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# Lignin as Potent Industrial Biopolymer: An Introduction



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**Abstract** Lignin is a complex biological molecule and well known as a second abundant biopolymer on the planet. It also produced as a by-product of lignocellulosic biomass, paper and pulp industry. It has not been well explored for industrial applications due to its poor solubility and complex molecular structure. Hence, since last two decades, lignin has gained the attention of researchers as a raw material for the synthesis of value-added products of commercial importance. However, the major part of the lignin derived from the pulp industry is being utilized as boiler fuel. The efficacy of lignin produced from lignocellulosic-based bio-ethanol industry to synthesize the renewable polymeric material is much higher as compared to the lignin obtained from pulp industry. These days lignin has also been exploited to synthesize various chemicals like esters, ethers, bio-adhesives, biolubricants, foams, nano-particles and nano-composites. The excessive production of lignin from paper or bio-ethanol industry has also appeared as critical environmental problem. The conversion of huge amount of lignin will not only help to solve the environmental threat but also boost the bio-economy of bio-ethanol and paper industry. In this chapter, we highlight the sources, extraction of lignin and its immense industrial importance.

**Keywords** Ethanol · Lignocellulosic biomass · Biofuel · Esters · Ethers · Adhesives · Foam

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## 1 Introduction

Lignin is the most abundant in plants and an important component of the cell wall. It is highly hydrophobic and insoluble in water and alcohol. Lignin is a complex organic polymer formed of monolignol units. Lignin waste is also appeared as an environmental issue as this waste is dumped or burned as low-grade fuel causes wastage of natural resources. Hence, upgradation of lignin valorization through technological improvements for the realization of sustainable resource management is very necessary. Due to the technological improvements like thermochemical tailor technologies of lignin, numerous value-added chemicals can be synthesized, e.g. ethylbenzene (vital intermediate for organic synthesis) (Regmi et al. 2017), guaiacol (phenolic resin making) (vom Stein et al. 2015) and *p*-hydroxyl acetophenone (cholagogue drug making and perfume synthesis) (Luo et al. 2018). Currently, more than 80 million tons of lignin is being produced as a by-product from lignocellulosic biorefinery and paper/pulp industry. On the other hand, only a small fraction of this lignin is used as fuel or energy source in the industry. Thus, researchers are intended to synthesize various fine chemicals of higher commercial value from lignin to make the biorefinery process more sustainable. However, the direct conversion of lignin into valuable chemicals is also challenging due to its poor solubility and complex phenolic ring structures with high bond energy. Lignin falls within important biomass resources due to the depletion of fossil resources and increasing environmental pollution by the excessive use of fuels (Peng et al. 2014).

Literature showed that lignin is a good source for manufacturing the phenolics as it is one of the potent sources of aromatic chemical compounds (Alonso et al. 2010). As stated in previous reports, lignin can be hydrolysed into phenolic resins and alkylphenols which can act as highly efficient fuels and energy sources (Graglia et al. 2015; Li et al. 2015; Xu et al. 2014; Zakzeski et al. 2010). The lignin-derived derivatives can also be used in the synthesis of polyurethane resins, polyols, foams, antifungal agents and various products of industrial use (Dos Santos et al. 2015; Mahmood et al. 2016; Rößiger et al. 2018). The major challenges in the lignin conversion are formation of char as a by-product, complexity in the purification and separation of products and also poor selectivity for product synthesis which are needed to be considered during operation of lignin-based biorefinery.

## 2 Sources and Structure of Lignin

### 2.1 Major Sources of Lignin

Lignin was primarily studied for its significance in the pulp and paper industry, where fibrous product rich in cellulose was produced by eliminating lignin from the wood. Therefore, the major studies were focused on the composition and structure of lignin (Chen et al. 2018; Fernández-Rodríguez et al. 2019; Glasser 2019; Rahimi

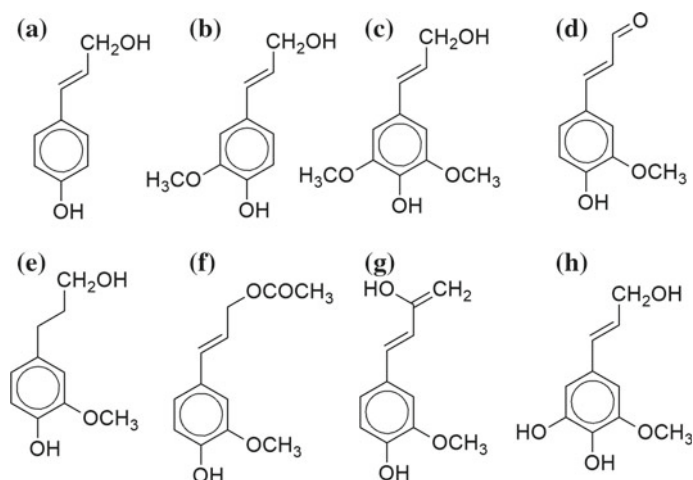
et al. 2014). Some studies of lignin were also related to herbaceous plants (Buranov and Mazza 2008; del Río et al. 2012a, b; Marques et al. 2010) where lignin partly triggered by digestibility and dietary conversion issues in animal feed (Campbell and Sederoff 1996). But nowadays, these lignocellulosic wood species and wastes provide opportunities for the production of green chemicals, bioproducts and energy within the biorefinery (de Gonzalo et al. 2016; Graglia et al. 2015; Keegstra 2010; Zakzeski et al. 2010). Lignin is mostly bound to polysaccharides in close association with cellulose and hemicelluloses in plants. But the distribution of lignin, cellulose and hemicellulose is not uniform throughout the plant body. Vascular plants contain lignin mainly between the cells, with second largest in quantity to cellulose among natural polymers (Gellerstedt 2015; Gierer 1985; Graglia et al. 2015; Keegstra 2010; Moura et al. 2010; Zakzeski et al. 2010). Lignin is proven fundamental source of complex organic polymers for the chemical industry in a biorefinery. More specifically in woody plants, the lignin content is approximately 15–40% (Fengel and Wegener 1984), whereas in herbs or annual plants, the lignin content is less than 15% (Table 1). So, the paper and pulp sectors yield a large quantity of lignin with greater potential in biorefineries. Negligible lignin is recovered from solid waste, where their content (lignin) is assessed to be less than 15%.

