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Chapter 6

LIGNIN-BASED THERMOSET RESINS

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ABSTRACT

Lignin as a polyphenolic non-toxic bio-renewable polymer has been considered a promising candidate to replace phenol – a relatively costly and toxic substance – to reduce the carbon footprint and cost of phenolic resins. A detailed look at the current status of research in regard to lignin-based resins is presented. The discussion includes resins synthesized using lignin sourced from traditional pulping processes and the more recent biorefinery-based technologies, as well as the challenges facing lignin valorization.

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INTRODUCTION

Conversion of biomass to renewable energy, materials and chemicals in biorefineries has long been considered a viable solution to the multifaceted problem of sustainability. However, competing in terms of economic viability with the petroleum industry is a major challenge for biorefineries. Both first and second generation biorefineries are focused on carbohydrate conversion, but it is becoming increasingly evident that valorization of the lignin streams delineates the success of the second generation lignocellulosic biorefineries. This is also emphasized in the Bioeconomy Initiative Implementation Framework report released by the US-BRDC in 2019 (Biomass Research and Development Committee 2019).

The pulp industry is the largest source of lignin, and the vast majority of currently produced energy-rich lignin is burned for regenerating chemicals. This is an indispensable phase in the kraft process, which is a world dominant chemical pulping process. However, lignin as an aromatic polymer holds tremendous potential for use in non-fuel applications either in its polymeric form or as low molecular weight aromatic compounds after depolymerization (Holladay et al. 2007). Lignin in the polymeric form has been studied as an alternative for the production of various synthetic materials including resins, thermoplastics, carbon fibers, and activated carbon (Kubo and Kadla 2004; N. E. Mansouri, Pizzi, and Salvadó 2006; Liou 2010; Montané, Torné-Fernández, and Fierro 2005). In comparison to their synthetic counterparts, lignin-based materials are eco-friendly and more economically feasible (Hill et al. 2006; Ragauskas et al. 2014). In addition, they are light weight (H. Zhang, Fu, and Chen 2020), and have UV-absorption, antioxidizing and antimicrobial properties, which can prolong the shelf-life of materials (Barclay, Xi, and Norris 1997; X. Pan et al. 2006).

Lignin as a polyphenol is of particular interest for substituting phenol in phenolic resins. Phenol-formaldehyde (PF) is a ubiquitous polymer with unrivaled mechanical strength, thermal stability, and chemical resistance with diverse applications including composites, laminates, coatings, molding compounds, friction materials, and abrasives (Pilato 2013). The PF resin market is valued at $10 billion globally, with an annual market value between $4.5 billion and $6 billion. Furthermore, ~ 95% of phenol used in the production of PF resins is derived from petroleum products (Siddiqui et al. 2017). Formaldehyde is manufactured by catalytic oxidation of methanol, with a global production of over 52 million t in 2017 and a projected annual growth of 4% in 2020. An estimated 70% of formaldehyde is used in the production of resins (Dugheri et al. 2017).

During the period of December 2019 to June 2020, the cost of phenol varied from $696/t to $1,107/t (EChemi n.d.). On the contrary, the price of kraft lignin is estimated to range from $260-500/t (Ludmila et al. 2015). The cost of LignoForce™ lignin is approximated at $600/t (Dessbesell et al. 2020).

Moreover, demands based on the ever-increasing societal pressure combined with environmental policies for a more sustainable world have initiated efforts to find more environmentally acceptable alternatives to both phenol and formaldehyde in the last several decades. In addition to being petrochemical products with ecotoxic effects, phenol and formaldehyde have adverse effects on human health. The LD_{50} values in rats are 317 mg/kg and 65 mg/kg for phenol and formaldehyde, respectively (Chung and Washburn 2013). In 2008, formaldehyde was classified as a carcinogen by the Environmental Protection Agency (EPA) urging for its removal from consumer products. These necessitate the search for alternatives that are safe for human use, eco-friendly and economical.

This report overviews select literature on lignin-based resins as alternatives to PF resins. In addition to the lignin regenerated from various pulping processes, potential routes for resin production from lignin-containing streams that remain underutilized in growing biorefineries focused on carbohydrate conversion are also highlighted. These include lignin-rich residues after enzymatic hydrolysis of pretreated biomass, and

lignin-containing liquor streams from various pretreatment processes such as steam explosion, hydrothermal, alkali or organosolv. The various approaches to improve reactivity via various modification methods such as hydroxymethylation or methyloylation (Vázquez et al. 1997; Gonçalves and Benar 2001), phenolation (Çetin, N.S; Özmen, N. 2003; Ma et al. 2011; Lee, Chang, and Tseng 2012), demethylation (Olivares et al. 1988), oxidation, reduction and alkali hydrolysis (L. Hu et al. 2011; Siddiqui et al. 2017), as well as natural crosslinkers – glyoxal, furfuryl alcohol, furfural, glutaraldehyde, and aromatic aldehydes as formaldehyde alternatives (Younesi-Kordkheili and Pizzi 2019; Dongre et al. 2015; Deka, Mohanty, and Misra 2014; da Silva et al. 2013; Gabriel Foyer et al. 2016) are also discussed. Challenges to lignin valorization including availability, heterogeneity of lignin, mechanical properties of resins, and frequently reported poor thermal stability are presented.

LIGNIN STRUCTURE

In addition to the polysaccharides, cellulose and hemicelluloses, the third structural constituent of lignocellulosics is lignin, an aromatic polymer whose incorporation leads to the stiffening of plants. By providing resistance against the gravitational force, lignin plays a vital role in the survival of land plants (Ralph, Brunow, and Boerjan 2007). This unprecedented reinforcing ability might have also sparked the original idea of using lignin in thermoset resins.

Lignin, which accounts for 12%–33% of lignocellulosic biomass, is composed of three phenylpropanoid C_9 units linked by randomly distributed ether and C-C bonds, with ether bonds being the major bonds; dominant β-aryl ether bonds. Three hydroxycinnamyl alcohols, lignin precursors, monomers or monolignols: *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol participate in the last phase of lignin biosynthesis, called dehydrogenative polymerization, DHP, (Rinaldi et al. 2016; Ralph, Brunow, and Boerjan 2007).

During DHP, monolignols, differing in degree of methoxylation on the aromatic ring, produce *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, respectively (Figure 1). Softwood, hardwood, and herbaceous/Gramineae lignins differ in the content of C_9 units. Softwoods consist of G-lignin which contains some H-units, (<5%). Hardwoods consist of SG-lignin with traces of H-units, while Gramineae consist of HSG-lignin, where the H-unit content is usually <15% (Ralph, Brunow, and Boerjan 2007). During DHP, *p*-coumaryl alcohol and coniferyl alcohol undergo coupling with participation of the C_3/C_5 available positions forming condensed structures, in contrast to sinapyl alcohol which cannot couple through these positions. Therefore, softwood G-lignin is more condensed than both SG- and HSG-lignins (Rinaldi et al. 2016). Lignin monomers may be acylated at the γ-carbon and participate in lignin biosynthesis as acetates, *p*-hydroxybenzoates (specifically in *Salicaceae*) or *p*-coumarates (specifically in Gramineae). The presence of "uncommon" lignin monomers, such as cinnamaldehydes and benzaldehydes has also been detected. Cinnamic acids, specifically ferulic acid may participate in DHP, especially in Gramineae (Ralph, Brunow, and Boerjan 2007; Boerjan, Ralph, and Baucher 2003). Therefore, lignin presents a versatile structure in regard to the presence of building units, although G- and S-units, followed by H-units dominate and govern lignin structure, properties, and reactivity. Lignin has been recognized as one of the major contributors to an intrinsic resistance of lignocellulosics to biodegradation; recalcitrance. An intertwined polymer network in combination with chemical bonds between lignin and polysaccharides/hemicelluloses promotes this resistance through the formation of impenetrable composite structure. Therefore, in a typical biorefinery design, lignocellulosics are pretreated to facilitate the access of enzymes and maximize yields of fermentable sugars/glucose during enzymatic hydrolysis of polysaccharides/cellulose (F. Hu and Ragauskas 2012).

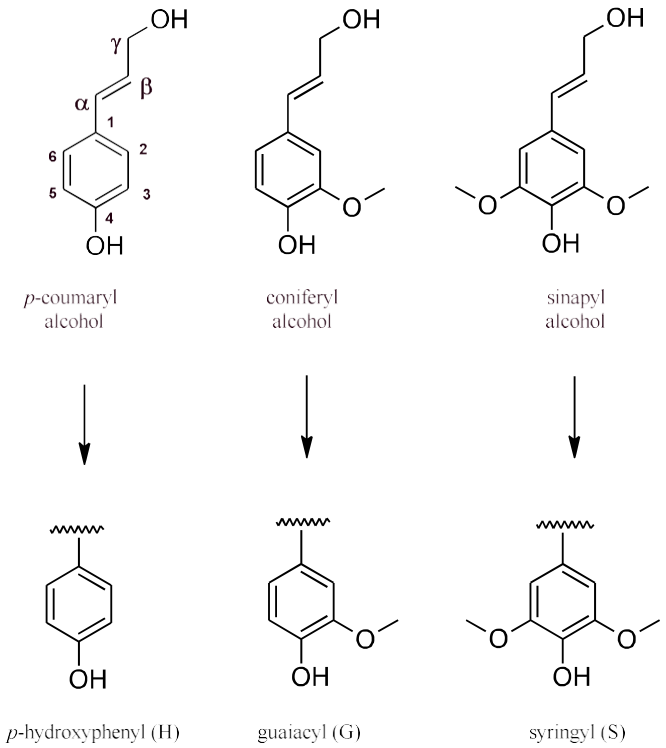

Figure 1. Lignin precursors, *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol and lignin phenylpropanoid H-, G-, and S-units, respectively. Adapted from (Vanholme et al. 2010).

