

# Reductive Partial Depolymerization of Acetone Organosolv Lignin to Tailor Lignin Molar Mass, Dispersity, and Reactivity for Polymer Applications

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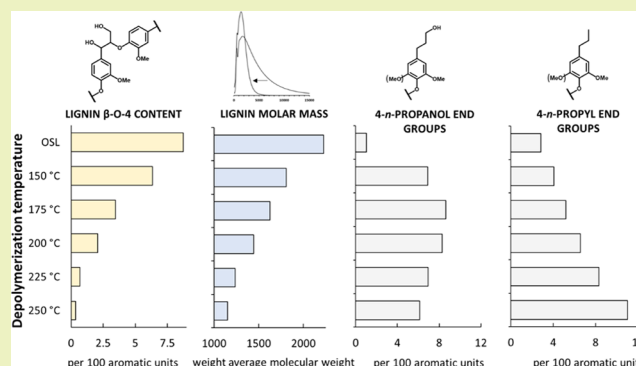
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**ABSTRACT:** Lignin partial depolymerization by reduction (PDR) was developed as a strategy to tailor a technical lignin's molar mass and reduce its heterogeneity and to potentially increase the reactivity of lignin hydroxyl groups in polymer applications such as PU foams and coatings. The process aims to cleave remaining lignin  $\beta$ -O-4 linkages, thereby reducing the molar mass of large lignin fragments and overall lignin dispersity. Acetone organosolv lignin from pilot-scale fractionation of industrial-size wood chips was depolymerized using methanol, a Ru/C catalyst, and externally supplied hydrogen. The effect of reaction temperatures (in the presence and absence of the catalyst) was fully detailed using SEC,  $^{31}\text{P}$  NMR, and 2D-HSQC NMR analyses of the depolymerized lignin. The Ru/C catalyst promoted molar mass reduction by hydrogenolysis and slightly increased the lignin aliphatic OH content. Process parameter screening showed effective depolymerization at high lignin concentrations but required relatively high catalyst loadings. PDR depolymerization efficiency proved to be dependent on the technical lignin's quality. A less-condensed lignin with a higher  $\beta$ -O-4 content showed improved ether cleavage, yielding a lower lignin molar mass after PDR and increased formation of 4-*n*-propanol end groups. Overall, the PDR process provides control over key lignin characteristics, which in turn offers potential to tailor biobased polymer properties for various applications.

**KEYWORDS:** biomass organosolv pretreatment, lignocellulose biorefinery, tailored lignin molar mass and reactivity, reductive depolymerization



## INTRODUCTION

Biorefinery concepts are major technology options for biomass to play an important role in the transition from a petroleum-based to a more sustainable and circular biobased society. Acetone organosolv pretreatment, the so-called Fabiola process, enables effective isolation of cellulose, hemicellulose, and lignin from lignocellulosic biomass.<sup>1</sup> The process has recently been validated at the pilot scale, using industrial-size beech and birch wood chips at low liquid-to-solid ratios, showing excellent translation from lab-scale operation.<sup>2</sup> At the pilot scale, the lignin could be isolated in high yield and purity from the pulping liquor using a continuous falling film lignin precipitation process known as LigniSep.

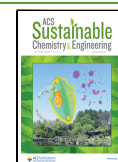
Solvent-based biorefinery processes require cost-effective valorization of cellulose pulp and hemicellulose sugars, as well as higher-value-added lignin applications to obtain both sustainability impact and a viable process economy. To this end, successful application of acetone organosolv lignin in polyurethane (PU) coatings and foams with a high lignin content have been reported.<sup>3,4</sup> Duval et al. modified acetone organosolv lignin with ethylene carbonate to fully convert

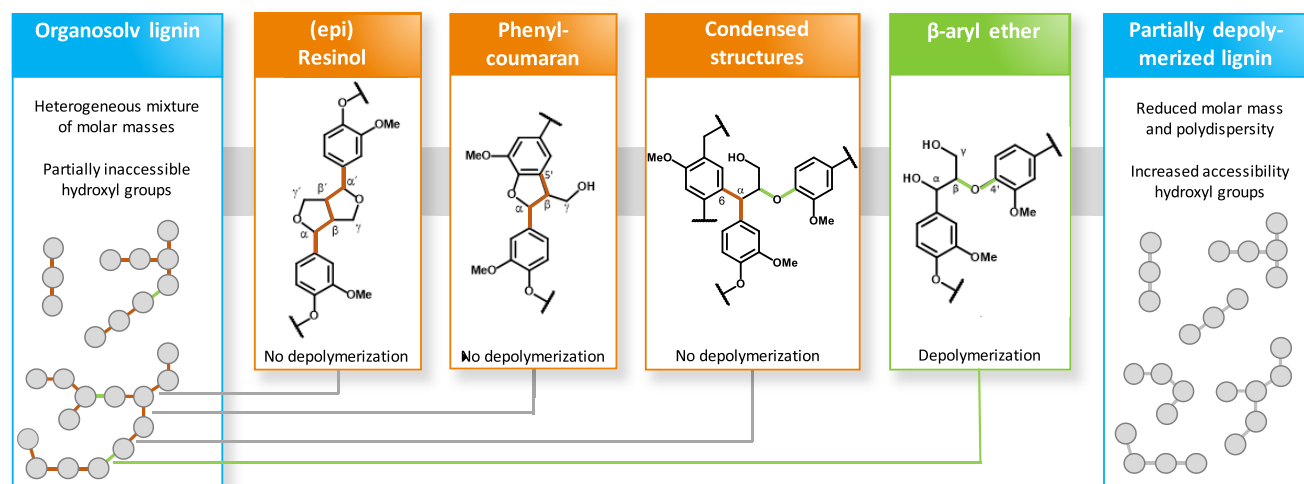
lignin's phenolic hydroxyl groups to primary aliphatic ones. The obtained polyol proved highly reactive and gave rigid PUR foams with good thermal insulation properties at 25% substitution of the standard polyol.<sup>4</sup> De Haro et al. developed a vanillin-based diisocyanate for cross-linking with unmodified acetone organosolv lignin to produce a 96% biobased coating.<sup>3</sup> While these studies present some promising leads, polyol replacement by lignin faces some significant challenges. Notably, the high molar mass heterogeneity of a typical technical lignin, and the associated broad range of physicochemical properties the individual components of the disperse sample add to the collective, hampers (optimization for) application. For the PU foams, for example, large lignin

