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## ARTICLE

## Pyrolysis-assisted catalytic hydrogenolysis of softwood lignin at elevated temperatures for the high yield production of monomers

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The catalytic hydrogenolysis of softwood lignins is normally conducted at temperatures below 200 °C but tends to provide monomer yields of less than 30 mol% as a consequence of the non-cleavable 4-*O*-5 and condensed (C–C) linkages of phenylpropane units in lignin. In the present study, catalytic hydrogenolysis at higher temperatures (250–350 °C) with the addition of Pd/C and H<sub>2</sub> in anisole provided very high monomer yields of 62 and 43.5 mol% (based on the quantity of aromatic rings in the original lignin) from milled wood lignin and organosolv lignin, respectively. Both these materials were isolated from Japanese cedar wood (a softwood). An analysis of the dimeric products and catalytic hydrogenolysis trials using model dimers established that the cleavage of 4-*O*-5 and condensed bonds was responsible for these high monomer yields. Specifically, C<sub>α</sub>-aryl-type condensed bonds formed by condensation reactions during pyrolysis and the organosolv process were efficiently cleaved. This cleavage favored the production of monomers because condensation forming C<sub>α</sub>-aryl bonds normally inhibits monomer formation to a significant extent. The undesirable saturation of aromatic rings was also suppressed at such high temperatures. The Pd/C catalyst but not the addition of H<sub>2</sub> was determined to be necessary for high monomer yields and the pyrolytic degradation of the lignin evidently played an important role in this transformation. On the basis of these data, the high temperature process reported herein is termed pyrolysis-assisted catalytic hydrogenolysis.

### Introduction

Lignin is the most abundant renewable source of aromatic compounds on the planet and accounts for 20–35 wt% of lignocellulosic biomass materials such as wood and herbaceous plants. Consequently, the conversion of lignin to aromatic monomers could represent a renewable source of commodity chemicals such as phenol and other aromatics and an alternative to the use of petroleum.<sup>1</sup> The selective depolymerization of lignin is a very important aspect of this strategy and catalytic hydrogenolysis has received a great deal of attention in this regard. It has been reported that catalytic hydrogenolysis conducted under extreme conditions (such as 250–260 °C and 220–240 bar) can convert lignin into saturated cycloalkanes such as cyclohexane that can be used as gasoline substitutes.<sup>2–5</sup> Recently, other work has shown that milder conditions (150–200 °C) can be used during catalytic hydrogenolysis to avoid hydrogenation of the aromatic rings<sup>2,6</sup> and has demonstrated the selective production of dihydroconiferyl alcohol and dihydrosinapyl alcohol from lignin and wood.<sup>2,7–9</sup> The monomer yields obtainable from hardwood lignins are generally high (on the order of 50 wt%) whereas those from softwood lignins are often less than 30 wt%.<sup>10–12</sup>

Accordingly, increasing the monomer yields from softwood lignin remains a challenge.

The varying chemical structures of different types of lignin are one reason for the low monomer yields from softwood lignin. Lignin macromolecules are constructed via the polymerization of cinnamyl alcohols serving as biosynthetic monomers based on one-electron oxidation. The composition of lignin and the types of linkages (that is, ether (C–O–C) or condensed (C–C) bonds) are determined by the benzene ring substitution pattern of the cinnamyl alcohols, which comprise guaiacyl (4-hydroxy-3-methoxyphenyl, G-type), syringyl (3,5-dimethoxy-4-hydroxyphenyl, S-type) and *p*-hydroxyphenyl (H-type). Softwood lignin contains almost exclusively G-type alcohols while hardwood lignin contains G- and S-types.<sup>13</sup> The G-type units each contain a site that allows for condensation at the C5 position whereas this position in an S-type unit is occupied by a methoxyl group. Therefore, as summarized in Table 1, softwood lignin has a higher proportion of β-5 and 5-5 condensed bonds but a lower proportion of β-*O*-4-type bonds. As a consequence of the higher dissociation energies of condensed bonds, these linkages are resistant to cleavage<sup>2,7,14,15</sup> during pyrolysis, treatment with acids or bases and exposure to reductive/oxidative environments. This is problematic because the cleavage of these highly stable bonds is required for the efficient conversion of softwood lignin into aromatic monomers.

The present work used a combination of catalytic hydrogenolysis and pyrolysis to induce the conversion of lignin within the temperature range of 250–350 °C, over which range this material is readily degraded even without the use of

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† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

**Table 1** Proportions of various inter-phenylpropane linkages<sup>14,16,17</sup> in softwood and hardwood lignins and the associated bond dissociation enthalpies (BDEs).<sup>18,19</sup>

Linkage type	Occurrence (%)		BDE (kcal/mol)
	Softwood	Hardwood	
<i>α</i> -O-4	6–8	6–8	48–57
<i>β</i> -O-4	45–50	60–65	54–72
<i>β</i> -5	9–12	6	104–108
<i>β</i> -1	7–10	15	101–128
<i>β</i> - <i>β</i>	3	3–7.5	83
diaryl	4–8	1.5–6.5	78–83
5-5	18–25	2.3–4.5	112–118

catalysts. During pyrolysis, the ether bonds between phenylpropane units in softwood lignin (other than the 4-O-5-type bonds) can be efficiently cleaved to produce coniferyl alcohol.<sup>20,21</sup> However, the major products from standard pyrolysis are high molar mass compounds rather than coniferyl alcohol owing to the extremely high condensation reactivity of such alcohol.<sup>22</sup> During pyrolysis, coniferyl alcohol transitions to a quinone methide serving as a key intermediate for re-condensation. The formation of this intermediate can be inhibited by the hydrogenation of C=C double bond on coniferyl alcohol to produce a saturated alkyl. This effect was thought to be obtainable using catalytic hydrogenolysis conditions. This possibility has been confirmed by observations of lignin pyrolysis in the presence of a hydrogen donor in diphenoxybenzene (an aprotic solvent) to give a thermally stable oligomer with a yield of approximately 80 wt%<sup>23</sup> together with various monomers at a yield of 16 wt%.<sup>24</sup> The monomer yield remained relatively low because the 4-O-5 and condensed bonds in the lignin were not cleaved. Therefore, if these bonds can be cleaved by high temperature catalytic hydrogenolysis, the monomer yield should be significantly improved.

It is known that substituents on aromatic rings in lignin can be removed by replacement with hydrogen radicals during pyrolysis.<sup>18</sup> Although these substitution reactions do not proceed rapidly, catalytic conditions could potentially improve the reactivity. There are several approaches to promoting cleavage of the condensed bonds in lignin, including the use of C<sub>α</sub>-aryl-type dimers with CoS<sub>2</sub> at 250 °C,<sup>25</sup> *β*-1-type dimers in supercritical water at 400 °C<sup>26</sup> and 5-5 type-dimers with a catalyst at 600 °C in conjunction with microwave irradiation.<sup>27</sup> However, trials using real lignin specimens have continued to provide low yields of aromatic monomers even using these optimized conditions.

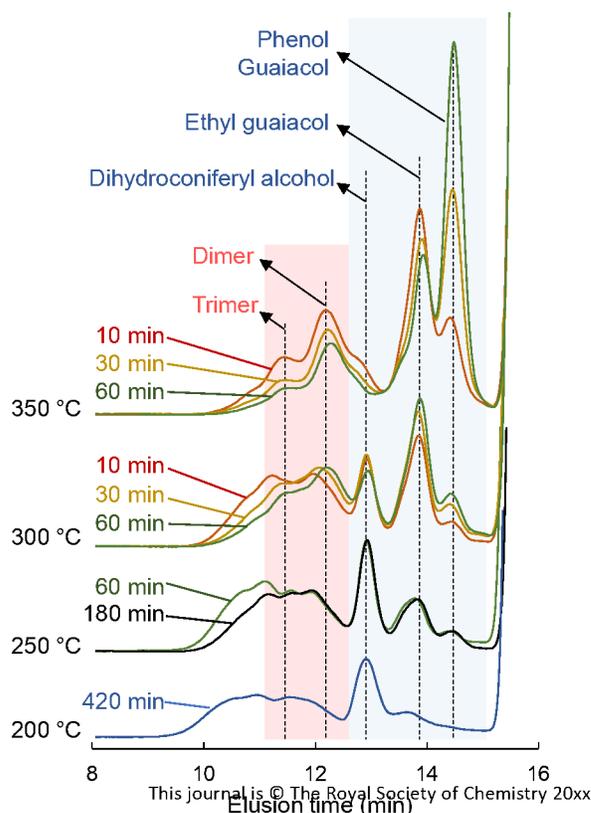
The work reported herein examined the catalytic hydrogenolysis of milled wood lignin (MWL) and organosolv lignin, both of which were isolated from Japanese cedar (*Cryptomeria japonica*, a softwood), using Pd/C in anisole (an aprotic solvent) over the temperature range of 200–350 °C. Various model dimers, including those containing 4-O-5, C<sub>α</sub>-aryl and 5-5 bonds, were also used to elucidate the conversion mechanisms.

