Chapter 2

Tailoring Lignin Structure to Maximize the Value from Lignin

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Lignin valorization is one of the most important topics across the biorefinery research community. The overdependence on petroleum-derived products has raised increasing concerns about the energy crisis and environmental pollution, which has warranted significant research on producing renewable chemicals and materials from lignin, replacing petroleum-derived carbons. Despite the potential promise of lignin derivatives, there are still major technical obstacles that need addressing to make lignin valorization more feasible and sustainable. In addition to developing processes, recent studies have focused more on tailoring lignin structures to make lignin a process-friendly feedstock. This review introduces recent studies on chemoselective alteration of lignin structures in an effort to maximize the value from lignin.

Introduction

Lignin is the second most abundant biopolymer next to cellulose, and nature's dominant aromatic polymer. Most lignin is currently produced from pulp and paper industries, and a large amount of technical lignin is expected from emerging biorefineries. Although lignin is an abundant and natural aromatic polymer, the heterogeneous, reactive, and inherent intractability of lignin limit its potential for various industrial applications. Until now, lignin is considered as one of the most challenging materials to work with. However, lignin valorization is still a key research area in the scientific community because the success of future biorefineries highly depends on lignin valorization (*1*, *2*).

Lignin valorization typically includes two different approaches; deconstruction and reconstruction, as shown in Figure 1. In the deconstruction approach, macromolecular lignin is thermochemically or biologically depolymerized into low-molecular-weight phenols to produce

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fuels and aromatic chemicals. However, it is often discussed that lignin depolymerization is challenging because lignin contains various C-O and C-C linkages with the broad distribution of bond strengths (3). Besides, the primary products from the thermal decomposition of lignin readily undergo irreversible recondensation reactions, which lead to the formation of recalcitrant species (4–7).

Reconstruction approaches utilize lignin as a raw material or an additive for the production of polymeric materials. For example, technical lignins obtained from lignocellulosic biomass can be used to produce plant-derived plastic and composites. Reducing the omnipresence of disposable plastics made from petroleum and the high demand for bio-derived materials have warranted intensive research on lignin valorization to produce green and renewable materials. The superficial similarities between lignin and petroleum-derived carbon fiber have encouraged efforts to utilize lignin for carbon fiber composite materials. In addition to the carbon fiber, other promising lignin application areas include electrochemicals (8–10) and pharmaceuticals (11–13). Despite the potential promise of lignin-derived materials, the nonuniformity and several reactive linkages of lignin structure make it process-unfriendly, resulting in poor material properties (14). Recent studies have focused on tailoring lignin structures to make lignin more suitable feedstocks for the production of polymeric materials. This chapter presents an overview of the recent efforts toward tailoring lignin structures for successful lignin valorization. Two different, but not competing, approaches on lignin utilization will be highlighted.
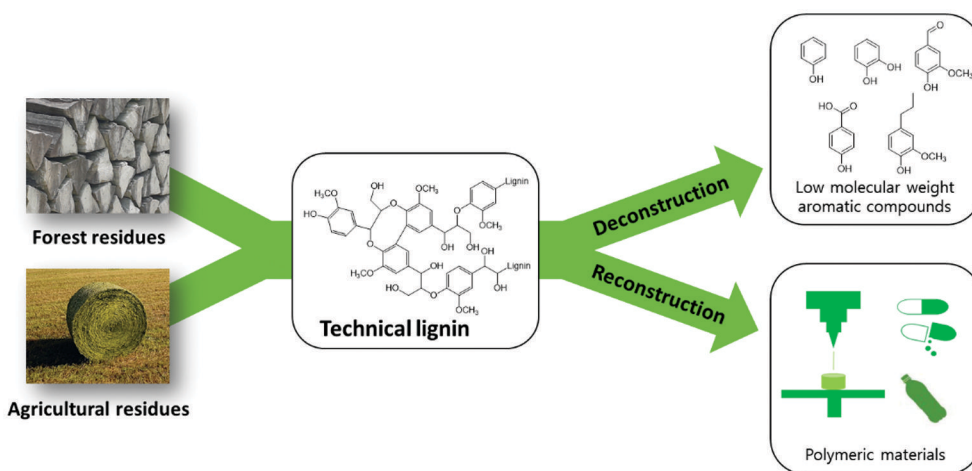

Figure 1. Two approaches in the lignin valorization.

Tailoring Lignin Structure for Depolymerization Approach

There have been significant efforts to produce low molecular weight aromatic compounds from technical lignins. In a typical thermochemical conversion process, heat and catalyst are employed to efficiently break down lignin to phenolic compounds. Besides, using a proper solvent(s) is important in solvent-mediated depolymerization (i.e., solvolysis). One major problem of lignin depolymerization is the recondensation of the lignin fragments, forming aromatic C-C bonds and undesirable condensed products, which significantly reduces the yield of low molecular weight phenolics. This unwanted and irreversible reaction significantly occurs between the primary products of lignin. To maximize the lignin conversion and yield of phenolic monomers, repolymerization has to be minimized. From the process development perspectives, the secondary condensation reactions

can be quenched by employing hydrogen-donor solvents (e.g., formic acid, isopropyl alcohol, and tetralin), molecular hydrogen, and scavenging agents. More recently, tailoring lignin structure has been focused on preventing the repolymerization reaction during the lignin depolymerization. In the following text, recent studies on the modification of lignin structures for enhancing lignin conversion to phenols are presented.

Protection of Reactive Sites in Lignin Structure

Altering specific sites in lignin structure can make lignin more amenable to thermochemical depolymerization, minimizing the undesirable condensation reactions. To this end, the selective blocking strategy of reactive functional groups in lignin was introduced. The addition of formaldehyde prevents lignin condensation during extraction by forming 1,3-dioxane structures with C_α-OH and C_γ-OH in the lignin sidechains (15). The protected lignin with a dioxane unit produced near theoretical yields of 47% lignin monomers after hydrogenolysis. Formaldehyde-incorporated lignin, forming a stable six-membered acetal structure, can suppress the formation of benzylic cations responsible for the condensation reactions and blocks reactive aromatic positions with hydroxyl methyl groups. Recently, a density functional theory (DFT) calculation study provided mechanistic insights into the reactions of formaldehyde-blocked lignin (16). Lignin preferably reacts with formaldehyde with a low energy barrier to form a 1,3-dioxane structure, which protects the reactive sites of lignin, including benzylic hydroxyl groups and aromatic rings. The formaldehyde-protected lignin eventually suppresses lignin condensation reactions, resulting in an enhanced yield of low-molecular-weight products.

The strategy of protecting benzylic hydroxyl groups was further extended with other protection groups. In addition to formaldehyde, Lan et al. reported that acetaldehyde and propionaldehyde could effectively stabilize the C_α-OH and C_γ-OH during the lignin extraction. The subsequent hydrogenolysis of protected lignin in the presence of Pd/C catalyst produced lignin-derived monomeric products at near-theoretical yields (17). The protected lignin was subjected to oxidation using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as oxidant and catalyst to selectively oxidize the C_α-OH to C_α=O. The oxidized lignin was depolymerized with a formic acid and sodium formate, resulting in a 36 mol% of aromatic monomers with high selectivity of syringyl propane dione and guaiacyl propane dione.

