PULP

1. Introduction

Pulp is the fibrous raw material utilized in the production of paper, paperboard, fiberboard and various wood-based composites, and absorbents. In purified form, dissolving pulp, it is a source of cellulose for rayon and other regenerated cellulose fibers, as well as cellulose derivatives including cellulose esters and ethers. Pulp is produced through mechanical, chemical, and/or biological treatment (pulping) of fibrous plants. At present, wood provides $>90\%$ of the world's virgin fiber requirement (Table 1), the remainder being made up of nonwood sources (bagasse, straws, bamboo, etc). Approximately one-third of all paper products are recycled as secondary fiber. The predominant pulping processes are chemical based, accounting for $>70\%$ of worldwide production, of which 80% is by Kraft pulping (sulfate).

2. Wood and Fibers

2.1. The Structure of Wood. Trees are perennial, seed bearing plants that are generally classified into two broad categories, known commercially as *softwoods* (gymnosperms) and *hardwoods* (angiosperms). The chemistry and anatomy of wood vary somewhat within the species of tree, but there are some gross similarities (Table 2). Wood is composed of elongated cells, most of which are oriented in the longitudinal direction of the stem. These cells vary in length and width, depending on the function within the tree, providing mechanical support, liquid transport, and the storage of reserve food supplies (1,2). A clear difference is seen in the presence of vessel elements in hardwoods that are oriented in the longitudinal direction of the stem. At the microstructural level further differences can be seen between hardwoods and softwoods. Softwoods contain fewer cell types resulting in a less complex and varied structure.

Softwoods are primarily made up of fibers or tracheids, which comprise $>90\%$ (by volume) of the xylem. They are thin and long cells with flat tapered closed edges and perform both conduction and support roles. Softwood fibers are significantly larger than those found in hardwoods (Table 3), and vary depending on species. Softwoods also contain parenchyma cells that are arranged both horizontally and vertically. The storage and transport of assimilates take place within the Ray parenchema cells. By contrast, hardwoods have a much larger variety of cell types, which in addition to fibers include vessel elements, and longitudinal and ray parenchyma cells. In hardwoods, vessel elements are the conducting cells, while fibers are support cells. As with softwoods, parenchyma cells transport and store nutrients.

Structural carbohydrates are the main chemical constituents of most plant tissues, and form the bulk of the plant cell's supporting structure: *the cell wall* or *extracellular matrix*. The plant cell wall is a highly organized composite of many different polysaccharides, proteins, and aromatic substances (Table 4) (1). Some structural molecules act as fibers, while others act as the cross-linking matrix. The molecular composition and arrangements of the wall polymers differ among species, among tissues of a single species, among individual cells and even among regions of the wall.

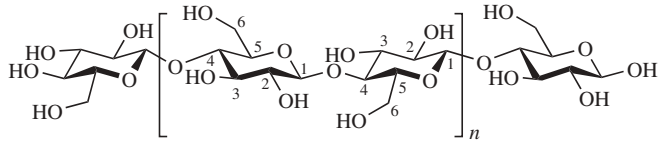
The plant cell wall consists of three layers: middle lamella, primary wall, and secondary wall (Fig. 1) (1). The primary wall is the first layer formed during cell-wall development (3). It is formed in the cell plate during cell division and rapidly increases in surface area during cell expansion. Substantial cell development, thickening, within the primary wall leads to the formation of the secondary wall. The secondary wall is highly organized and crucial to conferring rigidity on plant tissue. It is comprised of three layers: S1 (outer layer), S2 (middle layer), and S3 (inner layer), and is made up of cellulose, hemicellulose, and lignin (Table 5) (4). The middle lamella serves to form the interface between primary walls of adjacent cells, and is comprised of pectic compounds, protein, and lignin (Table 5). The layers of the cell wall are not only rigid, but extremely hard. Hardness is conferred by the deposition of lignin throughout the cell wall upon completion of cell-wall thickening. Lignin deposition is typically followed by cell death.

The cell wall consists of distinctive fibrillar structures embedded in an amorphous matrix. The fibrillar structures are microfibrils of cellulose (Fig. 2) and are largely crystalline. The microfibrils are not randomly oriented, implying a high degree of control over their biosynthesis and/or deposition. In a typical diagrammatic representation, the various cell-wall layers are distinguishable by their distinct microfibril orientations (5). Specifically, a thin primary wall with an apparent disordered array of microfibrils, and a thick, three layered secondary wall in which the microfibrils are highly ordered. In the outer S1, the microfibrils are orientated at a fairly high angle to the cell (fiber) axis, 50–70°. In the middle S2 layer, the microfibril orientation is very low, 5–20° relative to the fibre axis, while in the S3 layer they are at a very high angle to the cell axis, 50–90° (6).

2.2. Chemical Composition of Cell Wall. *Cellulose.* Cellulose constitutes the most abundant, renewable polymer resource (8). It is produced by Nature at an annual rate of 10^{11}–10^{12} tons. Cellulose is the main constituent of higher plants, including wood, cotton, flax, kemp, jute, bagasse, ramie, and the like, making up as much as 40–45% of the dry weight (9). Cellulose is produced by bacterium, *Acetobacter xylinum*, algae, *Valonia, Chladophora, Rhizoclonium and Microdictyon*, and several sources of animal origin, eg, tunicin, a cell wall component of ascidians. Industrially, the principal sources of cellulose are wood, cotton fiber, and cotton linters.

In 1838, Anselm Payen first proposed the elemental composition of cellulose to be $C_6H_{10}O_5$(10), classifying it as a carbohydrate. Cellulose is a polydispersed linear threodisyndiotactic homopolymer consisting of β-D-anhydroglucopyranose (β-D-glc) moieties linked via β(1-4) glycosidic bonds (trans or diequitorial linkages). The anhydroglucopyranose units (AGU) exist in the lowest energy $^4C_1$-chair conformation (11). Taking the dimer cellobiose as the basic repeat unit, cellulose can be classified as an isotactic homopolymer of cellobiose (**1**). Based on the $^4C_1$-chair conformation each AGU possesses hydroxyl groups at the C_2, C_3, and C_6 positions orientated in the ring plane, equatorially. The hydroxyl groups at both ends of the cellulose molecule show different behavior. The C_1 end has reducing properties, while the end with a free C_4 hydroxyl group is nonreducing. The molecular size of native cellulose, which can be defined by the degree of polymerization (DP) differs widely depending on the origin and method of isolation.

Native cotton has a DP range on the order of 15,000, while that of native wood cellulose is 10,000. This corresponds to a molecular mass of 2.4 and 1.6 million Da, respectively, or to a molecular length of 7.7 and 5.2 μm, respectively. In technical processes, eg, chemical pulping, the DP of cellulose can decrease to 500–2000.



nonreducing end-group (**1**) reducing end-group

The backbone conformation of the cellulose chain is determined by the bond angles, bond length, and torsion angles of the glycosidic bond. Generally, a bent backbone conformation is assumed, Fig. 3, which together with the equatorial orientation of the hydroxyl groups there is a strong tendency to form intra- and intermolecular hydrogen bonds. The intramolecular hydrogen bonds are responsible for the stiff and rigid nature, as well as the "twofold screw axis" of the cellulose molecule. The special chain conformation of crystalline native cellulose (cellulose I) is adequately represented by a 1,2 helix (12–15) although deviations have been observed and attributed to changes in hydrogen bonding or degree of order (16). From infrared (IR), nuclear magnetic resonance (NMR) spectroscopy and X-ray diffraction studies (17,18) it is known that intramolecular hydrogen bonds are formed along both sides of the cellulose chain, Fig. 3. One exists between the C_3-hydroxyl of one anhydroglucopyranose unit and the pyranose ring oxygen (O_5) of an adjacent unit (O_3-H-O_5), and the other is between the C_2-hydroxyl and the adjacent C_6-hydrogen ($O_{2'}-H-O_6$), which is in a *tg* (trans–guache) orientation. The $O_3-H-O_{5'}$ hydrogen-bond length is 2.75 Å, and that of the $O_{2'}-H-O_6$ hydrogen bond is 2.87 Å (19).

The intermolecular hydrogen bonding in cellulose is between the hydroxyl groups of the C_6 and $C_{3'}$ positions of cellulose molecules adjacently located in the same lattice plane (Fig. 3). Thus, the C_6 hydroxyl group, which is in a *tg* position, is involved in two secondary valence interactions, one intramolecular and one intermolecular; it is precluded from interacting with molecules in neighboring 020-planes, ie, above or below. Therefore, native cellulose is represented as a sheetlike structure with only weak van der Waals forces holding the sheets together.

Cellulose is the principal scaffolding component of all plant cell walls. The cellulose chains have a strong tendency to aggregate to highly ordered structural entities. This arises from the extensive intra- and intermolecular interactions, specifically intermolecular hydrogen bonding. The interchain cohesion is favored by the high spatial regularity of the hydrogen-bonding sites, which involves all three of the free hydroxyl groups within the AGU. The resulting cellulose aggregates are highly crystalline, although not uniform throughout the entire structure. A two-phase model assuming low ordered (noncrystalline) and highly ordered (crystalline) regions is generally accepted for cellulose and cellulose

fibers—fringed fibril model (20). The amount of highly ordered regions or the degree of crystallinity covers a wide range and depends on origin and treatment conditions, Table 6.

Cellulose exists in several crystal structures, differing in unit-cell dimensions and possible chain polarity (8). Native cellulose, referred to as cellulose I, is the predominate crystalline structure of algal, bacterial, some animal and most higher plants, and can be converted into the other polymorphs through a variety of treatments (22). Two forms of cellulose I exist, cellulose I_α, and cellulose I_β. Cellulose I_α is reportedly the dominant polymorph in bacterial and algal celluloses, while cellulose I_β is predominant in higher plants, eg, cotton and wood (23,24). Cellulose I_α is metastable, irreversibly converted to cellulose I_β by annealing in dilute alkali at high temperature (25). Electron diffraction studies have shown that cellulose I_α is a 1-chain, triclinic (P1) unit cell structure ($a = 6.74$ Å, $b = 5.93$ Å, and c (fiber axis) $= 10.36$ Å; $\alpha = 117^\circ$, $\beta = 113^\circ$, $\gamma = 81^\circ$) while cellulose I_β is a two chain monoclinic (P21) unit cell ($a = 7.85$ Å, $b = 8.17$ Å, c (fiber axis) $= 10.36$ Å; $\gamma = 97.3^\circ$) (25). Native cellulose has a parallel chain orientation (26,27). In the presence of alkali (mercerization) or via regeneration from solution, both cellulose I_α or I_β are transformed into an antiparallel cellulose II (22,28–33). The basic unit-cell structure of cellulose II is monoclinic consisting of two cellulose chains with a P21 space group: $a = 9.08$ Å, $b = 7.92$ Å, $c = 10.36$ Å (fiber axis), $\gamma = 117.1^\circ$. Although quite similar to I_β in unit cell dimensions, Cellulose II has a slightly larger b-lattice plane distance, 9.04 versus 8.17 Å, respectively. The hydrogen bonding in cellulose II is more complicated than cellulose I, with higher intermolecular cross-linking. Unlike cellulose I, the hydrogen bonding of the center and corner chains of the unit cell of cellulose II are not equivalent. The center chain of cellulose II forms sheets very similar to cellulose I with two intramolecular hydrogen bonds and an intermolecular hydrogen bond between the $O_6{-}H{-}O_3$ to the next chain within the same lattice plane (020). However, in the corner chain the C_6 hydroxymethyl group is in the *gt* position and forms two intermolecular hydrogen bonds, one within the same 020 plane ($O_6{-}H{-}O_2$) and the other between $O_2{-}H{-}O_{2'}$ along the diagonal in the 110 plane.

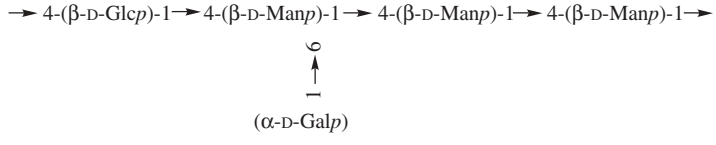
Native cellulose can also be converted to other polymorphs, eg, cellulose III, IV, with various treatment conditions. Crystalline modification to cellulose III is obtained by treating either cellulose I or cellulose II with liquid ammonia at low temperature and subsequently recrystallizing the preparation by evaporation of the ammonia. Cellulose III is a monoclinic unit cell, $a = 9.9$ Å, $b = 7.74$ Å, $c = 10.3$ Å (fiber axis), $\gamma = 122^\circ$, with small differences in lattice dimension existing between cellulose III_I and III_{II}. Cellulose IV is obtained by treating the various polymorphs in a suitable liquid at high temperature under tension, the average lattice spacing is $a = 7.9$ Å, $b = 8.11$ Å, $c = 10.3$ Å (fiber axis), $\gamma = 90^\circ$.

Hemicellulose. Hemicelluloses are typically defined as nonpectic polymers that make up the cell wall. A generally simplistic term, hemicelluloses are typically defined as the material that can be extracted from the cell wall by alkali. However, others refer to hemicelluloses as cell wall polymers with a particular type of molecular structure and a function within the cell wall. Hemicelluloses are heteropolysaccharides that interlock the cellulose scaffold through hydrogen bonding; hemicelluloses are cross-linking glycans. Depending on the

species of plant, the structure of the hemicelluloses will vary as will their abundance. Hemicelluloses are principally made up of hexoses, pentoses, deoxyhexoses, and small amounts of uronic acids (Fig. 4).

The most prevalent sugar moieties are β-D-glucopyranose (β-D-Glc*p*), β-D-mannopyranose (β-D-Man*p*), and β-D-xylopyranose (β-D-Xyl*p*), which constitute the backbone structure of glucomannans and xylans, respectively, while various other monosaccharides make up the short branches or side chains (34–38). Hemicelluloses are amorphous heteropolymers with low degrees of polymerization (DP∼100–200).

Hemicelluloses in Softwood. In softwoods, the primary hemicellulose components are galactoglucomannans (**2**) and arabinoglucuronoxylans (**3**). They are a heteropolysaccharides with heterolinkages. The glucomannans constitute as much as 15–20% of the dry wood mass. It has a backbone chain consisting of D-glucopyranose and D-mannopyranose residues linked via β(1-4) glycosidic bonds. The ratio of Glc*p* to Man*p* residues is ∼1 to 3, randomly orientated with the Man*p* residues partially acetylated at the C_2 and C_3 hydroxyl groups (1 acetyl group per 3-4 Man*p*). The glucomannan backbone carries short branches consisting of D-galactopyranose (α-D-Gal*p*) residues attached to 2–4% of the Man*p* residues by α(1-6) linkages. The other main constituent, arabino-4-*O*-methylglucuronoxylan, has a β-D-xylopyranose (β-D-Xyl*p*) backbone with β(1-4) linkages. Again the backbone carries short side chains consisting of α-L-arabinofuranose (α-L-Ara*f*), 4-*O*-methyl-α-D-glucuronic acid (4-*O*-Me-α-D-Glc*p*A). The 4-*O*-Me-α-D-Glc*p*A residues are linked via α(1-2) linkages to the xylan backbone, while the α-L-Ara*f* are linked α(1-3). The ratio of α-L-Ara*f* to 4-*O*-Me-α-D-Glc*p*A to β-D-Xyl*p* residues is 1:2:8.



