, the concentration in the cell corner middle lamella (ML_{cc}) was lower by the UV-EDXA technique.[56] The observed discrepancies are due probably to the uncertainty in estimating the guaiacyl-syringyl ratio, as the analysis is made by UV microscopy alone.

Table 8. Distribution of guaiacyl and syringyl residues in lignin in white birch. [56, 58]

Morphological region	Guaiacyl: syringyl	
	UV-EDXA [56]	UV spectral analysis [58]
Fiber S_2	12:88	0:100 (Syringyl)
Vessel S_2	88:12	100:0 (Guaiacyl)
Ray parenchyma S	49:51	0:100 (Syringyl)
$ML_{cc(F/F)}$ [a]	91:9	50:50
$ML_{cc(F/V)}$ [b]	80:20	100:0 (Guaiacyl)
$ML_{cc(F/R)}$ [c]	100:0	50:50
$ML_{cc(R/R)}$ [d]	88:12	50:50

[a] Fiber/fiber, [b] Fiber/vessel, [c] Fiber/ray, [d] Ray/ray.

Table 9. The distribution of lignin in white birch. [56, 59]

Element	Morphological region	Tissue volume (%)	Lignin concentration (g/g)	
			UV-EDXA[a] [56]	UV only[a] [59]
Fiber	S_1	11.4	0.14	-
	S_2	58.5	0.14	0.16
	S_3	3.5	0.12	-
	ML	5.2	0.36	0.34
	$ML_{cc(F/F)}$ [b]	2.4	0.45	0.72
Vessel	S_1	1.6	0.26	-
	S_2	4.3	0.26	0.22
	S_3	2.3	0.27	-
	ML	0.8	0.4	0.35
	$ML_{cc(F/V)}$ [c]	≅0	0.58	-
Ray parenchyma	S_3	8	0.12	0.22
	ML	2	0.38	-
	$ML_{cc(F/R)}$ [d]	≅0	0.47	-
	$ML_{cc(R/R)}$ [e]	≅0	0.41	-

[a] Calculated using xylem lignin content of 0.199 g/g.
[b] Fiber/fiber, [c] Fiber/vessel, [d] Fiber/ray, [e] Ray/ray.

(b) Distribution of Lignin in Softwoods

Table 10 shows the distribution of lignin in tracheids of black spruce (*Picea mariana* Miall.) as determined by UV microscopy.[4] The results show that the lignin concentration in the secondary wall (S) is considerably lower than that in the middle lamella (ML or ML_{cc}). However, the

secondary wall makes up a much larger proportion of the total tissue volume. Thus, the majority of the lignin is located in the secondary wall. Furthermore, as seen in Figure 10, the lignin is uniformly distributed across the secondary wall in black spruce tracheids.

Table 10. The distribution of lignin in black spruce tracheids as determined by UV microscopy.[4]

Wood	Morphological region	Tissue volume (%)	Lignin (% of total)	Lignin concentration (g/g)
Earlywood	S	87	72	0.23
	ML	9	16	0.5
	ML_{cc}	4	12	0.85
Latewood	S	94	82	0.22
	ML	4	10	0.6
	ML_{cc}	2	8	1

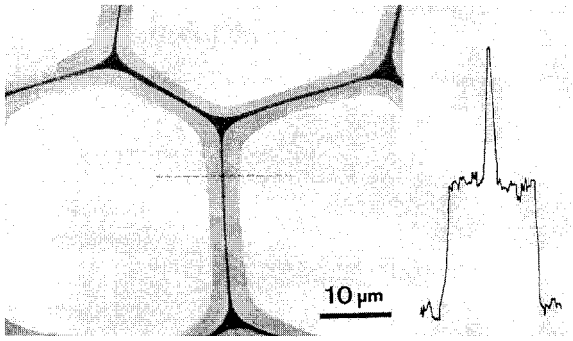

Figure 10. UV photomicrograph taken at 240 nm of the earlywood tracheid walls in black spruce. The densitometer tracing was conducted along the dotted line. (Courtesy of Prof. Emer. D. A. I. Goring, University of Toronto, Canada.).

