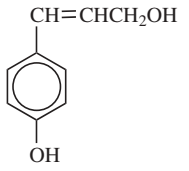
LIGNIN

1. Introduction

The word lignin is derived from the Latin word *lignum* meaning wood. It is a main component of vascular plants. Indeed, lignin is second only to polysaccharides in natural abundance, contributing 24–33% and 19–28%, respectively, to dry wood weights of normal softwoods and temperate-zone hardwoods.

According to a widely accepted concept, lignin [8068-00-6] may be defined as an amorphous, polyphenolic material arising from enzymatic dehydrogenative polymerization of three phenylpropanoid monomers, namely, coniferyl alcohol [485-35-5] (**2**), sinapyl alcohol [537-35-7] (**3**), and *p*-coumaryl alcohol (**1**).



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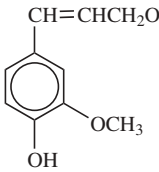

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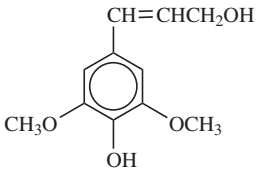


(**3**)

The traditionally held biosynthesis process, which consists essentially of random radical coupling reactions is sometimes followed by the addition of water, of primary, secondary, and phenolic hydroxyl groups to quinonemethide intermediates, leads to the formation of a three-dimensional polymer that lacks the regular and ordered repeating units found in other natural polymers such as cellulose and proteins. Traditionally, no other enzymes or proteins are thought to be required (1).

The random biosynthesis process is under review. Dirigent proteins, acting as templates, are proposed to assist the orientation of lignin precursers to afford steroselective phenoxy radical coupling (2,3).

Normal softwood lignins are usually referred to as guaiacyl lignins because the structural elements are derived principally from coniferyl alcohol (>90%), with the remainder consisting mainly of *p*-coumaryl alcohol-type units. Normal hardwood lignins, termed guaiacyl–syringyl lignins, are composed of coniferyl alcohol and sinapyl alcohol-type units in varying ratios. In hardwood lignins, the methoxyl content per phenylpropanoid unit is typically in the range of 1.2–1.5 (4). Grass lignins are also classified as guaiacyl–syringyl lignins. However, unlike hardwood lignins, grass lignins additionally contain small but significant amounts of structural elements derived from *p*-coumaryl alcohol. Grass lignins also contain *p*-coumaric, hydroxycinnamic, and ferulic acid residues attached to the lignin through ester and ether linkages (5).

The distribution of lignin in individual cells of lignified wood has been well examined. The lignin concentration is rather uniform across the secondary wall, but there is a significant increase in lignin concentration at the boundary of the middle lamella and primary wall region (6). This pattern of lignin distribution, with the highest concentration in the interfiber region and a lower, uniform concentration in the bulk of the cell walls, is typical for most wood cells. Thus

lignin serves the dual purpose of binding and stiffening wood fibers through its distribution between and in the cell walls.

Lignin performs multiple functions that are essential to the life of the plant. By decreasing the permeation of water across the cell wall in the conducting xylem tissues, lignin plays an important role in the internal transport of water, nutrients, and metabolites. It imparts rigidity to the cell walls and acts as a binder between wood cells, creating a composite material that is outstandingly resistant to compression, impact, and bending. It also imparts resistance to biological degradation.

In commercial chemical pulping of wood, the reverse process in nature is performed to isolate fibers for papermaking. In the process, wood is delignified by chemically degrading and/or sulfonating the lignin to water-soluble fragments. The industrial lignins thus obtained are used in many applications.

2. Structure and Reactions

The structural building blocks of lignin are linked by carbon–carbon and ether bonds (7,8). Units that are trifunctionally linked to adjacent units represent branching sites which give rise to the network structure characteristic of lignin (see Figs. 1 and 2). Thus lignin consists of complex and diverse structures, including in softwood lignin an eight-member ring configuration (dibenzodioxocin) (9). The types and frequencies of several prominent interunit lignin linkages are summarized in Table 1.

Because the interunit carbon–carbon linkages are difficult to rupture without extensively fragmenting the carbon skeleton of the lignin, solvolysis of the ether linkages is often utilized as the best approach for degrading lignin. Of the functional groups attached to the basic phenylpropanoid skeleton, those having the greatest impact on reactivity of the lignin include phenolic hydroxyl, benzylic hydroxyl, and carbonyl groups. The frequency of these groups may vary according to the morphological location of lignin, wood species, and method of isolation.

2.1. Electrophilic Substitution. The processes by which the aromatic ring in lignin is modified by electrophilic substitution reactions are chlorination, nitration, and ozonation. Chlorination, widely used in multistage bleaching sequences for delignifying chemical pulps, proceeds by a rapid reaction of elemental chlorine with lignin in consequence of which the aromatic ring is nonuniformly substituted with chlorine. In nitration, nitro groups are introduced into the aromatic moiety of lignin with nitrogen dioxide (13). As one of several competing processes, electrophilic attack of ozone on lignin ultimately leads to ring hydroxylation (14).

2.2. Conversion of Aromatic Rings to Nonaromatic Cyclic Structures. On treatment with oxidants such as chlorine, hypochlorite anion, chlorine dioxide, oxygen, hydrogen peroxide, and peroxy acids, the aromatic nuclei in lignin typically are converted to *o*- and *p*-quinoid structures and oxirane derivatives of quinols. Because of their relatively high reactivity, these structures often appear as transient intermediates rather than as end

products. Further reactions of the intermediates lead to the formation of catechol, hydroquinone, and mono- and dicarboxylic acids.

Aromatic rings in lignin may be converted to cyclohexanol derivatives by catalytic hydrogenation at high temperatures (250°C) and pressures [20–35 MPa (200–350 atm)] using copper–chromium oxide as the catalyst(11). Similar reduction of aromatic to saturated rings has been achieved using sodium in liquid ammonia as reductants (16).

2.3. Conversion of Cyclic to Acyclic Structures. Upon oxidation, the aromatic rings of lignin may be converted directly to acyclic structures (eg, muconic acid derivatives) or indirectly by oxidative splitting of *o*-quinoid rings. Further oxidation creates carboxylic acid fragments attached to the lignin network.

2.4. Ring Coupling and Condensation Reactions. Many oxidants (eg, ClO_2, O_2) generate free radicals in lignin. Coupling of such reactive radicals ultimately leads to diphenyl structures. In alkaline media, phenolic units may react with formaldehyde forming methylol derivatives that condense with themselves or with other phenols. This formaldehyde condensation reaction is the basis for using technical lignins in the preparation of adhesives.

2.5. Cleavage of Ether Bonds. Ether linkages at the α- and β-positions are the most abundant functional groups on the propanoid side chain of lignin. Under acid conditions these linkages undergo solvolytic cleavage initially forming secondary alcohols that are converted to carbonyl, ethylene, and carboxyl structures through a combination of dehydrations and allylic rearrangements, leading eventually to fragmentation of the side chain (17).

The alkali-promoted cleavage of α- and β-ether linkages, an important step in alkaline pulping processes, is mainly responsible for the fragmentation and dissolution of lignin in the pulping liquor. Addition of bisulfide ion to the aqueous alkaline media, as in the case of kraft pulping, enhances the rate and extent of β-aryl ether cleavage in phenolic units (18).

