

Chapter 1

Structure and Properties of Lignin

Abstract Lignin is a phenolic natural polymer, second only to cellulose. It can be extracted from lignocellulosic biomass through various chemical, physical, mechanical, and enzymatic treatments. The chemical structure and properties of the extracted lignin are mainly depended on the extraction method, vegetal species, location, season, etc. Based on the separation method, several types of lignin, also called technical lignin, could be obtained, including alkali lignin/kraft lignin, liginosulfonate, organosolv lignin, milled wood lignin (MWL), klason lignin, and hydrolytic lignin. The separation conditions can influence the cross-linked structure and molecular weight distributions of the technical lignin products. By far, lignin is mainly regarded waste or by-product streams from paper pulping mills and cellulosic ethanol plants with a limited application for heat and power generation. However, the abundant availability and unique structure of lignin make it a potential feedstock for the synthesis of biochemicals and biopolymers such as surfactants/dispersants, carbon fibers, phenolic resins, epoxy resins, and polyurethane resins, etc.

Keywords Lignin · Phenolic natural polymer · Technical lignin · Alkali lignin · Kraft lignin · Lignosulfonate · Organosolv lignin · Milled wood lignin (MWL) · Klason lignin · Hydrolytic lignin

1.1 Lignin

Wood, a heterogeneous, hygroscopic, cellular and anisotropic material, consists of cells, and the cell walls consist mainly of three organic components including cellulose (40–60 wt%), hemicelluloses (25–35 wt%), and lignin (15–30 wt%) (Fig. 1.1) [1]. Lignin can be extracted from lignocellulosic biomass (such as woody biomass and other plants) by various treatments such as chemical, biochemical, and physical processes. The properties of extracted lignin (so called technical lignin), and its chemical structure and purity are strongly dependent on the treatment

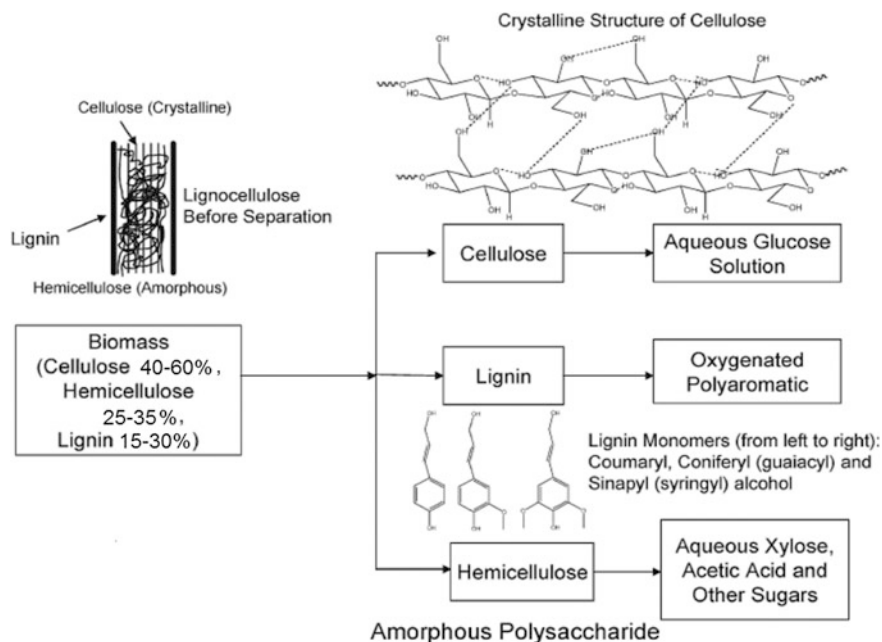


Fig. 1.1 Schematic structure of wood cells, reprinted with permission from Ref. [6] with modifications. Copyright (2006) American Chemical Society

method [2–4]. The industrial processes for lignin extraction can be classified into two different categories: sulfur processes and sulfur-free processes. Figure 1.2 shows various extraction processes and their corresponding products [2, 5]. Currently, the majority of technical lignin is generated in kraft pulping processes, and the annual kraft lignin (KL) generation is estimated to be 50 million tons, present in the form of “black liquor” that is used mainly in the recovery boilers for heat and power generation in the kraft pulping mills.

Lignin is the second most abundant natural renewable polymer after cellulose [7, 8] and accounts for between 15 and 30 wt% of lignocellulosic biomass as mentioned previously, contributing to the rigidity and strength of plant cell walls. Table 1.1 shows the contents of cellulose, hemicellulose, and lignin in common lignocellulosic biomass [9]. Unlike cellulose that has unique well-defined structure, lignin has a three-dimensional network structure and the structure depends on the vegetal species, location, season, etc. [3]. Elucidation of lignin structure plays an important role in its utilization for chemicals and materials. Different analytical methods such as FTIR [10], NMR [11–13] and GPC [14] have been widely used in exploring the structure of lignin.