**Table 1** Quantity of lignin in various classes of plants

Plant	Lignin contents (%)	Reference
<i>Piceaabies</i> sp.	20–40	Önnerud (2003), Önnerud and Gellerstedt (2003)
<i>Pinus pinaster</i>	25–35	Baptista et al. (2008)
<i>Pinus taeda</i>	28–45	Huang et al. (2011)
<i>Pinus radiata</i>	25–30	Sjöström (1993)
<i>Acasia mollissima</i>	20–25	Sjöström (1993)
<i>Acacia mangium</i>	27–35	Pinto et al. (2005)
<i>Cynara cardunculus</i>	16–25	Gominho et al. (2001)
<i>Betula verrucosa</i>	15–25	Önnerud (2003)
<i>Eucalyptus globulus</i>	20–25	Sjöström (1993)
<i>Populus tremula</i>	18–22	Önnerud and Gellerstedt (2003)
<i>Quercus suber</i>	25–40	Lourenço et al. (2016)
<i>Tectona grandis</i>	30–45	Lourenço et al. (2015)
<i>Arundo donax</i>	15–20	Shatalov and Pereira (2005)
<i>Miscanthus x giganteus</i>	15–20	Pascoal Neto et al. (1997)
<i>Musa acuminata</i>	10–25	Oliveira et al. (2007)

## 2.2 Structural Composition of Lignin

In order to understand the properties of lignin and to propose a lignin-based pathway, its structural aspects need to be understood deeply. Lignin is primarily constituted of three monolignol precursors: coniferyl alcohol (guaiacyl), *p*-coumaryl alcohol (hydroxyphenyl) and sinapyl alcohol (syringyl) (Fig. 1) which synthesizes lignin polymers in the cytoplasm via shikimate pathway (Boudet 2000; Glasser 2019; Rahimi et al. 2014; Rößiger et al. 2018). The chemical structure of lignin possessed abundance of the chemical sites which indicated that lignin might be a key precursor in the synthesis of aromatic chemicals. Few other non-conventional monolignol precursors are also identified in negligible amounts (Gellerstedt and Henriksson 2008). Also, these polyphenolic rings provide hydrophobicity in aqueous systems which ultimately gave resistance to chemical and biological degradation of plants (Keegstra 2010). The composition of these monolignol precursors in different types of plants is represented in Table 2. In angiosperms, syringyl–guaiacyl-type lignin is

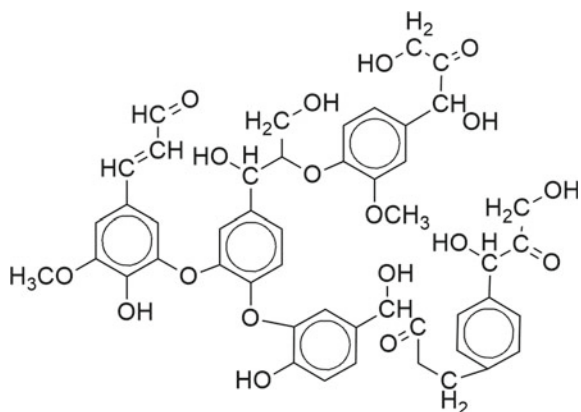


**Fig. 1** Types of monolignol precursors for lignin syntheses: **a** *p*-coumaryl alcohol, **b** coniferyl alcohol, **c** sinapyl alcohol, **d** coniferaldehyde, **e** dihydroconiferyl alcohol, **f** coniferyl alcohol-9-acetate, **g** ferulic acid and **h** 5-hydroxyconiferyl alcohol

**Table 2** Amount of monolignol precursors is in different types of plants (Gellerstedt and Henriksson 2008)

Plant	Hydroxyphenyl (H) (%)	Guaiacyl (G) (%)	Syringyl (S) (%)
Softwoods	5	95	0
Hardwoods	0–8	25–50	45–75
Grasses	5–35	35–80	20–55

**Fig. 2** Structure of lignin showing G, S and H units



present which makes angiosperm (hardwood) lignin more readily detached during pulping process, while in gymnosperm, only guaiacyl lignin is present (Fig. 2).

### 3 Lignin Extraction from Different Types of Biomass

The extraction of lignin from different types of biomass usually depends on a starting material or the wood to obtain the pulp (Chen et al. 2018; Radotić and Mičić 2016). The yield of the lignin is affected by various parameters such as the method of extraction, reaction time, type of reaction medium and temperature. There are several methods which have been developed for the extraction of lignin from cellulosic pulp which involves enzymatic, chemical and physical.

#### 3.1 Biological or Enzymatic Methods

Enzymatic methods involve the use of cellulolytic enzymes for carbohydrate's hydrolysis which produce the insoluble fraction of lignin (Radotić and Mičić 2016). Successive enzymatic treatments of the pulps ensure absolute hydrolysis of carbohydrates to enhance the recovery of lignin with good yield as compared to other methods like unbleached kraft pulps. These enzymes are quite effective to hydrolyse the entire pulp polysaccharides of the wood. The obtained fractions contain ~65 to 80% lignin with ~7 to 8% carbohydrates and some fraction of other impurities (Radotić and Mičić 2016). These impurities are difficult to remove by enzymatic methods. However, the residual lignin obtained from enzymatic hydrolysis or dissolution of carbohydrates is considered to be effective and economic as lignin structures remain unchanged with a higher yield. In order to remove the impurities and ensure the high purity of lignin, we need to apply an integrated approach which

involves the use of chemical agents and mechanical amenities along with enzymatic method.