2.6. Cleavage of Carbon–Carbon Bonds. Under appropriate conditions, the propanoid side chain in lignin may be ruptured to form three-, two-, or one-carbon fragments. This carbon–carbon fragmentation occurs in a variety of laboratory treatments and technical processes such as in bleaching of chemical pulps with Cl_2, ClO_2, and O_2, in microbial degradation (19), and in photooxidation (20).

2.7. Substitution Reactions on Side Chains. Because the benzyl carbon is the most reactive site on the propanoid side chain, many substitution reactions occur at this position. Typically, substitution reactions occur by attack of a nucleophilic reagent on a benzyl carbon present in the form of a carbonium ion or a methine group in a quinonemethide structure. In a reversal of the ether cleavage reactions described, benzyl alcohols and ethers may be transformed to alkyl or aryl ethers by acid-catalyzed etherifications or transetherifications with alcohol or phenol. The conversion of a benzyl alcohol or ether to a sulfonic acid group is among one of the most important side chain modification reactions because it is essential to the solubilization of lignin in the sulfite pulping process (21).

2.8. Formation and Elimination of Multiple Bond Functionalities. Reactions that involve the formation and elimination of multiple bond functional groups may significantly effect the color of residual lignin in bleached and unbleached pulps. The ethylenic and carbonyl groups conjugated with phenolic

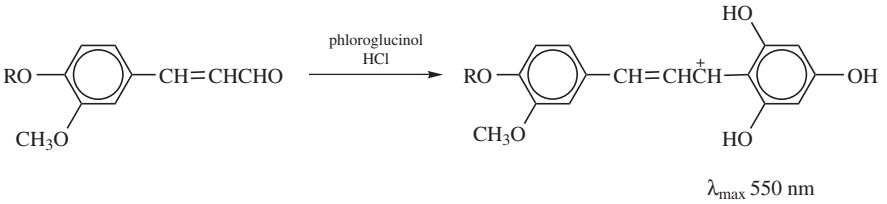
or quinoid structures are possible components of chromophore or leucochromophore systems that contribute to the color of lignin.

Reduction of ring-conjugated carbonyl groups to the corresponding primary and secondary alcohols is generally achieved by reaction with sodium borohydride. Ring-conjugated olefinic groups may be converted to their saturated components by hydrogenation.

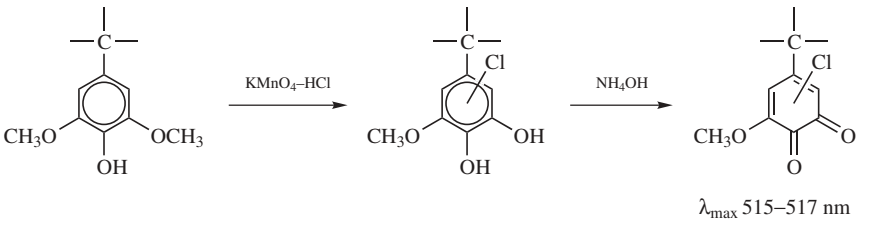
3. Analytical Methods

3.1. Detection of Lignin. The characteristic color-forming response of lignified tissue and some lignin preparations on treatment with certain organic and inorganic reagents was recognized in the early nineteenth century. More than 150 color reactions have now been proposed for the detection of lignin (22). Reagents used in these reactions may be classified into aliphatic, phenolic, and heterocyclic compounds, aromatic amines, and inorganic chemicals. Among the important reactions are the Wiesner and Mäule color reactions.

The Wiesner Reaction. The reaction of lignified tissue and phloroglucinol – hydrochloric acid gives a visible absorption spectrum with a maximum at 550 nm. This reaction has been attributed to coniferaldehyde units in lignin as the groups responsible for the color formation.



The Mäule Color Reaction. The procedure for this test consists basically of three sequential treatments of lignified material with 1% potassium permanganate, 3% hydrochloric acid, and concentrated ammonium hydroxide. A red-purple color develops for hardwoods and a brown color for softwoods. The steps comprising the Mäule reaction may be portrayed as follows (23,24):



3.2. Determination of Lignin Content. Lignin content in plants (wood) is determined by direct or indirect methods (25). The direct method includes measurement of acid-insoluble (ie, Klason) lignin after digesting wood with

72% sulfuric acid to solubilize carbohydrates (26). The Klason lignin contents of representative lignified materials are shown in Table 2.

In contrast to the direct determination of lignin content, indirect methods do not involve the isolation of a lignin residue. These include spectrophotometric methods and procedures that are based on oxidant consumption. An ultraviolet (uv) microspectrophotometric method has been used to determine the distribution of lignin in the various cell wall regions of softwoods (27). Supplementing the uv-microscopic technique is a method in which lignin is brominated and the bromine uptake, which is proportional to the lignin content, is determined by a combination of scanning or transmission electron microscopy (sem or tem) and energy dispersive x-ray analysis (edxa) (28). A number of spectral methods for determining lignin content are based on totally dissolving the sample in a suitable solvent and measuring the uv absorbance of the solution. Among the solvents used to dissolve lignocellulosic material are sulfuric acid, phosphoric acid, nitric acid, cadoxene, and acetyl bromide in acetic acid. The acetyl bromide method appears to have gained the most widespread acceptance (29).

The methods of oxidant consumption are used exclusively in the analysis of residual lignin in unbleached pulps. These procedures are all based on the common principle that lignin consumes the applied oxidants at a much faster rate than the carbohydrates, and oxidant consumption under carefully specified conditions can be regarded as a measure of lignin concentration in the pulp.

Two oxidants commonly used are chlorine and potassium permanganate. The Roe chlorine number, the uptake of gaseous chlorine by a known weight of unbleached pulp (ie, Technical Association of the Pulp and Paper Industry (TAPPI) Standard Method T202 ts-66) has been superseded by the simpler hypo number (ie, TAPPI Official Test Method T253 om-86), eg, chlorine consumption in treatment of the pulp with acidified sodium or calcium hypochlorite.

By far the most commonly used oxidation method is the corrected permanganate number test (30) in which the number of milliliters of 0.1*N* $KMnO_4$ consumed by 1 g of ovendried pulp under specified conditions (kappa number) is determined (TAPPI Historical Method T236 hm-85). Typical kappa numbers for representative pulps are shown in Table 3.

3.3. Characterization of Lignin. Lignin is characterized in the solid state by Fourier transform infrared spectroscopy (ftir), uv microscopy, interference microscopy, cross polarization/magic angle spinning nuclear magnetic resonance spectroscopy (cp/mas nmr), photoacoustic spectroscopy, Raman spectroscopy, pyrolysis-gas chromatography–mass spectroscopy, and thermal analysis. In solution, lignins are characterized by spectral methods such as uv spectroscopy, ftir, ^{1}H nmr, ^{13}C nmr, electron spin resonance spectroscopy (esr), and by several chemical degradation methods such as acidolysis, nitrobenzene and cupric oxidations, permanganate oxidation, thioacidolysis, hydrogenolysis, nuclear exchange reaction, ozonation and dfrc (derivitization followed by reductive cleavage). The details of these characterization methods have been discussed (31,32).