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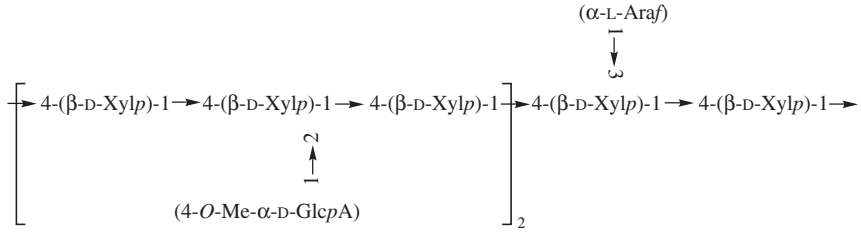
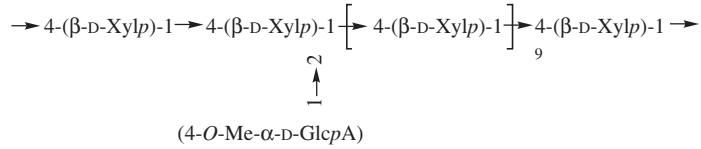


(3)

Hemicelluloses in Hardwood. Hardwoods contain hemicellulose polymers that are structurally similar to those found in softwoods. However, the principal hemicellulose polymer is a 4-*O*-methylglucuronoxylan (**4**) accompanied by a lesser amount of glucomannans (**5**). This is in contrast to softwoods wherein the glucomannans are the major hemicellulose and xylans are the minor compo-

nents. As with the galactoglucomannans in softwoods, the xylans in hardwoods are partially acetylated along the β-D-Xyl*p* backbone at the C_2 and/or C_3 hydroxyl groups. The acetyl content varies and is in the range of 8–17% of the total xylan, corresponding to ~3.5–7 acetyl groups per 10 xylose residues. The glucuronoxylans make up between 20–30% of the dry wood mass and are structurally very similar to those in softwoods, but contain much fewer 4-*O*-Me-α-D-Glc*p*A residues, 2-3 units per xylan polymer. In addition, xylans contain small amounts of L-rhamnose (α-L-Rha*p*) and β-D-galacturonic acid (β-D-Gal*p*A), wherein the reducing end is reportedly →4-(β-D-Xyl*p*)-1→3-(α-L-Rha*p*)-1→2-(α-D-Gal*p*A)-1→4-(β-D-Xyl*p*). The glucomannans also differ between hardwoods and softwoods. Hardwood glucomannans are linear heteropolymers with homolinkages, β(1-4), no branching (α-D-Gal*p*) residues, and the ratio of mannose to glucose is 2.



(4)

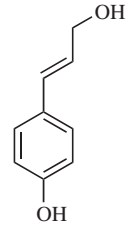
(5)

Hemicelluloses in Nonwoods. By contrast to both softwoods and hardwoods, hemicellulose from nonwood or agro-based crops consist predominately of xylans. The nonwood xylans have β(1-4) linked D-xylan backbones with a large variety of short side chains or branches. In addition to the 4-*O*-Me-α-D-Glc*p*A and α-L-Ara*f* residues that are attached to the xylan backbone, respectively, other monosaccharides are also link via α-linkages, Figure 5.

Lignin. Lignin is arguably the second most abundant biopolymer behind cellulose. The word lignin is derived from the Latin *lignum* meaning wood, and while it is not the major component of wood, it nonetheless serves an essential function in the cell wall of all vascular plants (39–41). Lignin provides mechanical strength and structural support. It prevents the permeation of water across the cell wall, thus facilitating conduction of water and nutrients, and plays a role in protecting plants against pathogens (39).

Lignins are complex racemic aromatic heteropolymers derived primarily from *p*-hydroxycinnamyl alcohol units: (42–45) *p*-coumaryl (**6**), coniferyl (**7**) and sinapyl (**8**) alcohols. Although interesting details regarding the biosynthetic pathways to these monolignols continue to be uncovered, and significant revisions continue to appear the pathway is relatively well characterized (46–51). Incorporation of these monolignols into the lignin polymer leads to *p*-hydroxyphenyl **H**, guaiacyl **G**, and syringyl **S** phenyl propanoid units, respectively. The amount and composition of lignins vary among taxa, cell types, and individual cell wall layers and are influenced by developmental and environmental cues (52). Although exceptions exist, dicotyledonous angiosperm

(hardwood) lignins consist principally of **G** and **S** units and traces of **H** units, whereas gymnosperm (softwood) lignins are composed mostly of **G** units with low levels of **H** units.



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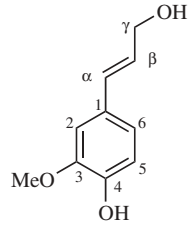

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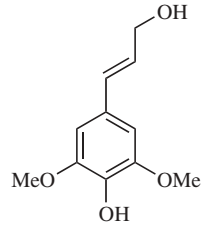


(8)

Lignification is the process by which monolignols are linked together via "random" radical coupling reactions (42,46,53). Although not statistically random, the process is essentially "combinatorial", ie, all of the various possible coupling modes are available, but are not equally probable (50,54). The actual polymerization step is controlled as in any chemical reaction by normal chemical concerns: coupling and cross-coupling propensities, reactant concentrations, the matrix, and conditions (46). The currently accepted theory is that the lignin macromolecule is formed by phenolic coupling reactions, via radicals generated by peroxidase-H_2O_2, where monolignol radicals react endwise with radicals on the growing polymer chain (41–45,49,50,53,55). Branching reactions are also prevalent, and important to the structure and properties of lignin. Branching occurs when two adjacent growing ends, ie, phenolic ends, of the lignin macromolecule undergo radical coupling. As a result, the actual structure of

the lignin macromolecule is not absolutely defined or determined, making the probability of two lignin macromolecules being identical extremely low.

Lignins are characterized by certain prominent interunit linkages, Fig. 6**a**. These linkages arise primarily from monomer–oligomer or oligomer–oligomer coupling reactions (monomer–monomer reactions likely occur, but are much less frequent and much less important), Fig. 6**b**. As has been well reviewed (39,41,45,46) lignins are characterized by certain prominent interunit linkages, Table 7. The main linkages are β-*O*-4 and β-5 (mainly from monomer–oligomer couplings), 5-5 and 4-*O*-5 (from oligomer–oligomer couplings), and β-β and β-1 couplings. The 5-5 and 4-*O*-5 structures are of particular importance as they represent branch points in the lignin macromolecule. Recently, new findings into the structure of 5-5 units has shown that the majority of these interunit linkages exist as dibenzodioxocin structures [5-5/β-*O*-4(α-*O*-4)] (56). These cross-coupling reactions to the growing polymer extend the complex three-dimensional lignin network. However, such reactions are radical quenching or termination steps, meaning each extension of the polymer network requires new radicals on each of the two coupling components. Radicals on the growing lignin polymer are thought to be generated by radical transfer from monolignols or other intermediaries (50), ie, the monolignols may act as the radical shuttles. When a monolignol radical encounters a polymer radical, it may cross-couple with it, but when the polymer is not electron-deficient, radical transfer may occur and the monolignol will diffuse back to the peroxidase/laccase to be reoxidized. Alternatively, redox shuttles, such as an Mn^{2+}/Mn^{3+} system (57), may be involved.

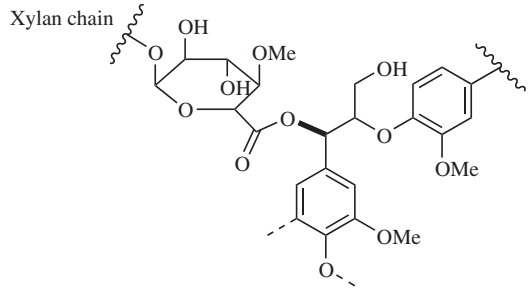
Lignin deposition is one of the final stages of wood cell wall development and proceeds in different phases, each preceded by the deposition of carbohydrates (58). Lignification starts at the cell corners in the region of the middle lamella and the primary wall when the formation of the outer (S1) layer of the secondary wall has started. It proceeds into the secondary wall only after the formation of the polysaccharide matrix of the middle (S2) layer of the secondary wall is completed. Lignification of the bulk of the cell wall (S2) follows cellulose and hemicellulose deposition in the S3 (inner) layer (58–60). In general, lignin concentration is highest in the middle lamella and cell corners, but the highest lignin content is found in the secondary wall (it occupies the largest portion of the cell wall). Lignin composition and amount are also influenced by environmental conditions, eg, reaction wood. The secondary cell walls of angiosperm tension wood are characterized by the presence of an unlignified gelatinous layer, which is composed of highly crystalline cellulose. Tension wood has higher cellulose content and lower lignin content than the corresponding normal wood. By contrast, compression wood in gymnosperms is highly lignified as compared to the rest of the secondary wall (60,61).

In addition to differences in lignin deposition within the cell wall, monolignol incorporation (**H** vs. **G** vs. **S**) also varies with cell wall development (60,62). Typically **H** units are deposited first, followed by **G** units, and ultimately **S** units, with the amounts of **S** units being obviously larger in angiosperms that gymnosperms. The **H** units are incorporated predominately into the cell corners and middle lamella, and are not present to a large extent in the secondary wall. Vessels are lignified earlier than fiber walls and contain larger amounts of **H** and **G** units than fibers (58) while ray parenchyma (63) the lignin is typically

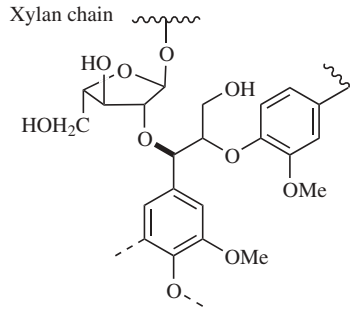
enriched in **S** units. The difference in timing of monolignol deposition is also associated with variations in lignin condensation in the individual cell wall layers (39).

Lignin deposition is influenced by the chemical nature of the carbohydrate matrix and the orientation of the cellulose microfibrils. In the middle lamella and the primary wall, lignin forms spherical structures, whereas in the secondary wall, lignin forms lamellae that follow the orientation of the microfibrils (60,64,65). During deposition, lignin forms chemical bonds with the polysaccharide components in the wall; this process leads to the gradual elimination of water and the formation of a hydrophobic environment. It has been postulated that lignin deposition, and the relative incorporation of the different monolignols are spatially and temporally regulated (46). Although the mechanisms controlling this process are not yet fully resolved, the process clearly involves the interplay between the expression of monolignol biosynthetic genes, the kinetics of monolignol delivery to the cell wall, and the chemistry of monolignol coupling to the growing polymer in the complex macromolecular environment of the cell wall.

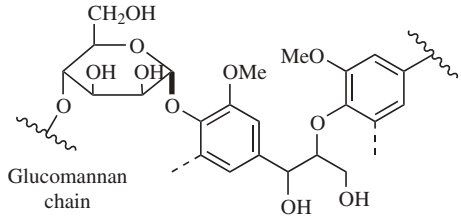
Lignin–Carbohydrate Linkages. The close association between lignin and carbohydrate components in wood strongly suggests the existence of chemical linkages between these constituents. Physical and chemical interactions (ie, hydrogen bonds, van der Waals forces, and chemical bonding) between lignin and carbohydrates (LC bonds) have been proposed to exist in wood (66–69) and pulp (70–73), however, ambiguity in the types, frequencies, and quantity exist. The nature of the different lignin–carbohydrate bonds is very complex and not completely understood. It is generally accepted that lignin is chemically linked with at least part of the hemicelluloses, but may also be in fact chemically linked directly to cellulose. Three main types of native LC bonds have been suggested in the literature, namely, benzyl esters (**9**), benzyl ethers (**10**), and phenyl glycosides (**11**), (4). Lignin carbohydrate linkages involve the hemicellulose side groups (L-arabinose, D-galactose, and 4-*O*-methyl-D-glucuronic acid), as well as end group of the hemicellulose chains (D-xylose in xylans and D-mannose/D-glucose in glucomannans). This is likely attributed to their sterically favored positions and to the fact that the polysaccharide matrix is already in place as lignin deposition occurs (see above).



(**9**)



(**10**)



(**11**)

Based on the mechanism of lignification and polymerization of the lignin macromolecule, the α-carbon (benzylic carbon) of the phenyl propanoid units is the most probable connection point between lignin and the polysaccharide macromolecules. During cross-coupling reactions and extension of the complex three-dimensional lignin network, incoming monolignol radicals couple preferentially via β-interunit linkages, ie, β-*O*-4 bonds. An important aspect of this cross-coupling is the postcoupling rearomatization reactions. The β-ether units that arise from β-*O*-4-coupling (of a monolignol with an oligomer), lead to the intermediary quinonemethide (Fig. 7). Depending on the chemical and physical environment in which the quinonemethide is generated, LC bonds can arise via nucleophillic addition. The resultant β-ether α-LC structure has two distinct, chemically different, isomeric forms, commonly referred to as *erythro*- and *threo*-isomers. Each of these isomers has different physical properties and dictates different spatial constraints on the resultant polymer. The formation of LC ether linkages are considerably more stable than those of glucosides, and constitute one of the primary reactions leading to a stable cross-link between lignin and the plant polysaccharides. Indications are that lignin in the middle lamella and primary wall is associated with pectic polysaccharides (galactan and arbinan) through ether linkages. In these cases, the primary alcohol, C_6 in D-galactose and C_5 in L-arabinose, seem to participate in the cross-linking (59).

Although the most prevalent of the LC linkages are the ether-type, ester bonds are also involved in the attachment of lignin to the cell wall polysaccharides, particularly in plants and grasses (74,75). Similarly, glucosidic linkages have been reported between lignin and polysaccharides (76). The LC linkage results via the reaction of the reducing end group of a polysaccharide chain and the phenolic hydroxyl group of the lignin macromolecule.

Extractives. Extractives constitute only a minor component in wood (Table 4), but comprise an extraordinarily large and diverse number of compounds (1,77,78). Extractives are nonstructural wood constituents that are primarily low molecular mass and are generally classified as either hydrophilic (water soluble) or lipophilic (organic solvent soluble). They are formed through secondary metabolism and their composition varies depending on species, environmental conditions and external stimuli. Extractives have been classified based on physiological, chemical, or utilization classes; however, it is chemical classification that is most generally used (1). Accordingly, extractives are generally classified as terpenoids and steroids (monoterpenes, diterpenes, or resin acids, triterpenes, etc), fats and waxes, and phenolics (lignans, flavanoids, stilbenes, tannins, etc) (79–82).

Extractives are biologically important to the survival of the tree (1). They are formed in response to mechanical damage, insect and fungi attack. Extractives are also of significant commercial importance. They constitute a valuable raw material for the production of organic chemicals, in fact terpenes and "tall oil" (resin acids and fatty acids collected as soap skimmings from pulping liquor) are important by-products of pulping and papermaking processes (83,84).