Table 11 shows the distribution of lignin in loblolly pine (*Pinus taeda* L.) tracheids as determined by bromination coupled with SEM-EDXA technique.[54] One of the advantages of this technique compared with UV microscopy is the ability to study the S_1, S_2 and S_3 layers in the secondary wall as a separate entity. Such resolution is often difficult with UV microscopy. It is interesting to note that the lignin concentration in the S_2 layer is lower than that in either the S_1 or S_3 layer. The line profile of the bromine X-rays in Figure 11 shows such differences clearly. Fukazawa and Imagawa [60] have also reported a similar finding of high UV absorbance near the lumen/ wall interface for juvenile wood tracheids of Japanese fir (*Abies sachalinensis* Fr. Schm.).

For the ray parenchyma cells constituting about 5% of the total xylem tissue in softwoods, Harada and Wardrop[16] have reported a lignin content of 0.44 g/g in Japanese cedar (*Cryptomeria japonica* D. Don). By a microdisection technique, Bailey[61] obtained a value of 0.41 g/g for the segregated ray parenchyma cells of Douglas fir. Fergus et al.[4] also determined by UV microscopy a lignin concentration of 0.40 g/g for black spruce. These results by a variety of methods are in good agreement with the data of 0.40 g/g for earlywood parenchyma cells in Douglas fir determined by UV microscopy.[62] It is interesting to note that the ray parenchyma cells in softwoods possess significantly higher lignin contents than the whole wood.

Table 11. The distribution of lignin in loblolly pine tracheids as determined by bromination with SEM-EDXA.[54]

Wood	Morphological region	Tissue volume (%)	Lignin (% of total)	Lignin concentration (g/g)
Earlywood	S_1	13	12	0.25
	S_2	60	44	0.2
	S_3	9	9	0.28
	ML	12	21	0.49
	ML_{cc}	6	14	0.64
Latewood	S_1	6	6	0.23
	S_2	80	63	0.18
	S_3	5	6	0.25
	ML	6	14	0.51
	ML_{cc}	3	11	0.78

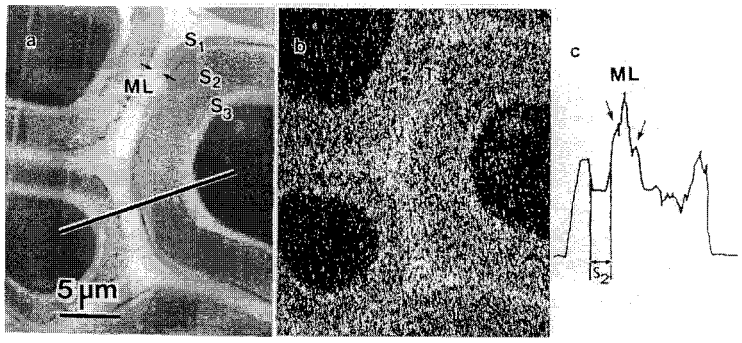

Figure 11. Scanning electron micrograph (a) of brominated latewood tracheids in loblolly pine (0.5 µm section). The distribution map (b) of Br-L X-rays was taken of the same area as the scanning electron micrograph. The distribution of bromine (c) was taken along the line across the double cell wall.[52]

2.1.5.3 Distribution of Inorganic Constituents

A fair amount of information is available on the inorganic constituents of wood[63-69] and bark.[70, 71] In woods from temperate zones, elements other than carbon, hydrogen, oxygen and nitrogen makes up between 0.1% and 0.5% of the weight of wood,[72, 73] whereas those from tropical regions makes up to 5%.[74] This proportion, although small, contains a wide variety of elements. For example, spectrographic analysis of grand fir[63] revealed as many as 32 elements.