Lignin is a phenolic polymer formed by radical coupling polymerization of three monolignols (Figs. 1.3 and 1.4) [14], and it has amorphous macromolecular structure comprising three types of phenyl-propanols, i.e., p-hydroxyl-phenyl propanol, guaiacyl-propanol and syringyl-propanol, linked mainly by ether linkages

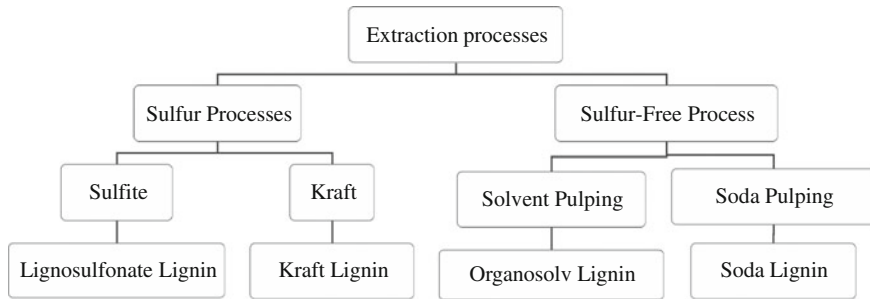


Fig. 1.2 Various lignin extraction processes and their dominant products (modified from Ref. [2])

Table 1.1 Contents of cellulose, hemicellulose, and lignin in common lignocellulosic biomass (reprinted with permission from Ref. [9])

Lignocellulosic materials	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwoods stems	40–55	24–40	18–25
Softwood stems	45–50	25–35	25–35
Nut shells	25–30	25–30	30–40
Corn cobs	45	35	15
Grasses	25–40	35–50	10–30
Paper	85–99	0	0–15
Wheat straw	30	50	15
Sorted refuse	60	20	20
Leaves	15–20	80–85	0
Cotton seed hairs	80–95	5–20	0
Newspaper	40–55	25–40	18–30
Waste papers from chemical pulps	60–70	10–20	5–10
Primary wastewater solids	8–15	NA	24–29
Swine waste	6.0	28	NA ^a
Solid cattle manure	1.6–4.7	1.4–3.3	2.7–5.7
Coastal Bermuda grass	25	35.7	6.4
Switch grass	45	31.4	12.0

Copyright (2002) Elsevier

^aNot available

(e.g., α -O-4, 5-O-4 and β -O-4) and condensed linkages (e.g., 5-5, β - β , β -5 and β -1 linkages) [15–17] (Fig. 1.3). Around 40–60% of total intermolecular linkages in the structure of lignin are ether bonds and the β -O-4 bond is a predominant ether linkage [14, 18]. The dominant monomer in softwood lignins is Guaiacyl (G) monomer, while hardwood lignins consist of both Syringyl (S) and Guaiacyl (G) units [19]. The reactivity of lignin depends on the form and composition of reactive functional groups within monomer units, in particular, its three types of functional groups: p-hydroxy-phenyl, aliphatic hydroxyl, and carboxylic acid groups [19].

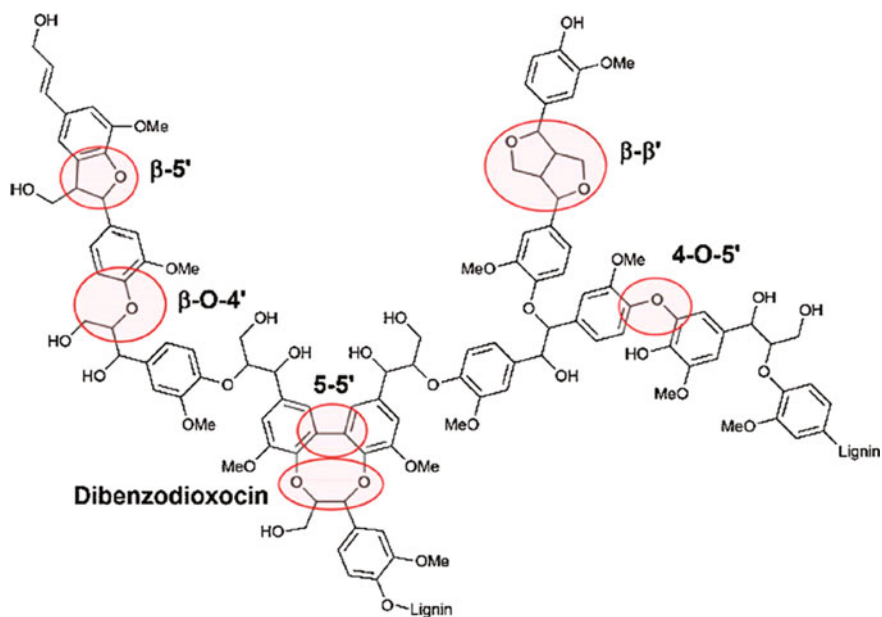


Fig. 1.3 A fraction of lignin model structure, reprinted with permission from Ref. [20]. Copyright (2013) Royal Society of Chemistry

