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Journal Name

ARTICLE

Mechanistic investigation of the Zn/Pd/C catalyzed cleavage and hydrodeoxygenation of lignin

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While current biorefinery processes use lignin only for its heat value, the conversion of lignin to high value chemicals is an area of increasing interest. Herein we present a detailed mechanistic study of the hydrodeoxygenation (HDO) of lignin by using a synergistic Pd/C and Zn^{II} catalyst through use of both lignin model compounds and lignocellulosic biomass. Spectroscopic data coupled with the study of lignin model compounds suggest that Zn^{II} activates and facilitates removal of the hydroxyl group at the C_γ position of the β-O-4 ether linkage. Activation is proposed to occur through formation of a six-membered ring complex of Zn^{II} coordinated to the oxygen atoms at C_α and C_γ of the lignin model compound guaiacylglycerol-β-guaiacyl.

Introduction

With an increased awareness of global climate change, the case for use of bio-renewable resources in production of liquid fuels and chemicals is compelling.¹ To meet this need, development of chemistry for making liquid fuels and chemicals from lignocellulosic biomass has become an area of intense research focus lately.² Carbohydrates constitute 50-60% by weight of lignocellulosic biomass³⁻⁴ and carbohydrate conversion to soluble sugars and liquid fuels has seen significant advances in recent years.⁵ Although lignin constitutes 15-30% by weight⁶⁻⁷ and ca. 40% of the energy⁵⁻⁷ of lignocellulosic biomass, it is currently of little utility and typically burned as a low value fuel in industrial applications.⁷ Lignin is an amorphous, three-dimensional polymer of methoxylated phenylpropane units bound through several types of linkages, with the most abundant being the β-O-4 ether linkage.⁷ The lignin model compound **1** (Figure 1) illustrates the β-O-4 ether linkage of lignin, which contains a benzylic OH at C_α and a primary aliphatic OH at C_γ.⁸

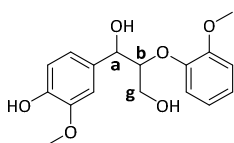


Figure 1: Lignin model compound **1**, guaiacylglycerol-β-guaiacyl ether.

Selective upgrading of lignin has proven challenging, with the fractionation method of organosolv pulping recently shown to produce hundreds of molecules from switchgrass lignin.⁹ While a number of catalysts have been reported for cleavage and hydrodeoxygenation (HDO) of ether C-O bonds in lignin model compounds, success with lignocellulosic biomass has been limited.¹⁰⁻¹⁷ Ford and co-workers have reported use of a copper-doped porous metal oxide catalyst for production of hydrogenated cyclic alcohols from lignocellulosic biomass in supercritical methanol.¹⁸ More recently Xu and co-workers have reported high yields and selectivity for methoxypropylphenols from reaction of birch powder with heterogeneous Ni/C catalyst.¹⁹ Pd/C was used in transfer hydrogenation to make propenyl aryls from birch wood.²⁰ Previously we reported on a bimetallic Pd/C and Zn^{II} catalyst system for the selective cleavage and HDO of the β-O-4 ether linkages in both lignin model compounds and intact lignocellulosic biomass under moderate temperatures and pressures (150-225 °C, 300-500 psig H₂).^{4,21} Most notably the Pd/C and Zn^{II} system catalytically depolymerized and upgraded a wide variety of wood lignin, producing a combined yield of up to 54% 4-propylguaiacol and 4-propylsyringol from lignin in intact biomass.⁴ Here we present a detailed mechanistic investigation into the synergistic Pd/C and Zn^{II} through use of both lignin model compounds and lignocellulosic biomass. The results illuminate the role of Zn^{II} in facilitating selective C-O cleavage by palladium hydride.

Results

Table 1 shows the effect of varying Zn^{II} concentrations in the bifunctional Pd/C + Zn^{II} catalyst system for the cleavage and HDO of lignin in intact biomass. The ratio of Zn:Pd was decreased from the previously reported⁴ Zn:Pd = 15.6 : 1 mol to Zn:Pd = 0.25 : 1 mol

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(Table 1, entries 1-4) with no reduction in the yield of propylguaicol (PG) and propylsyringol (PS) from poplar lignin. Further reduction in the ratio of Zn: Pd to 0.1 : 1 mol (entry 5),

Table 1: The effect of Zn^{II} and select Lewis acids on depolymerization and HDO of lignin in biomass with Pd/C catalyst.

