Green Chemistry

CRITICAL REVIEW

Check for updates

Grafting strategies for hydroxy groups of lignin for producing materials

Armin Eraghi Kazzaz, Zahra Hosseinpour Feizi and Pedram Fatehi (iD) *

Lignin is one of the most abundant biopolymers on Earth and is considered as the primary resource of aromatic compounds. Recently, lignin has attracted attention from scientists and industrialists due to its inherent potential arising from its unique structure, which leads to its possible use in many applications. Many efforts have been made to ameliorate the reactivity and compatibility of lignin in different areas. Although methods have been proposed for endowing lignin with different properties, there continues to be a considerable demand for discovering new and effective ways of unraveling the beneficial uses of this aromatic polymer. Considering the structure of lignin, different grafting modifications can occur on the aliphatic and/or aromatic groups of lignin. To date, there has been a lack of fundamental understanding of the modification pathways of lignin for generating lignin–based products. In this review paper, we discuss comprehensively the chemical reactions that were introduced in the literature for preparing lignin with different features *via* modifying its phenolic and aliphatic hydroxy groups for altered uses. This review paper critically and comprehensively elaborates on the recent progress in lignin reactions as well as the challenges, advantages and disadvantages associated with the reaction procedures and the product development processes. Furthermore, the research gap in reaction strategies and product development are described throughout this study.

Introduction

Lignin is an abundant, natural polymer representing between 15 and 30 wt% of lignocellulosic biomass.[1] This polymer exists in the cellular wall of cellulose fibers and provides structural support against oxidative stresses and microbial attacks for plants.[2–4] Lignin, an amorphous heteropolymer, is insoluble in water and has a limited reactivity.[5,6] It mainly comprises methoxylated phenylpropanoid (guaiacyl and syringyl) subunits that provide lignin with an energy density of 30% higher than that of polysaccharide polymers.[1,7] Lignin can be an alternative product to petroleum feedstocks for producing different chemicals.[8] The availability of lignin in the biosphere exceeds 300 billion tons, with a growth rate of around 20 billion tons every year.[9] However, a small fraction of the extracted lignin is used in the formulation of adhesives,[10] dispersants,[11] surfactants or as antioxidants in rubbers and plastics.[12–14] Thus, there is considerable room for taking greater advantage of the inherent potential of this abundant polymer in various fields.

Based on the types of plants (softwood, hardwood, and non-wood), the amount of each monolignol could be different. Hardwood lignin contains the highest amount of syringyl alcohol among the three classes of lignin with a smaller amount of coniferyl alcohol monolignols. Lignin extracted from soft-wood resources (also called coniferous or guaiacyl lignin) merely contains coniferyl alcohol monolignols. Meanwhile, lignin from grass (*i.e.*, non-wood lignin) contains all three monolignols while the highest amount of monolignols is uncertain.

Since methoxy groups provide steric hindrance to the aromatic hydroxy groups of monolignol, their amount in monolignol is very critical. This is due to the fact that the enzyme catalyzing monolignol units' polymerization severely attacks the hydroxy groups, which connect monomers to generate a polymer chain. Hence, the overall cross-linking in the lignin structure decreases due to the enhancement in the steric hindrance, which lowers the ability of the aromatic part of lignin to react with other monomers. In addition, considering the internal cross-linking of the lignin structure, hardwood lignin, by virtue of having numerous units of syringyl alcohol monolignol, exhibits minimal internal cross-linking, while, lignin from grasses has more of a cross-linked structure than other lignin classes. It is worth noting that this internal cross-linked structure affects both the lignin molecule and the characteristics of lignin-based materials.[15]

The polymeric nature of lignin presents technical restrictions when used directly for synthesizing with other chemicals, which raises the need for its structural modification. Lignin modification and its use in alternative products has become

Chemical Engineering Department, Lakehead University, 955 Oliver Road, Thunder Bay, Ontario P7B 5E1, Canada. E-mail: pfatehi@lakeheadu.ca

particularly popular in biorefining processes. Biorefining can be considered as analogous to petroleum refining that is supposed to create many biodegradable, non-toxic and recyclable chemicals from the biomass.[16] In the past, different modification pathways had been conducted on lignin to make it a valuable product. Based on the lignin structure, modification reactions can occur on aromatic, aliphatic, or both parts.

Lignin can be isolated from the spent pulping liquors of sulfite, kraft, organosolv, and soda processes. Among these, sulfite and kraft processes are the two dominant techniques that are commercially utilized in the pulping industry.[17–19] Lignin produced from the kraft process is usually used as a fuel and burned in mills, while lignin generated in the sulfite pulping process is extracted as lignosulfonate. The solubility of kraft lignin is much lower than that of lignosulfonate due to the lack of hydrophilic groups on kraft lignin.[20,21] Nonetheless, kraft lignin possesses some outstanding properties in comparison with other types of lignin, such as a higher phenolic hydroxide group content, which is raised from the cleavage of β-aryl bonds during the pulping process. Interest on lignosulfonate, on the other hand, has increased because its sulfonic acid groups are attached to its aliphatic part rendering it soluble in water and providing it with the capability of emulsifying and binding properties. There are two commercial techniques called LignoBoost and Lignoforce that utilize acidification for lignin isolation from black liquor with the lignin solid content of 50–60 wt%.[22,23]

Herein, the primary objective of this review is to discuss the fundamentals associated with the modification of the aromatic and aliphatic groups of lignin. Distinguishing the altered reaction pathways on lignin aromatic and aliphatic parts can possibly lead to the identification of an appropriate method for producing lignin-based products with desired properties for altered applications. Furthermore, the challenges and perspectives associated with the modification methods at both laboratory and commercial scale practices are discussed throughout this study. In addition, since reviews are available on the topics of polymerization,[24,25] catalytic reactions,[26,27] depolymerization,[8,24,28,29] redox-neutral strategies,[8] and photoredox catalysis,[30] this study has excluded the discussion on the above-mentioned strategies. Lignin oxidation has also been covered briefly in this study, while more comprehensive information on the oxidation of lignin and its derivatives could be found in the literature.[31–33] However, the graft modifications of lignin have not been studied comprehensively, which further begets the lack of studies on some curtail applications of lignin in industry. This study also excludes discussion on model compounds but provides comprehensive discussion on the modification of industrial lignin as the raw material.

Alternative methods for modification of phenolic structure of lignin

Phosphorylation

Phosphorus-containing compounds have been widely studied to develop non-toxic and environmentally friendly flame
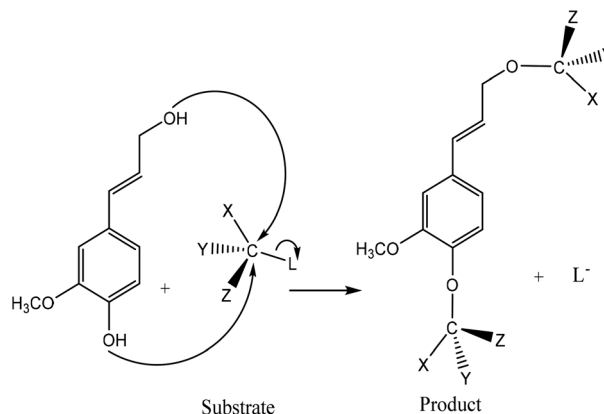

Fig. 1 General S_N2 reaction mechanism between lignin and substrate to form a new product and a leaving group (L). Substituents of the reacting carbon (X, Y, and Z) do not interfere with the reaction.[39–43]
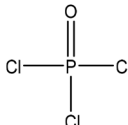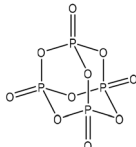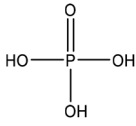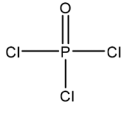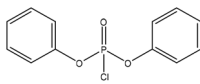
retardants to diminish the production of toxic fumes and smoke during burning and to hamper the combustibility of polymers.[34–36] Phosphorylation of lignin occurs *via* the addition of a phosphoryl group ($-PO_3$) to a molecule. This reaction proceeds through the S_N2 reaction mechan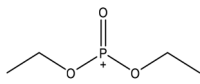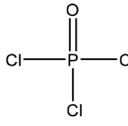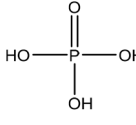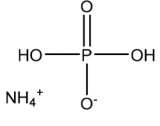ism (Fig. 1). Generally, in an S_N2 reaction, lignin's hydroxy groups, as a nucleophile, attack the carbon atom, an electrophilic center, due to the withdrawal of some electron density by the leaving-group (*e.g.*, bromine, chlorine) from carbon, which makes the carbon partially positive. This leads the nucleophile that is the lone pair of an electron on oxygen (hydroxyl of lignin) to attack the partially positive carbon. As the nucleophilic groups of lignin generate a bond with the carbon atom, the bond among the leaving group and the carbon atom breaks, simultaneously. At the same time, the bond between carbon and the leaving group breaks, which renders the leaving-group negatively-charged. Finally, the hydroxy groups of lignin form a bond with the carbon atom to generate the product. The reaction mentioned above was reported to occur on both aromatic and aliphatic hydroxy groups of lignin.[37,38]

Table 1 shows some of the phosphorylation reactions conducted on lignin. Lignin phosphorylation has been carried out under different conditions using various phosphorus reagents, such as phosphorus trihalides, phosphorus oxyhalides, phosphorus thiohalides, phosphorus oxides, and phosphorus sulfides, for instance.[44–47] Tetrahydrofuran,[38,48] pyridine,[39,49] acetonitrile,[47] dimethylformamide, formaldehyde[44,45] and urea[37] were also used as solvents for phosphorylation in different studies. The reaction conditions were reported to occur in the time range of 1–12 h and the temperature range of 25–180 °C.[38,49,50] After the reaction, lignin-based products were reported to be isolated from the reaction media using methanol, diethyl ether and ion exchange processes.[38,47,49,50]

The phosphorylated group on lignin has facilitated its use as a high-performance flame-retardant additive in polyurethane, polybutylene succinate, polypropylene, epoxy and polylactic acid.[39,44–47] The proposed application is attributed to the fact that the phosphorylation of aromatic compounds

Table 1 Phosphorylation of lignin

Lignin source/type	Reaction conditions					Separation	Property improvement	Yield (%)	Application	Ref.
	Time (h)	Temperature (°C)	pH	Reagent	Solvent					
Wheat straw alkali	12	95	3–4	$POCl_3$ (O=P(Cl)(Cl)Cl)	Triethylamine, dimethylformamide	Methanol	Thermal stability	92	Flame retardant	53
Kraft	7–8	20–25	N/A	P_4O_{10} (phosphorus pentoxide cage)	Tetrahydrofuran	Water	Thermal stability	N/A	Flame retardant	48 and 38
Spruce	1	80	N/A	H_3PO_4 (O=P(OH)(OH)OH)	Urea	Water and HCl	Phosphorus content	96	Sorbent	37
Black liquor	2	115	N/A	$POCl_3$ (O=P(Cl)(Cl)Cl)	Pyridine	N/A	N/A	N/A	Sodium and metal ion adsorbent	51
Kraft	12	N/A	N/A	diphenyl chlorophosphate (O=P(OPh)(OPh)Cl)	Pyridine	Water and DMSO	Oxidative stability	N/A	Flame retardant	39
Wheat straw alkali	5	70	5	diethyl phosphite (O=P(OEt)(OEt)H)	Dimethylformamide and formaldehyde	Water	Flame retardancy, thermal stability	N/A	Flame retardant	44 and 45
Cotton stalks	2	115	N/A	$POCl_3$ (O=P(Cl)(Cl)Cl)	Pyridine	HCl	Adsorption selectivity, thermal stability	N/A	Heavy metal ion adsorbent	51
Hydrolysis	3–6.5	140–180	N/A	H_3PO_4 (O=P(OH)(OH)OH)	Urea	Water	Thermal stability	70–75	Fire-retardant fillers for epoxy compounds	46
Alkali and an organosolv	15	80	N/A	ammonium phosphate (O=P(OH)(OH)O⁻ NH₄⁺)	Acetonitrile	Diethyl ether	Thermal stability	N/A	Flame retardant for polybutylene succinate	47

N/A: not available.

enhances char formation under fire conditions by acting either in the gas phase or in the condensed phase *via* interacting with the polymeric matrix.[38,39,48] Phosphorylated lignin has also been used as a cation exchange resin[49] and a sorbent of metal ions in wastewater treatment processes.[37,49,51]

While lignin phosphorylation has certain advantages, some drawbacks, such as long reaction times, use of toxic reagents, *e.g.*, phosphorus oxychloride and phosphorus oxychloride, or toxic solvents, such as dimethyl formaldehyde or dioxane, exist for the phosphorylation of lignin, which may be obstacles for the development of these reaction systems at commercial scales.[52]

Hydroxymethylation

Hydroxymethylation introduces a hydroxymethyl group (–CH₂OH) into lignin molecules, which is performed by elec-
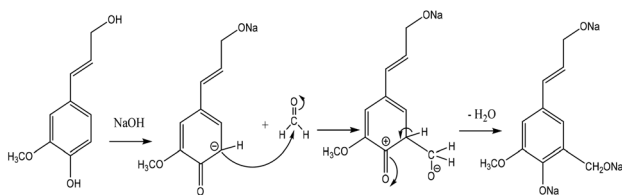
Fig. 2 Hydroxymethylation of lignin using formaldehyde.[57]

trophilic aromatic substitution (Fig. 2). Under alkaline conditions, the sigma complex of lignin loses a proton to regain its aromaticity, which makes the oxyanion become protonated. By reacting lignin and formaldehyde in hydroxymethylation, the hydroxymethyl group is introduced into the *para* and/or *ortho* position on the aromatic ring of lignin.[54,55] Since this reaction is endothermic, temperature elevation would improve reaction yields.[56]

Table 2 shows the results of hydroxymethylation reaction conducted on lignin in the past. In most cases, the reactions were carried out using formaldehyde in alkaline media in the temperature range of 25–90 °C for 2–8 h (or even 72 h) to produce hydroxymethylated lignin. Compared to other reagents, formaldehyde was reported to shorten the reaction time due to its high reactivity. The use of paraformaldehyde in this reaction prolongs the reaction time as it requires the release of formaldehyde monomers at a slower pace in the reaction.[58] It is worth noting that formaldehyde may polymerize by itself in the hydroxymethylation reaction, which is undesirable. The hydroxymethylated lignin was reported to be separated from the reaction media by acidification and washing with acids.[59] It is worth mentioning that hydroxymethylation is one of the most appealing methods used to produce lignin derivatives used for wood adhesive applications. This reaction can also be used prior to sulfonation and amination reactions to attach a methyl group to lignin for the desired reactions.[20,57,61]

Hydroxymethylated lignin is also found to have high antioxidant activity since the phenolic OH groups are remained intact in its structure.[61] Hydroxymethylated lignin has also been reported to be used in polyurethane foam production[62] and as a binder in adhesive applications.[63]

Phenolation

Phenolation is a reaction in which the number of phenolic OH groups of lignin are increased by the addition of phenol to lignin's aliphatic chain.[73,74] This reaction proceeds through S_N2 (Fig. 1) or addition reaction.[75] A reduction in lignin's molecular weight could be observed in some cases, which would be due to the breakage of ether bonds.[76] In general, the phenolation reaction improves the flexibility, tensile strength and glass transition temperature of lignin making it preferable to be used in polyurethane films' production.

Additionally, phenolated lignin has been mostly studied when producing phenol formaldehyde resins, in which lignin is primarily phenolated to react with formaldehyde. Thus, the

formaldehyde resins produced with phenolated lignin demonstrated an adequate curing time and viscosity required for panels' production which is comparable to those of commercial resins.[74]

Table 3 shows the phenolation reaction carried out on lignin. Generally, lignin is mixed with phenol or cardanol, an alkyl phenol isolated from the liquid shell of cashew nut,[77] mostly in water under harsh acidic conditions at a temperature range of 25–125 °C for 20 min–6 h. Phenolated lignin can be separated from the reaction mixture using filtration and/or washing with water, acetone or ether.

Additionally, phenolated lignin used in phenolic resins has been reported to have better mechanical properties than unmodified or hydroxymethylated lignin.[78,79] Nonetheless, the immense amount of sulfuric acid used in lignin phenolation is not economically or environmentally attractive since it requires an expensive recovery process.

Sulfonation

Sulfonation occurs through the substitution of a sulfonate group with lignin's aliphatic hydroxy groups through the addition reaction (Fig. 3),[86] rendering lignin negatively charged. This reaction primarily occurs on the carbon of the α position.[87] As an exception, sulfonation with chlorosulfonic acid occurs on the lignin's phenolic ring. Sulfonated lignin has a broad range of applications in various industries such as oil drilling,[88] paper coating,[89] cement and concrete production,[90,91] in ion-exchange,[80] and as a surfactant,[93] binder, and dispersant.[88,93–95] The anti-oxidant and UV absorbent properties of sulfonated lignin have also made this product attractive to be used in flame retardants and sunscreens' production, respectively.[96]
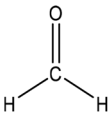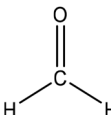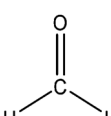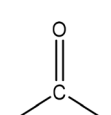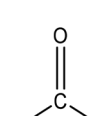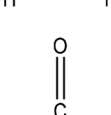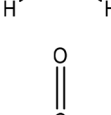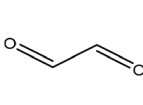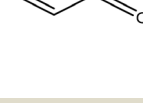
Table 4 shows sulfonation reactions performed on lignin. The sulfonation of lignin has been reported to be conducted using either sulfur dioxide (SO_2), sulfur trioxide (SO_3), sulfurous acid (H_2SO_3), sodium metabisulfite ($Na_2S_2O_5$), or bi-sulfite (M_2SO_3) (where M can be Ca, Na, H, Mg, K, or their combination) as a reagent. In this reaction, lignin is generally mixed with the reagent mostly in water under either acidic or alkaline conditions in a high-temperature range of 70–180 °C for 0.5 to 4 hours. Thus, the produced lignin samples could be separated and purified using filtration and a dialysis membrane.