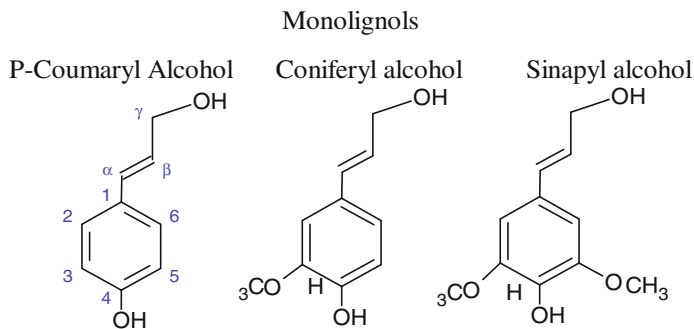


Fig. 1.4 Structure of three lignin monomers

1.2 Types of Lignin

Technical lignin is conventionally named after the separation (extraction) method, e.g., liginosulfonate lignin, kraft lignin, organosolv lignin, and soda lignin (Fig. 1.2). The lignin separation methods can also be categorized into two classes: (1) dissolving lignin into a solution, and (2) hydrolyzing cellulose and hemicellulose in acidic media and separating lignin as an insoluble residue [21, 22]. The

soluble lignin has an amorphous structure, and the insoluble one has the virginal morphological structure of the raw material fibers [22]. The presence of some functional groups such as phenolic hydroxyl and carboxyl on the structure of lignin facilitates its solubility in alkaline solutions. Organosolv lignin is soluble in various solvents such as dioxane, DMSO, methanol, ethanol, acetone, and pyridine. The common solvents for alkali lignin and lignosulfonate are dilute alkali, water, and salt solution. Acidic/enzymatic hydrolyzed lignin cannot be dissolved in any solvents [22]. The molecular weight and polydispersity of lignin are affected by the separation methods too due to the partial degradation of lignin during the extraction process [22]. In addition, the separation conditions including mechanical action, enzymes, or chemical reagents can influence the crosslinked structure of lignin and formed lignin fragments with different molecular weight distributions.

Some important types of technical lignin are described as follows:

- *Alkali Lignin/Kraft Lignin*

Alkali lignin is isolated from biomass in the presence of NaOH solution at high temperature and pressure. The linkages to polysaccharides are broken and lignin fragments are dissolved in the solvent, forming black liquor. The resulted lignin separated from black liquor with Na_2CO_3 is called soda lignin. The lignin separated in the presence of Na_2SO_4 is named kraft lignin [21, 23].

- *Lignosulfonate*

Lignosulfonates or sulfonated lignins are water-soluble anionic polyelectrolyte polymers, recovered from the sulfite pulping of wood (brown liquor) [24]. In the pulping process, an aqueous solution containing sulfur dioxide and a sulfurous acid salt are used to break down the linkages to polysaccharides [21]. Depending on the type of bases in pulping process, various lignosulfonates such as calcium [25, 26], sodium [27, 28], magnesium [29], and ammonium lignosulfonates [30] can be formed. Finally, lignosulfonates can be isolated from spent pulping liquors by various methods including precipitation in alcohol, dialysis, electrodialysis, ion exclusion, ultrafiltration, supported liquid membrane (SLM), and extraction with amines [24, 31, 32].

- *Organosolv Lignin*

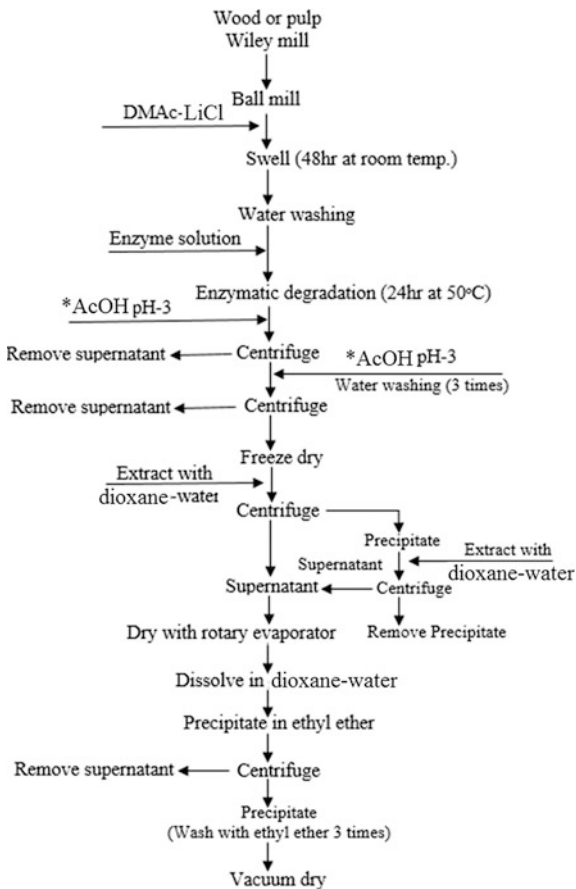
Organosolv pulping is conducted in the presence of an aqueous organic solvent at the temperature ranging from 140 to 220 °C. In this process, the alpha aryl-ether linkages of lignin are broken down by hydrolytic cleavage and the obtained fragments dissolve in the solvent [21, 33]. One of the suitable catalysts for organosolv pulping is HCl in the presence of water with different solvents including acetone, methanol, ethanol, butanol, ethylene glycol, formic acid or acetic acid, or their mixtures etc. [34, 35]. The concentration of solvent in water varies in the range of 40–80%. Dozens of organosolv methods have been reported in the literature and the obtained lignin was commonly named as organosolv lignin [34], among which four main organosolv pulping processes are Organocell process [34, 36, 37], Alcell process [34, 38], alkaline sulfite-antraquinone-methanol (ASAM) process [34, 39–41], and acetosolv