Fourier transform spectroscopy is a versatile, rapid, and reliable technique for lignin characterization. By Using this technique, the *p*-hydroxyphenyl, guaiacyl, and syringyl units, methoxyl groups, carbonyl groups, and the ratio of phenolic hydroxyl to aliphatic hydroxyl groups can be determined. The uv

microscopy method is best suited for investigating the topochemistry of lignin in wood, namely, for determining the concentration and chemical structure of lignin in different layers of the cell wall. The cp/mas nmr spectroscopy provide for another spectral technique whereby lignin can be characterized in the solid state. Results obtained by cp/mas nmr are in good agreement with Klason lignin contents for softwoods.

In solution, lignin is most conveniently analyzed qualitatively and quantitatively by uv spectroscopy. Typical absorptivity values, D, at 280 nm for milled wood (MW) lignins and other types of lignins are listed in Table 4. These values are used for quantitative determination of the lignins in suitable solvents.

^{1}H and ^{13}C nmr spectroscopy provide detailed information on all types of hydrogen and carbon atoms, thus enabling identification of functional groups and types of linkages in the lignin structure. Detailed assignments of signals in ^{1}H and ^{13}C nmr spectra have been published (34,35). A review of the use of ^{31}P nmr as an analytical tool for lignin is available (36). Through phosphitylation of the various hydroxyl groups present in lignin, unique quantitative and qualitative information has been obtained.

Electron spin resonance (esr) or electron paramagnetic resonance (epr) spectroscopy are essential tools for the study of structure and dynamics of molecular systems containing one or more unpaired electrons. These methods have found application as a highly sensitive tool for the detection and identification of free-radical species in lignin and lignin model compounds (37,38). Milled wood lignin generally exhibits a singlet esr signal with a g-value of 2.0023 and a line width of 1.6 mT (16 G), typical of a phenoxy radical.

Among the chemical degradation methods, acidolysis, nitrobenzene and cupric oxide oxidations, permanganate oxidation, thioacidolysis, and hydrogenolysis are all based on a common principle of chemically degrading lignin polymers to identifiable low molecular weight products through side-chain cleavages and maintaining the aromatic nature of the lignin units. By these methods, the makeup of monomeric units in the lignin (eg, guaiacyl–syringyl–p-hydroxyphenyl ratio) is determined. In addition, the identification of dimeric and trimeric degradation products reveals the types of linkages existing in the lignin. A new degradation method termed dfrc (derivatization followed by reductive cleavage) has been found to be simpler and is gaining acceptance (39). Combination of dfrc with ^{31}P nmr has reveiled information about the structural nature of hydroxyl bearing moieties of lignin (40).

A technique based on ozonation, in contrast, provides information on the structure of the lignin side chain by degrading the aromatic rings (41). Thus the side chain of the dominant structure in all native lignins, the arylglycerol–β-aryl ether moiety, can be obtained in the form of erythronic and threonic acids. Ozonation proves to be an elegant method for determination of the stereospecificity in lignin.

The quantities of noncondensed and condensed phenyl nuclei in various lignins and in the morphological regions of cell walls are determined by a nucleus exchange method (42). The data obtained from this method indicate that lignin in the middle lamella is more condensed than lignin in the secondary wall and that hardwood lignin is less condensed than softwood lignin. By combining nucleus exchange with nitrobenzene oxidation, the methylol groups formed in the

condensation of lignin with formaldehyde can be directly measured without isolation of the lignin.

3.4. Functional Group Analysis. The move toward instumental analysis and away from wet methods is illustrated in the methods of analysis of the various fuctional groups present in lignin. Nmr has become a particularly useful tool. Each section below contains information about both the classical wet method as well as references to the most current instumental techniques.

The total hydroxyl content of lignin is determined by acetylation with an acetic anhydride–pyridine reagent followed by saponification of the acetate, and followed by titration of the resulting acetic acid with a standard 0.05 *N* NaOH solution. Either the Kuhn-Roth (43) or the modified Bethge-Lindstrom (44) procedure may be used to determine the total hydroxyl content. The aliphatic hydroxyl content is determined by the difference between the total and phenolic hydroxyl contents. Total hydroxyl content as been determined, after derivitization, by ^{31}P, ^{13}C, ^{1}H and ^{19}F nmr techniques, which were recently reviewed (45).

The phenolic hydroxyl group is one of the most important functionalities affecting the chemical and physical properties of lignin. It facilitates the base-catalyzed cleavage of interunitary ether linkages and oxidative degradation, and has a pronounced influence in the reactivity of lignin polymers in various modification reactions such as sulfomethylation with formaldehyde, and bisulfite. Regarding classical analysis, the periodate method is based on the oxidation of a phenolic guaiacyl group with sodium periodate to orthoquinone structures, wherein nearly 1 mol of methanol per mole of phenolic hydroxyl group is released (46). Measurement of the methanol formed is approximately equivalent to the phenolic hydroxyl content. Another classic method is aminolysis, (44), consisting of acetylation of lignin and aminolysis with pyrrolidine to remove acetyl groups such as 1-acetylpyrrolidine. The amount of removed acetyl is a measure of the phenolic hydroxyl content of lignin. These and other procedures for determining phenolic hydroxyl groups have been compared (47). The advantages and disadvantages of each of these methods compared to NMR spectroscopy has also been discussed (45). A simple and reliable ^{1}H nmr method that does not require derivitization has been reported. This method relys on D_2O exchange of the phenolic proton. An instrument capable of 500 MHz or greater is required (48). Table 5 lists the total phenolic and aliphatic hydroxyl contents of some representative milled wood, bamboo, and technical lignins.

The presence of carbonyl groups in spruce lignin was postulated as early as 1922 (50).Coniferaldehyde [458-36-6] has definitely been identified as a building block in lignin, and the α-carbonyl content has been found to increase in the milling of wood and during pulping processes. The total carbonyl content of lignin is determined by a borohydride or hydroxylamine hydrochloride method (51), and the α-carbonyl content from analysis of uv alkaline difference spectra. An ^{19}F nmr method employing quantitative trifluoromethylation of lignin was recently reported that is claimed to be not only more precise than previous methods, but can differentiate between the various types of carbonyl groups (52).

The method of choice for determining carboxyl groups in lignin is based on potentiometric titration in the presence of an internal standard, *p*-hydroxybenzoic acid, using tetra-*n*-butylammonium hydroxide as a titrant (53). The

carboxyl contents of different lignins are shown in Table 6. In general, the carboxyl content of lignin increases upon oxidation.

Methoxyl groups are determined by the Viebock and Schwappach procedure (55). In treatment of lignin with hydroiodic acid, the methoxyl group is cleaved forming methyl iodide, which is quantitatively stripped from the reaction mixture and collected in a solution of sodium acetate and glacial acetic acid containing bromine. The bromine reacts with methyl iodide to form alkyl and iodine bromide. The iodine thus produced is titrated with a dilute standard sodium thiosulfate solution using 1% starch solution as an indicator. The methoxyl content can be quantitatively determined with high accuracy based on the quantity of iodine recovered. A technique that offers a simpler procedure using gas chromatography (gc) has been reported (56). This method relies on quantiative analysis of methyl iodide by gc after reaction with hydriodic acid. This bypasses the complex apparatus, as well as the distillation, trapping and titration steps.