3. Nonwood Fibers

Wood is the dominant pulp fiber source worldwide, occupying $> 90\%$ of the total global capacity. Fibers from plant sources other than wood have been used in papermaking throughout human history for thousands of years. Almost every type of plant fiber has been used in making paper. The main reasons for the world's current increased use of nonwood plant fibers in paper production are (*1*) rapid growth of the paper industry. The Technical Association of the Pulp and Paper Industry (TAPPI) projected that annual global consumption of paper will reach 400 million tons by 2010, up from 300 millions tons in 1997 (85); (*2*) wood fiber shortage. With the increase in population, the demand for mechanical and structural wood keeps increasing. The use of nonwood fibers will greatly reduce the need for nonsustainable cutting. For example, in China and India, where forest resources are limited, nonwood fibers are the dominant fiber source for papermaking; (*3*) environmental pressure. Most nonwood fibers are from agriculture residues. Using agriculture residues in papermaking will help reduce waste management problems for farmers, eliminate the burning of agriculture residues in the field, thereby reducing air pollution and emission of greenhouse gases. Nonwoods contain less lignin and nonwood fibers are naturally brighter than those of wood fibers. This results in less chemical and energy demands for pulping and bleaching, and less solid, liquid, and gas emissions. Industrial residues, eg, rags from textile production, though limited in volume, would clearly have a positive environmental aspect as compared to wood; (*4*) economic aspects. The use of nonwood fibers for papermaking will add value to farm crops. In regions where tree plantations do not exist or are not economically viable, growing fiber-dedicated annual crops for papermaking (hemp, kenaf) may provide an economic alternative.

3.1. Major Sources. There are a huge variety of nonwood, agro-based fibers that can be used for paper production. These include agricultural residues, nonwoody annual fiber crops (including by-product residues) and uncultivated natural fiber plants (Table 8). For sustainable commercial development, a long-term guaranteed supply of raw materials is necessary. Table 8 lists the rough estimate of potential nonwood fiber resources in the United States and worldwide. However, due to the costs of harvesting, storage, and shipping, the most economically viable source of nonwood fibers is residues from crop processing centers, eg, sugar cane bagasse and cotton linters.

3.2. Nonwood Fiber Characteristics and Chemical Composition. Compared to softwood and hardwood fibers, there are large differences in the physical and chemical characteristics of nonwood fibers. Most nonwood sources contain a wide variety of cell types and fibers. Nonwoody plants are usually described as either monocots, eg, cereal, sugarcane and corn, or dicots, such as flax, kenaf, and hemp. Both the dicots and monocots share the same cell types, but their composition and arrangement are different.

The stems of dicots mainly contain ground tissues and vascular tissues. There are three cell types in ground tissue: parenchyma, collenchyma, sclerenchyma. Parenchyma is the dominant cell type in ground tissue, with thin walls and large vacuoles. Its functions include storage, secretion and photosynthesis. Collenchyma is a supportive cell, with an elongated cell and thick primary wall. Sclerenchyma has a tough and thick cell wall with a rigid and lignified secondary cell wall. It consists of two cell types: fibers (long, slender supportive cells) and sclerids (short multishaped cells). As with wood cells the vascular tissues are comprised of xylem, phloem, and vascular cambium. The xylem is composed of tracheids and vessel cells. Vessel cells are large, open-ended cells used for conducting water and minerals. The phloem is composed of fibers, companion cells, and sieve tube cells, which are mainly for photosynthate conduction. The vascular cambium generates xylem to the inside and phloem to the outside and forms a complete ring. Generally, nonwoody dicots contain an inner core of short fibers and an outer layer of longer blast fibers.

Monocots share the same cell types as dicots, but the organization is different. In monocots, the vascular bundles (an organization of xylem to the inside and phloem to the outside) do not form a ring, but are scattered. The stem is supported by a layer of sclerenchyma in the cortex. Generally, fibers from nonwoody monocot stems have similar fiber lengths as hardwood fibers. However, they are more heterogeneous due to the large content of thin-walled cells, barrel-shaped parenchyma cells, and vessel and fine epidermal cells of different dimensions.

Fiber dimensions are very critical to determine the potential application of a given fiber for paper production. Compared to fibers from softwood and hardwood, nonwood fibers have a wide range of fiber lengths and fiber diameters (Table 9). Cereal straw and sugarcane bagasse are good sources for short fibers and readily available in large quantities. Separated kenaf bast and hemp bast are good sources for long fibers and can significantly increase the tensile and tear strength to paper due to their long fiber length.

Many factors affect the chemical composition of nonwood fibers, ie, type of plant, soil conditions, and growing conditions. Generally, nonwood fibers have lower lignin content and higher hemicellulose or pentosan content than wood

fibers. Stalk fibers, eg, cereal straw and sugarcane bagasse are close to hardwood fibers in chemical composition except high silica content. Long fibers (hemp, kenaf) are also close to hardwood fibers in chemical composition. However, their ash content is lower than that of stalk fibers. Table 10 lists the chemical composition of some common nonwood fibers.

Even though there are many possible nonwood fiber sources for papermaking, nonwood fibers will not take the dominant place of wood fibers in paper production. The use of agricultural residues and whole-stalk kenaf to make certain grades of pulps has potential from a technical, environmental, and economic perspective. However, other options are less promising. Even with agricultural residues, the high silica and hemicellulose content makes black liquor recovery difficult. Plantation farming of annual fiber-dedicated plants requires more fertilization per acre and better irrigation than for trees. Likewise, the costs associated with harvesting, collection, storage, and transportation are more than trees. Compounded on this is the fact that many nonwood fibers show inferior secondary fiber properties, affecting nonwood fiber recycling.

The utilization of nonwood fibers for papermaking will require a fundamental change in the industry's supply infrastructure. Currently, market conditions and demand–supply balance for pulp and wood make it difficult for a nonwood industry to development economically viable projects. The potential of nonwood fibers for paper production is still limited by site and grade.

4. Pretreatments of Lignocellulosics

The pretreatment of wood is of great importance for some pulping processes and pulp applications. Of primary concern is control or manipulation of extractives levels. This can be accomplished through mechanical, chemical, and biological treatments. For example, in the production of sulfite dissolving pulps wood is usually stored in the form of chips to reduce the "pitch problems". Extractive levels decrease rapidly with time, markedly faster in the form of chips than logs. Exposure to air facilitates evaporation and oxidation of extractives, as well as enabling fungal attack and enzymatic degradation. Extractive levels can also be reduced through mechanical fiber fractionation. As much of the resins are encapsulated within parenchyma cells extractives levels can be substantially reduced by removal of these cells.

5. Pulping

Pulping refers to the process wherein wood or other fibrous raw materials are reduced to a fibrous mass (88). It is accomplished by either mechanical, thermal, chemical or a combination of these treatments. Commercially, these treatments are classified as mechanical, chemical, or semichemical pulping. The most prevalent process is chemical pulping, which accounts for $> 70\%$ of the worldwide production of pulp, of which kraft pulping is the most prevalent (80%).

5.1. Mechanical Pulping. Mechanical pulping is a generic term given to a process in which fiber liberation is achieved by mechanical action (89–92).

Mechanical treatment disrupts the wood structure into fragments of varying dimensions. Up to 95% of the dry weight of wood is converted into pulp. As a result, mechanical pulps, which contain substantial amounts of lignin in the fibers, are stiff and woody in nature and easily discolored upon exposure to light (92). The mechanical pulping of wood chips rather than a block of wood, refiner mechanical pulp (RMP), results in more long fibers than stone groundwood, and subsequently stronger paper (93,94). Further enhancement in fiber properties and accepts can be achieved through pretreatment with steam (thermomechanical pulp, TMP) and/or chemicals (chemithermomechanical pulp, CTMP) (92,95).

Despite the high lignin content and stiff fibers, high yield mechanical pulps are desirable for many paper products (92). Mechanical pulps are composed mainly of fiber bundles and fragments, some whole fibers and high quantities of fines (93). Mechanical pulps have a small average particle length and because of the high lignin content do not pack closely together. The result is a network that is resistant to deformation through applied stress, regaining their shape upon release of external pressure. Mechanical pulps have high bulk, high opacity, low tensile strength and lack of durability. Although mechanical pulps have a high energy demand, they are relatively low in cost because of the high yield (92).

5.2. Steam Explosion. Steam explosion is an efficient physical processing method wherein wood is treated with the high pressure, saturated steam at a high temperature for a period of time (96). The wood, softened by the heat and moisture, is then rapidly decompressed resulting in defibrilization (97,98). The advantages of steam explosion are the ability to separate wood and nonwoody raw materials into its three relatively pure main components in relatively high yield. The disadvantages include that steam-treated products have to be washed to remove inhibitors and the products have relatively low bulk density. Initially, steam explosion was used to provide low cost fibers for wood fiber-polymer composites. Currently, it can be used to pretreat lignocellulosic residues to provide substrates for biofuels, to fractionate lignocellulosics to obtain hemicellulose and lignin by-products, to provide more reactive cellulose substrate for production of cellulose derivatives, and to lower the chemical energy usage and emission in later pulping stages (99–105).

Steam explosion is an effective way to liberate lignocellulosic components at a relatively low cost. Much of the hemicelluloses are hydrolyzed to monosugars, water-soluble oligomers and acetic and uronic acids during steam explosion, and a large amount of pentosans become soluble in water (106,107). Although only a small amount of lignin is solubilized during steam explosion, much of the water-insoluble residual lignin becomes extractable by 0.1 *M* aqueous alkali solution or by organic solvents. Depending on the severity of the stream explosion conditions mild to medium degradation of cellulose can occur (108,109). However, as substantial degradation of the hemicellulose and amorphous cellulose occurs, the crystallinity of cellulose generally is increased.

5.3. Chemical Pulping. Chemical pulping is a process in which the fiber liberation is achieved by lignin removal or "delignification", ie, to make lignin soluble in the cooking liquor (110). The dissolution of lignins is generally the result of increased hydrophilicity via the formation of hydrophilic groups and/

or degradation to low molecular weight fragments. Traditionally, chemical pulping has been performed in aqueous media, but recently organic solvent-based processes, eg, organosolv pulping, are attracting more and more attention (see below) particularly in biofuels applications (111).

The primary goal of chemical pulping is to selectively remove as much lignin as possible, especially from the middle lamella, without degrading the carbohydrate components and negatively effecting pulp properties. Therefore, the selectivity of delignification is determined by the weight ratio of lignin removal to carbohydrate removal. The degree of delignification is generally indicated by "kappa number" of the pulp, which is an index used by the pulp and paper industry to express the lignin content of a pulp (110). A high kappa number indicates high lignin content in the pulp. The kappa number of bleachable softwood and hardwood pulps is 30–40 and 18–20, respectively.

Depending on the pulping process different active chemicals are used. In general, chemical pulping can be classified as alkaline, acidic, or neutral pulping processes (110,112,113). The majority of chemical pulping is alkaline, in which kraft pulping dominates. The simplest alkaline pulping process is soda pulping; in which sodium hydroxide is the active chemical. The lignocellulosic materials are treated with aqueous sodium hydroxide solution at a temperature between 150 and 170°C. Since sodium hydroxide can attack both lignin and carbohydrates without much selectivity under soda pulping conditions, the selectivity of soda pulping is low (113). Currently, soda pulping is mainly used in preparing some nonwood fibers. To increase the selectivity of soda pulping and to keep the pulping process sulfur-free, many potential methods have been proposed. One intensively studied process is soda-anthraquinone (AQ) process. This process, as a catalyst, can significantly accelerate the delignification process, and at the same time stabilize the polysaccharide against alkaline hydrolysis (114,115). Under soda-AQ pulping conditions, AQ is reduced to anthrahydroquinone (AHQ) by a reducing end group of the polysaccharides. The reducing end group is oxidized to form a carboxylic acid group, which is stable under alkaline condition. Anthrahydroquinone can effectively cleave phenolic β-ether linkages in lignin and itself is oxidized to AQ. The cleaved lignin can be further degraded by NaOH. Due to the redox cycle of AQ-AHQ-AQ, as low as 0.01% AQ (based on the weight of dry wood) can effectively improve delignification. However, soda-AQ pulping processes cannot produce pulp with the properties and at a cost comparable to kraft pulp.

Kraft pulping is the dominant chemical pulping process (110). In North America $\sim 95\%$ of the chemical pulp is produced by the kraft process. This process utilizes an aqueous solution of sodium sulfide (Na_2S) and sodium hydroxide (NaOH), ie, "white liquor". The total amount of NaOH and Na_2S is defined as active alkali and the ratio of Na_2S to active alkali is defined as sulfidity. In a normal kraft process, the active alkali requirement is $\sim 15–20\%$ and the sulfidity is $\sim 25–35\%$. The lignocellulosic materials are treated with white liquor at a temperature between 150 and 175°C for a period of time. For wood chips, the dissolution of lignin can be divided into three stages. The first stage is "initial delignification", occurring at temperature < 140°C, characterized by lignin extraction and hemicellulose degradation. The second stage is "bulk delignification". The delignification rate is accelerated with increased temperature and

remains relatively high until ~90% lignin is removed. The last stage is "residual delignification". The rate of delignification is low and the degradation of polysaccharides becomes significant (116). Since hydrogen sulfide ions (HS^-) only react with lignin and degradation of carbohydrates is mainly affect by the strength of OH^- ions, the selectivity of kraft pulping is higher than that of soda pulping. Therefore, kraft pulping provides stronger pulps and higher yields than soda pulping.

Another prominent pulping process is sulfite pulping in which the active species are sulfur dioxide, hydrogen sulfite ions (HSO_3^-), and/or sulfite ions (SO_3^{2-}), depending on the pH of the pulping liquor (110,113,117). At pH ~4, HSO_3^- is the primary sulfur species. Above or below that pH value, the concentrations of SO_3^{2-} and SO_2 will increase. Different pH values in sulfite pulping are targeted for different types of pulps. The pH range of acid sulfite pulping is pH 1–2 and this process is mainly used for dissolving pulps due to the high removal ratio of cell corner lignin and hemicellulose. Bisulfite pulping is in the range of pH 2–6 and is mainly for chemical pulp. Neutral sulfite pulping, between pH 6–9 is mainly used for high yield pulps, as in chemimechanical pulping. Alkaline sulfite pulping is in the range of pH 9–13, usually used with AQ, and is mainly for chemical pulps. Although a once prominent pulping process, sulfite pulps have steadily been replaced by kraft pulps, due to their superior pulp strength, lower demand on wood species, established recovery of pulping chemicals, energy and by-products, and shorter pulping times. However, for certain applications sulfite pulps are still preferred. Sulfite pulps have higher brightness, higher yields at a given kappa, lower odor and lower investment costs as compared to kraft pulps.