Selective oxidation of the C_α alcohol into a ketone in lignin was previously found to enhance the lignin conversion into low molecular weight phenolics. Aspen-derived cellulolytic enzyme lignin (CEL) was oxidized using 4-acetamido-2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) before the depolymerization. Formic acid-induced depolymerization of the modified lignin under relatively mild conditions (110 °C) yielded 61.2 wt% of low-molecular-weight aromatics (18). A density functional theory study revealed that the conversion proceeds sequentially via formylation and elimination at C_γ, followed by hydrolysis of aryl-ether linkages (19). Wang et al. used DDQ to oxidize C_α alcohol of birch lignin (20). Hydrogenolysis of oxidized lignin with carbon-modified nickel catalyst promoted selective cleavage of aryl-ether linkages, resulting in a 22 wt% yield of aromatics.

The conversion of the active C_α-OH groups to C_α=O was also subjected to oxidative deconstruction (21). TEMPO-assisted oxidized lignin was depolymerized by polyoxometalate oxidation at 150 °C with 10 bar O_2. The extractable lignin-derived oil yield was 74.5%, with 32.8% of total monomer yields. Lignin oxidation to block the highly reactive C_α-OH can minimize

undesirable condensation reactions and weaken the β-O-4 ether bond, promoting the overall lignin degradation with a high yield of monomers.

Besides the oxidation of benzylic hydroxyl groups, stabilizing agents have been used to stabilize reactive sites in lignin. The addition of 2-naphthol as a carbocation scavenger to biomass fractionation can minimize lignin condensation reactions by attaching to the C_{α} position (22), providing opportunities to utilize intact lignin as a feedstock for the production of phenolic compounds (23). In addition, phenolic acids, including 4-hydroxybenzoic acid, vanillic acid, and syringic acid, are also electron-rich, lignin-derived, and reactive toward electrophilic carbocations, inhibiting secondary condensation reactions (24).

Zhang et al. reported a stepwise method to strategically defunctionalize the benzylic sidechain of the lignin (25). The ethanosolv process resulted in α-ethoxylated β-O-4 motif, followed by aerobic oxidation and subsequent decarbonylation of the primary hydroxyl group in the C_{γ} position. The resulting partially defunctionalized β-O-4 lignin motif showed enhanced C-O bond cleavage.

In addition to protecting sidechains in lignin, modification of functional groups in the aromatic ring was also studied. Roberts et al. investigated the effect of the addition of boric acid during hydrothermal lignin depolymerization (26). They observed inhibition of concurrent polymerization reactions because boric acid, as a capping agent, significantly suppressed these reactions by capping phenolic hydroxyl groups with the formation of strongly coordinated boric esters. It was found that the phenolic hydroxyl groups play an important role in the addition and polymerization reactions, which eventually lead to the formation of unwanted polymerization of primary phenolic products.

Kim et al. also investigated the effect of selective masking of the phenolic hydroxyl group on the depolymerization of lignin (27). The phenolic hydroxyl groups were blocked by simple methylation. Thermal degradation of the structurally altered lignin, where the reaction was coupled with the *in-situ* EPR monitoring system, showed a decrease in the formation of reactive quinone methide intermediates responsible for repolymerization reactions. Figure 2 summarizes recent efforts to increase the lignin depolymerization efficiency by structural alteration of lignin.

It is widely discussed that methoxylation is helpful in lignin degradation under anaerobic conditions. Because the methoxyl group is the main point of attack for many anaerobic microbes, having more methoxyl groups in lignin structure by pretreatment would benefit the biological depolymerization of lignin (28).
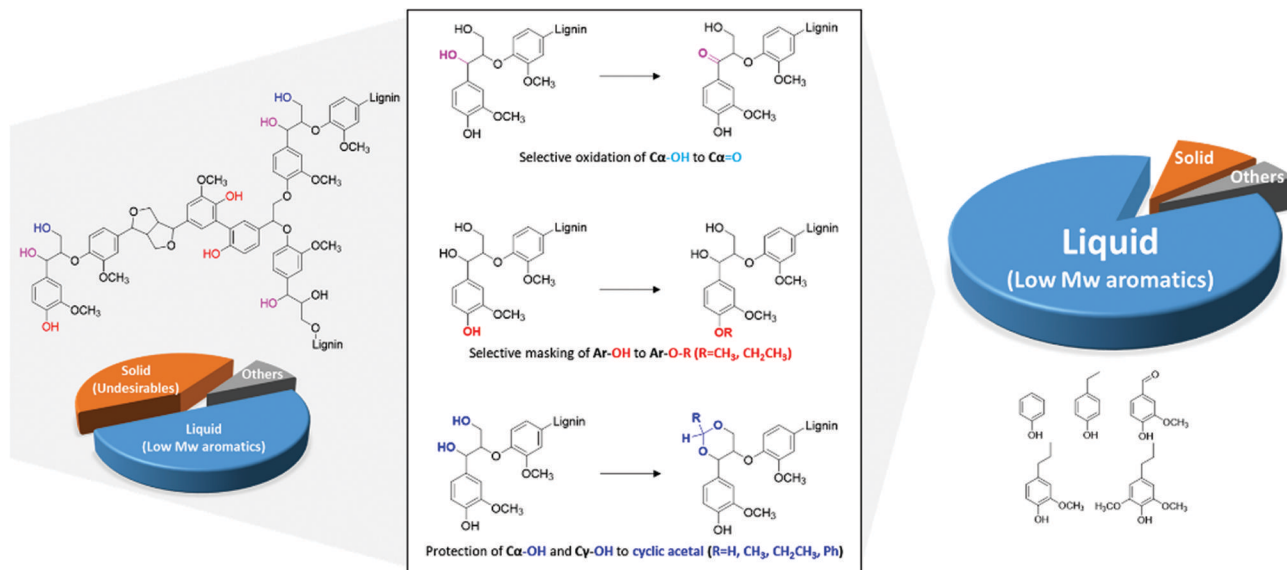
Figure 2. Tailoring lignin structure to enhance the yield of low-molecular weight phenols. Reprinted with permission from reference (1). Copyright 2018 Frontiers.

Lignin Modification to Increase the Selectivity of Final Products

Recently, many efforts to tailor the lignin structure have been made to increase the selectivity of the final products. Considering the heterogeneous structure of lignin, the depolymerized product is a mixture of hydroxyphenyl- (H-), guaiacyl- (G-), and syringyl- (S-) units with various sidechains, depending on the reaction conditions. From the downstream perspective, the complex distribution of the products is technically challenging to further processing. Lignin demethylation was introduced to selectively produce catechol and catechol derivatives. Kim et al. reported that the demethylation of softwood-derived lignin produces a catechol-like structure, and the subsequent hydrogenolysis reaction using a hydrogen donor solvent can produce a high yield of catechol and alkylcatechols (*29*) (Figure 3).

