



# Editorial: Advancements in Biomass Recalcitrance: The Use of Lignin for the Production of Fuels and Chemicals

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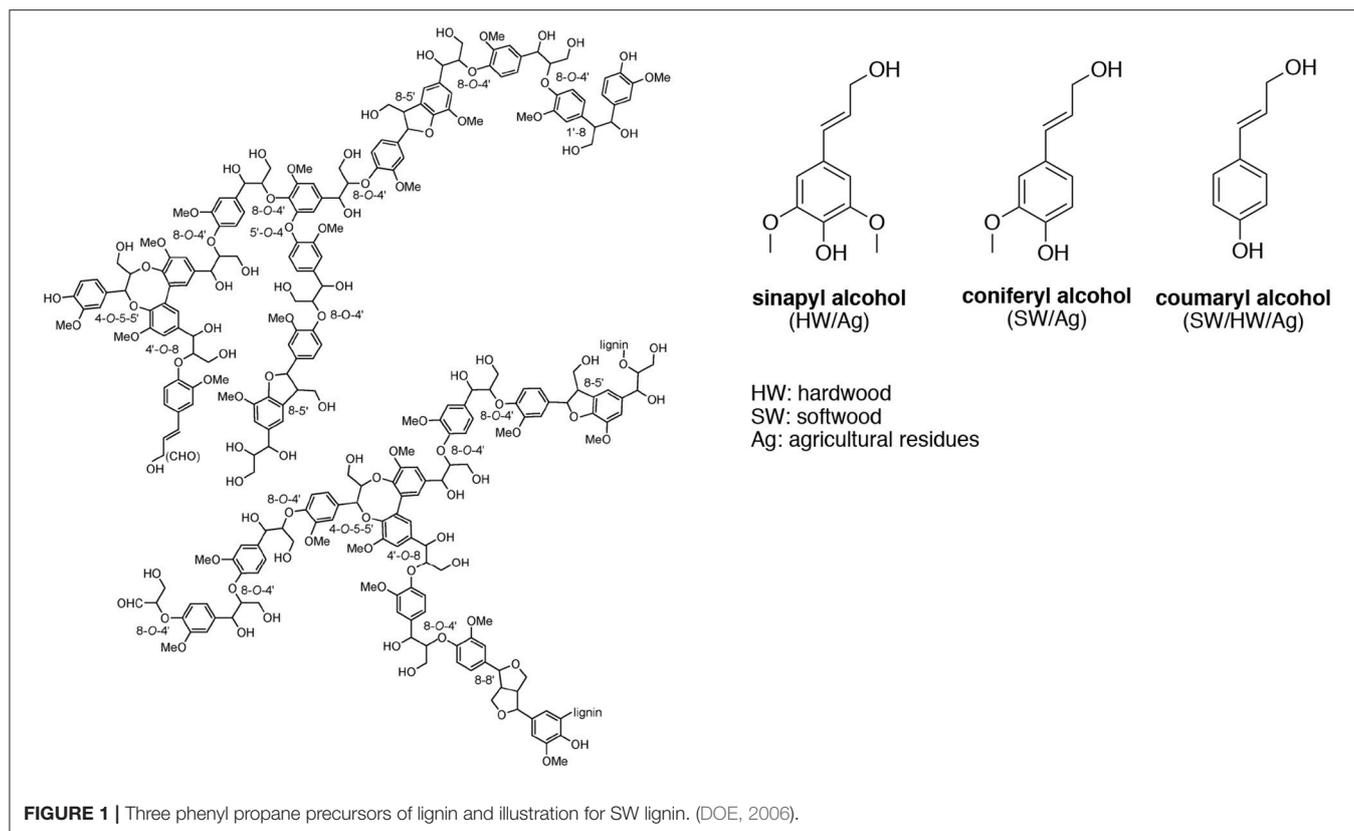
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## Advancements in Biomass Recalcitrance: The Use of Lignin for the Production of Fuels and Chemicals

The valorization of lignin has become a dominant translational research theme in biorefining in the last few years (Ragauskas et al., 2014). Historically, lignin has been sourced from kraft and sulfite pulping operations, and each of these sources provides some natural limitations to their usage. Commercially, this type of lignin has been used as a dispersant, dust suppression agent, surfactant, binder, and emulsifiers; however, most of these applications are low-value, and the markets are saturated (Gargulak and Lebo, 2000). The general limitation of these lignins is due to the presence of sulfur, extensive cross-linking, difficult process ability, purity, and low-molecular-weight profiles in the case of kraft lignin.

The next phase in lignin application is to use the intrinsic structural features of lignin to develop value-added products. Several studies have shown that lignin may be well suited for *bio-based* plastics and composite applications, in particular, for lignin resources isolated from biomass using an organosolv extraction protocol. Depending on the exact lignin extraction procedure used, the structure of lignin may be kept mostly intact. Several promising lignin applications include the use of oxypropylated lignin for polyurethane foams (Li and Ragauskas, 2012), inclusion into polystyrene (Henry et al., 2012), as a potential green antioxidant (Pouteau et al., 2003), or flame-retardant additive (Matsushita et al., 2017). Furthermore, lignin is also being actively developed as an adhesive for non-formaldehyde wood resins for flooring (Aracri et al., 2014), packaging, and composite wood board production (Li et al., 2018) which leverage the intrinsic reactivity between lignin and oxidoreductase enzymes, such as laccase, which catalyzes further lignin polymerization. The use of lignin has been leveraged with epoxy resins to yield printed circuit boards (Luukko et al., 2013), and for molding (Nam and Son, 2015). As reported by Stewart, the starting plant resource and lignin extraction process have a substantial impact on the resulting physical properties and the purification cost of lignin (Stewart, 2008). Finally, there is a growing interest in using lignin in the polyolefin markets (i.e., polyethylene and polypropylene) as the aromatic unit of lignin provides photo-stabilization, strength enhancement, and elongation effects (Lv et al., 2011). In addition to