TECHNICAL LIGNINS

Technical or industrially produced lignins are categorized as either sulfur-containing or sulfur-free lignins. Sulfur-containing lignins are extracted from lignocellulosics in chemical processes using sulfur-containing chemicals, specifically kraft and sulfite delignification, which produce kraft lignin and lignosulfonates (LSs), respectively. Sulfur-free lignins are either generated in non-sulfur based chemical delignification processes soda and organosolv, or in novel processes proposed for use in lignocellulosic biorefineries.

Kraft pulping is the world's leading chemical pulping process, with 184 million t of kraft pulp produced worldwide in 2017 (UN FOA 2019). It also produces the largest amount of technical lignin, as kraft lignin accounts for approximately 85% of the 50–70 million t/year total lignin produced worldwide (Thébault, Müller, et al. 2017). This lignin, valued at $732.7 million in 2015, is expected to be valued at $913.1 million by 2025 with a compound annual growth rate (CAGR) of 2.2%, indicating an increase in demand (Bajwa et al. 2019). However, only about 2–3% of the total lignin produced, 1.6 million t/year (Dessbesell et al. 2020), is used in non-fuel applications. In 2018, LSs dominated commercial use at 1.3 million t, followed by 0.265 million t of kraft lignin, and 0.075 million t of enzymatic hydrolysis lignin (EHL) and soda lignin (Dessbesell et al. 2020).

In the conventional kraft process, acidification of black liquor to recover kraft lignin is rare, as kraft lignin is burnt in the recovery boiler for the production of heat and power; e.g., LignoBoost has a HHV of 26.7 MJ/kg (Tomani 2010). However, kraft mills may experience an overload on the recovery boiler, especially if aged, exceeding their heat transfer capacity and experience bottlenecking. Debottlenecking can be achieved by recovering a portion of the kraft lignin from the black liquor to create new economic revenues (Tomani 2010). The LignoBoost process encompasses acidification of the black liquor, filtration, and resuspension of lignin in conjunction with an elaborate washing procedure has been patented to produce a low-ash high quality kraft lignin (Ohman et al. 2010). LignoBoost lignin has been produced by Domtar, Plymouth, NC with an annual production of 25,000 t (Biochoice™ lignin mainly from Southern pines), and by Stora Enso, Sunila, Finland with an annual production of 50,000 t (spruce and pine) (Valmet n.d.).

In line with the LignoBoost process mentioned earlier, a different method has been suggested in the patented production of LignoForce kraft lignin (Kouisni and Paleologou 2014). Here, black liquor is oxidized first to reduce emission of volatile sulfur-containing compounds in the following acidification step. This lignin has been produced at 30 t/day by West Fraser, Alberta, Canada since 2016 (Kouisni et al. 2016).

LSs represent sulfur-containing lignins recovered at the end of sulfite pulping and account for 79% of the commercially used lignin today (Dessbesell et al. 2020). Based on the pH and base used, LSs can be calcium or magnesium (acid sulfite pulping), ammonium (neutral sulfite semi-chemical pulping; NSSC), or sodium (NSSC, alkaline sulfite pulping) LSs. The main producers are Borregaard LignoTech (Norway) and Tembec (Canada), which produced almost 40% of the world LSs in October 2016. However, due to a decreased interest in sulfite pulps, the world annual production of LSs has decreased from 1.6 million tons in 2000 to 1.1. million tons in 2016 (Aro and Fatehi 2017), with a 1% CAGR only (Dessbesell et al. 2020).

Table 1. Acid-insoluble (AISL) and acid-soluble (ASL) lignin content of various lignins

Treatment	Source	Lignin content (% OD)			Species
		AISL	ASL	Total	
Kraft	SW	91.3	2.8	94.1	NS[1]
Soda	NS[1]	86.4	11.5	97.9	NS[1]
Organosolv	HW	38.8	3.7	42.5	NS[2]
	AG	88.2-96.2	1.1-2.7	88.4–97.7	Wheat straw[3]
		92.3	1.9	94.2	Miscanthus[1]
Steam explosion	HW	86.6	1.4	88.0	Poplar[1]
Hot-water extraction	HW	86.4	1.9	88.3	Sugar Maple[4]
		80.2	4.5	84.7	Willow[5]
	AG	74.7	4.7	79.4	Miscanthus[6]
		77.0	3.7	81.0	Wheat straw[6]
Mild acid hydrolysis	HW	71.2	6.2	77.4	Sugar Maple[6,a]
		87.7	10.3	98.0	Eucalyptus[7]
EHL	AG	83.47	3.69	87.16	Corn stalk[8]

1 (N.-E. E. Mansouri and Salvadó 2006); **2** (W. Zhang, Ma, Xu, et al. 2013); **3** (Huijgen et al. 2014): Lignins from 10 organosolv treatments; **4** (Dongre et al. 2015); **5** (Dongre and Bujanovic 2019); **6** (Dongre 2018); **7** (Vázquez et al. 1997): acetosolv process (acetic acid + HCl); **8** (G. Wang et al. 2018) **a**: weak acid treatment from Pure Lignin Environmental Technologies, Canada; **HW**: Hardwood; **SW:** Softwood; **AG**: Agricultural residue; **NS**: Not specified.

Table 2. Free phenolic hydroxyl groups (PhOH) and S/G ratio of various lignins

Treatment	Source	Phenolic hydroxyl groups (PhOH)		S/G ratio	Method	Species
		mmol/g	Method			
Kraft	HW	4.16	^{31}P NMR	-	-	NS[1]
		2.29	^{1}H NMR	-	-	NS[2]
	SW	3.01	^{31}P NMR	N/A	N/A	Indulin[1,3]
		3.86	^{31}P NMR			NS[1]
		4.5	UV			NS[4]
		4.1	^{1}H NMR			NS[4]
LS	Sulfite	0.16	^{31}P NMR	-	-	NS[1]
	Calcium	2.0	UV	-	-	NS[4]
Soda	AG	3.05	^{31}P NMR	-	-	Wheat straw[2]
		1.41	^{1}H NMR	-	-	NS[5]
		4.40	UV	-	-	NS[6]
		4.50	^{1}H NMR	-	-	NS[6]
Organosolv	HW	3.05	^{31}P NMR	-	-	NS[1]
		1.92	^{1}H NMR	-	-	NS[2]
	SW	2.39	^{31}P NMR	N/A	N/A	NS[3]
	AG	1.23	^{31}P NMR	-	-	Corn stover[1,a]
		0.63-1.36	Wet chemistry	0.48-0.55	^{31}P NMR	Wheat straw[5]
		1.81-3.31	^{31}P NMR	-	-	Wheat straw[5]
		2.47	Wet chemistry	1.62	^{31}P NMR	Alcell[5]
		3.99	^{31}P NMR	-	-	Alcell[5]
		2.66	UV	-	-	Miscanthus[4]
		3.33	^{1}H NMR			Miscanthus[4]

Table 2. (Continued)

Treatment	Source	Phenolic hydroxyl groups (PhOH)		S/G ratio	Method	Species
		mmol/g	Method			
Steam explosion	HW	2.39	UV	-	-	Poplar[4]
		2.65	^{1}H NMR	-	--	Poplar[4]
Hot-water extraction	HW	1.95	Periodate			Sugar Maple[7]
		1.97		1.25	HSQC	Willow[6]
	AG	1.19	Periodate	1.90	HSQC	Wheat straw [7]
		2.42	^{31}P NMR	1.84	^{31}P NMR	Wheat straw [8]
		1.96	Periodate	2.86	HSQC	Miscanthus [6]
		2.91	^{31}P NMR	1.35	^{31}P NMR	Corn cob[8]
Mild acid Hydrolysis	HW	0.84	Periodate	2.76	HSQC	Sugar Maple[3,b]
EHL	AG	2.2	^{31}P NMR	-	-	Corn stover[1,2]

1 (Kalami et al. 2018); **2** (Tejado et al. 2007); **3** (Kalami et al. 2017); **4** (N.-E. E. Mansouri and Salvadó 2006); **5** (Huijgen et al. 2014): Lignins from 10 different organosolv treatments; **6** (Dongre and Bujanovic 2019); **7** (Dongre 2018); **8** (S. Yang et al. 2014); **a** Dilute acid pretreatment prior to enzymatic hydrolysis; **b**: : weak acid treatment from Pure Lignin Environmental Technologies, Canada; **HW**: Hardwood; **SW:** Softwood; **AG**: Agricultural residue; **NS**: Not Specified; **N/A:** Not applicable.