## Results and discussion

### Monomer formation from Japanese cedar MWL

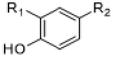
Fig. 1 presents the gel permeation chromatography (GPC) data acquired from the analysis of Japanese cedar MWL treated with Pd/C and H<sub>2</sub> in anisole at various temperatures and for different durations. During these trials, relatively low amounts of H<sub>2</sub> (3 mL at 0.1 MPa, corresponding to 2.4 equivalents relative to the moles of aromatic rings in each specimen) were used to avoid saturation of the aromatic moieties. These chromatograms indicate the retention times of the monomer and dimer/trimer fractions based on prior analyses of model compounds. Note that, during the trial performed at 350 °C, a small amount of the anisole was converted to phenol.

In the case of the sample reacted at 200 °C, a peak assigned to dihydroconiferyl alcohol (DHCA) can be observed together with various high molecular weight (MW) products that eluted over the time span of 9–12 min. Increasing the processing temperature evidently reduced the product MWs, with this effect especially apparent at 300 and 350 °C, indicating that depolymerization proceeded in this temperature range. The intensity of the various peaks in the monomer region of each



**Fig. 1** Gel permeation chromatograms of the reaction mixtures obtained from the pyrolysis-assisted catalytic hydrogenolysis of Japanese cedar MWL in anisole at 200–350 °C (MWL: 10 mg, Pd/C: 10 mg, anisole: 2 mL, H<sub>2</sub>: 3 mL at 0.1 MPa). GPC column exclusion limit: 1500 Da at 9.5 min.

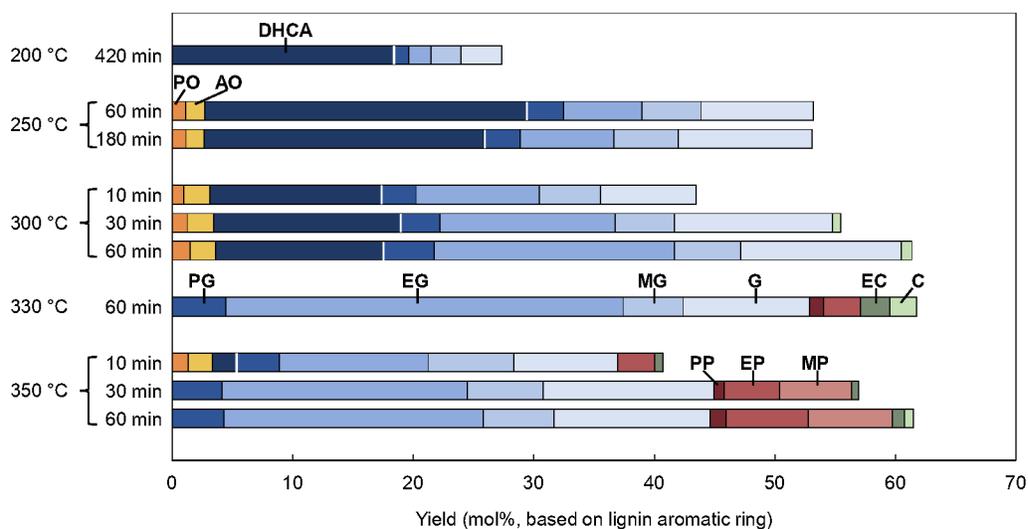
**Table 2** Molecular structures and abbreviations for the various monomeric products.

	Legends		
		R <sub>1</sub>	R <sub>2</sub>
Vanillic acid	<b>VA</b>	OCH <sub>3</sub>	COOH
Isoeugenol ( <i>cis</i> )	<b>IE (<i>cis</i>)</b>	OCH <sub>3</sub>	CHCHCH <sub>3</sub>
Isoeugenol ( <i>trans</i> )	<b>IE (<i>trans</i>)</b>	OCH <sub>3</sub>	CHCHCH <sub>3</sub>
Eugenol	<b>E</b>	OCH <sub>3</sub>	CH <sub>2</sub> CHCH <sub>2</sub>
Vinyl guaiacol	<b>VG</b>	OCH <sub>3</sub>	CHCH <sub>2</sub>
Coniferyl aldehyde	<b>CALD</b>	OCH <sub>3</sub>	CHCHCHO
Vanillin	<b>VO</b>	OCH <sub>3</sub>	CHO
Propiovanillone	<b>PO</b>	OCH <sub>3</sub>	COCH <sub>2</sub> CH <sub>3</sub>
Acetovanillone	<b>AO</b>	OCH <sub>3</sub>	COCH <sub>3</sub>
Dihydroconiferyl alcohol	<b>DHCA</b>	OCH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH
Propyl guaiacol	<b>PG</b>	OCH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>
Ethyl guaiacol	<b>EG</b>	OCH <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>
Methyl guaiacol	<b>MG</b>	OCH <sub>3</sub>	CH <sub>3</sub>
Guaiacol	<b>G</b>	OCH <sub>3</sub>	H
Propyl phenol	<b>PP</b>	H	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>
Ethyl phenol	<b>EP</b>	H	CH <sub>2</sub> CH <sub>3</sub>
Methyl phenol	<b>MP</b>	H	CH <sub>3</sub>
Ethyl catechol	<b>EC</b>	OH	CH <sub>2</sub> CH <sub>3</sub>
Catechol	<b>C</b>	OH	H

chromatogram also changed at these higher temperatures, confirming variations in the types or proportions of monomers.

Table 2 presents the molecular structures of the monomers discussed herein while the yields of the products (in mol%, based on the quantity of aromatic rings in the lignin) obtained from these conversions are summarized in Fig. 2. At 200 °C, the monomer yield increased by extending the duration from 180 min (18.0 mol%) to 360 min (26.0 mol%) and tended to plateau at 420 min (27.4 mol%), where DHCA was obtained in a yield of 18.4 mol% and accounted for 67% of all monomers. The monomer yield increased to 53 mol% upon increasing the temperature to 250 °C, indicating that temperature had a very important effect on monomer production. It should also be noted that the monomer yield and composition did not change with variations in the treatment duration at 250 °C (based on trials running for 60 and 180 min), suggesting that these monomers were stable and did not decompose on prolonged heating. The proportions of guaiacol and alkyl guaiacols (methyl, ethyl and propyl) in the monomers were also found to increase at 250 °C. These results also indicate that 60 min is sufficient to generate monomers from MWL at temperatures above 250 °C.

The overall monomer yield was further increased at 300 °C, reaching 61 mol% after 60 min. Ethyl guaiacol and guaiacol were the primary monomeric products from this trial while the DHCA yield was slightly decreased. At 330 °C, no DHCA was obtained but a significant amount (33 mol%) of ethyl guaiacol was produced. From these data, it is evident that the DHCA was converted to ethyl guaiacol. The maximum monomer yield was on the order of 60 mol% over the temperature range of 300–350 °C. Lignin itself is known to rapidly degrade via pyrolysis within 10 min at 350 °C and 60 min at 300 °C in aromatic solvents without the addition of catalysts.<sup>23</sup> Therefore, pyrolysis would have played a role in the decomposition of lignin in the present work at these high temperatures.



**Fig. 2** The yields of monomers obtained from the pyrolysis-assisted catalytic hydrogenolysis of Japanese cedar MWL at varying temperatures and for different durations (MWL: 10 mg, Pd/C: 10 mg, anisole: 2 mL, H<sub>2</sub>: 3 mL at 0.1 MPa). PO: propiovanillone, AO: acetovanillone, DHCA: dihydroconiferyl alcohol, PG: propyl guaiacol, EG: ethyl guaiacol, MG: methyl guaiacol, G: guaiacol, PP: propyl phenol, EP: ethyl phenol, MP: methyl phenol, EC: ethyl catechol, C: catechol.

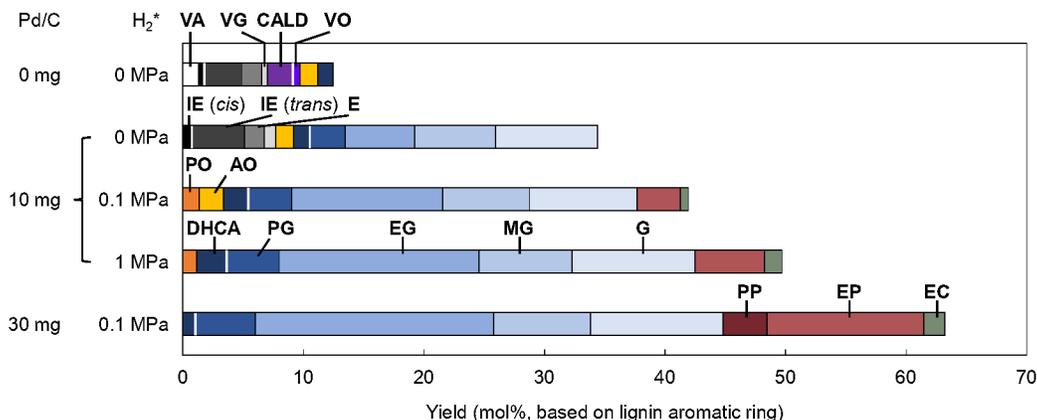


Fig. 3 The yields of monomers obtained from the pyrolysis-assisted catalytic hydrogenolysis of Japanese cedar MWL at 350 °C for 10 min with varying amounts of Pd/C and H<sub>2</sub> (MWL: 10 mg, anisole: 2 mL, H<sub>2</sub>: 3 mL at 0.1 or 1.0 MPa).