Finally, the sulfonate content of lignin is determined by two main methods: one typified by conductometric titration in which sulfonate groups are measured directly, and the other that measures the sulfur content and assumes that all of the sulfur is present as sulfonate groups. The method of choice for determining the sulfonate content of lignin samples that contain inorganic or nonsulfonate sulfur, however, is conductometric titration (57).

4. Properties

4.1. Molecular Weight and Polydispersity. Because it is not possible to isolate lignin from wood without degradation, the true molecular weight of lignin in wood is not known. Different methods for measuring the molecular weight of isolated lignins give various results, and aggregation of lignin molecules may prevent determination of real molecular weight. Light scattering and vapor phase pressure osmometry are the traditional methods of analysis. By using these methods, the weight-average molecular weight, M_w, of softwood milled wood lignin is estimated to be 20,000; lower values have been reported for hardwoods (58).

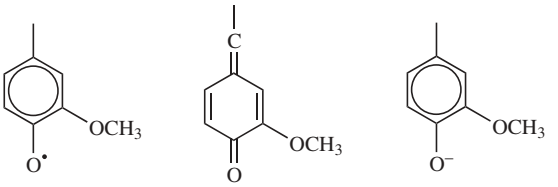
Various methods based on size exclusion chromatography (sec) have been reported. An initial stumbling block for this method was an affinity between lignin and early sec columns, and the use of linear polystyene sulfonate standards (59). Since that time, various standardization techniques such as universal calibration, multiple angle light scattering (mals), and matrix assisted laser desorption ionization–time of flight (maldi–tof) mass spectrometry have been coupled with sec (60,61). With the maldi–tof method the $\overline{M}_w$ of softwood kraft lignin was found to be close to 3000. Purified softwood lignosulfonates has been estimated to have a M_w of 30,000 by mals (62). Kraft lignins invariably have lower molecular weights than lignosulfonates, indicative of a more extensive degradation of the lignin during the kraft pulping process. Hopefully, a method that gives the actual molecular weight of isolated lignins will be verified by one of the above listed techniques.

4.2. Solution Properties. Lignin in wood behaves as an insoluble, three-dimensional network. Isolated lignins (milled wood, kraft, or organosolv

lignins) exhibit maximum solubility in solvents having a Hildebrand's solubility parameter, δ, of $20.5 - 22.5(J/cm^3)^{1/2}(10 - 11(cal/cm^3)^{1/2}$, and $\Delta\mu$ in excess of 0.14 μ, where $\Delta\mu$ is the ir shift in the O–D bond when the solvents are mixed with CH_3OD. Solvents meeting these requirements include dioxane, acetone, methyl cellosolve, pyridine, and dimethyl sulfoxide (dmso).

4.3. Thermal Properties. As an amorphous polymer, lignin behaves as a thermoplastic material undergoing a glass-transition at temperatures that vary widely depending on the method of isolation, sorbed water, and heat treatment (62). Lignin stores more energy than cellulose (qv) in wood. For example, the glass-transition temperature, T_g, and heat capacity at 350 K for dioxane lignin are 440 K and 1.342 J/(g K), respectively (63). Thermal softening of lignin at elevated temperatures accelerates the rate of delignification in chemical pulping and enhances the bond strength of fibers in paper- and boardmaking processes. In commercial thermomechanical pulping, a pretreatment of wood chips with sulfite lowers the glass-transition temperature of lignin to 70–90°C (63), thus decreasing the power consumption in defibration. Other physical properties of lignin have been comprehensively reviewed (51).

4.4. Chemical Properties. Lignin is subject to oxidation, reduction, discoloration, hydrolysis, and other chemical and enzymatic reactions. Many are briefly described elsewhere (64). Key to these reactions is the ability of the phenolic hydroxyl groups of lignin to participate in the formation of reactive intermediates, eg, phenoxy radical (**4**), quinonemethide (**5**), and phenoxy anion (**6**):



(**4**) (**5**) (**6**)

The free-radical intermediate initiates light-induced discoloration (yellowing) and enzymatic degradation of lignin (38,65). Nucleophilic addition occurs at the quinonemethide center, of which the most important reactions are the addition of sulfonate groups to the α-carbon during sulfite pulping and the sulfide assisted depolymerization in kraft pulping (Fig. 3).

The significance of phenoxy anions is well recognized in the isolation of kraft and other water-insoluble technical lignins by acid precipitation. The ionization of phenolic hydroxyl groups coupled with the reduction of molecular size renders native lignin soluble in the aqueous pulping solution, thus enabling its separation from the polysaccharide components of wood.

The aromatic ring of a phenoxy anion is the site of electrophilic addition, eg, in methylolation with formaldehyde (qv). The phenoxy anion is highly reactive to many oxidants such as oxygen, hydrogen peroxide, ozone, and peroxyacetic acid. Many of the chemical modification reactions of lignin utilizing its aromatic and phenolic nature have been reviewed elsewhere (66).

During the last decade there has been increased interest in the use of ligninolytic enzymes that degrade lignin, either for the pulping of wood, bleaching of fiber, or for modification of lignin based chemical feedstocks. The pretreatment of pulpwood with enzymes has seen limited to commercial use. With a number of research groups dedicated to this technology, it should continue to gain commercial acceptance (67).

5. Industrial Lignins

Industrial lignins are by-products of the pulp and paper industry.Lignosulfonate [8062-15-5], derived from sulfite pulping of wood and kraft lignin [8068-05-1], derived from kraft pulping, of wood [8068-05-1] are the principal commercially available lignin types. In the past organosolv [8068-03-9] derived from the alcohol pulping of wood were also reported to be available commercially in the past, but they are no longer available in any quantity (68).

The production capacity of lignin in the Western world is estimated to be $\sim 8 \times 10^5$ tons/yr (Table 7). Although the production of lignosulfonates has been declining, kraft lignin production has increased. Of the companies listed in Table 7, LignoTech Sweden and Westvaco produce kraft lignins. The rest produce lignosulfonates.

Advances in technology have increased the importance of lignin products in various industrial applications. They are derived from an abundant, renewable resource, and they are nontoxic and versatile in performance.

5.1. Lignosulfonates. Lignosulfonates, also called lignin sulfonates and sulfite lignins, are derived from the sulfite pulping of wood. In the sulfite pulping process, lignin within the wood is rendered soluble by sulfonation, primarily at benzyl alcohol, benzyl aryl ether, and benzyl alkyl ether linkages on the side chain of phenyl propane units (69). Some demethylation also occurs during neutral and alkaline sulfite pulping, which leads to the formation of catechols and methane sulfonic acid (see Fig. 3).

Depending on the type of pulping process, lignosulfonates of various bases, including calcium [904-76-3], sodium [8061-51-6], magnesium [8061-54-9], andammonium lignosulfonates [8061-53-8], can be obtained. Typical compositions for hardwood and softwood spent sulfite liquors are given in Table 8. In addition to whole liquor products, commercial forms of lignosulfonates include chemically modified whole liquors, purified lignosulfonates, and chemically modified forms thereof.

Isolation of Lignosulfonates. Various methods have been developed for isolating and purifying lignosulfonates from spent pulping liquors. One of the earliest and most widely used industrial processes is the Howard process, where calcium lignosulfonates are precipitated from spent pulping liquor by addition of excess lime. Lignin recoveries of 90–95% are obtainable through this process. Other methods used industrially include ultrafiltration and ion-exclusion (69), which uses ion-exchange resins to separate lignin from sugars.