### 3.2 *Chemical Methods*

Various chemical methods for extraction of lignin are employed; some of them are acid hydrolysis, kraft process, lignosulphonate process and organosolvlysis. In acid hydrolysis, the extracted pulp from the wood is refluxed under N<sub>2</sub> or Ar (argon) and HCl to solubilize the lignin (Fernández-Rodríguez et al. 2019; Gellerstedt et al. 1994). The solubilized lignin is free from contaminants with minimum impurities and makes this method better and rapid as compared to enzymatic hydrolysis. However, strong acidic environment results in structural changes in the lignin like the cleavage of aryl and alkyl ethers in benzyl alcohol moiety, alterations of molecular structure, which could be the possible drawbacks of this method.

The extraction of lignin through lignosulphonate process involves the treatment of wood at high temperatures with sodium sulphite (aqueous) under acidic conditions. The functional moieties, e.g. carboxylic, phenolic and –SH, allow their use as surfactants, additives, dispersants and flocculants (Aro and Fatehi 2017). Approximately, 1 million tons of lignosulphonates are produced every year as dry solids. Nowadays, kraft process is more preferred as compared to sulphite pulping because of its better product quality and fibre strength obtained in lignin extracts (Zhu et al. 2009).

Presently, the usage of volatile organic solvents (VOS) is growing to prevent environmental pollution and minimization of the greenhouse effect (Dos Santos et al. 2015; Mahmood et al. 2016). Also, ionic liquids are in trend for biomass treatment due to their low volatility as well as reusable behaviour. Lignin obtained by organosolvents like ethanol or alkaline NaOH is assisted with the combined treatment of ionic liquid 1-butyl-3-methylimidazolium methylsulphate [Bmim][MeSO<sub>4</sub>] (Meng et al. 2012). Overall, when compared to lignosulphonates or kraft lignins, the alkaline and organosolv lignins are sulphur-free and most suitable for the synthesis of various value-added products (Zhang 2011).

### 3.3 *Physical Methods*

Various physical or mechanical methods like pyrolysis and heat steams are used in lignin isolation from wood. Pyrolysis is known to be a thermochemical process as it can convert 60–75% of the original biomass into crude oil (Garcia-Perez et al. 2007; Jiang et al. 2010). This crude oil of biomass can replace the petroleum-based fuels (Czernik and Bridgwater 2004). Pyrolysis is generally operated at relatively high heating rate, ambient temperature range and short residence time of gas in order to obtain more liquid products (Demirbaş 2001). There are only a few reports on

extracting pyrolytic lignin from bio-oils (Jiang et al. 2010; Scholze et al. 2001). It may be separated by adding water to precipitate lignin-derived hydrophobic components.

Another method for lignin extraction is steam-assisted process. In this process, wood is subjected to high temperature (200 °C) and quick release of pressure which ultimately liberates bundles of fibres. Nowadays, this process has gained more attention due to its low-cost ease of polymer separation. However, chances of homolytic cleavage reactions of lignin are higher due to the high temperature (200 °C) which could be the major drawbacks of this method. After condensation reaction, this method results in a highly heterogeneous lignin-containing discrete fragments as well as recombined bundles (Tian et al. 2017).

### ***3.4 Miscellaneous Processes of Lignin Extraction and Conversion***

Lignin content is isolated from plant tissues and purified cell wall regions. Cell breakage is mostly used technique for lignin isolation. These techniques enable to achieve pure cell wall material. FastPrep method for isolation of lignin helps to preserve its native structure which is free from proteins and other contaminants. This type of lignin is principally used for accurate determination of structure and sensitive assays of its functions (Chen et al. 2000). The major advantage of using FastPrep method is improved homogenization which accelerates the purification and product recovery and also making this process faster than other methods. Similarly, Saisu et al. (2003) conducted a study on conversion of lignin using supercritical H<sub>2</sub>O and phenol. They evaluated that biomass of plants consists of cellulose (50 wt%), hemicellulose (20wt%) and lignin (30wt%). In a previous study, the gasification of lignin with a nickel catalyst in supercritical water was carried out at 673 K (Hagaman and Lee 1999). The conversion of lignin by hydrothermal reaction using alkali has also been used to convert lignin into chemicals/fuels. Hydrothermal degradation has also been reported to perform under subcritical or supercritical conditions for the improved production of phenolics (Peng et al. 2014).

## **4 Challenges in Lignin Conversion**

Presently, the main challenge is to convert lignin into valuable chemicals by improving the overall economics of production to make it suitable for commercial scale. The development of competent methods for product separation, complexities in purification and minimizing the char formation are major challenges of lignin processing (Rößiger et al. 2018). Thus, the valorization of lignin is one of the most important challenges in the development of sustainable and economic biorefinery processes. However, the biological strategies for lignin valorization hold the stance



by overcoming the complexity of lignin in the improvement of bioprocesses. The polyalkylphenolic lignin molecule can be cleaved into low-molecular-weight products like phenols, alkylphenols and phenol resins using enzymes or chemical catalysts (Graglia et al. 2015; Zakzeski et al. 2010). These products are extremely efficient fuels, fuel additives (Li et al. 2015; Xu et al. 2014) antifungal components (Dos Santos et al. 2015) and can synthesize polyols or polyurethane resins (Mahmood et al. 2016). Till date, the highly stable intramolecular bonds in the lignin make its depolymerization as a difficult task. In addition to this, efficient technologies for the selectivity of defined products, downstreaming process, product recovery and their purification from the reaction cocktail are still the major subjects of concern related to lignin conversion.