VA: vanillic acid, IE (*cis*): isoeugenol (*cis*), IE (*trans*): isoeugenol (*trans*), E: eugenol, VG: vinyl guaiacol, CALD: coniferyl aldehyde, VO: vanillin, PO: propiovanillone, AO: acetovanillone, DHCA: dihydroconiferyl alcohol, PG: propyl guaiacol, EG: ethyl guaiacol, MG: methyl guaiacol, G: guaiacol, PP: propyl phenol, EP: ethyl phenol, EC: ethyl catechol.

\*H<sub>2</sub> pressure at room temperature prior to the reaction. A value of 0 MPa indicates that N<sub>2</sub> was used instead of H<sub>2</sub>.

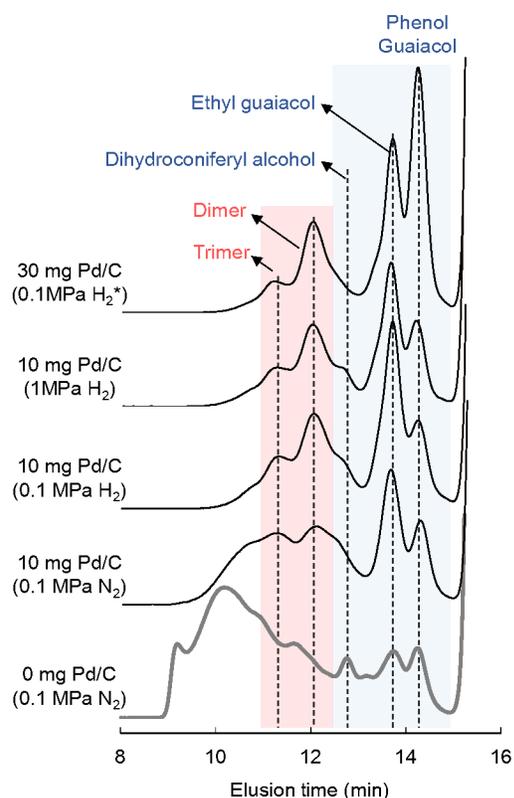


Fig. 4 Gel permeation chromatograms of the reaction mixtures obtained from the pyrolysis-assisted catalytic hydrogenolysis of Japanese cedar MWL in anisole at 350 °C for 10 min with varying amounts of Pd/C and H<sub>2</sub> (MWL: 10 mg, anisole: 2 mL, H<sub>2</sub>: 3 mL at 0.1 or 1.0 MPa).

GPC column exclusion limit: 1500 Da at 9.5 min.

\*H<sub>2</sub> pressure at room temperature prior to the reaction

At 350 °C, alkylphenols (representing the demethoxylation products) were generated at a proportion of approximately 15 mol%. Phenol may also have been produced but the yield could not be determined because the anisole used as a solvent also generated a small amount of phenol throughout the reaction. The demethylation products catechol and ethyl catechol were also detected, although the yields of both were minimal. The demethylation and demethoxylation of the guaiacol moiety evidently began to occur over the temperature range of 300–330 °C.

To better understand the effects of pyrolysis, the catalyst (Pd/C) and the H<sub>2</sub>, Japanese cedar MWL specimens were heated at 350 °C for 10 min in anisole under either N<sub>2</sub> or H<sub>2</sub> and with or without the Pd/C catalyst. The resulting monomer yields and GPC profiles are presented in Figs. 3 and 4, respectively. The trial with N<sub>2</sub> but without Pd/C in anisole produced coniferyl aldehyde, DHCA, isoeugenol (both *cis* and *trans*), eugenol, vinyl guaiacol, acetovanillone, vanillin and vanillic acid as typical pyrolysis monomers at a total yield of 12.5 mol%. Coniferyl alcohol, which was predicted to form in significant amounts based on cleavage of the β-ether bonds in the lignin, was not detected, likely as a result of secondary degradation (Fig. 5). In prior work, coniferyl aldehyde, DHCA, isoeugenol and vinyl guaiacol were obtained from the pyrolysis of coniferyl alcohol.<sup>22</sup> The acetovanillone, vanillin and vanillic acid may have been formed via different pyrolysis pathways. As noted, coniferyl alcohol also tends to re-condense via a quinone methide intermediate to form thermally stable condensed products containing C<sub>α</sub>- and C<sub>γ</sub>-aryl bonds,<sup>28</sup> although this condensation is suppressed in aromatic solvents such as anisole. The low monomer yield from this trial is attributed to the 4-*O*-5 and condensed bonds in the sample, which resisted cleavage.<sup>23</sup>

The addition of Pd/C significantly increased the monomer yield (from 12.5 to 34.4 mol%) even under N<sub>2</sub>, with the

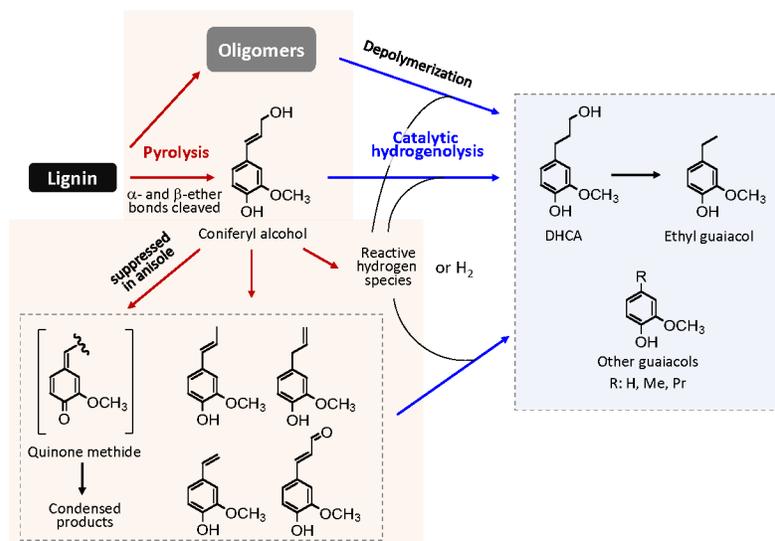


Fig. 5 Proposed reaction pathways for monomer production via the catalytic hydrogenolysis of lignin with pyrolysis, Pd/C and H<sub>2</sub> at 250–350 °C.

appearance of guaiacol and alkyl guaiacols (methyl, ethyl, and propyl) among the products. The GPC data also show that the peaks related to a high MW fraction in the products (Fig. 4) appearing over the range of 9–12 min were shifted to a lower MW region. This result demonstrates that some bonds in the oligomers produced by pyrolysis were cleaved by the incorporation of the Pd/C, resulting in an improved monomer yield.

Although the monomer yield was increased further upon using H<sub>2</sub> instead of N<sub>2</sub> (from 34.4 to 41.9 mol% at 0.1 MPa and to 49.8 mol% at 1.0 MPa), these relative improvements were much less than those obtained by adding Pd/C. This finding was supported by the GPC data, which exhibited minimal change on going between H<sub>2</sub> and N<sub>2</sub> in the presence of Pd/C. Consequently, the incorporation of Pd/C was more important than the addition of H<sub>2</sub> with regard to promoting the depolymerization of lignin-derived oligomers, although using H<sub>2</sub> did slightly increase the degree of conversion. Reactive hydrogen species may have been present in the reaction mixtures but further studies will be required to identify these species. The monomers obtained with N<sub>2</sub> but without Pd/C (as described above) were not produced under H<sub>2</sub> with Pd/C, presumably as a result of the hydrogenation of side-chain double bonds.