Table 3. Thermal properties and molecular weight distribution, number average (Mn), weight average (Mw) and polydispersity (PD), of various lignins

Treatment	Source	Tg, (°C)	Td (°C)	MWD			Species
				Mn	Mw	PD	
Kraft	HW	-	-	1300	3100	2.3	NS[1]
	SW	144	421	-	-	-	Pine[2]
		-	-	1790	4600	2.6	Indulin[1]
		-	-	1910	4590	2.4	NS[1]
		-	-	545	1099	2.0	NS[3]
		158	378	-	-	-	NS[4]
LS	SW	133	-	-	-	-	Mixed softwoods[5]
Soda	ASP	138	356	1500	2600	1.8	Flax[2]
		-	-	1600	4580	2.7	Wheat straw[3]
		-	-	647	1300	2.0	NS[6]
		189	365	-	-	-	Herbaceous[4]
Organosolv	HW	100	413	-	-	-	NS[2]
		-	-	1540	4080	2.6	NS[3]
		-	-	450	760	1.7	NS[7]
	SW	-	-	1450	5770	4.0	NS[3]
	AG	-	-	2300	9350	4.0	Corn stover[3]
		-	-	1123	2500	2.5	Miscanthus[6]
Steam explosion		-	-	795	2107	2.7	Poplar[6]
	HW	149	316	-	-	-	HW/Herbaceous[4]

Table 3. (Continued)

Treatment	Source	Tg, (°C)	Td (°C)	MWD			Species
				Mn	Mw	PD	
Hot-water extraction	HW	143	356	-	-	-	Sugar Maple[8]
		159	358	2186	5962	2.7	Willow[9]
		-	-	1825	3058	1.7	Sugar Maple[10]
	AG	123	358	2124	4672	2.2	Miscanthus[9]
		143	356	2850	12114	4.3	Wheat Straw[8]
EHL	AG	-	-	2400	5460	2.3	Corn stover[3]

1 (Kalami et al. 2018); 2 (Tejado et al. 2007); 3 (Kalami et al. 2017); 4 (Sameni et al. 2014); 5 (Tejado A. et al. 2007); 6 (N.-E. E. Mansouri and Salvadó 2006); 7 (W. Zhang, Ma, Xu, et al. 2013); 8 (Dongre 2018); 9 (Dongre and Bujanovic 2019); 10 (Dongre et al. 2015); ASP: Angiosperms; HW: Hardwood; SW: Softwood; AG: Agricultural residue; Tg: Glass transition temperature; Td: Thermal degradation temperature; NS: Not specified.

Sulfur-free lignins are organosolv lignins, soda lignins, and lignin recovered as a byproduct from biomass conversion technologies - biorefineries. Organosolv lignins are recovered from different organosolv delignification processes conducted mostly using Angiosperms. These include using organic solvents such as the ethanol-based Alcell process (Lora and Glasser 2002), and organic acids such as acetic acid-based acetosolv and formic-acid-based formasolv. Soda lignins are recovered from spent liquors of soda pulping, which is conducted mainly using herbaceous species; thus, soda lignins are mostly non-wood lignins such as LPS® lignins (Lora and Glasser 2002). Lignins from biorefineries include hydrolytic lignins as byproducts of autohydrolysis-based pretreatments such as steam explosion (for example Angiolin lignin from steam-explosion of hardwoods) (Lora and Glasser 2002) and liquid-hot water (Bozell et al. 2018), and enzymatic hydrolysis lignin-rich (EHL) residue (W. Zhang, Ma, Wang, et al. 2013; Jing et al. 2015; Qiao et al. 2015).

Technical lignins differ in their structure from lignin *in situ,* which is closely represented by lignins isolated in mild procedures such as milled wood lignin (MWL) (Sjöström and Alen 2013). The extent of lignin modification depends on the treatment severity. In this context, organosolv lignins and lignins recovered from mild pretreatment processes may be considered less modified, while kraft lignin undergoes significant changes (Argyropoulos and Crestini 2016; X. Pan et al. 2006). The properties of lignins, which primarily govern their reactivity and suitability for different polymer applications include purity (Table 1; lignin content), content of free phenolic hydroxyl groups (Table 2; PhOH-groups), and thermal properties and molecular weight distribution, including polydispersity, PD (Table 3). The wide range of properties make apparent the diversity of lignins available for use.

PHENOL-FORMALDEHYDE RESINS (PF)

PF resins are of two types—novolacs and resoles. Novolacs are prepared in acid conditions, and have a phenol to formaldehyde ratio of greater than 1. Novolacs require a curing agent owing to the lesser amount of formaldehyde present. The most common curing agent used in industry is hexamethylenetetramine (HMTA; $(CH_2)_6N_4$). In contrast, resoles are prepared in alkaline conditions and have a phenol to formaldehyde ratio of less than 1. No curing agent is required as there is a sufficient amount of formaldehyde in the mixture for curing to occur (H. Pan 2011). General chemical reactions producing novolac and resole resins are shown in Figure 2.

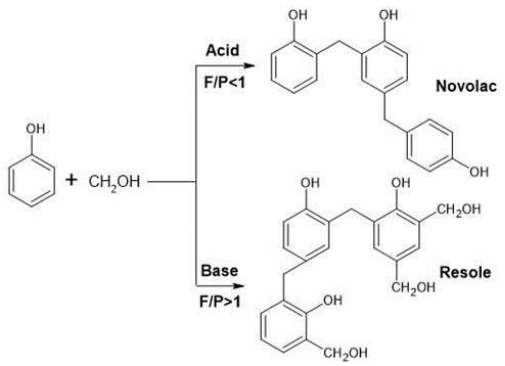

Figure 2. Production of phenol-formaldehyde (PF) resins. Figure adapted from (Y. Zhang 2014).

Novolacs

Novolacs are typically used in binder or fiber reinforcement applications such as brake friction materials. They act as a binder to maintain structural integrity when the friction materials are exposed to mechanical and thermal stresses. Brake friction materials contain several other components such as reinforcing fibers, abrasives, lubricants, and fillers. The amount of binders in brake friction materials can range from 20-40% (Chan and Stachowiak 2004). Important characteristics of friction materials are wear resistance and thermal stability, as temperatures in automotive brake parts can reach up to

1000 °F. Novolacs are also used for coating proppants in hydraulic fracturing indicating their greater expected growth rate in comparison to resoles (Pilato 2013).

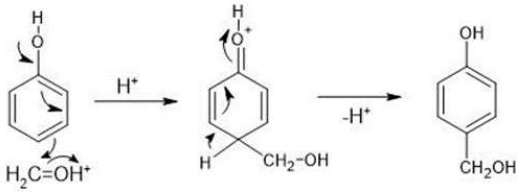

Figure 3. Step 1 of novolac formation: Formaldehyde reacts with phenol to form methylol phenol. Figure adapted from (Y. Zhang 2014).

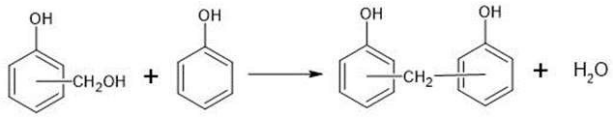

Figure 4. Step 2 of novolac formation: methylol phenol and phenol self-condense to form linear polymers. Figure adapted from (Y. Zhang 2014).

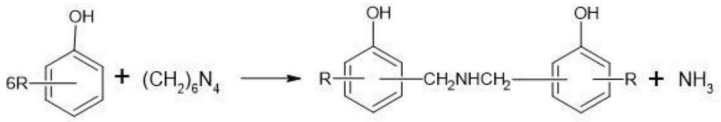

Figure 5. Step 3 of novolac formation: HMTA crosslinking novolac resin during curing process. Figure adapted from (Y. Zhang 2014).

Novolacs are synthesized with a molar excess of phenol to formaldehyde and in the presence of an acidic catalyst. The initial attack can occur at the 2-, 4- or 6- positions. The initial reaction is between formaldehyde and phenol (Pizzi 2003) (Figure 3). Subsequently, the methylol phenol reacts with phenol or other methylol phenol moieties to form a linear polymer (Pizzi 2003) (Figure 4). Methylene bridges are formed via this reaction and owing to the three potential sites for polymerization, branching occurs. As the reaction progresses, the random orientations and branching produce a complex polymer network. The reaction is terminated when the formaldehyde reactant is quenched. For further crosslinking to

occur, a curing agent such as HMTA is required to provide excess formaldehyde (Figure 5).