Laboratory methods for isolating lignosulfonates include dialysis (71,72), electrodialysis (73), ion exclusion (73,74), precipitation in alcohol (75,76), and

extraction with amines (77–79). They can also be isolated by precipitation with long-chain substituted quarternary ammonium salts (80–82).

Physical and Chemical Properties of Lignosulfonates. Even unmodified lignosulfonates have complex chemical and physical properties. Their molecular polydispersities and structures are heterogeneous and they are soluble in water at any pH but are insoluble in most common organic solvents.

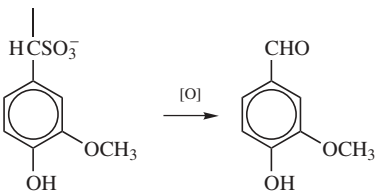
Typical C_9 formulas reported for isolated softwood and hardwood lignosulfonates are $C_9H_{8.5}O_{2.5}\,(OCH_3)_{0.85}\,(SO_3H)_{0.4}$ and $C_9H_{7.5}O_{2.5}\,(OCH_3)_{1.39}\,(SO_3H)_{0.6}$, respectively. These correspond to monomer unit molecular weights of 215 for softwood lignosulfonates and 254 for hardwoods. Polymer molecular weights are polydisperse and difficult to determine precisely. However, a range of from 1000–140,000 has been reported for softwood lignosulfonates (83) with lower values reported for hardwoods (84).

A number of different functional groups are present in lignosulfonates. ^{13}C-nmr analysis of a purified sulfonated lignin from Western hemlock revealed 2.0% phenolic hydroxyl, 17.5% sulfonate, 12.5% methoxyl, and 0.6% carboxyl groups per unit weight of lignosulfonates (85). Additional studies indicate that lignosulfonates also contain limited numbers of olefinic, carbonyl, and catechol groups (86).

Lignosulfonates exhibit surface activity but have only a slight tendency to reduce interfacial tension between liquids. When compared to true surface-active agents, they are not effective in reducing the surface tension of water or for forming micelles (87). Their surface activity can be improved, however, by introducing long-chain alkyl amines into the lignin structure (88), by ethoxylation of lignin phenolic structures (89), or by conversion to oil-soluble lignin phenols (90).

Lignosulfonate Uses. Worldwide, the single largest use of lignosulfonates is as water reducers for concrete. Both hardwood and softwood lignosulfonates are widely used as lower end water reducers. Recently, higher molecular weight products produced by fractionation of softwood lignosulfonates have been used as mid-range water reducers, and efforts are underway to modify lignosulfonates for use as superplasticizers.

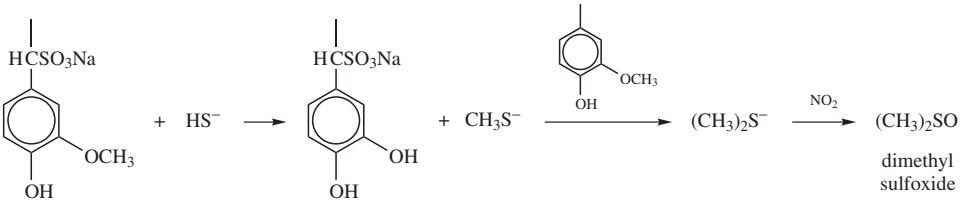
From a historical perspective, two other large-volume uses include production of vanillin (qv) and dmso (91). Commercially, softwood spent sulfite liquors or lignosulfonates can be oxidized in alkaline media by oxygen or air to produce vanillin [121-33-5].



vanillin

Through reaction with sulfide or elemental sulfur at 215°C, lignosulfonates can also be used in the commercial production of dimethyl sulfide and methyl

mercaptan (92). Dimethyl sulfide produced in the reaction is further oxidized to dmso, a useful industrial solvent (see SULFOXIDES).



Additional large-volume uses of lignosulfonates include animal feed pellet binders, dispersants (qv) for gypsum board manufacture, thinners/fluid loss control agents for drilling muds, dispersants/grinding aids for cement (qv) manufacture, and in dust control applications, particularly road dust abatement.

Lignin technology has advanced significantly, and increased research and development efforts have resulted in specialty uses in several key market areas.

Dye Dispersants. One such area is dye manufacture, where lignosulfonates act as primary dispersants, extenders, protective colloids, and grinding aids. Products produced by the reaction of lignosulfonates with benzyl alcohols have low azo dye reduction properties, low fiber-staining properties, high dispersion efficiency, good grinding aid qualities, and increased heat stability (66). Lignosulfonates prepared by sulfonation of kraft lignin are also widely used in this application. Such products are particularly useful in applications requiring superior heat stability.

Pesticide Dispersants. Modified lignosulfates and lignosulfonates derived from kraft lignins are used in the formulation of pesticides. In wettable powders, suspension concentrates, and water dispersible granules, they act as dispersants and prevent sedimentation. They also act as binders in the production of granular pesticides. Typical usage levels in these types of products range from 2 to 10%.

Carbon Black Dispersant. Specially modified lignosulfonates are used in a wide range of pigment applications to inhibit settling and decrease solution viscosity. Applications include dispersants for dark pigment systems used to color textile fibers, coatings, inks (qv), and carbon black. Lignosulfonates are also used as grinding aids and binders in the pelletizing of carbon black (qv).

Water Treatment/Industrial Cleaning Applications. Boiler and cooling tower waters are treated with lignosulfonates to prevent scale deposition (93). In such systems, lignosulfonates sequester hard water salts and thus prevent their deposition on metal surfaces. They can also prevent the precipitation of certain insoluble heat-coagulable particles (94). Typical use levels for such applications range from 1 to 1000 ppm.

In industrial cleaning formulations, lignosulfonates function as dirt dispersants and suspending agents (95). Rinsing properties are improved, corrosivity is reduced and the amount of wetting agent needed is lowered when lignosulfonates are added to acid and alkaline industrial cleaning formulations. Typical use levels in such formulations range from 0.05 to 2.0%.

Complexing Agent for Micronutrients. Complexes of lignosulfonates and iron, copper, zinc, manganese, magnesium, boron, or combinations of such are used to provide essential micronutrients to plants growing in metal-deficient soils. In most instances application of such complexes is by foliar spray. When applied in this manner the micronutrients can be readily absorbed by the plant without undesired leaf burn (96). Lignosulfonate complexes can also be used in soil treatment where they maintain availability longer than if metals are applied alone (97).

Lignosulfonate–metal complexes are weaker complexes than those formed from amine-based complexing agents such as ethylenediaminetetracetic acid (edta). They are compatible with most pesticides/herbicides, but their use in phosphate fertilizers is not recommended.

Oil Well Cement Retarders. Sodium and calcium lignosulfonates are the most commonly used retarders for oil well cements (98). They are effective with all Portland cements and are generally added in concentrations from 0.1–2%. Depending on their structure and purity and on the nature of the cement, they are effective to about 250°F bottom hole circulating temperature. This range can be extended to 400°F by addition of sugar acids or sodium borate.

Expanders for Lead-Acid Batteries. Oxylignin, a sodium lignosulfonate derived from the vanillin process, is the premier expander for lead acid batteries (99). Added to the negative plate at dosages of 0.1–0.5%, battery lifetimes are expanded from days to years.