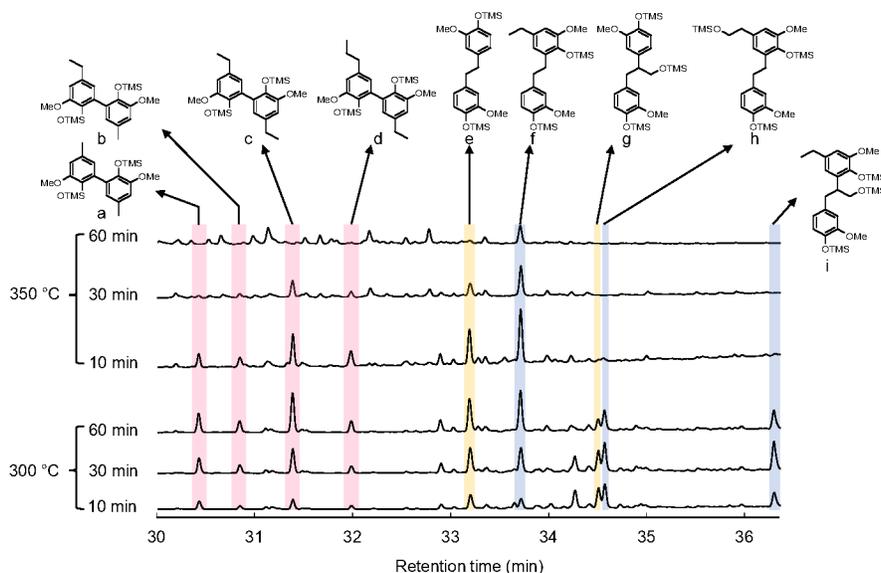
Increasing the amounts of H<sub>2</sub> and Pd/C improved the extent of lignin conversion but did not significantly change the composition of the monomeric product mixture. It should also be noted that extensive saturation of the aromatic rings in the lignin did not occur even with the use of H<sub>2</sub> at 1.0 MPa, corresponding to 24 equivalents relative to the moles of aromatic rings in the MWL. As discussed below, efficient ring saturation did not proceed at such high temperatures. Ethyl phenol and ethyl catechol were detected only after reactions under H<sub>2</sub> and in the presence of Pd/C, suggesting that both H<sub>2</sub>

and Pd/C were required for demethoxylation and demethylation.

Fig. 5 summarizes the proposed roles of pyrolysis, Pd/C and H<sub>2</sub> during high-temperature catalytic hydrogenolysis at 250–350 °C. Although the MWL was not soluble in anisole, this material underwent thermal depolymerization to generate soluble oligomers along with monomers via the cleavage of  $\alpha$ - and  $\beta$ -ether bonds as a consequence of the pyrolysis. As a result, the subsequent conversion of oligomers to monomers proceeded more efficiently on the surface of the solid Pd/C catalyst. Reactive hydrogen species formed during the pyrolysis were also important and the addition of very small amounts of H<sub>2</sub> ensured a sufficient supply of these species. The monomers generated in this system had alkyl side chains (methyl, ethyl and propyl). In particular, ethyl groups were formed via the pathway  $\gamma$ -hydroxypropenyl (representing a coniferyl alcohol)  $\rightarrow$   $\gamma$ -hydroxypropyl (a DHCA)  $\rightarrow$  ethyl. A large amount of unsubstituted guaiacol was also produced. One possible pathway for guaiacol formation proceeded via vanillin and related intermediates, and this possibility will be examined in a future paper.

#### Dimer production from Japanese cedar MWL

The data discussed above suggest that bonds in the lignin-derived oligomers that are normally difficult to cleave were broken after adding Pd/C. An analysis of the chemical structures of the dimers was therefore performed to better understand the associated reactions. Fig. 6 shows the dimer regions of the gas chromatography-mass spectrometry (GC/MS) total ion chromatograms of the mixtures obtained from Japanese cedar MWL after reactions using 0.1 MPa H<sub>2</sub> and Pd/C in anisole at 300 and 350 °C, following trimethylsilylation. The standard mass spectra used to identify the various components are provided in Fig. S1.

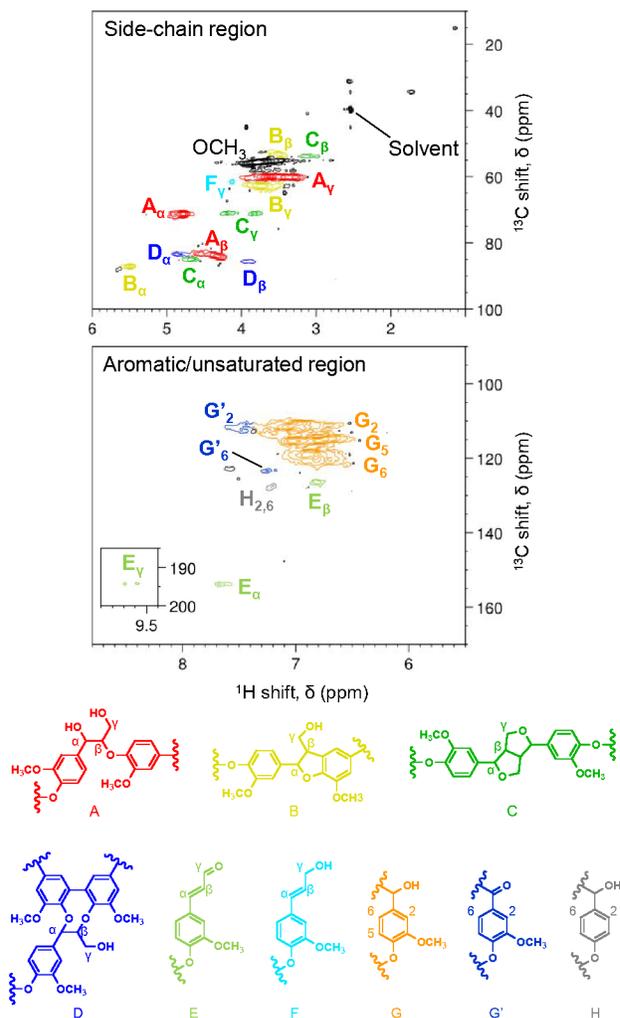


**Fig. 6** The dimer regions of GC/MS total ion chromatograms acquired from the trimethylsilyl (TMS) derivatives of products obtained from the pyrolysis-assisted catalytic hydrogenolysis of Japanese cedar MWL in anisole at 300 or 350 °C (MWL: 10 mg, Pd/C: 10 mg, anisole: 2 mL, H<sub>2</sub>: 3 mL at 0.1 MPa).

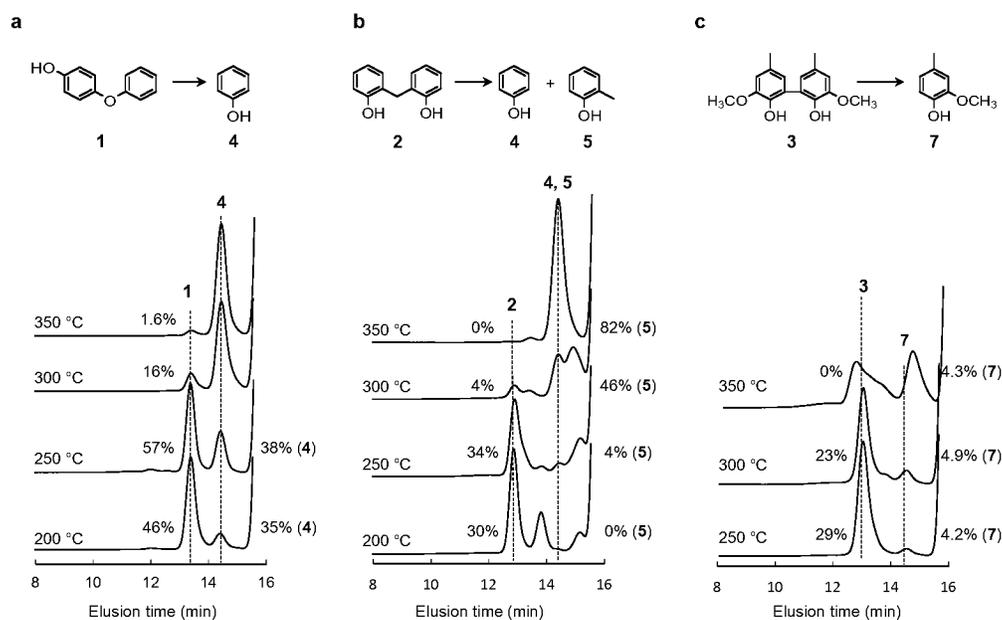
Biphenyl (5-5, a-d) and  $\beta$ -aryl ( $\beta$ -1 and  $\beta$ -5, e-i)-type dimers were detected within the retention time ranges of 30–32 and 33–37 min, respectively, indicating that these bonds were relatively stable even under the pyrolysis-assisted catalytic hydrogenolysis conditions. It should also be noted that the chromatograms were quite complex as a consequence of the conversion reactions of side chains on the products. As was observed when assessing the monomers,  $\gamma$ -hydroxypropyl, methyl, ethyl and propyl side chains were attached to the various products, although unsubstituted compounds were also generated. Accordingly, similar side chain transformations evidently occurred in the case of the dimers and possibly the oligomers.

Stilbene, which is a typical pyrolysis product of  $\beta$ -aryl-type structures, can be hydrogenated to produce the diarylethane-type dimers labeled e-i in Fig. 6. Dimers g, h, and i tended to be converted to dimers e and f, as can be clearly seen in the chromatogram of the sample processed at 300 °C. Dimers h and i, each of which contained two alkyl side chains, were derived from the  $\beta$ -5 bonds in lignin and converted to dimer f, whereas dimer g (with only one alkyl side chain) was obtained from a  $\beta$ -1 bond and converted to dimer e. For these reasons, the peaks related to dimers e and f were more intense in the chromatogram of the sample heated at 350 °C for 10 min. However, these signals were decreased in intensity after the treatment time was extended to 30 or 60 min, suggesting that even stable  $\beta$ -aryl bonds could be cleaved at such high temperatures. Similar trends were observed for the 5-5-type dimers.

