

Lignin Hydrogenolysis: Improving Lignin Disassembly through Formaldehyde Stabilization

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Lignocellulosic biomass is available in large quantities and constitutes an attractive feedstock for the sustainable production of bulk and fine chemicals. Although methods have been established for the conversion of its cellulosic fractions, valorization of lignin has proven to be challenging. The difficulty in disassembling lignin originates from its heterogeneous structure and its propensity to undergo skeletal rearrangements and condensation reactions during biorefinery fractionation or

biomass pretreatment processes. A strategy for hindering the generation of these resistive interunit linkages during biomass pretreatment has now been devised using formaldehyde as a stabilizing agent. The developed method when combined with Ru/C-catalyzed hydrogenolysis allows for efficient disassembly of all three biomass fractions: (cellulose, hemicellulose, and lignin) and suggests that lignin upgrading can be integrated into prevailing biorefinery schemes.

The depletion of fossil-based resources and the environmental burden associated with their use requires society to find sustainable alternatives. However, the transition from a petroleum-based society to one that utilizes biomass will require the development of novel methodologies for this ambitious goal to be realized. Lignocellulose, the main nonfood component of biomass, consists of cellulose, hemicellulose, and lignin, and is a potential feedstock for the production of liquid fuels and value-added chemicals as it is available in feedstock quantities ($> 10^{11}$ tonnes per year worldwide). Although advancements have been made in converting the cellulosic moieties derived from lignocellulose to liquid fuels and commodity chemicals, lignin currently represents an underutilized carbon feedstock.^[1]

Lignin, which accounts for up to 30% of lignocellulosic biomass, is the only renewable feedstock of aromatics on the earth and would thus represent an ideal source for accessing value-added aromatic platform chemicals. However, lignin is currently treated as waste by the paper and pulp industry and is simply burned to provide heat rather than an opportunity for commodity chemical synthesis.^[1] Lignin research dates back to the 1930s when the focus was directed toward structural elucidation of native lignin.^[2] Although significant research has been devoted during the past decades to affect selective depolymerization of lignin to produce lignin-derived aromatic monomers, this has proven to be a formidable challenge. The difficulty in valorizing lignin originates from its structural hetero-

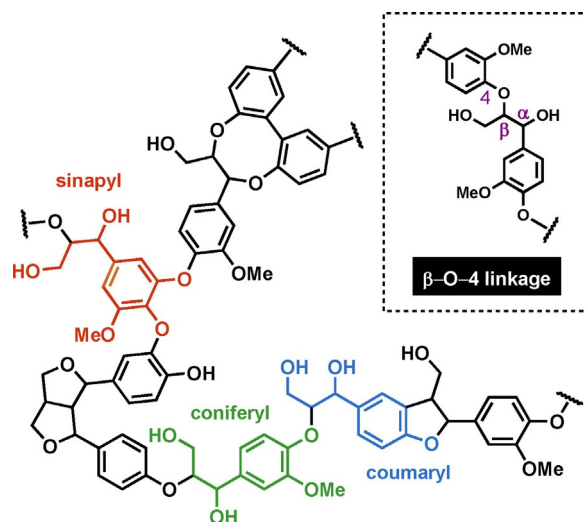


Figure 1. Representative structure of lignin. The three monolignols that are used in the biosynthesis of lignin as well as the β -O-4 linkage are highlighted.

ogeneity and recalcitrance. Lignin is comprised of three simple phenolic building blocks (monolignols): coumaryl, coniferyl, and sinapyl alcohols. During biosynthesis, these monolignols are oxidized to phenoxy radicals that undergo radical-radical coupling to produce the heterogeneous lignin biopolymer that is random in both monomer sequence and linkage motif (Figure 1).^[3-5]

Of the various linkages found in native lignin, the β -O-4 motif is the most prevalent one and has been primarily targeted by researchers for disassembly of lignin. Recently developed strategies for cleavage of the β -O-4 linkage rely on two-step processes in which an initial oxidation event produces a benzylic ketone.^[6-9] The oxidation decreases the bond dissociation energy (BDE) of the generated " β -O-4 ketone" linkage, thereby facilitating scission of the C-O bond in the subsequent step.^[10] However, it is essential to realize that an optimal procedure for isolation of lignin does not currently exist, which is a vital feature for obtaining high-quality lignin extracts. Commercial ligno-