Sulfoalkylation

Sulfomethylation. Sulfomethylation reaction introduces a methylene sulfonate group mainly into the *ortho* position of the aromatic ring of lignin.[99] Sulfoalkylation of lignin occurs through the S_N2 route as the electrophilic S attacks the carbon in the CH_2OH group of lignin while the OH group leaves the molecule (Fig. 4). In this case,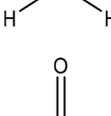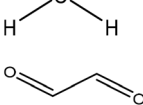 sodium sulfonate methyl derivatives are formed by the addition of nucleophilic sodium sulfite anions into alkaline media. In this reaction, unsubstituted carbon-5 sites in phenolic units of lignin are the primary targets.[100] Under alkaline conditions, the reaction occurs with equimolar alkali metal sulfite salt and phenolic units.[101] In sulfomethylation, formaldehyde introduces the methoxy group

Table 2 Hydroxymethylation of lignin

Lignin source/type	Reaction conditions					Separation	Property improvement	Yield (%)	Application	Ref.
	Time (h)	Temperature (°C)	pH	Solvent	Reagent					
Organosolv	2	40	Alkaline	Water	(formaldehyde)	Acidification	Reactivity, thermal stability	N/A	N/A	64
Wheat straw, and grass	3	90	10.5	Water	(formaldehyde)	Acidification and centrifugation	Molecular weight	N/A	N/A	55 and 65
Kraft, and sodium lignosulfonate	0.25–4	50	Alkaline	Water	(formaldehyde)	N/A	Thermal stability	N/A	Phenolic resin	66
Kraft	72	20–25	12–12.5	Water	(formaldehyde)	N/A	Cross-linking ability	N/A	Adhesives and resins	54
Wheat straw, and grass	3	90	9.7–9.9	Water	(formaldehyde)	Acidification and centrifugation	Reactivity	N/A	N/A	67
Calcium lignosulfonate	2	80	11	Water	(formaldehyde)	N/A	Foaming ability, foam half-life time	N/A	N/A	57
Wheat straw	N/A	55–90	10–10.5	Water	(formaldehyde)	Acidification and centrifugation	Carbonyl groups, thermal degradation	N/A	As bio-protection in wood and adhesive	68
Alkali	3	60–90	10.5–12	Water	(formaldehyde)	N/A	Reactivity with resol resin, viscosity	N/A	Phenolic adhesive substitution	69
Softwood alkali	8	60	Alkaline	Water	(glyoxal)	N/A	Decrease in molecular weight	N/A	Wood adhesive	70
Calcium lignosulfonate	8	58	12–12.5	Water	(glyoxal)	N/A	N/A	N/A	Wood adhesive	71
Soda bagasse	8	58	12–12.5	Water	(glyoxal)	N/A	N/A	N/A	Wood adhesive	72
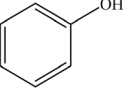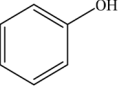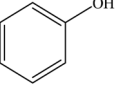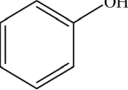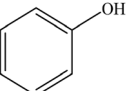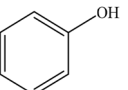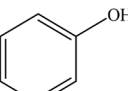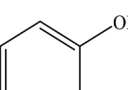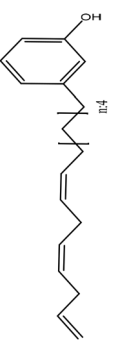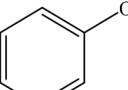
N/A: not available.

into lignin, which is the reacting location in the sulfonation reaction with sodium sulfite.[102] Table 5 shows the data available on the sulfomethylation of lignin. Generally, the sulfomethylation reaction has been carried out in the pH range of 7–13 at 60–140 °C for 0.5–9 hours. The sulfomethylated lignin can be separated and purified *via* neutralizing the pH and using membrane dialysis, respectively.[20] Filtration[103,104] and ion exchange resin were also reported as the practical options for purifying the product.[100] In the meantime, sodium thiosulfate is observed to be produced in the side reaction, which is

Table 3 Phenolation of lignin

Lignin source/type	Reaction conditions					Separation	Property improvement	Yield (%)	Application	Ref.
	Time (h)	Temperature (°C)	pH	Reagent	Solvent					
Black liquor	5	60	Acidic	(phenol)	Water	Filtration and water	Ion-exchange capacity	N/A	Making resin	80
Enzymatic hydrolysis	2	110–120	Acidic	(phenol)	Ether	Filtration and water	Molecular weight	100–120	Adhesive	73
Sulfuric acid	6	60	Acidic	(phenol)	Water	Filtration and water	Solubility and reactivity	N/A	N/A	81
Organosolv	1	50–80	N/A	(phenol)	Water	N/A	Curing time	N/A	Resins for particleboard	78
Organosolv	1–2	70–110	Acidic	(phenol)	Acetone and water	Filtration and water	Molecular weight and dispersity	71–96	Thermoset resin	82
Eucalyptus/ acetosolv	1.5	125	Acidic	(phenol)	Water	N/A	Reactivity	N/A	Resin	83
BioChoice, and a pine (softwood) kraft	2	90–110	Acidic	(phenol)	Water	Ether, and filtration	Molecular weight decreased	30–60	Thermosets	75
Sulfuric acid	N/A	20–25	Acidic	(phenol)	Ethanol or water	Acetone, and centrifugation	Light colored	~93–110	Selective phenolation	84
Softwood kraft	N/A	50	Acidic	(cardanol, n:4)	Water	N/A	Tensile strength, glass transition temperature	20–40	Polyurethane film	77
Beech organosolv	0.33	110	Acidic	(phenol)	Water	N/A	Strength	N/A	Wood veneer and particle board adhesion	85

N/A: not available.

Fig. 3 Sulfonation of lignin with sodium sulfite.[97]

reported to affect the yield of the sulfomethylation reaction adversely. This yield could be enhanced by increasing the temperature from 100 °C to 150 °C.

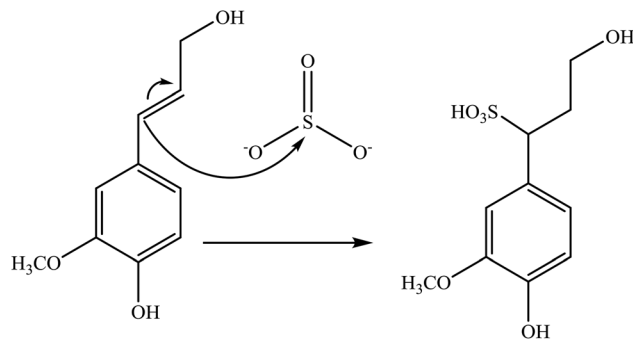However, the reactivity of this reaction is rather low and highly depends on the lignin type. In order to improve lignin reactivity toward sulfomethylation, oxidation was reported to be conducted prior to sulfomethylation.[20,101]

Overall, sulfomethylated lignin has been investigated to have various applications in industry, such as a dispersant for coal–water slurry[21,57] and concrete paste[20,101] or a flocculant for aluminum oxide suspension[105] due to its augmented hydrophilicity and charge density.

However, using formaldehyde in sulfomethylation can be considered as the main drawback of this modification pathway since it is toxic, carcinogenic and mutagenic, which raises environmental concerns.

Sulfobutylation. Sulfobutylation reactions have been conducted on lignin by introducing $-C_4H_8-SO_3H$ into hydroxy groups on both aromatic and aliphatic sites, with long alkyl chains using a 1,4-butane sultone reagent. This reaction occurs through the S_N2 mechanism with ring-opening under alkaline conditions (Fig. 5). The reaction mechanism for sulfobutylation is different from those using conventional sulfomethylation reagents, such as Na_2SO_3 or $Na_2S_2O_5$ with formaldehyde. Also, sulfobutylation occurs on both aromatic and aliphatic groups.[109] The sulfobutylation reaction has been reported to enhance the water-solubility of the polymer, which is highly desirable in aqueous based applications. The molecular weight of sulfobutylated lignin was reported to be greater than that of sulfomethylated lignin.[110] The long alkyl chain and sulfonic acid groups of the reagent were reported to play key roles in improving dispersibility performance by developing steric hindrance and electrostatic repulsion.[110]

Table 6 shows the sulfobutylation reactions conducted on lignin. In general, sulfobutylation was conducted using 1,4-butane sultone at 70 °C for 6–7 hours at pH 12. In order to separate the produced polymer from the reaction media, the ion-exchange resin and dialysis membrane have been used. Sulfobutylated lignin has been used as a dopant and a dispersant for coal–water slurry and carbendazim.[109–111]

Sulfobutylation seems to be a more favorable reaction over sulfomethylation because (1) sulfobutylation needs lower

temperature and pressure (Tables 5 and 6), which results in using less expensive and simpler equipment, (2) the use of toxic formaldehyde in sulfomethylation is another downside of this reaction,[109] and (3) sulfomethylation can only occur on the phenolic part of lignin, while sulfobutylation can occur on both aliphatic and aromatic parts. However, the 1,4-butane sultone reagent used in sulfobutylation is substantially more expensive than sulfomethylation reagents (Na_2SO_3, $Na_2S_2O_5$), which may make this modification process expensive.

Carboxyalkylation

Carboxymethylation. Carboxymethylation is applied to lignin by introducing a carboxymethyl group ($-C_2H_3O_2$) following the S_N2 reaction, as discussed earlier (Fig. 1).[40] In the carboxymethylation reaction with sodium chloroacetate, salt (*i.e.*, NaCl) and glycolic acid are observed to be generated as by-products. Since aromatic hydroxy groups ionize easier than aliphatic hydroxy groups in an alkaline environment, the reaction would occur primarily on the aromatic ring.
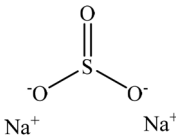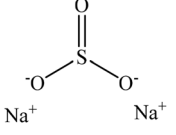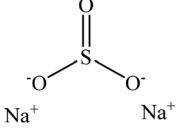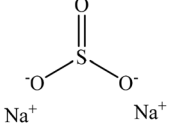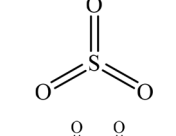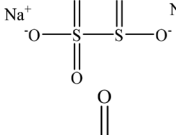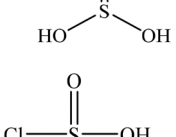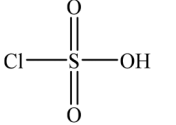
Table 7 shows the lignin carboxymethylation reactions performed in the literature. The carboxymethylation reaction has been carried out by mixing lignin with NaOH followed by sodium chloroacetate or monochloroacetic acid in the time and temperature range of 1–6 h and 30–90 °C, respectively.[40,115–119] Alternative pathways were considered for purifying the products, such as acidification,[118] membrane dialysis,[40] and washing with ethanol.[116,119,120]

Carboxymethylated lignin has been proposed as an effective dispersant for oil–water emulsions,[109] crude bitumen emulsions,[121] and clay,[40] cement,[116] and graphite suspensions.[122] Carboxymethylated lignin was also used as a stabilizer in kerosene-in-water emulsions[117] and as a foaming agent.[110] The composite of carboxymethylated lignin–tetra ethoxysilane was tested as a packaging and antimicrobial formula as well as in wound dressings. In addition, due to its potential in adsorbing heavy metals, such as nickel and cadmium, this product has been suggested to be used in wastewater treatment and biofilters.[119] Carboxymethylated lignosulfonate was also reported to improve the heat capacity of leather when it was used along with tanning chromium in leather production.[115]

Carboxyethylation. Carboxyethylation is the grafting of the $-CH_2-CH_2-COOH$ group to lignin. Fig. 6 shows the mechanism of carboxyethylation of lignin in an alkaline environment. The reaction proceeds through an S_N1 mechanism in the basic medium by the substitution of the carboxyethylate group with the aromatic and aliphatic hydroxy groups of lignin. Carboxyethylation of lignin by 2-chloropropionic acid has been proceeded by the dissociation of the carbon–halogen bond, which generates negatively charged chloride ions (as the leaving group) and positively charged carbocation intermediate (on the reagent) in the first stage. In the second stage, the alkoxide ion (of lignin) attacks the planar carbocation and bonds to the reagent. In the meantime, sodium lactate and homopropionic acid polymer could be produced as the by-products of carboxyethylation with 2-chloropropionic acid. Carboxyethylation of lignin would improve its hydrophilicity

Table 4 Sulfonation of lignin

Lignin source/type	Reaction conditions					Separation	Property improvement	Yield (%)	Application	Ref.
	Time (h)	Temperature (°C)	pH	Reagent	Solvent					
Esparto grass	4	140	4–9	Na_2SO_3	Water	Filtration	Solubility	N/A	Plasticizing for cement	91
Washed aqueous slurry	2	140	~7	Na_2SO_3	Water	N/A	Solubility	N/A	Dispersant in dye	95
Kraft	1–5	100–180	Alkaline	Na_2SO_3	Water	Dialyzed	Molecular weight decreased	N/A	N/A	97
Corn stalks	0.5–1	95	Alkaline	Na_2SO_3	Water	N/A	N/A	~70–85	N/A	98
Kraft	1–2	70–120	Acidic	SO_3; $Na_2S_2O_5$; H_2SO_3	Water	N/A	N/A	N/A	Sulfonation of alkali pulp	92
Phenolyzed	1.5	100	Alkaline	$ClSO_3H$	Tetrachloroethane	Filtration and water	Ion-exchange capacity	~33–58	Making resin	80

N/A: not available.

and generate a highly charged anionic lignin, which could be a pathway to produce pH sensitive anionic lignin[123] for use as a dispersant and flocculant in industry. This reaction reported to slightly increase the molecular weight of lignin as well.[123]

In this reaction, lignin can be mixed with 2-chloropropionic acid, the donor of the carboxyethyl group, in a mixture of water and isopropyl alcohol in the basic environment at 60–90 °C for 0.5–2 h (Table 8). The production of sodium lactate is the undesired side reaction.[123] Due to the insolubility of the produced lignin in solvents, the reaction mixture can be mixed with ethanol for lignin isolation.[123] Alternatively, membrane dialysis and filtration can be used for isolating the product from the reaction media.

In opposition to carboxymethylation reactions, carboxyethylation can occur on both aromatic and aliphatic hydroxyl groups of lignin. Therefore, carboxyethylation may be considered as a more influential modification pathway for lignin than carboxymethylation.[122,123] However, the main drawback of carboxyethylation is the solvent used in the reaction (e.g., isopropyl alcohol), which may not be an attractive pathway to develop green processes for lignin modification.

Epoxidation

Chemicals possessing amino or hydroxy groups have good reactivity with epoxy groups. Lignin can be rendered lipophilic when it is modified with epoxy containing materials. This reac-
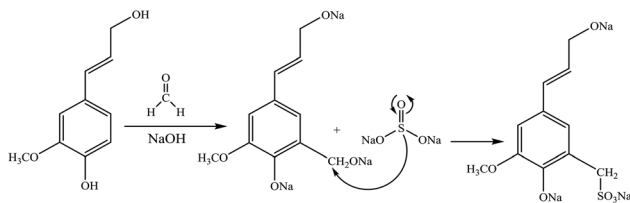
Fig. 4 Sulfomethylation of lignin with sodium sulfite.[20,57]

tion facilitates the dissolution of lignin in organic solvents, such as methylene chloride, tetrahydrofuran, acetone, and chloroform for generating value-added products.[124] Epoxy resins are used in a broad variety of applications in electrical and electronic laminates, high-performance composites, industrial coatings, adhesives, paving applications, and feedstock for emulsifiers and detergents.[122,124–126] Epoxidation of lignin proceeds through the S_N2 mechanism as discussed earlier (Fig. 1) under alkaline conditions.[112] Epoxidation was reported to occur on the aromatic ring of lignin by the substitution of hydroxy groups with epoxy groups.[61,127]

Table 9 shows the epoxidation reactions of lignin reported in the literature. In this reaction, lignin is mixed with either di-epoxides, such as polyethylene glycol diglycidyl ether (PEGDGE), with different chain lengths, or epichlorohydrin in an alkaline environment (pH > 12) at 30–90 °C for 1–18 h.[50,112,126–128] The epoxidized lignin product is then isolated by neutralizing the reaction mixture with sodium dihydrogen phosphate (NaH_2PO_4) and centrifugation. The solid epoxy lignin can then be recrystallized in chloroform for further use.[61–67] Stronger alkalinity could enhance the lignin degradation and produce more phenolic hydroxy groups to react with epichlorohydrin, which increases the reaction yield.[112] In this case, lignin macromolecules will be converted to more of lignin monomers, and then monomers would have a higher tendency to epoxidize. However, using epichlorohydrin has some disadvantages, such as toxicity and limited rheological characteristics associated with the gel-like dispersion.[129,130]

Epoxy resins produced by lignin usually have low thermal stability and T_g value over the mercantile ones (i.e., a synthetic bisphenol A). In this regard, the limited number of epoxy rings in lignin prevents the generation of dense crosslinks in cured epoxy systems. Hence, it would be more favorable to produce lignin-based curing agents to be used in generating epoxy systems with efficient performance.[131] Similarly, the epoxy lignin was reported to have antibacterial activity and was mostly resistant to *Bacillus* sp. and *Klebsiella* sp. strains.[61] Nonetheless, the disadvantages associated with lignin-based epoxy resins include low water solubility, slow curing rate, high cost and brittleness.[24,132–135]

Oxyalkylation/oxypropylation

Oxyalkylation is a process by which hydroxy groups of lignin are converted to oxyalkylated groups. The oxyalkylation of lignin proceeds through the S_N2 mechanism (Fig. 7). In the

reaction of cyclic organic carbonates with hydroxyl groups of lignin (Fig. 7), cyclic carbonate (e.g., propylene carbonate) can react with aliphatic and aromatic hydroxyl groups[136] according to two reaction pathways; aliphatic hydroxy tends to attack the carbonyl carbon atom leading to carbonate linkages, while aromatic hydroxy can attack the alkylene carbon atoms and ether linkage with a subsequent loss of CO_2, which allows the production of polyether polyols with primary and secondary hydroxy groups.[136,137] At temperature lower than 170 °C, the rate of oxyalkylation trend on the aromatic hydroxy groups is higher than that on the aliphatic ones due to the lower nucleophilicity of aliphatic hydroxy groups. At a higher temperature (>170 °C) and in the presence of the basic catalyst (e.g., K_2CO_3), only 0.3% of carbonate linkages could be developed, while etherification of the aliphatic hydroxy groups was found to be favored at high temperatures.[136,138] Oxyalkylation liberates the lignin's hydroxy groups, especially that of the aromatic OH, and induces moieties of ether that presents uniformity, solubility, and reactivity to lignin. In this case, lignin can be converted to a liquid polyol product[139] that could be a potential alternative to replace typical ones in polyurethanes. Among all, oxypropylation is the most popular oxyalkylation reaction, which could be feasible to conduct under both alkaline and acidic conditions, while it was suggested to be more efficient and economically favorable if performed in an alkaline environment.[140]

