1

General Background and Introduction

Abstract

Lignin, a complicated organic polymer, plays a significant structural function in the support tissues of vascular plants. It is particularly prevalent in woody plants and is highly polymerized. Lignin is one of the three crucial elements of wood, along with extractives and carbohydrates. Lignin, a three-dimensional amorphous polymer made of methoxylated phenylpropane structures, is important for the survival of vascular plants. In nature, lignin polymer generally forms ether or ester linkages with hemicellulose which is also connected with cellulose. The structural and chemical composition of lignin; representative linkages in lignin molecules and types of lignin are presented in this chapter.

Keywords *Lignin; Phenylpropane units; Monolignols; Sinapyl alcohol; Coniferyl alcohol; p-coumaryl alcohol; Hardwood lignin; Softwood lignin;*

With the rapid growth of populations and rising living standards in developing nations, global energy demand is rapidly rising. To meet this rising energy demand, fossil resources alone will not be sufficient. At the same time, there are significant concerns regarding the impact of climate change, which may be linked to the combustion of fossil fuels that are not renewable. As a result, it is crucial to develop technologies that can use new energy solutions on a large scale and provide more environmentally friendly alternatives to the current economy based on fossil fuels. Because this renewable feedstock can theoretically be incorporated into a carbon dioxide-neutral energy cycle, biomass is an option for the production of sustainable fuels and chemicals. Cellulose, hemicellulose, and lignin are the three main components of biomass.

Aromatic compounds, which can be used as fuel or as intermediate chemicals in the industry, can be obtained from lignin, the organic biopolymer that is found in the second highest concentration anywhere on the planet. Biomass conversion technology's viability can be improved by incorporating lignin into biorefineries. The recalcitrant and complicated nature of the lignin feedstock presents the primary obstacle in this situation. It is a huge challenge to properly convert lignin into functional polymers, but this is a fascinating area of research in both industry and academia (Guvenatam, 2015).

Depolymerization of Lignin to Produce Value Added Chemicals, First Edition. Pratima Bajpai.

1.1 Structural and Chemical Composition of Lignin

The Swiss botanist Augustin Pyramus de Candolle was the first person to use the term lignin, which comes from the Latin word *lignum*, which means wood (Candolle et al., 1821). Lignin, a complicated organic polymer, plays a significant structural role in the support tissues of vascular plants. It is particularly prevalent in woody plants and is highly polymerized. Lignin is one of the three crucial elements of wood, along with extractives and carbohydrates (Sarkanen and Ludwig, 1971; Sjöström, 1982). Protolignin is the name given to lignin when it is in its natural state, as it is in plants. Lignin, a three-dimensional amorphous polymer made of methoxylated phenylpropane structures, is essential for the survival of vascular plants. In nature, lignin polymer usually forms ether or ester linkages with hemicellulose which is also associated with cellulose. Therefore, these natural polymers construct a complicated and valuable lignocellulose polymer (Figure 1.1).

1.2 Major Backbone Units and Representative Linkages in Lignin Molecules

It is generally acknowledged that the polymerization of three types of phenylpropane units, also known as monolignols, initiates the biosynthesis of lignin (Freudenberg and Neish, 1968; Lewis, 1999; Ralph, 1999; Sarkanen and Ludwig, 1971). These units, sinapyl, coniferyl, and p-coumaryl alcohol, are linked by the chemical bonds of aryl ether (β-O-4), phenylcoumaran (β-5), resinol (β-β), biphenyl ether (5-O-4), and dibenzodioxocin (5–5) (Figure 1.2). In Figure 1.3, the three structures are shown. The most typical linkage among the various typical linkages (β-O-4, β-5, β-1, 5–5, α-O-4, 4-O-5, β-β) (Figure 1.4) is the β-aryl ether (β-O-4), which accounts for more than half of the structure of lignin (Dutta et al., 2014; Rinaldi et al., 2016). Figure 1.5 shows model lignin structures: A softwood, B hardwood, and C grass (Lu and Gu, 2022).