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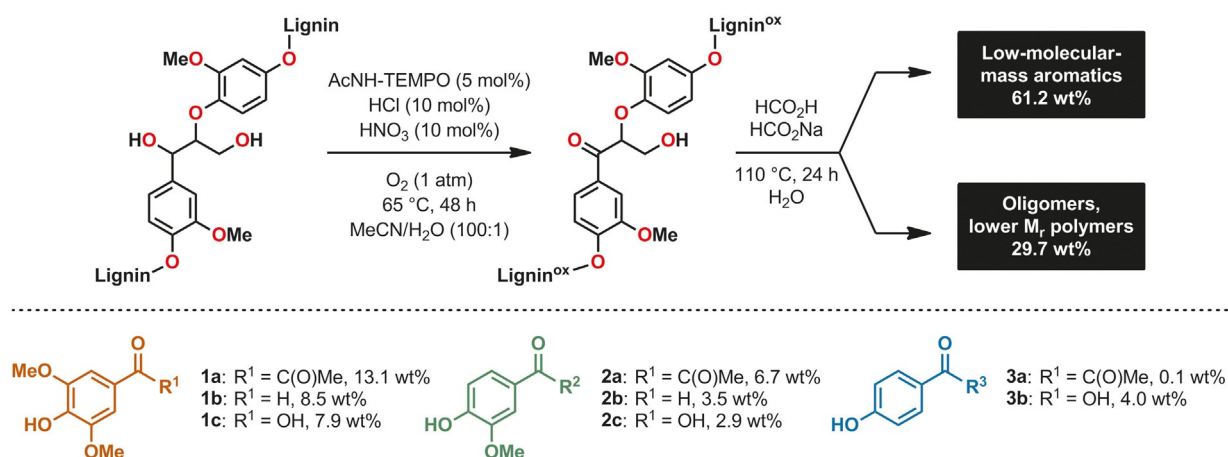


Figure 2. Two-step approach for depolymerization of aspen lignin (top) and major depolymerization products (bottom).

cellulosic fractionation or pretreatment processes, such as sulfite, kraft, and soda, are conducted at high temperatures, generally in the presence of an acid or base; however, these pulping methods are focused on producing delignified cellulose. Under these pulping conditions, native lignin inevitably undergoes structural rearrangements where C–C and C–O bond cleavage occurs, followed by irreversible formation of unnatural C–C bonds, thus introducing new interunit linkages when lignin is isolated from the lignocellulosic matrix. Current research in improving lignin extraction involves the use of water, organic solvent, γ -valerolactone (GVL), and ionic liquids (ILs), generally in combination with mineral acids at elevated temperatures.^[3–5]

Stahl and co-workers showed that the issues associated with the pretreatment process can be minimized using cellulolytic enzyme lignin (CEL) employing a two-step fragmentation approach. Here, the initial metal-free aerobic oxidation delivered the oxidized lignin, which was subsequently treated with formic acid to affect cleavage of the original β -O-4 linkages, thus giving a total yield of approximately 61 wt% of the low-molecular weight aromatics 1–3 (Figure 2) and ethyl acetate-soluble aromatic dimers and trimers.^[11] Although the yield of the enzymatically derived lignin extract is good and the enzymatic hydrolysis is believed to introduce minimal structural changes,^[12] the enzymatic process requires prolonged reaction times and also results in a residual lignin that contains a small fraction of nonhydrolyzable polysaccharides. Furthermore, sufficient quantities of CEL are currently impossible to produce, thereby limiting its applicability for large-scale applications.^[13]

In contrast, the hydrogenolysis of isolated lignin or direct hydrogenolysis of lignocellulosic biomass employing heterogeneous metal-based catalysts represents an appealing approach for converting lignin into low-molecular weight compounds,^[4,14–17] however, such reductive approaches are not new.^[18,19] Early studies in this area by Hibbert and co-workers using lignin derived from maple and spruce wood meal in combination with a copper–chromium oxide catalyst showed that lignin could be hydrogenolyzed and hydrogenated to furnish 4-propylcyclohexanol-based aliphatic alcohols.^[18] Although the yields of the monomeric products were relatively low, these studies were mainly aimed at structural elucidation of

native lignin. Recent examples include the use of heterogeneous nickel-,^[20] palladium-,^[21] ruthenium-^[22] or mixed metal-based catalysts^[23] for achieving deconstruction of lignin to monomers. In addition to the catalytic heterogeneous metal-based systems that have been designed, metal-free hydrosilylation strategies have also been reported.^[24]