Table 10 shows reports on the oxypropylation of lignin. To produce oxypropylated lignin, lignin is mixed with reagents, such as propylene oxide or propylene carbonate, and NaOH or KOH, and is reacted in the temperature range of 40–285 °C for 4 min to 24 h under atmospheric and pressurized (up to about 40 bar) conditions.[136,138,141,144,150] To extract the product from the reaction media, the reaction mixture is acidified to pH 2.5, which facilitates the precipitation of oxypropylated lignin.[136,138,141]

Oxypropylated lignin has found application in polyurethane foams.[142,143] It was reported that oxypropylated lignin has remarkably enhanced the mechanical properties of foams compared to commercial polyols.[145] In addition, the produced lignin polyols were suggested to be a valuable substitution for oil-based polyols, which are extensively used in polyester and polyurethane productions.[136–138] However, the use of propylene oxide, which is obtained from oil-based chemicals may be unattractive, as the final product may contain less than 50% lignin.[145] In addition, this reagent is very expensive which makes the reaction unfavorable for commercial purposes. This reaction also suffers from safety concerns due to the high vapor pressure as well as high toxicity, carcinogenicity, and flammability of propylene oxide in the reaction media. Instead, cyclic organic carbonates, such as propylene carbonate, could be used in this reaction to reduce the precautions since it is non-toxic and eco-friendly.[137] Furthermore, high boiling and flash points, as well as low vapor pressure and high solubility make this reagent more attractive than propylene oxide to be used in the oxypropylation of lignin.[136,137,146]

Table 5 Sulfomethylation of lignin

| Lignin source/type	Reaction conditions		pH	Reagent	Solvent	Separation	Property improvement	Yield (%)	Application	Ref.
	Time (h)	Temperature (°C)								
Enzymatic hydrolysis	3	95	Alkaline	[structure]	Formaldehyde	Filtration	Steric energy reduction	N/A	Dispersion for graphite suspension	106
Alkaline, and enzymatic hydrolysis	1–5	80–130	N/A	[structure]	Formaldehyde	H_2SO_4	Compressive strength of concrete	~60–90	Dispersant for concrete paste	107
Oxidized	1–3	100	Alkaline	[structure]	Water and formaldehyde	Membrane dialysis	Molecular weight, charge density	33–38	Flocculant for aluminum oxide suspension	105
Aminated alkaline	2	90	10	[structure]	Water	Filtration	N/A	N/A	Heavy metal ion removal	109
Oxidized softwood kraft	0.5–4	60–100	7	[structure]	Water, and formaldehyde	Membrane dialysis	Molecular weight, charge density	N/A	Dispersant for cement	101
Hardwood kraft	1–7	80–140	N/A	[structure]	Formaldehyde	Membrane dialysis	Molecular weight, charge density	N/A	Dispersant for cement	20
Kraft	3	75	3–4	[structure]	Formaldehyde, H_2O_2	Dialyzed	Molecular weight decreased, and lighter color	N/A	N/A	97
Calcium lignosulfonate	2	90	10	[structure]	Formaldehyde	N/A	N/A	N/A	Dispersant for cement	57
Alkali	5	90	10	[structure]	Water, and formaldehyde	N/A	Adsorption selectivity, wettability	N/A	Dispersant for coal–water slurry	21
Alkali-corn stalk	2–9	75	9	[structure]	Formaldehyde	Filtration	N/A	N/A	Dispersant for dye	100
Hydroxymethylated alkali	4	95	13	[structure]	Formaldehyde	Neutralization and Buchner funnel	Charge density, solubility	N/A	Adsorbent	103
Wheat straw alkali	4	95	N/A	[structure]	Formaldehyde	Neutralization and Buchner funnel	Charge density	N/A	Dispersion for TiO_2	104

N/A: not available.
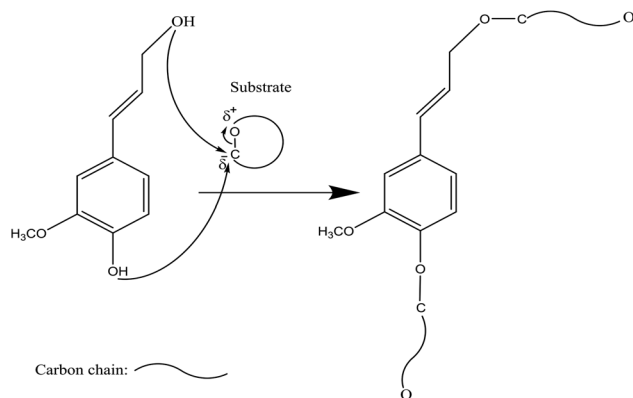
Fig. 5 General S_N2 reaction with ring-opening. Electrophilic center (carbon) is partially negatively-charged, and oxygen is partially positively-charged.[109,111,112]

Esterification

Generally, esterification is the conversion of alcohols to esters.[152] The esterification of lignin is performed by nucleophilic substitution (Fig. 8). In this reaction, the lone pair electron of the aromatic hydroxy group will attack the carbon of the ester group on the reagent (Fig. 8). As a result, the carboxylic acid group will leave, and hydroxy groups of the aromatic ring are replaced with carbonyl groups.[153] This reaction is feasible using mono- or dicarboxylic acids, their anhydrides, acid chlorides, or *via* transesterification with carboxylic acid esters. For instance, maleic acid, acetic acid, phthalic acid, fumaric acid, or fatty acids such as oleic acid, lauric acid or their anhydrides, acid chlorides or simple esters can be used in the esterification of lignin.[153–155] Esterification occurs on both aromatic and aliphatic hydroxy groups of lignin but is

Table 6 Sulfobutylation of lignin

| Lignin source/type | Reaction conditions | | | Reagent | Solvent | Separation | Advancement in properties | Yield (%) | Application | Ref. |
	Time (h)	Temperature (°C)	pH							
Alkali	7	70	12		Water	Ion-exchange resin	Molecular weight	N/A	As dopant and dispersant	111
Alkali	6	65	12		Water	Ion-exchange resin	Molecular weight	N/A	Dispersant for coal–water slurry	109
Eucalyptus kraft	3	70	12		Water	Ethanol	Brightness	N/A	Dispersant for dye	113
Alkali	7	70	12		Water	Dialysis membrane	Molecular weight	N/A	Dispersant for carbendazim	110
Alkali	7	50	12		Water	Filtration and dialysis	Hydrodynamic size	N/A	Aggregation-induced emission	114
Kraft	1–6	50–90	Alkaline		Water	Dialyzed	Molecular weight decreased, and lighter color	N/A	N/A	97

N/A: not available.

Table 7 Carboxymethylation of lignin

Lignin source/type	Reaction conditions									
	Time (h)	Temperature (°C)	pH	Reagent	Solvent	Separation	Property improvement	Yield (%)	Application	Ref.
Organosolv	3.5	55	N/A		Ethanol	Filtration	N/A	N/A	Stabilizer in ceramic industries	116
Harwood kraft	1–6	30–70	Alkaline		Water	Membrane dialysis	Charge density, solubility, molecular weight	N/A	Dispersant for clay suspension	40
Kraft	3.5	55	N/A		Ethanol	Filtration and ethanol	Surface tension	N/A	Stabilizer for oil-in-water emulsions	117
Kraft and organosolv	3.5	55	N/A		Ethanol	Filtration and HCl	Decrease in heat capacity, and surface tension	90	Stabilizer of crude bitumen	121
Wheat straw alkali	1–3	50–90	N/A		Water	HCl	N/A	~80	Dispersant	122
Kraft	N/A	N/A	Alkaline		Water/ ethanol	HCl	Adsorption to fibre-laden	N/A	Stabilizer of fiber-laden foams	120

N/A: not available.
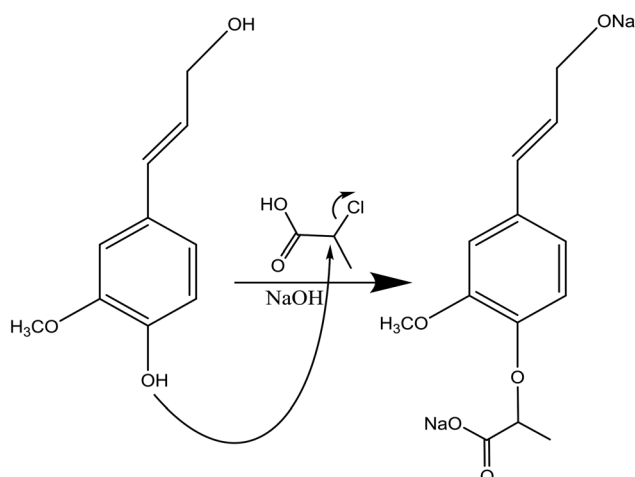
Fig. 6 Carboxyethylation of lignin under alkaline conditions by using 2-chloropropionic acid.[123]

more favored to occur on the aromatic hydroxy group.[156] The reason for this tendency could be the lower pK_a of the aromatic hydroxy groups than the aliphatic counterparts of lignin since the acetylation reagents, *e.g.*, pyridine or imidazole, act as both catalysts and bases accelerating the production of nucleophiles.[157]
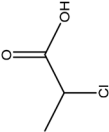
Table 11 shows the esterification reaction conducted on lignin. Generally, lignin is mixed with different acid anhydrides (succinic, phthalic, acetic and maleic anhydrides) in solvents, such as pyridine, tetrahydrofuran, dimethylformamide, acetone, dioxin, and 1-methylimidazole, in the temperature range of 25–120 °C for the period of 5 min and 48 h.[143,148–151] After the reaction, acidification or solvent (*e.g.*, acetone, ethanol) addition and membrane dialysis were used as means of the product purification strategy.[153,158,160,161]

Esterification has been commonly used to reduce the hydrophilicity and solvophilicity of lignin, which makes it favorable to be used for composite productions.[162–164] Lignin esterification by butylation, for instance, transforms the alcohol groups to butyl esters and improves lignin miscibility in low-polar solvents, which would facilitate its use in the construction industry.[165–167] Esterifying lignin also enhances its compatibility with plastic blends such as polystyrene, polyethylene, and poly(3-hydroxybutyrate-*co*-3-hydroxy valerate) blends.[160,161,168] In addition, esterified kraft lignin was

Table 8 Carboxyethylation of lignin

Lignin source/type	Reaction conditions			Reagent	Solvent	Separation	Advancement in properties	Yield (%)	Application	Ref.
	Time (h)	Temperature (°C)	pH							
Lignosulfonate	0.5–2.0	60–90	Alkaline		Water/isopropyl alcohol	Ethanol/water	Charge density, molecular weight	N/A	Dispersant	123

N/A: not available.

reported to remarkably improve the interfacial tension between the resin and reinforcing flax fibers.[169] Furthermore, lignin esterification increases the thermal mobility of lignin molecules by diminishing the intermolecular interaction, which further leads to a reduction in the glass transition temperature of lignin.[170]

The esterification was reported to improve the morphology of lignin-based materials. For example, carbon fibers made from phthalic anhydride-modified lignin were revealed to have reasonably high micro-scale porosity in comparison with carbon fibers made from unmodified lignin.[158] It is also worth mentioning that the structural properties of carbon fibers produced from lignin depend on the reagent used in the esterification reaction. For instance, lignin with a cyclic anhydride such as succinic, maleic or phthalic may form di-esters, whereas lignin could only form a monoester with acetic anhydride. In addition, the esterification of lignin using phthalic anhydride would render lignin more hydrophobic. Using maleic anhydride, a reagent with a double bond in its structure may increase cross conjugation between lignin's structural units.

These reports also suggested that the esterified lignin could be a green alternative to replace petroleum-based fillers in thermoplastics[159,161,169] as well as being a potential photosensitizer.[171] Esterification has also promoted lignin's application as an oxygen and water-vapor barrier in the packaging.[172] However, esterification was observed to reduce the antioxidant activity of lignin, which may be due to lowering its phenolic hydroxyl groups.[61]

Propargylation

Propargylation takes place by adding a propargyl group to a molecule. Lignin propargylation occurs *via* an S_N2 mechanism, as shown in Fig. 1. This reaction occurs only on the phenolic hydroxy groups of lignin since these groups have a higher ionization efficiency compared to aliphatic ones.[41,147]

Table 12 shows the propargylation reaction on lignin carried out in the previous studies. In propargylation, lignin is mixed with propargyl containing bromide and NaOH or KOH at 70–90 °C for 1–4 h in an alkaline environment.[41,178] Then, the generated product is separated by acidifying the reaction mixture.[41,178] Lignin propargylation increases the reactivity of lignin in a uniform and modulated way, thus increasing the potential use of the propargylated lignin in carbon fibers.[147,178] According to the US Department of Energy, using propargylated lignin in carbon fibers would reduce the final price of carbon fibers by half.[179] Similarly, propargylated lignin has been reported to be used in transportation applications such as tire production and composite production as the curable thermosetting resin.[178] However, using propargyl bromide can be considered as the main problem of this modification because it is toxic and may cause environmental issues.

Methylation

Methylation reaction is the addition of a methyl group ($-CH_3$) to lignin. The methylation of lignin occurs by nucleophilic aro-

Table 9 Epoxidation of lignin

| Lignin source/type	Reaction conditions					Separation	Property improvement	Yield (%)	Application	Ref.
	Time (h)	Temperature (°C)	pH	Reagent	Solvent					
Alkaline	5	90	Alkaline	[tetrabutylammonium bromide; epichlorohydrin structures]	Water	Neutralization and water	Molecular weight	~12	Feedstock for an emulsifier, detergent, and additive	124
Alkali	6	50–80	N/A	[epichlorohydrin structure]	Diethanolamine, and formaldehyde	N/A	Thermal stability	N/A	Thermal stable resin	126
Organosolv lignin	3–5	50–90	N/A	[epichlorohydrin structure]	Water	Water and filtration	Molecular weight	107–126	Bio-based epoxy resin	125
Wheat straw	2	60	Alkaline	[epoxy structure]	Water	N/A	N/A	N/A	Bio-based epoxy resin	127
Sugarcane bagasse	3–6	70	Alkaline	[epichlorohydrin structure]	Water	Neutralization and centrifugation	Antibacterial activity, lower radical scavenging activity	N/A	Natural antibacterial	61
Sarkanda, and wheat straw, Protobind 1000	3–7	50–90	Alkaline	[epichlorohydrin structure]	Water	Neutralization and centrifugation	Thermal stability decreased	61–88	Composite formation	67
Alkaline	8	50	N/A	[epichlorohydrin structure]	Water	Filtration and ethane/water	Decomposition temperature decreased	37–91	Epoxy resin additive	112
Alkali	3	30	Alkaline	[epoxy structure]	Water	Centrifugation	Viscosity	N/A	Thickener in bio-lubricant	129

N/A: not available.
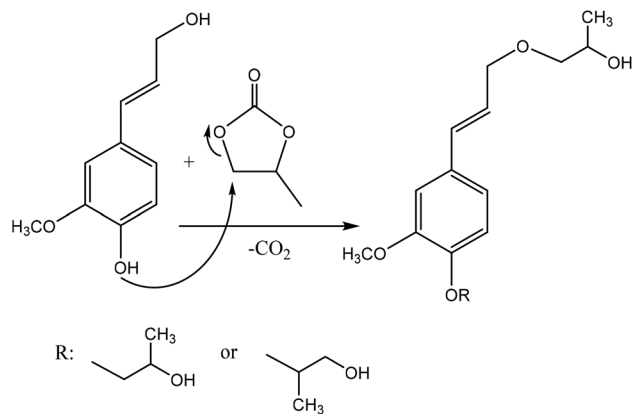
Fig. 7 Oxypropylation of lignin by using propylene carbonate.[136]

matic substitution (Fig. 9). Under alkaline conditions, the lone pair electron of aromatic hydroxide of lignin attacks the carbon of the methyl group. As a result, hydroxy groups are replaced with a methyl group in lignin. Methylation is considered as an alkylation in which a methyl group is exchanged with a hydrogen atom. This reaction had been used to cover the phenolic hydroxy groups to render lignin hydrophobic, or to analyze whether the desired reaction tends to occur on the phenolic or aliphatic hydroxy groups of lignin. The selective methylation of lignin's phenolic hydroxy groups converts these groups to phenyl methyl ether, which are remarkably less reactive compared to hydroxy groups.