More recently, catechyl lignin was discovered in the seed coats of vanilla and cactus species. Catechyl lignin is a benzodioxane homopolymer without condensed units, representing ideal lignin for valorization. Hydrogenolysis of catechyl lignin resulted in a near-quantitative yield of catechyl-type monomers with a selectivity of 90% to a single monomer (*30*). Wang et al. reported that catalytic depolymerization of catechyl lignin yielded 30 wt% monomeric catechol derivatives with 86% selectivity toward catechylpropanol (*31*). Considering that catechyl lignin is highly acid-resistant with structural uniformity (*30*), chemo- or bioselective alteration of lignin structure to a catechyl-like structure would be a promising strategy for lignin valorization.
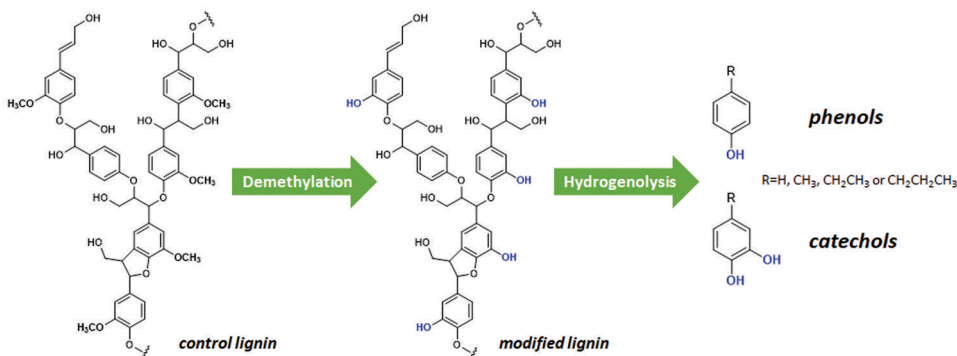

Figure 3. Selective demethylation of lignin followed by hydrogenolysis to produce catechols. Reprinted with permission from reference (29). Copyright 2021 ELSEVIER.

Lignin Modification for the Production of Carbohydrates

Traditionally, biomass pretreatment technologies tried to remove as much lignin in the biomass cell wall typically using strong and toxic acid or base catalyst at harsh conditions. Although the conventional approach has been successfully demonstrated in lignin removal, it often results in poor lignin quality, devaluing the overall process efficiency. Modern biorefineries, however, have been developing a milder treatment process to modify lignin rather than targeting complete lignin removal (*32*), which enables better utilization of lignin and maximizes the value from biomass.

Alkali-oxygen treatment was found to effectively modify lignin structure, producing a high yield of fermentable sugars (*33, 34*). Biomass chips treated with sodium carbonate and oxygen before mechanical refining resulted in modified lignin with a greater amount of carboxylic acid groups retaining most of the carbohydrates in the solid fraction. The modified substrates showed increased

swelling and a decrease in the tendency of the lignin to bind enzymes, resulting in a high yield of fermentable sugars.

Lai et al. developed an integrated pretreatment process combining an in-situ lignin modification with 2-naphthol and poly (ethylene glycol) diglycidyl ether (PEGDE) (35). Lignin modification with 2-naphthol and PEGDE showed suppressed lignin repolymerization and lowered the non-productive binding on lignins of enzymes, respectively, synergistically facilitating enzymatic hydrolysis of the substrates. Similarly, 2-naphthol-7-sulfonate was used as a carbocation scavenger in the biomass pretreatment (36). The addition of scavenger to the acid pretreatment resulted in acid group-incorporated lignin with enlarged biomass porosity, and the hydrolysis yield increased by more than 48% after dilute acid pretreatment.

Tailoring Lignin Structure for the Production of Lignin-Derived Materials

Chemical modification of lignin to develop new materials is another promising way of lignin value-addition. Lignin has plenty of reactive functional groups, such as hydroxyl, carbonyl, benzyl alcohol, and carboxyl groups. However, the structural complexity and heterogeneity of lignin, attributed to the various functional groups, decrease its processability toward making lignin-derived materials. Therefore, proper structural transformation to introduce new functionalities on lignin has been performed. One way is the incorporation of functional groups that have not existed in raw lignin material. Another is to modify the hydroxyl group, the most frequent and reactive functional group in lignin polymer, for further development. In addition, controlled functionalization by polymer chemistry improves the performance of lignin-based materials. In the next sections, several technical approaches on the functionalization of the lignin structure for material production are presented. Also, the material properties of lignin-derived products are compared with those of commercial products where applicable.
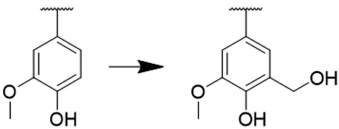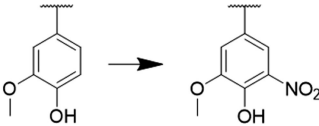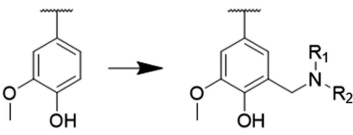
Incorporation of New Functional Groups on Lignin Aromatic Region

Several types of chemical reactions have been used to synthesize new functional groups onto lignin; hydroxyalkylation, nitration, amination, etc. (Table 1) Each modification method can contribute to the change of physicochemical properties of lignin.

Hydroxyalkylation is a reaction that can replace the carboxyl group and hydroxyl group of lignin using formaldehyde and strong bases, such as NaOH or Na_2CO_3. This reaction includes the condensation of an aldehyde with activated lignin aromatic regions for further functionalization or improving solubility and mechanical properties of the lignin-derived resin. Several studies were conducted to use hydroxyalkylated lignin-derived resin as a high-performance and greener binder replacement in particleboard or plywood. Yang et al. (37) synthesized hydroxymethyl lignin from four kinds of technical lignin (corncob lignin, two different poplar wood lignins, and wheat straw lignin) obtained from black liquor or biorefinery mills. In this study, an aromatic region of lignin and formaldehyde were reacted in the presence of NaOH (pH 9–10) at 80 °C to form a methylol group on the *para* or *ortho* positions of a phenolic hydroxyl group. These functionalized lignins were then copolymerized with phenol to produce lignin-phenol-formaldehyde resin adhesive, which showed similar structure and curing behavior with the commercial one, in the preparation of plywood. A similar experiment of lignin modification was described by Wang and Chen. (38). Alkaline lignin solution extracted from corn stalk (pH 10.5–12.0) was methylolated at 60–80 °C. The authors noticed that high temperatures at over 90 °C could accelerate the self-condensation process of methylolated lignin. The methylol groups in the aromatic C_5 position of lignin were subsequently

condensed with phenolic resin as plywood adhesives under hot pressing conditions (0.8 MPa at 160 °C). Another study of lignin hydroxyalkylation was conducted by Jiao et al. (*39*). In their study, corncob lignin was methylolated at 80 °C and pH 11.5 to enhance the reactivity of lignin toward making a hydroxymethylurea polymer. This three-dimensional lignin polymer network captures hydroxymethylurea and slowly releases nitrogenous compounds (NH_4^+ and NO_3^-). As a result, the authors suggested that the hydroxymethylated lignin could act as a diffusional barrier of controlled-release nitrogen fertilizer.

Table 1. Examples of Incorporation of New Functionalities to Lignin Aromatic Structure

Reactions	Scheme	References
Hydroxyalkylation		(37-39)
Nitration		(40)
Mannich reaction	For dimethylamine, $R_1 = R_2 = CH_3$ For diethylamine, $R_1 = R_2 = CH_2CH_3$ For triethylenetetramine, $R_1 = H$, $R_2 = CH_2CH_2(NHCH_2CH_2)_2NH_2$	(41, 43, 44)

Nitration and Mannich reaction are used to add nitrogen-containing functional groups in an aromatic region of lignin structure. Lignin nitration is used not only for further substitution reactions or add directing group that enables the incoming electrophile to react at specific positions on the aromatic ring, but also to produce nitrated aromatics, which is an important intermediate in chemical industries. Graglia et al. (*40*) reported the preparation of nitrogen-doped carbon using functionalized lignin via aromatic nitration followed by carbonization in molten eutectic $KCl/ZnCl_2$. It was reported that the nitrogen doping enhances the electroactivity of carbon. Residual lignin obtained from lactic acid production was reacted with inorganic acid catalysts in acetic anhydride and quenched at 0 °C. The obtained acetylated nitrogen-functionalized lignin (NL) with 6.7% nitrogen content was employed for the synthesis of nitrogen-doped carbon via carbonization in molten eutectic $KCl/ZnCl_2$. Compared to further deacetylated NL and aminated lignin, NL was reported to show slightly better electrocatalytic activity for the oxygen reduction reaction when carbonized.