Other Uses. Other uses of specially modified lignosulfonates include leather (qv) tanning (100), as flotation and wetting aids in ore processing, as sacrificial agents in enhanced oil recovery (101), as precipitating agents in protein recovery (102,103), in deicing formulations (104), and as wood preservatives (105). Medicinally, lignosulfonates have been purported to have value as antithrombotic (106) and antiviral (107,108) agents.

Interest in acrylic-graft copolymers of lignosulfonates is also growing. Commercially such products have found use as dispersants/fluid loss control agents for oil-well drilling muds and cements (109,110), as scale control agents in water treatment (111), as water reducing agents in the manufacture of bricks and ceramic materials (112), and as low inclusion animal feed binders (113).

5.2. Kraft Lignins. Kraft lignins, also called sulfate or alkali lignins, are obtained from black liquor by precipitation with acid. Generally, acidification is conducted in two steps. In the first step, carbon dioxide from the waste gases of boiler fires or from lime kilns is used to reduce the pH of the liquor from 12 to 9–10. About three quarters of the lignin is precipitated in this step as a sodium salt. After isolation, the material thus obtained can be used as is or further refined by washing. By suspending the salt in water and lowering the pH to 3 or less with sulfuric acid, refined lignin is obtained.

Typical compositions for softwood and hardwood kraft black liquors are shown in Table 9. Most commercial kraft lignins are sulfonated kraft lignins or lignin amines. A few nonsulfonated products are, however, available.

Physical and Chemical Properties of Kraft Lignins. Kraft lignins are soluble in alkali (pH $>$ 10.5), dioxane, acetone, dimethylformamide, and methyl cellosolve. They are insoluble in water at neutral and acidic pH, have number average molecular weights in the 2000–3000 range, and are less polydisperse

than lignosulfonates. A C_9 formula of $C_9H_{8.5}O_{2.1}S_{0.1}$ $(OCH_3)_{0.8}$ $(CO_2H)_{0.2}$ has been reported for softwood kraft lignin corresponding to a monomer molecular weight of ~180 (116). Due to the high degree of degradation during pulping, they also have a large number of free phenolic hydroxyl groups (4.0%).

The aromatic rings of kraft lignins can be sulfonated to varying degrees with sodium sulfite at high temperatures (150–200°C) or sulfomethylated with formaldehyde and sulfite at low temperatures (<100°C). Oxidative sulfonation with oxygen and sulfite is also possible.

Many of the chemical reactions used to modify lignosulfonates are also used to modify kraft lignins. These include ozonation, alkaline–air oxidation, condensation with formaldehyde and carboxylation with chloroacetic acid (117), and epoxysuccinate (118). In addition, cationic kraft lignins can be prepared by reaction with glycidylamine (119).

The physical and chemical properties of kraft lignin differ greatly from those of lignosulfonates. A summary of these differences is presented in Table 10.

Applications of Kraft Lignins. Because of the high fuel value of black liquor, kraft lignin products are generally used in high value applications. In many applications, the base lignin must be modified (ie, through sulfonation or oxidation) prior to use. Once modified, kraft lignins can be used in most of the same applications in which lignosulfonates are used. These include usage as emulsifying agents/emulsion stabilizers (120), as sequestering agents (121) as pesticide dispersants (122), as dye dispersants (66,123,124), as additives in alkaline cleaning formulations (125), as complexing agents in micronutrient formulations, as flocculants (126), and as extenders for phenolic adhesives (127). In addition, kraft lignins can also be used as an extender/modifier, and as a reinforcement pigment in rubber compounding (128,129).

Sulfonated kraft lignins derivatized via ethoxylation have recently been used as dispersants in numerous applications including pesticides and dyestuffs (114). Propoxylated lignosulfonates have found use commercially as nonretarding dispersants for oil well cements (115)

Toxicology of Lignosulfonates and Sulfonated Kraft Lignins. Rather extensive testing has shown that lignosulfonates are nontoxic. In most cases, LD_{50} values are >5 g/kg. The safe use of lignosulfonates in the manufacturing and processing of a wide variety of food and food packaging applications is covered under the following United States Food and Drug Administration (FDA) regulations: (*1*) as adjuvants in pesticide formulations exempt from the requirements of tolerance when applied pre- or post-harvest (21 CFR 182.99, 40 CFR 180.1001); (*2*) as dispersant or stabilizers in pesticides applied pre- or post-harvest to bananas (21 CFR 172.715); (*3*) as a boiler water additive used in the preparation of steam that will contact food (21 CFR 173.310); (*4*) as components of paperboard or paper in direct contact with moist, fatty, or dry food (21 CFR 176.170, 178.3120, 176.120, 176.180); (*5*) as component in food packaging (qv) adhesives (21 CFR 175.105); (*6*) as component of defoamers (qv) used in manufacturing food packaging-grade paper or paperboard (21 CFR 176.210); (*7*) in animal feed as pelleting or binder aid (limit of 4%), surfactant in molasses (limit of 11%), source of metabolizable energy (limit 4%) (21 CFR 573.600).

5.3. Organosolv Pulping Lignins. In organosolv pulping processes, hardwood chips are batch cooked for set times at appropriate temperatures

and pH in an aqueous ethanol or methanol liquor. In the process lignin, hemicelluloses, and other miscellaneous components of the wood are extracted into the alcoholic pulping liquor forming a black liquor. Organosolv lignin is recovered from the black liquor by precipitation, settled, centrifuged or filtered, and dried (129,130). The resulting lignin is a fine, brown, free-flowing powder.

Physical and Chemical Properties. Organosolv lignins are soluble in some organic solvents and in dilute alkali. They are insoluble in water at neutral or acidic pH. They have number average molecular weights <1000 and polydispersities between 2.4 and 6.3 (68). A C_9 formula of $C_9H_{8.53}O_{2.45}$ $(OCH_3)_{1.04}$ has been reported for one organosolv lignin (68). Which corresponds to a monomer molecular weight of 188.

Applications. These materials are still in developmental infancy, and are not currently available commercially. The lignins produced in these processes have potential application in wood adhesives, as flame retardants (qv), as slow-release agents for agricultural and pharmaceutical products, as surfactants (qv), as antioxidants (qv), as asphalt extenders, and as a raw material source for lignin-derived chemicals.

5.4. Other Lignins. In addition to main commercial lignins, there are a number of other lignins of no or limited commercial value. One of these is produced almost exclusively in the former Soviet Union where wood is used to produce glucose by acid hydrolysis. The lignin isolated as a by-product of this process is called acid hydrolysis lignin. It is claimed that in modified form such lignins can be used as rubber filling agents, as binders in wood adhesives, as additives in fabric treating compounds where they impart decay resistance, and as flotation aids in ore processing.

Numerous lignins have also been isolated in the laboratory including milled wood lignins, dioxane lignins, and enzymatically liberated lignins. These laboratory prepared lignins have different chemical and physical properties depending on the chemical modifications undergone during their isolation. Quantities are limited.

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STUART E. LEBO, JR.
JERRY D. GARGULAK
TIMOTHY J. MCNALLY
LignoTech USA, Inc.