In addition, a carefully controlled and monitored methylation of lignin may reduce lignin's reactivity, which could provide possibilities for its self-polymerization at high temperatures (above 130 °C).[147] However, this radically initiated self-polymerization of lignin could be inhibited entirely by methylating the phenolic hydroxyl groups.[181] In methylation, methyl groups replace only phenolic hydroxyl groups due to their remarkably higher (about 80 times) ionization efficiency.[123,141]

Table 13 shows the methylation reaction implemented on lignin. In the past, lignin was mixed with dimethyl sulfate, methyl iodide, diazomethane or tetramethylammonium hydroxide in an alkaline medium or it was dissolved in anhydrous N,N-dimethylformamide (DMF) for methylation. The reaction generally occurs at room temperature for 72 h or at 75–150 °C for 2–24 h.[123,141,150,182,183] To collect lignin derivatives, the reaction mixture is acidified, if conducted under the alkaline conditions and purified *via* filtration, for instance.[123,141] The methylation reduces the glass transition temperature of lignin since most of the intra-molecular hydrogen bonding becomes eliminated in this reaction.[150]

Methylation was reported to enable the use of lignin in thermoplastics and carbon fibers.[141,150] However, methyl iodide and dimethyl sulfate, the most common reagents used for methylation, are very toxic and hazardous, which is the major drawback of this process. One advantage of lignin methylation is that the by-products, methanol and carbon

dioxide, could be recycled and reused in the production of dimethyl carbonate.[181,184] Among other reagents, dimethyl carbonate has the supremacy of safe and straightforward handling since it is not mutagenic or hazardous. However, the chemical reactivity of dimethyl carbonate depends on the temperature in a way that at a temperature higher than 120 °C, it participates in methylation reaction *via* a base mediated alkyl cleavage nucleophilic substitution mechanism, and at a lower temperature (*e.g.*, 90 °C), it can act as a carboxymethylating agent *via* a base mediated acyl cleavage nucleophilic substitution mechanism.[181] Therefore, to use dimethyl carbonate as a methylating agent, the reaction temperature needs to be higher than 120 °C, and since this temperature is higher than the dimethyl carbonate's boiling point (90 °C), the reaction has to be carried out in a closed reactor and pressurized system.[181]

Alkylation

Alkylation introduces an alkyl group ($-C_nH_{2n+1}$) to a lignin macromolecule *via* the S_N2 mechanism (Fig. 1). Lignin can be readily alkylated through nucleophilic substitution on its active aromatic hydroxy groups with an alkyl chain having different chain lengths.[42] It has been reported that the alkylation reaction increases the thermal resistance of lignin while reducing its hydrophilicity.[42,181,185] Alkylated lignin could be used as a plasticizer in polymer blends.[186] It was also used in polypropylene composites along with synthetic polymers and it was reported to improve the composite's stiffness and storage moduli.[181,185,187]

Table 14 shows the alkylation reaction of lignin. In general, bromododecane or lead acetate, as the alkylating agent, can be mixed with lignin at pH 8–12 at 25 or 80 °C for 24–72 h in isopropanol, water, and dioxane as a solvent.[42,185] As a drawback, alkylated lignin could be quite brittle, which might not be favorable in polymer blends.[188]

Halogenation

Halogenation is a method used for introducing a halogen group into the lignin molecule. The halogenation of lignin occurs by electrophilic aromatic substitution. As an example of halogenation, Fig. 10 shows the bromination reaction of lignin with bromine in a hydrophilic (polar) protic solvent of acetic acid. Halogenation has been reported to occur on the aromatic ring of lignin since the aromatic hydroxy group could activate the adjacent positions for the electrophoretic attack.[189]

Table 15 shows the halogenation reactions of lignin. Typically, lignin is mixed with a halogen (hydrogen bromide, N-bromosuccinimide, and an ionic liquid, liquid chlorine) in the temperature range of 20–164 °C for 1–2 h.[189–191] Halogenated lignin can be precipitated using a mixture of diethyl ether and ethyl acetate.[191]

Bromination of lignin was reported to restrict lignin's agglomeration.[192] Meanwhile, halogenated compounds are intensively used as fungicides, herbicides, insecticides, and precursors in the synthesis of pesticides. They could also be used as intermediates in the synthesis of dyes, agricultural
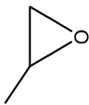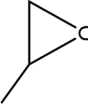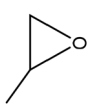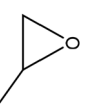
Table 10 Oxyalkylation of lignin
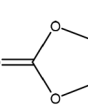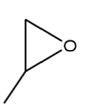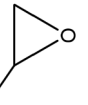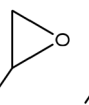
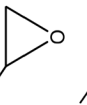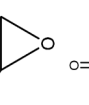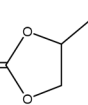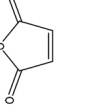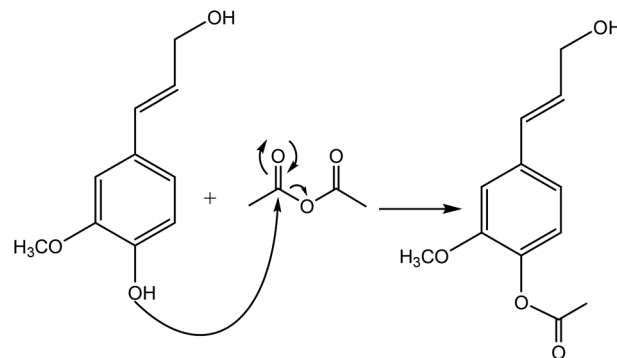| Lignin source/type	Reaction conditions			Reagent	Catalyst/solvent	Separation	Property improvement	Yield (%)	Application	Ref.
	Time (h)	Temperature (°C)	pH							
Kraft	12	40	Alkaline	[epoxide]	Potassium hydroxide	HCl	Molecular weight decreased	N/A	Use in carbon fiber	147
Soda	0.08–0.16	120–140	Alkaline	[epoxide]	Potassium hydroxide	N/A	Molecular weight decreased	N/A	Use in polyurethane foam	142
Organosolv, kraft, and oxidized organosolv	0.3–15	140–190	Alkaline	[epoxide]	Potassium hydroxide	Vacuum removal	Dimensional stability of the foam	N/A	Use in polyurethane foam	143
Kraft	2	140	Alkaline	[epoxide]	Potassium hydroxide	Tartaric acid	Viscosity of the polyester–polyether polyol	N/A	Use in the polyurethane production	148
Sodium lignosulfonate	4	175	Alkaline	[cyclic carbonate]	Sodium carbonate	Distillation	Darkness, viscosity	N/A	As dispersants for carbon black, as emulsifiers	149
Wheat straw soda	24	70	Alkaline and acidic	[epoxide]	Water	Ethyl ether anhydrous	Molecular weight, smother morphology	N/A	As a substitute for polyols in view of polyurethane	140
Kraft, soda, organosolv	~0.58–1.8	169–271	Alkaline	[epoxide]	Potassium hydroxide	N/A	Viscosity	N/A	As a substitute for polyols in view of polyurethane	140
Kraft	18	40	Alkaline	[epoxide]	Water	HCl	Thermal stability decreased	N/A	Thermoplastic materials	150
Kraft	0.15	150–285	Alkaline	[epoxide]	Potassium hydroxide	N/A	Molecular weight decreased	N/A	As a substitute for polyols in view of polyurethane	144
Softwood kraft	18	20–25	Alkaline	[epoxide]	Water	N/A	Molecular weight decreased	N/A	N/A	141
Organosolv	3	170	N/A	[cyclic carbonate]	Methylimidazole, 1,4-dioxane	Acidification and filtration	Molecular weight	N/A	As a substitute for polyols in view of polyurethane and polyesters	136
	21	50		[maleic anhydride]						

Fig. 8   The esterification reaction of lignin with acetic anhydride.[61]

chemicals and pharmaceuticals.[193] As is well-known, the reagents used in halogenation have different levels of reactivity. For example, chlorine and halogen fluorine are the most aggressive reagents compared to bromine[194] due to their high electrophilicity while bromine is a weaker reagent, and iodine is classified as the least reactive reagent of the halogens. It is advised that the chlorination reaction should be carried out with caution due to toxicity issues, which may require additional control. Furthermore, fluorination is mostly used in the production of fluorocarbons.[194] Since halogenated organics are highly toxic, the halogenation process has serious disadvantages, which requires health caution.[195]

Amination

Amination is a simple method for introducing amine groups onto lignin. This reaction occurs through the S_N2 route (Fig. 1). Generally, the amination reaction has been applied to lignin with the aim of generating cationic surfactants, slow-release fertilizers, flocculants, heavy metal adsorbents, coagulants, cationic asphalt emulsifiers, curing agents of epoxy resin, anion-exchange resins and retention aids.[108,112,196–201] Lignin amination could enhance the surface activity, water solubility, charge density and molecular weight of lignin.[69,202]

Logically, introducing nitrogen-containing groups into lignin can render lignin an efficient adsorbent for heavy metals. This phenomenon arises since the nitrogen-containing bases tend to chelate with acidic metallic ions.[203,204]

Table 16 shows the amination reactions of lignin. Generally, lignin is mixed with amination agents, such as diethylenetriamine, dimethylamine, methylamine, propane diamine, and triethylamine in water or a solvent, such as formaldehyde or dioxane, in the temperature range of 20–90 °C under both acidic and alkaline conditions for 1–17 h. Produced aminated lignin samples can be precipitated *via* mixing the reaction mixtures with hydrochloric acid, acetone, ethyl acetate or isopropanol.[189] Although inducing amine groups on lignin through amination reaction is selective and straightforward, using the toxic, carcinogenic and mutagenic chemical of formaldehyde in most of the reactions can be unsafe and cause environmental problems.

Table 10 (*Contd.*)

Lignin source/type	Reaction conditions			Reagent	Catalyst/solvent	Separation	Property improvement	Application	Yield (%)	Ref.
	Time (h)	Temperature (°C)	pH							
Beech wood organosolv	0.5–24	100–170	N/A		1,8-Diazabicyclo[5.4.0]undec-7-ene/potassium carbonate	Acidification and filtration	Molecular weight	Substitution of conventional petroleum-based polyols	N/A	137
Beechwood, wheat straw Organosolv	3	170	N/A		1,8-Diazabicyclo[5.4.0]undec-7-ene	Water and filtration	Molecular weight	Biobased polyols	N/A	138
Organosolv	3	170	Alkaline		1,8-Diazabicyclo[5.4.0]undec-7-ene/dimethyl sulfoxide	Acidification	Molecular weight	Prepolymer for nonisocyanate polyurethanes	97–99	151

N/A: not available.

Table 11 Esterification of lignin

Lignin source/type	Reaction conditions			Reagent	Solvent/Catalyst	Separation	Property improvement	Yield (%)	Application	Ref.
	Time (h)	Temperature (°C)	pH							
Organosolv	2	20	N/A		N,N,1-Dimethylformamide/pyridine	Filtration and ethanol	Hydrophobicity	N/A	As a dispersant and a protective agent	173
Pulp and paper industries	0.6	80	N/A		Pyridine	HCl	Molecular weight	122	Mold lubricant	164
Organosolv	3	100	N/A		Pyridine containing 4-dimethylaminopyridine	Water or diethyl ether	Strength	N/A	Blend with poly(ε-caprolactone)	163
Organosolv	6	70	N/A		Tetrahydrofuran	Methanol and filtration	Surface area, pore volume	~36–46	Lignin-based carbons	158
Kraft	5	100	N/A		Triphenyl antimony	Acetone	Thermal stability	N/A	N/A	153

Table 11 (*Contd.*)

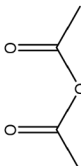| Lignin source/type	Reaction conditions			Reagent	Solvent/Catalyst	Separation	Property improvement	Yield (%)	Application	Ref.
	Time (h)	Temperature (°C)	pH							
Softwood and hardwood kraft	20	20–25	N/A	(structure, Cl, n:8 or 12)	Dimethylformamide	Ethanol, Soxhlet extraction in chloroform	Molecular weight	N/A	Oxygen and water vapor barrier	152
Hardwood and softwood kraft	3	50	N/A	(structure)	Acetic, and propionic	Filtration	Molecular weight, reduce water adsorption	88–99	Polyethylene blends	160
Softwood kraft	24	65	N/A	(structures)	1-Methylimidazole	Ethanol and centrifugation	Tensile strength, reduced water adsorption	24	Fillers for thermoplastics	161
		95						29		
		120						46		
Organosolv	1	100	N/A	(structure)	Pyridine	N/A	Solubility	~96	N/A	174
Softwood kraft	48	65	N/A	(structure, tetrahydrofuran)	Pyridine	Soxhlet extraction using tetrahydrofuran	T_g and melt torque reduced	60–80	Thermoplastic	159
Hardwood kraft	Overnight	20–25	Alkaline	(structures)	Water	Acetone and filtration	Compatibility of lignin	86	Polyethylene blends	168

Table 11 (Contd.)
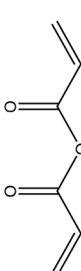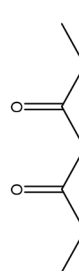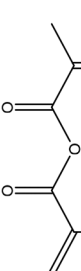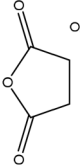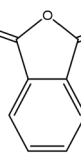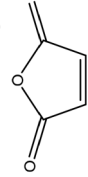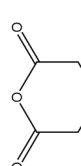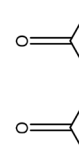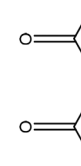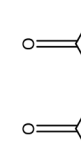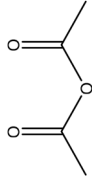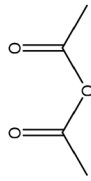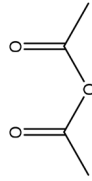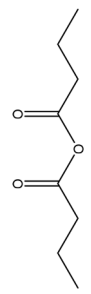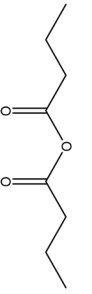
| Lignin source/type | Reaction conditions | | | Reagent | Solvent/Catalyst | Separation | Property improvement | Yield (%) | Application | Ref. |
	Time (h)	Temperature (°C)	pH							
Hardwood and softwood kraft	Overnight	50	N/A		1-Methylimidazole/1,4-dioxane	Ethyl ether	Solubility in non-polar solv, molecular weight	N/A	Use in unsaturated thermosets	169
Enzymatic hydrolysis	1.5	80	N/A		4-Dimethylamino pyridine, sodium acetate, and sulfuric acid	Ethanol	N/A	N/A	N/A	155
Kraft	7	60	N/A		Acetone	Filtration, water or toluene	Hydrophobicity, molecular weight, thermal stability	N/A	Reinforced wood plastic composites	175
Bagasse	4	90	N/A		1-Allyl-3-methylimidazolium chloride	Ethanol	Surface adhesion compatibility	N/A	N/A	132
Sugarcane bagasse	72	20–25	N/A		Pyridine	Filtration, water	Radical scavenging index decreased	N/A	Antioxidant	61
Synthetic	48	30	N/A		Pyridine	HCl, centrifugation	Secondary cinnamaldehydes prohibited	N/A	N/A	176
Kraft	48	N/A	N/A		Pyridine	Methanol	Molecular weight decreased	N/A	Chromatographic eluent	177
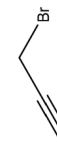
Table 11 (Contd.)

Lignin source/type	Reaction conditions			Reagent	Solvent/Catalyst	Separation	Property improvement	Yield (%)	Application	Ref.
	Time (h)	Temperature (°C)	pH							
Alkaline soda	18	20–25	N/A		Pyridine	Ethanol, or HCl	Thermal stability decreased	N/A	In polyolefins	157
Organosolv	48	25	N/A		Pyridine	Filtration	Solubility in tetrahydrofuran	N/A	Photosensitizers	171
Hardwood	N/A	N/A	N/A		Dioxin	N/A	Photodiscoloration behavior under decreased	77	Studying photoyellowing properties	162
Organosolv	3	60	N/A		1-Methylimidazole	n-Hexane	Viscosity decreased	N/A	Additive for plasticizing	165
Hardwood kraft	N/A	50	N/A		1-Methylimidazole	Ethyl ether	Flexural strength, viscosity	N/A	Resin and flax fibers	156

N/A: not available.

Table 12 Propargylation of lignin

Lignin source/type	Reaction conditions			Reagent	Solvent	Separation	Property improvement	Yield (%)	Application	Ref.
	Time (h)	Temperature (°C)	pH							
Kraft	1	90	13.7		Potassium hydroxide	HCl	Molecular weight	N/A	Carbon fiber, tires	178
Paper factory	4	70	Alkaline		Water/ethanol	Filtration	Solubility, thermal properties	98	Resin for composite matrix	180
Softwood kraft	2	75	Alkaline		Water	Acidification	Thermal stability, molecular weight	91–96	To increase thermal stability	41
Methylated softwood kraft	2	75	Alkaline		Water	Acidification	Molecular weight	N/A	Carbon fiber	178

N/A: not available.
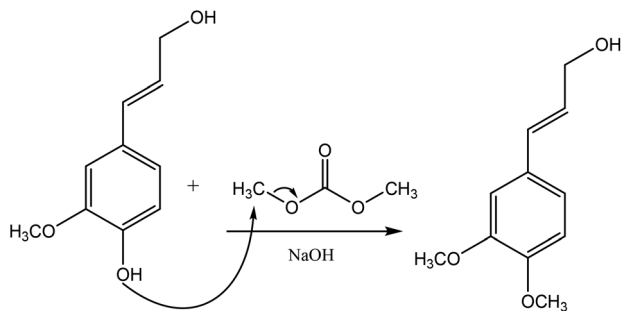
Fig. 9 Methylation of lignin by dimethyl carbonate.[181]

Oxidation

Recently, the oxidation of lignin has become popular because of the extensive need for replacing fossil fuel feedstock with sustainable materials to produce fuels and chemicals. Oxidation occurs through the electron loss of a molecule. In lignin oxidation, the cleavage of C–O bonds occurs leading to the generation of carboxylic acids and aromatic aldehydes.[210] The type of catalyst used in the oxidation reaction is responsible for its low molecular weight reduction or phenolic product generation.[210–212]

It is worth mentioning that the reaction pH plays a critical role in lignin oxidation. In one study,[212] hydrogen peroxide was used to oxidize lignin under both acidic and alkaline conditions. As a result of the reaction under acidic conditions, formic acid and acetic acid were produced as the main components, while no aromatic acids, aldehydes, chromophoric groups, and phenolic components was detected.[212] However, in an alkaline environment, lignin with a high amount of carboxylic acid was produced along with oxalic, formic, acetic, malonic, and succinic, as well as vanillin, syringaldehyde, and chromophoric groups. These chromophoric groups also undergo a ring cleavage reaction and further degradation to form low molecular weight acids. Interestingly, reactions conducted under strong alkaline conditions proceed at low temperatures of 80–90 °C, while those under acidic conditions need higher temperatures of 130–160 °C.[212] That being said, most of the oxidation reactions have been performed in an alkaline environment since it helps solubilize lignin and accelerates the deprotonation of hydroxy groups.[211,212]

Harsh oxidation. In a severe oxidation reaction, the lignin's aromatic ring is destroyed, and acids with low molecular weight are produced.[211] The oxidation reaction depolymerizes lignin *via* cleavage of C–O and C–C bonds. Comparing these linkages, it is harder to break the linkages in C_α–C_β since the bonding energies in C_α–C_β (264.3–294.2 kJ mol^{-1}) linkages are stronger than those in C_β–O (161.1–247.9 kJ mol^{-1}) linkages.[213–216] Due to the non-polarity and robustness of the C–C bond, its selective cleavage is a challenge.[216] Table 17 shows the oxidation reaction on lignin that results in ring opening products. A wide range of reagents were used to oxidize lignin, such as hydrogen peroxide (H_2O_2) (in acidic medium),[212,217] nitrobenzene and copper oxide[218] and

oxygen.[197,219–221] The reaction time and temperature have been reported to vary between 2–20 h and 80–160 °C, respectively, while the pressure of the reaction systems is mostly reported to be 10 bar.[212,218]