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**Figure 1.** Partial depolymerization of acetone organosolv lignin through the cleavage of  $\beta$ -O-4 bonds.

fragments increase the viscosity of the foam polyol mixture, which negatively affects foam expansion kinetics at lignin loadings above 30% w/w. In turn, for PU coating applications, lignin reactivity is directly dependent on the accessibility of its aliphatic hydroxyls to the cross-linkers. Accessibility depends on local steric hindrance, which can be larger for higher-molecular-weight components, as the hydroxyl can be located inside the macromolecular lignin structure, ultimately resulting in a lower cross-linking density and thus control over the PU coating characteristics.

Lignin fractionation methods have been developed to produce lignin samples of reduced dispersity in distinct molar mass ranges.<sup>5–7</sup> For acetone organosolv lignin, for example, fractionation could be achieved by consecutive solubilization in a variety of solvents or by stepwise precipitation by water dilution of the liquor.<sup>2,8,9</sup> The beech and birch wood lignin fractions thus obtained showed that a significant part of the lignin consists of large lignin fragments with weight-average molecular weights ( $M_w$ ) roughly between 2500 and 10 000 g/mol.

As fractionation does not change the overall  $M_w$  of a lignin sample, but just the distribution over the fractions, another strategy is required to gain further control over  $M_w$ , one that would allow tailoring it for the entire sample, including its fractions. As the  $M_w$  of a large part of the sample is too high for optimal application, controlled depolymerization of especially the large lignin fragments to a lower molar mass may have potential to tailor lignin characteristics for a better control over its solubility, reactivity, and thermal properties. Most literature examples however focus on deep polymerization and target the production of monomeric phenolics via full lignin depolymerization using thermochemical, oxidative, reductive, photocatalytic, and biochemical processes.<sup>10–16</sup> Only very few studies report on, e.g., optimization of the oligomer product instead.<sup>17,18</sup> Indeed, the strategy of tailoring macromolecular properties via partial depolymerization of an isolated lignin (and its fractions) remains to be demonstrated. Within the deep depolymerization examples, reductive approaches have gained particular interest as they achieve high monomer yields, in particular when applied in a lignin-first-type strategy. Efficient stabilization of the depolymerization products largely prevents undesired radical-mediated lignin repolymerization

and generation of complex product mixtures as observed for, e.g., most oxidative or acid- or base-mediated processes.<sup>19</sup> Typically, transition metals such as Ru, Pd, Pt, Rh, and Ni on carbon, alumina, or zeolite supports are used as catalysts for such reductive catalytic depolymerizations.<sup>20–27</sup> The degree of deoxygenation and thus product composition can be influenced by both catalyst composition and hydrogen availability, i.e., by using either an external  $H_2$  supply or hydrogen donating solvents.<sup>19,28</sup>

The efficiency of depolymerization to (mono)aromatics is largely determined by lignin quality, in particular defined here by the amount of cleavable ether linkages. As ether linkages, specifically the most reactive  $\beta$ -aryl ether ( $\beta$ -O-4) bond, are most abundant in native lignin, i.e., in planta, reductive catalytic depolymerization approaches (RCF) are most successful if applied as part of a lignin-first strategy<sup>27,29–31</sup> or on lignins isolated with high retention of such linkages;<sup>32</sup> high yields of monomeric aromatic products such as 4-*n*-propyl and 4-*n*-propanol syringol/guaiacol are typically reported in these cases. However, most technical (i.e., isolated) lignins are generally considered to be ill-suited for reductive depolymerization. This is because most biomass pretreatment processes require relatively high process severities to obtain sufficient biomass delignification, resulting in extensive ether bond cleavage and formation of condensed lignin structures.<sup>33</sup> Most technical and organosolv lignins thus have limited potential for deep depolymerization to give high monomer yields.<sup>20,34–36</sup> As also technical lignins still contain varying amounts of cleavable ethers, reductive depolymerization, while not suited for monomer production, may have considerable potential for tailoring the  $M_w$  of the macromolecules (Figure 1). Additionally, the depolymerized lignin product, lean in residual ethers, may prove to be a more resilient polyol, thus introducing improved durability and circularity options to the polymer products.

Notably, the acetone organosolv process yields a high purity lignin which is, importantly, relatively rich in ether linkages. This offers an opportunity to tailor the lignin characteristics post isolation by reductive partial depolymerization. Compared to RCF, such post isolation partial depolymerization by reduction (PDR) can in principle be performed at higher

lignin loadings and with reduced risk of catalyst fouling by other components of the biomass.<sup>37,38</sup>

Here, we demonstrate that such a strategy of tailoring the macromolecular properties by reductive partial depolymerization can be successfully applied to high-quality acetone organosolv lignin. The aim is to controllably reduce molar mass and dispersity to preserve hydroxyl groups and, in the combination thereof, improve accessibility and reactivity of these groups, providing an opportunity to control PDR lignin characteristics toward optimal utilization in polymer applications.