The advantage of performing reductive processes on whole lignocellulosic biomass might obviate the structural rearrangements and condensation reactions that occur during lignocellulosic fractionation while producing less complex product mixtures than those produced by other fragmentation methods.^[25] Seminal work by Pepper and Fleming showed that aspen wood lignin (hardwood) could be degraded using Rh/C as catalyst at 195 °C and 3.4 MPa H₂. This afforded >40% yield of the four monomeric products **4a–7a** with 4-*n*-propanolsyringol (**4a**) and 4-*n*-propylsyringol (**5a**) being the major products (Table 1, entry 1).^[19b] In previous work, the authors studied the hydrogenolysis of spruce wood.^[19a] However, this afforded lower yields of fragmentation products, suggesting that liberation of lignin degradation products is facilitated from hardwoods compared to softwoods. Other heterogeneous metal catalysts have also been employed in the direct hydrogenolysis of lignins, for example Pd/C, which is a frequently used catalyst in organometallic chemistry. Torr et al. examined the Pd/C-catalyzed hydrogenolysis of in situ and isolated lignins from *Pinus radiata* wood in dioxane/H₂O (1:1 v/v) solutions at 195 °C and 3.45 MPa H₂ pressure.^[21b] The major monomeric components from both in situ and isolated *Pinus radiata* lignins consisted of 4-*n*-propanolguaiacol (**6a**) and 4-*n*-propylguaiacol (**7a**), which were isolated in 20–22% yield (Table 1, entry 2), illustrating that the carbohydrate residues have negligible effect on the reactivity of the lignin under the investigated reaction conditions. However, hydrogenolysis of steam exploded wood afforded lower yields of monomeric products (7%) compared to the unmodified wood. This was attributed to lower levels of releasable β -O-4 moieties in the starting lignin, suggesting that the condensation reactions that occur during steam explosion produce a lignin fraction that is less amenable to hydrogenolysis.^[26]

Zhang and co-workers prepared a variety of metal catalysts supported on activated carbon (AC) for the direct catalytic con-

Table 1. Comparison of the direct hydrogenolysis of lignocellulosic biomass using heterogeneous metal catalysts.

Entry	Feedstock	Catalyst	Hydrogen source	Major products [%]			
				4a	5a	6a	7a
1 ^[a]	aspen	Rh/C	H ₂	21.9	11.0	3.6	6.3
2 ^[b]	pine	Pd/C	H ₂	–	–	20.8	1.6
3 ^[c]	birch	NiW ₂ C/AC	H ₂	9.6	18.2	5.0	5.4
4 ^[c]	birch	Pd/AC	H ₂	31.1	4.7	9.5	0.5
5 ^[d]	birch	Pd/C + ZnCl ₂	H ₂	–	36	–	16
6 ^[d]	poplar	Pd/C + ZnCl ₂	H ₂	–	28	–	12
7 ^[d]	pine	Pd/C + ZnCl ₂	H ₂	–	–	–	19
8 ^[e]	birch	Ru/C	H ₂	3.1	31.9	1.3	9.8
9 ^[e]	birch	Pd/C	H ₂	35.2	1.4	9.7	0.4
10 ^[f]	birch	Ni/C	MeOH	–	36	–	12

[a] Reaction conditions: H₂ (3.4 MPa), 195 °C, 5 h in dioxane/H₂O (1:1 v/v) (see Ref. [19b]). [b] Reaction conditions: H₂ (3.45 MPa), 195 °C, 24 h in dioxane/H₂O (1:1) (see Ref. [21b]). [c] Reaction conditions: H₂ (6.0 MPa), 235 °C, 4 h in H₂O (see Ref. [23b]). [d] Reaction conditions: H₂ (3.4 MPa), 225 °C, 12 h in methanol (see Ref. [23e]). [e] Reaction conditions: H₂ (3.0 MPa), 250 °C, 3 h in methanol (see Ref. [21c]). [f] Reaction conditions: 200 °C, 6 h in methanol (see Ref. [20b]). AC = activated carbon.