Lignin oxidation by the aliphatic and aromatic hydroxy groups of lignin leads to the generation of ketones, quinones, aldehydes, vanillin (shown in Table 17).[7,222,223] Also, some of the most advanced oxidative routes are used in pulp and paper industries to depolymerize or remove lignin from cellulosic materials.[224,225]

Based on the literature reports,[226,227] a correlation could be found between the resulting product and the oxidative breaking of specific linkage. Fig. 11 depicts this correlation under aerobic oxidation conditions. As depicted, the cleavage of the C_α–C_β bond forms phenolic aldehydes, while C_{ph}–C_α bond cleavage leads to the generation of para-quinones and oxirane structures. The cleavage of the lignin aromatic ring also yields the production of muconic acid derivatives.[226,227]

Meanwhile, aromatic aldehydes, such as vanillin, could be the main product of lignin oxidation.[228] Vanillin is the only mercantile product achieved from lignin through oxidation with a market volume of around 20 000 tonnes per year. Nonetheless, a majority (90%) of the synthetic vanillin used today is oil-based implying a need to improve and develop the lignin-based vanillin production, which is closer in flavor/taste to natural vanilla than vanillin produced from petrochemical guaiacol.[8] However, these oxidation pathways are accompanied by some disadvantages, such as long reaction times and use of toxic catalysts, such as sodium periodate or palladium chloride.[229,230]

Mild oxidation. Mild oxidation of lignin introduces carboxylic acid groups into lignin and does not necessarily depolymerize lignin.[239] In this paper, the oxidation that reduced the molecular weight of lignin by less than 10% is considered mild. Undoubtedly, increasing the amount of carboxylate groups in lignin improves its anionicity and hydrophilicity.[211,239] This reaction has been performed by using hydrogen peroxide (in alkaline medium),[57,240] nitrobenzene,[218] metal oxides,[218] and catalysts with oxygen.[211]

Hydrogen peroxide is widely available in pulp mills and is extensively used for bleaching pulp worldwide. As an oxidant, it can also be used for oxidizing lignin to introduce carboxylate groups. It is reported that hydrogen peroxide generally decomposes the phenolate group of lignin, whereas it induces the carboxylate group into lignin.[42,240,241] It was reported that the majority of hydrogen peroxide molecules was utilized for the partial decomposition of the lignin structure by the bond cleavage of lignin's ether bonds.[240]

Fig. 12 shows the mild oxidation by using different sources of lignin and oxidizing reagents. Lignin undergoes two different reaction sets in lignin oxidation with hydrogen peroxide; perhydroxyl anions attack nucleophilically while removing lignin chromophores. Meanwhile, free radical species generated by the decomposition of hydrogen peroxide yield oxidative degradation of the phenolic structures of lignin and converts them to carboxylic acid groups.[242] The perhydroxyl anion cleaves the side
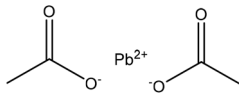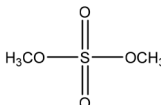
Table 13 Methylation of lignin

| Lignin source/type	Reaction conditions			Reagent	Solvent	Separation	Property improvement	Yield (%)	Application	Ref.
	Time (h)	Temperature (°C)	pH							
Milled wood	72	20–25	Acidic		Methanol and hydrochloric acid	N/A	N/A	N/A	Mask phenolic hydroxide groups	182
Lignosulfonate	2	80	11–11.5		Water	HCl	Molecular weight	N/A	Mask phenolic hydroxide groups	123
Softwood and hardwood kraft	2, 10	25, 80	Alkaline		N,N-Dimethylformamide	HCl	Molecular weight	N/A	Mask phenolic hydroxide groups	141
Softwood kraft	2–24	120 and 150	Alkaline		Dimethyl sulfoxide	HCl	T_g decreased	N/A	N/A	181
Softwood kraft	2	75	Alkaline		Water	HCl	Molecular weight, T_g	N/A	N/A	150
Softwood kraft	2	75	Alkaline		Water	HCl	N/A	N/A	Carbon fiber	178

N/A: not available.

Table 14 Alkylation of lignin

| Lignin source/type | Reaction conditions | | | | | | | |
	Time (h)	Temperature (°C)	pH	Reagent	Solvent	Separation	Application	Ref.
Unbleached hardwood kraft	24	80	8–10	[structure: alkyl chain, n:9, Br]	Isopropanol	Water	Retardant and toughening agent for polypropylene	185
Pulping industry	N/A	50	N/A	[structure: lead acetate, Pb²⁺]	Distilled water	Filtration, water	Surfactants	42
Kraft	72	20–25	11–12	[structure: dimethyl sulfate, H₃CO–SO₂–OCH₃]	Dioxane	Water, centrifuged	Plasticizer	186

N/A: not available.
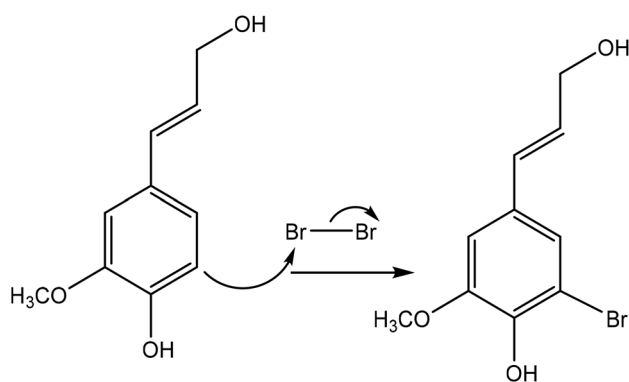
Fig. 10 Bromination reaction of lignin by using bromine.[191]
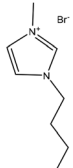
chains of lignin, opens the benzene ring, and produces new compounds, which have carboxylate or chromophore groups.[212,242,243] These groups may undergo the ring cleavage reaction under severe reaction conditions and further degrade

to form different low molecular weight compounds, such as oxalic acid, formic acid, and malonic acid.[212]

The oxidation of lignin *via* hydrogen peroxide would promote the solubility and increase the charge density of lignin, and therefore it could be used as an anionic dispersant for kaolin and other suspensions.[240] Employing nitrobenzene to oxidize lignin generates aromatic aldehydes as main products; however, using nitrobenzene have some disadvantages, such as difficulties in recovering the oxidant as well as the complexity of the reaction raised from the formation of phenylhydroxylamine, aniline, and nitrobenzene products, leading to a condensation among them. Also, the respective carboxylic acids produced in mild oxidation have lower yields than in harsh oxidation.[218]

Oxygen, Cu(ii), Co(ii), and CuO have also been used to oxidize lignin (Table 18). Protolignin oxidation with CuO has claimed to have a lower yield compared with nitrobenzene as the oxidant.[218,244,245] Co(ii) is a better oxidant than nitrobenzene, as the oxidant recovery is easier and harmful byproducts are not produced in the reaction.[246] Although oxygen (or air) as a catalyst

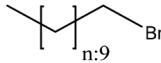**Table 15** Halogenation of lignin

| Lignin source/type | Reaction conditions | | | | | | | |
	Time (h)	Temperature (°C)	pH	Reagent	Solvent	Separation	Application	Ref.
Hardwood and softwood	2	163–164	N/A	Br–Br	Glacial acetic acid	N/A	N/A	191
Hydrolysis	1	20	N/A	Br–Br	Carbon tetrachloride and water	Water	N/A	190
depolymerized	N/A	20–25	N/A	[structure: 1-Butyl-3-methylimidazolium bromide]	1-Butyl-3-methylimidazolium bromide	Diethyl ether and ethyl acetate	Surfactant	189

N/A: not available.

Table 16 Amination of lignin

Lignin source/type	Reaction conditions			Reagent	Solvent	Separation	Property improvement	Yield (%)	Application	Ref.
	Time (h)	Temperature (°C)	pH							
Epoxidated	3	80	Alkaline		Formaldehyde	Filtration and water	N/A	N/A	Heavy metal adsorbent	197
Oxidized	5	90	10		Formaldehyde	Filtration	N/A	N/A	Heavy metal adsorbent	60
Alkaline	2–6	40–90	8–13		Water	HCl	Molecular weight, nitrogen content	N/A	Lead removal	108
LignoBoost	4	60	Acetic		Dioxane, and formaldehyde	Membrane dialysis	Molecular weight, nitrogen content	N/A	Surfactant and slow-release fertilizers	196
Epoxidated	4–6	80	Alkaline	$H_2N{-}R{-}NH_2$	Water	Acetone	Decomposition temperature decreased	N/A	Curing agents of epoxy resin	112
Carboxylated	3	80	Alkaline		Water	Membrane dialysis	Removing both anionic and cationic dyes	N/A	Flocculant	205
Sulfuric acid treated	4–48	50	Acetic		Formaldehyde, and dioxane	Ethyl acetate	Solubility	~0.6–63	Retention aid	199
Kraft	1	20–25	N/A		Formaldehyde	Filtration and isopropanol	N/A	97	Coagulant in wastewater	198
Enzymatic hydrolysis	2	20	3		Formaldehyde, and acetone	Membrane dialysis	Efficiency in higher pH	N/A	Flocculant for anionic azo dyes	201
Sulfonated	4	85	12		Water	Membrane dialysis	Hydrophilicity	N/A	Enhanced the enzymatic hydrolysis of lignocellulose	206

Table 16 (*Contd.*)

Lignin source/type	Reaction conditions			Reagent	Solvent	Separation	Property improvement	Yield (%)	Application	Ref.
	Time (h)	Temperature (°C)	pH							
Lignosulfonate	4	85	12		Water	Membrane dialysis	Fluidity	N/A	Clay-tolerance sacrificial agent	207
Softwood kraft	1	70	12.5		Water	Membrane dialysis	Solubility, charge density	N/A	Flocculant for dye removal	208
Hardwood organosolv, and enzymatic hydrolysis	20	60	Alkaline		Water	Dialyzed	Solubility	N/A	Removal of sulfate, kaolin, and humic acid	209
Sulfuric acid treated	4–72	60	N/A		Formaldehyde	Membrane dialysis	Brightness of the paper	78–90	Retention aid in papermaking	200

N/A: not available.

Table 17 Harsh oxidation reaction on lignin

Lignin source/type	Reaction conditions				Oxygen pressure atm	Solvent	Separation	Remark	Yield (%)	Ref.
	Time (h)	Temperature (°C)	pH	Catalyst						
Organosolv beech wood	1.5–3	N/A	N/A		1	Water	Ethyl acetate	Formation of quinones and phenol derivatives	N/A	231
Precipitated hardwood	0.08–0.016	95–160	Acidic	HO-OH	N/A	H_2SO_4	H_2SO_4	Formic acid and acetic acid	41	212
Alkali	0.15–2	20	N/A		N/A	Acetic acid	N/A	N/A	N/A	229
Organosolv beech wood	5	20–25	N/A		N/A	Acetonitrile-d3	Filtration	One-pot two-step reaction	N/A	231
Eucalyptus black liquor	2	150–190	Alkaline	Cu^{2+}, Co^{2+}	10–15	Water	N/A	Phenolic compound production	3.5	211
Aspen	12–48	110	Acidic		2	HNO_3, CH_3CN, HCl, water	Evaporation	Two-step reaction	N/A	232

Table 17 *(Contd.)*

| Lignin source/type | Reaction conditions | | | | | | Separation | Remark | Yield (%) | Ref. |
	Time (h)	Temperature (°C)	pH	Catalyst	Oxygen pressure atm	Solvent				
Curaua fibers and sugar cane bagasse	0.5	55	N/A	O=Cl=O	N/A	CH_3COOH	Centrifuging and water	Lower molecular weight products. Elimination of quinones	N/A	233
Kraft	1	450	N/A	TiO_2, Ta_2O_5–IrO_2	N/A	Ethanol–isopropanol	N/A	Lower molecular weight products	N/A	223
Softwood and hardwood	0.5–12	100	N/A	Polyoxometalate, and HO–OH	N/A	Water	N/A	Vanillin and syringaldehyde	5	7
Softwood and hardwood kraft	0.08–4	90–110	Alkaline	O_2	~5.9–8.8	Water	HCl	Lower molecular weight products	N/A	220
Softwood kraft	0.5	95	Alkaline	Fe^{3+}	~9.8	Water containing Fe^{3+}	H_2SO_4	Lower molecular weight products and vanillin	20	219
Organosolv	40	135	N/A	(HTc) and $V(acac)_3$/Cu $(NO_3)_2 \cdot 3H_2O$	9.8	Pyridine	N/A	Veratraldehyde and veratric acid	22–30	234
Softwood kraft / Softwood	N/A / N/A	150 / 160	14 / 13	O_2 / $CuSO_4$	~9.8 / ~1.9	Water / Water	N/A / N/A	Vanillin / Vanillin	~3.5–8 / N/A	235 / 217
Poplar, maple, and maize	28	65	Acetic		2	HNO_3, CH_3CN, HCl	Evaporation	Low-molecular-weight aromatics	N/A	236
Hydrolyzed	N/A	80	Acidic	HO–OH	N/A	Sulfuric acid	Filtration and acidification	Forming soluble fraction of oxidized hydrolyzed lignin	22–78	237
Sugar-cane / Soda	N/A / 10–120	~99.8–139.8 / N/A	N/A / Acidic	$PdCl_2$, and γ-alumina / HO–OH	~1.9–9.8 / N/A	Water / Water	N/A / Filtration	Aromatic aldehyde / More carboxylic groups rather than ketones or aldehydes	12 / N/A	221 / 238

N/A: not available.
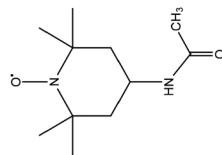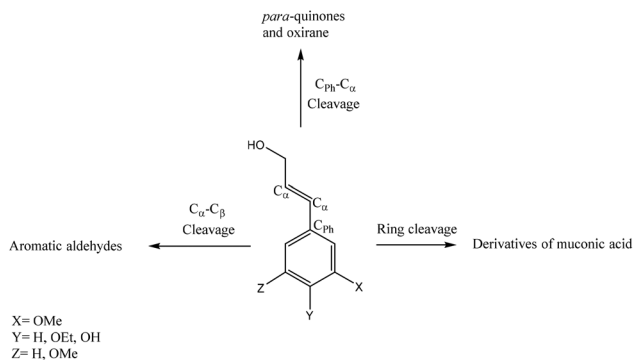
Fig. 11 Potential bond cleavage pathways in lignin aerobic oxidation.[226,227]

Fig. 12 Mild oxidation of lignin by hydrogen peroxide under alkaline conditions.[240]

will not contribute significantly to the oxidation cost, it has lower selectivity and produces low molecular weight acids.

Generally, although the mild oxidation pathways could be affordable, they are not effective in significantly altering the hydrophobicity of lignin.[239] Therefore, the lignin-based materials produced in some pulping and biorefining processes may need a stronger oxidizing agent.[42,247]

Silylation

Silica can be introduced on both phenolic and aliphatic hydroxy groups of lignin[252] under an S_N2 reaction mechanism (Fig. 1). Silica and derivatives of silane have been used as flame retardants. Dissimilar to carbon-based polymers, silicas generate inorganic silica under combustion. Silica residues could hamper fire deployment by restraining mass and heat transfer. Basically, no toxic emissions are produced from the combustion of silicas.[253,254] Hence, silica foams are highly favorable to be used in applications, such as construction building (*e.g.*, acoustic designs). Lignin–silica products have been used as gaskets, sealing materials, metal and organic adsorbents, as well as adsorbents for heavy metal ions and dyes.[43,252,255] They have also been reported as effective electrochemical sensors, polymer fillers,[252] and biosorbents for removing toxic substances from aqueous solutions.[42,252,255]

Table 19 shows the grafting of various silica on lignin. This reaction is generally conducted by introducing reagents including tetraethyl orthosilicate, silicon dioxide, sodium metasilicate, and tetraethoxysilane into lignin in a solvent (pyridine, ethanol, water, and dioxane) environment at 25–35 °C for 1.5 to 24 h. Although the lignin–silica reaction is popular in producing composites, these reactions are associated with drawbacks. For example, the two-step method used to produce lignin/silica composites intensely agglomerates composite particles. Also, the consumption of surfactants and various costly coupling agents in the preparation process of lignin/silica composites makes this process complicated and costly. Thus, there is a need for the expansion of a one-pot method for the lignin/silica composites' preparation, mainly in aqueous media.[256]

Modified lignin's characteristics

Hydrophilic lignin

Lignin is known for its complexity due to having hydrophilic groups attached to its hydrophobic rings. Chemical modifications (*e.g.*, carboxyalkylation and sulfoalkylation) would render it more hydrophilic.[40,100,175] The applications for hydrophilic lignin products can expand extensively to an adsorbent, stabilizer, and dispersant for emulsions, clay suspensions, coal/water slurry, dye suspensions, and cement admixtures. However, it is mostly favored to be used as a dispersant or flocculant for emulsion and suspension systems.

Various reactions render lignin anionic by introducing a negative charge into its backbone, of which carboxyalkylation, sulfoalkylation, and oxidation are the most common ones. The reaction temperature preferred for performing carboxymethylation, carboxyethylation, and sulfobutylation is mostly below 90 °C, but sulfomethylation is generally carried out at higher temperature (Tables 5–8). In addition, sulfobutylation has mostly been performed in a solvent-free environment, which is highly favorable.