Resoles

Resoles are typically used in the production of composites, mineral wool/glass insulation, and as wood adhesives for plywood and particle board applications; although new regulations on free formaldehyde concentration adversely affect this use (Pilato 2013). A basic (alkaline) catalyst such as sodium hydroxide, and a molar excess of formaldehyde are required to make resole resins (Pizzi 2003). First, phenol reacts with formaldehyde to form methylene glycol (Figure 6).

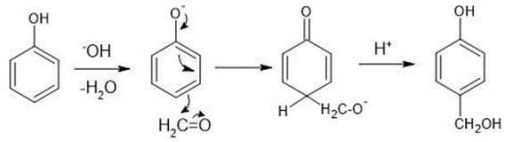

Figure 6. Step 1 of resole formation: Formaldehyde reacts with phenol to form methylol phenol. Figure adapted from (Y. Zhang 2014).

In the second step, methylol phenol can either react with itself or form dimethylene ether bridges with the release of water (Figure 7).

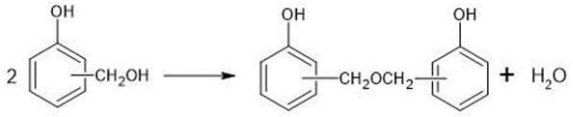

Figure 7. Step 2 of resole formation: Methylol phenol forms dimethylene ether bridges. Figure adapted from (Y. Zhang 2014).

LIGNIN-BASED RESINS

The use of lignin phenolic resins is not new, e.g., patents from the 1950s proposed to replace phenol with lignin-containing spent sulfite liquor in the production of thermosets and resins (Shen 1974).

Most reports attempt to use lignin to partially substitute phenol in PF resins in the production of lignin-based phenol formaldehyde (LPF) resins. Resole applications of these LPF resins as wood adhesives in plywood and particle board are more abundant (Alonso et al. 2011; Ma et al. 2011; Tejado et al. 2007; Tejado A. et al. 2007; Yang Sheng et al. 2015; Y. Zhang 2014). High pressure laminates (HPL) have been of particular interest for both resole and novolac resins. The commercial HPLs are manufactured when stacks of kraft papers are impregnated with PF resins cured at high temperature and pressure. This results in a composite material for durable decorative surfaces such as countertops. Resole resins for HPLs are found in furniture applications; novolacs are typically used in filters, battery separators and automotive brake parts (Dodiuk and Goodman 1999; Jing et al. 2015; Kuroe Motoki et al. 2012; Yan et al. 2017), with focus on partial substitution of phenol by lignin (Jing et al. 2015; J. M Pérez et al. 2011; J. M. Pérez et al. 2009; Juan Manuel Pérez et al. 2007). More recently novolacs have gained interest for use in electrical laminates in industry (Elvers 2016) offering new opportunities for incorporating lignin into resins, even if partially. Furthermore, technical sulfur-containing lignins, kraft lignin and/or LSs, are the primary sources of lignin in most studies. In addition, phenol- and formaldehyde-free eco-friendly resins are being investigated abetting efforts to produce sustainable chemicals.

The efficiency of lignin in this role is controlled by its ability to participate in polymerization reactions. The phenolic and aliphatic hydroxyl groups are considered essential in activating lignin for crosslinking with formaldehyde. In this context, in alkaline conditions used in the formulation of resole resins, free phenolic hydroxyl groups promote reactivity of lignin by formation of quinone methide intermediates with the activation of the *C_3/C_5 positions* for condensation with other phenolic units, and for the reaction with formaldehyde (Figure 8). In acid conditions used in the formulation of novolac resins, the presence of secondary aliphatic hydroxyl groups leads to the formation of carbocation, which results in the activation of the *C_2/C_6 positions* for reacting with lignin units and formaldehyde.

There are two methods of preparing lignin to synthesize lignin-based resins. The first method involves lignin purification (Jin, Cheng, and Zheng

2010) followed by modification by various methods, including methyloylation (hydroxymethylation) (Vázquez et al. 1997; Gonçalves and Benar 2001), phenolation (Çetin, N. S; Özmen, N. 2003; Ma et al. 2011; Lee, Chang, and Tseng 2012), demethylation (Olivares et al. 1988), oxidation, reduction, and alkali hydrolysis (L. Hu et al. 2011; Siddiqui et al. 2017). Modification is performed to improve the reactivity of lignin before incorporating it into the phenolic resins, in order to replace phenol more effectively.

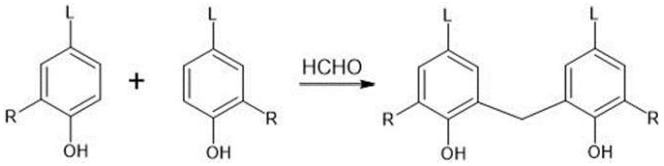

Figure 8. Proposed scheme for lignin-based resins in alkaline conditions. (R = H or OCH_3). Adapted from (Sen, Patil, and S. Argyropoulos 2015).

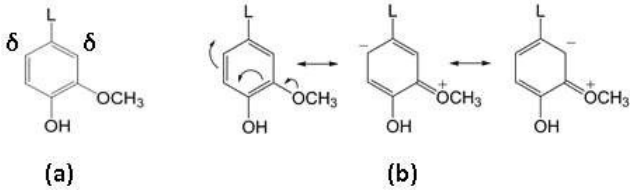

Figure 9. Mechanism that governs the presence of higher electron density on Position 2 and 6 on lignin units in acidic medium: (a) the induction effect of the alkyl group at Position 1; and (b) the resonance effect of the electron pairs on the methoxy oxygen (van der Klashorst 1989). Figure adapted from (Dongre et al. 2015).

Methoxyl groups on the G- and S-units on the *ortho* position (Figure 1) limit access to the PhOH groups, lowering reactivity; thus, should be removed. During demethylation, methoxyl groups are replaced with hydroxyl groups (PhOH-groups), which are new available sites for crosslinking. Chemical sulfur-mediated demethylation has commonly been used in the past (L. Hu et al. 2011). The objective of hydroxymethylation is to introduce reactive species, CH_2OH-groups into the lignin structure. The Wooten method is one of the most widely used methods where lignin and formaldehyde react for 5 h at 75 °C in the presence of sodium hydroxide (L.

Wooten, Sellers Jr, and M. Tahir 1988). Phenolation aims to increase the content of PhOH-groups in lignin by reacting lignin with phenol in acidic or in a cosolvent medium (mixture of organic solvents and acid catalysts). The oxidation treatment breaks the lignin down into phenolic monomers, while catalytic reduction transforms the ketone and aldehyde moieties of lignin into alcohols. Hydrolysis mainly promotes the cleavage of alkyl-aryl ether bonds to produce phenolic low molecular weight fractions and monomers. Additionally, it has been demonstrated that lignin reactivity can be improved by the producing nanoscale lignin particles, which increases their specific surface area (W. Yang et al. 2019). Detailed and optimized methodologies of modification methods have recently been discussed (Ang et al. 2019). A disadvantage of lignin modification is that processing operations increase the production costs making it a less viable option, especially in regard to producing more cost-competitive alternatives to phenolic resins (W. Zhang, Ma, Wang, et al. 2013).

The second method is called the "catch all" pathway (Stewart 2008), which utilizes unpurified or unmodified lignin for synthesis of lignin based resins (Çetin, N.S; Özmen, N. 2003; Cavdar, Kalaycioglu, and Hiziroglu 2008; Dongre et al. 2015; Dongre and Bujanovic 2019). The absence of a purification and/or modification step makes this method more attractive for scale up considering a lower cost and a more facile incorporation into an industrial process. The "catch all" pathway may be more suitable for lignins derived from sulfur-free biorefinery processes, as these lignins are considered to have higher reactivity and may not require purification and/or modification.

While extensive research has been performed in replacing phenol with lignin in thermoset resins, substituting formaldehyde with other crosslinkers is less studied. However, viable alternatives to formaldehyde to reduce emissions due to its toxicity and carcinogenic properties must be proposed. Some crosslinkers that have been studied include glyoxal, furfural, furfuryl alcohol, glutaraldehyde, and aromatic aldehydes (Younesi-Kordkheili and Pizzi 2019; Dongre et al. 2015; Deka, Mohanty, and Misra 2014; da Silva et al. 2013; Gabriel Foyer et al. 2016).

Challenges

The objective of mature pulping technologies and emerging biorefineries is the production of cellulosic fibers and fermentable sugars, respectively, while lignin is considered and treated as a waste or energy source at best. These technologies are not focused on the quality of lignin; therefore, it is not controlled. Substantial variations in lignin structure and properties due to species of origin and extent of transformation imposed by the processing conditions during removal and recovery are documented in Table 1–3. The lack of consistent quality complicates using lignin in the production of LPF resins. In comparison to phenol, lignin also has high molecular weight and a much more complex structure, which creates steric hindrance for polymerization to occur as access to reactive sites is restricted.