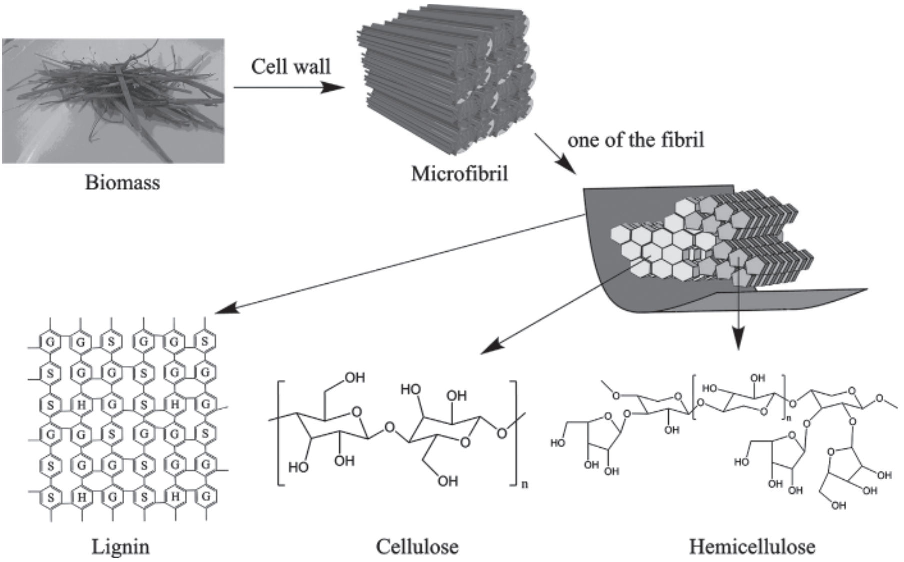
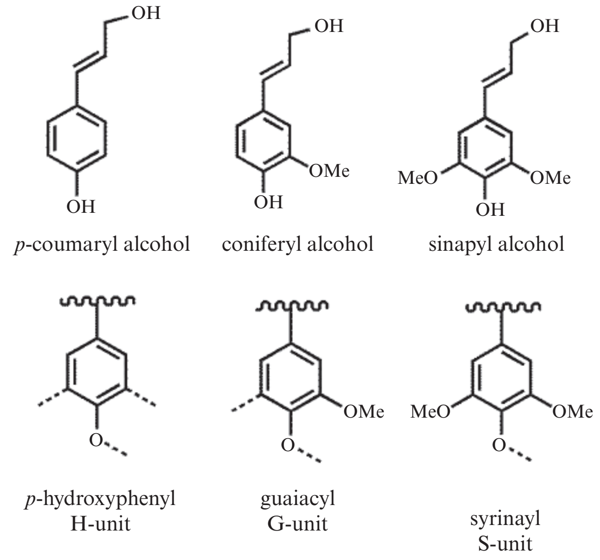


Figure 1.1 Lignocellulose in biomass and its composition. Chonlong Chio et al. 2019 / Reproduced with permission from Elsevier.

(a) Basic units



(b) Main linkages

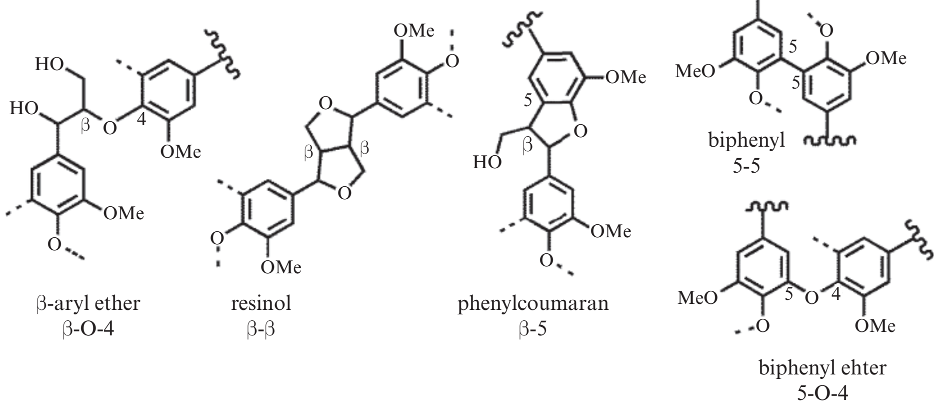
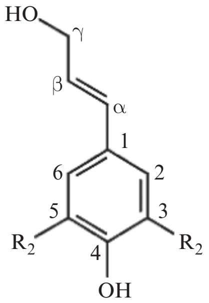


Figure 1.2 Major backbone units and representative linkages in lignin molecules. (a) The building blocks of lignin consist of three primary types of monolignols, namely *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. The alcohols form the corresponding phenylpropanoid units like p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) in lignin polymer, respectively. (b) Backbone units are conjugated via different chemical bonds (e.g., β-O-4, β-β, 5–5, and β-5) resulting in high resistance to lignin depolymerisation Weng et al. (2021) / Springer Nature / Public Domain CC BY 4.0.

Figure 1.6 demonstrates the phenoxy radicals that are resonance-stabilized and the dehydrogenation of coniferyl alcohol (Chakar and Ragauskas, 2004). The polymerization interaction is set up by the oxidation of the monolignol phenolic hydroxyl groups. It has been demonstrated that an enzymatic pathway catalyzes the oxidation itself. An electron transfer initiates the enzymatic dehydrogenation, resulting in reactive monolignol species and free radicals, which are able to pair with one another. The aromaticity of the benzene ring will be restored by a subsequent nucleophilic attack by water, alcohols, or phenolic hydroxyl groups on the benzyl carbon of the quinone methide intermediate. Polymerization will continue on the produced dilignols.