Comparing the reaction routes stated above, while both carboxyalkylation and sulfomethylation are conducted in alkaline media, sulfomethylation seems to be less favorable due to several reasons: (1) an oxidation reaction is suggested to perform prior to sulfomethylation to increase the reaction yield, which is unfavorable since it has a dramatic impact on the performance of the sulfomethylation reaction; (2) the use of formaldehyde in sulfomethylation is a major downside due to its toxicity; and (3) the sulfomethylation reaction is a slow reaction that occurs at high temperature.
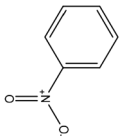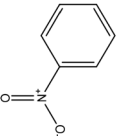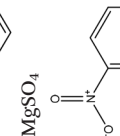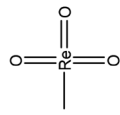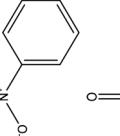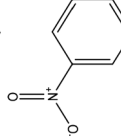
Carboxyethylation and sulfobutylation have more advantages than carboxymethylation and sulfomethylation, since they grant lignin with a higher anionic charge density stemming from the occurrence of the reaction on both aromatic and aliphatic hydroxy groups of lignin.[110,122,123]

Cationic lignin is produced by the addition of a positively charged group to its backbone. While lignin cationization has not been carried out as extensive as the anionization in the past, producing cationic lignin through amination is a well-known method of cationization, which further fosters its potential use in various applications, *e.g.*, flocculant, adsorbent, surfactant.[108,196–198]
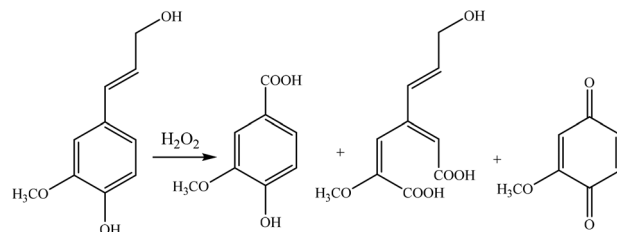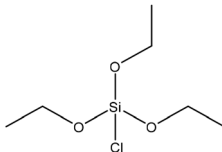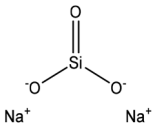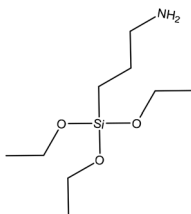
Table 18 Mild oxidation of lignin

Lignin source/type	Reaction conditions			Catalyst	Oxygen pressure atm	Solvent	Separation	Remark	Yield (%)	Ref.
	Time (h)	Temperature (°C)	pH							
Proto Alkali	2.5	170–180	Alkaline	(nitrobenzene)	N/A	Water	N/A	Product ratio depends on the material source	Syringaldehyde 36%, vanillin 15%; Syringaldehyde 25%, vanillin 10%	244
Hardwood Calcium lignosulfonate Eucalyptus black liquor	N/A 1.5 2–2.30	80–160 80 150	Alkaline 9 Alkaline	$HO-OH$ $HO-OH$ Cu(II), and Co(II)	N/A N/A 10–15	Water Water Water	N/A N/A N/A	Lower molecular weight products; Foam height and half-life decreased; Lower phenolic aldehyde compared to other lignin oxidants CuO and nitrobenzene	30–50 N/A 4	212 57 211
Eucalyptus black liquor	2–4	170–190	Alkaline	(nitrobenzene)	N/A	Water	N/A	Nitrobenzene is more effective than copper(II) oxide	15–18% by using nitrobenzene, 7–8% by using CuO	218
Alkali Thio	2	180	Alkaline	(nitrobenzene)	N/A	Water	Filtration	Product ratio depends on the material source	Vanillin 17% Vanillin 6.6%	248
Softwood kraft	1	78–110	Alkaline	$MgSO_4$	2.72	Water	Water	Increase in tensile strength	43–50	249
Proto Alkali	4	160	Alkaline	(nitrobenzene)	N/A	Water	N/A	N/A	Vanillin 4% Vanillin 3%	245
Sugar cane, red spruce kraft, and hardwood organosolvent	N/A	20–25	N/A	$HO-Re$ (methyltrioxorhenium)	N/A	Acetic acid	Filtration	Increase in carboxylic acid content	98	243
Softwood kraft	1–3	60–100	Alkaline	$HO-OH$	N/A	Water	Membrane	Decrease in molecular weight, increase in charge density and degree of the carboxylate group. Dispersant for kaolin suspensions	N/A	240
Proto	3	160	Alkaline	(nitrobenzene)	N/A	Water	Filtration	Half of lignin combined through C–C linkages	Syringaldehyde 13%, vanillin 8.5%	250
Native Alkali	2	180	Alkaline	(nitrobenzene)	8.9	Water	Filtration	N/A	Vanillin 25% Vanillin 14%	251

N/A: not available.

Table 19 Lignin–silica reaction

| Lignin source/type | Reaction conditions | | | | Solvent | Separation | Property improvement | Yield (%) | Application | Ref. |
	Time (h)	Temperature (°C)	pH	Reagent						
Alkali	24	20–25	N/A		Pyridine	Pyridine	Thermal stability, surface area	N/A	Wastewater treatment	43
Magnesium lignosulfonate	1.5	N/A	N/A	O=Si=O	Water	Vacuum evaporator	Thermal stability	N/A	Polymer filler, and metal adsorbent	252
Quaternized alkali	4	35	Alkaline		Ethanol and water	Water	UV-absorption ability, mechanical properties	N/A	Blend with polyurethane films	256
Ultrafiltered LignoBoost kraft	24	N/A	Acetic		Dioxane and water	Ethanol and water	Thermal stability surface area	N/A	Sorbents for organic molecules	255

N/A: not available.

Hydrophobic lignin

Hydrophobic lignin and its derivatives have a strong interaction with other materials in organic solvents,[12] and are almost insoluble in water. Reactions improving the hydrophobicity of lignin include esterification, alkylation, methylation, epoxidation, propylation, and oxypropylation, as they introduce hydrophobic groups into lignin's structure.

In comparing these reaction routes, while all are mostly conducted under alkaline conditions, alkylation and epoxidation benefit from a relatively lower reaction temperature (below 90 °C). On the other hand, a broad and high reaction temperature range in oxypropylation (40–285 °C) and prolonged reaction time (72 h) in alkylation, as well as in methylation (if conducted at room temperature) might be the drawbacks of some of these modification pathways. In addition, oxypropylation could render lignin more hydrophobic than esterification,[12] which is favorable for some applications, such as foams and composites.

Although the abovementioned reactions improve the hydrophobicity of lignin, each endows lignin with different features; the thermal resistance of lignin was reported to be improved *via* alkylation, and thus it promotes the application of alkylated lignin as a plasticizer in polymer blends.[42,181] On the other hand, epoxy lignin was reported to have antibacterial activity,[61] while esterified and methylated lignin were both reported to have a lower glass transition temperature than untreated lignin. Therefore, these reactions make products suitable for thermoplastics, plastic blends and carbon fibers.[150,158] However, none of the mentioned reactions are environmentally friendly, as reagents in these reactions are mostly toxic and carcinogenic.

Applications for modified lignin

Lignin is a polymer with tremendous potential for its use in various industries. Table 20 shows the reactions conducted on lignin for specific applications, as well as drawbacks of lignin properties for the desired applications, which were improved through modification reactions. As seen, various reactions have been carried out on lignin to improve its charge density and solubility/hydrophilicity to be used as a dispersant, such as sulfomethylation for coal–water slurry and concrete admixture, sulfobutylation for coal–water slurry and carbendazim, carboxymethylation for oil–water emulsions, crude bitumen emulsion, clay, cement, and graphite suspensions, halogenation for surfactant, animation of cationic surfactants, and cationic asphalt emulsifier productions.

Phosphorylation, hydroxymethylation, and oxypropylation reactions make modified lignin a good alternative for oil-based polyols used in polyester and polyurethane productions through improving lignin properties, such as tensile strength,

Table 20 Different reactions conducted for desired applications

Application	Shortcomings of lignin	Reaction	Ref.
Dispersant	Charge density	Sulfomethylation	20, 21, 57, 100, 101, 104 and 107
	Solubility/wettability	Sulfonation	95
		Sulfobutylation	109, 110 and 111
		Carboxymethylation	40, 116 and 120–122
		Carboxyethylation	123
		Oxidation	240
		Esterification	173
		Oxyalkylation	149
Surfactant	Hydrophilicity/phobicity	Halogenation	189
	Molecular weight	Sulfonation	92
		Alkylation	42
		Amination	196
Plasticizer	Charge density	Esterification	159 and 175
	Hydrophilicity	Sulfonation	90 and 91
		Oxyalkylation	150
		Esterification	159
		Alkylation	186
Flame-retardant	Thermal and oxidative stability	Phosphorylation	38, 39, 45, 47, 48, 53 and 139
		Lignin–silica	256
Additive in polyurethane	Tensile strength	Phosphorylation	47
	Glass-transition temperature	Phenolation	77
	Molecular weight	Oxypropylation	136–140, 142–144 and 148
	Viscosity		
Adsorbent of metal ions in wastewater treatment	Selectivity	Phosphorylation	49 and 51
	Thermal stability	Lignin–silica	252
		Sulfomethylation	60
		Amination	60 and 197
Flocculant/coagulant	Molecular weight	Sulfomethylation	105
	Charge density	Amination	198, 201, 205, 208 and 209
Epoxy	Thermal stability	Phosphorylation	46
	Molecular weight	Epoxidation	112 and 125
		Amination	112
Adhesive	Viscosity	Hydroxymethylation	54, 66 and 68–72
	Molecular weight	Sulfonation	88 and 93
Anti-oxidant and anti-bacterial	High radical-scavenging activity	Epoxidation	61
		Sulfonation	96
Resin	Thermal stability	Phenolation	78, 80 and 83
	Cross-linking		

molecular weight, viscosity, and glass-transition temperature. In addition, phosphorylation, carboxyethylation, amination, silylation, and sulfomethylation make lignin a polyelectrolyte with applications in aqueous systems by enhancing its selectivity and thermal stability.

Phosphorylation, epoxidation, and amination (curing agents of epoxy resin) increase lignin's molecular weight and thermal stability, which further promote lignin's application in the epoxy resin industry. Epoxy resins possess a wide range of applications, such as flooring, electronic laminates, industrial coatings and adhesives and high-performance composites. However, a slow curing rate, limited water solubility, and brittleness are the negative aspects of lignin-based epoxy resins. Lignin-based adhesives could be produced by hydroxymethylation and epoxidation. They could also be applied to mimic lignin antioxidant and anti-bacterial properties.

Miscibility of the polymers is a critical factor in applications such as polymer blends. Although two polymers' miscibility is not favorable entropically, it could be improved if the polymers involved in blending have intermolecular interactions since the negative enthalpy of mixing overcomes the opposite entropy.[257] Using lignin in polymer blends develops a convenient and powerful pathway to produce novel and functional green materials. It should be stated that polar synthetic polymers generate an intermolecular hydrogen bonding with lignin, while non-polar ones generally generate immiscible blends, showing distinct T_g points for two immiscible phases. In the past, lignin had been used in blending with synthetic polymers.[181] Lignin's phenolic hydroxy groups tend to contribute more in forming hydrogen bonds with other polymers in a blend than its aliphatic ones due to the higher acidity of lignin's phenolic hydroxy group.[257] Previously, alkylation, acetylation, methylation, and esterification of lignin have been carried out to increase the compatibility of lignin with various synthetic polymers in polymer blend applications.

Lignin alkylation and acetylation have reported modulating its chemical and thermal reactivities, which further leads to a thermal improvement in a polymer blend. Comparing alkylated and acetylated lignin with the unmodified lignin, it is found that the thermal stability of the polymer blends was improved when modified lignins were used in blends' composition.[185]

Table 21 Markets of lignin-based products

Industrial products from lignin	Est. total market value per year (billion dollar)	Est. scale produced per year (lignin-based) (MTon)	Est. lignin-based price ($ per kg)	Est. fossil-based price ($ per kg)	Ref.
Carbon fiber	4.5	N/A	6.5–12	17–26	261 and 262
Phenol	12–15	8	1–1.5	N/A	261–263
Vanillin	0.2	0.016	12	12	261 and 262

N/A: not available.

Lignin methylation was also observed to impact the thermal stability of the lignin/polyethylene blend, diminishing the degradation temperature of the polyethylene remarkably. Nevertheless, since the lignin's phenolic hydroxyl groups become entirely masked through methylation, the tendency to form intermolecular hydrogen bonding in polymer blends can be reduced significantly.[257]

Lignin esterification was also performed to increase lignin compatibility in polymer blends.[163] On the other hand, the esterified lignin's miscibility strongly depends on the carbon numbers presented in the side chain of the ester in that the miscibility improves with an increase in the ester groups' chain length. However, the esterified lignin's interaction in a polymer blend might be similar to the methylated lignin's interaction due to the masking of the phenolic hydroxy groups *via* esterification, hindering the hydrogen bonding development.

Current and future trends

Lignin has been used as fuel. The price of lignin as fuel varies between 70–150 USD per ton, which is dependent on its moisture content and contaminants.[258] Two technologies have been developed to generate lignin in dried powder forms. Lignoboost™ that has been implemented at Stora Enso, Sweden, with the production capacity of 50 000 ton per year, and Domtar, NC, USA with the production capacity of 25 000 ton per year. Lignoforce™ has also been commercialized at West Fraser Inc, AB, Canada, with the production capacity of 30 t per day. The production of lignin in such quantities will undeniably pave the way to generate lignin derivatives at commercial scales. Table 21 shows the addressable markets of lignin-based products. This table also comprises the estimated market values and capacities as well as the price of the lignin or fossil-based products. As seen, there are products, such as vanillin and phenol, which have been commercially available since 1933 and 2015, respectively, with lower or equal prices to their fossil-based counterparts. Lignin-based carbon fiber is also estimated to be produced commercially in 2020–2025.

While the utilization of lignin might seem limited with current technologies, it is anticipated that lignin would be even more available in future due to the production of lignin in commercial processes, such as LignoForce and LignoBoost,[259,260] which can pave the way for its further valorization. Although various modifications have been performed on lignin, there are still some unexplored reactions that could further improve the properties of lignin for different applications. For example, in carboxyalkylation, there is room for carboxypropylation and carboxybutylation of lignin to tune its charge density and hydrophilicity/hydrophobicity. Although sulfomethylation and sulfobutylation reactions have been conducted on lignin, no specific reports have been found in the literature on sulfoethylation and sulfopropylation of lignin, which could be a case of study since different reactions of carboxyalkylation or sulfoalkylation lead to the production of lignin with different properties as they introduce different carbon chain lengths and mimic the hydrophilicity/phobicity of lignin alterably. In the case of oxyalkylation, by far, oxypropylation has been the only reaction carried out on lignin, leaving room for investigating other routes in oxyalkylation. Generally, the solvent use and recovery impact the operation costs and ultimately the price of lignin derivatives and the environmental footprints of the developed technologies. If solvent use is necessary for lignin modification, the solvent recovery process is an important aspect of the process from finance and environment perspectives. For developing more industrially attractive and environmentally friendly pathways for lignin valorization, non-toxic reagents and chemistry should be discovered. Furthermore, the use of aqueous systems for lignin alteration would help reduce the environmental impacts of any lignin valorization processes.

As mentioned earlier, lignin has been studied in many applications, such as a dispersant, flocculant, adsorbent, and flame retardant (Table 20), while biological applications for lignin have been barely touched in the literature. For example, lignin's interaction with organic molecules, such as proteins, antibiotics, bacteria, and viruses could be studied for expanding either lignin-based biomedical applications as well as water and wastewater treatment systems. Using lignin in drug delivery systems, wound dressing, tissue engineering, and pharmaceutical applications could also be investigated. However, proceeding with such applications for lignin requires broad and detailed studies on the toxicity analysis of lignin, which has not been covered extensively as of yet.

Conclusions

Lignin is the most abundant aromatic polymer in nature, while its utility has been untapped in industry. Thanks to the numerous studies conducted in exploring lignin chemistry

and structure over the last few years, the applications of lignin have been growing tremendously. This trend shows the increasing level of enthusiasm and interest of researchers in developing lignin-based applications and more importantly, the replacement of aromatic substances with petrochemical origins. Thus, various modifications have been performed on lignin to alleviate or remove the restrictions in the nature of lignin that limits its applications in industry. Some of these reactions are very promising to improve lignin's reactivity with other materials and compatibility in different environments. This work comprehensively reviewed and compared various modification routes while highlighting the strength and weak points. Despite the reactions mentioned, there is still room for expanding the other possible modification methods. In addition, biological applications of lignin could be studied more extensively to explore further and expand the functionality of this biobased and abundant material. In conclusion, distinguishing the modifications occurring on different parts of lignin, knowing the precise manner of reactions and reaction sites of the modifications, as well as pros and cons of each reaction, can pave the way for understanding and expanding the use of lignin in various processes.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

References

1 L. Shuai, M. T. Amiri, Y. M. Questell-Santiago, F. Heroguel, Y. Li, H. Kim, R. Meilan, C. Chapple, J. Ralph and J. S. Luterbacher, *Science*, 2016, **354**, 329–333.

2 A. Scalbert, C. Morand, C. Manach and C. Rémésy, *Biomed. Pharmacother.*, 2002, **56**, 276–282.

3 G. Janusz, A. Pawlik, J. Sulej, U. Świderska-Burek, A. Jarosz-Wilkołazka and A. Paszczyński, *FEMS Microbiol. Rev.*, 2017, **41**, 941–962.

4 J. C. M. S. Moura, C. A. V. Bonine, J. de Oliveira Fernandes Viana, M. C. Dornelas and P. Mazzafera, *J. Integr. Plant Biol.*, 2010, **52**, 360–376.

5 J. Pérez, J. Muñoz-Dorado, T. de la Rubia and J. Martínez, *Int. Microbiol.*, 2002, **5**, 53–63.

6 J. Chen, A. Eraghi Kazzaz, N. AlipoorMazandarani, Z. Hosseinpour Feizi and P. Fatehi, *Molecules*, 2018, **23**, 868.

7 G. F. D. Gregorio, R. Prado, C. Vriamont, X. Erdocia, J. Labidi, J. P. Hallett and T. Welton, *ACS Sustainable Chem. Eng.*, 2016, **4**, 6031–6036.

8 R. Rinaldi, R. Jastrzebski, M. T. Clough, J. Ralph, M. Kennema, P. C. Bruijnincx and B. M. Weckhuysen, *Angew. Chem., Int. Ed.*, 2016, **55**, 8164–8215.

9 M. Alekhina, O. Ershova, A. Ebert, S. Heikkinen and H. Sixta, *Ind. Crops Prod.*, 2015, **66**, 220–228.

10 Y. Liu and K. Li, *J. Adhes.*, 2006, **82**, 593–605.

11 M. Zhou, X. Qiu, D. Yang, H. Lou and X. Ouyang, *Fuel Process. Technol.*, 2007, **88**, 375–382.

12 S. Laurichesse and L. Averous, *Prog. Polym. Sci.*, 2014, **39**, 1266–1290.

13 V. P. Saraf and W. G. Glasser, *J. Appl. Polym. Sci.*, 1984, **29**, 1831–1841.

14 N. Alwadani and P. Fatehi, *Carbon Resour. Convers.*, 2018, **1**, 126–138.

15 A. Lourenco and H. Pereira, *Lignin: Trends and Applications*, InTech, Croatia, 2018.

16 L. Christopher, J. H. Clark and G. A. Kraus, *Integrated forest biorefineries*, Royal Society of Chemistry, Cambridge, 2012.