## 5 Lignin-Derived Products of Industrial Importance

### 5.1 Lignin-Based Foams

Foam is generally formed by mixing suspension of lignin and carbohydrates which results in the formation of small particles, long fibres, sheets and fibreboards. A variety of foams have been developed from lignin such as polyurethane lignin foams (PUL foam), phenolic resin lignin foams (PRL foam), silicone–lignin foams (SiL foam), lignin–furan foams (LF foam) starch–lignin foams (SL foams), polystyrene–lignin foams (PS foams) and tannin–lignin foams (TL foam). These foams have immense applications in goods packaging and foundries' cushioning of utensils and machinery. PU foams are synthesized from isocyanate and polyol components of lignin-containing various free OH groups (Cateto et al. 2014; Obaid et al. 2016). The PU foams can be soft or hard types. The synthesis of hard or rigid PU foam was reported by Li and Ragauskas (2012). PRL foams are generally synthesized from phenol urea-formaldehyde resin, and these are widely used as insulating material (Ghorbani et al. 2017). SL foams have been prepared by moulding and compression of the lignin mixture and widely employed for the packing of goods and machinery (Obaid et al. 2016). Another important class of foam is lignin furan foam which can be synthesized from used spent liquor of pulp industry. The industrial liquor produced in magnesium bisulphite pulping reaction was precipitated using 30–40% of surfactant (Tondi and Pizzi 2009). Similarly, PS–lignin foams are the polymeric foams produced from styrene and lignin which have various applications in transportation industries for packaging.

Silicone–lignin foams are prepared by hydrosilanes and lignin polymerization as reported previously (Brook et al. 2011; Zhang et al. 2015). Tannin–lignin foams are well known for their high flame resistance and low chemical reactivity (Sánchez-Martín et al. 2013; Szczurek et al. 2014). The synthesis of TL foams was carried out by a mechanical frothing process as reported for PU foam preparation. Thus, all these lignin-based foams have high commercial value and numerous applications in day-to-day life.

## 5.2 *Epoxy Resins from Lignins*

The petroleum-based epoxy resins are synthesized using bisphenol A and epoxy resin in the presence of thiols, phenols or amines. The bisphenol A component is not environmentally friendly. Lignin is one of the biological components which can replace the bisphenol A and can be used to synthesize the epoxy resin with better stability and physicochemical properties (Delmas et al. 2013). To prepare the epoxy resins, the liquefied wood was subjected to glycidyl etherification using NaOH and epichlorohydrin under boiling conditions (Kishi and Fujita 2008; Kishi et al. 2006).

## 5.3 *Lignin-Based Ethers*

Ethers are fragrance and flavouring agents used in the cosmetics, food and confectionary industry. The ethers are usually produced by chemical reactions, but these can be synthesized from the lignin too. A polyoxyethylene is industrially important ether which can be synthesized from kraft lignin (KL) and polyethylene glycol (PEG). In a recent study, alkaline lignin derivatives were synthesized by etherification and epoxidation reactions. These can be used to increase enzymatic hydrolytic reaction in detergents and fermentation industry (Chen et al. 2016). In a previous study, the addition of hydrophilic and lipophilic groups in the lignin using dodecyl glycidyl ether in the presence of dimethyl benzylamine and followed by sulphonation using chlorosulphonic acid yields the ethers of commercial value.

## 5.4 *Lignin-Based Esters*

Esters are also one of the important organic compounds synthesized by the chemical reaction of acid and alcohol in the presence of catalyst such as alkali (NaOH). The esters of fatty acids are essential oils and many naturally occurring flavours. In the last decades, enzymatic synthesis of esters also becomes popular due to environmentally friendly biocatalytic reaction (Chandel et al. 2011; Sharma et al. 2017). The microbial lipolytic enzymes and esterases have also been reported to catalyse the conversion of fatty acid in the presence of alcohol into their respective esters (Kumar and Kanwar 2011, 2012; Kumar et al. 2013, 2015; Ramesh et al. 2014; Sharma et al. 2018). Zhao et al. (2017) have proposed the mechanism of esterification of lignin which involved the mechanical activation of solid-phase synthesis technology. In this reaction, sodium acetate and sulphuric acid were used as the catalyst. Generally, the esterification was carried out using acid chloride, acid anhydride, imidazole, pyridine or dimethylaminopyridine (DMAP) under controlled conditions (Nevárez et al. 2011; Thielemans and Wool 2005). In the literature, the esterification of hardwood and softwood was performed using various anhydrides. These conventional processes of

esterification are more time-consuming and laborious. Thus, with the advancement of technology, the rate of reaction and recovery of product can be enhanced using supercritical CO<sub>2</sub> and ionic liquid as solvent (Cachet et al. 2014). The rate of reaction can also be enhanced using microwaves and mixture of ionic liquids (Monteil-Rivera and Paquet 2015; Wang et al. 2018). In a recent study, the esters of *p*-coumaric acid and ferulic acid were obtained by esterification of lignin (Tana et al. 2019). Conclusively, the esterification of lignin can reduce the amount of waste product and improve the bio-economy of the process.

### 5.5 Lignin-Based Paints and Coatings

Lignin-based paints can be prepared by mixing the lignin liquor with paints and treatment with phenol oxidizing agents such as enzymes (Sena-Martins et al. 2008). The enzyme-treated mixture will be incubated to increase the viscosity of paint. The lignin has also been used to coat the fertilizers such as urea for its controlled release in the soil and increase its availability to the plants. Urea has been partly soluble in aqueous lignin dispersion, and the lignin layer results in fine coatings around the urea particles. Lignin has a broad range of molecular mass and various free functional groups which make it easier to modify with various polymeric materials to form insulation coating (Kai et al. 2016).

## 6 Conclusion

Despite various challenges in lignin valorisation and conversion into products of commercial value, it still holds the potential of alternative of various harsh chemicals and fossil fuels. Continuous efforts have been made by the researchers to scale up the lignin-based biorefineries and replace the chemical products by these biobased products. The question arises whether the lignin-based industries are sustainable and economical or not? How the formation of by-products such as char, phenols and alcohols can be controlled and materialized for mankind use? The presence of oxygen-rich contents in the lignin and its by-products hinders the easy implementation in industries. New strategies for the easy recovery of lignin with high purity level are the need of hour which should be scaled up for industrial usage.