Entry	Poplar Type	Catalyst	Co-catalyst	Molar Ratio Co-catalyst : Palladium	Yield (wt%)				Total Yield (wt%) ^c
					PG	PS	PG-OH	PS-OH	
1	WT-717 ^a	Pd/C	Zn(OAc) ₂	10:1	15	26	-	-	41
2	WT-717 ^a	Pd/C	Zn(OAc) ₂	2:1	14	28	-	-	42
3	WT-717 ^a	Pd/C	Zn(OAc) ₂	1:1	14	28	-	-	43
4	WT-717 ^a	Pd/C	Zn(OAc) ₂	0.25:1	13	28	-	-	41
5	WT-717 ^a	Pd/C	Zn(OAc) ₂	0.1:1	8	16	13	24	61
6	WT-717 ^a	Pd/C	-	-	-	7	17	35	59
7	WT-717 ^a	Pd/C	FeCl ₃	2:1	10	19	10	13	53
8	WT-717 ^a	Pd/C	NiCl ₂	2:1	8	15	13	22	57
9	WT-717 ^a	Pd/C	AlCl ₃	2:1	10	18	9	12	48
10	WT-717 ^a	Pd/C	ZnCl ₂	2:1	15	29	-	-	44
11	High-S ^b	Pd/C	Zn(OAc) ₂	2:1	6	30	-	-	36
12	High-S ^b	Pd/C	-	-	3	12	4	19	38

Reaction conditions: milled poplar = 1.0 g, catalyst (5% Pd/C) = 0.01 g (10 wt%), co-catalyst varied according to listed molar ratio. T = 225 °C, 25 ml methanol, 500 psig H₂ and 12 h reaction time. ^a Poplar WT-717 contains 19% lignin, comprised of 44% G-lignin and 51% S-lignin.

^b High-S poplar (717-F5H) contains 20% lignin, comprised of 20% G-lignin and 71% S-lignin. ^c yields (%) are calculated from the theoretical lignin content in wood and the mass of the products quantified by GC-FID (Supporting Information). Yields factor in the loss of two atoms of oxygen per each mole of products PG and PS produced, and one atom of oxygen lost per each mole of products PG-OH and PS-OH produced. Additional reactions with ethanol solvent listed in Table S1. Lignin content of biomass determined by Lignin content as determined by ABSL (acetyl bromide-soluble lignin) lignin analysis. ⁴ Ratio of S and G lignin determined by DFRC (derivatization followed by reductive cleavage).⁴

significantly reduced the yields of propylguaicol and propylsyringol, and resulted in the production of PG-OH (4-(3-hydroxypropyl)-2-methoxyphenol) and PS-OH (4-(3-hydroxypropyl)-2,6-dimethoxyphenol), increasing the total yield of phenolics from lignin to 61%. Reaction of poplar alone with Pd/C (entry 6) induced a shift in the distribution of phenolic products from lignin to favour PG-OH and PS-OH over propylguaicol and propylsyringol. Additional reactions utilized poplar wood genetically modified to contain 73% S-lignin, an increase from the 51% S-lignin found in the wild type poplar. Due to the increased S-lignin content of the genetically modified biomass, reaction of the High-S poplar with Pd/C/Zn^{II} yielded PS and PG in a ratio of 5:1, an increase from the PS:PG ratio of 2:1 observed with WT-poplar (Table 1, entries 2,11). Additionally, reaction of High-S poplar with Pd/C alone produced PS-OH and PG-OH in a ratio of 4.75:1, an increase from the PS-OH:PG-OH ratio of 2.06:1 when WT-poplar was used (Table 1, entries 12,6).