As stated above, lignin is also less reactive than phenol and needs to be purified and/or modified to improve its reactivity. Reactivity is measured by determining the free formaldehyde content at the end of the LPF resin synthesis (N. E. E. Mansouri, Farriol, and Salvadó 2006; Tejado A. et al. 2007). Free formaldehyde content measured after synthesis is desired to be below 1%, which indicates a good lignin reactivity. Lignin purification and modification can be a challenge during upscaling, as current industrial processes need to be modified to accommodate using lignin as a raw material. Moreover, the chemicals that are used for modification are often hazardous and pose concerns regarding handling, safety, and disposal if they were to be used in large scale industrial processes. Currently, other more reactive lignins are less available. However, they are expected to be produced in comparatively milder treatments such as processes based on autohydrolysis (Dongre and Bujanovic 2019; K. T. Wang et al. 2017) or recently suggested fractionation processes conducted in the presence of hydrotropes such as *p*-toluenesulfonic acid or maleic acid at relatively low temperatures $\leq$ 100 °C (Z. Wang et al. 2019; Cai et al. 2020) (Wang et al. 2019, Cai et al. 2020). These processes promote lignin dissolution where the native structure is relatively more preserved resulting in a lighter colored lignin. In contrast, common technical lignins are darker in color, which poses an aesthetic problem in high value applications (Holladay et al. 2007).

Most studies report up to 40% phenol replacement, beyond which properties are compromised. There are a few studies that report higher percentage of substitution, but lignins used in those studies are yet to become readily available in large quantities (Dongre and Bujanovic 2019; Kalami et al. 2017).

In general, lignin-based resins are less thermally stable than PF resins as they inherently contain ether bonds which are more susceptible to thermal degradation than C-C bonds. Due to the presence of ether bonds, lignin-based resins are also more hydrophilic and more prone to water absorption (Younesi-Kordkheili and Pizzi 2019). Even though lignin-based resins can often compete with PF resins in terms of mechanical properties, comparable thermal stability is difficult to achieve. However, some studies demonstrate improvements in thermal stability with lignin purification as carbohydrate contaminants are removed (Çetin and Özmen 2002). In addition, they often require longer curing times, which increase with increasing lignin substitution amounts.

RESINS FROM SULFUR-CONTAINING LIGNINS

Kraft Lignin

Due to the harsh conditions of kraft pulping, lignin undergoes drastic changes in structure (Figure 10). Compared to its native form, kraft lignin contains low amounts of β-aryl ether bonds, some minor carbon-carbon moieties (β-5 and β-β), reduced side chain s, and sulfur mainly as thiol groups, but appears abundant in uncharacteristic lignin structures such as stilbenes and aryl enol ethers (Crestini et al. 2017).

Kraft lignin is soluble in alkali and in select organic solvents. Kraft lignin rarely follows the "catch all" pathway for phenol substitution in phenolic resins. Due to its limited reactivity it is most often modified, commonly via phenolation and methylolation methods. Kraft lignin has been used to synthesize both novolacs and resoles, which are discussed below.

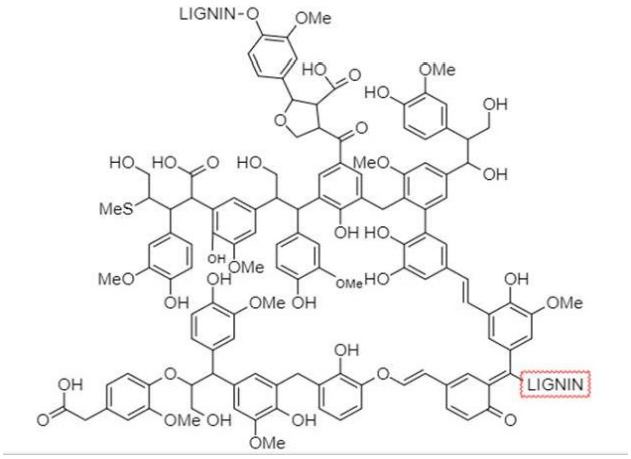

Figure 10. Structure of kraft lignin. Figure adapted from (Lange, Decina, and Crestini 2013).

Novolac

Researchers were able to replace up to 20% of phenol with hydroxymethylated kraft lignin in high pressure multilayered laminates (up to 26 layers) without compromising viscosity, and thermal and mechanical properties (Taverna et al. 2019). The flexural strength results suggested that resins with 30% phenol replaced would be more suitable for post-formable laminates, where some flexibility is tolerated. Novolac resins from pine kraft and sodium-LS for outdoor laminate usage were synthesized with up to 40% phenol substitution. The laminates impregnated with resins were tested for water absorption, thickness swelling, flexural strength, elastic modulus, and relative impact energy in conditions with rapid temperature change. Laminates impregnated with LS performed poorly in these conditions owing to their hydrophilic nature. This indicates that resins from LS may be limited to applications where the temperature and humidity are more stable (Ghorbani et al. 2018).

Three types of unmodified lignins–kraft pine (L1), soda-anthraquinone lignin (L2) and sulfonated softwood kraft lignin (L3) were used to synthesize novolacs (Tejado A. et al. 2007). A comparison of DSC curves showed that resins from L1 and L2 showed two well-defined Tgs suggesting non-homogenous material (Kubo and Kadla 2004). Regardless of lignin type, the

LPF resins were more viscous than PF resins demonstrated by the gel times at increasing curing temperatures from 145 °C–185 °C. LPF with L3 at 45% substitution of phenol showed comparable gel times to that of PF. During hardening the LPF resins experienced a volume shrinkage of up to 200%. This can be attributed to the lignin fragments self-condensing and polymerizing, most likely due to the presence of branched lignin fragments imparting more free volume. Overall, the authors suggested that kraft pine lignin (L1) is the superior candidate for phenolic resins due to its more reactive sites and higher decomposition temperature. Higher molecular weight of L1 was also suggested as a positive attribute, although several studies report lower molecular weight being more advantageous (N.-E. E. Mansouri and Salvadó 2006; Lourençon et al. 2020).

Resole

A study (Lourençon et al. 2020) demonstrated that resins prepared form hydroxymethylated hardwood kraft lignin from eucalyptus showed better reactivity towards formaldehyde compared to resins from softwood lignin. The reported bonding strength measured was also comparable. This is contrary to the observations of (Kalami et al. 2018) where resins from hardwood kraft showed less reactivity towards formaldehyde and lower bonding strength. A significant difference between the hardwood kraft lignins used by (Lourençon et al. 2020) and those used by (Kalami et al. 2018) was that the molecular weight of the former was lower. Lignins with low molecular weight have greater access to reactive sites resulting in resins with better performance in terms of mechanical properties. This has been confirmed by other studies as well (Tejado et al. 2007). On the contrary, an in depth look at the impact of molecular weight has been studied (Solt et al. 2018) with conflicting results. Pine kraft lignin, which was fractionated by an ethanol-based solvent to produce four fractions with polydispersity ranging from 1.5–3.2 and Mw ranging from 1,600–5,000 Da was used to make resole resins with 50% phenol substitution. The resins from high molecular weight lignin had lower condensation times as the desired viscosity was obtained faster. The mechanical properties of the resins prepared from the four fractions did not show any significant differences and were inferior to the control PF resin.

Lignosulfonates (LSs)

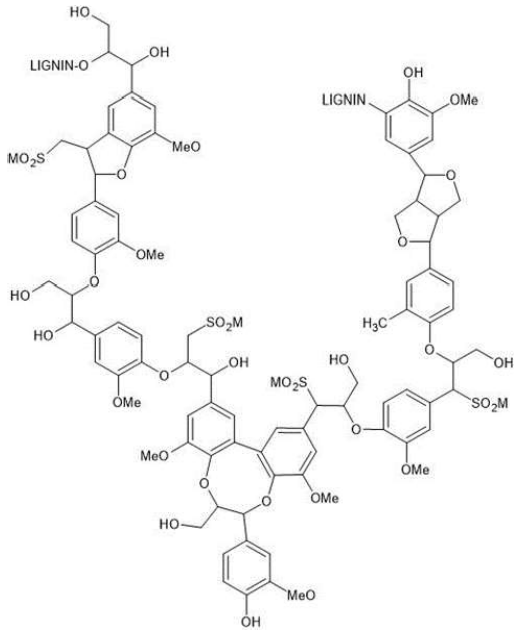

Figure 11. Structure of lignosulfonates (LS). (M = calcium, sodium, ammonium or magnesium). Figure adapted from (Lange, Decina, and Crestini 2013).

In contrast to kraft lignin, LSs carry hydrophilic sulfonate groups rendering them soluble in water (Figure 11). In addition, LSs contain a higher amount of sulfur ranging from 3.5–8% (1–3% in kraft lignin), and have a higher molecular weight (Mw 1,000–150,000 for LSs vs. 1,500 – 25,000 for kraft lignin) and charge density (Aro and Fatehi 2017; Thébault, Kandelbauer, et al. 2017). They are used in a broad range of applications such as concrete admixtures, carbon black, cement additives, animal feed pellets, pesticides, and surfactants.