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## References

- Alonso DM, Bond JQ, Dumesic JA (2010) Catalytic conversion of biomass to biofuels. *Green Chem* 12(9):1493–1513. <https://doi.org/10.1039/C004654J>
- Aro T, Fatehi P (2017) Production and application of lignosulfonates and sulfonated lignin. *ChemSuschem* 10(9):1861–1877. <https://doi.org/10.1002/cssc.201700082>
- Baptista C, Robert D, Duarte AP (2008) Relationship between lignin structure and delignification degree in *Pinus pinaster* kraft pulps. *Bioresour Technol* 99(7):2349–2356. <https://doi.org/10.1016/j.biortech.2007.05.012>
- Boudet A-M (2000) Lignins and lignification: selected issues. *Plant Physiol Biochem* 38:81–96. [https://doi.org/10.1016/S0981-9428\(00\)00166-2](https://doi.org/10.1016/S0981-9428(00)00166-2)
- Brook MA, Grande JB, Ganachaud F (2011) New synthetic strategies for structured silicones using B(C6F5)3. In: Muzafarov AM (ed) *Silicon polymers*. Springer, Berlin, Heidelberg, pp 161–183
- Buranov AU, Mazza G (2008) Lignin in straw of herbaceous crops. *Ind Crops Prod* 28(3):237–259. <https://doi.org/10.1016/j.indcrop.2008.03.008>
- Cachet N, Camy S, Benjelloun-Mlayah B, Condoret J-S, Delmas M (2014) Esterification of organosolv lignin under supercritical conditions. *Ind Crops Prod* 58:287–297. <https://doi.org/10.1016/j.indcrop.2014.03.039>
- Campbell MM, Sederoff RR (1996) Variation in lignin content and composition (mechanisms of control and implications for the genetic improvement of plants). *Plant Physiol* 110(1):3–13. <https://doi.org/10.1104/pp.110.1.3>
- Cateto CA, Barreiro MF, Ottati C, Lopretti M, Rodrigues AE, Belgacem MN (2014) Lignin-based rigid polyurethane foams with improved biodegradation. *J Cell Plast* 50(1):81–95. <https://doi.org/10.1177/0021955x13504774>
- Chandel C, Nadda A, Kanwar S (2011) Enzymatic synthesis of butyl ferulate by silica-immobilized lipase in a non-aqueous medium. *J Biomater Nanobiotechnol* 2:400–408
- Chen M, Sommer AJ, McClure JW (2000) Fourier transform-IR determination of protein contamination in thioglycolic acid lignin from radish seedlings, and improved methods for extractive-free cell wall preparation. *Phytochem Anal* 11(3):153–159. [https://doi.org/10.1002/\(sici\)1099-1565\(200005/06\)11:3%3c153:aid-pca502%3e3.0.co;2-z](https://doi.org/10.1002/(sici)1099-1565(200005/06)11:3%3c153:aid-pca502%3e3.0.co;2-z)
- Chen C, Zhu M, Li M, Fan Y, Sun R-C (2016) Epoxidation and etherification of alkaline lignin to prepare water-soluble derivatives and its performance in improvement of enzymatic hydrolysis efficiency. *Biotechnol Biofuels* 9(1):87. <https://doi.org/10.1186/s13068-016-0499-9>
- Chen J, Dong J, Yang G, He M, Xu F, Fatehi P (2018) A process for purifying xylosugars of pre-hydrolysis liquor from kraft-based dissolving pulp production process. *Biotechnol Biofuels* 11(1):337. <https://doi.org/10.1186/s13068-018-1336-0>
- Czernik S, Bridgwater AV (2004) Overview of applications of biomass fast pyrolysis oil. *Energy Fuels* 18(2):590–598. <https://doi.org/10.1021/ef034067u>
- de Gonzalo G, Colpa DI, Habib MH, Fraaije MW (2016) Bacterial enzymes involved in lignin degradation. *J Biotechnol* 236:110–119. <https://doi.org/10.1016/j.jbiotec.2016.08.011>
- del Río JC, Prinsen P, Rencoret J, Nieto L, Jiménez-Barbero J, Ralph J, Gutiérrez A (2012a) Structural characterization of the lignin in the cortex and pith of elephant grass (*Pennisetum purpureum*) stems. *J Agric Food Chem* 60(14):3619–3634. <https://doi.org/10.1021/jf300099g>
- del Río JC, Rencoret J, Prinsen P, Martínez ÁT, Ralph J, Gutiérrez A (2012b) Structural characterization of wheat straw lignin as revealed by analytical Pyrolysis, 2D-NMR, and reductive cleavage methods. *J Agric Food Chem* 60(23):5922–5935. <https://doi.org/10.1021/jf301002n>
- Delmas G-H, Benjelloun-Mlayah B, Bigot YL, Delmas M (2013) Biolignin™ based epoxy resins. *J Appl Polym Sci* 127(3):1863–1872. <https://doi.org/10.1002/app.37921>
- Demirbaş A (2001) Biomass resource facilities and biomass conversion processing for fuels and chemicals. *Energy Convers Manag* 42(11):1357–1378. [https://doi.org/10.1016/S0196-8904\(00\)00137-0](https://doi.org/10.1016/S0196-8904(00)00137-0)