Zn^{II} was also replaced with several common Lewis acids (Table 1, entries 7-9). While the total phenolic yield increased, the reactions lacked selectivity and produced a mixture of

propylguaicol, propylsyringol, PG-OH, and PS-OH. These results indicate that Zn^{II} plays a greater role than that of a simple Lewis acid in the HDO of lignin using the bifunctional Pd/C + Zn^{II} catalyst.

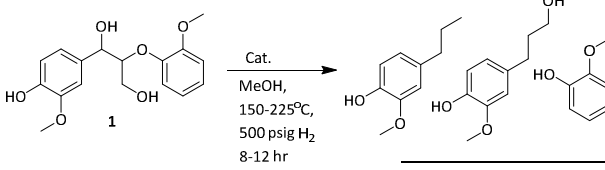
To further evaluate the synergistic effect of Pd/C and Zn^{II} in the hydrodeoxygenation of the β-O-4 ether linkage, lignin model compound **1** (Figure 1) was studied. In agreement with previous work,²¹ the bifunctional Pd/C + Zn^{II} catalyst was shown to selectively cleave and hydrodeoxygenate the β-O-4 ether linkage of lignin model compound **1** to yield primarily propylguaicol and guaicol, in methanol solvent under H₂ pressure at 150 °C (Table 2, entry 1). Previous work has shown treatment of lignin model compound **1**, under identical reaction conditions at 150 °C with Pd/C alone as a catalyst, to yield mainly unreacted starting material and starting material with methoxy substitution at hydroxyl group positions.²¹ However, Table 2, entry 2 shows treatment of the model lignin compound with Pd/C alone, under conditions optimized for HDO of lignin in native biomass (225 °C, 10 wt% Pd/C), to produce PG-OH and guaicol in high yields. A decrease in selectivity in the reaction of lignin model compound **1** with the bifunctional Pd/C + Zn^{II} catalyst is observed at elevated temperatures (225 °C), yielding propylguaicol (69%) and PG-OH (20%) (Table 2, entry 3). The

observed decrease in selectivity for the conversion of lignin model compound **1** to PG with Pd/C/Zn^{II} catalyst at 225 °C is likely due to competing reaction pathways accessible at elevated temperatures, allowing for Pd/C catalyzed production of PG-OH.

These findings show Pd/C to be an effective catalyst for the cleavage of β-O-4 ether linkages and removal of the benzylic OH at the Cα position, in both model lignin compounds (Table 2, entry 2) and lignocellulosic biomass (Table 1, entry 6). Furthermore, the results of Table 1 (entries 1-4), and Table 2 (entries 1,3) suggest that under the conditions studied, Zn^{II} must be used in combination with the Pd/C for the removal of the hydroxyl group at Cγ position in both lignocellulosic biomass and model lignin compounds.

Several control reactions were conducted to confirm the importance of Pd/C in the selective conversion of lignin model compound **1** to guaiacol, propylguaiacol, and/or PG-OH. Reaction of lignin model compound **1** with Zn(OAc)₂ at 150 °C under H₂ pressure, yielded primarily unreacted starting material and starting material with methoxy substitution at Cα (Figure S15). When heated to 225 °C in methanol without catalyst, lignin model compound **1** showed significant thermal decomposition to multiple products including 4-hydroxy-3-methoxybenzaldehyde, (E)-3-(4-hydroxy-3-methoxyphenyl)acrylaldehyde, and 2-methoxy-4-(1-methoxybut-3-en-1-yl)phenol (Figure S16). When heated to 225 °C in methanol under H₂ pressure, in the presence of Zn(OAc)₂, lignin model compound **1** produced several decomposition products with 4-hydroxy-3-methoxybenzaldehyde as the major product (Figure S17). These control reactions further illustrate the important role of Pd/C, in the catalytic system studied, for the selective production of guaiacol, propylguaiacol, and/or PG-OH from lignin model compound **1**.

Table 2: Effect of Zn^{II} on the cleavage and HDO of β-O-4 ether linkage of lignin model compound **1** with Pd/C.