process [34, 42–44]. It was reported that the organosolv process with ethanol-water mixed solvent produces a higher pulp yield than that of kraft process, and the tensile and tear strength of softwood organosolv pulps fall between the corresponding values of kraft pulp and sulphite pulp [45].

- *Milled Wood Lignin (MWL)*

The milled wood lignin is obtained from milling wood in a ball-mill for tens of hours and the linkages to polysaccharides are broken mechanically. The fragmented lignin is dissolved in solvents such as 0.2 mol/L NaOH solution followed by extraction with dioxane-water mixture [21, 46, 47]. Crestini et al. [48] investigated the chemical structure of different softwood and hardwood milled wood lignins by combining quantitative data arising from ^{31}P NMR and QQ-HSQC analyses. It was suggested that the milled wood lignin is a linear oligomer rather than a network polymer. The yield of isolated lignin from MWL is often low and many studies have been conducted to improve this process. Lin and Dence [49] proposed a novel process called milled wood enzyme lignin

Fig. 1.5 SEL process for isolation of lignin, reprinted with permission from Ref. [50]. Copyright (1995) Springer



(MWEL) process with higher yield of lignin by treating the milled wood with enzymes to solubilize the carbohydrate components. However, this process requires ten or more days to accomplish due to the high crystalline structure of cellulose. To overcome this challenge, swelled enzyme lignin (SEL) was tested by Chen et al. [50]. The procedure of SEL is displayed in Fig. 1.5. Lignin yields were as high as 24–67% based on the total amount of lignin present.

Some typical types of lignin isolated by insoluble methods are listed below:

- *Klason Lignin*

Klason method is a standard method for determination the lignin content in wood [51]. In this process, all polysaccharide linkages are hydrolyzed with 72% sulfuric acid and leaving the solid lignin residue [21, 52].

- *Hydrolytic Lignin*

In a dilute acid, most of the polysaccharides linkages are hydrolyzed into fermentable sugar and the resulted residue is hydrolytic lignin [9, 21]. The hydrolytic lignin, extracted from the residues of the cellulosic ethanol production, is commonly known as “enzymatic hydrolysis lignin (EHL)”. As enzymatic hydrolysis processes of biomass normally operates under relatively mild conditions, the most active functional groups such as phenolic hydroxyl and alcoholic hydroxyl can be preserved [53]. As a consequence, the resulting EHL is expected to be more reactive in comparison with lignosulfonate or kraft lignin [53, 54]. However, in practice, the hydrolytic lignin has a very large molecular structure with strong steric hindrance and normally contains sugar impurities, so it is not as reactive as organosolv or kraft lignin in chemical applications. As such, enzymatic hydrolysis lignin is usually used as a fuel in combustion or gasification processes to generate steam or electricity [53].

1.3 Utilization of Lignin

Until recently, lignin has been considered as a waste by-product of paper pulping mills and cellulosic ethanol plants. It is mainly consumed in the mills/plants in recovery boilers for heat and power generation [55], and a small quantity of lignin (<1%) is used as fillers such as ink varnishes, paints, and elastomeric matrices or surfactants/dispersants [3]. While in recent decades, there is a growing interest in utilization of lignin as a feedstock for the synthesis of bioaromatic chemicals (such as vanillin and phenols) and bio-based polymeric materials (resins and polymers) due to the following driving forces [56]:

- (1) The material is sustainable and renewable,
- (2) There is immense generation of lignin as a by-product in pulp/paper industry and cellulosic ethanol industry,

- (3) There are various functional groups present in lignin structure which enable a variety range of chemical reactions,
- (4) Lignin has intrinsic biodegradability and it is believed that the incorporated polymers with lignin would be more biodegradable than the petroleum based polymers.