The heteronuclear single quantum coherence (HSQC) nuclear magnetic resonance (NMR) spectrum obtained from the Japanese cedar MWL indicated the presence of 5-5,  $\beta$ -aryl and  $\beta$ - $\beta$ -type condensed bonds along with  $\alpha$ - and  $\beta$ -ether bonds (Fig. 7). The  $\alpha$ - and  $\beta$ -ether bonds (structures A, B, C and D in



**Fig. 7** The HSQC NMR spectrum of Japanese cedar MWL in DMSO-*d*<sub>6</sub>.



**Fig. 8** Gel permeation chromatograms of the reaction mixtures obtained from the pyrolysis-assisted catalytic hydrogenolysis of the model dimers **a** (having 4-O-5 bonds; **1**), **b** (having  $\alpha$ -aryl bonds; **2**) and **c** (having 5-5 bonds; **3**) at 200–350 °C for 60 min in anisole (Model: 10 mg, Pd/C: 10 mg, anisole: 2 mL, H<sub>2</sub>: 3 mL at 0.1 MPa). The numerical value attached to each signal indicates the recovery or yield (mol%, based on aromatic rings). GPC column exclusion limit: 1500 Da at 9.5 min.

Fig. 7) could be pyrolytically cleaved within the temperature range of 250–350 °C.<sup>23</sup> However, dimers containing  $\beta$ - $\beta$  bonds (structure C) and 4-O-5 bonds (undetectable in the HSQC spectra) were not present in the dimer regions of the various chromatograms (Fig. 6). These bonds might therefore have been cleaved following the addition of Pd/C and H<sub>2</sub>.

#### Model compound study

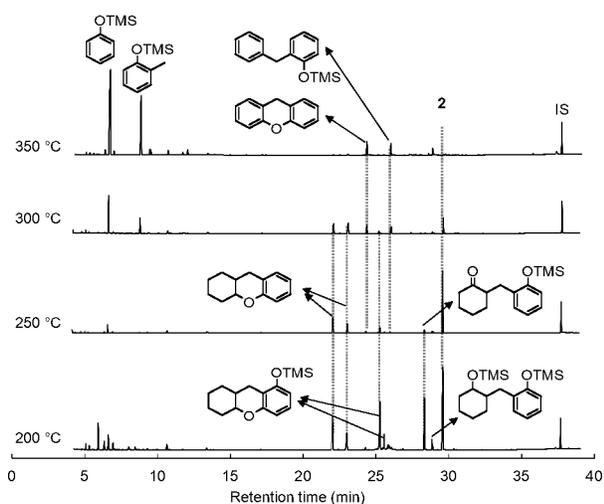
Three model dimers having 4-O-5 (**1**, 4-phenoxyphenol),  $\alpha$ -aryl (**2**, 2,2'-methylendiphenol) and 5-5 (**3**, 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-dimethyl biphenyl)-type bonds were treated at

200, 250, 300 or 350 °C for 60 min in anisole with Pd/C and H<sub>2</sub>. The GPC data obtained from the reaction mixtures are shown in Fig. 8. Here, the number attached to each peak represents either the dimer recovery or the product yield (in mol%) as determined by GC/MS (Figs. 9, 10 and S2). Phenol yields at temperatures above 300 °C were not determined because the anisole used as a solvent produced some phenol under these conditions, as noted earlier.

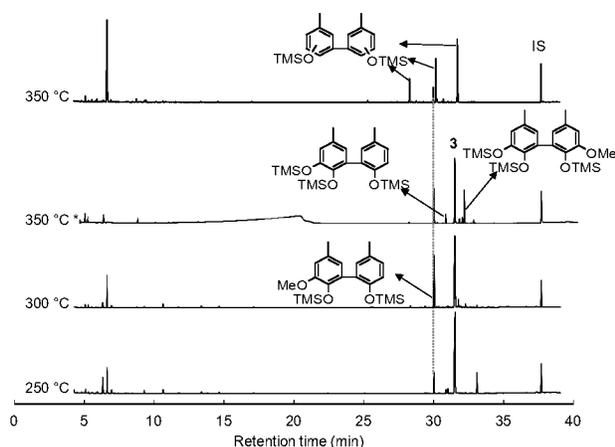
In all experiments, no GPC peaks appeared at retention times shorter than those of the model dimers, suggesting that these dimers did not condense under these conditions. However, the reactivity of each dimer was dependent on its structure. Specifically, the 4-O-5 bond of dimer **1** was broken at the lowest temperature of 200 °C and increasing reactivity was observed with increases in temperature. In contrast, the  $\alpha$ -aryl bond of dimer **2** was cleaved at 300 and 350 °C to form 2-methylphenol. These data suggest that these two types of bonds were cleaved during pyrolysis-assisted catalytic hydrogenolysis at high temperatures.

Although  $\alpha$ -aryl bonds are not present in natural lignins, these bonds can be formed by the re-condensation of quinone methide intermediates during pyrolysis, pulping and other conversion processes. Therefore, the efficient cleavage of  $\alpha$ -aryl bonds under the current reaction conditions promoted the production of monomers from the lignin. In particular, this effect could be demonstrated using organosolv lignin, as discussed below. Thus, even if these bonds were formed, they could be cleaved under the current pyrolysis-assisted catalytic hydrogenolysis conditions.

On the contrary, the 5-5 bond in dimer **3** was much less reactive with regard to monomer formation. The amounts of the monomers resulting from this type of bond cleavage were



**Fig. 9** The GC/MS total ion chromatograms of the TMS-derivatives of reaction mixtures obtained from the pyrolysis-assisted catalytic hydrogenolysis of the  $\alpha$ -aryl model compound (**2**) in anisole at 200–350 °C for 60 min (Compound **2**: 10 mg, Pd/C: 10 mg, anisole: 2 mL, H<sub>2</sub>: 3 mL at 0.1 MPa).



**Fig. 10** The GC/MS total ion chromatograms of the TMS-derivatives of reaction mixtures obtained from the pyrolysis-assisted catalytic hydrogenolysis of the 5-5 model compound (**3**) in anisole at 250–350 °C for 60 min (Compound **3**: 10 mg, Pd/C: 10 mg, anisole: 2 mL, H<sub>2</sub>: 3 mL at 0.1 MPa). \*Treatment time: 10 min.

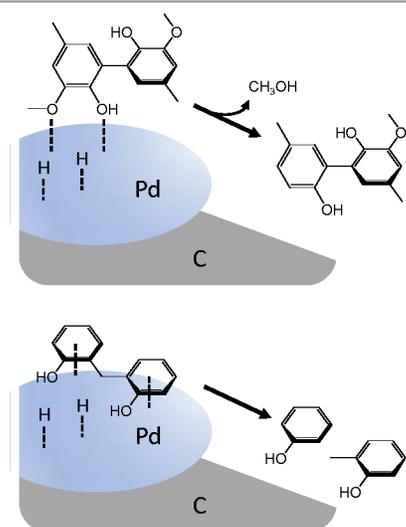
minimal at 250 °C, and the yields of the cleavage product 4-methyl guaiacol were less than 5% (compared with a theoretical yield of 200%, based on the quantity of aromatic rings in the model) in the temperature range of 250–350 °C. These results are consistent with the composition of the dimer fraction obtained from the MWL (products labeled a-d, Fig. 6). As discussed below, demethylation and demethoxylation occurred selectively in the case of the 5-5-type dimer.

Fig. 10 provides the GC/MS total ion chromatograms of the reaction mixtures generated in trials using the 5-5 dimer model **3**. Although the bond attaching the methyl substituent of this compound was not cleaved, demethoxylation and demethylation occurred efficiently to form dimers having catechol and phenol moieties, in contrast to the results

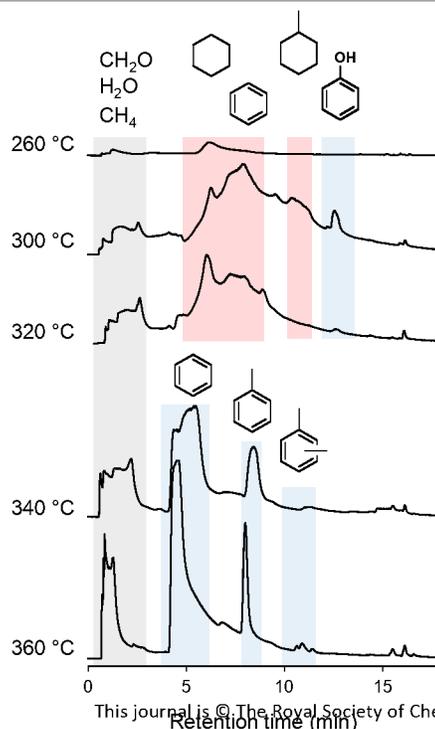
obtained with dimers **1** and **2**. This specificity is attributed to the unique conformation of the 5-5 dimer, in which two aromatic rings are arranged perpendicular to one another as a consequence of the steric repulsion between the hydrogens and hydroxyl groups at ortho positions,<sup>29</sup> as depicted in Fig. 11. In this conformation, the parallel association of the two benzene rings of the 5-5 dimer with Pd is difficult, such that one ring must be positioned vertically with respect to the Pd. This scenario could lead to increases in demethoxylation and demethylation reactivity. The association of the benzene ring with the catalyst in a perpendicular configuration during catalytic hydrogenation is known to result in deoxygenation whereas a planer configuration favors hydrogenation of the ring.<sup>30</sup> However, both rings of the 4-*O*-5 and  $\alpha$ -aryl dimers can be associated in parallel with the Pd atom.