## RESULTS AND DISCUSSION

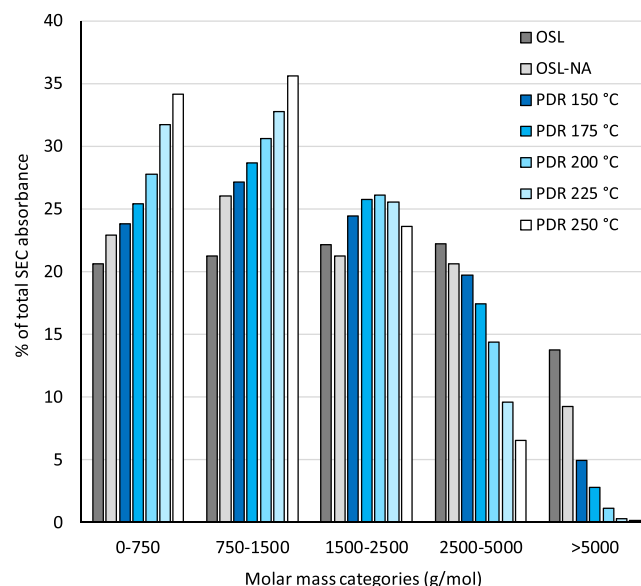
**Lignin Selection.** Beech wood acetone organosolv lignin (OSL) was produced at the pilot scale from industrial-size beech wood chips by pretreatment in 50% aq acetone at 140 °C using a low liquid-to-solid ratio (L/S 3.3 based on dry wood). Lignin was precipitated from the pulping liquor using the LigniSep technology of a continuous falling film precipitator to enable the isolation of OSL lignin in high yield and purity, whose characteristics have been detailed previously (as P-BEC-3).<sup>2</sup>

**Lignin Partial Depolymerization by Reduction (PDR).** PDR process development was conducted using 10 g/L OSL in methanol, 0.5 g 5% Ru/C per g lignin, and 30 bar H<sub>2</sub> (pressure at ambient temperature) for 2 h. A temperature screening (150–250 °C) was conducted in the presence and absence of the catalyst under the selected process conditions. Details of the downstream processing and analysis methods, including alkaline size-exclusion chromatography (SEC) to determine lignin molar mass and polydispersity; <sup>31</sup>P NMR for quantification of lignin hydroxyl groups; and 2D-HSQC NMR for the semiquantitative analysis of lignin aromatic structures, interunit linkages, and end groups, can be found in the [Supporting Information](#).

A relatively mild PDR treatment at 150 °C in the absence of Ru/C led to an apparent drop in lignin weight-average molecular weight ( $M_w$ , here referred to as molar mass) of untreated OSL from 2830 to 2120 g/mol ([Figure 3A](#), open circle). However, 2D-HSQC NMR analysis showed no cleavage of  $\beta$ -O-4 linkages in depolymerized (PDR) lignin and thus provided no support for any actual depolymerization of OSL. This led us to suspect lignin molar mass to be overestimated for as-is OSL by the SEC analysis, as a result of lignin aggregation. While the tendency of lignin for self-assembly or aggregation through noncovalent interactions such as hydrogen bonding, hydrophobic, and  $\pi$ - $\pi$  interactions is well known,<sup>39–42</sup> aggregation in methanol or aqueous acetone is not expected, given the high solubility of Fabiola lignin in these solvents. Possibly, lignin aggregation occurs during lignin precipitation from the process liquor where the energetically most favorable assembly is formed during this step. Indeed, Wang et al. explored the dissolution and aggregation behavior of enzymatic hydrolysis lignin in water–solvent mixtures and found a good lignin solubility in aqueous acetone mixtures with only weak interactions between lignin hydrophilic and hydrophobic groups. More aqueous mixtures (as during lignin precipitation) induced strong attractive forces and lignin aggregation.<sup>43</sup>

As lignin aggregation effects needed to be resolved to allow for proper analysis of any extent of depolymerization by PDR, a series of experiments were conducted ([Figures S1 and S2](#)) comprising a short heat treatment of a lignin/methanol

mixture to 150 °C, showing a significant reduction in lignin molar mass to 2230 g/mol without altering its structural characteristics and linkage abundance as evidenced by 2D-HSQC NMR (OSL-NA, [Table S2](#)). The  $M_w$  distribution obtained by SEC analysis of OSL and OSL-NA over selected  $M_w$  ranges is presented in [Figure 2](#) (gray bars), showing an