these efforts, the conversion of lignin to chemicals and fungible fuels for ground and aviation transportation is being aggressively developed using thermal and/or catalytic processes (Ben and Ragauskas, 2011; Bi et al., 2015). As an alternative to these chemical technologies, the power of biology is also being investigated to convert lignin to fatty acids and esters using *Rhodococcus* (Le et al., 2017), and *Pseudomonas putida* for PHAs (Liu et al., 2017), to name just a few promising pathways.

In each of these applications, the structure and purity of lignin play a critical role in determining its chemical and physical properties. Lignin is one of the most complex natural polymers in regards to its chemical structure and composition. It is synthesized by enzymatic dehydrogenative polymerization of 4-hydroxyphenyl propanoid units (**Figure 1**). Major types of interunit linkages and the reported abundance in softwood (SW) and hardwood (HW) lignins are presented in **Table 1**. Also, the molecular weights of various lignins isolated from native and pretreated biomass are presented in **Table 2**. There are several techniques that can be used to determine the molecular weight of lignin, but one of the most commonly used methods is lignin acetylation followed by gel permeation chromatography (GPC) analysis conducted via external standards or using multi-angle laser light scattering (MALLS) (Tolbert et al., 2014).

The breadth of lignin molecular weight and its structural features have become significantly more complex as genetic engineering of the monolignol pathways have demonstrated the ability to significantly alter the S (syringyl): G (guaiacyl):

H (*p*-hydroxyl) ratio in plants. In these days, the structure of lignin is widely determined using advanced 1D and 2D NMR techniques (Yoo et al., 2016b) supplemented with selected lignin functionalization techniques followed by heteronuclear single quantum coherence (HSQC) NMR techniques (Pu et al., 2011). These techniques have been refined so that all the key functional groups of lignin can now be established quantitatively or semi-quantitatively. Also, they made it possible to detect the acetylation of lignin in nature and the incorporation of *p*-hydroxybenzoate, ferulate, *p*-coumaric acid, and other structures in lignin (Yoo et al., 2016a, 2017b). The presence of lignin-carbohydrate complexes (LCCs) in native and process lignin remains difficult to establish fully and yet is believed to cause challenges in the processing of lignin. This special issue highlights recent advances in lignin characterization, conversion, and valorization.

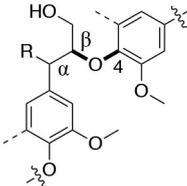
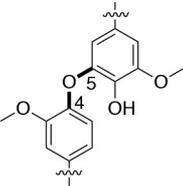
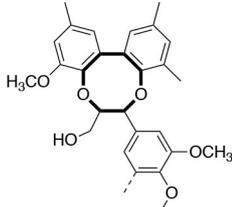
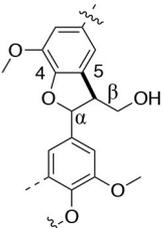
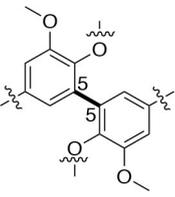
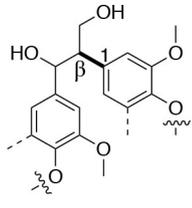
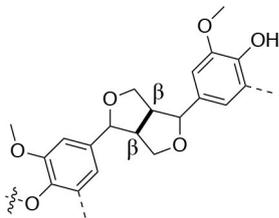
## AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication.

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**TABLE 1** | Reported abundance of major linkages in softwood and hardwood lignins (Chakar and Ragauskas, 2004; Zakzeski et al., 2010).

Linkage	$\beta$ -O-4 (%)	4-O-5 (%)	Dibenzodioxocin (%)	
C-O linkage Abundance Per 100 C <sub>9</sub> -units				
Softwood	45–50	4–8	5–7	
Hardwood	60–62	7–9	0–2	
Linkage	$\beta$ -5 (%)	5-5 (%)	$\beta$ -1 (%)	$\beta$ - $\beta$ (%)
C-C linkage Abundance Per 100 C <sub>9</sub> -units				
Softwood	9–12	18–25	7–10	2–4
Hardwood	3–11	3–9	1–7	3–12

**TABLE 2** | Weight-average molecular weight ( $M_w$ ), number-average molecular weight ( $M_n$ ), and polydispersity index (PDI) of various lignins.

Origin	$M_w$	$M_n$	PDI
Switchgrass	5,000	2,940	1.7
<i>Buddleja davidii</i>	16,800	7,260	2.3
<i>Populus</i>	13,260	5,047	2.6
Sugarcane Bagasse	3,176	1,673	1.9
Kraft softwood lignin	6,300	955	6.6
Ammonia lignin (Corn stover)	3,975	1,827	2.2
Ethanol organosolv lignin (Miscanthus)	13,800	8,300	1.6

David and Ragauskas (2010); Zeng et al. (2014); Sen et al. (2015); Bezerra and Ragauskas (2016); and Yoo et al. (2016a, 2017a).

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**Conflict of Interest Statement:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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