LSs have been extensively studied to produce phenolic resins. Ammonium-LSs have displayed a better reactivity than LSs of other bases (Ca, Mg, or Na) due to their higher PhOH-group content. LSs with lower S/G ratio also exhibit higher reactivity and may be more suitable for indoor applications as previously indicated (Alonso et al. 2004). Their use in novolacs and resoles is discussed below.

Novolac

Six hydroxymethylated technical lignins–five samples recovered from black liquor of sugarcane bagasse and one from ammonium-LSs sample recovered from pine were used to partially substitute phenol in PF resins. The LS-PF resins performed better than PF resins with regard to elastic modulus. Their superior performance was attributed to the G-origin of LS, i.e., the absence of S-units. The presence of S-units leads to greater steric hindrance and limited access to PhOH-groups, resulting in fewer methylene bridges; thus, compromising properties. (Martínez and Velásquez 2013).

Resole

Alkali hydrolysis has been conducted as a relatively simple method for increasing lignin reactivity for use in resole resins. The added advantage of alkaline hydrolysis is that the end products can directly be used for resole synthesis which is conducted in alkaline environments (N.-E. E. Mansouri, Farriol, and Salvadó 2006). In this study, ammonium-LS was subjected to alkaline hydrolysis in ten different conditions (time and temperature) and its reactivity with formaldehyde was measured. Formaldehyde reactivity improved (more than 50%) for samples treated in more severe conditions that generated reactive PhOH groups more readily through an advanced cleavage of alkyl-aryl-ether bonds and yielded a greater decrease in molecular weight and polydispersity.

Formaldehyde has been replaced by glyoxal, noncarcinogenic less toxic and less reactive dialdehyde to synthesize eco-friendly resins. Prior to incorporation in PF resins, glyoxalation of lignin has been performed with alkali-purified calcium-LS. The lignin-glyoxal resins showed comparable internal bonding strength to PF resins as well as press times indicating good lignin-glyoxal reactivity (N. E. E. Mansouri, Pizzi, and Salvador 2007).

Indoor applications, such as decorative laminates and phenolic foams have also been explored in literature. Hydroxymethylated sodium-LSs were used to replace 10% phenol in resole resins for decorative laminate application and exhibited higher tensile, flexural and impact strength (Taverna et al. 2016). LS-based laminates swelled and gained more mass, but resisted delamination, compared to PF laminates in a boiling water. Once

more, the increase in mass and thickness is attributed to the hygroscopic nature of LS and confirm the aforesaid indoor applicability of LS-based laminates.

Phenolic foams have excellent chemical and fire resistance, compression strength, and self-extinguishing properties; moreover, they do not smoke if exposed to fire. Their applications include, but are not limited to insulation materials, building materials, and frozen foods. Phenolic resins require further processing in the presence of foaming agents, surfactants to manufacture phenolic foams. Phenolated LSs were used to make resole resins and further processed in the presence of sulfuric acid as a catalyst and Tween-80 as a surfactant to make phenolic foams (L. Hu et al. 2012). The LS-phenolic foams showed higher compression strength and Young's modulus, lower density and comparable thermal resistance to PF foams, proving to be a promising material warranting further research.

RESINS FROM SULFUR-FREE LIGNINS

Sulfur-free lignins are considered closer in structure to native lignins than sulfur-containing lignins, which are produced in the presence of sulfur-containing delignification agents and undergo more severe modifications (Lora and Glasser 2002). Therefore, sulfur-free lignins are also expected to exhibit superior biological activities such as antioxidizing and antimicrobial properties. This section will discuss the sulfur-free lignins obtained from the organosolv process (pulping and pretreatment technologies), soda pulping, hydrothermal pretreatment, and enzymatic hydrolysis.

Soda Lignins

Research on the use of soda lignins resulted from pulping of mostly herbaceous lignocellulosic biomass to produce lignin-based resins has also been conducted, although less frequently compared to other technical

lignins. Two studies where formaldehyde has been replaced with non-toxic crosslinkers are also discussed and are an important contribution to the field.

Novolac

An LPF resin with a methanol soluble fraction of soda lignin from straw was produced for use in brake friction material with 75% phenol substitution and oxalic acid catalyst (Kuroe Motoki et al. 2012). The resins were then incorporated into friction materials and tested for mechanical and friction properties. LPF resins showed comparable flexural strength to that of PF and an improvement in fade resistance. However, the lower thermal stability of LPF resins resulted in a reduced wear resistance.

Straw and grass soda lignin were blended with furfuryl alcohol in the presence of maleic acid as the catalyst to synthesize eco-friendly resins and compared to neat poly-furfural alcohol resins (PFA). The blends exhibited similar thermal degradation behavior to that of PFA resins. However, it was observed that beyond 46% lignin concentration in the resin, phase separation occurred (Guigo et al. 2010).

Resole

Soda lignin was unmodified and modified with four demethylation agents ~~S~~, NaSH, Na_2SO_3, and n-dodecyl mercaptan, and used to replace 30% of phenol in resole resins (Li et al. 2016). The Na_2SO_3-modified LPF resins were most successful in terms of bonding strength, formaldehyde emission, gel time, and thermal stability compared to PF.

One recent study (Younesi-Kordkheili and Pizzi 2019) attempted to produce lignin-phenol-glyoxal resins. The proposed mechanism is shown in Figure 12. Soda bagasse lignin was used to replace up to 40% phenol and the resins were tested on particleboard panels for mechanical properties. Although slightly lower than PF, the mechanical properties passed the European Standards. More than 40% phenol substitution with lignin compromised the mechanical properties and dimensional stability. This study is an important step forward to more renewable formaldehyde-free resins, although further research is needed.

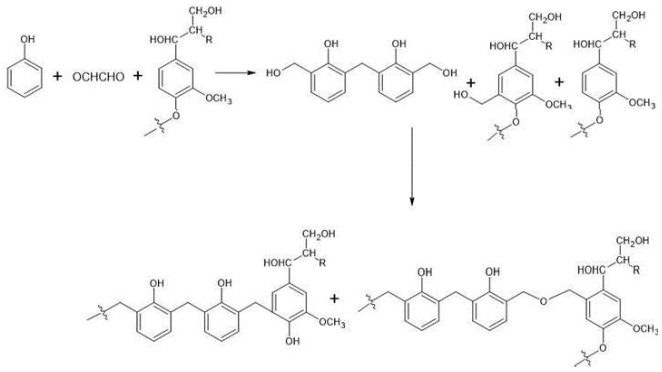

Figure 12. Possible reaction between lignin, phenol and glyoxal (R = H, Oar or Ar) Adapted from (Younesi-Kordkheili and Pizzi 2019).

Four biorefinery lignins from corn cob (L1), poplar (L2 and L3) and wheat straw (L4) were used to synthesize resole resins with 50% phenol substitution. The lignins were prepared in the following ways: L1 was derived from hydrothermally treating corn cob followed by alkali extraction to remove lignin. Poplar was hydrothermally treated, and a lignin fraction isolated from the extract (L2). The treated poplar wood was then subjected to kraft pulping and the L3 fraction was isolated from the black liquor. Lastly, L4 was extracted from steam explosion of wheat straw followed by alkali extraction. The resins prepared from these lignins were tested for bonding strength in plywood with satisfactory performance and low formaldehyde free emissions. However, the lignin-based resins required higher curing temperatures compared to the control PF resin. (S. Yang et al. 2014; Yang Sheng et al. 2015).

Organosolv Lignins

Organic solvents such as ethanol, methanol, and acetone, and organic acids such as acetic acid and formic acid are used to remove lignin in delignification processes either in the production of pulp or increasingly in pretreatments in biorefineries. In the proposed conditions at temperatures ranging from 150–200 ºC cellulose remains largely insoluble (Carvalheiro,

Duarte, and Gírio 2008). Selectivity of the delignification process can be improved by adding catalysts such as oxalic, salicylic, and acetylsalicylic acid (Taherzadeh and Karimi 2008). Organosolv methods can yield lignin, which is relatively pure, low molecular weight lignin, more reactive for use as a raw material for value-added products. Nevertheless, modifying the lignin has also been investigated to further improve reactivity. Environmental and economic concerns present a challenge during recovery of the products due to the use of organic solvents. Owing to the limited availability of organosolv lignin, research in recent years has been focused at the small scale with testing mostly limited to curing time, free formaldehyde content, and viscosity. Fewer studies have investigated mechanical properties as they often require larger amounts of lignin.

Earlier studies on lignin from organosolv pulping processes Alcell, acetosolv, or formasolv (Lora and Glasser 2002; Vázquez et al. 1997; Gonçalves and Benar 2001; Çetin and Özmen 2002) and more recently, lignin from organosolv pretreatment technologies (M. Wang, Leitch, and Xu 2009; Tachon, Benjelloun-Mlayah, and Delmas 2016; Kalami et al. 2018; da Silva et al. 2013) are discussed in this section.