The Mannich reaction is a condensation reaction of ammonia, primary or secondary amine in the presence of formaldehyde. This reaction introduces amine groups to the unsubstituted *ortho* position in the lignin and is used for the synthesis of building blocks to prepare nitrogen-containing compounds or nitrogen-doped materials.

Du et al. (*41*) performed the amination of the lignin model compound (apocynin) and LignoBoost softwood kraft lignin (*42*) by the Mannich reaction. In this research, the lignin was dissolved in 1,4-dioxane, then 10 molar equivalents of dimethylamine and formaldehyde were subsequently introduced in the solution. The Mannich reaction between lignin, amine, and formaldehyde was carried out under sealing conditions at 60 °C for 4 h. Du et al. identified a new $ArCH_2N$ signal in ^{13}C NMR and 2D-HSQC NMR from the resulting aminated lignin and determined that 28 amine groups were successfully introduced per 100 aromatic rings. Furthermore, 42 amine groups were introduced per 100 aromatic rings by the Mannich reaction after phenolation. The aminated lignin products were hydrophilic and showed higher zeta potential (max. 31.6 mV) and charge density (max. 1.6×10^{-7} equiv./mL) that could form surfactant chemicals or polycationic materials.

Work by Li et al. (*43*) applied the Mannich reaction to synthesize the aminated lignin-polylactic acid (PLA) blend. Softwood kraft lignin was reacted with diethylamine and formaldehyde at 60 °C for 4 h under sealing and stirring. ^{31}P NMR spectra showed the complete disappearance of the guaiacyl hydroxyl group peak and rise of C_5 substituted (dialkylaminomethyl) guaiacyl hydroxyl group peak, which indicates the complete introduction of dialkylaminomethyl group at the C_5 position of the lignin aromatic ring. They reported that blend coating of PLA-aminated lignin on the urea pellet fertilizer for food production provides additional bound nitrogen (high molecular amine groups) to the fertilizer to supply a slow-release effect. On the other hand, Mendis et al. (*44*) performed the Mannich reaction of lignin to increase dispersion in epoxy through lignin–amine interaction. Kraft lignin was introduced to triethylenetetramine and quickly homogenized for 5 min. Then formaldehyde solution (38 wt%) was introduced at a rate of 0.1 g/min to the lignin-triethylenetetramine solution. Increased hydroxyl and tertiary amine functional groups in the Mannich-functionalized lignin enhanced the dispersion ability of the lignin in an epoxy matrix but discouraged thermomechanical properties.

Modification of Lignin Functional Groups

Lignin functionalization has been performed to increase the chemical reactivity and processability of lignin. Among the modification strategies, alteration of the hydroxyl group is considered to be the simplest to increase the potential of lignin applications in the polymer industry, which includes allylation, esterification, etherification and silylation. Table 2 presents several examples of structural modification of lignin.

In the allylation, the hydroxyl groups of lignin are converted into allyl ether groups which can be further functionalized or directly applied to various chemical reactions, including epoxidation, thiol-end click chemistry and bromination.

Llevot et al. (*45*) reported an allylation of bio-based phenols (guaiacol, eugenol, vanillyl alcohol, and syringol) and organosolv lignin in the Tsuji–Trost reaction with a Pd nanoparticle catalyst. The study revealed that selective allylation of the phenolic hydroxyl groups was employed by 1 mol% of Pd catalyst in an H_2O/dimethylacetamide solvent mixture (44% allylated) and an H_2O/ethyl acetate solvent mixture (83% allylated). Dumont et al. (*46*) also described the Pd-catalyzed selective allylation of kraft lignin for the production of malleable materials. Dumont et al. described that the telomerized lignin showed a decreased glass-transition temperature of 50 °C, and can be easily shaped. Furthermore, ^1H NMR analysis determined the presence of unsaturated sidechains in the

telomerized lignin, which could be further functionalized to synthesize fillers, macromonomers, and compatibilizing agents.

Traditionally, lignin esterification with acid derivatives has been widely used for structural analysis of lignin since it functionalizes the lignin hydroxyl group, decreases intermolecular hydrogen bonding, and thus increases lignin solubility in nonpolar solvents. Also, lignin esters with larger-chain derivatives showed increased thermal mobility compared to unmodified lignin, which has lead to research for several applications in carbon fibers, thermoset plastics, and coating polymers.
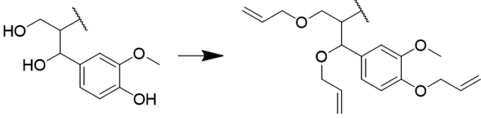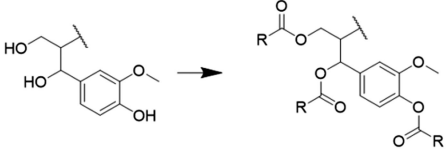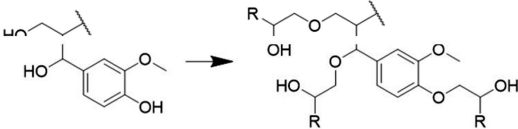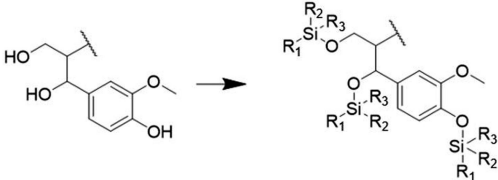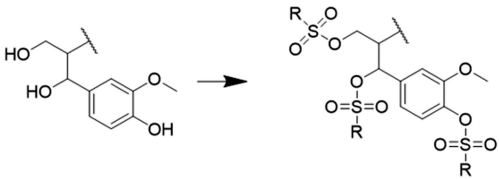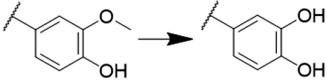
Koivu et al. (47) carried out a detailed study of lignin esterification with different acids (C2–C16) to determine the effect of chain length and substitution degree on the thermal properties of the lignin ester. In this study, softwood kraft lignin was dissolved with the mixture of tetrahydrofuran (THF), dimethylformamide (DMF), and pyridine. Acyl chlorides with four different fatty acid chains (C2, C8, C12, and C16) were introduced in the lignin solution and further reacted. All the synthesized esters showed a decrease in the glass-transition temperature (ΔTg max. -100 °C) and melting temperature with a high loading of fatty acids, which suggests the potential of the lignin ester as additives for polymer blends by melt extrusion.

Lignin has been viewed as a promising feedstock of renewable carbon fiber. However, there has been critical issues of decreasing tensile properties (instability or surface defects) for lignin-based carbon fibers. Zhang & Ogale (48), to overcome the problem, synthesized partially acetylated lignin and used to prepare dry-spinning carbon fiber. The acetylated lignin with low acetic anhydride concentration (0.66 mL/g lignin) was dissolved in acetone and successfully dry-spun into lignin as-spun fibers (i.d. 30 μm). Finally carbonized fibers obtained in this study (i.d. 6-8 μm) displayed higher tensile modulus (52 ± 2 GPa), larger surface area, and higher reactivity due to its less graphitic surfaces.