- Dos Santos P, Erdocia X, Gatto DA, Labidi J (2015) Bio-oil from base-catalyzed depolymerization of organosolv lignin as an antifungal agent for wood. *Wood Sci Technol* 50. <https://doi.org/10.1007/s00226-015-0795-8>
- Fengel D, Wegener G (1984) Reactions in alkaline medium. *Wood: chemistry, ultrastructure, reaction*, Walter de Gruyter, Berlin, New York, pp 296–318
- Fernández-Rodríguez J, Erdocia X, Hernández-Ramos F, Alriols MG, Labidi J (2019) Lignin separation and fractionation by ultrafiltration. In: *Separation of functional molecules in food by membrane technology*, Academic Press, pp 229–265. <https://doi.org/10.1016/C2017-0-02808-2>
- García-Pérez M, Chaala A, Pakdel H, Kretschmer D, Roy C (2007) Characterization of bio-oils in chemical families. *Biomass Bioenerg* 31(4):222–242. <https://doi.org/10.1016/j.biombioe.2006.02.006>
- Gellerstedt G (2015) Softwood kraft lignin: raw material for the future. *Ind Crops Prod* 77:845–854. <https://doi.org/10.1016/j.indcrop.2015.09.040>
- Gellerstedt G, Henriksson G (2008) Lignins: major sources, structure and properties. In: Belgacem MN, Gandini A (eds) *Monomers, polymers and composites from renewable resources*. Elsevier, Amsterdam, pp 201–224 (Chap. 9)
- Gellerstedt G, Pranda J, Lindfors EL (1994) Structural and molecular properties of residual birch kraft lignins. *J Wood Chem Technol* 14(4):467–482. <https://doi.org/10.1080/02773819408003108>
- Ghorbani M, Konnerth J, Budjav E, Silva AR, Zinovyev G, Van Herwijnen HWG, Liebner F (2017) Ammonoxidized fenton-activated pine kraft lignin accelerates synthesis and curing of resolite resins. *Polymers* 9(2):43. <https://doi.org/10.3390/polym9020043>
- Gierer J (1985) Chemistry of delignification. *Wood Sci Technol* 19(4):289–312. <https://doi.org/10.1007/bf00350807>
- Glasser WG (2019) About making lignin great again—some lessons from the past. *Front Chem* 7(565). <https://doi.org/10.3389/fchem.2019.00565>
- Gominho J, Fernandez J, Pereira H (2001) *Cynara cardunculus* L.—a new fibre crop for pulp and paper production. *Ind Crops Prod* 13:1–10. [https://doi.org/10.1016/S0926-6690\(00\)00044-3](https://doi.org/10.1016/S0926-6690(00)00044-3)
- Graglia M, Kanna N, Esposito D (2015) Lignin refinery: towards the preparation of renewable aromatic building blocks. *ChemBioEng Rev* 2(6):377–392. <https://doi.org/10.1002/cben.201500019>
- Hagaman EW, Lee SK (1999) Acid-catalyzed cross-linking reactions at benzylic sites in fluorene monomers, polymers, and lignin<sup>1</sup>. *Energy Fuels* 13(5):1006–1014. <https://doi.org/10.1021/ef980269s>
- Huang F, Singh PM, Ragauskas AJ (2011) Characterization of milled wood lignin (MWL) in loblolly pine stem wood, residue, and bark. *J Agric Food Chem* 59(24):12910–12916. <https://doi.org/10.1021/jf202701b>
- Jiang X, Ellis N, Zhong Z (2010) Characterization of pyrolytic lignin extracted from bio-oil. *Chin J Chem Eng* 18:1018–1022. [https://doi.org/10.1016/S1004-9541\(09\)60162-2](https://doi.org/10.1016/S1004-9541(09)60162-2)
- Kai D, Tan MJ, Chee PL, Chua YK, Yap YL, Loh XJ (2016) Towards lignin-based functional materials in a sustainable world. *Green Chem* 18(5):1175–1200. <https://doi.org/10.1039/C5GC02616D>
- Keegstra K (2010) Plant cell walls. *Plant Physiol* 154(2):483–486. <https://doi.org/10.1104/pp.110.161240>
- Kishi H, Fujita A (2008) Wood-based epoxy resins and the ramie fiber reinforced composites. *Environ Eng Manag J* 7:517–523. <https://doi.org/10.30638/eemj.2008.074>
- Kishi H, Fujita A, Miyazaki H, Matsuda S, Murakami A (2006) Synthesis of wood-based epoxy resins and their mechanical and adhesive properties. *J Appl Polym Sci* 102(3):2285–2292. <https://doi.org/10.1002/app.24433>
- Kumar A, Kanwar SS (2011) Synthesis of ethyl ferulate in organic medium using celite-immobilized lipase. *Bioresour Technol* 102(3):2162–2167. <https://doi.org/10.1016/j.biortech.2010.10.027>