version of raw woody biomass.^[23b] Using birch as the feedstock, it was demonstrated that the bimetallic NiW₂C/AC catalyst efficiently converted the carbohydrate component in the biomass to ethylene glycol and related diols with a total yield of up to 75.6%. The lignin component could also be converted to monophenols with a yield up to 46.5% (Table 1, entry 3). Noble metal-modified W₂C catalysts were also prepared but did not show any superior activity compared to monometallic catalysts. Of the monometallic catalysts, the Pd/AC catalyst was able to provide monomeric phenolic products in a total yield of 55.1% and also displayed different product selectivity compared to the investigated bimetallic NiW₂C/AC catalyst (cf. Table 1, entries 3 and 4). The authors also demonstrated that the chemical compositions and structures of different sources of lignocellulose exerted notable influence on the catalytic efficiency and the product distribution. For example, ash tree, basswood, and poplar, for which the lignin content were determined to be <20% of the biomass, afforded the monophenolic products in a total yield of 40.5, 37.3, and 32.4%, respectively. In comparison, both pine- and yate-derived biomass with >30% lignin content gave poor yields of monomeric products (10.1 and 10.9%, respectively).^[23b] A related study was also conducted by Abu-Omar and co-workers in which a bimetallic catalyst system consisting of Pd/C and ZnCl₂ was evaluated. Also here, lignocellulosic biomass derived from birch and poplar could undergo efficient hydrogenolysis to afford 4-*n*-propylsyringol (**5a**) and 4-*n*-propylguaiacol (**7a**) as the major products (Table 1, entries 5 and 6). However, the use of pine resulted in low conversion to monomeric products, giving **7a** in only 19% yield (Table 1, entry 7).^[23e]

The product selectivity in the hydrogenolysis can be effectively tuned using different metal catalysts. This was nicely il-

lustrated in recent work by Sels and co-workers in which a difference in selectivity was observed between Ru/C and Pd/C. Although the yields of the monomeric products were similar for the Ru/C- and Pd/C-catalyzed reactions (46 and 47%, respectively), a complete change in selectivity was observed. The use of Ru/C as hydrogenolysis catalyst had a preference for generating *para*-propyl phenolics **5a** and **7a**, whereas Pd/C favored the formation of *para*-propanol phenolics **4a** and **6a** (cf. Table 1, entries 8 and 9). This effect was attributed to the low C–O hydrogenolysis activity of Pd/C, allowing the *para*-propanol phenolics to remain stable during hydrogenolysis.^[21c] The use of alcohols for performing transfer hydrogenolysis of lignocellulosic biomass represents a more sustainable option than the direct use of H₂. The Xu laboratory could successfully degrade native birch wood lignin into monomeric phenols over a Ni/C catalyst at 200 °C using methanol as the hydrogen source (Table 1, entry 10).^[20b] The group of Abu-Omar subsequently applied the same catalyst system on different lignins and demonstrated that the product spectrum and yield was highly dependent on catalyst loading and biomass type and origin.^[20d]

To minimize the issues associated with the lignin pretreatment process, Luterbacher and co-workers now report a strategy that addresses the detrimental condensation reactions that occur, allowing for improved hydrogenolysis of extracted lignin.^[27] The authors reasoned that protecting the reactive benzylic positions could prevent the structural rearrangements and undesired linkages from occurring. Initial experiments on a simple coniferyl model compound using formaldehyde as protecting/stabilizing agent revealed that subjecting the substrate to acid treatment (as in a representative biomass fractionation process) followed by hydrogenolysis afforded high yields of the hydrogenolyzed products. However, in the absence of formaldehyde, low overall yields of hydrogenolyzed products were obtained, supporting the occurrence of condensation reactions before hydrogenolysis. The authors suggested that the beneficial effect that formaldehyde exerts is owed to two operating mechanisms: i) in acidic media, formaldehyde facilitates conversion of the α - and γ -hydroxyl groups in lignin to yield stable six-membered 1,3-dioxane/acetal motifs, thereby blocking the formation of benzylic cations, and ii) the unfunctionalized positions on the aromatic rings that are susceptible to electrophilic aromatic substitution are functionalized by formaldehyde to generate hydroxymethyl groups, thereby preventing these positions from undergoing undesirable condensation reactions (Figure 3, top). The formation of the 1,3-dioxane structures in the presence of formaldehyde could be confirmed by two-dimensional heteronuclear single-quantum coherence nuclear magnetic resonance (2D HSQC NMR) spectroscopy. The second stabilization mechanism was established through isolation of several hydroxymethylated products, which were derived from coniferyl model substrates subjected to acid/formaldehyde treatment followed by hydrogenolysis.