Table 1. **Types and Frequencies of Interunitary Linkages in Softwood and Hardwood Lignins (Number of Linkages per 100 C_9 Units)**

Linkage	Softwood lignin[a]	Hardwood lignin[b]
β-*O*-4	49–51	65
α-*O*-4	6–8	
β-5	9–15	6
β-1	2	15
5-5	9.5	2.3
4-*O*-5	3.5	1.5
β-β	2	5.5

[a]Ref. 12.
[b]Ref. 11.

Table 2. **Klason Lignin Contents of Lignified Materials**[a]

Material	Klason lignin, %
softwoods	26–28.8
hardwoods	22
nonwood fibers	
bagasse	19.6
bamboo	22.2
wheat straw	17.0
kenaf	10.9
sorghum	7.9
pulp	
pine kraft	4.8
birch kraft	5.0
spruce kraft	2.8
birch acid sulfite	3.2
birch bisulfite	4.0

[a]Ref. 25.

Table 3. **Kappa Numbers for Typical Pulps**[a]

Pulp	Kappa number range
kraft (bleached grade)	
softwood	25–35
hardwood	14–18
neutral sulfite semichemical (softwood)	80–100
bisulfite (softwood)	30–50
acid sulfite	
softwood	16–22
hardwood	14–20
kraft (chlorinated and alkali extracted)	
softwood	5–8
hardwood	3–6

[a]Ref. 25.

Table 4. **Absorptivity Values, D, of Lignin at 280 nm**[a]

Lignin	D,L$(g \cdot cm)^{-1}$	Solvent
spruce MW	16.7	2-methoxyethanol
spruce MW	20.7	formamide
spruce MW	19.5	dioxane
pine MW	18.8	2-methoxyethanol/ethanol
beach MW	13.3	formamide
maple MW	12.9	2-methoxyethanol/ethanol
poplar dioxane	12.6	dioxane
spruce lignosulfonate	11.9	water
beech lignosulfonate	10.4	water
pine kraft	24.6	water
	26.4	2-methoxyethanol/water

[a]Ref. 33.

Table 5. **Phenolic and Aliphatic Hydroxyl Contents of Milled Wood and Technical Lignins**[a]

	Hydroxyl content, mol/C_9 unit		
Lignin	Total	Phenolic	Aliphatic
spruce MWL	1.46	0.28	1.18
bamboo MWL	1.49	0.36	1.13
pine kraft lignin	1.35	0.58	0.77
bamboo kraft lignin	1.00	0.44	0.56

[a]Ref. 49.

Table 6. **Carboxyl Contents of Various Lignins**[a]

Lignin	COOH, meq/g
hardwood kraft	1.44
hardwood native	0.92
lignosulfonates	0.31–2.08
wheat straw MWL	0.81
spruce MWL	0.12
decayed spruce	0.55
softwood kraft	0.80

[a]Ref. 55.

Table 7. **European and U.S. Lignin Manufacturers**

Producer	Country	Annual capacity, tonnes/yr
Borregaard LignoTech	Europe	400,000
	U.S.	70,000
Tembfibre	Europe	40,000
	Canada	40,000
Fraser Paper	U.S.	50,000
Tolmozzo	Italy	35,000
Westvaco	U.S.	30,000
Inland Paper	U.S.	20,000
Others		100,000
Total		*785,000*

Table 8. **Compositions of Spent Sulfite Liquors**[a]

	Percentage of total solids	
Component	Softwood	Hardwood
lignosulfonate	55	42
hexose sugars	14	5
pentose sugars	6	20
noncellulosic carbohydrates	8	11
acetic and formic acids	4	9
resin and extractives[b]	2	1
ash	10	10

[a]Ref. 70.
[b]For example, polyphenolic oils and tall oils.

Table 9. **Compositions of Kraft Black Liquors**[a]

Component	Total solids, %	
	Softwood	Hardwood
kraft lignin	45	38
xyloisosaccharinic acid	1	5
glucoisosaccharinic acid	14	4
hydroxy acids	7	15
acetic acid	4	14
formic acid	6	6
resin and fatty acids	7	6
turpentine	1	
others	15	12

[a]Ref. 48.

Table 10. **Properties of Kraft Lignins and Lignosulfonates**[a]

Property	Kraft lignins	Lignosulfonates
molecular weight	2,000–3,000	20,000–50,000
polydispersity	2–3	6–8
sulfonate groups,meq/g	0	1.25–2.5
organic sulfur, %	1–1.5	4–8
solubility	soluble in alkali (pH > 10.5), acetone, dimethylformamide, methyl cellosolve	soluble in water at all pHs; insoluble in organic solvents
color	dark brown	light brown
functional groups	many phenolic hydroxyl,carboxyl, and catecholgroups; some side-chain saturation	fewer phenolic hydroxyl, carboxyl, and catechol groups; little side-chain saturation

[a]Ref. 70.