In the study by García-Mateos et al. (49), carbonyl and hydroxyl groups of Alcell lignin were esterified with phosphoric acid to generate phosphate and/or polyphosphate esters during electrospinning lignin fiber preparation in ethanol. Product fibers containing phosphorus-functionalities have shown an increased glass transition temperature and a much shorter stabilization time (105 min) than the pure lignin fibers (more than 90 h) without fiber fusion issue. The fiber also has submicron size (i.d. ≤ 1 μm), higher surface area, and uniformly distributed O and P surface functionalities that has potential for use as heterogeneous catalyst, adsorbent, and electrode. In contrast, Ding et al. (50) described that the butylation of organosolv lignin in the presence of 1-methylimidazole catalyst at 60 °C for 3 h decreased the glass transition temperature of lignin-polyacrylonitrile blend when compared to pure lignin-polyacrylonitrile blend. Also, a carbon fiber mat from a butylated lignin blend at 1,000 °C showed higher tensile strength and Young's modulus than that from the pure lignin-polyacrylonitrile blend.

Li et al. (43) additionally performed both acetylation and palmitoylation of the hydroxyl group of lignin to coat urea pellet fertilizer. The esterification of lignin was conducted using acetic anhydride or palmitic anhydride together with pyridine as a both solvent and catalyst at room temperature for 24 h. The esterification increased the hydrophobicity of the esterified lignin, especially with long-chain palmitic acid. Compared to the aminated lignin blend, PLA-palmitoylated lignin blend coating displayed a longer nitrogen release delay due to largely increased hydrophobicity.

Table 2. Examples of Structural Modifications of Lignin Functional Groups

Reactions	Scheme	References
Allylation		(45, 46)
Esterification	 For carboxylic acids, R = $CH_3(CH_2)_n$ For t-butyl acetoacetate, R = CH_3COCH_2	(43, 47-53)
Etherification	 For styrene oxide, R = C_6H_6	(54)
Silylation	 For divinyldisilazane, R_1 = CH_3CH, R_2 = R_3 = CH_3 For t-butyldimethylsilylchloride, R_1 = $(CH_3)_3C$, R_2 = R_3 = CH_3	(55, 56)
Tosylation	 For 4-toluenesulfonyl chloride, R = $C_6H_6C_3$	(65, 66, 76)
Demethylation		(57)

Scarica et al. (*51*) performed aliphatic hydroxyl group-specific esterification of Indulin AT kraft lignin using succinic anhydride. Lignin and succinic anhydride with different weight ratios were dissolved in THF in the presence of 1-methylimidazole catalyst. The authors reported that glass-transition temperature of lignin decreased from 92 °C to 69 °C resulting from the plasticization effect of succinic anhydride on lignin. The thermal stability was significantly increased by following reactions (crosslinking with an external agent or self-polyesterification of the succinylated lignin) to obtain fully cross-linked lignin-based polyester coatings. Both following reactions were successfully performed and the high water repellence, hardness, and adhesion strength of the lignin-based thermoset coating were evaluated. Work by Krall et al. (*52*) also esterified Indulin AT kraft lignin without catalyst and determined its structure for bio-based thermoset coating application. Kraft lignin dissolved in 1,4-dioxane was reacted with *t*-butyl acetoacetate at 130 °C for 3 h to be directly acetoacetylated.

On the other hand, Liu et al. (*53*) suggested low environmental impact esterification of lignin using a weak organic acid as the solvent and reagent rather than a strong acid. Softwood kraft lignin and hardwood organosolv lignin were mixed with propionic acid and magnetically stirred at 90–120 °C for 24–96 h. Interestingly, this reaction only functionalized the aliphatic hydroxyl group in the lignin, keeping the phenolic hydroxyl and carboxylic groups unchanged. The authors synthesized hydroxyethyl lignin derivatives followed by direct esterification with organic acid to obtain highly substituted lignin (max. 91% esterified).
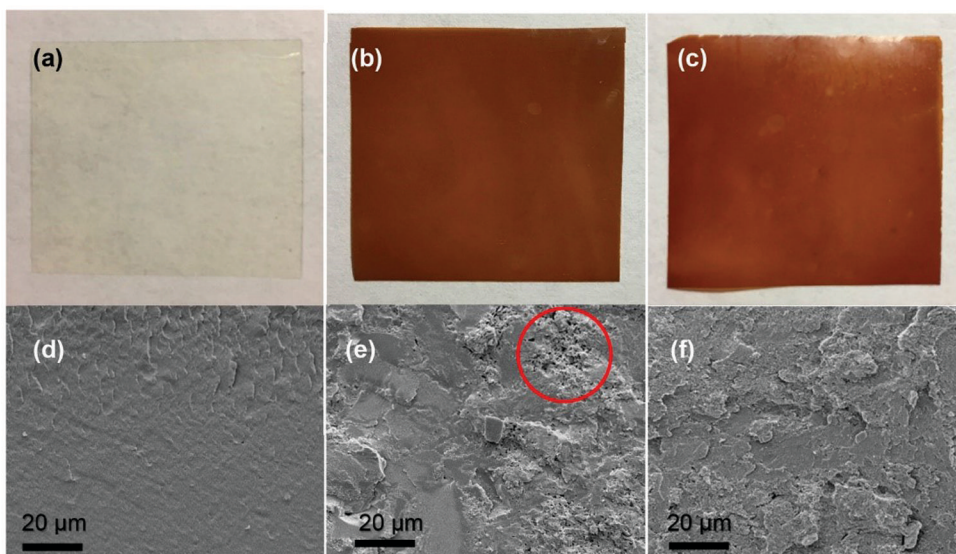

Figure 4. Optical images of (a) PAN, (b) lignin-g-PAN, and (c) vinyl silylated lignin-g-PAN films. Cross-section SEM images (1000×) of (d) PAN, (e) lignin-g-PAN, and (f) vinyl silylated lignin-g-PAN films. Reprinted with permission from reference (55). Copyright 2018 American Chemical Society.

Functionalization with an alkylene oxide applied to lignin is the most well-known etherification process, giving lignin not only higher solubility in organic solvents but also additional active sites. Duval et al. (*54*) applied epoxide ring-opening etherification with the lignin hydroxyl group to give the benzene ring site to lignin for further modifications. Phenolic hydroxyl groups of kraft lignin were selectively reacted with ring-opened styrene oxide in an alkaline solution (NaOH) at 50 °C. The new benzene rings in this benzylated lignin were further reacted with diazotized *N,N*-dimethyl-*p*-

phenylenediamine to contain diazobenzene groups, granting pH- and light-responsive properties to it.

Silylation is also one of the candidate modifications to improve the mechanical properties of lignin as polymer alternatives. Li et al. (55) performed an experiment of lignin modification with 1,1,3,3-tetramethyl-1,3-divinyldisilazane, which increases film flexibility and can partially replace polyacrylonitrile (PAN) in applications. Given its properties as light weight and stiffness, PAN is the most commonly used precursor for the production of carbon film. Pine kraft lignin was mixed with 1,1,3,3-tetramethyl-1,3-divinyldisilazane using a twin-screw extruder at 120 °C for 15 min (31 % sylilated). This vinyl silylated lignin was then copolymerized with acrylonitrile to form the PAN-grafted vinyl silylated lignin with improved thermal stability. Moreover, the films based on lignin-*graft* (g)-PAN showed much higher tensile strength (18 MPa) and strain (55% by a dynamic mechanical analyzer) than that of unmodified lignin-based copolymer (10 MPa and 10%, respectively) (Figure 4).