- Kumar A, Kanwar S (2012) An efficient immobilization of *Streptomyces* sp. STL-D8 lipase onto photo-chemically modified cellulose-based natural fibers and its application in ethyl ferulate synthesis. *Trends Carbohydr Res* 4:13–23
- Kumar A, Sharma V, Sharma P, Kanwar SS (2013) Effective immobilisation of lipase to enhance esterification potential and reusability. *Chem Pap* 67(7):696–702. <https://doi.org/10.2478/s11696-013-0377-x>
- Kumar A, Zhang S, Wu G, Wu CC, Chen J, Baskaran R, Liu Z (2015) Cellulose binding domain assisted immobilization of lipase (GSlip-CBD) onto cellulosic nanogel: characterization and application in organic medium. *Colloids Surf B Biointerfaces* 136:1042–1050. <https://doi.org/10.1016/j.colsurfb.2015.11.006>
- Li Y, Ragauskas AJ (2012) Kraft lignin-based rigid polyurethane foam. *J Wood Chem Technol* 32(3):210–224. <https://doi.org/10.1080/02773813.2011.652795>
- Li C, Zhao X, Wang A, Huber GW, Zhang T (2015) Catalytic transformation of lignin for the production of chemicals and fuels. *Chem Rev* 115(21):11559–11624. <https://doi.org/10.1021/acs.chemrev.5b00155>
- Lourenço A, Neiva D, Gominho J, Marques A, Pereira H (2015) Characterization of lignin in heartwood, sapwood and bark from *Tectona grandis* using Py–GC–MS/FID. *Wood Sci Technol* 49:159–175. <https://doi.org/10.1007/s00226-014-0684-6>
- Lourenço A, Rencoret J, Chemetova C, Gominho J, Gutiérrez A, del Río JC, Pereira H (2016) Lignin composition and structure differs between Xylem, Phloem and Phellem in *Quercus suber* L. *Front Plant Sci* 7(1612). <https://doi.org/10.3389/fpls.2016.01612>
- Luo M, Lin H, Li B, Dong Y, He Y, Wang L (2018) A novel modification of lignin on corncob-based biochar to enhance removal of cadmium from water. *Bioresour Technol* 259:312–318. <https://doi.org/10.1016/j.biortech.2018.03.075>
- Mahmood N, Yuan Z, Schmidt J, Tymchyshyn M, Xu C (2016) Hydrolytic liquefaction of hydrolysis lignin for the preparation of bio-based rigid polyurethane foam. *Green Chem* 18(8):2385–2398. <https://doi.org/10.1039/C5GC02876K>
- Marques G, Rencoret J, Gutiérrez A, del Río J (2010) Evaluation of the chemical composition of different non-woody plant fibers used for pulp and paper manufacturing. *Open Agric J* 4:93–101. <https://doi.org/10.2174/1874331501004010093>
- Meng LY, Kang SUM, Zhang X, Yu-Ying WU, Sun RC (2012) Isolation and physico-chemical characterization of lignin from hybrid poplar in dmsol/licl system induced by microwave-assisted irradiation. *Cellul Chem Technol* 46:409–418
- Monteil-Rivera F, Paquet L (2015) Solvent-free catalyst-free microwave-assisted acylation of lignin. *Ind Crops Prod* 65:446–453. <https://doi.org/10.1016/j.indcrop.2014.10.060>
- Moura JC, Bonine CA, de Oliveira Fernandes Viana J, Dornelas MC, Mazzafera P (2010) Abiotic and biotic stresses and changes in the lignin content and composition in plants. *J Integr Plant Biol* 52(4):360–376. <https://doi.org/10.1111/j.1744-7909.2010.00892.x>
- Nevárez LAM, Casarrubias LB, Celzard A, Fierro V, Muñoz VT, Davila AC, Sánchez GG (2011) Biopolymer-based nanocomposites: effect of lignin acetylation in cellulose triacetate films. *Sci Technol Adv Mater* 12(4):045006. <https://doi.org/10.1088/1468-6996/12/4/045006>
- Obaid N, Kortschot MT, Sain M (2016) 12—Lignin-based foaming materials. In: Faruk O, Sain M (eds) *Lignin in polymer composites*. William Andrew Publishing, pp 217–232
- Oliveira L, Cordeiro N, Evtuguin D, Torres IC, Silvestre A (2007) Chemical composition of different morphological parts from ‘Dwarf Cavendish’ banana plant and their potential as a non-wood renewable source of natural product. *Ind Crops Prod* 26:163. <https://doi.org/10.1016/j.indcrop.2007.03.002>
- Önnerud H (2003) Lignin structures in normal and compression wood. Evaluation by thioacidolysis using ethanethiol and methanethiol. *Holzforschung* 57:377–384. <https://doi.org/10.1515/HF.2003.056>
- Önnerud H, Gellerstedt G (2003) Inhomogeneities in the chemical structure of spruce lignin. *Holzforschung* 57:165–170. <https://doi.org/10.1515/HF.2003.025>