Normally, lignin can be used as a filler or can substitute <20–30 wt% of some reactive components in polymers (such as phenols for phenolic resins and polyols for polyurethane, or bisphenol-A for epoxy resins, etc.) [3, 16, 57]. Limited by lignin's detrimental properties (large M_w with steric hindrance effects, poor solubility in organic solvent and low reactivity), a greater substitution ratio of lignin in polymer materials is challenging, but can be achieved by modifications on its structure. Different lignin modification technologies have been explored, which include chemical [58, 59], biological [60], photochemical [61, 62], and electrochemical [61, 63] methods. Among these methods, chemical modification processes have attracted significant interest. It is well known that lignin is a polydisperse natural phenolic polymer, as shown in Figs. 1.3 and 1.4. Lignin contains both polar (hydroxyl) groups and nonpolar hydrocarbon and benzene rings, it is thus expected to act as a compatibilizer between hydrophilic natural fibers and a hydrophobic matrix polymer [7, 64–66]. The presence of the phenolic hydroxyl groups in lignin has also enabled its utilization in the synthesis of various polymers such as phenolic resins [67], epoxy resins [68, 69], polyurethanes [56, 57, 70], and polyesters [70, 71]. These lignin-based polymers will be introduced in details in the subsequent chapters.

1.4 Summary

Lignin is the second most abundant natural renewable polymer after cellulose. Natural lignin is a phenolic polymer formed by radical coupling polymerization of three monolignols, and it has amorphous macromolecular structure comprising three types of phenyl-propanols, i.e., p-hydroxyl-phenyl propanol, guaiacyl-propanol and syringyl-propanol, linked mainly by ether linkages (e.g., α -O-4, 5-O-4 and β -O-4) and condensed linkages (e.g., 5-5, β - β , β -5 and β -1 linkages). Technical lignin can be extracted from lignocellulosic biomass by various separation methods. The chemical structure and the properties of technical lignin are mainly affected by the delignification process. The typical types of technical lignin are kraft lignin, organosolv lignin, liginosulfonate, milled wood lignin, and hydrolysis lignin. Currently, the annual kraft lignin generation is estimated to be 50 million tons, present in the form of “black liquor” that is used mainly in the recovery boilers for heat and power generation in the kraft pulping mills. However, the availability and the presence of various functional groups (aromatic and hydroxyl) on lignin make it as a potential candidate for the synthesis of bioaromatic chemicals (such as vanillin and phenols) and bio-based polymeric materials (resins and polymers).