Coniferyl alcohol/guaiacyl: R_1=OMe, R_2=H
Sinapyl alcohol/syringyl: R_1=R_2=OMe
*p*Coumaryl alcohol: R_1=R_2=H

Figure 1.3 The three building blocks of lignin. Chakar and Ragauskas, 2004 / with permission of ELSEVIER.

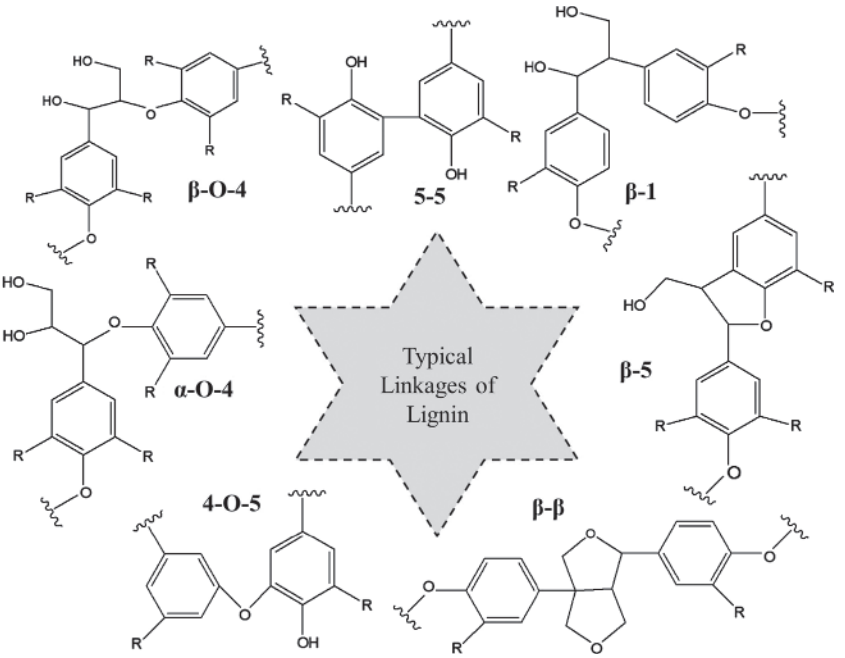


Figure 1.4 Typical linkages present in lignin. Agarwal et al. (2018) / with permission of ELSEVIER.

Architecturally, lignin forms a complex, three-dimensional heterogeneous network thanks to the chemical bonds it forms with cellulose and hemicellulose via covalent and non-covalent bonds (Figure 1.7) (Agarwal et al., 2018). Due to lignin's irregular, heterogeneous structure, it remains difficult to produce commodity chemicals with added value.

The primary sources of lignin that can be utilized on a larger scale are spent cooking liquor and the chemical extraction of wood fibers from the pulp and paper industry. Over 50 million tons of lignin-based materials and chemicals are produced annually worldwide. Despite the fact that most lignin in the world is still used as boiler fuel in facilities that process carbohydrates, its low value and abundance indicate that it might be used to create high-value new products.

If converted into chemical compounds, bioproducts based on lignin could lead to a multibillion-dollar industry. Several million tonnes of lignin are produced as a low-value byproduct of industrial cellulosic bioethanol production. It is anticipated that the US bioethanol industry alone will produce up to 60 Mt./year of lignin by the end of 2022 (Holladay et al., 2007a; Joffres et al., 2014).