Buono et al. (56) produced silylated lignin and its thermal, physicochemical, and blending properties were compared to acetylated lignin. Soda lignin (Protobind 1000™) was silylated with *t*-butyldimethylsilylchloride using imidazole as a catalyst and base at room temperature. The authors noted that the whole lignin phenolic hydroxyl group was functionalized quickly; however, around 15% of the aliphatic hydroxyl group could not be reacted possibly due to the steric hindrance. The silylated lignin was well melt-blended with low-density polyethylene (LDPE) at 10% loading and showed better thermal stability and compatibility with LDPE matrix than the neat or acetylated lignins.

So far, approaches to modify the hydroxyl group in the lignin has been increasingly studied. Sawamura et al. (57) investigated the effect of demethylation of the lignin methoxyl group to convert it to hydroxyl group with three different chemicals (1-dodecanethiol, hydroiodic acid, and iodocyclohexane). Synthetic lignin, guaiacyl-type dehydrogenation polymer (GDHP), was used in this study. Among the chemicals used, iodocyclohexane found to be the most effective for increasing the number of phenolic hydroxyl groups.

Strategies for Lignin Copolymerization

The incorporation of lignin into new polymeric materials could be achieved by derivatization using polymer chemistry. There are diverse processing techniques to form chain or three-dimensional networks by combination of monomers/polymers; free radical addition polymerization, ionic polymerization, vinyl polymerization with complex coordination catalysts, step-reaction polymerization, ring-opening polymerization, cycloaddition polymerization, atom transfer polymerization, block and graft copolymer formation, etc. Various types of copolymerization processes have been applied to modify lignin into a useful bio-based polymer. Among them, graft copolymerization that uses the lignin as the polymer core unit (backbone) and covalently bonded monomers (branch), is the most common process to control the architecture and use of the resulting copolymer.

Panesar et al. (58) synthesized lignin-g-vinyl acetate copolymer with potassium persulfate as an initiator and ammonium iron(II) sulfate hexahydrate as a catalyst at 60–80 °C. The authors noted that the highest grafting efficiency (60%) was observed for 2:3 ratio of lignin and vinyl acetate at 70 °C. The copolymer displayed decreased glass transition temperature from 118 °C to 103 °C and increased hydrophobicity. In another study of lignin copolymerization by Hu et al. (59), grafting of polyacrylic acid with alkali lignin was performed by adding an ammonium persulfate/DMF solution

as initiators and *N,N*-methylenebisacrylamide/DMF solution as a cross-linker at room temperature. The highly increased content of carboxylic acid group in lignin after copolymerization could contribute to improving the biosorption capacity of heavy metals, such as Cu(II) or Cd(II).

Several researches modified lignin before copolymerization to change the lignin as a proper macroinitiator, which enhances the reactivity or dispersion in the monomer mixture. Abdollahi et al. (*60*) carried out ring-opening polymerization of ε-caprolactone with three different lignin (kraft lignin, silica-lignin hybrid, and hydroxymethylated lignin) to prepare lignin-derived macroinitiators for thermoplastic synthesis. Lignin-g-polycaprolactone (PCL) with different polymer chain length was synthesized in the presence of a $ZnCl_2$ catalyst at 150 °C for 24 h with stirring, which showed relatively low grafting efficiency (52–55%). The authors suggested that water generation induced by $ZnCl_2$ contributed to reduced efficiency; therefore, $ZnCl_2$ can be replaced with another catalyst. Thermal properties of the lignin-g-PCL thermoplastics depended on the grafted chain length rather than the types of lignin. In another way, grafting of poly-L-lactide (PLLA) on fractionated lignin was conducted by Park et al. (*61*). Soda lignin was fractionated by sequential extraction with five different solvents (ethyl acetate, 2-butanone, methanol, acetone, and 1,4-dioxane). Obtained lignin fractions were reacted with L-lactide and triazabicyclodecene (ring-opening catalyst) to produce lignin-g-PLLA copolymer at 130 °C for 4 h under stirring. Finally, the lignin-PLA composite was synthesized by mixing each lignin-g-PLLA and PLA. The authors mentioned that high molecular weight lignin fraction, showing lower hydroxyl group content, achieved a slightly lower rate of conversion L-lactide to PLLA chains (min. 88.3%) than low molecular weight one (max. 91.2%). But the PLA composite with lower conversion rate presented better elastic modulus and UV blocking ability.

Cannatelli and Ragauskas (*62, 63*) synthesized kraft lignin-based copolymer by laccase-catalyzed grafting with low molecular weight quinone compounds to form the hyperbranched polymer. Methylhydroquinone and tris(2-mercaptoethyl)amine were introduced to the lignin/1,4-dioxane solution, followed by laccase-assisted thiol-Michael addition at 50 °C for 20 h. The resulting product, which has potential as a lignin-based biocomposite thermoplastic, showed moderate glass transition temperature (50–60 °C) and good thermostability.

Ring-opening chain-growth polymerization is utilized to obtain a grafted thermoset polymer of lignin with small molecules. Hydroxyl or other functional groups in lignin are etherified to produce polymers in processes such as the curing of epoxy resin. Li et al. (*64*) conducted the synthesis of epoxy resin by the formation of an ether bond between hydroxyl groups in lignin and glycerol diglycidyl ether (GDE)-derived crosslinker epoxide without the use of modifiers or catalysts. A mixture of lignin and GDE was cured at 130–150 °C. Lignin-GDE copolymer showed comparable characteristics (water-tolerance, fast curing, and adhesion performance) as conventional formaldehyde-based resins. Mahata et al. (*65*), formed hydrogel for the use of anti-infective ointment. A hydrophilic polyoxazoline chain was grafted through ring-opening polymerization between tosylated lignin macroinitiator (*66*) and 2-ethyl oxazoline in dimethyl sulfoxide at 100 °C for 10 h under nitrogen atmosphere. This copolymer has undergone further copolymerization with 3-amino-1H-1,2,4 triazole to achieve antimicrobial and antibiofilm properties.

Free-radical polymerization (FRP) is a kind of polymerization method of successive addition induced by free-radical monomers. In work by Gupta et al. (*67*), FRP of kraft lignin and acrylamide was conducted. First, hydroxyl groups in kraft lignin was functionalized by ring-opening polymerization of epoxide ring in glycidyl methacrylate (GM). Then lignin-GM macromolecule was reacted with acrylamide dissolved in DMF in the presence of azobisisobutyronitrile (AIBN) at 70 °C for 1 h. The authors compared the plasticizing ability of lignin-polyacrylamide copolymer with a commercial superplasticizer (polycarboxylate ether) in cement suspensions. Lignin-polyacrylamide

by FPR showed comparable viscosity at low superplasticizer concentration and compressive strength but poor slump flow spread value.