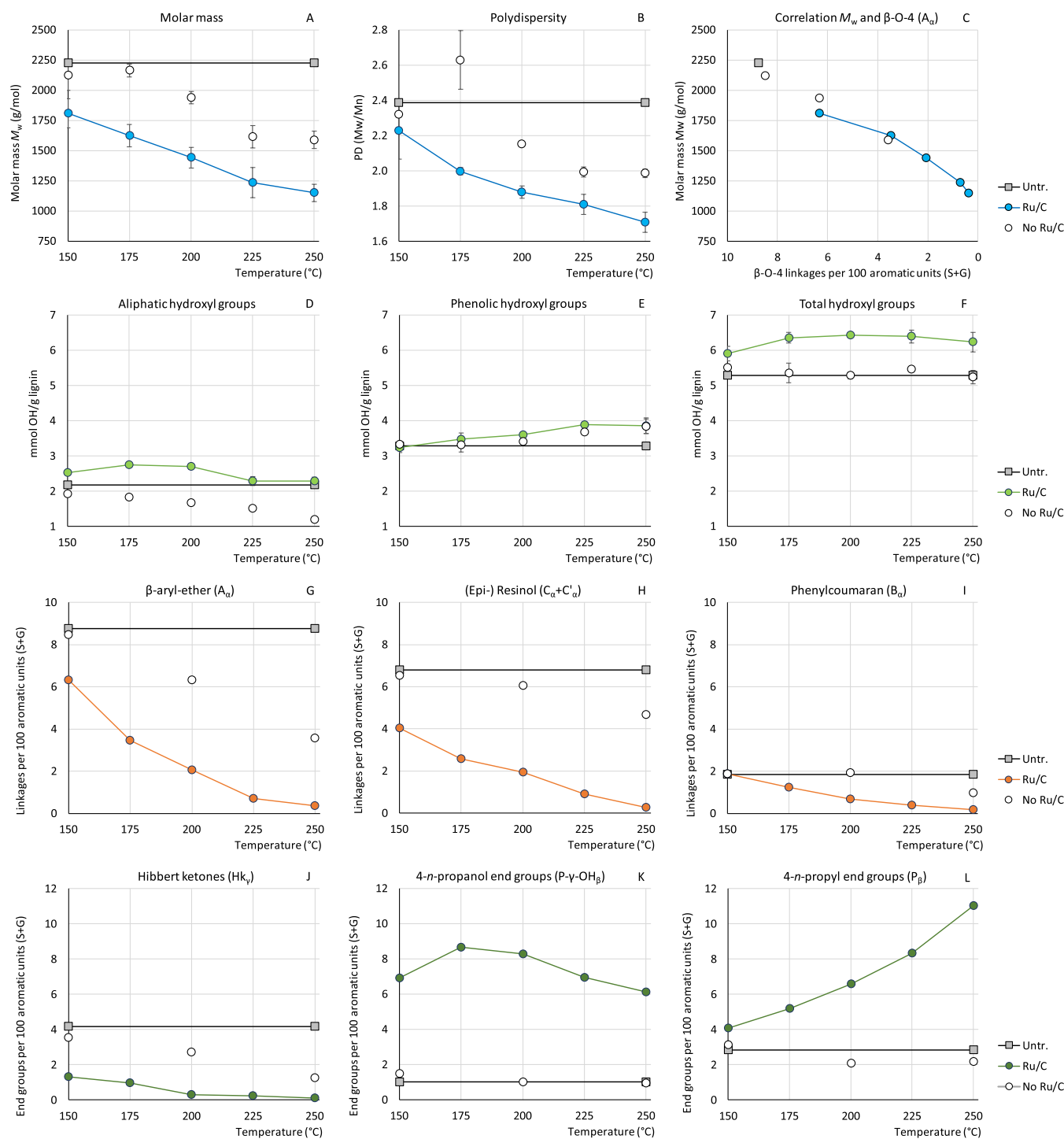


**Figure 2.** Molar mass distribution of isolated, nonaggregated (-NA) and partially depolymerized OSL.

increase in the amount of smaller lignin fragments in the range of 0–1500 g/mol and a decrease for lignin components with a molar mass larger than 2500 g/mol. To enable differentiation between lignin aggregation and depolymerization, the molar masses of nonaggregated (i.e., shortly heat-treated) parent lignins (-NA) are used throughout this study. Recent work on lignin fractionation showed that lignin aggregation exclusively occurs between large lignin fragments, and therefore, no aggregation is expected for the depolymerized lignin product.<sup>44</sup>

[Figure 3](#) shows how the structural characteristics of OSL-NA are affected by PDR process temperature and by the addition of the Ru/C catalyst. The reference experiment at 150 °C (without catalyst) showed a negligible decline in molar mass and lignin  $\beta$ -O-4 content ([Figure 3A,G](#)). However, significant cleavage of  $\beta$ -O-4 linkages and subsequent reduction of lignin molar mass are observed when the Ru/C catalyst is added (see also [Figure 2](#)). At higher temperatures, cleavage of lignin  $\beta$ -O-4 linkages and subsequent depolymerization increase, especially in the presence of the catalyst. Multiple studies support the understanding that noncatalytic lignin solvolysis is prevalent at higher process severities, while catalytic hydrogenolysis of lignin  $\beta$ -O-4 linkages occurs at milder conditions.<sup>45–47</sup> However, cleavage pathways will likely depend on the bond dissociation energy of and accessibility of the catalyst to each specific  $\beta$ -O-4 linkage.

Repolymerization of reactive intermediates after lignin solvolysis at higher temperatures can play a major role in the formation of larger condensed lignin fragments.<sup>48,49</sup> Here, such effects are not observed; the extent of  $\beta$ -O-4 bond cleavage and depolymerized lignin molar mass shows a surprisingly strong correlation regardless of the presence or absence of the catalyst ([Figures 3C and S4](#)). The polydispersity ( $M_w/M_n$ , PD)



**Figure 3.** Characteristics of OSL-NA (nonaggregated, gray squares) and OSL depolymerized at a range of temperatures in the absence (open circles) and presence of Ru/C (colored circles). Process conditions: 10 g OSL/L methanol, 150–250 °C, 120 min, 0.5 g Ru/C per g lignin, 30 bar H<sub>2</sub>.

decreased from 2.4 for OSL-NA to 1.7 after treatment with Ru/C at 250 °C. Lignin polydispersity also dropped for the uncatalyzed reaction (Table S3), indicating that lignin recondensation is limited in the presence of methanol and hydrogen.