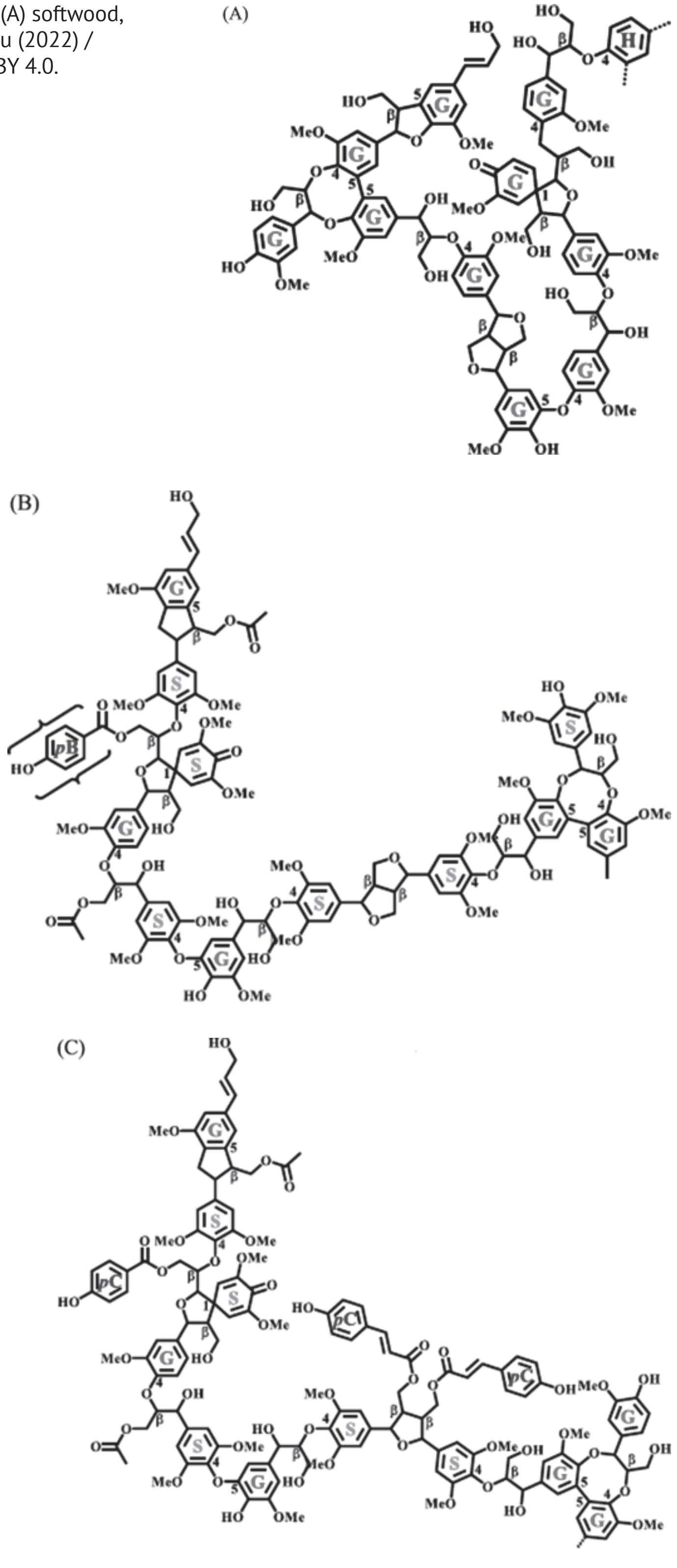


Figure 1.5 Model lignin structures: (A) softwood, (B) hardwood, and (C) grass. Lu and Gu (2022) / Springer Nature / Public Domain CC BY 4.0.

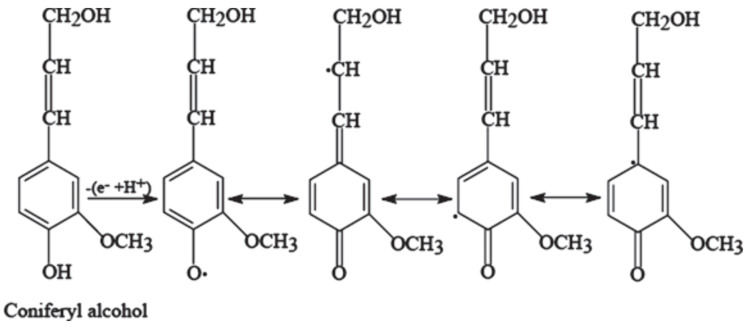


Figure 1.6 Dehydrogenation of coniferyl alcohol and the mesomeric radicals. Chakar and Ragauskas, 2004 / with permission of ELSEVIER.