References

1. Ragauskas AJ, Williams CK, Davison BH et al (2006) The path forward for biofuels and biomaterials. *Science* 311:484–489. doi:[10.1126/science.1114736](https://doi.org/10.1126/science.1114736)
2. Laurichesse S, Avérous L (2014) Chemical modification of lignins: towards biobased polymers. *Prog Polym Sci* 39:1266–1290
3. Belgacem MN, Blayo A, Gandini A (2003) Organosolv lignin as a filler in inks, varnishes and paints. *Ind Crops Prod* 18:145–153. doi:[10.1016/S0926-6690\(03\)00042-6](https://doi.org/10.1016/S0926-6690(03)00042-6)
4. Kouisni L, Holt-hindle P, Maki K, Paleologou M (2012) The Lignoforce System™: a new process for the production of high-quality lignin from black liquor. *J Sci Technol For Prod Process* 2:6–10
5. Lora JH, Glasser WG (2002) Recent industrial applications of lignin: a sustainable alternative to nonrenewable materials. *J Polym Environ* 10:39–48
6. Huber GW, Iborra S, Corma A (2006) Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chem Rev* 106:4044–4098. doi:[10.1021/cr068360d](https://doi.org/10.1021/cr068360d)
7. Wool RP, Sun XS (2005) Bio-based polymer and composites. Elsevier Academic Press, California
8. Vfizquez G, Gonzfilez J, Freire S, Antorrena G (1997) Effect of chemical modification of lignin on the gluebond performance of lignin-phenolic resins. *Bioresour Technol* 60:191–198
9. Sun Y, Cheng J (2002) Hydrolysis of lignocellulosic materials for ethanol production: a review. *Bioresour Technol* 83:1–11. doi:[10.1016/S0960-8524\(01\)00212-7](https://doi.org/10.1016/S0960-8524(01)00212-7)
10. Pandey KK (1999) A study of chemical structure of soft and hardwood and wood polymers by FTIR spectroscopy. *J Appl Polym Sci* 71:1969–1975. doi:[10.1002/\(SICI\)1097-4628\(19990321\)71:12<1969:AID-APP6>3.0.CO;2-D](https://doi.org/10.1002/(SICI)1097-4628(19990321)71:12<1969:AID-APP6>3.0.CO;2-D)
11. Sette M, Wechselberger R, Crestini C (2011) Elucidation of lignin structure by quantitative 2D NMR. *Chem Eur J* 17:9529–9535. doi:[10.1002/chem.201003045](https://doi.org/10.1002/chem.201003045)
12. Crestini C, Argyropoulos DS (1997) Structural analysis of wheat straw lignin by quantitative ³¹P and 2D NMR spectroscopy. The occurrence of ester bonds and r-O-4 substructures. *J Agric Food Chem* 45:1212–1219
13. Knut L (1980) NMR studies of lignin. 4. Investigation of spruce lignin by HNMR spectroscopy. *Acta Chem Scand B* 34:21–26
14. Ghaffar SH, Fan M (2013) Structural analysis for lignin characteristics in biomass straw. *Biomass Bioenergy* 57:264–279. doi:[10.1016/j.biombioe.2013.07.015](https://doi.org/10.1016/j.biombioe.2013.07.015)
15. Faulon J-L, Hatcher PG, Fadon J (1994) Is there any order in the structure of lignin? *Energy Fuels* 8:402–407. doi:[10.1021/ef00044a018](https://doi.org/10.1021/ef00044a018)
16. Delmas G-H, Benjelloun-Mlayah B, Le Bigot Y, Delmas M (2013) Biolignin™ based epoxy resins. *J Appl Polym Sci* 127:1863–1872. doi:[10.1002/app.37921](https://doi.org/10.1002/app.37921)
17. Vanholme R, Demedts B, Morreel K et al (2010) Lignin biosynthesis and structure. *Plant Physiol* 153:895–905. doi:[10.1104/pp.110.155119](https://doi.org/10.1104/pp.110.155119)
18. Marković JP, Štrbanović RT, Terzić DV et al (2012) Changes in lignin structure with maturation of alfalfa leaf and stem in relation to ruminants nutrition. *Afr J Agric Res* 7:257–264. doi:[10.5897/AJAR11.1485](https://doi.org/10.5897/AJAR11.1485)
19. Ahvazi B, Wojciechowicz O, Ton-That T-M, Hawari J (2011) Preparation of lignopolyols from wheat straw soda lignin. *J Agric Food Chem* 59:10505–10516. doi:[10.1021/jf202452m](https://doi.org/10.1021/jf202452m)
20. Forsythe WG, Garrett MD, Hardacre C et al (2013) An efficient and flexible synthesis of model lignin oligomers. *Green Chem* 15:3031–3038. doi:[10.1039/c3gc41110a](https://doi.org/10.1039/c3gc41110a)
21. Jiang G, Nowakowski DJ, Bridgwater AV (2010) A systematic study of the kinetics of lignin pyrolysis. *Thermochim Acta* 498:61–66. doi:[10.1016/j.tca.2009.10.003](https://doi.org/10.1016/j.tca.2009.10.003)
22. Chen H (2014) Biotechnology of lignocellulose. Theory and practice. doi:[10.1007/978-94-007-6898-7](https://doi.org/10.1007/978-94-007-6898-7)
23. Macek A (1999) Research on combustion of black-liquor drops. *Prog Energy Combust Sci* 25:275–304. doi:[10.1016/S0360-1285\(98\)00027-6](https://doi.org/10.1016/S0360-1285(98)00027-6)