The authors subsequently evaluated the effect of formaldehyde during the extraction of native lignin (beech wood lignin from *Fagus grandifolia*). The lignin extracted in the presence of formaldehyde showed that the 1,3-dioxane motif was present, analogous to the results obtained with lignin model com-

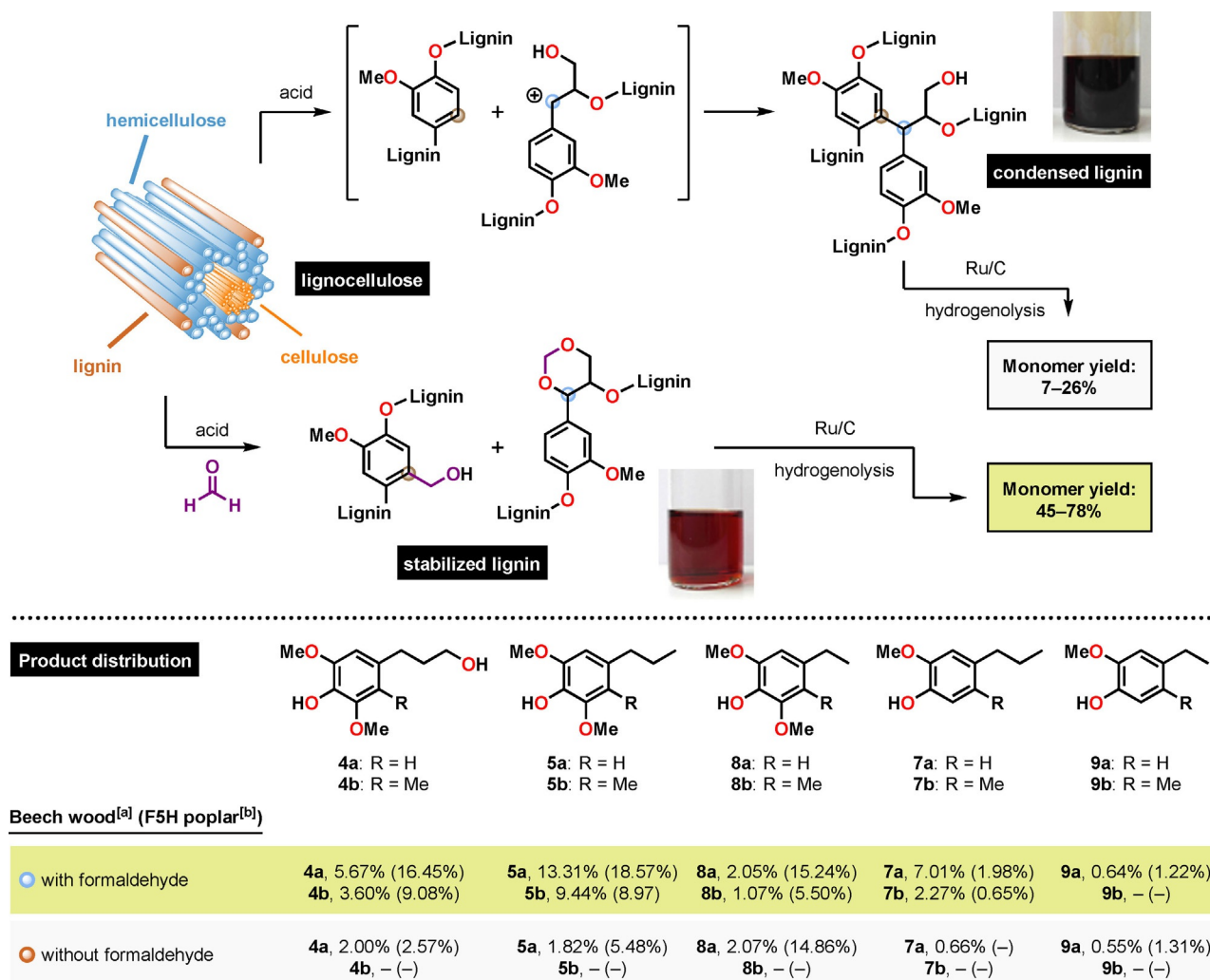


Figure 3. Improved disassembly of lignin through formaldehyde stabilization (top) and product distribution for beech wood and F5H poplar lignin (bottom). [a] For beech wood lignin, the extraction step was done in acidic 1,4-dioxane/H₂O (9:1 v/v) at 80 °C for 5 h in the presence or absence of formaldehyde. Hydrogenolysis was performed in THF at 200 °C for 6 h using Ru/C as catalyst. [b] For F5H poplar, the extraction was done in acidic 1,4-dioxane/H₂O (9:1 v/v) at 80 °C for 5 h in the presence or absence of formaldehyde. Hydrogenolysis was performed in THF at 250 °C for 15 h using Ru/C as catalyst.

pounds. Performing the pretreatment process without formaldehyde addition did not produce any signals in the HSQC spectra corresponding to the dioxane structure, and also revealed that the native lignin side-chains were absent. The color of the extract functioned as a qualitative indicator of the extent of condensation, as the lignin derived from formaldehyde treatment had a considerably lighter color than the sample recovered when formaldehyde was omitted. After hydrogenolysis with Ru/C at 200 °C for 6 h, a combined yield of 45% of monomeric species was achieved for the formaldehyde-treated lignin extract, which can be compared to a monomer yield of merely 7% for the extracted lignin without formaldehyde addition (see Figure 3, bottom).^[27]

Employing lignin derived from poplar with an over-expressed ferulate 5-hydroxylase gene (F5H poplar)^[28] produced monomer yields of up to 78% with formaldehyde as a stabilizing agent after being subjected to hydrogenolysis with Ru/C at 250 °C for 15 h. In contrast, the absence of formaldehyde gave a monomer yield of only 24%^[29] under similar hy-

drogenolysis conditions (see Figure 3, bottom). In the presence of acid, the formaldehyde-extracted lignin was also amenable to depolymerization at lower hydrogenolysis temperatures (a reaction time of 20 h at 150 °C instead of 15 h at 250 °C), producing 60% yield of monomers.