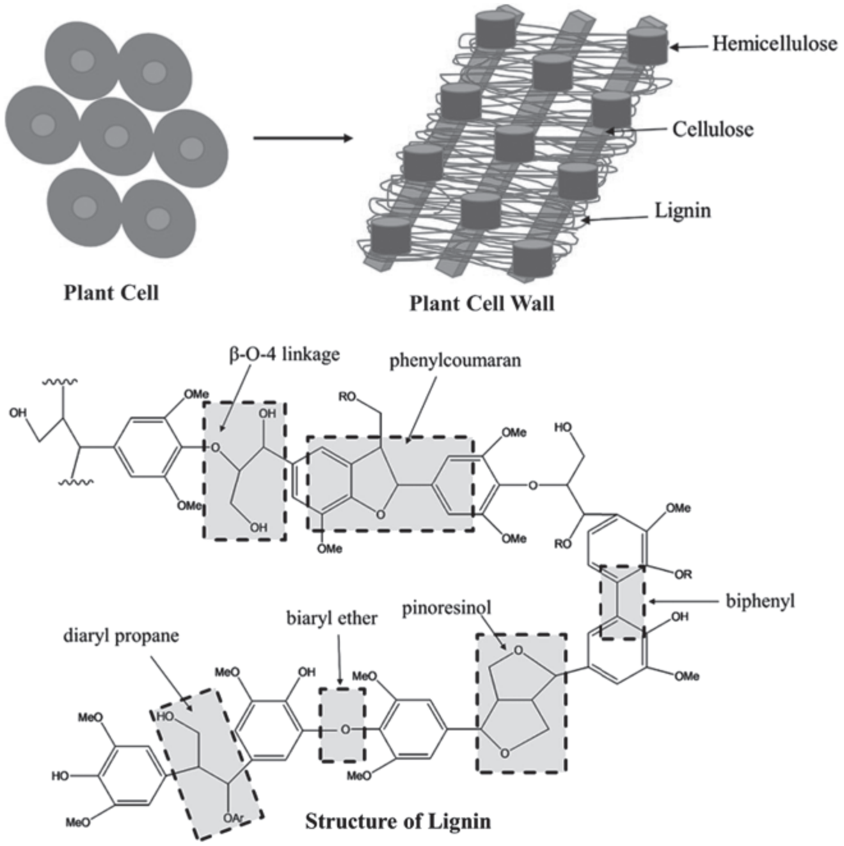


Figure 1.7 Structure of lignin in lignocellulosic material. Agarwal et al. (2018) / with permission of ELSEVIER.

1.3 Types of Lignin

Sinapyl alcohol, coniferyl alcohol and p-coumaryl alcohol, are frequently joined by non-hydrolysable linkages during the dehydrogenation of phenylpropanoid precursors that is carried out by free radicals with the assistance of peroxidase and results in the formation of lignin. The aromatic amorphous heteropolymer lignin lacks any optical activity. These three monoolignols are present in varying amounts in various plant species. For instance, softwood lignin contains a lot of coniferyl alcohol, whereas hardwood lignin contains both sinapyl and coniferyl alcohols and grass lignin contains all the three monolignols (Duval and Lawoko, 2014). The extracted lignin has been divided into four major categories—lignosulfonates, kraft lignin, soda lignin, and organosolv lignin based on the chemical pre-treatment method used: sulfur-free soda lignin is produced when biomass is treated with sodium hydroxide, whereas kraft lignin is produced when biomass is treated with sodium sulfide and sodium hydroxide. The ethanol-water extraction method and the pre-treatment of biomass with aqueous sulfur dioxide produce lignosulfonates and organosolv lignin, respectively. In addition to the four primary types of lignin, ionic liquid lignin, which is produced by treating biomass with ionic liquid is attracting a lot of interest because of its condensed structure and a low β-O-4 content (Wen et al., 2013). Due to the structural changes that take place when lignin is separated from lignocellulose biomass, chemical properties vary between lignin types. Contrary to kraft lignin and lignosulfonates, organosolv lignin, which is practically insoluble in water and natural solvents, contains a higher level of β-O-4 linkages (Bauer et al., 2012).

Even though lignin accounts for 15–40% of a plant's dry weight, it is still not considered a high-value-added product in biorefinery processes (Cao et al., 2017). Indeed, the utilization of lignin has the potential to significantly boost the cost-effectiveness of biorefinery processes based on biomass (Ragauskas et al., 2014). Only 5% of the lignin produced by the paper and pulp industry is used to produce low-quality fuel for use in heat and electricity applications through combustion (Cao et al., 2018). The well-organized valorization of lignin produced by various industrial processes may result in the proliferation of economic and environmental sustainability (Wu et al., 2018).

The highly asymmetrical polymeric structure is the most significant impediment to the lignin conversion process. The fractionation process's effect on product recovery was discussed by a number of researchers (Anderson et al., 2019). Bio-oil yield and quality could be impacted by minor structural changes. By selectively fractionating lignin from other biomass components with fewer structural changes for efficient lignin application, attempts have been made to valorize the lignin conversion process. Compared to extracted lignin whose structure has been altered, the direct hydrogenolysis process yielded aromatic monomers from native lignin at rates of 40–50%, which is five to ten times higher (Shuai et al., 2016).

There have been a number of studies on lignin valorization, in which the monomers and oligomers produced by depolymerizing lignin through thermal, chemical, and biological, pre-treatments can be turned into fuels and other chemicals (Beckham et al., 2016; Ragauskas et al., 2014).

Typically, heterogeneous aromatic compounds are produced following lignin depolymerization based on the feedstock and pre-treatment used (Schutyser et al., 2018). Fine chemicals can only be made with aromatic compounds of high purity. As a result, lignin upgrade is hindered by the heterogeneity of aromatics produced by depolymerization (Liu et al., 2017; Schutyser et al., 2018).