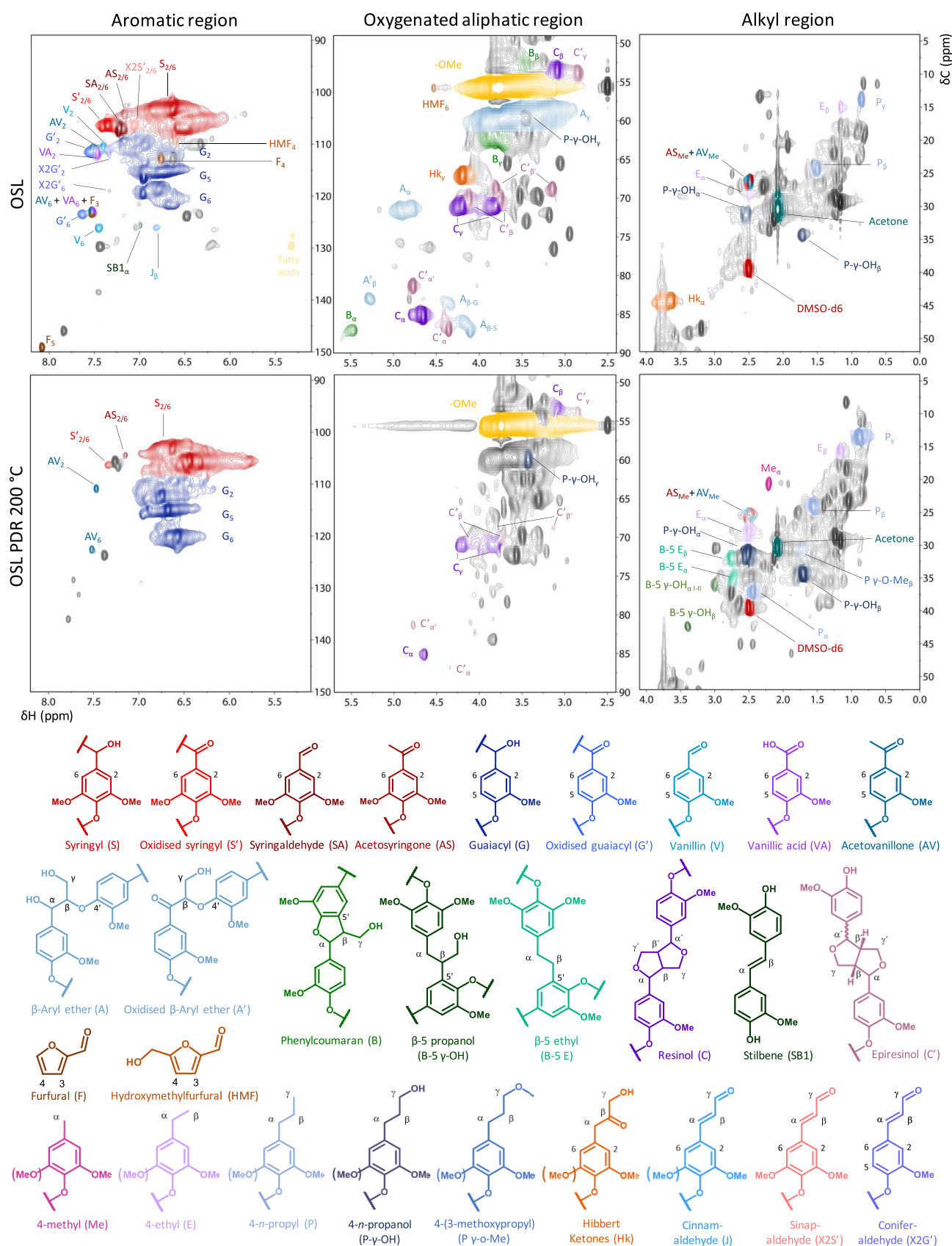
Overall, proper selection of process temperature clearly provides control over lignin molar mass reduction and polydispersity. Furthermore, deeper depolymerization is

achieved in the presence of a Ru/C catalyst allowing for milder process conditions to control lignin molar mass.

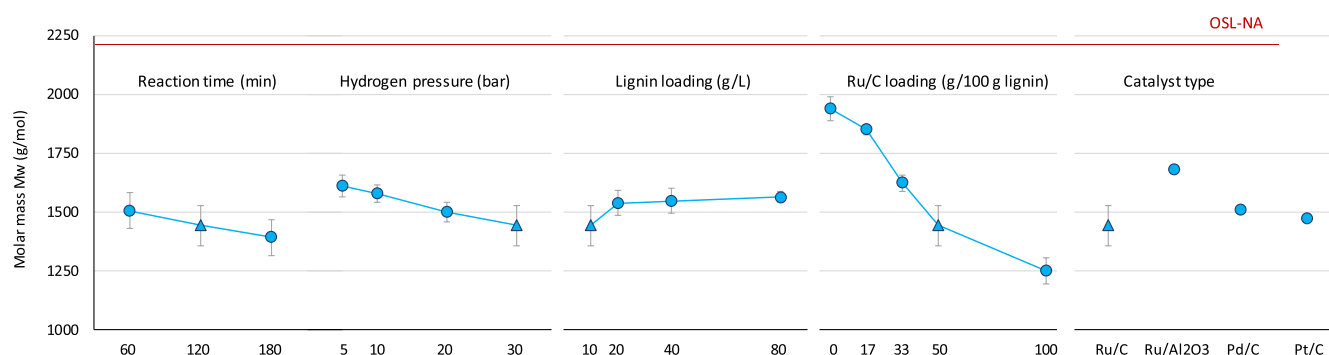
Despite some variation in lignin recovery, attributed to experimental error, the average recovery of PDR lignin was similar for catalyzed and uncatalyzed depolymerization at 89 and 88%, respectively.

Hydrogenolysis of  $\beta$ -O-4 bonds typically produces a phenolic hydroxyl group and an aliphatic chain which, depending on catalyst type and process conditions, may





**Figure 4.** Aromatic region, oxygenated aliphatic region, and alkyl region of 2D-HSQC NMR spectra of untreated and depolymerized OSL lignin. The main identified structures are shown at the right and bottom. Full spectra of catalyzed PDR lignin are available in the Supporting Information (Figure S14).



**Figure 5.** Effect of variations in PDR process conditions on the molar mass of depolymerized OSL.

consist of 4-*n*-propanol and 4-*n*-propyl end group structures. Here, increased depolymerization roughly correlated with an increase in phenolic hydroxyl group content (Figure 3E) for both catalyzed and noncatalyzed PDR. Contrarily, the PDR lignin aliphatic hydroxyl group content (Figure 3D) decreased in the absence of the catalyst.

Semiquantitative analysis of lignin end groups (Figure 3J,K,L) provided more insight, showing significant (catalyzed) formation of 4-*n*-propanol end groups already at low PDR temperatures. The extent of formation of such structures at low PDR temperatures did not correlate with the extent of  $\beta$ -O-4 bond cleavage and may partly originate from hydrogenation of Hibbert ketones. 4-*n*-Propanol end group abundance reached a maximum at 175–200 °C showing a good correlation with the lignin aliphatic hydroxyl group content. In the presence of Ru/C, formation of 4-*n*-propyl end groups steadily increased at higher PDR temperatures.

These structures may be formed directly from  $\beta$ -O-4 bond cleavage as well as hydrodeoxygenation of 4-*n*-propanol end groups. The role of Ru/C in the formation of both 4-*n*-propanol and 4-*n*-propyl end groups is clearly demonstrated as no such structures are formed during noncatalyzed PDR. What structures are formed during noncatalyzed PDR is not immediately evident from the 2D-HSQC NMR analysis.