One of the major drawbacks of FRP is uncontrolled molecular weight distribution due to the rapid irreversible termination process. On the other hand, controlled radical polymerization through a degenerative chain transfer process can be performed by reversible addition-fragmentation chain transfer (RAFT) of a wide range of monomers and RAFT agents which mediate the polymerization. In this reaction, lignin is usually transformed into a RAFT agent. Gupta et al. (67) also performed RAFT to synthesize polyacrylamide-grafted kraft lignin. Lignin-based RAFT macroinitiator, obtained by reaction of lignin and acyl chloride xanthate at room temperature for 12 h (68), was then grafted with acrylamide in the presence of AIBN initiator. Almost comparable slump spread to commercial polycarboxylate ether was reported in synthesis of lignin-polyacrylamide by RAFT.

Xu et al. (69) converted organosolv lignin into the RAFT agent by reacting to lignin hydroxyl groups with 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid at 25 °C for 48 h in the presence of N,N-dicyclohexylcarbodiimide, 4-dimethylaminopyridine, and dichloromethane. This lignin-derived RAFT agent and soybean oil-derived methacrylate monomers (SBMAs) were grafted as a RAFT reaction at 70 °C for 48 h under nitrogen gas. The authors cured a mixture of lignin-g-poly(SBMAs), maleic anhydride, and tri-n-propylamine at 120 °C for 12 h to form lignin epoxy resin. The presence of hydrogen bonding between secondary amides resulted in grafted copolymers with different tensile behaviors, lower stress at the break with higher strain at break.

Atom transfer radical polymerization (ATRP) is another popular method that enables control of polymer structure and composition while grafting various types of monomer. Among the important components of ATRP, lignin usually acts as an initiator. In the study by Liu et al. (70), kraft lignin-derived ATPR macroinitiator was produced first by esterification of the lignin hydroxyl group with 2-bromoisobutyryl bromide. Next, ATRP of 2-dimethylaminoethyl methacrylate (DMAEMA) with the lignin macroinitiator was carried out in the presence of copper(I) bromide (catalyst) and 1,1,4,7,10,10-hexamethyltriethylenetetramine as a ligand. Lignin-g-poly(DMAEMA) copolymer had a hyperbranched structure with a hydrophobic backbone (lignin) and multiple cationic hydrophilic arms (poly(DMAEMA)) which can bind and condense plasmid DNA to form a nano-sized gene delivery system . Kim et al. (71) also synthesized a graft polymer by ATRP of styrene with a bromoisobutyrylated kraft lignin macroinitiator in the presence of copper(I) bromide and N,N,N',N",N"-pentamethylenediethylenetriamine as a ligand. Thermal decomposition properties of lignin-g-polystyrene copolymer was improved with increase of number average molecular weight, while the radical polymerization process were less controlled.

Polyurethanes are the most commonly used polymers to make foams, synthesized by the reaction of a polyol (an organic compound containing multiple hydroxyl groups) with a polyisocyanate. Since lignin is a natural polyol, the urethanization of lignin to produce bio-based polyurethane has been steadily explored. Zhang et al. (72) reported the preparation of rigid polyurethane (RPU) foams from kraft lignin via surface functionalization followed by urethane bonding. A mixture of kraft lignin and diisocyanate was heated at 80 °C for 1 h under 800 RPM stirring to form urethane moiety by interaction of lignin hydroxyl group and highly reactive isocyanate group. This functionalized lignin was reacted with a commercial polyester polyol, R-23-015, in the presence of HFC-365mfc (blowing agent) and an amine catalyst to crosslink the RPU system. The authors revealed that lignin-based RPU foams with 30% of lignin substitution of the commercial polyol showed comparable thermal and mechanical properties to conventional RPU foams. Specific compressive strength and modulus were increased by increasing lignin ratio from 0 to 20% but decreased by further increasing the ratio. In a similar study from Gómez-Fernández et

al. (73), hydroxyl groups in kraft lignin were reacted with secondary isocyanate groups of isophorone diisocyanate and dibutyltin dilaurate (catalyst) at 60 °C under 600 RPM stirring and nitrogen atmosphere. Then RPU was subsequently synthesized by blending the lignin-diisocyanate copolymer, castor oil derived polyether polyol, water (blowing agent), and additives at room temperature under stirring.
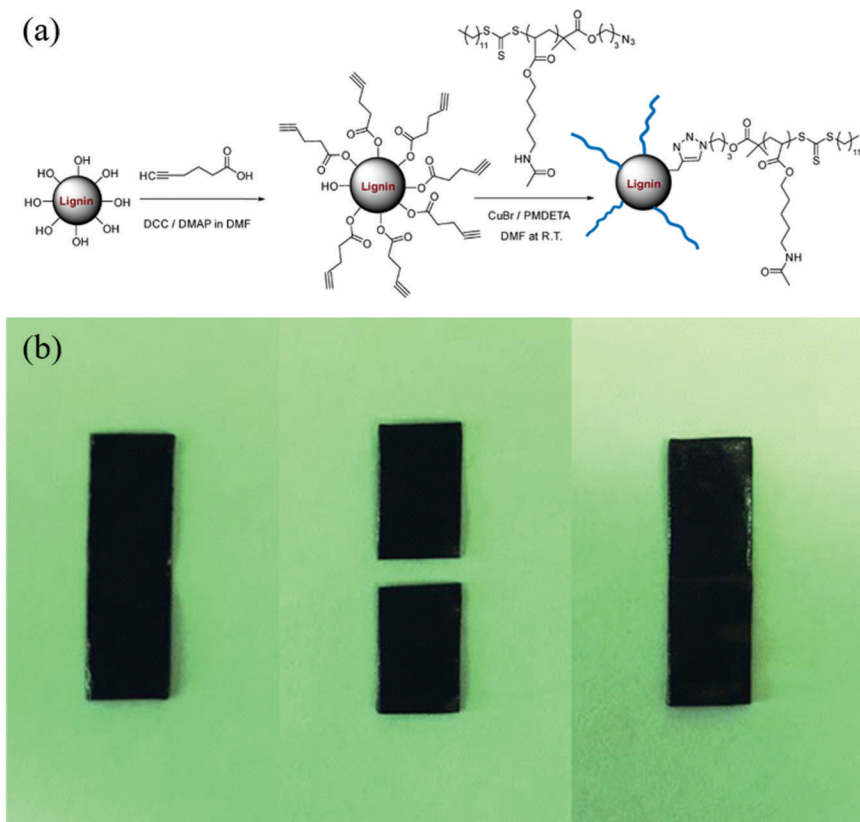

Figure 5. (a) Alkynylation and copper-catalyzed click reaction of poly(5-acetylaminopentyl acrylate) and natural lignin. (b) Self-healing test of 20 wt % lignin containing lignin-g-PAA under ambient conditions (23 °C and 55% humidity). Reprinted with permission from reference (75). Copyright 2018 American Chemical Society.

Work by de Haro et al. (74) developed lignin-based polyurethane coatings by urethanization of vanillic acid-derived diisocyanate (VA-NCO) and hydroxyl groups in lignin. Three different lignins (Indulin AT kraft lignin, acetone organosolv lignin, and soda lignin) were used in this study. VA-NCO and lignin were dissolved at room temperature in THF at 20 wt% concentration under stirring. The authors estimated a maximum lignin content in the obtained PU coatings in the 92–96 wt % range in a desirable condition.