Saturated ring products were also formed from the 4-*O*-5 and  $\alpha$ -aryl dimers while no such products were detected in trials using the 5-5 dimer, most likely because of the unique conformation discussed above. The GC/MS total ion chromatograms obtained from the 4-*O*-5 and  $\alpha$ -aryl dimers are shown in Figs. S2 and 9, respectively. Interestingly, the signals assigned to the saturated ring products decreased with increases in the reaction temperature and almost disappeared at 300 and 350 °C. The signal observed as a large peak around 14 min only at 200 °C in Fig. 8b would originate from the ring-saturation products identified in Fig. 9. Ring saturation therefore occurred at a relatively low temperature of 200 °C as reported in literature<sup>32,33</sup> but was not significant at higher temperatures. This effect illustrates the advantage of high-temperature catalytic hydrogenolysis for the production of aromatic monomers.

The same results were obtained from the gas phase catalytic conversion of guaiacol using Pd/C with a tandem micro-reactor GC/MS system under a H<sub>2</sub> flow at different temperatures. The results are shown in Fig. 12 and the MS data in Fig. S3. Here, the



**Fig. 11** Diagrams showing the proposed interactions of biphenyl (**3**)- and diarylmethane (**1**)-type dimers on a Pd surface determining reaction selectivity.



**Fig. 12** The GC/MS total ion chromatograms obtained from reactions mixtures following the catalytic hydrogenolysis of gas phase guaiacol over Pd/C at different temperatures in a micro-reactor with H<sub>2</sub> as the carrier gas.

peaks obtained sooner than 3 min are attributed to formaldehyde, methane and water. At 260 °C, only trace amounts of cyclohexane were detected and most of the guaiacol was adsorbed on the Pd/C. A mixture of cyclohexane and benzene was obtained upon raising the temperature to 300 or 320 °C along with small amounts of methylcyclohexane and phenol. The product composition changed to benzene, toluene and xylenes at 340 and 360 °C. These results indicate that the extent of ring saturation decreased with increasing temperature. The less efficient adsorption of H<sub>2</sub> at such high temperatures<sup>34</sup> evidently reduced the degree to which ring saturation occurred.

### Japanese cedar organosolv lignin

The present pyrolysis-assisted catalytic hydrogenolysis conditions were also applied to organosolv lignin isolated from Japanese cedar wood using 65% ethanol with 1% H<sub>2</sub>SO<sub>4</sub> in conjunction with heating at 195 °C for 40 min. Organosolv lignin is an emerging resource in the biorefinery industry. As indicated

by the HSQC NMR spectrum of this material (Fig. 13), the bond types were very different from those in the MWL (see Fig. 7). Specifically, the majority of  $\alpha$ - and  $\beta$ -ether bonds were cleaved during the extraction process and a large number of  $\alpha$ -aryl bonds were formed by re-condensation, in agreement with literature reports.<sup>35,36</sup>

The GPC data and monomer yields obtained from processing organosolv lignin are summarized in Figs. 14 and 15, respectively. Unlike the results obtained from the MWL trials, the MW distribution of the products was not significantly different from that of the original organosolv lignin even after processing at 250 °C. This stability can be explained by the type of linkages in this material, which primarily comprised condensed bonds. As a result, the monomer yields were limited to 5.5 mol% (at 200 °C) and 9.9 mol% (at 250 °C).

Depolymerization was greatly enhanced above 300 °C and the monomer yields showed corresponding increases to 17.8 mol% (at 300 °C) and 43.5 mol% (at 350 °C). Based on the reactivity of the  $\alpha$ -aryl type dimer **2** (Fig. 8), the  $\alpha$ -aryl bonds that are abundant in organosolv lignin are likely to be cleaved in this temperature range. High-temperature catalytic

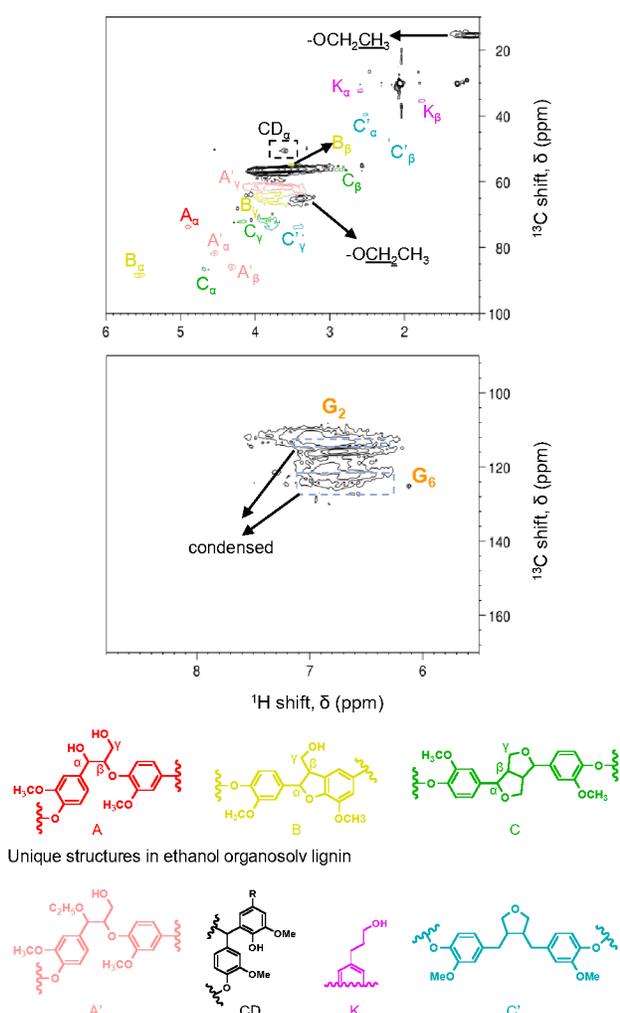


Fig. 13 The HSQC NMR spectrum of Japanese cedar organosolv lignin, acquired in acetone-*d*<sub>6</sub>.

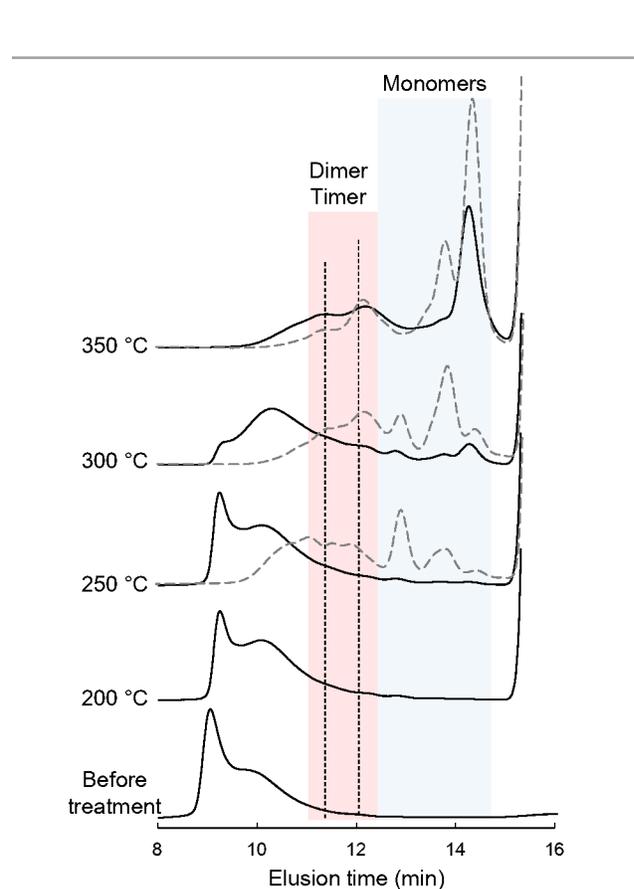
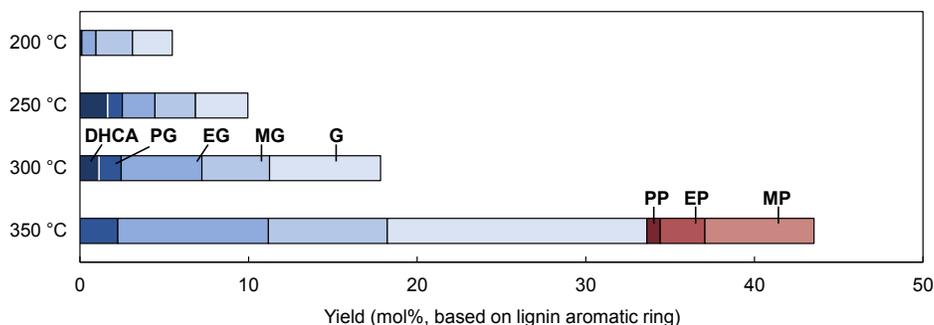


Fig. 14 Gel permeation chromatograms of the reaction mixtures obtained from the pyrolysis-assisted catalytic hydrogenolysis of Japanese cedar organosolv lignin in anisole at 200–350 °C for 60 min. Chromatograms obtained from MWL are also included as dashed gray curves for comparison (Organosolv lignin: 10 mg, Pd/C: 10 mg, anisole: 2 mL, H<sub>2</sub>: 3 mL at 0.1 MPa). GPC column exclusion limit: 1500 Da at 9.5 min.



