Chemical Composition of Wood

Wood is essentially composed of cellulose, hemicelluloses, lignin, and extractives. Table 1 presents major chemical compositions of some wood species. Each of these components contributes to fiber properties, which ultimately impact product properties.

Table 1. Chemical Composition of Some Wood Species[1]

Constituent	Scots Pine *(Pinus sylvestris)*	Spruce *(Picea glauca)*	Eucalyptus *(Eucalyptus camaldulensis)*	Silver Birch (*Betula verrucosa)*
Cellulose (%)	40	39.5	45.0	41.0
Hemicellulose				
-Glucomannan (%)	16.0	17.2	3.1	2.3
-Glucuronoxylan (%)	8.9	10.4	14.1	27.5
-Other polysaccharides (%)	3.6	3.0	2.0	2.6
Lignin (%)	27.7	27.5	31.3	22.0
Total extractives (%)	3.5	2.1	2.8	3.0

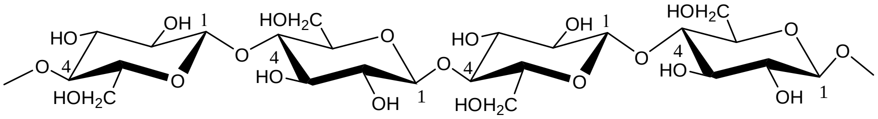

Figure 1. The Structure of Cellulose

Cellulose

Cellulose, the major chemical component of fiber wall and contributing 40-45% of the wood's dry weight, is composed of linear chains of D-glucose linked by ß-1,4-glycosidic bonds (Figure 2.1) with the degree of polymerization from 10,000 in native wood to 1,000 in bleached kraft pulps. Each D-anhydroglucopyranose unit possesses hydroxyl groups at C2, C3, and C6 positions, capable of undergoing the typical reactions known for primary and secondary alcohols. The molecular structure imparts cellulose with its characteristic properties: hydrophylicity, chirality, degradability, and broad chemical variability initiated by the high donor reactivity of hydroxyl groups.

Cellulose has a strong tendency to form intra- and inter-molecular hydrogen bonds by the hydroxyl groups on these linear cellulose chains, which stiffen the straight chain and promote aggregation into a crystalline structure and give cellulose a multitude of partially crystalline fiber structures and morphologies.[2] The degree of crystallinity of different cellulose samples are presented in Table 2.[3]

Table 2. X-Ray Crystallinity of Some Cellulose Materials

Sample	X-ray crystallinity (%)
Cotton linters	56-63
Sulfite dissolving pulp	50-56
Prehydrolyzed sulfate pulp	46
Viscose rayon	27-40
Regenerated cellulose film	40-45

The ultrastructure of native cellulose (cellulose I) has been discovered to possess unexpected complexity in the form of two crystal phases: I_α and I_β.[4] The relative amounts of I_α and I_β have been found to vary between samples from different origins. The I_α-rich specimens have been found in the cell wall of some algae and in bacterial cellulose, whereas I_β-rich specimens have been found in cotton, wood, and ramie fibers.[5] The crystal and molecular structure, together with hydrogen-bonding system in cellulose I_α and I_β has been determined recently by Nishiyama *et al* using atomic-resolution synchrotron and neutron diffraction data recorded from oriented fibrous samples prepared by aligning cellulose microcrystals from the cell wall of the freshwater alga [18] and tunicin.[6]

The presence of crystalline cellulose, with regions of less order, and the size of the elementary fibrils work together to produce interesting combination of contrary properties such as stiffness and rigidity on one hand and flexibility on the other hand.[7] Crystalline cellulose has a very limited accessibility to water and chemicals. Chemical attack can therefore be expected to occur primarily on amorphous cellulose and crystalline surface.