Liu and Chung (75) utilized a copper-catalyzed azide-alkyne cycloaddition or "click" reaction, forming a triazole ring in very high yields with little byproduct, of alkyne-functionalized softwood lignin and poly(5-acetylaminopentyl acrylate) (PAA). Alkyne functionalization of lignin was performed using 5-hexynoic acid in the presence of N,N'-dicyclohexylcarbodiimide and DMF for 48 h followed by further purification processes. Next, alkyne groups of functionalized lignin and azide terminal groups of PAA were reacted by copper(I) bromide-catalyzed alkyne-azide cycloaddition

at room temperature (Figure 5). The resulting copolymer showed superior mechanical properties (maximum tensile strength, energy-to-break, and Young's modulus) with longer PAA chains. Interestingly, acetylamino groups on the polymers led directly to autonomic healing properties in bulk lignin-g-PAA, showing 93% of maximum strength recovery after the self-healing process when severely damaged.

Work by Panovic et al. (76) selectively modified the β-O-4 γ-position of organosolv lignin with a high level of α-alkoxylated β-O-4 units (walnut shell butanol alkoxasolv lignin) via tosylation, azidation, and copper-catalyzed azide-alkyne triazole formation. First, hydroxyl groups in organosolv lignin was tosylated with 3 equivalents of toluenesulfonyl chloride at room temperature for 6 h. Next, azidation of the tosylated group was achieved with 2 equivalents of NaN_3 at 50 °C for 24 h, followed by copper-catalyzed click chemistry with several alkynes, $CuSO_4 \cdot 5H_2O$, and ascorbic acid dissolved in DMF/water at room temperature for 16 h . They described that the click reactions can only occur from the γ-position of β-O-4 linkage in this process because phenolic end groups are tosylated and the α-hydroxyl groups are replaced with butyl ethers. The authors concluded that this grafting method has potential to meet suitable and novel applications since it is a highly regioselective reaction.

Diels–Alder reaction is a versatile reaction linking an azido and a thermally reversible alkynyl group. Duval et al. (77) carried out a reversible crosslinking of lignin via Diels–Alder reaction. Both furan-functionalized moieties and maleimide-functionalized moieties were synthesized based on softwood kraft lignin. To prepare furan moieties, kraft lignin dissolved in NaOH solution was reacted with furfuryl glycidyl ether at 50 °C overnight. Maleimide moieties were synthesized by the reaction between the lignin/DMF solution and 6-maleimidohexanoic acyl chloride in the presence of K_2CO_3 at 50 °C for 1 h. Diels-Alder reaction of each functionalized lignins has occurred in DMSO at 70 °C until the resulting gelatin was formed. By heating up to 120 °C, the gel turned back into the liquid state due to a retro-Diels-Alder reaction (Figure 6). This new reversible crosslinking ability of lignin-based copolymer can be applied to manufacture material with recyclability or self-healing ability.
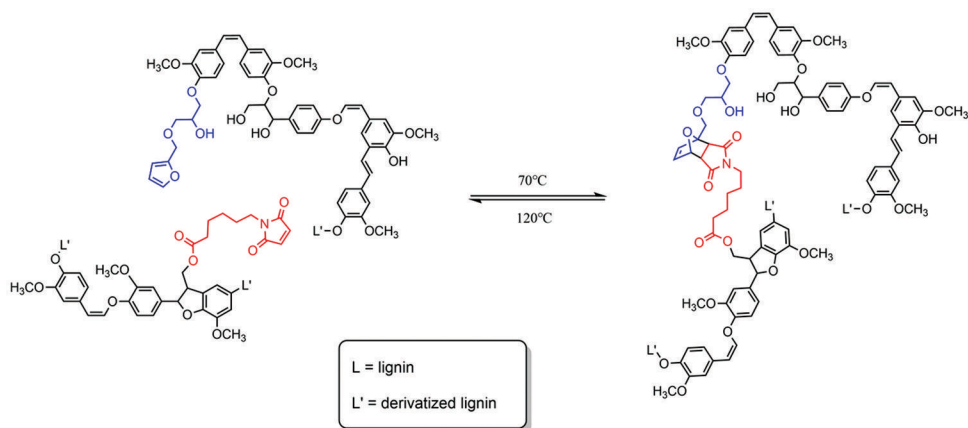

Figure 6. Crosslinking of the furfurylated lignin with furfuryl glycidyl ether (blue) and esterified lignin with 6-maleimidohexanoic acyl chloride (red) via the Diels–Alter reaction. Reprinted with permission from reference (77). Copyright 2015 Royal Society of Chemistry.

Future Perspectives

In the past years, lignin valorization has become a hot topic of developing sustainable biorefineries. The network map of keywords in the recent 500 scientific publications on "lignin valorization" was created using the full counting method of VOSViewer (*78, 79*), and the resulting keyword network map is shown in Figure 7. As shown in the figure, the major keywords are "valorization," "biomass," "lignin," "conversion" "depolymerization," "lignocellulosic biomass," "pretreatment," "kraft lignin," and "chemicals." This network map shows what recent studies focused on under the area of lignin valorization. However, we recognize that, despite efforts to utilize lignin in many applications, significant improvement in conversion technologies is needed to meet the rigorous requirements of the market of the products. It is often discussed that inherent physical and chemical properties of lignin negatively impact properties of final materials, limiting the amount of lignin in the products. Also, several technical challenges, including separation and recovery of the final products and catalyst recycling, need to be tackled to make lignin valorization more sustainable. Considering the long history of petroleum refining, lignocellulosic biorefineries are still in their early-stage, yet are the best non-petroleum alternatives for sustainable development. Lignin valorization, as a key research area in this field, requires continued, but more strategic efforts to maximize the value from lignin. It is also important to note that product cost and quality were the primary criteria of the past; future products need to meet environmental and social sustainability for achieving a sustainable carbon economy.
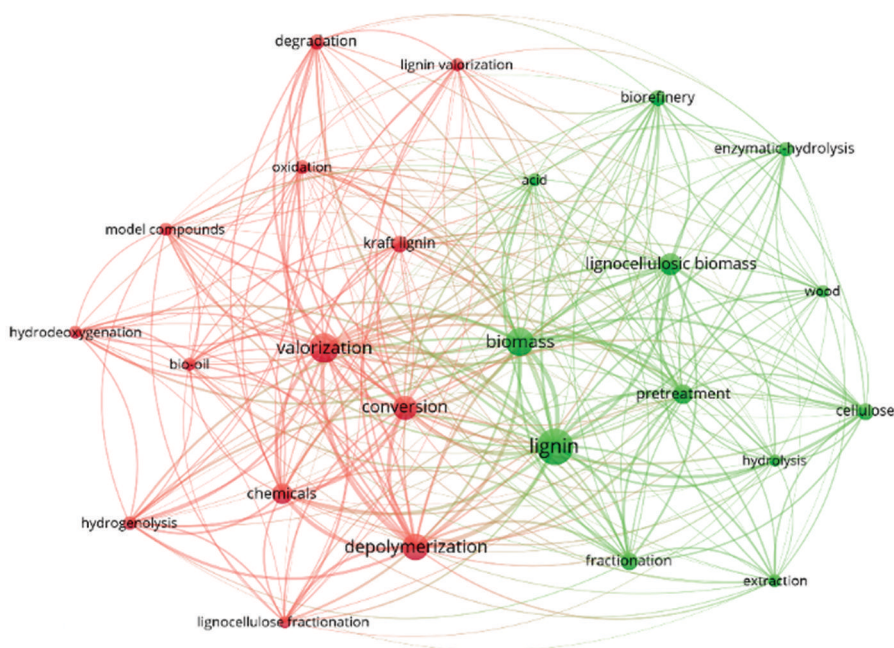

Figure 7. The keyword network of lignin valorization.

Acknowledgments

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