**Fig. 15** The yields of monomers obtained from the pyrolysis-assisted catalytic hydrogenolysis of Japanese cedar organosolv lignin in anisole at 200–350 °C for 60 min (Organosolv lignin: 10 mg, Pd/C: 10 mg, anisole: 2 mL, H<sub>2</sub>: 3 mL at 0.1 MPa).  
DHCA: dihydroconiferyl alcohol, PG: propyl guaiacol, EG: ethyl guaiacol, MG: methyl guaiacol, G: guaiacol, PP: propyl phenol, EP: ethyl phenol, MP: methyl phenol.

hydrogenolysis can therefore efficiently convert highly condensed lignin-derived products to monomers.

The compositions of the monomer mixtures generated by the organosolv lignin and MWL were also slightly different. Specifically, the proportions of guaiacol and methyl guaiacol were greater in the case of the former material. This result can possibly be ascribed to differences in the side-chain reactions involved in the organosolv pulping and pyrolysis processes. Organosolv lignins tended to preferentially form unsubstituted guaiacol, likely due to their high content of  $\alpha$ -aryl linkages, as discussed in Fig. 13. This bond is cleaved at 350 °C to produce guaiacol.

## Experimental

### Materials

The sapwood of Japanese cedar (*Cryptomeria japonica*) was ground into a fine flour and sieved to obtain particles less than 150  $\mu\text{m}$  in size, after which the material underwent Soxhlet extraction with acetone. The MWL was subsequently prepared from the extracted wood flour according to a procedure previously reported by Björkman.<sup>37</sup> The MWL was determined to contain the hydrolysable sugars glucose (at 0.6 wt%), xylose (0.7 wt%), mannose (0.3 wt%) and arabinose (0.2 wt%). Organosolv lignin was prepared using an acid-assisted ethanol organosolv process.<sup>38</sup> Briefly, a 500 mg quantity of the extracted wood flour was dispersed in 5 mL of an aqueous ethanol solution (65%, v/v) containing H<sub>2</sub>SO<sub>4</sub> (1%, w/w) and then heated at 195 °C for 40 min. Only 0.07 wt% carbohydrates and 1.14 wt% acid-soluble lignin remained in the resulting organosolv lignin. The compounds 4-phenoxyphenol (**1**), 2,2'-methylenediphenol (**2**) and 2,2'-dihydroxy-3,3'-dimethoxy-5,5'-dimethylbiphenyl (**3**) were selected as model dimers having 4-O-5,  $\alpha$ -aryl and 5-5 linkages, respectively. Compounds **1** (>99%, Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) and **2** (98%, Sigma-Aldrich Co. LLC, St. Louis, MO, USA) were purchased while **3** was synthesized from methyl guaiacol (guaranteed reagent grade, Nacalai Tesque, Inc., Kyoto, Japan) according to a literature

procedure.<sup>39</sup> The purity of this compound was confirmed by <sup>1</sup>H-NMR to be 99%.

### Pyrolysis-assisted catalytic hydrogenolysis

Samples of the model dimers, Japanese cedar MWL and organosolv lignin were subjected to pyrolysis-assisted catalytic reactions in a batch reactor (Fig. S4).<sup>40</sup> In each case, a sample mass of approximately 10 mg was placed in a sealed 5 mL reaction vessel together with a specific amount of 5% Pd/C (extra pure reagent, Nacalai Tesque, Inc.) and 2 mL of anisole (>99%, guaranteed reagent, Nacalai Tesque, Inc.). The free space in the vessel (approximately 3 mL) was filled with H<sub>2</sub> at 0.1 or 1.0 MPa using a compressor. After being filled, the reactor was immersed in a salt bath preheated to a temperature in the range of 200–350 °C and agitated by imparting a swinging motion. After a set time, the reactor was transferred to a water bath to quench the reaction. The time spans required to heat the reactor to the target temperature and to cool it to the quenching temperature were approximately 30 sec each and so were negligibly short compared with the reaction time. It should be noted that the 3 mL of H<sub>2</sub> at 0.1 and 1.0 MPa added to the reactor equated to approximately 0.13 and 1.3 mmol and so was equivalent to 2.4 and 24 times the number of guaiacyl propanoid (C9) units in 10 mg of the lignin sample (approximately 0.056 mmol), respectively. During the reaction, the pressure in the reactor would have increased to the vapor pressure of anisole. Calculations based on the Soave-Redlich-Kwong model using the Pro/II simulator 2021 software package (AVEVA Group plc, London, UK) indicated that the pressure was between 0.3 and 3.3 MPa when the reaction temperature was between 200 and 350 °C, such that the majority of the 2 mL of anisole was in the liquid phase.

After the reaction, the reactor was washed several times using a total of 18 mL of methanol to recover the reaction mixture, giving a turbid dispersion with a volume of approximately 20 mL containing a solid residue, the Pd/C and anisole. A portion of this suspension was centrifuged to remove solids after which the reaction products were analyzed.

### Product analysis

GPC was used to analyze the methanol-soluble portion of the product mixture as a means of determining the MW distribution of the products. This analysis was performed using an LC-10A system (Shimadzu Corporation, Kyoto, Japan) with a Shodex KF-801 column (exclusion limit 1500 Da as the polystyrene equivalent; Showa Denko K.K., Tokyo, Japan), tetrahydrofuran as the eluent at 0.6 mL/min, a column oven temperature of 40 °C and an ultraviolet detector operating at 280 nm.

GC/MS was also used to assess the methanol-soluble portion of the reaction mixture following trimethylsilyl derivatization. This analysis employed a GCMS-QP2010 Ultra instrument (Shimadzu Corporation) with a CPSil 8CB column (length: 30 m, inner diameter: 0.25 mm, film thickness: 0.25 µm; Agilent Technologies, Inc., Santa Clara, CA, USA), He as the carrier gas at 2.09 mL/min, an injector temperature of 250 °C and a split ratio of 1/10. The column oven temperature was initially 70 °C (2 min hold) then ramped at 4 °C/min to 150 °C (1 min hold) and subsequently ramped at 10 °C/min to 300 °C (1 min hold). Prior to each analysis, the methanol was removed from the methanol-soluble portion by heating at 30 °C under vacuum. This relatively low temperature was used because some products, such as guaiacol, were partly lost by heating at 40 °C or above. An aliquot of 1,3,5-triphenylbenzene was added to the resulting specimen as an internal standard, followed by the addition of pyridine (100 µL), hexamethyldisilazane (150 µL) and trimethylchlorosilane (80 µL) with subsequent heating at 60 °C for 30 min for trimethylsilylation. The products were quantified using calibration curves prepared from the analysis of standards. The molar yield,  $M_i$ , of each monomeric product,  $i$ , was calculated as

$$M_i \text{ (mol\%)} = \frac{\text{Mass of } i}{\text{MW of } i \times n_{C9}} \times 100,$$

where  $n_{C9}$  is the moles of phenylpropanoid (C9) units in the lignin sample, calculated as

$$n_{C9} \text{ (mol)} = \frac{\text{Sample mass (approximately 0.01 g)}}{\text{Average MW of phenylpropanoid units}}$$

The average MW values of the phenylpropanoid units in the MWL and in the ethanol organosolv lignin obtained from softwood have been reported to be 182 and 168 Da,<sup>41,42</sup> respectively, and these values were used in the present study.

NMR analyses were conducted using an AC-400 spectrometer (400 MHz, Varian Medical Systems, Palo Alto, CA, USA). The chemical shifts and coupling constants ( $J$ ) are presented herein as  $\delta$  (ppm) and in units of Hz, respectively. Prior to each analysis, the methanol was removed from the methanol-soluble portion by heating under vacuum at 30 °C and the resulting dry oil was dissolved in dimethyl sulfoxide- $d_6$  for the analysis of MWL or in acetone- $d_6$  for the analysis of organosolv lignin.