Chemistry of Delignification. The delignification process in chemical pulping is very complicated, and depending on the make-up and pH of the pulping liquor, the reactions of lignin can vary (118–120). Not all lignin bonds are reactive. Some linkages, such as carbon–carbon bonds and diaryl ether linkages, are stable under both acid and alkaline conditions. Under alkaline conditions, eg, soda, kraft or alkaline sulfite processes, the main delignification process is the degradation of lignin to low molecular weight fragments (118,121,122). The main alkaline delignification reactions include cleavage of phenolic α-ethers; cleavage of phenolic β-ethers; cleavage of etherified phenolic β-ethers; demethylation; sulfonation; condensation.

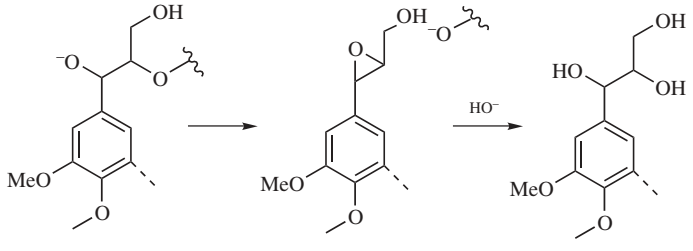
In acid pulping, eg, acid sulfite, the main delignification reactions are lignin hydrolysis and sulfonation (122). Condensation reactions are also very common and the frequency of condensation reactions is increased with the increase in acidity of the pulping liquor.

Reactions of Lignin under Alkaline Pulping Conditions. Lignin α- and β-aryl ether linkages in free phenolic structures are readily cleaved during the initial phase of delignification (Fig. 8) (121). Under alkaline conditions elimination of the α- substituent (hydroxide, alkoxide, or phenoxide ion) occurs with the formation of a quinonemethide intermediate (123,124). The subsequent reactions depend on the pulping process and the active ions present (125). In soda pulping, the reactive chemical is sodium hydroxide, which can lead to hydroxylation and subsequent oxirane formation and cleavage of the β-aryl ether bond (Fig. 8 center reaction), or elimination of the γ-hydroxymethyl group from the

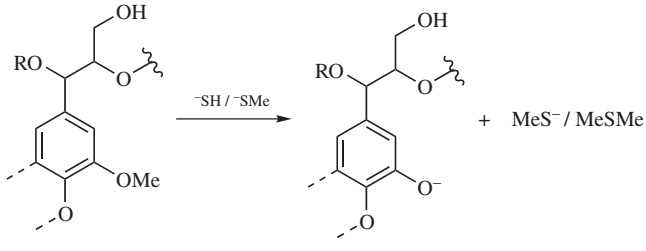
quinonemethide with formaldehyde generation and formation of a vinyl ether structure (Fig. 8 top reaction) (121). The latter reaction does not lead to cleavage of the β-aryl ether bond and is responsible for the poor delignification associates with soda pulping of softwoods.

In kraft pulping, hydrogen sulfide ions in addition to hydroxide ions are present to react with the quinonemethide intermediate (Fig. 8 bottom reaction) (126). Although a better nucleophile than hydroxide, it is the low pK_a of the corresponding thiol derivative that leads to cleavage of the β-aryl ether linkage with concurrent thiirane intermediate formation. Depending on the pulping temperature the thiirane can dimerize to a 1,4-dithiane structure (∼100°C) or decompose to form elemental sulfur and the corresponding styrene-type structure (∼170°C) (127,128).

Although the predominant reaction in alkaline pulping is with phenolic moieties, certain etherified phenolic units react during alkaline pulping. Etherified phenolic β-aryl ether linkages are cleaved analogous to the phenolic counterparts, but at a much slower rate (eq. 1) (129,130). Likewise, demethoxylation takes place during alkaline pulping, occurring more severely in kraft than soda pulping (eq. 2) (121). In softwoods, ∼10% of the methoxyl groups are eliminated during kraft pulping. The product, methyl mercaptan can further react with lignin to produce dimethyl mercaptan. Methyl mercaptan and dimethyl mercaptan are volatile malodorous compounds that contribute to the characteristic odor associated with kraft pulping.



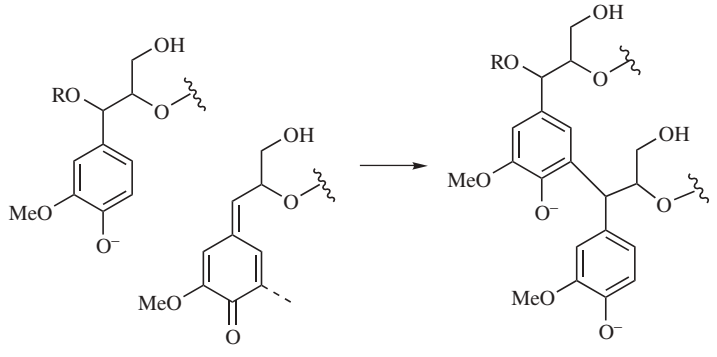
(1)



(2)

During alkaline pulping conditions a variety of condensation reactions can occur (121,131). One of the most prevalent condensation reactions occur between a phenolate anion and a quinonemethide intermediate, forming a new carbon–carbon (α-5) linkage (eq. 3). Likewise, condensation between phenolate anions can occur in the presence of elimination products, eg, formaldehyde (eq. 4) producing diarylmethane structures (132). As most condensation reactions occur at

the C-5 position of the aromatic ring, softwood lignin can be expected to be more prone to condensation reactions than hardwoods. As a result, condensation of lignin fragments leads to an increase in lignin molecular weight and reduces lignin solubility.



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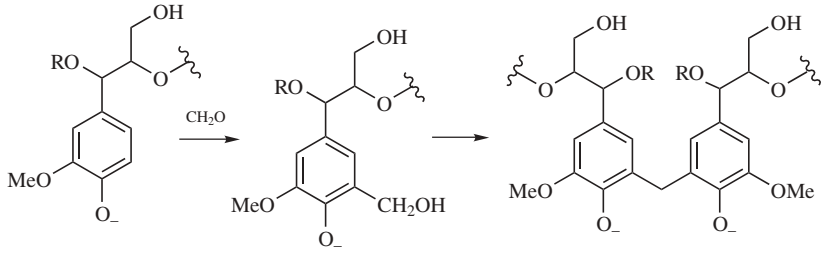
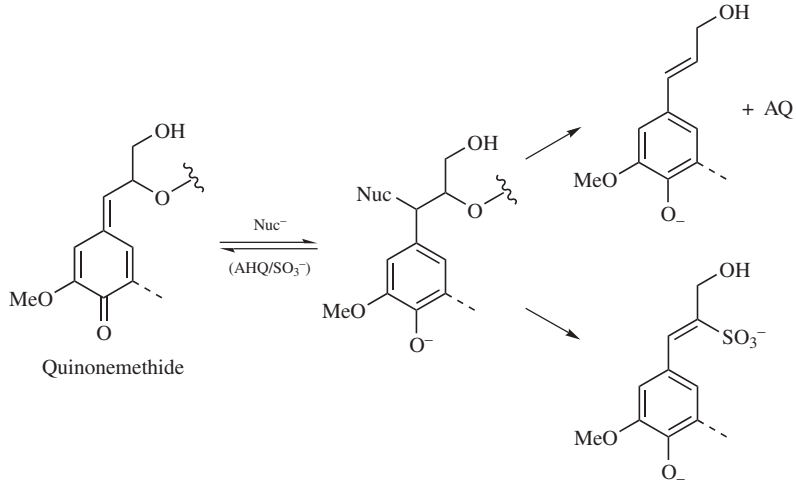


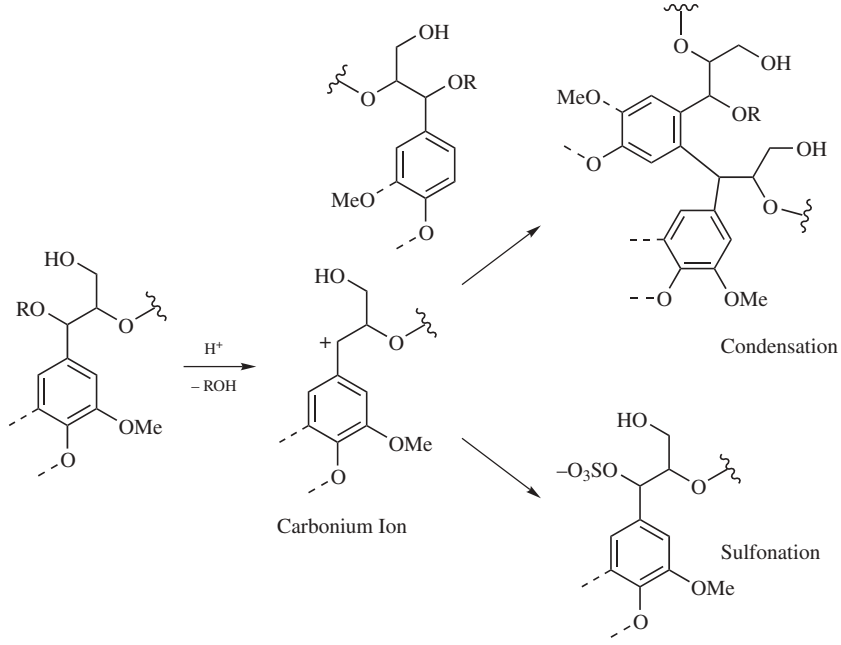
(4)

Analogous to kraft pulping, alkaline sulfite, and soda-AQ processes exhibit enhanced lignin degradation due to the addition of nucleophilic species, eg, SO_3^{2-} and anthrahydroquinone (AHQ) to the quinonemethide intermediate (eq. 5) (112,133).



(5)

Reactions of Lignin under Acid Pulping Conditions. Acid sulfite is the most common industrial acid pulping process (88,110,118,120). In acid sulfite pulping, α-hydroxyl, and α-ether groups are readily eliminated to form carbonium ion intermediates (eq. 6) and lignin fragmentation (α-aryl ethers) (122,134). The carbonium ions subsequently react with hydrated SO_2 and/or HSO_3^-, leading to sulfonation, or with other lignin fragments, via condensation to form carbon–carbon bonds. Under acidic conditions, α-substituted lignin moieties react regardless of whether they are phenolic or etherified phenolic structures (122). Sulfonation leads to increased hydrophilicity and solubility of the lignin, while condensation that is enhanced with decreasing pH leads to an increase in molecular weight and decrease in lignin solubility.



(6)

Reaction of Carbohydrates During Chemical Pulping. Depending on the processing conditions, the selectivity of delignification can vary greatly. Alkaline pulping generally has greater degradation of carbohydrate components than acid pulping (110). However, due to the high crystallinity of cellulose and high degree of polymerization the most significant losses are due to hemicelluloses. Under alkaline conditions, the main reactions of carbohydrates are peeling–stopping reactions that are responsible for pulp yield loss, and random hydrolysis, which decreases the molecular weight of cellulose, decreasing pulp strength and contributes to further losses in pulp yield (119,120,135). Under acid conditions, the most prominent reaction of carbohydrates is the cleavage of glycosidic bonds. As in alkaline pulping, the major carbohydrate degradation occurs with the hemicelluloses, with little loss in cellulose unless extreme acidic conditions are utilized (136,137).

Reaction of Carbohydrates under Alkaline Conditions. In alkaline pulping carbohydrate degradation occurs during the initial stage of pulping processing. The concentration of alkali is high and saponification of the acetate groups along the hemicellulose chain occurs (40–50°C). During the heating-up period the primary reaction is the peeling reaction (initiates at 60–70°C), or primary peeling which involves the successive elimination of monosaccharide units from the reducing end of the polysaccharide (Fig. 9). Primary peeling leads to the formation of a new reducing end unit and the corresponding isosaccharinic acid. This process repeats itself for several iterations until a stopping reaction occurs wherein the reducing end unit is converted to a nonreducing metasaccharinic acid moiety. The carboxylic group is stable to alkaline conditions and will not undergo further peeling reactions.

As pulping proceeds, the pH of the pulping liquor drops with increasing generation of acetic and isosaccharinic acids. The peeling and stopping reactions are highly dependent on pH, such that early in the cook (high pH, low temp) the rate of stopping reaction is greater than that of the peeling reaction. High alkali concentrations allow for benzyl-benzylic acid (BBA) rearrangement and hydroxide elimination to dominate over isomerization and β-elimination of the polysaccharide chain (Fig. 10). Increasing temperature results in increased reaction rates, such that for every 10°C increase in temperature the reaction rate doubles. At temperatures beyond 60–70°C the rate of peeling reaction is greater than that of the stopping reaction; with 50–60 monosaccharide units being eliminated until a stopping reaction occurs and terminates the degradation.

Although hemicelluloses are more readily degraded by primary peeling than cellulose, the structure of the hemicellulose can have an effect on the observed reaction rate. The presence of side groups along the hemicellulose backbone can prevent peeling/facilitate stopping. For example, xylans possess 4-*O*-methyl-D-glucuronic acid moieties at the C-2 position of the D-xylopyranose unit, thereby preventing the initial isomerization of the reducing end unit. Likewise, the L-arabinofuranose unit in softwood xylans (linked to the C-3 position of the D-xylopyranose) facilitates β-elimination (L-arabinofuranose) and metasaccharinic acid formation (119).

As temperature is further increased and the final pulping temperature, 160–170°C, is achieved there is sufficient thermal energy in the reaction system to facilitate ring distortion and internal nucleophilic substitution and glycosidic bond hydrolysis. The glycosidic linkages are randomly hydrolyzed, forming a new reducing end group, which can initiate new peeling reactions (secondary peeling) and further carbohydrate degradation (Fig. 11). As a result of random hydrolysis the molecular weight of polysaccharides is significantly reduced, and is a major contributor to the decrease in pulp physical properties.

Reaction of Carbohydrates under Acid Conditions. Under acid conditions, the primary reaction is acid catalyzed glycosidic bond hydrolysis. During acid pulping α-linked side-chain moieties, eg, galactosidic bonds in galactoglucomannans are rapidly hydrolyzed as are acetyl groups. Acid hydrolysis of glycosidic bonds proceed via an oxonium ion intermediate (Fig. 12). The sensitivity of the glycosidic linkages toward acid hydrolysis is dependent on the structure of the hemicellulose and the ability to form the oxonium ion intermediate. Galactosidic linkages in galactoglucomannan are completely hydrolyzed with glucoman-

nan are left in the pulp. In hardwoods, the highly uronic acid substituted xylans where in the substitute groups are completely hydrolyzed. Xylans with low side chain substitutions are retained in the pulp. Generally, for acid pulping, the hemicellulose yield for hardwoods is lower than that of softwoods.

Organosolv Pulping. Organic solvents have been used to separate wood into its constituent components for >100 years. Organic chemicals were first used to isolate and study lignin and carbohydrates (138–140). More recently organic solvent processing of wood has been investigated to try to overcome some of the short comings of traditional chemical pulping; poor selectivity, environmental impact, malodorous emissions, etc (141–143). Most recently, organosolv processing has been investigated in conjunction with biofuels production. Of the numerous organosolv methods investigated, few were able to produce pulps with properties comparable to those of kraft pulp (144–149). Most organosolv processes are based on the addition of an organic solvent to a conventional chemical process, eg, ASAM (alkaline-sulfite-AQ-methanol), OrganoCell (soda-AQ-methanol), or a nonconventional process, eg, Alcell (acid-catalyzed ALcohol-CELLulose), Acetosolv and Acetocell (acetic acid pulping), MILOX (peroxyformic acid).