24. Lebo SE, Gargulak JD, McNally TJ (2001) Lignin. Kirk-Othmer Encycl Chem Technol 15:1–32. doi:[10.1002/0471238961.12090714120914.a01.pub2](https://doi.org/10.1002/0471238961.12090714120914.a01.pub2)
25. Ansari A, Pawlik M (2007) Floatability of chalcopyrite and molybdenite in the presence of lignosulfonates. Part I. Adsorption studies. Miner Eng 20:600–608. doi:[10.1016/j.mineng.2006.12.007](https://doi.org/10.1016/j.mineng.2006.12.007)
26. Ouyang X, Qiu X, Chen P (2006) Physicochemical characterization of calcium lignosulfonate—a potentially useful water reducer. Colloids Surf A Physicochem Eng Asp 282–283:489–497. doi:[10.1016/j.colsurfa.2005.12.020](https://doi.org/10.1016/j.colsurfa.2005.12.020)
27. Li B, Lv W, Zhang Q et al (2014) Pyrolysis and catalytic pyrolysis of industrial lignins by TG-FTIR: kinetics and products. J Anal Appl Pyrol 108:295–300. doi:[10.1016/j.jaap.2014.04.002](https://doi.org/10.1016/j.jaap.2014.04.002)
28. Zhou H, Yang D, Wu X et al (2012) Physicochemical properties of sodium lignosulfonates (NaLS) modified by laccase. Holzforschung 66:825–832. doi:[10.1515/hf-2011-0189](https://doi.org/10.1515/hf-2011-0189)
29. Kang S, Li B, Chang J, Fan J (2011) Antioxidant abilities comparison of lignins with their hydrothermal liquefaction products. BioResources 6:243–252
30. Peter D, Schlegel SL (1988) Method of producing improved amine salts of lignosulfonates. US Patent 4748235 A, 31 May 1988
31. Ringena O, Saake B, Lehnen R (2005) Isolation and fractionation of lignosulfonates by amine extraction and ultrafiltration: a comparative study. Holzforschung 59:405–412
32. Xiana CK, Othmana N, Harruddina N et al (2014) Extraction of lignosulfonate using TOA-kerosene-PVDF in supported liquid membrane process. J Teknol 2:59–63
33. Alcaide LJ, Domonguez JCG, Perez OTIP (2003) Influence of cooking variables in the organosolv pulping of wheat straw using mixtures of ethanol, acetone, and water. Tappi J 2:27–31
34. Muurinen E (2000) Organosolv pulping. A review and distillation study related to peroxyacid pulping. Dissertation, University of Oulu, Finland
35. Rodriguez A, Jiménez L (2008) Pulping with organic solvents other than alcohols. Afinidad LXV 65:188–196
36. Lindnera A, Wegener G (1988) Characterization of lignins from organosolv pulping according to the organocell process. Part 1. Elemental analysis, nonlignin portions and functional groups. J Wood Chem Technol 8:323–340
37. Lindnera A, Wegener G (1990) Characterization of lignins from organosolv pulping according to the Organocell process. Part 3. Permanganate oxidation and thioacidolysis. J Wood Chem Technol 10:331–350
38. Pye E, Lora J (1991) The Alcell process. A proven alternative to kraft pulping. Tappi J 74:113–118
39. Sridach W (2010) The environmentally benign pulping process of non-wood fibers. J Sci Technol 17:105–123
40. Kordsachia O, Wandinger B, Patt R (1992) Some investigations on ASAM pulping and chlorine free bleaching of Eucalyptus from Spain. Holz Roh-Werkst 50:85–91
41. Kirçi H, Bostançi S, Yalinkiliç MK (1994) A new modified pulping process alternative to sulphate method “Alkali-Sulfite-Antraquinone-Ethanol (ASAE)”. Wood Sci Technol 28:89–99. doi:[10.1007/BF00192688](https://doi.org/10.1007/BF00192688)
42. Vázquez G, Antorrena G, Gonzalez J (1995) Acetosolv pulping of *Eucalyptus globulus* wood. Part I. The effect of operational variables on pulp yield, pulp lignin content and pulp potential glucose content. Holzforschung 49:69–74
43. Vázquez G, Antorrena G, González J et al (1997) Acetosolv pulping of pine wood. Kinetic modelling of lignin solubilization and condensation. Bioresour Technol 59:121–127. doi:[10.1016/S0960-8524\(96\)00168-X](https://doi.org/10.1016/S0960-8524(96)00168-X)
44. Abad S, Santos V, Parajó JC (1999) Simulation of acetosolv pulping of *Eucalyptus* wood. J Wood Chem Technol 19:225–246. doi:[10.1080/02773819909349610](https://doi.org/10.1080/02773819909349610)
45. Johansson A, Aaltonen O, Ylinen P (1987) Organosolv pulping—methods and pulp properties. Biomass 13:45–65