According to Abdelaziz et al. (2016), large quantities of lignin have been produced, estimated at $5–36 \times 10^8$ tons annually. The pulp and paper and biomass refinery industries each contribute approximately 6.2×10^7 and 5×10^7 tons of lignin annually, respectively, which includes soda lignin, kraft lignin, and lignosulfonate (Zakzeski, 2010).

Most of the time, lignin is used for energy or thrown away as waste. Due to its rich aromatic skeleton and high carbon-to-oxygen ratio, lignin is a promising feedstock for the production of biofuels and biochemicals (Vishtal and Kraslawski, 2011). In order to take advantage of lignin valorization, it is urgently necessary to acquire an understanding of the degradation procedure and create an efficient metabolic pathway for conversion. Lignin's recalcitrance and complicated structure make it difficult to depolymerize and use effectively. Currently, the most common approaches for lignin depolymerization are thermochemical and biological ones. Pyrolysis (thermolysis), gasification, hydrogenolysis, and chemical oxidation are thermochemical processes that call for extreme conditions, a lot of energy, and costly facilities (Bandounas, 2011). On the other hand, bioprocessing lignin has the advantages of higher specificity, reduced energy consumption, and affordability (Chen and Wan, 2017). In the specific cleavage of lignin linkages, biological depolymerization has demonstrated a number of benefits, and its nature makes this process environmentally friendly (Xu et al., 2019). But there are some disadvantages, such as the difficulty of genetically altering the microbes and their high sensitivity to changes in pH, temperature, and oxygen levels in the reaction system (Chauhan, 2020). Thermochemical methods have been used frequently for a long time, and these can be categorized into various groups based on the catalyst, heating technology, solvents, temperature ranges, and other factors. The liquid that comes out of lignin depolymerization, bio-oil, will have different percentage yields and different kinds of monomers and oligomers because of these factors (Agarwal et al., 2018; Lopez-Camas et al., 2020).

Holladay et al. (2007b) provide an economical evaluation of lignin feedstock-based chemical conversion technologies. Despite its potential, lignin is underutilized by industry as a chemical conversion raw material (Doherty et al., 2011; El Mansouri and Salvadó, 2006).

Biorefining natural feedstocks looks like a good way to use more lignin. The intricate utilization of biomass-derived feedstocks like lignocelluloses, oil and sugar crops, and algae is the foundation of the biorefinery concept (Cherubini, 2010; Demirbas, 2009). The three main components of lignocellulosic materials are: lignin, cellulose, and hemicelluloses (Sjöström, 1982). The majority of biorefineries are presently concentrating on the sugar-based platform for the valorization of hemicelluloses and cellulose (FitzPatrick et al., 2010), whereas lignin is typically regarded as a low-value product (Cherubini et al., 2010; Doherty et al., 2011). In contrast to sugars, which are released as uniformly monomeric carbohydrates, lignin is released as a complex and polydisperse compound. Limited use of lignin in biorefineries is primarily due to its complex structure and uncertain reactivity.

One strategy for realizing the full potential of lignin is through its transformation into useful products. Table 1.1 shows value-added chemicals formed from lignin through various treatments.

Technical lignins, such as kraft lignin, soda lignin, and lignosulphonates, are obtained in processes that deal with treating lignocelluloses, making them an intriguing raw material. Additionally, many technical lignins can be obtained in large quantities and are readily available. However, hydrolysis, organic solvents, and ionic liquids only yield a small fraction of the potentially valuable lignins. These are produced in relatively smaller quantities but may eventually

Table 1.1 Value-added chemicals formed from lignin through various treatments.

Lignin						
Hydrogenation	**Pyrolysis**	**Oxidative hydrolysis**	**Fast thermolysis**	**Alkali fusion**	**Enzymatic oxidation**	**Microbial conversion**
Phenol, cresols, substituted phenols	Phenol, acetic acid, carbon monoxide, methane	Vanillin, dimethyl sulfide dimethyl sulfooxide	Ethylene, acetylene	Catechol and phenolic acid	Oxidized lignin	Lignin with high level of polymerization ferulic, coumaric, vanollic, and other acid

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develop into products on a commercial scale. Removing lignin from the product streams of small non-wood mills permits the elimination of recovery boiler bottlenecks and offers a solution to some environmental issues but may eventually develop into products on an industrial scale (Gosselink et al., 2004).

Bibliography

Abdelaziz OY, Brink DP, Prothmann J, Ravi K, Sun M, García-Hidalgo J, Sandahl M, Hulteberg CP, Turner C, Lidén G, and Gorwa-Grauslund MF (2016). Biological valorization of low molecular weight lignin. *Biotechnol Adv*, *34*: 1318–1346. https://doi.org/10.1016/j.biotechadv.2016.10.001.