In organosolv pulping, delignification follows similar reaction mechanisms to that of acid or alkaline chemical pulping. The most common reaction of carbohydrates is hemicellulose deacetylation and subsequent autohydrolysis. However, in acetic acid pulping acetylation of the hemicelluloses and amorphous cellulose regions occurs. In alkaline organosolv pulping, selectivity is enhanced as primary peeling is greatly suppressed due to the alkali–alcohol reaction medium. In the presence of sulfur compounds, eg, ASAM process, the selectivity of delignication is even further enhanced.

Compared to traditional chemical pulping processes, organosolv pulping has several advantages: (*1*) more lignin can be removed; (*2*) wood can be processed under mild conditions—free of strong acids or alkalis and low temperature; (*3*) reduction and/or elimination of sulfur-containing compound emissions; (*4*) a generally simplified chemical recovery system (as compared to kraft or sulfite processes); and (*5*) recovery of lignocellulosic chemical by-products. However, the quality of organosolv pulps is generally lower than that of kraft pulps, but is suitable for certain specialty applications. Due to the low extractive content, organosolv pulp is suitable for archival grade paper, and Alcell hardwood pulp, eg, can be used as dissolving pulp for viscose rayon. Perhaps one of the most promising applications of organosolv pulping is in the production of biofuels and the development of value-added coproducts. The relatively high purity of the chemical constituents is ideal for biofuels development and support the biorefinery concept.

6. Bleaching

Bleaching is a chemical process applied to chemical and mechanical pulps to primarily increase their brightness. However, bleaching also improves the cleanliness of pulp through removing extractives and other contaminants, and purity, for dissolving pulps through hemicellulose removal. Pulping, in particular kraft pulping, substantially increases the color of unbleached pulp. The increase in

color, or decrease in brightness, is primarily associated with the formation of certain light absorbing unsaturated structures or chromophores. In wood, native lignin is only slightly colored, but as a result of pulping reactions chromophoric groups; conjugated double bonds, complexed metal ions, and the like, are introduced into the residual lignin and lead to an increase in color. Residual lignin in alkaline pulps is more difficult to bleach than that of acid pulps, and that of softwoods is more difficult than hardwoods. To reach acceptable brightness levels, the residual lignin should either be removed from the pulp (lignin degrading bleaching) or freed of chromophoric groups (lignin preserving bleaching). Lignin-degrading bleaching is usually performed in several stages, called a bleaching sequence, and typically with chlorine- and/or oxygen-based chemicals (Table 11). By contrast, lignin-preserving bleaching is predominately a one or two stage process performed using hydrogen peroxide (H_2O_2) and/or sodium dithionite ($Na_2S_2O_4$).

To fully remove lignin from pulp multiple bleaching stages are required. In a typical bleaching process, individual bleaching stages are generally separated by washing stages to remove residual chemical and degraded lignin. Table 12 lists examples of typical bleaching sequences for softwood kraft and sulfite pulps. Each stage is optimized to contribute to the overall delignification and brightening of the pulp, and operated to obtain a maximum delignification/brightening without decreasing pulp strength (150). For chemical pulps, the bleaching sequence is generally divided into two parts. The initial stages of a bleaching sequence are delignification stages, eg, CE in CEDED sequences, while the latter are brightening stages (eg, DED). In the delignification stages, large amounts of lignin are removed, but little enhancement in brightness is achieved. The opposite is observed in the latter brightening stages where chromophoric groups are selectively removed and brightness levels are substantially increased.

6.1. Bleaching Chemistry. Pulps may be bleached by a variety of processes comprising various combinations of chemicals making it extremely difficult to fully characterize the reactions taking place. Compounded on this is the complex structure of residual lignin and the numerous oxidative species present in each of the individual bleaching stages. For example, most chlorine- and oxygen-containing bleaching chemicals give rise to a number of other oxidative species during reaction with lignin. Thus, comprehensive simplifications must be made if the individual bleaching reactions and their interrelations are to be studied in detail. This includes (*1*) the use of model compounds representing structural features assumed to be present in residual lignin, and (*2*) division of bleaching reactions into two categories with respect to the initial reacting species; electrophilic and nucleophilic (Table 13). Electrophilic reactions can be either ionic- or radical-based processes, whereas nucleophilic reactions are solely ionic. Table 13 lists various primary (eg, ClO_2, HO_2^-, O_2) and secondary (eg, $HO^\bullet$, $Cl^\bullet$) initial reacting bleaching species.

Depending on the bleaching stage, several initial reacting species can be present during the bleaching process. For example, during chlorine dioxide bleaching, numerous chlorine-based reagents are generated and consumed and include: $ClO_2^\bullet$, Cl_2, HOCl, $Cl^\bullet$. Likewise, in oxygen or hydrogen peroxide bleaching where in addition to molecular oxygen (O_2) or hydrogen peroxide (H_2O_2)

numerous oxygen-based radicals ($HO^{\bullet}$, $HO_2^{\bullet}$, $^{\bullet}O_2^{-}$) are formed as are a number of peroxides (ROO^{-}).

Electrophilic reactions, whether ionic (eg, Cl_2) or radical (eg, $ClO_2^{\bullet}$, $HO_2^{\bullet}$, O_2), preferentially attack electron-rich aromatic and olefinic structures by either two- or one-electron-transfer mechanisms (Fig. 13**a**) (151). By contrast, nucleophilic species preferentially attack electron deficient carbonyl and conjugated carbonyl structures (ie, coniferaldehyde and quinonemethide/quinine structures) (Fig. 13**b**). Although these structures do not exist to any large extent in native lignins, they due arise during pulping and preceding bleaching stages.

Reactions of Lignin During Bleaching. In the degradation of lignin during pulp bleaching, both electrophilic and nucleophilic reactions are utilized to enable complete removal of lignin. This typically involves acidic and alkali bleaching stages in which each process is designed to activate the lignin structure for the subsequent chemical treatment.

Electrophilic Substitution and Oxidation. Some of the most widely studied lignin bleaching reactions are those involving cationic electrophilic bleaching reagents, eg, Cl_2 and peroxy acids (CH_3CO_3H, H_2SO_5, H_2CO_3) (151). Although the reactions are highly dependent on residual lignin structure, the initial reaction step involves electrophilic aromatic substitution (Fig. 14). Depending on the position of substitution, subsequent reaction can lead to oxidation with concurrent dealkylation, or side-chain elimination. Electrophilic substitution ipso to the aromatic side chain (C1) can lead to lignin degradation via cleavage of the C1−Cα bond (pathway B); however, this can only occur if the side-chain structure is such that stabilization of the resulting cationic fragment occurs. Benzyl alcohol groups (α-OH), which make up a majority of the Cα substituent in residual lignin, are readily eliminated with formation of an aldehyde terminated side chain fragment (39). Likewise, electrophilic substitution ipso to the methoxyl group (pathway D) leads to oxidation of the aromatic unit to *o*-quinoid moieties, which in the case of etherified phenolic aromatic units involves cleavage of lignin interunit linkages (ie, α-*O*-4, β-*O*-4), and consequently lignin degradation. Substitution of an aromatic ring carbon that is not substituted (pathway A) does not immediately lead to lignin degradation. Depending on the bleaching agent, it can lead to chlorinated organic formation, in the case of elemental chlorine (150), or hydroxylation (peroxy acids) and "activation" of the aromatic ring to further electrophilic reaction (151,152).

In addition to cationic electrophilic reactions, radical initiated electrophilic reactions can also lead to lignin oxidation and degradation (151). The reaction mechanism typically proceeds through a charge-transfer complex (π-complex) and subsequent electron abstraction and formation of a cation radical intermediate (Fig. 15). Depending on the bleaching reagent or secondary radicals present, both etherified phenolic and/or phenolic lignin moieties react. Strong oxidants, eg, chlorine dioxide, hydroxyl, and chlorine radicals react with both phenolic and etherified phenolic units, while weaker oxidants like molecular oxygen, perhydroxyl, and superoxide anion radicals only react with phenolic structures.

The intermediate phenoxy or cyclohexadienonyl radical mesomers undergo homolytic rearrangement and side-chain cleavage (Fig. 16, pathway A) or radical coupling with a primary or secondary radical species (Fig. 16, pathway B or C). Coupling with a reactant radical leads to ring opening and formation of a muco-

nic acid derivative product. The formation of such structures enhances the hydrophilicity of lignin and contributes to the solubility in water and alkali. In the case of etherified phenolic moieties, this results in cleavage of lignin interunit linkages (ie, α-*O*-4, β-*O*-4) and consequently degradation of the lignin macromolecule. By contrast, oxidative coupling of two phenol-derived radicals (Fig. 16, pathway C) leads to the formation of biphenyl-type structures, and the formation of lignin interunit linkages. Although likely a minor reaction in residual lignin during bleaching, it may negate the desirable effect of lignin-degrading reactions.

Nucleophilic Substitution and Oxidation. Nucleophilic attack of electron-deficient carbonyl and conjugated carbonyl lignin moieties constitutes the initial step in lignin-preserving bleaching, and a secondary step in lignin degrading bleaching. In lignin degrading bleaching nucleophilic reactions play an important and complementary role to that of the electrophilic reactions. Electrophilic aromatic substitution reactions introduce numerous quinoid and carbonyl structures into the residual lignin structure (151,153). These structural moieties are stable to further electrophilic reaction, requiring nucleophilic reagents to be further degraded (154).

In the presence of nucleophiles, quinoid-type chromophoric structures are rapidly degraded to mono- and/or difunctional carboxylic acids (Fig. 17). *Ortho*- and *para*-quinoid rings are comprised of dual enone structures offering multiple sites for attack by nucleophiles like hydroperoxyl anion. Nucleophilic attack of one of the electron deficient carbon atoms in the quinoid ring is followed by either elimination and epoxide formation (initial scheme in Fig. 17) or ring closure to a dioxetane structure (in the case of perhydroxyl anion, lower pathway in Fig. 17) and subsequent ring opening to yield the final carboxylic acid products.

In addition to quinoid-type moities, α-carbinol and α-carbonyl structures are present in residual lignin (153). In the degradation of aryl-α-carbonyl structures, both free and etherified phenolic hydroxyl compounds undergo oxidation by nucleophiles, eg, alkaline hydrogen peroxide (152,154). The initial step is nucleophilic attack at the α-carbonyl carbon. In the presence of a free-phenolic hydroxyl group, the reaction proceeds by way of the Dakin reaction. This reaction involves, as a rate-determining step, the formation of an intermediate epoxide, which under alkaline conditions is rapidly hydrolyzed accompanied by cleavage of the C_1-C_α bond [Fig. 18, pathway A (**a**)]. In the absence of a free-phenolic hydroxyl group, the initially formed addition product is precluded from undergoing the Dakin reaction. In the case of peroxide bleaching, the hydroperoxide addition product undergoes intramolecular nucleophilic attack leading to the formation of a new phenolic hydroxyl group and a dioxetane intermediate. This unstable intermediate subsequently decomposes to the corresponding benzaldehyde, which is susceptible to further oxidation. Free-phenolic moieties react an order of magnitude faster than the etherified counterpart (152).

For α-carbinol structures, whether β-aryl ethers, β-1 or β-5 diols, only free-phenolic lignin moieties react with nucleophiles in alkaline conditions, even at extreme reaction conditions. The reaction proceeds by way of a quinonemethide intermediate followed by the Dakin-like reaction. In this reaction, the quinonemethide intermediate rapidly reacts with the nucleophile, hydroperoxyl anion to produce the corresponding hydroperoxide. It then rearranges in a Dakin

reaction-like fashion, resulting in the cleavage of the C_1-C_α bond. Compared to the Dakin reaction, the Dakin-like reaction is extremely slow and does not occur at any appreciable rate at temperatures below 50°C (152). Although the predominant reaction of α-carbinol containing phenolic compounds is the Dakin-like reaction, numerous investigators have reported that the oxidation to the corresponding α-carbonyl compound also takes place (155). However, in the absence of peroxide decomposition, this oxidation does not occur, even at extreme temperatures (156).

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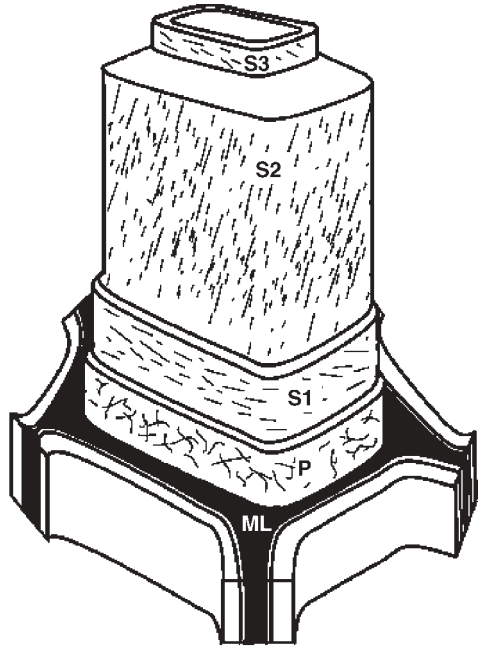

Fig. 1. Simplified structure of a wood cell wall, showing the middle lamella (ML), the primary wall (P), the outer (S1), middle (S2), and inner (S3) layers of the secondary cell wall (2).

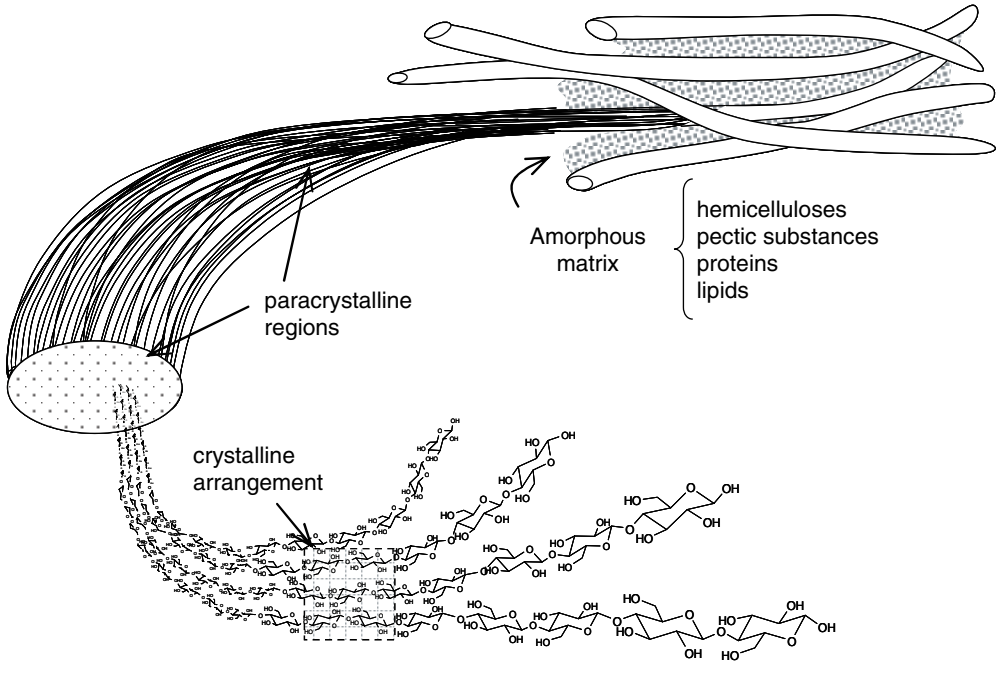

Fig. 2. Arrangement of cellulose chains within a microfibril (7).