Figure 3H,I shows that the resinol ( $\beta$ - $\beta$ , C<sub>a</sub>), epiresinol ( $\beta$ - $\beta'$ , C'<sub>a</sub>), and phenylcoumaran ( $\beta$ -5, B<sub>a</sub>) linkages decrease in abundance after partial depolymerization, especially at higher temperatures and in the presence of Ru/C. Cleavage of the ether bonds in those linkages mostly do not result in depolymerization as the C–C backbone remains intact (Figure 1). Structural analysis on dimers produced by reductive catalytic fractionation has shown that the  $\beta$ -5 bonds are converted to an ethylene bridge, which is either unsubstituted or contains a –CH<sub>2</sub>OH group.<sup>50</sup> Van Aelst et al. reported on the detailed 2D-HSQC NMR characterization of structures and linkages found in RCF lignin oils. From this work, typical products from hydrogenolysis of (epi)resinol and phenylcoumaran structures were identified.<sup>51,52</sup> Hydrogenolysis of  $\beta$ -5 ether bonds at increasing depolymerization temperatures is accompanied by a subsequent increase in  $\beta$ -5 propanol linkages ( $\beta$ -5  $\gamma$ -OH). At a PDR temperature of 200 °C, the drop in  $\beta$ -5 ether bond abundance is similar to the formation  $\beta$ -5 propanol linkages (Figures 4 and S6). A significant increase in  $\beta$ -5 ethyl linkage ( $\beta$ -5 E) abundance is observed over temperature, resulting in up to twice the amount of  $\beta$ -5 ether bonds present in OSL, suggesting that the  $\beta$ -5 ethyl moiety must partly originate from other sources than the  $\beta$ -5 linkages. Hydrogenation of stilbenes can in principle contribute to the

formation of  $\beta$ -5 ethyl linkages, but the abundance of stilbenes in the OSL is too low to make a significant contribution.

Finally, cleavage of resinol and epiresinol ether bonds may result in the formation of lariciresinol (not identified) and secoisolariciresinol, whose abundance remained low over the temperature series, corresponding to <3% of cleaved (epi)-resinol linkages.

Generally, syringyl and guaiacyl units were relatively stable under the applied conditions in accordance with previous studies.<sup>50</sup> The abundance of oxidized syringyl and guaiacyl units (4 and 2% of total aromatic units, respectively) decreased rapidly but only in the presence of Ru/C; the same holds for syringaldehyde and vanillin (3 and 1% of total aromatic units, respectively), suggesting reduction of the ketones to alcohol functionalities. The probable products, syringyl alcohol and vanillyl alcohol, could not be quantified as the identified signals are located in the syringyl and guaiacyl cross peaks (Figure S15). Acetovanillone hydrogenation may produce apocynol, but no Me<sub>a</sub> cross peak was detected. Surprisingly, acetovanillone and acetosyringone remained partially present in all PDR lignins, and the Me<sub>β</sub> signal (Figure S14) of both structures did not change significantly. Further details of the 2D-HSQC NMR analysis, including the abundance of major and minor structures and full spectra can be found in the supporting information (Figures S6, S7, and S14). Overall, the results show that the catalytic reductive cleavage of lignin  $\beta$ -O-4 bonds provides control over lignin molar mass as well as functionality with phenolic hydroxyl and 4-*n*-propanol/4-*n*-propyl as the main end groups.

**Processing Aspects.** Catalytic PDR at 200 °C was selected for further process development as it combines sufficient depolymerization with an increase in lignin aliphatic hydroxyl group content. Variations from the previously selected process parameters (10 g/L lignin in methanol, 120 min, 0.5 g Ru/C per g lignin, 30 bar H<sub>2</sub>) were tested to assess its impact on lignin depolymerization (Figure 5). Process intensification by using a shorter reaction time, reduced H<sub>2</sub> pressure, or increased lignin loading reduced the extent of lignin depolymerization. Note that the effect is limited and the optimal molar mass (distribution) will differ for specific lignin-based applications.

A larger effect is observed for catalyst loading where a significant amount of Ru/C is needed to ensure effective depolymerization. Replacing Ru/C with Ru/Al<sub>2</sub>O<sub>3</sub>, Pd/C, and Pt/C did not improve depolymerization. Van den Bosch et al. showed how changing the catalyst from Ru/C to Pd/C in a one-pot RCF process significantly increased the hydroxyl content of the products. Where Ru/C-catalyzed depolymeriza-

tion favored the production of 4-*n*-propyl end chains, the Pd/C predominantly produced 4-*n*-propanol moieties.<sup>26</sup> In this study, the Pd/C-catalyzed PDR lignin showed a slightly lower aliphatic hydroxyl group content (Figure S11). The work reported by Ouyang et al. provides interesting insights as it confirms these findings with a one-pot approach but found a significant shift toward the formation of 4-*n*-(3-methoxy) propyl in a two-pot process (i.e., auto- and acid-catalyzed lignin solvolysis, followed by Pd-catalyzed hydrogenolysis).<sup>53</sup> Lower-cost catalysts such as Ni may have potential for an improved PDR process economy as these catalysts have shown high activity for C–O bond cleavage, producing either monomers with *n*-propyl end chains<sup>25,28,54</sup> or *n*-propanol end chains when sufficient molecular hydrogen is applied.<sup>21</sup> However, besides catalyst cost and performance, catalyst stability and regeneration are important aspects to consider for further PDR process development.