Novolac

Brake pads were produced with Alcell lignin replacing 10% and 20% of phenol in novolacs resulting in reduction of wear resistance. It is noteworthy that the lignin addition also improved the thermal stability of friction coefficient (Lora and Glasser 2002). Alcell lignin has also been used to replace 20% of phenol in PF resins in the production of oriented strand boards (OSB) yielding comparable mechanical properties in finished boards to PF resins (Lora and Glasser 2002).

Resole

A study compared the effect of hydroxymethylation and phenolation of eucalyptus lignins obtained from the acetosolv process on the mechanical properties of LPF resole resins where 40% of phenol was replaced. Modified-LPF resins demonstrated similar gel times to commercial PF resins, but shorter to those of unmodified-LPF resins. Phenolated-LPF resins

fared poorly compared to hydroxymethylated-LPF in terms of mechanical properties. Moreover, the mixtures of phenolated LPF and commercial PF resins showed enhanced mechanical properties than the individual resins (Vázquez et al. 1997).

Resole resins produced with unmodified and phenolated Alcell lignin to substitute up to 40% phenol were tested for formaldehyde reactivity and hardening time. The phenolated lignins showed improved reactivity and lower curing times compared to unmodified lignins, as well as PF resins, indicated by the lower free formaldehyde content measured in the respective experiments (Çetin and Özmen 2002).

Organosolv lignins recovered from ethanol-based pretreatment of pine sawdust, and purified in 72% sulfuric acid to remove carbohydrate contaminants were used to substitute up to 50% phenol in resins. There was no improvement in curing time, but the purified LPF resins exhibited higher thermal degradation temperature than unpurified-LPF. This can be attributed to two possible explanations: 1. Purification results in freeing lignin from carbohydrate contaminants and improving lignin thermal stability, and 2. An increase in lignin condensation in the presence of strong sulfuric acid results in the formation of more stable C-C bonds (M. Wang, Leitch, and Xu 2009).

Non-modified wheat straw lignin obtained from the CIMV process™, which utilizes acetic acid, formic acid and water for pretreatment of biomass was used to synthesize LPF wood adhesives. The resulting linear and low molecular weight polymer was used to substitute 50-70% phenol and tested on plywood panels. The researchers reported that formaldehyde requirements could be reduced from 64% for PF to 35% in LPF experiments. Due to the self-condensation mechanism of lignin, a pre-polymer network was formed with similar characteristics to that of PF network; thus, reducing the amount of required formaldehyde. The resins also exhibited formaldehyde emission of less than 1%, and comparable viscosity. Furthermore, the resin with 50% phenol replacement exhibited higher strength than PF (Tachon, Benjelloun-Mlayah, and Delmas 2016).

More recently, nine resin samples consisting of three organosolv samples obtained from a hardwood, softwood, and corn stover (Kalami et al. 2018) were used to make resole LPF resins and tested for shear strength on

bonded veneers, gelation time, viscosity and free formaldehyde content. Compared to the PF control, the gelation times of softwood and hardwood samples were much shorter, but that of the corn stover was longer. The viscosities of all three LPF resins were higher than that of PF. The lignin-based resins also exhibited free formaldehyde content of $\simeq$ 1%, while the PF value was 2.4%. However, the LPF resins were not able to perform adequately in terms of shear strength.

Eco-friendly phenol- and formaldehyde-free resins made from sugarcane bagasse organosolv lignin with glutaraldehyde as a crosslinker were used to make a composite with sugarcane bagasse fibers. Glutaraldehyde is a dialdehyde that can be sourced from natural resources. The resins were compared to PF and lignin-formaldehyde resins in terms of impact strength, flexural strength and flexural modulus. The lignin-glutaraldehyde resins exhibited highest impact strength and flexural modulus, but lower flexural strength indicating good elasticity and stiffness (da Silva et al. 2013).

Hydrolytic Lignins

Hydrothermal pretreatment uses water with no additional (catalytic) chemicals at temperatures generally ranging from 150 °C to 230 °C (Alvira et al. 2010; Carvalheiro, Duarte, and Gírio 2008; Mosier et al. 2005) to mostly target hemicelluloses, and some readily accessible lignin in lignocellulosic biomass. (Garrote, Dominguez, and Parajo 1999). Hydrothermal pretreatment has been documented as particularly effective on Angiosperms, which are abundant in autohydrolysis-prone xylans.

Lignin recovered from hot-water extraction (160 °C and two hours) was analyzed and used to synthesize lignin-furfural novolac resins. These resins were both phenol- and formaldehyde-free and eco-friendly (Dongre et al. 2015; Dongre and Bujanovic 2019). The lignins tested were from several species (sugar maple, willow, miscanthus and wheat straw); properties are listed in Table 1–3. This lignin was shown to contain xylose-based carbohydrates, which may be converted to furfural in acid conditions; i.e.,

furfural may be produced *in situ*. Furfural has been shown to be a good crosslinking agent for lignin; thus, can serve as a non-toxic substitute for carcinogenic formaldehyde (Figure 13).

The synthesized resins were tested for their mechanical properties by subjecting resin impregnated glass fiber filters to tensile tests. The tensile index and Young's modulus were comparable to those of a commercial novolac resin. The resins were further tested on kraft paper for potential application in HPLs (Dongre and Bujanovic 2019). Miscanthus lignin demonstrated the best mechanical properties attributing to the PhOH-group content and S/G ratio values, which resulted in the optimized level of crosslinking determined by molecular weight distribution. It was concluded that extremely low and high molecular weights of the resins adversely affect tensile strength indicating a lack of mobility required for good tensile strength and Young's modulus.

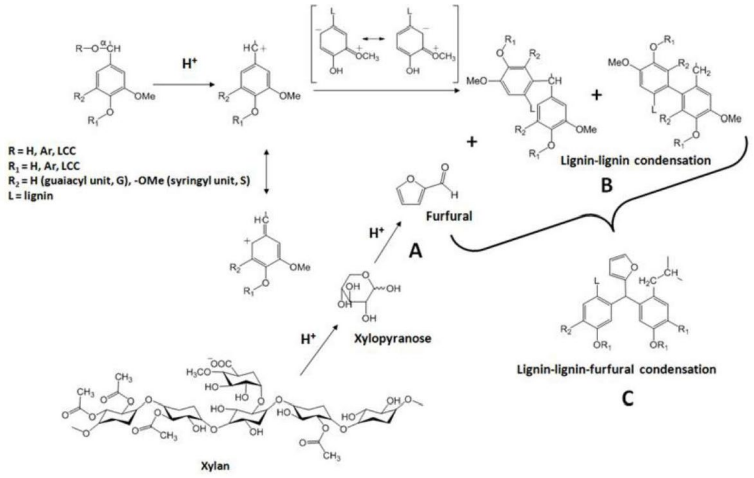

Figure 13. Proposed mechanism of lignin-lignin and lignin-furfural condensation products in acid conditions; *in situ*, xylan-containing lignin. (Samuel et al. 2013; Bu et al. 2011; Binder et al. 2009). Figure adapted from (Dongre et al. 2015).

Enzymatic Hydrolysis Lignin (EHL)

Enzymatic hydrolysis of pretreated biomass is widely studied and EHL, which is the solid residue remaining after enzymatic hydrolysis of pretreated biomass, has garnered considerable interest in recent studies. Sulfur-free EHL exhibits greater chemical reactivity than kraft, lignosulfonates or organosolv lignins; thus, appears as an attractive candidate for phenolic resins (Jin, Cheng, and Zheng 2010). Several approaches regarding EHL as a raw material for phenolic resins are discussed.

Novolac

A study tested liquefaction of hardwood EHL to increase its reactivity before its incorporation into novolac resins. The EHL was liquefied in the presence of oxalic acid and phenol. The Mn and Mw were reduced from 1,288 to 655, and 3,107 to 1,448, respectively, indicating formation of lignin dimers and oligomers during liquefaction. Up to 55% phenol could be replaced with this liquefied EHL in novolac resins. It was reported that the gelation time, flowing distance, and softening point of the resins were within the acceptable range (Jing et al. 2015). It can be hypothesized that a certain amount of phenolation occurs during liquefaction resulting in better reactivity.

EHL and furfuryl alcohol (FA) were blended to produce phenol- and formaldehyde-free, eco-friendly resins and compared to neat poly-furfuryl alcohol (PFA) resins. The resin blend containing 20% EHL showed an increase in flexural strength (55%), flexural modulus (70%) and storage modulus (14%) when compared to PFA resin (Deka, Mohanty, and Misra 2014). In context of efforts toward more benign industrial practices and products, it is beneficial to observe results with higher lignin content. As previously mentioned, soda lignin was blended with furfuryl alcohol and a phase separation occurred above 46% (Guigo et al. 2010).

Resole

Resins from corn stalk EHL showed higher free formaldehyde content with increasing phenol substitution. (Jin, Cheng, and Zheng 2010).