46. Rencoret J, Marques G, Gutiérrez A et al (2009) Isolation and structural characterization of the milled-wood lignin from *Paulownia fortunei* wood. *Ind Crops Prod* 30:137–143. doi:[10.1016/j.indcrop.2009.03.004](https://doi.org/10.1016/j.indcrop.2009.03.004)
47. Min DY, Smith SW, Chang HM, Jameel H (2013) Influence of isolation condition on structure of milled wood lignin characterized by quantitative ¹³C nuclear magnetic resonance spectroscopy. *BioResources* 8:1790–1800
48. Crestini C, Melone F, Sette M, Saladino R (2011) Milled wood lignin: a linear oligomer. *Biomacromolecules* 12:3928–3935. doi:[10.1021/bm200948r](https://doi.org/10.1021/bm200948r)
49. Lin SY, Dence CW (eds) (1992) *Methods in lignin chemistry*. Springer, Heidelberg
50. Chen J, Shimizu Y, Takai M, Hayashi I (1995) A method for isolation of milled-wood lignin involving solvent swelling prior to enzyme treatment. *Wood Sci Technol* 29:295–306. doi:[10.1007/BF00202089](https://doi.org/10.1007/BF00202089)
51. Schwanninger M, Hinterstoisser B (2005) Klason lignin: modifications to improve the precision of the standardized determination. *Holzforschung* 56:161–166
52. Hatfield RD, Jung HG, Ralph J et al (1994) A comparison of the insoluble residues produced by the Klason lignin and acid detergent lignin procedures. *J Sci Food Agric* 65:51–58. doi:[10.1002/jsfa.2740650109](https://doi.org/10.1002/jsfa.2740650109)
53. Yin Q, Yang W, Sun C, Di M (2012) Preparation and properties of lignin-epoxy resin composite. *BioResources* 7:5737–5748
54. Jin Y, Cheng X, Zheng Z (2010) Preparation and characterization of phenol-formaldehyde adhesives modified with enzymatic hydrolysis lignin. *Bioresour Technol* 101:2046–2048. doi:[10.1016/j.biortech.2009.09.085](https://doi.org/10.1016/j.biortech.2009.09.085)
55. Hu TQ (2002) *Chemical modification, properties and usage of lignin*. Kluwer Academic/Plenum Publisher, New York
56. Cateto CA, Barreiro MF, Rodrigues AE (2008) Monitoring of lignin-based polyurethane synthesis by FTIR-ATR. *Ind Crops Prod* 27:168–174. doi:[10.1016/j.indcrop.2007.07.018](https://doi.org/10.1016/j.indcrop.2007.07.018)
57. Cateto CA, Barreiro MF, Rodrigues AE, Belgacem MN (2011) Kinetic study of the formation of lignin-based polyurethanes in bulk. *React Funct Polym* 71:863–869. doi:[10.1016/j.reactfunctpolym.2011.05.007](https://doi.org/10.1016/j.reactfunctpolym.2011.05.007)
58. Mu H, Liu C, Zheng T, Huang Y (2006) Chemical modification of lignin and its utilization. *J Agro-Environ Sci* 1:1–10
59. Gellerstedt G, Majtnerova A, Zhang L (2004) Towards a new concept of lignin condensation in kraft pulping. Initial results. *C R Biol* 327:817–826. doi:[10.1016/j.crv.2004.03.011](https://doi.org/10.1016/j.crv.2004.03.011)
60. Pérez J, Muñoz-Dorado J, de la Rubia T, Martínez J (2002) Biodegradation and biological treatments of cellulose, hemicellulose and lignin: an overview. *Int Microbiol* 5:53–63. doi:[10.1007/s10123-002-0062-3](https://doi.org/10.1007/s10123-002-0062-3)
61. Tian M, Wen J, McDonald D et al (2010) A novel approach for lignin modification and degradation. *Electrochem Commun* 12:527–530
62. Kaneko M, Nemoto J, Ueno H et al (2006) Photoelectrochemical reaction of biomass and bio-related compounds with nanoporous TiO₂ film photoanode and O₂-reducing cathode. *Electrochem Commun* 8:336–340. doi:[10.1016/j.elecom.2005.12.004](https://doi.org/10.1016/j.elecom.2005.12.004)
63. Antunes CSA, Bietti M, Salamone M, Scione N (2004) Early stages in the TiO₂-photocatalyzed degradation of simple phenolic and non-phenolic lignin model compounds. *J Photochem Photobiol A Chem* 163:453–462. doi:[10.1016/j.jphotochem.2004.01.018](https://doi.org/10.1016/j.jphotochem.2004.01.018)
64. Simionescu CI, Rusan V, Macoveanu MM et al (1993) Lignin/epoxy composites. *Compos Sci Technol* 48:317–323
65. Raikila S (2008) The effect of lignin content and lignin modification on Norway spruce wood properties and decay resistance. Dissertation, University of Helsinki
66. Acha BA, Marcovich NE, Reboredo MM (2009) Lignin in jute fabric–polypropylene composites. *J Appl Polym Sci* 113:1480–1487. doi:[10.1002/app.29999](https://doi.org/10.1002/app.29999)
67. Wang M, Leitch M, Xu CC (2009) Synthesis of phenol–formaldehyde resol resins using organosolv pine lignins. *Eur Polym J* 45:3380–3388
68. Simionescu CI, Cazacu G, Macoveanu MM (1987) Lignin-epoxy resins. II Physical and chemical characterization. *Cellul Chem Technol* 21:525–534

69. Miyagawa H, Misra M, Drzal LT, Mohanty AK (2005) Biobased epoxy/layered silicate nanocomposites: thermophysical properties and fracture behavior evaluation. *J Polym Environ* 13:87–96. doi:[10.1007/s10924-005-2940-1](https://doi.org/10.1007/s10924-005-2940-1)
70. Bonini C, D'Auria M, Emanuele L et al (2005) Polyurethanes and polyesters from lignin. *J Appl Polym Sci* 98:1451–1456. doi:[10.1002/app.22277](https://doi.org/10.1002/app.22277)
71. Evtugin DV, Gandini A (1996) Polyesters based on oxygen-organosolv lignin. *Acta Polym* 47:344–350. doi:[10.1002/actp.1996.010470805](https://doi.org/10.1002/actp.1996.010470805)