In many cases, alkali and alkali earth elements such as Ca, Mg and K make up about 80% of the total inorganic constituents.[75] These elements probably occur in wood as salts, e.g., oxalates, carbonates and sulfates,[76] or inorganic moiety bound to the cell wall components such as carboxyl groups of pectic materials.[75, 77, 78]

Some of the inorganic elements present in wood are essential for wood growth, whereas others are not necessarily required. Metallic elements are often absorbed into the tree though the root system and are transported to all areas within the growing tree.[63] Unlike major cell wall components such as cellulose and lignin, the content of inorganic constituents varies to a great extent with the environmental conditions under which the tree has grown.[65, 73]

Saka and Goring[75] have studied the distribution of inorganic constituents from the pith to the outer ring of black spruce (*Picea mariana* Mill.) by means of TEM-EDXA. The TEM-EDXA technique is a powerful tool detecting any element above neon and recently above boron in the periodic table. Seven morphological regions of the tracheids, ray tracheids and ray parenchyma cells were investigated by the point analysis with a resolution of 400 nm. Detected were 15 different elements, such as Na, Mg, Al, S, K, Ca, Cr, Fe, Ni, Cu, Zn and Pb above neon in the periodic table. Secondary walls of tracheids, ray tracheids and ray parenchyma cells usually contain detectable concentrations of only four elements: sulfur, chlorine, potassium and calcium. In contrast, almost all the elements were found to be located and concentrated in the torus and half-bordered pit membrane regions (Figure 12). The total content of inorganic constituents decreased in the order of torus (2%) > half-bordered pit membrane (1%) > middle lamella (4%) > ray parenchyma cell wall (3%) > tracheid secondary wall (0.1-0.15%). The total content of inorganic constituents was found to be higher in earlywood than latewood for any of the morphological regions studied. This is probably because the earlywood tracheids that have large

lumens and abundant pits are the major water-conducting tissues, whereas thick-walled latewood tracheids with fewer pits may act as a physical or mechanical support for the wood.

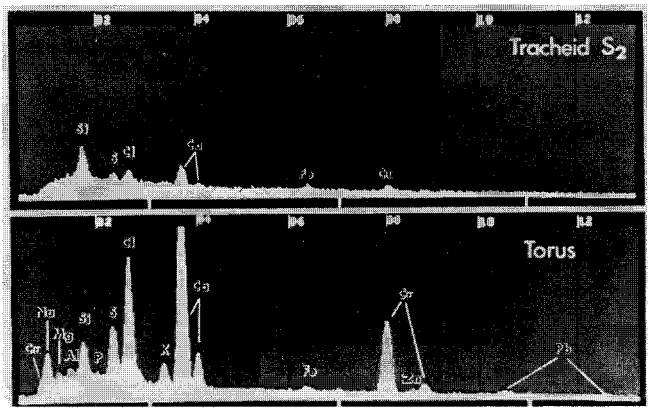

Figure 12. EDXA spectra from the tracheid secondary wall and tracheid torus[75].

Later, Saka and Mimori[79] have studied the distribution of inorganic constituents of Japanese birch wood (*Betula platyphylla* Sukatchev var. *Japonica* Hara) by the SEM-EDXA technique with thin sections. Six morphological regions of the fibers, vessels and ray parenchyma cells were investigated by the point analysis with a resolution of 800 nm. Detected were 11 different elements: Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe and Zn. The secondary walls of wood fibers, vessels and ray parenchyma cells usually contained detectable concentrations of three elements, S, Cl and Ca, while, in the amorphous layer of ray parenchyma cell and pit membrane between vessel and ray parenchyma cell, almost all of the detected elements were found to be localized and concentrated. The total content of inorganic constituents was found to be decreased in the order, amorphous layer (0.68%) > fiber middle lamella (0.54%) > vessel middle lamella (0.48%) > ray parenchema cell wall (0.15%) > fiber secondary wall (0.14%) > vessel secondary wall (0.10%). This observed trend is basically the same as found in black spruce by Saka and Goring.[75]

Conclusion

Knowledge of the chemical constituents of wood is essential for studying the physical and chemical properties of wood, and it becomes more important as wood dissolving pulps are used as cellulose materials for cellulose acetate production. However, it can provide nothing but the average of the cell wall constituents. For a better understanding of wood pulp fibers as raw materials, more detailed information is required about their distribution across the wood cell wall. Knowledge in this chapter will therefore provide basic information of the wood cell wall constituents and its distribution.

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