Similarly, resins from corn stalk steam explosion lignin (RPF) and enzymatic hydrolysis of pretreated corn stalk (LPF) were synthesized with up to 50% phenol substitution. With an increase in phenol substitution by lignin, free formaldehyde content of resin increased, although it has been suggested that formaldehyde adsorbents can be used to reduce this effect (Qiao et al. 2015). It was also observed that LPF resins exhibited superior adhesion properties in plywood than RPF. The authors proposed that higher purity and reactivity of EHL gave it the advantage over lignin from steam explosion. Higher free formaldehyde content was also observed in experiments conducted to analyze effects of using lignin isolated from steam pretreated poplar either after enzymatic hydrolysis or alkaline extraction to replace phenol in PF resole resin. Furthermore, the free-formaldehyde content increased with an increase in molecular weight of lignin, indicating less reactive sites in lignin of higher molecular weight (Stücker et al. 2016).

A complete, 100% replacement of phenol by alkali-purified residue of enzymatic hydrolysis of dilute-acid pretreated corn stover; alkali purified EHL in the production of resole PF adhesive has been reported (Kalami et al. 2017). This lignin-based resin showed a slightly higher curing temperature than commercial PF resole, but the energy required for its curing was twice as less. The shear strength was equal with no statistically-significant difference. However, free formaldehyde content in lignin-based resin was higher than in commercial resin. Exceptionally high reactivity of this alkali purified EHL from corn stover compared to other lignins such as Indulin (kraft lignin, softwood, G-lignin) was attributed to a high content of *p*-hydroxylphenyl groups and *p*-coumaric acid implying its high reactivity (Kalami et al. 2017; 2018). It was also suggested that hardwood lignins are not suitable for resole applications as the presence of S-units decreases reaction with formaldehyde. Additionally, adhesives prepared with softwood lignin showed a reduction of 50% in formaldehyde emissions.

DEPOLYMERIZATION APPROACH

Lignin obtained from various delignification processes can be activated by depolymerization for use in formulation of lignin-based resins. The advantage of this approach is that the phenol produced via lignin depolymerization can be easily introduced into industrial processes with little to no modification. In contrast, using lignin as a macromolecule will require considerable changes to existing industrial processes. This remains a crucial hurdle to extensive lignin valorization.

Depolymerization of lignin has been attempted via several techniques – catalytic (metal and enzymes) and thermochemical (pyrolysis, hydrogenolysis, gasification and hydrolysis). In recent years, several studies have focused on depolymerizing lignin to its phenolic derivatives and/or aromatic aldehydes prior to use in the production of phenolic resins.

Lignin structure and linkages must be considered in selecting catalytic processing. Lignins from chemical pulping processes such as kraft and soda lignins contain fewer β-O-4 linkages and more C-C bonds, which are significantly more resistant (bond dissociation energyβ-O-4 bonds 54–72 kcal/mol vs. C_5-C_5 115–118 kcal/mol, (Rinaldi et al. 2016)); thus, less condensed lignins are more attractive for catalytic processing. The catalytic processes can be divided into convergent and stepwise approaches (Rinaldi et al. 2016). The objective of catalytic processing is to maximize the yields of the monomeric moieties from which platform chemicals can be built.

(Cheng et al. 2013) used metal catalysts in hydrothermal depolymerization of white pine sawdust organosolv lignin (OL). The original OL and the depolymerized lignin (DL) were used to partially substitute (50% and 75%) phenol in resoles–OLPF and DLPF, respectively. Resins were tested for viscosity, free formaldehyde content, thermal behavior and mechanical properties on plywood panels. Both the resins showed comparable viscosity to PF, but exhibited higher free formaldehyde content indicating poor reactivity. The OLPF and DLPF resins were less thermally stable than PF resin. Nevertheless, the mechanical properties (dry and wet strength) of OLPF were highest, followed by DLPF and PF. This suggests that in the case of OLPF, a polymer network formed due to the self-

condensation of lignin, which provides the necessary strength characteristics as was observed by (Tachon, Benjelloun-Mlayah, and Delmas 2016) who also studied organosolv lignin.

Depolymerization of alkali lignin in the presence of NaOH/urea resulted in a product mixture (DAL) of low molecular weight aromatic compounds, characterized by higher PhOH-group content, greater number of reactive sites and fewer methoxyl groups. The original alkali lignin (AL) and DAL were used to synthesize resole resins with 50% substitution of phenol – ALPF and DALPF. The bonding strength, formaldehyde emission and gel time of DALPF were superior to ALPF and comparable to the PF control resin (Li et al. 2018).

Corn stalk EHL was treated with the solid acid catalyst process (SACP) with the purpose of depolymerization. The obtained lignin was then used to synthesize resole resin for incorporation into light weight phenolic foams with phenol substitution of up to 60%. The depolymerization resulted in significant decrease of PhOH and increased reactivity with formaldehyde. The authors observed that the increased reactivity enabled the lignin to polymerize to form a network rather than just act as a filler. The phenolic foam with 50% phenol substitution exhibited better thermal insulation and satisfactory compression strength compared to the control PF resin (G. Wang et al. 2018).

It is also noteworthy that oxidative depolymerization of lignin yields aromatic aldehydes such as 4-hydroxybenzaldehyde, vanillin and syringaldehyde, which have been proposed as alternatives to formaldehyde. The resins synthesized via this method are phenol-aldehyde resins where the aldehydes were functionalized to improve reactivity (Gabriel Foyer et al. 2016; G. Foyer et al. 2016).

The depolymerization approach offers several benefits in lignin utilization for thermoset resins and a glimpse into some, more recent approaches has been provided here.

CONCLUSION

In order to create a more sustainable world and conserve non-renewable resources, finding alternatives to petrochemical products has become vital. Lignin-based resins are sustainable, economical, and have the potential to offer comparable mechanical properties. In addition, the chemical and structural diversity of lignin enables its utilization in a multitude of applications. This review outlines recent literature on lignin-based phenolic resins synthesized from lignins derived from various biochemical processes such as kraft, sulfite pulping, organosolv, soda, enzymatic hydrolysis, and hydrothermal pretreatment. However, despite the interest and vast body of literature including patents in the field, lignin valorization is yet to become a commercial reality.

Lignins from mature pulping processes, kraft lignin and lignosulfonates, are currently the most available; therefore, the most studied. Even though kraft lignin is less reactive, modification methods substantially improve reactivity yielding resins that exhibit adequate physical and mechanical properties presenting a potential advantage in outdoor applications. LS-based resins are more suitable for indoor applications owing to their hydrophilicity, and currently find utilization in low-value applications such as cement mixtures and animal feed pellets, but have the potential in decorative laminates and phenolic foams. Organosolv lignins are capable of forming polymer networks and often produce resins with low free formaldehyde content indicating higher reactivity. In addition, the higher reactivity of biorefinery lignins is of a particular advantage in phenolic resins. However, owing to their limited availability, our thorough knowledge and understanding regarding their scale up and mechanical properties remains limited as well.

The heterogeneity of lignin, which is mostly governed by the nature of the raw material/origin and processing conditions, is apparent from its diverse properties. The amount of free phenolic hydroxyl groups, S/G ratio and molecular weight determine its route of valorization. In general, a lignin that is characterized by a low molecular weight, higher polydispersity, low

Tg, high PhOH-group content, and low S/G ratio proved to be a better candidate for resin production.

Resins from high molecular weight lignin attain the desired viscosity, as well as high impact strength compared to resins made with low molecular weight. In contrast, high molecular weight prevents access to reactive sites, hindering the crosslinking process, which compromises the tensile strength.

Thermal stability is a major challenge for lignin-based resins. Lignin-based resins will often surpass mechanical properties of PF, but tend to degrade at lower temperatures than PF. This is due to the inherent presence of ether bonds in lignin, as well as the presence of carbohydrate contaminants. Purification of lignin has shown to improve its thermal properties. Studies indicate that kraft lignin, which contains fewer ether bonds, may be a better candidate for applications where high temperatures are common. In comparison, the ether bonds in lignins from other processes are more likely to be preserved rendering them more susceptible to thermal degradation.

It is well-known that tailoring synthesis conditions (time, temperature, pH, curing agent) of PF resins produces a diverse set of properties with applications in wide range of fields making it an ubiquitous material. The heterogeneity of lignin offers a similar advantage where conditions can be fine-tuned to meet the requirements of the end application. However, resins that are completely phenol- and formaldehyde-free are less studied, and currently, LPF resins dominate the literature. Moreover, most studies report inferior mechanical properties of resins when the phenol substitution exceeds 50%, with a few that report successful phenol substitution above 50% to completely phenol-free resins. Suitable substitutes for formaldehyde, which is the main toxic component of phenolic resins, have also been pursued. However, they are unable to compete in terms of cost or mechanical properties thus far; although some have shown adequate mechanical properties.

Lignin is a promising raw material for phenolic resins given its natural abundance, phenolic nature, and its ability to form robust polymer networks to produce resins with excellent physical and mechanical properties, but remains severely underutilized as a low-grade fuel. However, new and

emerging processes for lignin valorization, as well as techniques that can elucidate the structure and reaction routes are likely to open a host of possibilities for lignin use.

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