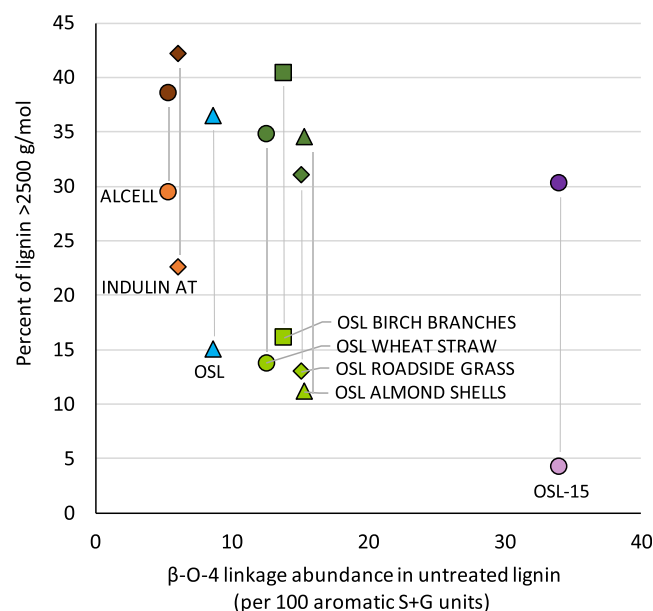
Multiple studies have reported on how solvents such as water, methanol, ethanol, isopropanol, and ethylene glycol affect lignin depolymerization toward bioaromatics.<sup>22,54–56</sup> The results reported vary, however, considerably, likely due to the variety of applied lignins, catalysts, and process conditions in these studies. Jahan et al. showed that pure methanol is an excellent solvent for lignin that leads to progressively extended coil conformation of the lignin, suggested to be the catalytically competent conformations that expose the linkages to the surroundings solvents.<sup>57</sup> Ethanol and isopropanol were tested as alternative PDR solvents, showing similar results as methanol with respect to OSL depolymerization and PDR lignin hydroxyl group content (Figure S10). However, process intensification efforts using higher lignin loadings may be impaired by the low solubility of lignin in isopropanol.<sup>54</sup> Water–solvent mixtures were not tested as reduced solubility of large (and aggregated) lignin fragments in these mixtures may hamper depolymerization and reduce the role of the solvent as a capping agent to stabilize free radicals.<sup>56,58</sup>

A PDR experiment with 80 g/L OSL and aforementioned process conditions resulted in a 79% lignin recovery, which increased to 93% after more extensive catalyst washing (Table S4). Lignin obtained in the PDR mixture and after (extensive) washing showed no significant differences in molar mass, indicating limited preferential entrapment of large (condensed) lignin fragments or adsorption of monomers on the activated carbon (data not shown). The catalyst weight increase corresponded to 7% of the initial lignin and is most likely present on the catalyst as carbonaceous insoluble deposits. A preliminary study into catalyst regeneration shows that these deposits can mostly be dissolved in hexane at ambient temperature and acetone at 120 °C (data not shown).

**Effect of Lignin Quality.** The extent of lignin partial depolymerization largely depends on lignin quality (i.e., abundance of  $\beta$ -O-4 linkages). PDR was conducted on a selection of lignins to assess this relationship. Indulin AT (Kraft lignin) and Alcell (organosolv lignin), characterized previously by Constant et al., were selected as technical lignins.<sup>59</sup> Lignins obtained from acetone organosolv pretreatment of wheat straw, roadside grass, and almond shells were characterized in recent work (as WA-WS, WA-RG, and WA-AS, respectively).<sup>60</sup> The shorter fractionation time applied for these feedstocks (60 min) leads to less extensive acidolysis of ether bonds and thus a higher  $\beta$ -O-4 content compared to OSL. In addition, a beech wood lignin (OSL-15) was isolated

under milder pretreatment process conditions for 90 min at 140 °C using 60% aq acetone and 40 mM sulfuric acid. The pulping liquor was replaced by reaction liquid every 15 min, thereby limiting the residence time of solubilized lignin at process temperature. This approach minimizes further cleavage of ether linkages and repolymerization caused by long residence time of solubilized lignin in the hot liquor as reported in the literature, while maintaining a similar degree of delignification.<sup>20,34,53</sup> Beech wood delignification was 82%, which is comparable to OSL fractionation; however, the lignin  $\beta$ -O-4 bond content of OSL-15 is much higher with 33 linkages per 100 aromatic units. Cellulolytic enzymatic lignin (CEL) extracted from this beech wood, representing the native lignin, had a  $\beta$ -O-4 bond content of 53 per 100 aromatic units, showing that more than half of the native  $\beta$ -O-4 linkages are retained in OSL-15. The lignins were then processed using the standard PDR conditions (200 °C, 10 g lignin/L methanol, 120 min, 0.5 g Ru/C/g lignin, 30 bar H<sub>2</sub>).

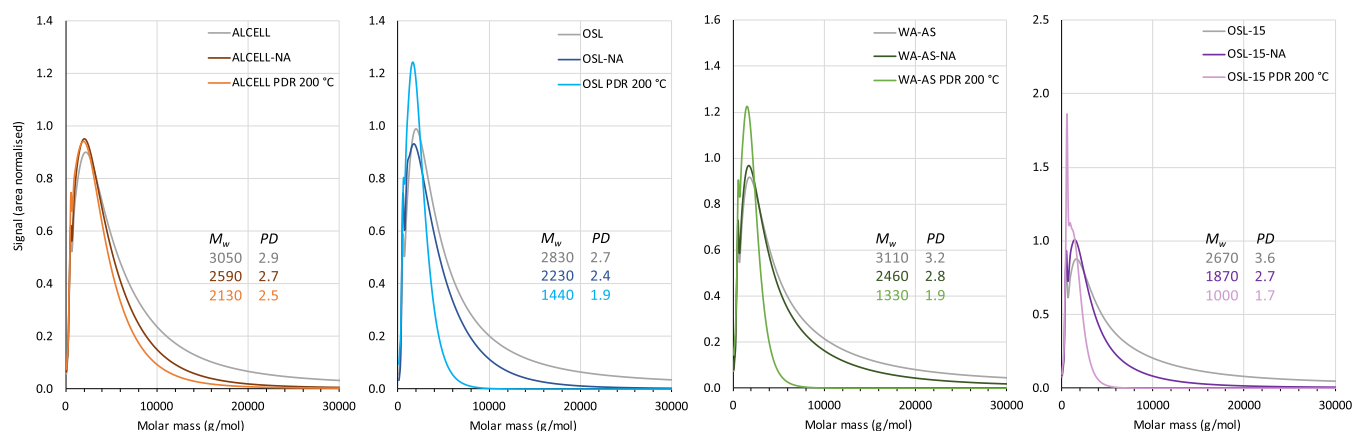
To reduce molar mass and polydispersity, cleavage of available  $\beta$ -O-4 linkages, in particular the ( $\beta$ -O-4 rich<sup>44</sup>) larger lignin fragments, is of specific interest in PDR. Here, we arbitrarily set the cutoff for large lignin fragments at to >2500 g/mol and expressed these as percent of the total lignin in Figure 6. The SEC curves in Figure 7 show the total molar