17 A. G. Vishtal and A. Kraslawski, *BioResources*, 2011, **6**, 3547–3568.

18 Z. H. Feizi, A. E. Kazzaz, F. Kong and P. Fatehi, *Sep. Purif. Technol.*, 2019, **222**, 254–263.

19 D. Tarasov, M. Leitch and P. Fatehi, *Biofuels*, 2018, **11**, 269.

20 M. K. Konduri and P. Fatehi, *ACS Sustainable Chem. Eng.*, 2015, **3**, 1172–1182.

21 Y. Qin, D. Yang, W. Guo and X. Qiu, *J. Ind. Eng. Chem.*, 2015, **27**, 192–200.

22 M. A. Hubbe, R. Alén, M. Paleologou, M. Kannangara and J. Kihlman, *BioResources*, 2018, **14**, 2300–2351.

23 A. N. Evdokimov, A. V. Kurzin, O. V. Fedorova, P. V. Lukanin, V. G. Kazakov and A. D. Trifonova, *Wood Sci. Technol.*, 2018, **52**, 1165–1174.

24 B. M. Upton and A. M. Kasko, *Chem. Rev.*, 2015, **116**, 2275–2306.

25 W. Boerjan, J. Ralph and M. Baucher, *Annu. Rev. Plant Biol.*, 2003, **54**, 519–546.

26 Z. Sun, B. Fridrich, A. de Santi, A. Elangovan and K. Barta, *Chem. Rev.*, 2018, **118**, 614–678.

27 C. Li, X. Zhao, A. Wang, G. W. Huber and T. Zhang, *Chem. Rev.*, 2015, **115**, 11559–11624.

28 W. Schutyser, T. Renders, S. Van den Bosch, S. F. Koelewijn, G. T. Beckham and B. F. Sels, *Chem. Soc. Rev.*, 2018, **47**, 852–908.

29 V. M. Roberts, V. Stein, T. Reiner, A. Lemonidou, X. Li and J. A. Lercher, *Chem. – Eur. J.*, 2011, **17**, 5939–5948.

30 J. Zhang, *ChemSusChem*, 2018, **11**, 3071–3080.

31 S. Gharehkhani, Y. Zhang and P. Fatehi, *Prog. Energy Combust. Sci.*, 2019, **72**, 59–89.

32 J. Zakzeski, P. C. Bruijnincx, A. L. Jongerius and B. M. Weckhuysen, *Chem. Rev.*, 2010, **110**, 3552–3599.

33 S. Gillet, M. Aguedo, L. Petitjean, A. R. C. Morais, A. M. da Costa Lopes, R. M. Lukasik and P. T. Anastas, *Green Chem.*, 2017, **19**, 4200–4233.

34 X. Chen, L. Song and Y. Hu, *J. Appl. Polym. Sci.*, 2010, **115**, 3332–3338.

35 H. Vothi, C. Nguyen, K. Lee and J. Kim, *Polym. Degrad. Stab.*, 2010, **95**, 1092–1098.

36 P. A. Song, L. Xu, Z. Guo, Y. Zhang and Z. Fang, *J. Mater. Chem.*, 2008, **18**, 5083–5091.

37 G. L. Bykov and B. G. Ershov, *Russ. J. Appl. Chem.*, 2010, **83**, 316–319.

38 B. Prieur, M. Meub, M. Wittemann, R. Klein, S. Bellayer, G. Fontaine and S. Bourbigot, *Polym. Degrad. Stab.*, 2016, **127**, 32–43.

39 G. P. Mendis, S. G. Weiss, M. Korey, C. R. Boardman, M. Dietenberger, J. P. Youngblood and J. A. Howarter, *Green Mater.*, 2016, **4**, 1–11.

40 M. K. Konduri, F. Kong and P. Fatehi, *Eur. Polym. J.*, 2015, **70**, 371–383.

41 S. Sen, H. Sadeghifar and D. S. Argyropoulos, *Biomacromolecules*, 2013, **14**, 3399–3408.

42 L. R. Morrow, M. G. DaGue and L. E. Whittington, *US Pat*, 4790382, 1988.

43 R. Saad and J. Hawari, *J. Porous Mater.*, 2013, **20**, 227–233.

44 L. Liu, G. Huang, P. Song, Y. Yu and S. Fu, *ACS Sustainable Chem. Eng.*, 2016, **4**, 4732–4742.

45 L. Liu, M. Qian, P. A. Song, G. Huang, Y. Yu and S. Fu, *ACS Sustainable Chem. Eng.*, 2016, **4**, 2422–2431.

46 A. A. Alalykin, R. L. Vesnin and D. A. Kozulin, *Russ. J. Appl. Chem.*, 2011, **84**, 1616.

47 L. Ferry, G. Dorez, A. Taguet, B. Otazaghine and J. M. Lopez-Cuesta, *Polym. Degrad. Stab.*, 2015, **113**, 135–143.

48 B. Prieur, M. Meub, M. Wittemann, R. Klein, S. Bellayer, G. Fontaine and S. Bourbigot, *RSC Adv.*, 2017, **7**, 16866–16877.

49 A. M. Nada, N. F. Kassem and S. H. Mohamed, *BioResources*, 2008, **3**, 538–548.

50 J. Qin, M. Woloctt and J. Zhang, *ACS Sustainable Chem. Eng.*, 2014, **2**, 188–193.

51 A. A. M. Nada and M. L. Hassan, *J. Appl. Polym. Sci.*, 2003, **89**, 2950–2956.

52 G. B. Quistad, N. Zhang, S. E. Sparks and J. E. Casida, *Chem. Res. Toxicol.*, 2000, **13**, 652–657.

53 Y. Yu, S. Fu, P. A. Song, X. Luo, Y. Jin, F. Lu and J. Ye, *Polym. Degrad. Stab.*, 2012, **97**, 541–546.

54 M. R. Clarke and A. J. Dolenko, *U.S. Patent*, 4113675, 1978.

55 A. M. Capraru, V. I. Popa, T. Malutan and G. Lisa, *Cellul. Chem. Technol.*, 2009, **43**, 409–418.

56 A. R. Goncalves and P. Benar, *Bioresour. Technol.*, 2001, **79**, 103–111.

57 Y. X. Pang, X. Q. Qiu, D. J. Yang and H. M. Lou, *Colloids Surf., A*, 2008, **312**, 154–159.

58 X. L. Liu, Y. H. Liao, Z. J. Wu, L. F. Cun, X. M. Zhang and W. C. Yuan, *J. Org. Chem.*, 2010, **75**, 4872–4875.

59 T. Malutan, R. Nicu and V. I. Popa, *BioResources*, 2007, **3**, 13–20.

60 Y. Ge, Z. Li, Y. Kong, Q. Song and K. Wang, *J. Ind. Eng. Chem.*, 2014, **20**, 4429–4436.

61 R. Kaur, S. K. Uppal and P. Sharma, *Sugar Tech*, 2017, **19**, 675–680.

62 R. V. Gadhave, P. A. Mahanwar and P. T. Gadekar, *Open J. Polym. Chem.*, 2018, **8**, 1.

63 S. Pietarinen, O. Ringena, K. Eskelinen and S. Valkonen, *US Pat*, 9464219, 2016.

64 P. Benar, A. R. Gonçalves, D. Mandelli and U. Schuchardt, *Bioresour. Technol.*, 1999, **68**, 11–16.

65 A. M. Capraru, E. Ungureanu, L. Trinca, T. Malutan and V. I. Popa, *Cellul. Chem. Technol.*, 2012, **46**, 589–597.

66 M. E. Taverna, F. Felissia, M. C. Area, D. A. Estenoz and V. V. Nicolau, *J. Appl. Polym. Sci.*, 2019, 47712.

67 T. Malutan, R. Nicu and V. I. Popa, *BioResources*, 2008, **3**, 1371–13767.

68 E. Ungureanu, O. Ungureanu, A. M. Capraru and V. I. Popa, *Cellul. Chem. Technol.*, 2009, **43**, 263.

69 X. Wang, Y. Zhang, C. Hao, F. Feng, H. Yin and N. Si, *Ind. Eng. Chem. Res.*, 2014, **53**, 6585–6592.

70 A. Ang, Z. Ashaari, E. S. Bakar and N. A. Ibrahim, *BioResources*, 2015, **10**, 4795–4810.

71 N. E. E. Mansouri, A. Pizzi and J. Salvado, *J. Appl. Polym. Sci.*, 2007, **103**, 1690–1699.

72 H. Younesi-Kordkheili and A. Pizzi, *J. Adhes.*, 2017, **14**, 1120–1130.

73 F. Zhang, X. Jiang, J. Lin, G. Zhao, H. M. Chang and H. Jameel, *New J. Chem.*, 2019, **43**, 2238–2246.

74 A. Effendi, H. Gerhauser and A. V. Bridgwater, *Renewable Sustainable Energy Rev.*, 2008, **12**, 2092–2116.

75 X. Jiang, J. Liu, X. Du, Z. Hu, H. M. Chang and H. Jameel, *ACS Sustainable Chem. Eng.*, 2018, **6**, 5504–5512.

76 L. Hu, H. Pan, Y. Zhou and M. Zhang, *BioResources*, 2011, **6**, 3515–3525.

77 T. T. M. Tan, *Polym. Int.*, 1996, **41**, 13–16.

78 N. S. Cetin and N. Özmen, *Int. J. Adhes. Adhes.*, 2002, **22**, 477–480.

79 N. S. Cetin and N. Özmen, *Int. J. Adhes. Adhes.*, 2002, **22**, 481–486.

80 S. Kamel, *Int. J. Polym. Mater.*, 2005, **55**, 283–291.

81 Y. Matsushita and S. Yasuda, *Bioresour. Technol.*, 2005, **96**, 465–470.

82 J. Podschun, B. Saake and R. Lehnen, *Eur. Polym. J.*, 2015, **67**, 1–11.

83 G. Vazquez, J. Gonzalez, S. Freire and G. Antorrena, *Bioresour. Technol.*, 1997, **60**, 191–198.

84 M. Funaoka, M. Matsubara, N. Seki and S. Fukatsu, *Biotechnol. Bioeng.*, 1995, **46**, 545–552.

85 J. Podschun, A. Stücker, R. I. Buchholz, M. Heitmann, A. Schreiber, B. Saake and R. Lehnen, *Ind. Eng. Chem. Res.*, 2016, **55**, 5231–5237.

86 E. Rojo, M. S. Peresin, W. W. Sampson, I. C. Hoeger, J. Vartiainen, J. Laine and O. J. Rojas, *Green Chem.*, 2015, **17**, 1853–1866.

87 D. Fengel and G. Wegener, *Wood: chemistry. ultrastructure. Reaction*, Walter de Gruyter, New York, 2011.

88 C. I. Chiwetelu, V. Hornof, G. H. Neale and A. E. George, *Can. J. Chem. Eng.*, 1994, **72**, 534–540.

89 G. Telysheva, T. Dizhbite, E. Paegle, A. Shapatin and I. Demidov, *J. Appl. Polym. Sci.*, 2001, **82**, 1013–1020.

90 A. Macias and S. Goni, *Mater. J.*, 1999, **96**, 40–46.

91 A. Kamoun, A. Jelidi and M. Chaabouni, *Cem. Concr. Res.*, 2003, **33**, 995–1003.

92 W. L. Ng, D. Rana, G. H. Neale and V. Hornof, *J. Appl. Polym. Sci.*, 2003, **88**, 860–865.

93 R. Chen and Q. Wu, *J. Appl. Polym. Sci.*, 1994, **52**, 437–443.

94 T. Aro and P. Fatehi, *ChemSusChem*, 2017, **10**, 1861–1877.

95 P. Dilling, *US Pat*, 4546173, 1985.

96 S. E. Lebo Jr., J. D. Gargulak and T. J. McNally, *Encycl. Polym. Sci. Technol.*, 2002, DOI: 10.1002/0471440264.pst179.

97 H. Zhang, Y. Bai, W. Zhou and F. Chen, *Int. J. Biol. Macromol.*, 2017, **97**, 201–208.

98 A. J. Latibari, M. Roohnia, A. Tajdini, F. Darvishqadima and M. Moradbak, *J. Appl. Chem. Res.*, 2008, **2**, 34–44.

99 P. Dilling, *US Pat*, 4732572, 1988.

100 H. Wu, F. Chen, Q. Feng and X. Yue, *BioResources*, 2012, 7, 2742–2751.

101 W. He and P. Fatehi, *RSC Adv.*, 2015, **5**, 47031–47039.

102 P. Dilling, *US Pat*, 4670482, 1987.

103 D. Yang, Y. Chang, X. Wu, X. Qiu and H. Lou, *RSC Adv.*, 2014, **4**, 53855–53863.

104 H. Zhou, Y. Chang, X. Wu, D. Yang and X. Qiu, *ACS Sustainable Chem. Eng.*, 2015, **3**, 518–523.

105 A. E. Kazzaz, Z. H. Feizi and P. Fatehi, *Colloid Polym. Sci.*, 2018, **296**, 1867–1878.

106 B. Zhang, D. Yang, H. Wang, Y. Qian, J. Huang, L. Yu and X. Qiu, *ACS Sustainable Chem. Eng.*, 2018, **7**, 1120–1128.

107 C. Huang, J. Ma, W. Zhang, G. Huang and Q. Yong, *Polymer*, 2018, **10**, 841.

108 Y. Ge, Q. Song and Z. Li, *J. Ind. Eng. Chem.*, 2015, **23**, 228–234.

109 X. Qiu, W. Zeng, W. Liang, Y. Xue, N. Hong and Y. Li, *J. Dispersion Sci. Technol.*, 2016, **37**, 472–478.

110 X. Qiu, W. Zeng, W. Yu, Y. Xue, Y. Pang, X. Li and Y. Li, *ACS Sustainable Chem. Eng.*, 2015, **3**, 1551–1557.

111 Y. Li, Y. Wu, W. Zeng, Y. Li, L. Xu, X. Qiu and W. Huang, *ACS Sustainable Chem. Eng.*, 2016, **4**, 2004–2011.

112 H. Pan, G. Sun and T. Zhao, *Int. J. Biol. Macromol.*, 2013, **59**, 221–226.

113 H. Zhang, B. Yu, W. Zhou, X. Liu and F. Chen, *Int. J. Biol. Macromol.*, 2018, **109**, 1232–1238.

114 Y. Xue, X. Qiu, Y. Wu, Y. Qian, M. Zhou, Y. Deng and Y. Li, *Polym. Chem.*, 2016, **7**, 3502–3508.

115 V. I. Chursin, *Russ. J. Appl. Chem.*, 2010, **83**, 312–315.

116 B. M. Cerrutti, C. S. de Souza, A. Castellan, R. Ruggiero and E. Frollini, *Ind. Crops Prod.*, 2012, **36**, 108–115.

117 S. Li, J. A. Willoughby and O. J. Rojas, *ChemSusChem*, 2016, **9**, 2460–2469.

118 W. Lange and W. Schweers, *Wood Sci. Technol.*, 1980, **14**, 1–7.

119 K. Shweta and H. Jha, *Bioresour. Bioprocess.*, 2016, **3**, 31.

120 S. Li, W. Xiang, M. Jarvinen, T. Lappalainen, K. Salminen and O. J. Rojas, *ACS Appl. Mater. Interfaces*, 2016, **8**, 19827–19835.

121 S. Li, D. Ogunkoya, T. Fang, J. Willoughby and O. J. Rojas, *J. Colloid Interface Sci.*, 2016, **482**, 27–38.

122 L. H. Gan, M. S. Zhou and X. Q. Qiu, *Adv. Mater. Res.*, 2012, **550**, 1293–1298.

123 K. Bahrpaima and P. Fatehi, *ChemSusChem*, 2018, **11**, 2967–2980.

124 C. Chen, M. Zhu, M. Li, Y. Fan and R. C. Sun, *Biotechnol. Biofuels*, 2016, **9**, 87.

125 F. Ferdosian, Z. Yuan, M. Anderson and C. C. Xu, *J. Sci. Technol. For. Prod. Processes*, 2012, **2**, 11–15.

126 N. Ding, X. Wang, Y. Tian, L. Yang, H. Chen and Z. Wang, *Polym. Eng. Sci.*, 2014, **54**, 2777–2784.

127 G. H. Delmas, B. Benjelloun-Mlayah, Y. L. Bigot and M. Delmas, *J. Appl. Polym. Sci.*, 2013, **127**, 1863–1872.

128 Y. Nonaka, B. Tomita and Y. Hatano, *Holzforschung*, 1997, **51**, 183–187.

129 E. Cortes-Trivino, C. Valencia, M. Delgado and J. Franco, *Polymer*, 2018, **10**, 670.

130 A. L. Brocas, G. Cendejas, S. Caillol, A. Deffieux and S. Carlotti, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 2677–2684.

131 S. Nikafshar, O. Zabihi, Y. Moradi, M. Ahmadi, S. Amiri and M. Naebe, *Polymer*, 2017, **9**, 266.

132 S. Wang, S. Ma, C. Xu, Y. Liu, J. Dai, Z. Wang and J. Zhu, *Macromolecules*, 2017, **50**, 1892–1901.

133 K. Hofmann and W. G. Glasser, *J. Adhes.*, 1993, **40**, 229–241.

134 T. A. Khan, J. H. Lee and H. J. Kim, *Lignocellulose for Future Bioeconomy*, Elsevier, Amsterdam, 2019.

135 Q. Yin, W. Yang, C. Sun and M. Di, *BioResources*, 2012, 7, 5737–5748.

136 I. Kuhnel, J. Podschun, B. Saake and R. Lehnen, *Holzforschung*, 2015, **69**, 531–538.

137 I. Kuhnel, B. Saake and R. Lehnen, *React. Funct. Polym.*, 2017, **120**, 83–91.

138 I. Kuhnel, B. Saake and R. Lehnen, *Ind. Crops Prod.*, 2017, **101**, 75–83.

139 C. A. Cateto, M. F. Barreiro, A. E. Rodrigues and M. N. Belgacem, *Ind. Eng. Chem. Res.*, 2009, **48**, 2583–2589.

140 B. Ahvazi, O. Wojciechowicz, T. M. Ton-That and J. Hawari, *J. Agric. Food Chem.*, 2011, **59**, 10505–10516.

141 H. Sadeghifar, C. Cui and D. S. Argyropoulos, *Ind. Eng. Chem. Res.*, 2012, **51**, 16713–16720.

142 B. Berrima, G. Mortha, S. Boufi, E. El Aloui and M. N. Belgacem, *Cellul. Chem. Technol.*, 2016, **50**, 941–950.

143 H. Nadji, C. Bruzzèse, M. N. Belgacem, A. Benaboura and A. Gandini, *Macromol. Mater. Eng.*, 2005, **290**, 1009–1016.