As a comparison, direct biomass hydrogenolysis under acidic conditions provided monomer yields of 48%, and also caused a considerable loss of the polysaccharide portion. This highlights the advantage of employing formaldehyde-extracted hardwood lignin for the generation of monomeric building blocks at relatively mild hydrogenolysis temperatures. Attempts to apply the developed formaldehyde method to softwood (spruce, *Picea abies*), which has a lower natural abundance of cleavable β-O-4 ether bonds,^[5,30,31] afforded 21% of monomeric products. Here, the direct hydrogenolysis with Ru/C produced a similar monomer yield, highlighting that the origin of lignin has a dramatic influence on the reaction outcome.^[27]

In summary, catalytic upgrading of lignin represents an attractive approach for production of value-added aromatic

chemicals that would otherwise only be attainable from petroleum-based feedstocks. Although direct hydrogenolysis of lignocellulosic biomass has proven to be a valuable catalytic platform for deconstructing lignin, it is also vital to address the detrimental structural rearrangements and irreversible formation of interunit C–C bonds that occur during traditional lignin pretreatment processes, which result in the production of large amounts of relatively intractable solid residues, a feature that significantly hampers the development of methods for efficient fragmentation of isolated lignin fractions. Devising methods that limit the condensation reactions that occur under biomass pretreatment could provide an opportunity for generation of lignin-derived monomers. Luterbacher and co-workers have now demonstrated that the addition of formaldehyde during biomass pretreatment facilitates the production of uncondensed lignin. The formaldehyde-treated lignin can subsequently be subjected to hydrogenolysis, giving high yields of aromatic monomers. Although the ultimate goal of controlled disassembly of lignin will undoubtedly require the collective efforts from a variety of scientific disciplines, the established strategy represents a significant advance in lignin processing and will facilitate the development of other novel lignin extraction and depolymerization methodologies in the future.

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