**Figure 6.** Lignin molar mass fraction of  $M_w > 2500$  g/mol before (dark colored markers) and after depolymerization (light colored markers) of a selection of lignins as a function of the parent lignin  $\beta$ -O-4 linkage content ( $\beta$ -O-4 content of Alcell and Indulin AT from Constant et al.<sup>59</sup>).

mass distribution of untreated (gray lines), nonaggregated (-NA, dark colored lines), and depolymerized (light colored lines) lignin.

As anticipated,<sup>20,34</sup> the lignins with a higher  $\beta$ -O-4 content showed improved depolymerization resulting in a more extensively reduced lignin molar mass and dispersity. Note that lignins obtained from herbaceous biomass (wheat straw and roadside grass in this study) are structurally different from the hardwood lignins with a relatively high content of *p*-coumarate and ferulate units. Multiple studies using lignin from herbaceous biomass have shown higher solvolysis rates



**Figure 7.** Alkaline size-exclusion chromatography curves of untreated, nonaggregated (-NA), and depolymerized (PDR 200 °C) Alcell, OSL, almond shell lignin (WA-AS), and a beech wood OSL with a high  $\beta$ -O-4 content (OSL-15).

and cleavage of  $\beta$ -O-4 lignin bonds even in the absence of a hydrogenation catalyst and hydrogen.<sup>37,61</sup> On the other hand, the study by Ebikade et al. showed a negative correlation between the lignin ferulate content and lignin monomer yield, indicating that ferulates are prone to condensation reactions.<sup>37</sup> In this study, no large differences were found between the organosolv lignins from hardwood and herbaceous biomass (see also Figure S13).

As expected, OSL-15 was most susceptible for depolymerization, showing a large dimer/trimer peak in the SEC curve (note that recovery and quantification of lignin monomers were not included in the downstream processing).

2D-HSQC NMR analysis of depolymerized OSL-15 lignin showed a much lower  $\beta$ -O-4 content compared to the OSL PDR lignin with 0.6 and 2.1 linkages per 100 S + G units, respectively (Table 1). A similar trend was observed for (epi-

effectiveness and sustainability impact by applying lower temperatures and/or less catalyst. Overall, this shows the importance of lignin quality for successful PDR.

## CONCLUSIONS

Lignin isolated by pilot-scale acetone organosolv treatment of beech wood chips was successfully depolymerized to a lignin with reduced molar mass and dispersity. A temperature of 200 °C balances lignin molar mass reduction with a slight increase in lignin aliphatic hydroxyl groups. Efficient depolymerization of especially the large lignin fragments results in significantly reduced molar mass heterogeneity and potentially the reactivity of lignin hydroxyl groups in polymer applications. Partial depolymerization of acetone organosolv lignins from a variety of feedstocks gave similar results. This strengthens the connection between sustainable feedstock supply chains and, through feedstock flexible biorefining and PDR, the industrial end users.

The process presented in this study will introduce additional costs to the lignin valorization chain. More cost-effective processing may be pursued by using low-cost catalysts at lower doses, high lignin concentrations, and milder process conditions. Further improvements in biomass pretreatment process design, producing less-condensed lignin with a high  $\beta$ -O-4 content seems to provide the highest potential for achieving these goals.

An important next step is to test the partially depolymerized lignin in polymer applications and establish lignin structure–polymer performance relationships. More control over the lignin structure may provide both advance as well as tuneability of lignin-based polymers. The effect of PDR treatment on lignin application in PU coatings, including its sustainability impact, has shown promising results, as reported in separate contributions.<sup>44,62</sup>

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.3c00617>.

Additional experimental details, materials, methods, and 2D-HSQC NMR spectra (PDF)

**Table 1.** OSL-15 Linkages and End Group Abundance before and after PDR

per 100 S + G units		OSL	OSL PDR	OSL-15	OSL-15 PDR
Linkages					
$\beta$ -O-4	$A_\alpha$	8.6	2.1	33.2	0.6
$\beta$ -5	$B_\alpha$	1.9	0.7	2.9	0.2
$\beta$ - $\beta$	$C_\alpha$	3.9	1.2	4.1	0.6
$\beta$ - $\beta'$	$C'_\alpha$	3.1	0.7	4.4	0.4
End Groups					
4- <i>n</i> -propanol	$P\text{-}\gamma\text{-OH}_\beta$	1.0	8.3	1.0	18.7
4- <i>n</i> -propyl	$P_\beta$	2.4	6.6	1.9	14.5

)resinol and phenylcoumaran linkages. This indicates that a less-condensed and thus more linear lignin structure limits steric hindrance allowing for better interaction between the heterogeneous Ru/C catalyst and the lignin linkages, promoting its catalytic function.

The high  $\beta$ -O-4 content of OSL-15 and near-complete cleavage of these linkages resulted in an increased formation of 4-*n*-propyl end groups (14.5 per 100 aromatic units) and 4-*n*-propanol end groups (18.7 per 100 aromatic units). Note that the extensive depolymerization of OSL-15 is outside the target molar mass range of the PDR process, which aims to recover lignin in macromolecular form, to be used as a functional polymer. However, the susceptibility of OSL-15 to depolymerization does provide potential for improved process cost-



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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

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