144 Y. Li and A. J. Ragauskas, *J. Wood Chem. Technol.*, 2012, **32**, 210–224.

145 A. Arbenz and L. Averous, *RSC Adv.*, 2014, **4**, 61564–61572.

146 J. Busch, *J. Am. Coll. Toxicol.*, 1987, **6**, 23–51.

147 D. S. Argyropoulos, *US Pat*, 61601181, 2012.

148 W. G. Glasser and O. H. H. Hsu, *US Pat*, 4017474, 1977.

149 L. T. Monson and W. J. Dickson, *US Pat*, 2854444, 1958.

150 C. Cui, H. Sadeghifar, S. Sen and D. S. Argyropoulos, *BioResources*, 2013, **8**, 864–886.

151 I. Kühnel, B. Saake and R. Lehnen, *Macromol. Chem. Phys.*, 2018, **219**, 613.

152 M. Wanga, Z. Wanga, Z. Sun and H. Jiang, *React. Kinet. Catal. Lett.*, 2005, **84**, 223–228.

153 J. Lisperguer, C. Nunez and P. Perez-Guerrero, *J. Chil. Chem. Soc.*, 2013, **58**, 1937–1940.

154 N. Blank, I. Schober, P. R. Von Rohr and T. Voitl, *US Pat*, 13257733, 2010.

155 X. Zhao, Y. Zhang, L. Wie, H. Hu, Z. Huang, M. Yang, A. Huang, J. Wua and Z. Fenga, *RSC Adv.*, 2017, **7**, 52382–52390.

156 L. Li, Y. Hu and F. Cheng, *BioResources*, 2015, **10**, 3181–3196.

157 P. Buono, A. Duval, P. Verge, L. Averous and Y. Habibi, *ACS Sustainable Chem. Eng.*, 2016, **4**, 5212–5222.

158 S. Chatterjee, A. Clingenpeel, A. McKenna, O. Rios and A. Johs, *RSC Adv.*, 2014, **4**, 4743–4753.

159 K. A. Koivu, H. Sadeghifar, P. A. Nousiainen, D. S. Argyropoulos and J. Sipilä, *ACS Sustainable Chem. Eng.*, 2016, **4**, 5238–5247.

160 L. Dehne, C. V. Babarro, B. Saake and K. U. Schwarz, *Ind. Crops Prod.*, 2016, **86**, 320–328.

161 S. Luo, J. Cao and A. G. McDonald, *Ind. Crops Prod.*, 2017, **97**, 281–291.

162 Y. Pu and A. J. Ragauskas, *Can. J. Chem.*, 2005, **83**, 2132–2139.

163 Y. Teramoto, S. H. Lee and T. Endo, *Polym. J.*, 2009, **41**, 219.

164 H. F. Lewis and F. E. Brauns, *US Pat*, 2429102, 1947.

165 R. Ding, H. Wu, M. Thunga, N. Bowler and M. R. Kessler, *Carbon*, 2016, **100**, 126–136.

166 W. G. Glasser and R. K. Jain, *Holzforschung*, 1993, **47**, 225–233.

167 M. Thunga, K. Chen, D. Grewell and M. R. Kessler, *Carbon*, 2014, **68**, 159–166.

168 L. Dehne, C. Vila, B. Saake and K. U. Schwarz, *J. Appl. Polym. Sci.*, 2017, **134**, 44582.

169 W. Thielemans and R. P. Wool, *Composites, Part A*, 2004, **35**, 327–338.

170 J. H. Lora and W. G. Glasser, *J. Polym. Environ.*, 2002, **10**, 39–48.

171 G. Marchand, C. A. Calliste, R. M. Williams, C. McLure, S. Leroy-Lhez and N. Villandier, *ChemistrySelect*, 2018, **3**, 5512–5516.

172 E. L. Hult, K. Koivu, J. Asikkala, J. Ropponen, P. Wrigstedt, J. Sipilä and K. Poppius-Levlin, *Holzforschung*, 2013, **67**, 899–905.

173 O. Gordobil, R. Herrera, R. Llano-Ponte and J. Labidi, *Prog. Org. Coat.*, 2017, **103**, 143–151.

174 N. Cachet, S. Camy, B. Benjelloun-Mlayah, J. S. Condoret and M. Delmas, *Ind. Crops Prod.*, 2014, **58**, 287–297.

175 Y. Chen, N. M. Stark, Z. Cai, C. R. Frihart, L. F. Lorenz and R. E. Ibach, *BioResources*, 2014, **9**, 5488–5500.

176 T. Sonoda, T. Ona, H. Yokoi, Y. Ishida, H. Ohtani and S. Tsuge, *Anal. Chem.*, 2001, **73**, 5429–5435.

177 N. E. Mansouri and J. Salvadó, *Ind. Crops Prod.*, 2006, **24**, 8–16.

178 H. Sadeghifar, S. Sen and S. V. Patil, *ACS Sustainable Chem. Eng.*, 2016, **4**, 5230–5237.

179 D. A. Baker and T. G. Rials, *J. Appl. Polym. Sci.*, 2013, **130**, 713–728.

180 M. Wang and L. Yang, *J. Polym. Environ.*, 2012, **20**, 783–787.

181 S. Sen, S. Patil and D. S. Argyropoulos, *Green Chem.*, 2015, **17**, 1077–1087.

182 K. Iiyama and R. Pant, *Wood Sci. Technol.*, 1988, **22**, 167–175.

183 D. E. McKinney, D. M. Carson, D. J. Clifford, R. D. Minard and P. G. Hatcher, *J. Anal. Appl. Pyrolysis*, 1995, **34**, 41–46.

184 D. Delledonne, F. Rivetti and U. Romano, *J. Organomet. Chem.*, 1995, **488**, 15–19.

185 F. Chen, H. Dai, X. Dong, J. Yang and M. Zhong, *Polym. Compos.*, 2011, **32**, 1019–1025.

186 S. Sarkanen and Y. Li, *US Pat*, 6172204, 2001.

187 M. Tajvidi, R. H. Falk and J. C. Hermanson, *J. Appl. Polym. Sci.*, 2006, **101**, 4341–4349.

188 Y. Li and S. Sarkanen, *Macromolecules*, 2002, **35**, 9707–9715.

189 A. Sequeiros, L. Serrano and J. Labidi, *J. Chem. Technol. Biotechnol.*, 2016, **91**, 1809–1815.

190 N. N. Shorygina and L. I. Kolotova, *Russ. Chem. Bull.*, 1953, **2**, 505–508.

191 S. C. Puri, S. M. Anand and C. K. Atal, *Indian J. Chem.*, 1985, **16**, 294–295.

192 W. Zhao, L. P. Xiao, G. Song, R. C. Sun, L. He, S. Singh and G. Cheng, *Green Chem.*, 2017, **19**, 3272–3281.

193 A. Longoria, R. Tinoco and R. Vázquez-Duhalt, *Chemosphere*, 2008, **72**, 485–490.

194 J. G. Speight, *Environmental organic chemistry for engineers*, Butterworth-Heinemann, Oxford, 2016.

195 D. N. S. Hon, *Chemical modification of lignocellulosic materials*, CRC Press, New York, 1995.

196 X. Du, J. Li and M. E. Lindstrom, *Ind. Crops Prod.*, 2014, **52**, 729–735.

197 X. Liu, H. Zhu, C. Qin, J. Zhou, J. R. Zhao and S. Wang, *BioResources*, 2013, **8**, 2257–2269.

198 H. Dong, W. Peng and L. N. Lewis, *US Pat*, 9181405, 2013.

199 Y. Matsushita and S. Yasuda, *J. Wood Sci.*, 2003, **49**, 166–171.

200 Y. Matsushita, A. Iwatsuki and S. Yasuda, *J. Wood Sci.*, 2004, **50**, 540–544.

201 R. Fang, X. Cheng and X. Xu, *Bioresour. Technol.*, 2010, **101**, 7323–7329.

202 H. Ruihua, Y. Bingchao, D. Zheng and B. Wang, *J. Mater. Sci.*, 2012, **47**, 845–851.

203 H. Harmita, K. G. Karthikeyan and X. Pan, *Bioresour. Technol.*, 2009, **100**, 6183–6191.

204 J. Aguado, J. M. Arsuaga, A. Arencibia, M. Lindo and V. Gascón, *J. Hazard. Mater.*, 2009, **163**, 213–221.

205 J. Tian, S. Ren, G. Fang, Y. Ma and Q. Ai, *BioResources*, 2014, **9**, 6290–6303.

206 C. Cai, X. Zhan, M. Zeng, H. Lou, Y. Pang, J. Yang and X. Qiu, *Green Chem.*, 2017, **19**, 5479–5487.

207 T. Zheng, D. Zheng, X. Li, C. Cai, H. Lou, W. Liu and X. Qiu, *ACS Sustainable Chem. Eng.*, 2017, **5**, 7743–7750.

208 F. Kong, K. Parhiala, S. Wang and P. Fatehi, *Eur. Polym. J.*, 2015, **67**, 335–345.

209 R. Wahlstrom, A. Kalliola, J. Heikkinen, H. Kyllonen and T. Tamminen, *Ind. Crops Prod.*, 2017, **104**, 188–194.

210 C. Cheng, J. Wang, D. Shen, J. Xue, S. Guan, S. Gu and K. Luo, *Polymer*, 2017, **9**, 240.

211 J. C. Villar, A. Caperos and F. Garcia-Ochoa, *Wood Sci. Technol.*, 2001, **35**, 245–255.

212 Q. Xiang and Y. Y. Lee, *Appl. Biochem. Biotechnol.*, 2000, **84**, 153–162.

213 J. M. Chan, S. Bauer, H. Sorek, S. Sreekumar, K. Wang and F. D. Toste, *ACS Catal.*, 2013, **3**, 1369–1377.

214 S. K. Hanson, R. Wu and L. A. P. Silks, *Angew. Chem.*, 2012, **124**, 3466–3469.

215 S. Son and F. D. Toste, *Angew. Chem., Int. Ed.*, 2010, **49**, 3791–3794.

216 M. Wang, J. Lu, X. Zhang, L. Li, H. Li, N. Luo and F. Wang, *ACS Catal.*, 2016, **6**, 6086–6090.

217 V. E. Tarabanko, N. A. Fomova, B. N. Kuznetsov, N. M. Ivanchenko and A. V. Kudryashev, *React. Kinet. Catal. Lett.*, 1995, **55**, 161–170.

218 J. C. Villar, A. Caperos and F. García-Ochoa, *React. Kinet. Catal. Lett.*, 1997, **17**, 259–285.

219 G. Tong, Y. Matsumoto and G. Meshitsuka, *J. Wood Sci.*, 2000, **46**, 371–375.

220 S. Rovio, S. Kuitunen, T. Ohra-aho, S. Alakurtti, A. Kalliola and T. Tamminen, *Holzforschung*, 2011, **65**, 575–585.

221 F. G. Sales, C. A. M. Abreu and J. A. F. R. Pereira, *Braz. J. Chem. Eng.*, 2004, **21**, 211–218.

222 T. A. D. Nguyen, A. M. Wright, J. S. Page, G. Wu and T. W. Hayton, *Inorg. Chem.*, 2014, **53**, 11377–11387.

223 M. Tian, J. Wen, D. MacDonald, R. M. Asmussen and A. Chen, *Electrochem. Commun.*, 2010, **12**, 527–530.

224 C. Zhu, W. Ding, T. Shen, C. Tang, C. Sun, S. Xu and H. Ying, *ChemSusChem*, 2015, **8**, 1768–1778.

225 R. Behling, S. Valange and G. Chatel, *Green Chem.*, 2016, **18**, 1839–1854.

226 J. Gierer, *Wood Sci. Technol.*, 1986, **20**, 1–33.

227 R. Ma, Y. Xu and X. Zhang, *ChemSusChem*, 2015, **8**, 24–51.

228 R. Prado, A. Brandt, X. Erdocia, J. Hallet, T. Welton and J. Labidi, *Green Chem.*, 2016, **18**, 834–841.

229 J. Marton, S. C. Charleston and E. Adler, *US Pat*, 3071570, 1963.

230 T. Okamoto, H. Takeda, T. Funabiki, M. Takatani and R. Hamada, *React. Kinet. Catal. Lett.*, 1996, **58**, 237–242.

231 S. Dabral, H. Wotruba, J. G. Hernández and C. Bolm, *ACS Sustainable Chem. Eng.*, 2018, **6**, 3242–3254.

232 A. Rahimi, A. Ulbrich, J. J. Coon and S. S. Stahl, *Nature*, 2014, **515**, 249.

233 W. Hoareau, W. G. Trindade, B. Siegmund, A. Castellan and E. Frollini, *Polym. Degrad. Stab.*, 2004, **86**, 567–576.

234 J. Mottweiler, M. Puche, C. Räuber, T. Schmidt, P. Concepción, A. Corma and C. Bolm, *ChemSusChem*, 2016, **8**, 2106–2113.

235 J. D. Araújo, C. A. Grande and A. E. Rodrigues, *Chem. Eng. Res. Des.*, 2010, **88**, 1024–1032.

236 A. Das, A. Rahimi, A. Ulbrich, M. Alherech, A. H. Motagamwala, A. Bhalla and B. E. Dale, *ACS Sustainable Chem. Eng.*, 2018, **6**, 3367–3374.

237 E. I. Evstigneyev, O. S. Yuzikhin, A. A. Gurinov, A. Y. Ivanov, T. O. Artamonova, M. A. Khodorkovskiy and A. V. Vasilyev, *J. Wood Chem. Technol.*, 2016, **36**, 259–269.

238 A. Mancera, V. Fierro, A. Pizzi, S. Dumarçay, P. Gérardin, J. Velásquez and A. Celzard, *Polym. Degrad. Stab.*, 2010, **95**, 470–476.

239 R. L. Couch, J. T. Price and P. Fatehi, *ACS Sustainable Chem. Eng.*, 2016, **4**, 1954–1962.

240 W. He, W. Gao and P. Fatehi, *ACS Sustainable Chem. Eng.*, 2017, **5**, 10597–10605.

241 J. J. Meister, *J. Macromol. Sci., Polym. Rev.*, 2002, **42**, 235–289.

242 Y. Sun, M. Fenster, A. Yu, R. M. Berry and D. S. Argyropoulos, *Can. J. Chem.*, 1999, **77**, 667–675.

243 C. Crestini, P. Pro, V. Neri and R. Saladino, *Bioorg. Med. Chem.*, 2005, **13**, 2569–2578.

244 K. R. Kavanagh and J. M. Pepper, *Can. J. Chem.*, 1955, **33**, 24–30.

245 S. Kagawa, *Jpn. TAPPI J.*, 1970, **24**, 424–428.

246 Y. Sang, B. Wang, Q. Wang, G. Zhao and P. Guo, *Sci. Rep.*, 2014, **4**, 6321.

247 M. N. Alam and T. G. Van De Ven, *J. Sci. Technol. For. Prod. Processes*, 2014, **4**, 22–26.

248 D. E. Bland, G. Ho and W. E. Cohen, *Aust. J. Chem.*, 1950, **3**, 642–648.

249 R. Yang, L. Lucia, A. J. Ragauskas and H. Jameel, *J. Wood Chem. Technol.*, 2003, **23**, 13–29.

250 T. Higuchi, *J. Biochem.*, 1985, **45**, 675–685.

251 J. C. Pew, *J. Am. Chem. Soc.*, 1955, **77**, 2831–2833.

252 L. Klapiszewski, J. Zdarta, T. Szatkowski, M. Wysokowski, M. Nowacka, K. Szwarc-Rzepka and T. Jesionowski, *Open Chem.*, 2014, **12**, 719–735.

253 S. Hamdani, C. Longuet, D. Perrin, J. M. Lopez-cuesta and F. Ganachaud, *Polym. Degrad. Stab.*, 2009, **94**, 465–495.

254 J. Zhang, E. Fleury, Y. Chen and M. A. Brook, *RSC Adv.*, 2015, **5**, 103907–103914.

255 T. Budnyak, S. Aminzadeh, I. Pylypchuk, A. Riazanova, V. Tertykh, M. Lindström and O. Sevastyanova, *Nanomaterials*, 2018, **8**, 950.

256 W. Xiong, X. Qiu, D. Yang, R. Zhong, Y. Qian, Y. Li and H. Wang, *Chem. Eng. J.*, 2017, **326**, 803–810.

257 J. F. Kadla and S. Kubo, *Composites, Part A*, 2004, **35**, 395–400.

258 P. Bruijnincx, B. Weckhuysen, G. J. Gruter and E. Engelen-Smeets, *Lignin valorisation: The importance of a full value chain approach*, Utrecht University, Google Books, 2016.

259 L. Kouisni, A. Gagné, K. Maki, P. Holt-Hindle and M. Paleologou, *ACS Sustainable Chem. Eng.*, 2016, **4**, 5152–5159.

260 J. Kihlman, *Nord. Pulp Pap. Res. J.*, 2016, **31**, 573–582.

261 M. Abraham, *Encyclopedia of sustainable technologies. Elsevier*, Cambridge, 2017.

262 N. Smolarski, Frost & Sullivan, https://www.greenmaterials.fr/wp-content/uploads/2013/01/High-value-Opportunities-for-Lignin-Unlocking-its-Potential-Market-Insights.pdf, (accessed August 2019).

263 LigniMATCH online, https://www.gmv.gu.se/digitalAssets/1448/1448662_roadmap.pdf, (accessed August 2019).