Agarwal A, Rana M, and Park JH (2018). Advancement in technologies for the depolymerization of lignin. *Fuel Process Technol*, *181*: 115–132.

Anderson EM, Stone ML, Katahira R, Reed M, Muchero W, Ramirez KJ, Beckham GT, and Roman-Leshkov Y (2019). Differences in S/G ratio in natural poplar variants do not predict catalytic depolymerization monomer yields. *Nat Commun*, *10*: 2033.

Bandounas L (2011). Isolation and characterization of novel bacterial strains exhibiting ligninolytic potential. *BMC Biotechnol*, *11*: 94. https://doi.org/10.1186/1472-6750-11-94.

Bauer S, Sorek H, Mitchell VD, Ibanez AB, and Wemmer DE. (2012). Characterization of Miscanthus giganteus lignin isolated by ethanol organosolv process under reflux condition. *J Agric Food Chem*, *60*: 8203–8212.

Beckham GT, Johnson CW, Karp EM, Salvachua D, and Vardon DR (2016). Opportunities and challenges in biological lignin valorization. *Curr Opin Biotech*, *42*: 40–53.

Candolle AP (1821). *Regni Vegetabilis Systema Naturale 2*. Argentorati et Londini, Paris, p. 266.

Cao L, Yu IKM, Liu Y, Ruan X, Tsang DCW, Hunt AJ, Ok YS, Song H, and Zhang S (2018). Lignin valorization for the production of renewable chemicals: state-of-the-art review and future prospects. *Bioresour Technol*, *269*: 465–475.

Cao L, Zhang C, Chen H, Tsang DCW, Luo G., Zhang S, and Chen J (2017). Hydrothermal liquefaction of agricultural and forestry wastes: State-of-the-art review and future prospects. *Bioresour Technol*, *245*: 1184–1193.

Chakar FS and Ragauskas AJ (2004). Review of current and future softwood kraft lignin process chemistry. *Ind Crops Prod*, *20*: 131–141.

Chauhan PS (2020). Role of various bacterial enzymes in complete depolymerization of lignin: a review. *Biocatal Agric Biotechnol*, *23*: 101498.

Chen Z and Wan C (2017). Biological valorization strategies for converting lignin into fuels and chemicals. *Renew Sust Energ Rev*, *73*: 610–621. https://doi.org/10.1016/j.rser.2017.01.166.

Cherubini F (2010). The biorefinery concept: using biomass instead of oil for producing energy and chemicals. *Energy Convers Manag*, *51*(7): 1412–1421.

Chio C, Sain MM, and Qin W (2019). Lignin utilization: a review of lignin depolymerization from various aspects. *Renewable Sustainable Energy Rev*, *107*: 232–249.

Demirbas A (2009). *Biorefineries: For Biomass Upgrading Facilities*. Springer, Berlin, ISBN: 1848827202.

Doherty W, Mousaviouna P, and Fellows *C* (2011). Value-adding to cellulosic ethanol: lignin polymers. *Ind Crops Prod*, *33*(2): 259–276.

Dutta S, Wu KCW, and Saha B (2014). Emerging strategies for breaking the 3D amorphous network of lignin. *Catal Sci Technol*, *4*: 3785–3799.

Duval A and Lawoko M (2014). A review on lignin-based polymeric, micro- and nanostructured materials. *React Funct Polym*, *85*: 78–96.

El Mansouri N-E and Salvadó J (2006). Structural characterization of technical lignins for the production of adhesives: application to lignosulphonate, kraft, sodaanthraquinone, organosolv and ethanol process lignins. *Ind Crops Prod*, *24*(1): 8–16.

FitzPatrick M, Champagne P, Cunningham MF, and Whitney RA (2010). A biorefinery processing perspective: treatment of lignocellulosic materials for the production of value-added products. *Bioresour Technol*, *101*(23): 8915–8922.

Freudenberg K and Neish AC (1968). *Constitution and Biosynthesis of Lignin*, Kleinzeller A., Springer G.F., and Whittman H.G. (eds.). Springer-Verlag, New York.

Gosselink RJA, Abächerli A, Semke H, Malherbe R, Käuper P, Nadif A, and van Dam JEG (2004). Analytical protocols for characterization of sulphur-free lignin. *Ind Crops Prod*, *19*(3): 271–281.

Guvenatam B (2015). Catalytic pathways for lignin depolymerization. *PhD Thesis (Research TU/e / Graduation TU/e), Chemical Engineering and Chemistry*. Technische Universiteit Eindhoven.

Holladay JE, Bozell JJ, White JF, and Johnson D (2007a). Top value-added chemicals from biomass. *Vol. 2 Results of Screening for Potential Candidates From Biorefinery Lignin*. U.D.o. Energy, United States of America, p. 79.