- Peng C, Zhang G, Yue J, Xu G (2014) Pyrolysis of lignin for phenols with alkaline additive. *Fuel Process Technol* 124:212–221. <https://doi.org/10.1016/j.fuproc.2014.02.025>
- Pascoal Neto C, Seca A, Nunes AM, Coimbra MA, Domingues F, Evtuguin D, Silvestre A, Cavaleiro JAS (1997) Variations in chemical composition and structure of macromolecular components in different morphological regions and maturity stages of *Arundo donax*. *Ind Crops Prod* 6(1):51–58. [https://doi.org/10.1016/S0926-6690\(96\)00205-1](https://doi.org/10.1016/S0926-6690(96)00205-1)
- Pinto PC, Evtuguin DV, Pascoal Neto C (2005) Chemical composition and structural features of the macromolecular components of plantation *Acacia mangium* wood. *J Agric Food Chem* 53(20):7856–7862. <https://doi.org/10.1021/jf058081b>
- Radotić K, Mičić M (2016) Methods for extraction and purification of lignin and cellulose from plant tissues. Sample preparation techniques for soil, plant, and animal samples, Humana Press, New York, NY, pp 365–376. [https://doi.org/10.1007/978-1-4939-3185-9\\_26](https://doi.org/10.1007/978-1-4939-3185-9_26)
- Rahimi A, Ulbrich A, Coon JJ, Stahl SS (2014) Formic-acid-induced depolymerization of oxidized lignin to aromatics. *Nature* 515(7526):249–252. <https://doi.org/10.1038/nature13867>
- Ramesh K, Ashok K, Shamsher SK (2014). Synthesis of methyl succinate by natural-fibre immobilized lipase of *Streptomyces* sp. STL-D8. *Curr Biotechnol* 3(2):152–156. <https://doi.org/10.2174/2211550102666140107232547>
- Regmi YN, Mann JK, McBride JR, Tao J, Barnes CE, Labbé N, Chmely SC (2017) Catalytic transfer hydrogenolysis of organosolv lignin using B-containing FeNi alloyed catalysts. *Catal Today*. <https://doi.org/10.1016/j.cattod.2017.05.051>
- Rößiger B, Unkelbach G, Pufky-Heinrich D (2018) Base-catalyzed depolymerization of lignin: history, challenges and perspectives. *Lignin Trends Appl* 21:99–120. <https://doi.org/10.5772/intechopen.72964>
- Saisu M, Sato T, Watanabe M, Adschiri T, Arai K (2003) Conversion of lignin with supercritical water-phenol mixtures. *Energy Fuels* 17(4):922–928. <https://doi.org/10.1021/ef0202844>
- Sánchez-Martín J, Beltrán-Heredia J, Delgado-Regaña A, Rodríguez-González MA, Rubio-Alonso F (2013) Optimization of tannin rigid foam as adsorbents for wastewater treatment. *Ind Crops Prod* 49:507–514. <https://doi.org/10.1016/j.indcrop.2013.05.029>
- Scholze B, Hanser C, Meier D (2001) Characterization of the water-insoluble fraction from fast pyrolysis liquids (pyrolytic lignin): Part II. GPC, carbonyl groups, and <sup>13</sup>C-NMR. *J Anal Appl Pyrol* 58–59:387–400. [https://doi.org/10.1016/S0165-2370\(00\)00173-X](https://doi.org/10.1016/S0165-2370(00)00173-X)
- Sena-Martins G, Almeida-Vara E, Duarte JC (2008) Eco-friendly new products from enzymatically modified industrial lignins. *Ind Crops Prod* 27:189–195. <https://doi.org/10.1016/j.indcrop.2007.07.016>
- Sharma A, Kumar A, Meena K, Rana S, Singh M, Kanwar S (2017) Fabrication and functionalization of magnesium nanoparticle for lipase immobilization in n-propyl gallate synthesis. *J King Saud University Sci* 29. <https://doi.org/10.1016/j.jksus.2017.08.005>
- Sharma A, Sharma T, Meena KR, Kumar A, Kanwar SS (2018) High throughput synthesis of ethyl pyruvate by employing superparamagnetic iron nanoparticles-bound esterase. *Process Biochem* 71:109–117. <https://doi.org/10.1016/j.procbio.2018.05.004>
- Shatalov A, Pereira H (2005) Kinetics of organosolv delignification of fibre crop *Arundo donax* L. *Ind Crops Prod* 21:203–210. <https://doi.org/10.1016/j.indcrop.2004.04.010>
- Sjöström E (1993) Wood chemistry: fundamentals and applications. Academic Press San Diego. <https://doi.org/10.1016/C2009-0-03289-9>
- Szczurek A, Fierro V, Pizzi A, Stauber M, Celzard A (2014) A new method for preparing tannin-based foams. *Ind Crops Prod* 54:40–53. <https://doi.org/10.1016/j.indcrop.2014.01.012>
- Tana T, Zhang Z, Beltramini J, Zhu H, Ostrikov K, Bartley J, Doherty W (2019) Valorization of native sugarcane bagasse lignin to bio-aromatic esters/monomers via a one pot oxidation–hydrogenation process. *Green Chem* 21(4):861–873. <https://doi.org/10.1039/C8GC03655A>
- Thielemans W, Wool RP (2005) Lignin esters for use in unsaturated thermosets: lignin modification and solubility modeling. *Biomacromol* 6(4):1895–1905. <https://doi.org/10.1021/bm0500345>

- Tian D, Chandra RP, Lee JS, Lu C, Saddler JN (2017) A comparison of various lignin-extraction methods to enhance the accessibility and ease of enzymatic hydrolysis of the cellulosic component of steam-pretreated poplar. *Biotechnol Biofuels* 10:157. <https://doi.org/10.1186/s13068-017-0846-5>
- Tondi G, Pizzi AP (2009) Tannin-based rigid foams: Characterization and modification. *Ind Crops Prod* 29:356–363. <https://doi.org/10.1016/j.indcrop.2008.07.003>
- vom Stein T, den Hartog T, Buendia J, Stoychev S, Mottweiler J, Bolm C, Klankermayer J, Leitner W (2015) Ruthenium-catalyzed C–C bond cleavage in lignin model substrates. *Angew Chem Int Ed Engl* 54(20):5859–5863. <https://doi.org/10.1002/anie.201410620>
- Wang H, Chen W, Zhang X, Wei Y, Zhang A, Liu S, Liu C (2018) Structural changes of bagasse during the homogeneous esterification with maleic anhydride in ionic liquid 1-Allyl-3-methylimidazolium chloride. *Polymers* 10:433. <https://doi.org/10.3390/polym10040433>
- Xu C, Arancon RAD, Labidi J, Luque R (2014) Lignin depolymerisation strategies: towards valuable chemicals and fuels. *Chem Soc Rev* 43(22):7485–7500. <https://doi.org/10.1039/C4CS00235K>
- Zakzeski J, Bruijninx PCA, Jongerius AL, Weckhuysen BM (2010) The catalytic valorization of lignin for the production of renewable chemicals. *Chem Rev* 110(6):3552–3599. <https://doi.org/10.1021/cr900354u>
- Zhang Y-HP (2011) What is vital (and not vital) to advance economically-competitive biofuels production. *Process Biochem* 46:2091–2110. <https://doi.org/10.1016/j.procbio.2011.08.005>
- Zhang J, Fleury E, Brook MA (2015) Foamed lignin–silicone bio-composites by extrusion and then compression molding. *Green Chem* 17(9):4647–4656. <https://doi.org/10.1039/C5GC01418B>
- Zhao X, Zhang Y, Wei L, Hu H, Huang Z, Mei Y, Huang A, Wu J, Feng Z (2017) Esterification mechanism of lignin with different catalysts based on lignin model compounds by mechanical activation-assisted solid-phase synthesis. *RSC Adv* 7(83):52382–52390. <https://doi.org/10.1039/C7RA10482K>
- Zhu JY, Pan XJ, Wang GS, Gleisner R (2009) Sulfite pretreatment (SPORL) for robust enzymatic saccharification of spruce and red pine. *Bioresour Technol* 100(8):2411–2418. <https://doi.org/10.1016/j.biortech.2008.10.057>