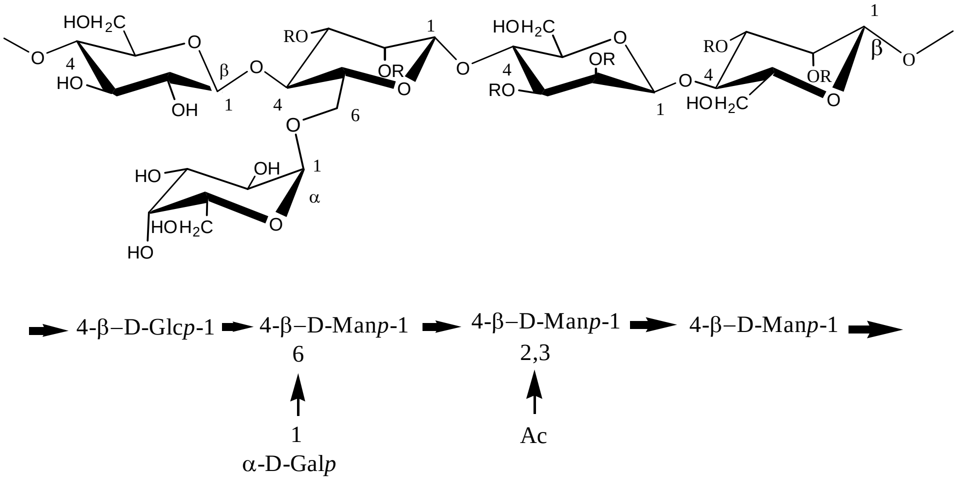

Figure 2. Principal Structure of Galactoglucomannans in Softwood

Sugar units: β-D-glucopyranose (Glc*P*); β-D-mannopyranose (Man*p*); β-D-galactopyranose (Gal*p*). R = CH_3CO or H. The lower representation is the abbreviated formula showing the proportions of the units (galactose-rich fraction)

Hemicellulose

Unlike cellulose, hemicelluloses have lower DP (only 50-300) with side groups on the chain molecule and are essentially amorphous. The main hemicelluloses of softwood are galactoglucomannans (Figure 2) and arabinoglucuronoxylan (Figure 3), while in hardwood is glucuronoxylan (Figure 4). Table 2 summarizes the main structural features of hemicelluloses appearing in both softwood and hardwood.

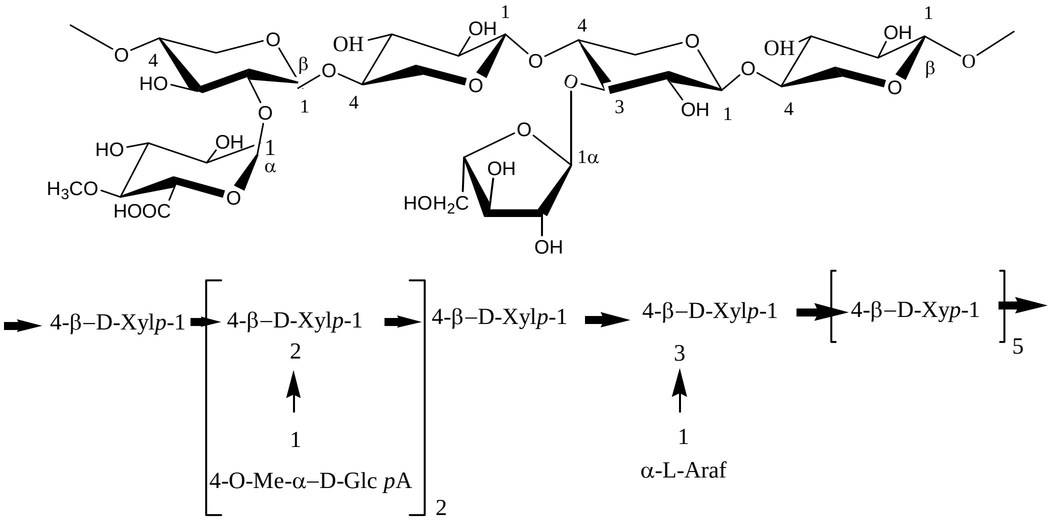

Figure 3. Principal Structure of Arabinoglucuronoxylan in Softwood

Sugar units: β-D-xylopyranose (Xyl*P*); 4-O-methyl-α-D-glucopyranosyluronic acid (Glc*p*A); α-L-Arobinofuranose (Ara*f*). The lower representation is the abbreviated formula showing the proportions of the units.

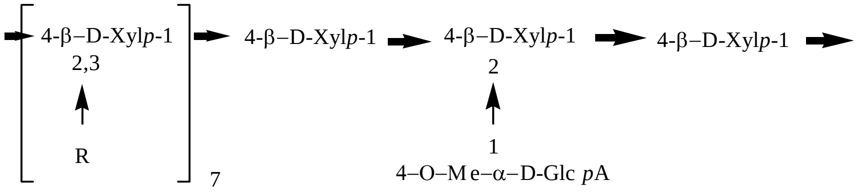

Figure 4. Principal Structure of Glucuronoxylan in Hardwood

Sugar units: β-D-xylopyranose (Xyl*P*); 4-O-methyl-α-D-glucopyranosyluronic acid (Glc*p*A); R = Acetyl group (CH_3CO).