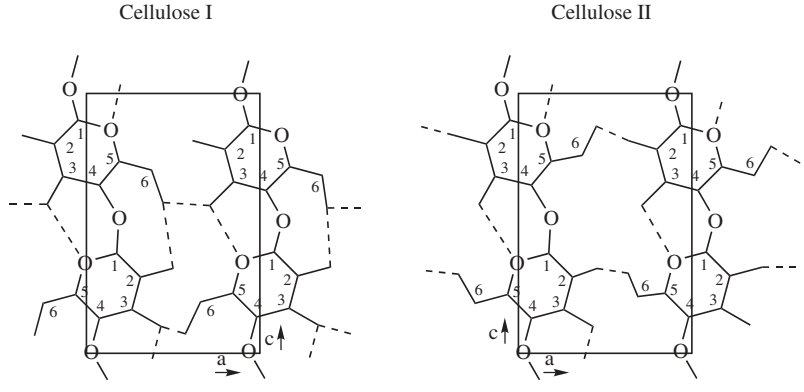

Fig. 3. Intra- and intermolecular hydrogen bonding in cellulose I and cellulose II. Cellulose I: intramolecular hydrogen bonding between O_3-H-O_5 and O_2-H-O_6, and Intermolecular hydrogen bonding between O_6-H-O_3 within the same lattice plane (020). Cellulose II: center chain same as cellulose I; corner chain O_3-H-O_5 intramolecular hydrogen bond and O_2-H-O_6 intermolecular hydrogen bond (020 plane), and $O_2-H-O_{2'}$ intermolecular hydrogen bond along the diagonal in the 110 plane (not shown). Hydrogen bonds are represented by dashed lines.

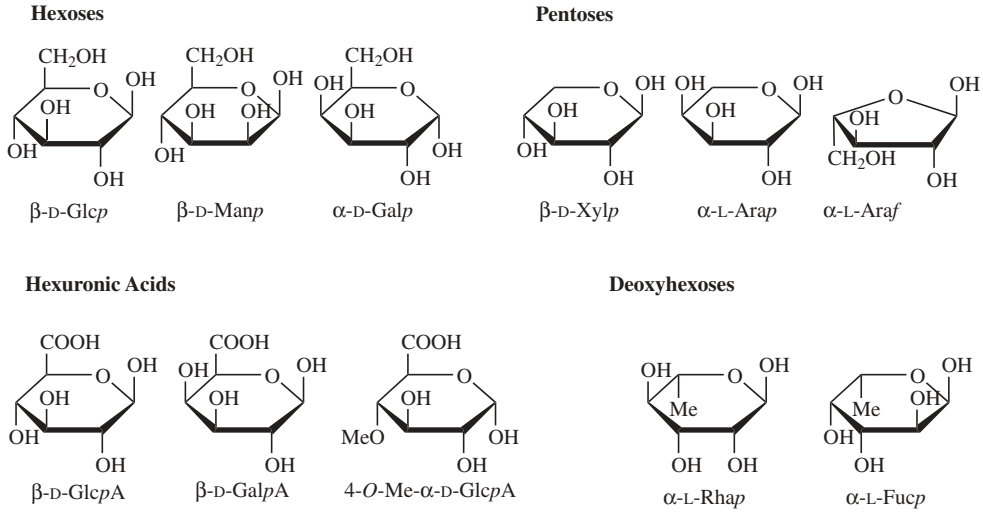

Fig. 4. The sugar moieties of wood hemicelluloses: β-D-glucopyranose (β-D-Glc*p*), β-D-mannopyranose (β-D-Man*p*), α-D-galactopyranose (α-D-Gal*p*), β-D-xylopyranose (β-D-Xyl*p*), α-L-arabinopyranose (α-L-Ara*p*), α-L-arabinofuranose (α-L-Ara*f*), 4-*O*-methyl-α-D-glucuronic acid (4-*O*-Me-α-D-Glc*p*A), β-D-galacturonic acid (β-D-Gal*p*A), α-L-rhamnopyranose (α-L-Rha*p*), α-L-Fucopyranose (α-L-Fuc*p*).

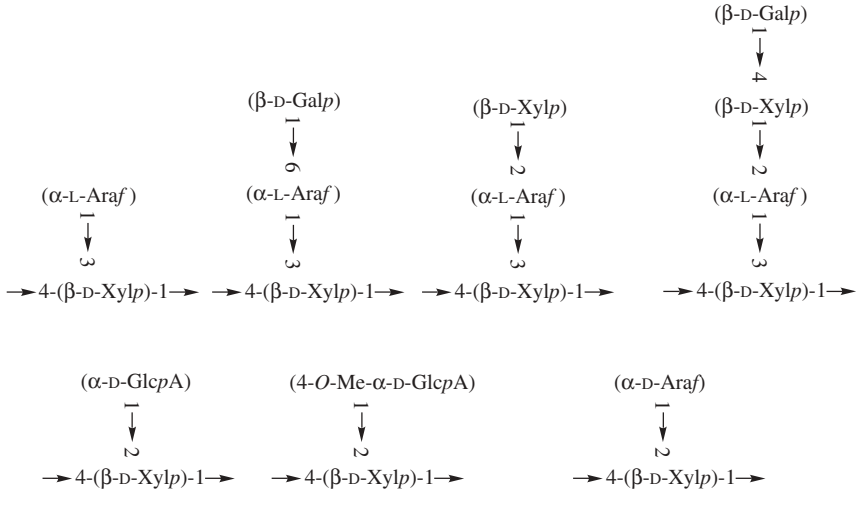

Fig. 5. Structural representation of the various side chains present in xylans from non-woods.

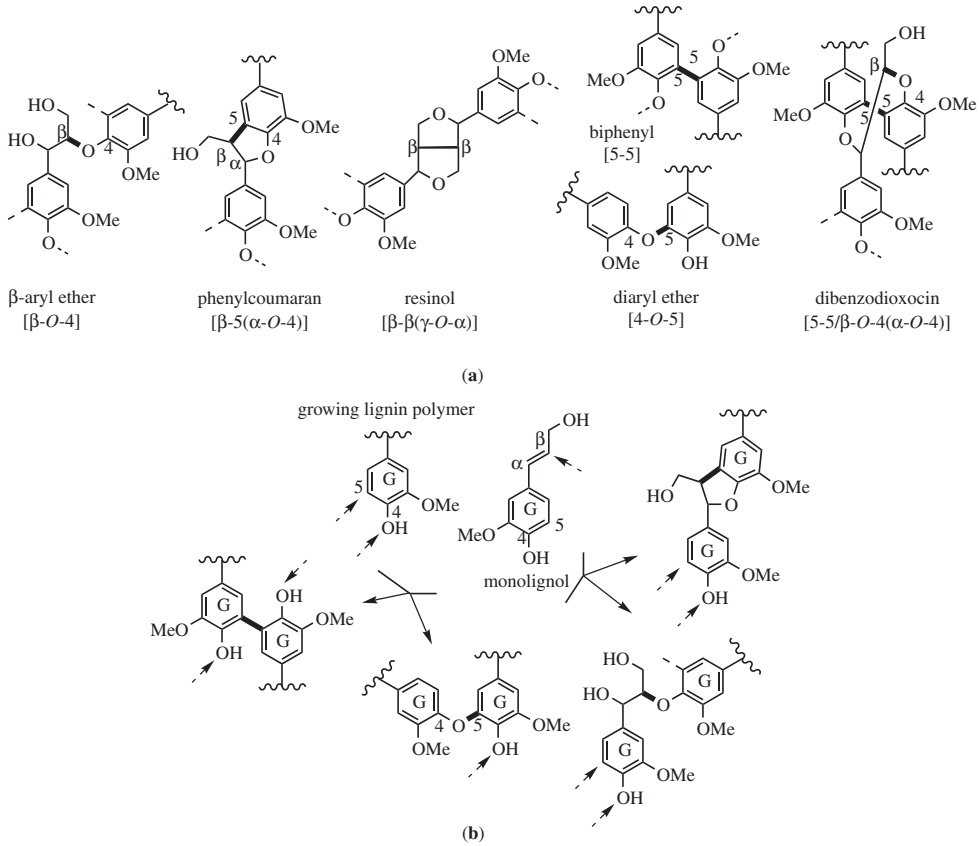

Fig. 6. Lignification. (**a**) Major structural units in lignin; bold lines represent the bonds formed during radical coupling reactions. (**b**) Lignification scheme for **G** lignin; potential reaction sites between monomer and oligomer (right) and between oligomers (left). Sites of further coupling reactions during lignification are indicated by dashed arrows. For **G**-polymer units cross-coupling only affords β-*O*-4 or β-5 structures. In **S** lignin (not shown) elevated β-*O*-4 structures are present due to the syringyl phenyl propanoid units (45).

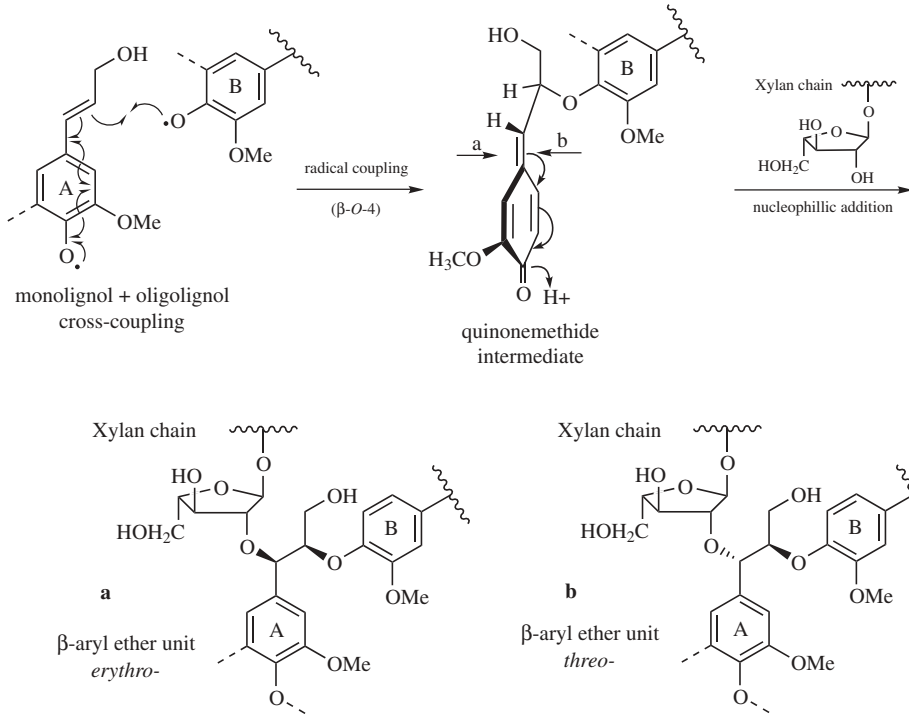

Fig. 7. Lignin–carbohydrate bond formation. Any coupling reaction of a hydroxycinnamyl alcohol at its favored β-position produces a quinonemethide intermediate. Nucleophillic addition can occur from either face of the planar quinonemethide intermediate, producing two possible isomers, (**a**) the threo- (or anti-) and (**b**) the erythro- (or syn-) isomers. The stereochemical preference is dictated by the **G**- / **S**- nature of the rings, but primarily influenced by the nature of the **B**-ring (46).

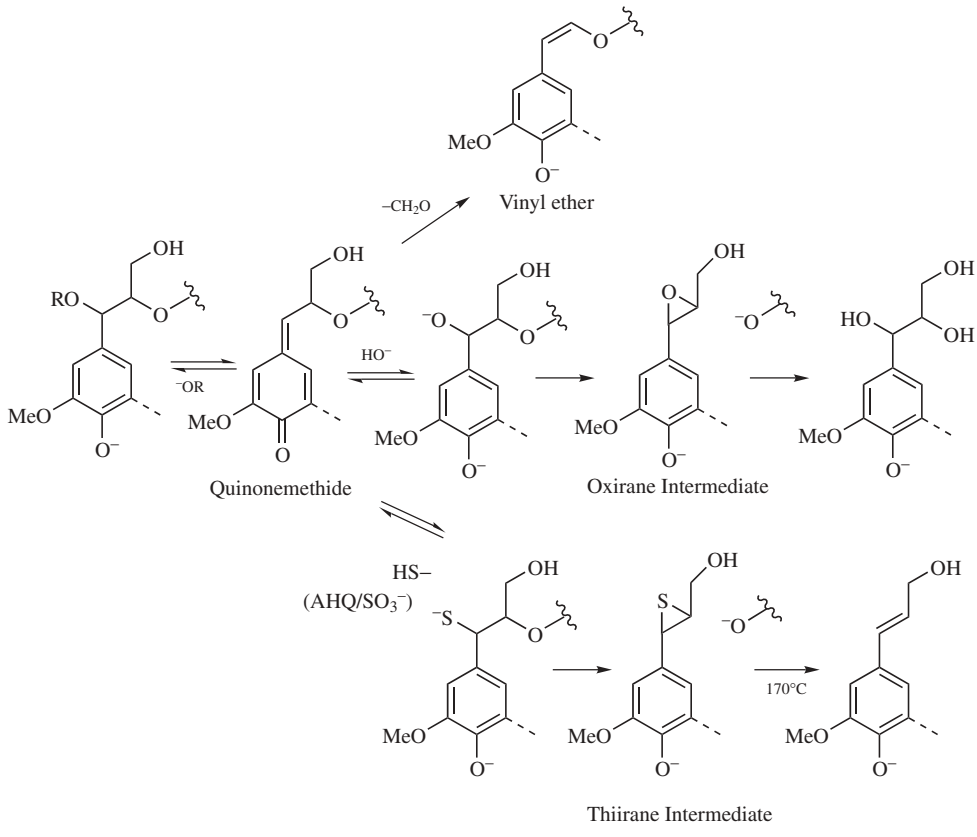

Fig. 8. Cleavage of phenolic α- and β-aryl ethers under alkaline pulping conditions (R = alkyl, aryl).