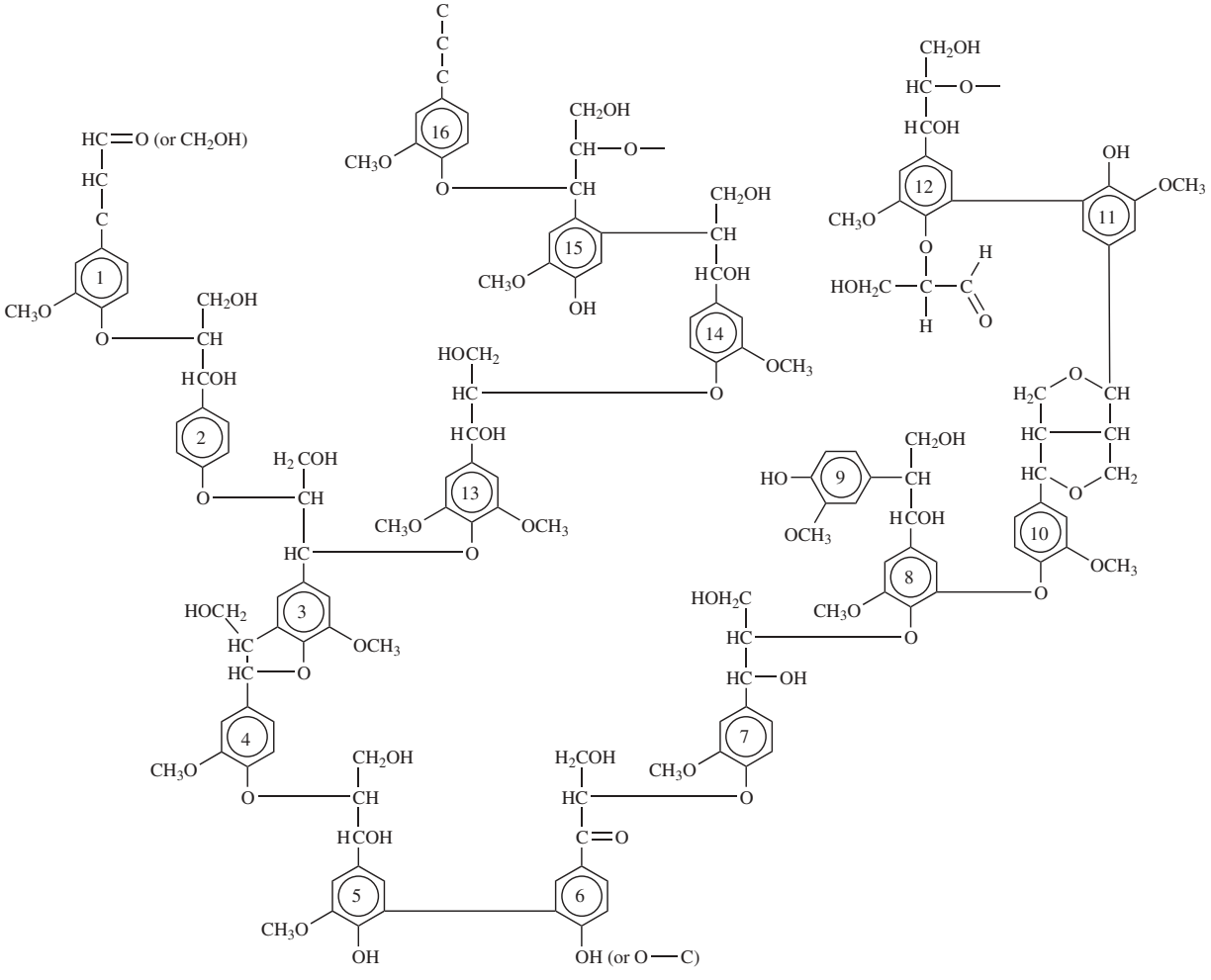

Fig. 1. Structural model of spruce lignin(10).

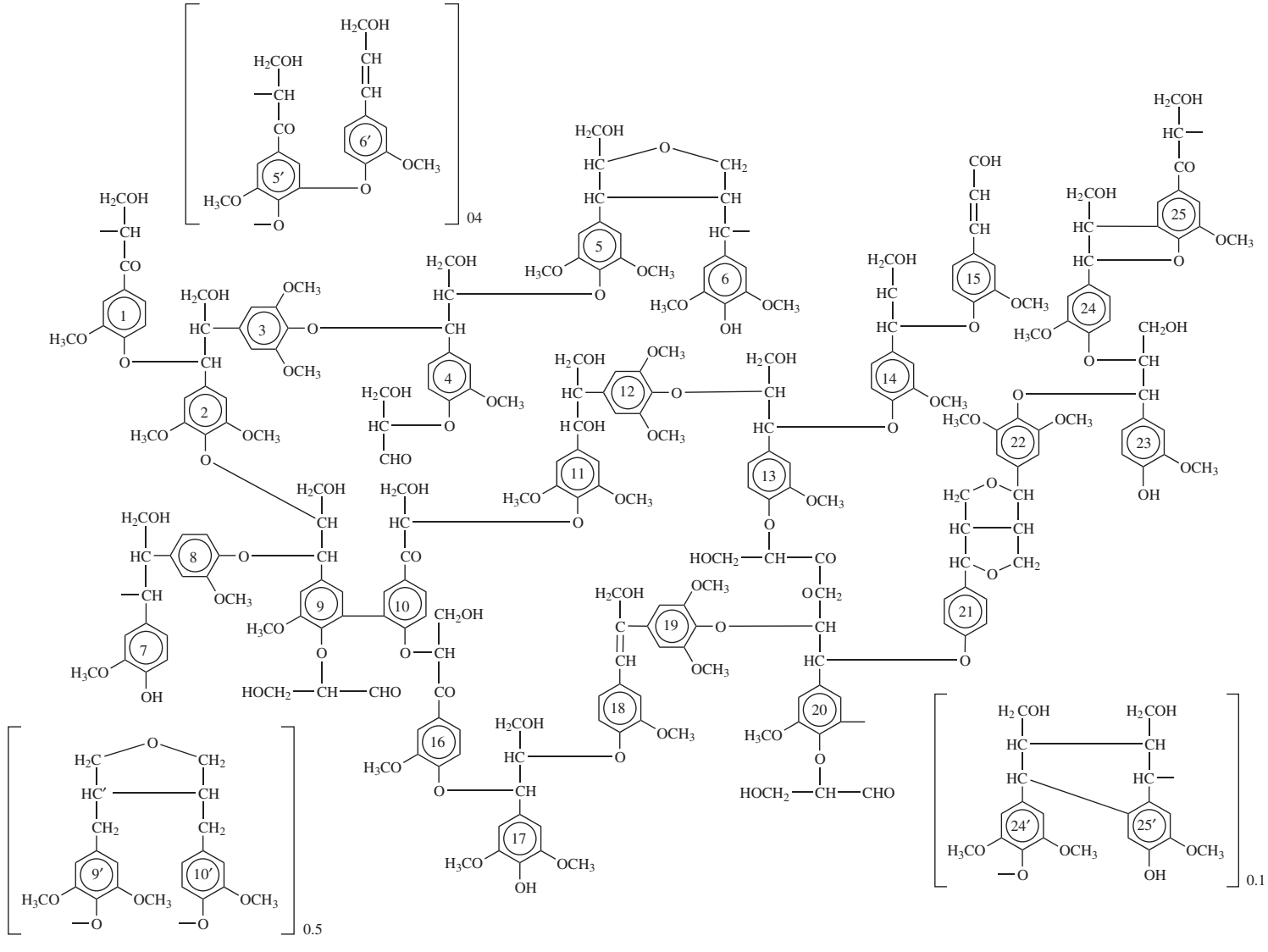

Fig. 2. Structural model of beech lignin (11).

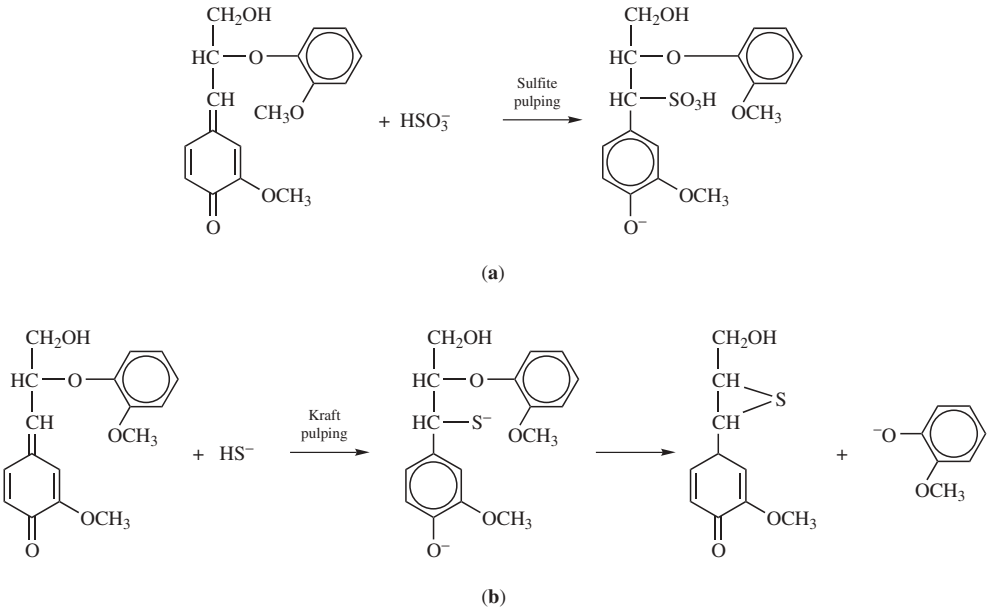

Fig. 3. Reactions at the quinonemethide center during pulping: (**a**) sulfite pulping, and (**b**) kraft pulping.