Table 2. The Major Hemicellulose Components in Softwood and Hardwood[1]

Wood	Hemicellulose type	Amount (% on wood)	Composition			DP
			Units	Molar ratios	Linkage	
SW	Galacto-glucomannan	5-8	β-D-Man*p* β-D-Glc*p* α-D-Gal*p* Acetyl	3 1 1 1	1 → 4 1 → 4 1 → 6	100
	(Galacto)-glucomannan	10-15	β-D-Man*p* β-D-Glc*p* α-D-Gal*p* Acetyl	4 1 0.1 1	1 → 4 1 → 4 1 → 6	100
	Arabino-glucuronoxylan	7-10	β-D-Xyl*p* 4–O–Me–α-D-Glc*pA* α-L-Araf	10 2 1.3	1 → 4 1 → 2 1 → 3	100
HW	Glucuronoxylan	15-30	β-D-Xyl*p* 4–O–Me–α-D-Glc*pA* Acetyl	10 1 7	1 → 4 1 → 2	200
	Glucomannan	2-5	β-D-Man*p* β-D-Glc*p*	1-2 1	1→ 4 1→ 4	200

Unlike glucomannan, xylan contains acidic groups (glucuronic acid) (Figure 3 and Figure 4) and has a molecular structure similar to cellulose when their branches are removed from xylan, which may make xylan combine with cellulose in more ordered structure after kraft pulping.[8]

Glucomannan is very sensitive to kraft cooking conditions and is already dissolved to a large extent at the beginning of kraft cooking, whereas xylan is more resistant.[7] Therefore, the content of xylan in chemical softwood kraft pulp becomes almost the same as that of glucomannan in spite of considerably higher content of glucomannan in softwood (Table 3). Hemicelluloses in hardwood kraft pulps are dominated by xylan. Furthermore, relocation of xylan in fiber can occur during kraft cooking due to the sorption of xylan from cooking liquor. Consequently, enhanced hemicellulose (xylan) levels on pulp fiber surfaces have been reported for both softwood and hardwood kraft pulps.[9]

Table 3. The Change of Chemical Composition of Birch and Pine

Constituents	Pine *(Pinus sylvestris)*	Birch (*Betula verrucosa)*
Cellulose (%)	40.0	41.0
Hemicellulose		
-Glucomannan (%)	16.0	2.3
-Glucuronoxylan (%)	8.9	27.5
-Other polysaccharides (%)	3.6	2.6
Lignin (%)	27.7	22.0
Total extractives (%)	3.5	3.0

In addition, all sugar components can take part in the formation of lignin carbohydrate complexes by covalent linkages between lignin and carbohydrates in both wood and pulps.[10] The most frequently suggested LCC-linkages in native wood are benzyl ester, benzyl either, and glycosidic linkages. However, the benzyl ester linkage is alkali-labile and may therefore be hydrolyzed during kraft pulping process. The latter two linkages are alkali-stable and would survive from the hydrolysis during kraft pulping process.

Proximate Analysis of Wood

Typical Wood Properties

Wood Species	**Oven Dry Density***	**Calorif Value Wood****	**% Lignin**	**% α Cellulose**	**% Pentosan**	**% Extractives**	**% Ash**
Softwoods							
Western White Pine	35 .0		25.4	42.3	7.9	8.3	0.3
White Spruce	416		27.8	42.1	12.1	2.3	
Black Spruce	400		27.3	45.8	12.5	2.2	0.29
Norway Spruce	368		26.9	42.3	11.0	0.9	0.31
Loblolly Pine	545	4381	28.1	43.3	12.6	3.8	0.4
Slash Pine	560	4281	28.0	46.1	8.6	2.6	0.6
Jack Pine		4962 (bone-dry)	28.3	45.2	11.3	4.0	1.3

Hardwoods							
Wood Species	**Oven Dry Density***	**Calorif Value Wood****	**% Lignin**	**% α Cellulose**	**% Pentosan**	**% Extractives**	**% Ash**
Yellow Birch	657	3215	21.2	49.4	21.4	2.6	2.9 – 1.7
Red Maple	561		22.8	44.5	17.1	2.5	5.2
Yellow Poplar	432	4275 (oven-dry)	25.3	33.5	20.1	3.6	2.8
Quaking Aspen	400	3215	18.2	50.2	17.5	2.4	4

*kg/cu m; ** kcal/kg aid dry

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