### Gas phase catalytic reaction of guaiacol

Approximately 1 µL of guaiacol (>99%, Wako Pure Chemical Industries, Ltd., Osaka, Japan) was injected into a tandem

micro-reactor system (Rx-3050TR, Frontier Laboratories Ltd., Fukushima, Japan) as shown in Fig. S4b. This aliquot was volatilized in the first reactor after which the resulting vapor was transferred to the second reactor via a flow of H<sub>2</sub> carrier gas. A column packed with Pd/C (inner diameter: 3 mm, height of Pd/C layer: 20 mm) was situated in this second reactor to promote the catalytic conversion of the guaiacol. The first and second reactors were both held at the same temperature of between 260 and 360 °C. The resulting products were introduced into a GC/MS system (GCMS-QP2010 SE, Shimadzu Corporation) and analyzed in real-time. This system included an Ultra ALLOY<sup>+</sup>-1 column (length: 30 m, inner diameter: 0.25 mm, film thickness: 2 µm; Frontier Laboratories Ltd.) connected to a vent-free adaptor N-50 (length: 50 cm, inner diameter: 0.15 mm), H<sub>2</sub> as the carrier gas at 1.20 mL/min, an injector temperature of 250 °C and a split ratio of 1/24.9. The column oven temperature was initially 50 °C (5 min hold) followed by a ramp at 10 °C/min to 270 °C (3 min hold).

### Conclusions

This work examined the catalytic hydrogenolysis of MWL isolated from Japanese cedar wood (a softwood) in anisole using Pd/C over the temperature range of 250–350 °C, within which lignin is pyrolyzed. A high yield of monomers (over 60 mol%, based on the lignin aromatic rings) could be achieved when the catalytic process was carried out at temperatures above 250 °C. The insoluble MWL was first thermally converted to soluble oligomers and monomers by pyrolysis, after which depolymerization of the oligomers and monomer conversion occurred under catalytic conditions. Based on the dimer composition and the reactivity of 4-*O*-5-,  $\alpha$ -aryl- and 5-5-type model dimers, the high monomer yield is attributed to the cleavage of these normally stable bonds in the oligomers. Ring saturation was also found to be significantly suppressed at these high temperatures. DHCA was the predominant monomer below 200 °C whereas guaiacol and alkyl guaiacols (methyl, ethyl and propyl, especially ethyl guaiacol) were formed above 300 °C. Demethylation and demethoxylation were initiated above 330 °C, particularly in the case of the 5-5 dimer, which had a unique conformation in which the two aromatic rings were arranged perpendicular to one another. The presence of the Pd/C catalyst was determined to be more important than the addition of H<sub>2</sub> with regard to catalytic depolymerization. The data from this work allowed the roles of pyrolysis, the catalyst and hydrogen in monomer production to be evaluated. This high temperature process, termed pyrolysis-assisted catalytic hydrogenolysis, was also effectively applied to organosolv lignin isolated from Japanese cedar, giving monomers in 43.5 mol% yield at 350 °C based on the cleavage of  $\alpha$ -aryl bonds formed by re-condensation during organosolv pulping.

### Conflicts of interest

There are no conflicts of interest to declare.

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## References

- S. S. Wong, R. Shu, J. Zhang, H. Liu and N. Yan, *Chem. Soc. Rev.*, 2020, **49**, 5510–5560.
- Z. Sun, B. Fridrich, A. De Santi, S. Elangovan and K. Barta, *Chem. Rev.*, 2018, **118**, 614–678.
- H. P. Godard, J. L. McCarthy and H. Hibbert, *J. Am. Chem. Soc.*, 1941, **63**, 3061–3066.
- L. M. Cooke, J. L. Mccarthy and H. Hibbert, 1941, **63**, 3056–3061.
- E. E. Harris, J. D'anni and H. Adkins, *J. Am. Chem. Soc.*, 1938, **60**, 1467–1470.
- D. Tang, X. Huang, W. Tang and Y. Jin, *Int. J. Biol. Macromol.*, 2021, **190**, 72–85.
- W. Schutyser, T. Renders, S. Van Den Bosch, S. F. Koelewijn, G. T. Beckham and B. F. Sels, *Chem. Soc. Rev.*, 2018, **47**, 852–908.
- S. Gillet, M. Aguedo, L. Petitjean, A. R. C. Morais, A. M. Da Costa Lopes, R. M. Łukasik and P. T. Anastas, *Green Chem.*, 2017, **19**, 4200–4233.
- K. M. Torr, D. J. van de Pas, E. Cazeils and I. D. Suckling, *Bioresour. Technol.*, 2011, **102**, 7608–7611.
- M. V. Galkin and J. S. M. Samec, *ChemSusChem*, 2014, **7**, 2154–2158.
- S. Van Den Bosch, W. Schutyser, R. Vanholme, T. Driessen, S. F. Koelewijn, T. Renders, B. De Meester, W. J. J. Huijgen, W. Dehaen, C. M. Courtin, B. Lagrain, W. Boerjan and B. F. Sels, *Energy Environ. Sci.*, 2015, **8**, 1748–1763.
- X. Luo, Z. Gong, G. Yang, L. Huang, L. Chen and L. Shuai, *Chem. Eng. J.*, 2022, **429**, 132365.
- J. R. Obst and L. L. Landucci, *Holzforschung*, 1986, **40**, 87–92.
- J. Zakzeski, P. C. A. Bruijninx, A. L. Jongerius and B. M. Weckhuysen, *Chem. Rev.*, 2010, **110**, 3552–3599.
- C. Li, X. Zhao, A. Wang, G. W. Huber and T. Zhang, *Chem. Rev.*, 2015, **115**, 11559–11624.
- F. S. Chakar and A. J. Ragauskas, *Ind. Crops Prod.*, 2004, **20**, 131–141.
- M. Balakshin, E. A. Capanema, X. Zhu, I. Sulaeva, A. Potthast, T. Rosenau and O. J. Rojas, *Green Chem.*, 2020, **22**, 3985–4001.
- H. Kawamoto, *J. Wood Sci.*, 2017, **63**, 117–132.
- R. Parthasarathi, R. A. Romero, A. Redondo and S. Gnanakaran, *J. Phys. Chem. Lett.*, 2011, **2**, 2660–2666.
- T. Nakamura, H. Kawamoto and S. Saka, *J. Anal. Appl. Pyrolysis*, 2008, **81**, 173–182.
- M. T. Klein and P. S. Virk, *Ind. Eng. Chem. Fundam.*, 1983, **22**, 35–45.
- T. Kotake, H. Kawamoto and S. Saka, *J. Anal. Appl. Pyrolysis*, 2013, **104**, 573–584.
- J. Wang, E. Minami and H. Kawamoto, *ChemistryOpen*, 2022, **11**, e202200104.
- T. Kotake, H. Kawamoto and S. Saka, *J. Anal. Appl. Pyrolysis*, 2014, **105**, 309–316.
- L. Shuai, J. Sitisson, S. Sadula, J. Ding, M. C. Thies and B. Saha, *ACS Catal.*, 2018, **8**, 6507–6512.
- A. Yamaguchi, N. Mimura, M. Shirai and O. Sato, *Sci. Rep.*, 2017, **7**, 1–7.
- W. Wang, M. Wang, X. Li, L. Cai, S. Q. Shi, C. Duan and Y. Ni, *ACS Sustain. Chem. Eng.*, 2020, **8**, 38–43.
- T. Nakamura, H. Kawamoto and S. Saka, *J. Wood Chem. Technol.*, 2007, **27**, 121–133.
- F. Grein, *J. Phys. Chem. A*, 2002, **106**, 3823–3827.
- J. Zhang, J. Sun and Y. Wang, *Green Chem.*, 2020, **22**, 1072–1098.
- J. He, C. Zhao, D. Mei and J. A. Lercher, *J. Catal.*, 2014, **309**, 280–290.
- C. Zhao, J. He, A. A. Lemonidou, X. Li and J. A. Lercher, *J. Catal.*, 2011, **280**, 8–16.
- Q. Song, F. Wang and J. Xu, *Chem. Commun.*, 2012, **48**, 7019–7021.
- Carlos A. Leon y Leon and M. A. Vannice, *Appl. Catal.*, 1991, **69**, 269–290.
- F. P. Bouxin, A. McVeigh, F. Tran, N. J. Westwood, M. C. Jarvis and S. D. Jackson, *Green Chem.*, 2015, **17**, 1235–1242.
- Y. Guo, J. Zhou, J. Wen, G. Sun and Y. Sun, *Ind. Crops Prod.*, 2015, **76**, 522–529.
- Björkman A, *Sven Papperstidn*, 1956, **59**, 477–485.
- X. Pan, N. Gilkes, J. Kadla, K. Pye, S. Saka, D. Gregg, K. Ehara, D. Xie, D. Lam and J. Saddler, *Biotechnol. Bioeng.*, 2006, **94**, 851–861.
- K. Kratzl and F. W. Vierhapper, *Monatshfte für Chemie*, 1971, **102**, 425–430.
- K. Ehara and S. Saka, *Cellulose*, 2002, **9**, 301–311.
- S. Y. Lin and C. W. Dence, *Methods in lignin chemistry*, Springer-Verlag, 1992.
- W. Lange and W. Schweers, *Wood Sci. Technol.*, 1980, **14**, 1–7.