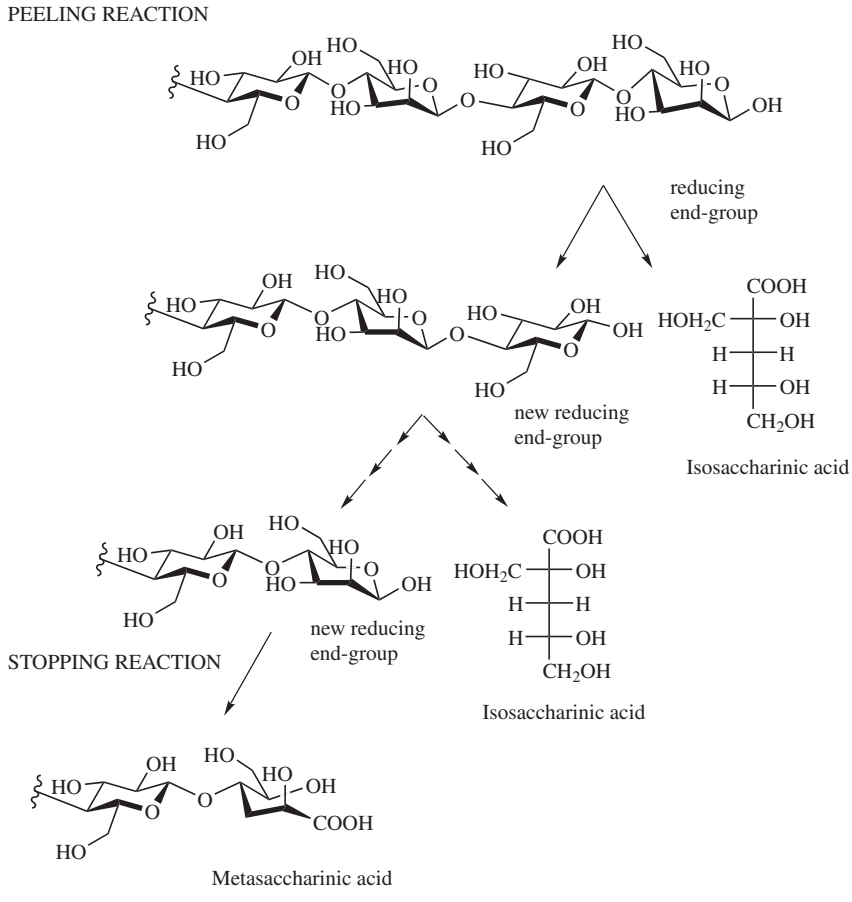

Fig. 9. Peeling and stopping reactions of polysaccharides under alkaline conditions.

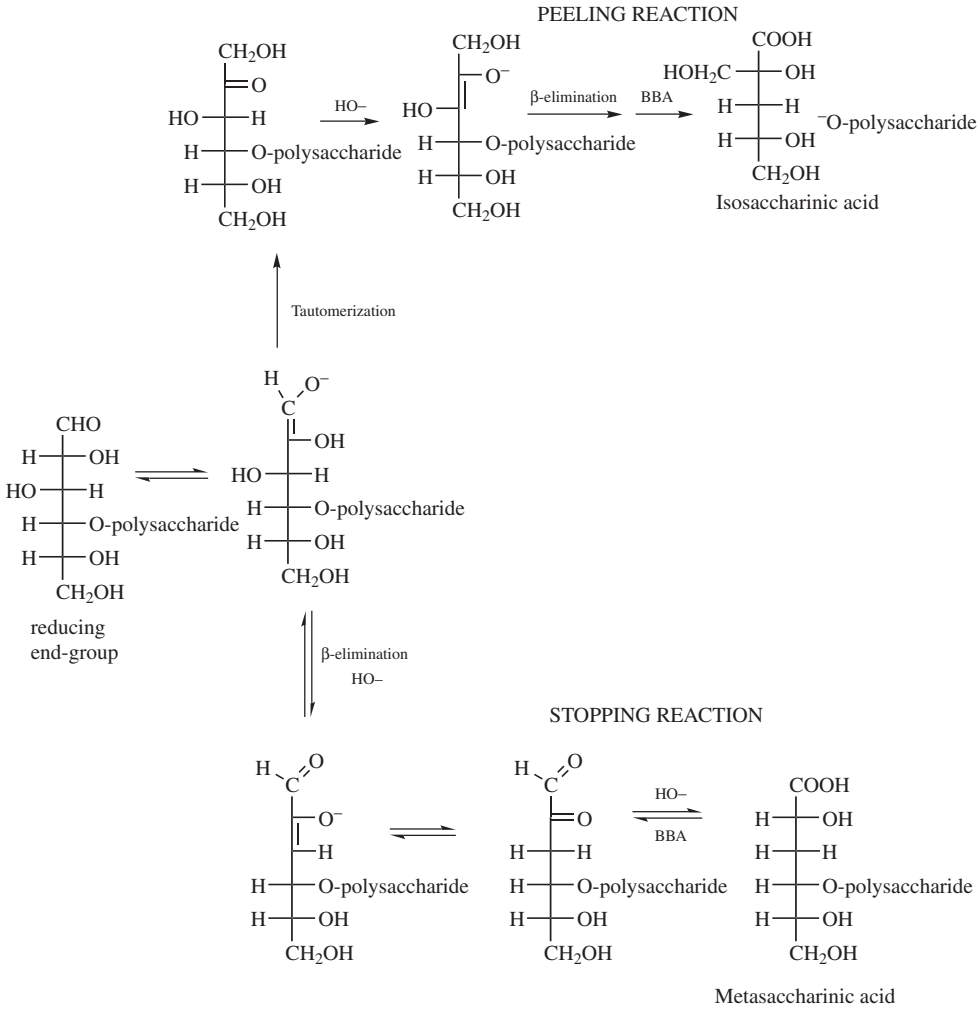

Fig. 10. Reaction mechanism of peeling and stopping reactions in alkaline pulping.

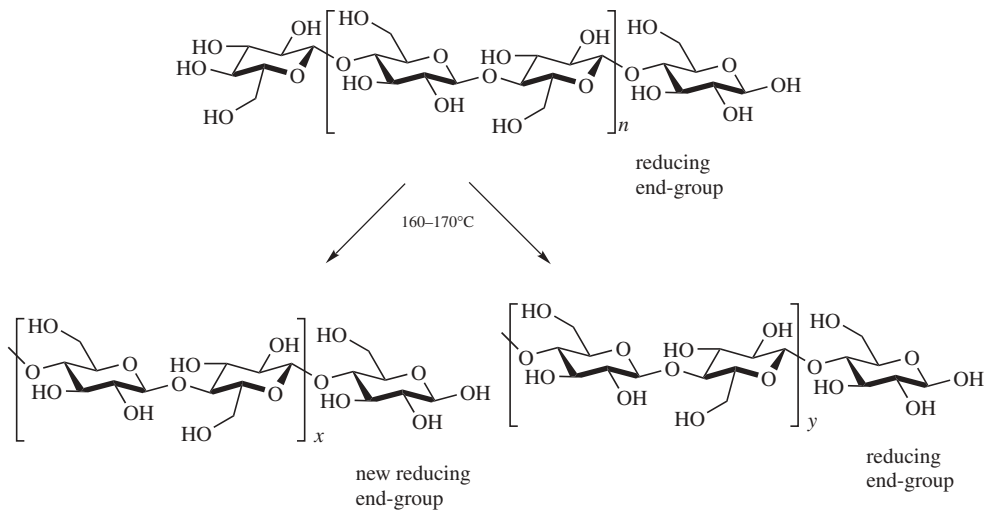

Fig. 11. Random hydrolysis of polysaccharides under alkaline conditions.

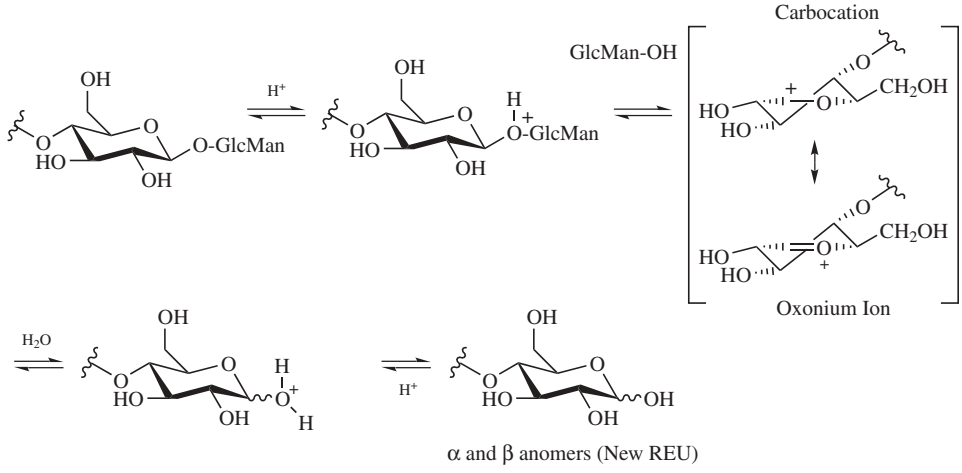

Fig. 12. Hydrolysis of polysaccharides under acid conditions.

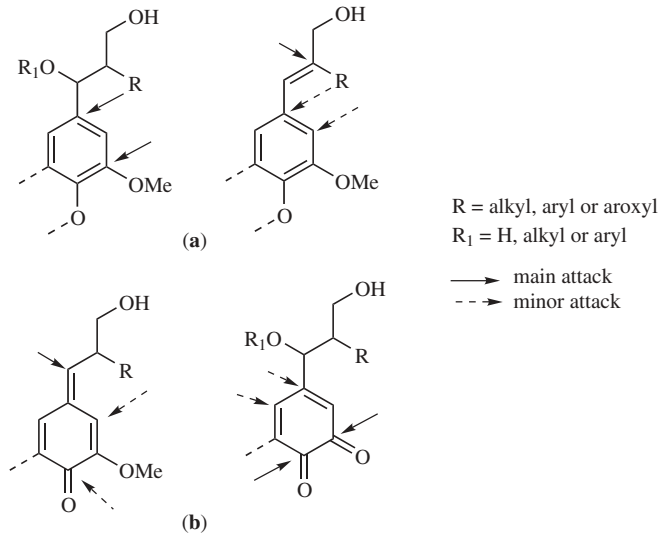

Fig. 13. Reaction sites of (**a**) aromatic and olefinic structures by electrophilic reagents and (**b**) carbonyl structure with nucleophilic reagents.

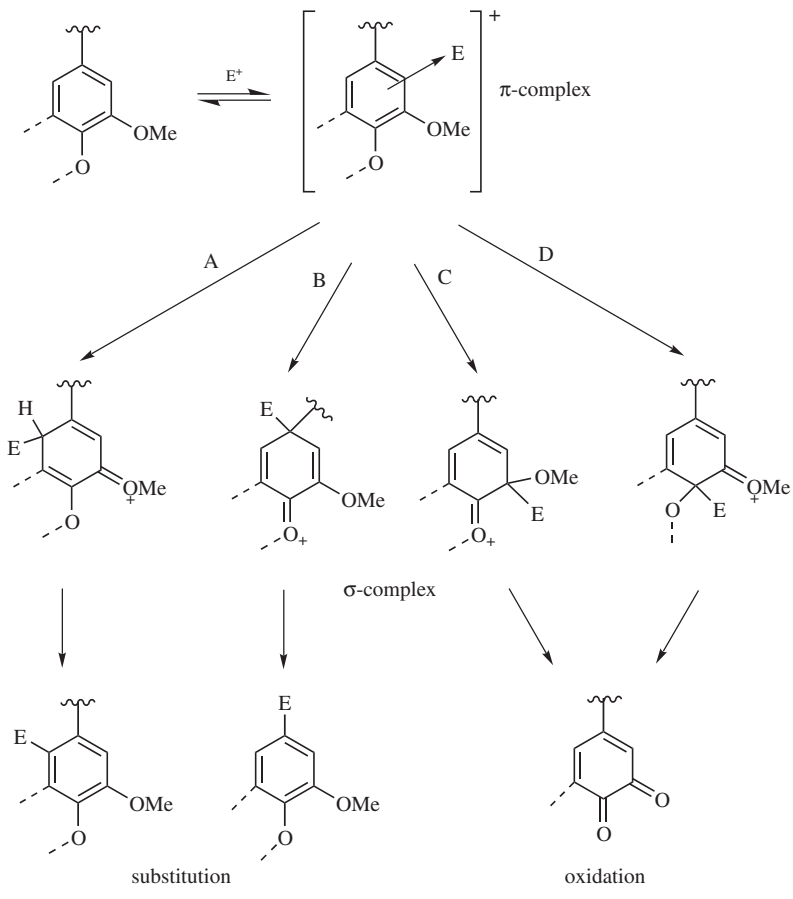

Fig. 14. General reaction scheme of an electrophilic (E) bleaching reagent with lignin; E = Cl_2, CH_3CO_3H, H_2SO_5, H_2CO_3 (151).

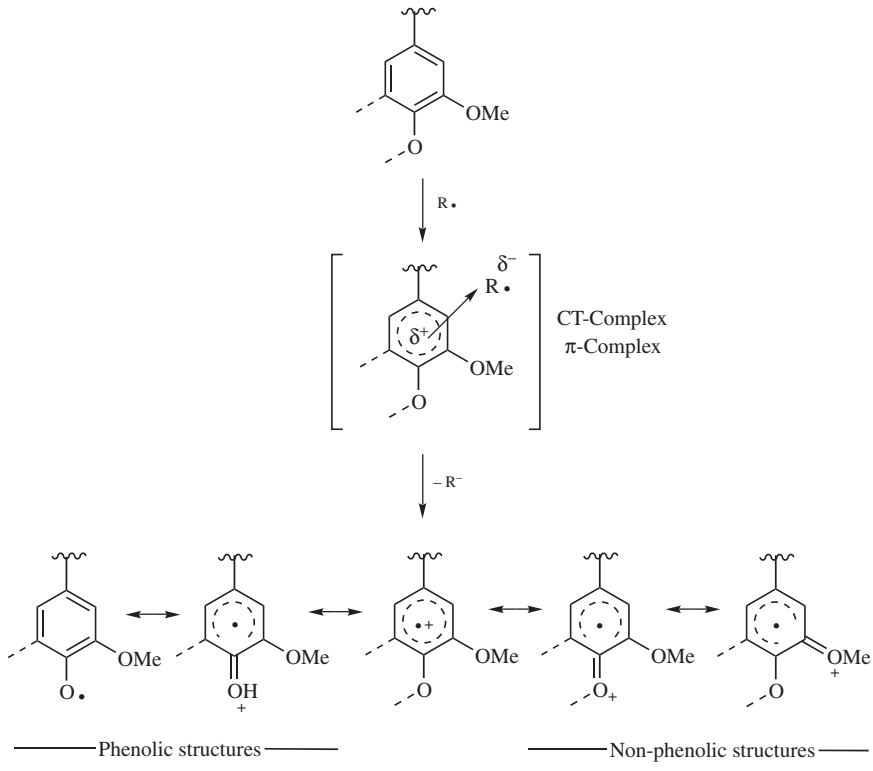

Fig. 15. General reaction scheme of an electrophilic radical (R) bleaching reagent with lignin; $R^{\bullet} = ClO_2^{\bullet}$, $Cl^{\bullet}$, $HO^{\bullet}$, which react with both phenolic and etherified phenolic lignin moieties; and $^{\bullet}O_2^{\bullet}$, $HO_2^{\bullet}$, $^{\bullet}O_2^{-}$, which react only with phenolic lignin moieties.