Holladay, JE, Bozell, JJ, White, JF, and Johnson, D. (2007b). Top value-added chemicals from biomass. *Volume II- Results of Screening for Potential Candidates from Biorefinery Lignin, A Report*. Available via http://www1.eere.energy.gov/biomass/pdfs/pnnl-16983.pdf.

Joffres B, Lorentz C, Vidalie M, Laurenti D, Quoineaud AA, Charon N, Daudin A, Quignard A, and Geantet C (2014). Catalytic hydroconversion of a wheat straw soda lignin: characterization of the products and the lignin residue. *Appl Catal B Environ*, *145*: 167–176.

Lewis NG (1999). A 20th century roller coaster ride: a short account of lignification. *Curr Opin Plant Biol*, *2*(2): 153–162.

Liu ZH, Olson ML, Shinde S, Wang X, Hao NJ, Yoo CG, Bhagia S, Dunlap JR, Pu Y, Kao KC, and Ragauskas AJ (2017). Synergistic maximization of the carbohydrate output and lignin processability by combinatorial pretreatment. *Green Chem*, *19*: 4939–4955.

Lopez-Camas K, Arshad M, and Ullah A (2020). Chemical modification of lignin by polymerization and depolymerization. *Lignin: Biosynthesis and Transformation for Industrial Applications*, *Sharma S.* and *Kumar A.* (eds.). Springer, Cham, p. 139–180.

Lu X and Gu X (2022). A review on lignin pyrolysis: pyrolytic behavior, mechanism, and relevant upgrading for improving process efficiency. *Biotechnol Biofuels*, *15*: 106.

Ragauskas AJ, Beckham GT, Biddy MJ, Chandra R, Chen F, Davis MF, Davison BH, Dixon RA, Gilna P, and Keller M (2014). Lignin valorization: improving lignin processing in the biorefinery. *Science*, *344*: 1246843.

Ralph J (1999). Lignin structure: recent developments. *Proceedings of the 6th Brazilian Symposium Chemistry of Lignins and Other Wood Components*, Guaratingueta, Brazil, October, p. 97–112.

Rinaldi R, Jastrzebski R, Clough MT, Ralph J, Kennema M, Bruijnincx PCA, and Weckhuysen BM (2016). Paving the way for lignin valorisation: recent advances in bioengineering, biorefining and catalysis. *Angew Chem Int Ed*, *55*: 8164–8215.

Sarkanen KV and Ludwig CH (1971). *Lignin, Occurrence, Formation, Structure and Reactions*. Wiley/Interscience, New York, p. 95–240.

Schutyser W, Renders T, Van den Bosch S, Koelewijn SF, Beckham GT, and Sels BF (2018). Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading. *Chem Soc Rev*, *47*: 852–908.

Shuai L, Amiri MT, Questell-Santiago YM, Héroguel F, Li Y, Kim H, Meilan R, Chapple C, Ralph J, and Luterbacher JS (2016). Formaldehyde stabilization facilitates lignin monomer production during biomass depolymerization. *Science*, *354*: 329–333.

Sjöström E (1982). *Wood Chemistry: Fundamentals and Applications*. Academic Press, p. 223. ISBN 0-12-647480-x.

Ullah M, Liu P, Xie S, and Sun S (2022). Recent advancements and challenges in lignin valorization: green routes towards sustainable bioproducts. *Molecules*, *27*: 6055.

Vishtal AG and Kraslawski A (2011). Challenges in industrial applications of technical lignins. *Bioresources*, *6*: 3547–3568.

Wen JL, Sun SL, Xue BL, and Sun RC (2013). Quantitative structures and thermal properties of birch lignins after ionic liquid pretreatment. *J Agric Food Chem*, *61*: 635–645.

Weng C, Peng X, and Han Y (2021). Depolymerization and conversion of lignin to value-added bioproducts by microbial and enzymatic catalysis. *Biotechnol Biofuels*, *14*: 84. https://doi.org/10.1186/s13068-021-01934-w.

Wu X, Fan X, Xie S, Lin J, Cheng J, Zhang Q, Chen L, and Wang Y (2018). Solar energy-driven lignin-first approach to full utilization of lignocellulosic biomass under mild conditions. *Nat Catal*, *1*: 772–780.

Xu Z, Lei P, Zhai R, Wen Z, and Jin M (2019). Recent advances in lignin valorization with bacterial cultures: microorganisms, metabolic pathways, and bio-products. *Biotechnol Biofuels*, *12*: 32. https://doi.org/10.1186/s13068-019-1376-0.

Zakzeski J (2010). The catalytic valorization of lignin for the production of renewable chemicals. *Chem Rev*, *110*: 3552–3599. https://doi.org/10.1021/cr900354u.