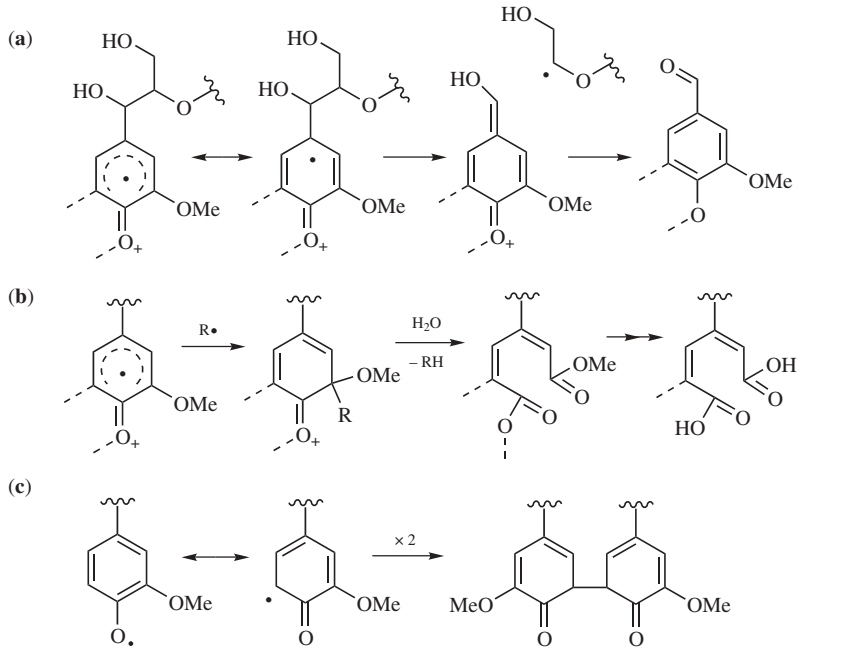

Fig. 16. Possible reaction schemes of initially formed radical cations and phenoxy radicals leading to (**a**) splitting of Cα–Cβ bonds, (**b**) ring cleavage, and (**c**) oxidative coupling of lignin moieties.

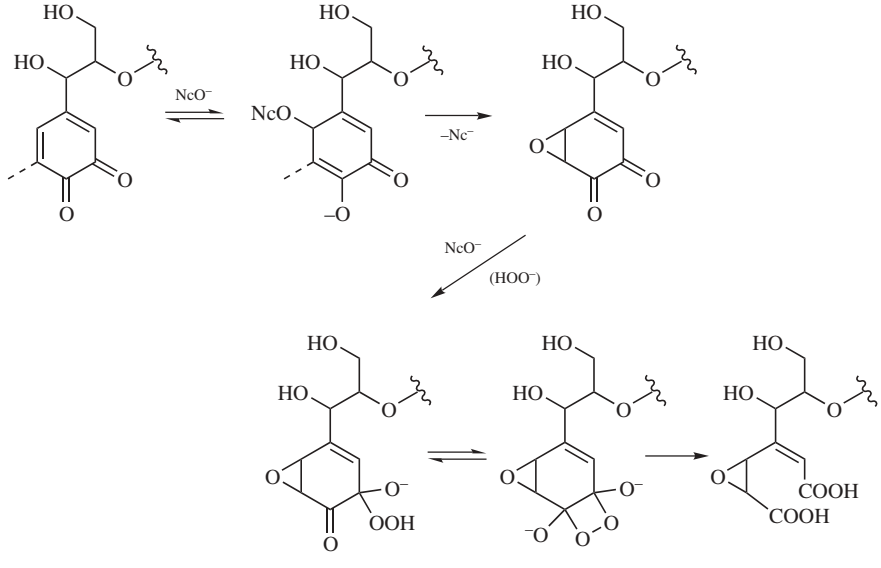

Fig. 17. Possible reactions of quiniod-type structures with nucleophilic (NcO^-) bleaching reagents. ($NcO^- = HOO^-$ and ClO^-.)

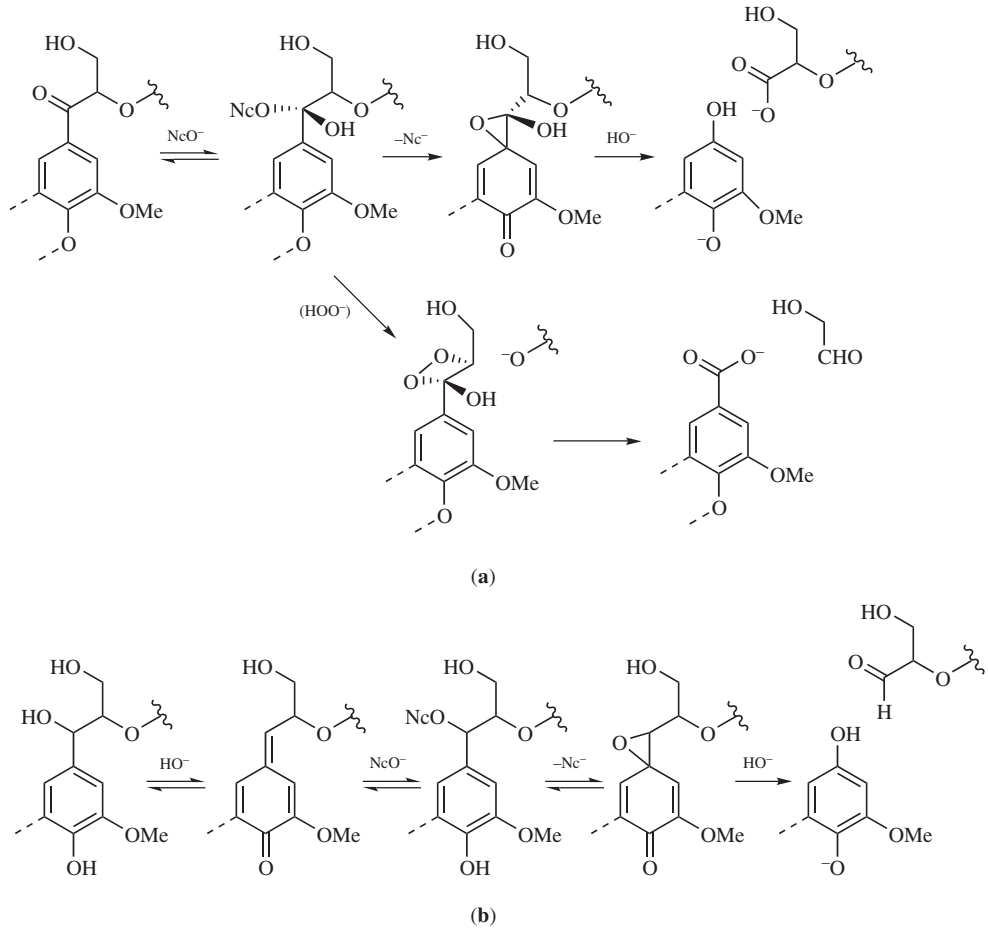

Fig. 18. Reaction of (**a**) α-carbonyl (Dakin reaction) and (**b**) α-carbinol (Dakin-like reaction) structures with nucleophilic (NcO^-) bleaching reagents. ($NcO^- = HOO^-$ and ClO^-.)

Table 1. **Pulpwood Species by Main U.S. Pulp-Producing Regions**

	Softwoods		Hardwoods	
Region	Dominant	Secondary	Dominant	Secondary
northeast	spruce and fir	hemlock, tamarack, and white pine	oak, hickory, and maple	aspen and poplar
south	yellow pine		oak and gums	
northwest	douglas fir and hemlock	true firs and spruce	red alder	
lake states	jack pine and red pine	white pine and tamarack	red oak, aspen and maple	birch

Table 2. **Major Cell Types in Softwood and Hardwood Xylem**

Cell type	Orientation	Function	Amount, %	Length, mm	Width, μm
		Softwoods			
trachied (fiber)	vertical	support/conduction	90	1.4–6.0	20–50
ray trachied	horizontal	conduction	< 5	0.01–0.16	2–50
ray parenchyma	horizontal	storage	<10		
epithelial parenchyma	vertical/ horizontal	resin excretion	< 1		
		Hardwoods			
fibers	vertical	support	55	0.4–1.9	10–40
vessel elements	vertical	conduction	30	0.2–0.6	10–300
longitudinal parenchyma	vertical	storage	< 5	<0.1	<30
ray parenchyma	horizontal	storage	15		

Table 3. **Properties of Various Pulpwood Species**

Species	Fiber length, mm	Fiber diameter, μm
	Softwoods	
loblolly pine	3.6	35–45
slash pine	4.6	35–45
black spruce	3.5	25–30
Douglas fir	3.9	35–45
redwood	6.1	50–65
	Hardwoods	
Aspen	1.04	10–27
Birch	1.85	20–36
Oak	1.40	14–22
Red gum	1.70	20–40

Table 4. **Average Chemical Composition of the Main Constituents in the Cell Wall of a Typical Softwood and Hardwood**[a]

Component	Softwood[b], %	Hardwood[b], %
carbohydrates	65–75	68–84
cellulose	40–45	38–49
hemicellulose	25–30	30–35
lignin	25–30	20–25
extractives	2–5	3–7

[a]See Ref. 1.
[b]Values are given as % woody dry solids.

Table 5. **Distribution of the Main Constituents in the Cell Wall of Softwood Trachieds**[a]

Constituent	Morphological region[b]			
	(ML + P)		(S1 + S2 + S3)	
lignin	21	(65)	79	(25)
carbohydrates	5	(35)	95	(75)
cellulose	3	(12)	97	(45)
glucomannan	2	(3)	98	(20)
xylan	5	(5)	95	(10)
pectic substances	75	(15)	25	(<1)

[a]Percent constituent.
[b]Values in brackets refer to relative mass proportions of constituents.

Table 6. **Crystallinity of Various Cellulose Materials as Determined by X-Ray (21)**

Sample	Crystallinity, %
cotton linters	56–68
sulfite pulp	50–56
kraft pulp	46–52
regenerated cellulose film	40–45
cellulose powder	54–58

Table 7. **Relative Amounts of Interunit Linkages in a Softwood (SW) and Hardwood (HW) Milled Wood Lignin**[a]

Linkage	SW[b]	HW[c]
β-*O*-4	48	60
α-*O*-4[d]	8	7
β-5	9–12	6
β-1	7	7
5-5[e]	10–12	5
4-*O*-5	4	7
β-β	2	3

[a]Ref. 45. Approximate values per 100 C_9-units.
[b]Spruce MWL.
[c]Birch MWL.
[d]Noncyclic α-*O*-4.
[e]Do not include dibenzodioxocin.

Table 8. **Availability of Some Nonwood Fibers**[a]

Fiber source	US[b]	Worldwide[c]
Agricultural residues		
wheat straw	78.9	600.0
rice straw	7.5	360.0
corn stalk	300.8	750.0
seed flax stalk	0.7	2.0
sugar cane bagasse	3.0	102.2
annual fiber crops		
stem fibers	0.02	13.9
hemp, kenaf, jute, flax		
leaf fibers	0	0.6
manila hemp, sisal		
seed hair fibers		
cotton fibers	4.0	21.0
uncultivated natural fiber		
bamboo	0	30.0
papyrus	0	5.0

[a]In million metric tons.
[b]Ref. 85.
[c]Ref. 86.

Table 9. **Dimensions of Common Nonwood Fibers**[a]

Fiber source	Mean length, mm	Mean diameter, μm	L/D ratio
rice straw	1.41	8	175
wheat straw	1.48	13	110
corn stalk	1.26	16	80
cotton stalk	0.86	19	45
cotton linters	3.50	21	165
sugarcane bagasse	1.70	20	85
hemp	20	22	1000
kenaf bast	2.74	20	135
kenaf core	0.60	30	20
seed flax	27	16	1250
bamboo	2.70	14	190
papyrus	1.50	12	125
softwood	*3.00*	*30*	*100*
hardwood	*1.25*	*25*	*50*

[a]Ref. 87.

Table 10. **Chemical Composition of Common Nonwood Fibers**

Fiber source	Cellulose, %[a]	Lignin, %[a]	Ash %, Silica, %[b]
rice straw	28–36	12–16	15–20 (9–14)
wheat straw	33–39	16–23	4–9 (3–7)
corn stalk	32–35	16–27	6.4*
cotton linters	89–95	0.7–1.6	1–1.2 (<1)
sugarcane bagasse	32–37	18–26	1.5–5 (0.7–3)
hemp	55–77	9–13	
kenaf bast	44–57	15–19	2–5
seed flax	43–47	21–23	2–5
bamboo	26–43	21–31	1.7–5 (1.5–3)
papyrus	38–44	16–19	
softwood	*40–45*	*25–30*	*1 (<1)*
hardwood	*38–49*	*20–25*	*1 (<1)*

[a]Ref. 85.
[b]Ref. 87.

Table 11. **Description of Main Chemicals Used in Bleaching**

Reagent	Designation
chlorine (Cl_2)	C
chlorine dioxide (ClO_2)	D
oxygen (O_2)	O
ozone (O_3)	Z
sodium hypochlorite (NaOCl)	H
hydrogen peroxide (H_2O_2)	P
sodium hydroxide (NaOH)	E
enzymes (xylanase)	X
chelants (DTPA/EDTA)[a]	Q

[a]ethylenediaminetetraacetic acid = EDTA. diethylenetriaminepentaacetic acid = DTPA.

Table 12. **Examples of Typical Bleaching Sequences Used for Softwood Kraft and Sulfite Pulps**

Kraft pulps	Sulfite pulps
C-E-D-E-D	C-E-D-E-D
C-E-H-D-E-D	C-E-H
C/D-E-D-E-D	C-E-H-P
D/C-EO-D-E-D	C-E-H-D
D-EOP-D-P-D	EPO-H-P
D-EOP-P-P	DC-E-H-P
O-EOP-P-P	
Q-P-Z-P	
X-EOP-D-EOP-D	

Table 13. **Division of Initial Reacting Species in Pulp Bleaching**

Electrophilic		Nucleophilic
Cationic[a] Acidic	Radical Acidic–alkali	Anionic Alkali
Cl^+, HO^+	$ClO_2^\bullet$, $^\bullet O_2^\bullet$, $Cl^\bullet$, $HO^\bullet$, $HO_2^\bullet$	ClO^-, HOO^-

[a]Both Cl^+ and HO^+ are the reactive component of elemental chlorine (Cl_2) and peroxy acids (ROOH)/Hypochlorite (HOCl), respectively.