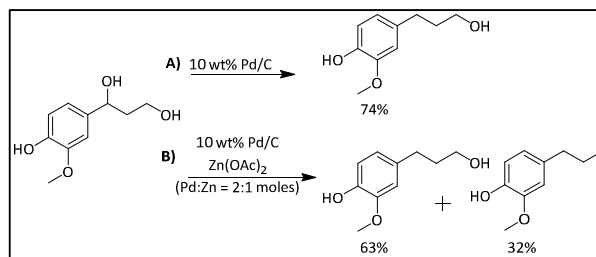
Entry	Substrate	Catalyst	T(°C)	Yield (%)		
				PG	PG-OH	G ^b
1	1	10 wt% Pd/C, Zn(OAc) ₂ ·2H ₂ O Zn:Pd = 2:1	150	84	nd ^a	84
2	1	10 wt% Pd/C,	225	nd ^a	74	74
3	1	10 wt% Pd/C, Zn(OAc) ₂ ·2H ₂ O Zn:Pd = 2:1	225	69	20	98

Lignin model compound **1** dissolved in methanol, then added to 5% Pd/C in stainless steel Parr reactor (10 wt % Pd/C loading relative to substrate). To entries 1 and 3 was added Zn(OAc)₂·2H₂O. Reactions

pressurized with 500 psig H₂. ^and = compound not detected in GC analysis. ^bGuaiacol abbreviated as (G).

HDO of hydroxyl Groups at Cα vs Cγ in Lignin Model Compounds

A series of experiments were conducted to clarify the synergistic effect of Pd/C and Zn^{II} in the HDO of the hydroxyl groups at Cα vs Cγ in lignin model compound 1-(4-hydroxy-3-methoxyphenyl)propane-1,3-diol (PG-diol). Reaction of PG-diol with Pd/C resulted in removal of the benzylic OH at the Cα position of PG-diol, yielding PG-OH (Scheme 1A). This result is reflective of those observed with the model lignin compound (Table 2, entry 2), further indicating that Pd/C can effectively remove the benzylic OH of the β-O-4 ether linkage in lignin. Reaction of PG-diol with Pd/C and Zn^{II} (Pd: Zn = 1:2 moles) also removed the benzylic OH at the Cα position of PG-diol, yielding PG-OH as the major product (Scheme 1B). Additionally, Scheme 1B shows treatment of PG-diol with Pd/C and Zn^{II} to produce propylguaiacol as a minor product (32%), indicating a reaction pathway for the removal of the primary OH at Cγ of the β-O-4 ether linkage when Zn^{II} is used in combination with Pd/C. Reaction of PG-diol with Pd/C and an increased loading of Zn^{II} (Scheme S1) did not change the product distribution from the lower Zn^{II} loading of Scheme 1B. In a control experiment, PG-OH was shown to undergo no reaction with a Pd/C and Zn^{II} catalyst system under our standard HDO conditions. Therefore, PG-OH cannot be an intermediate in the production of propylguaiacol and results from a catalytic pathway not involving Zn^{II}. It is proposed that addition of Zn^{II} to the reaction of Pd/C with PG-diol opens a reaction pathway where the primary OH at Cγ position is activated and undergoes HDO before the benzylic OH at Cα position of PG-diol to yield propylguaiacol. However, the highly reactive nature of the benzylic OH in the Cα position of PG-diol allows for a competing reaction in which Pd/C removes the benzylic OH before the OH at Cγ position is activated by Zn^{II}, leaving the reaction product trapped as the unreactive PG-OH.



Scheme 1: Effect of Zn^{II} loading in reaction of PG-diol with Pd/C. 50 mg 1-(4-hydroxy-3-methoxyphenyl)propane-1,3-diol (PG-diol) dissolved in 20 ml methanol, then added to 5 mg Pd/C in stainless steel Parr vessel. To reaction **B** was added 38.12 μL of 0.123 M Zn(OAc)₂. Reactions pressurized with 500 psig H₂, and heated to 150 °C for 8 hours. Products were analyzed by GC-FID and HPLC/MS (Figures S4, S5, S6, and S7).

Investigation of Zn^{II} Coordination to Lignin Dimer

To probe the mechanism by which Zn^{II} activates the primary OH at Cy position of the lignin model compound **1** (Figure 1), Zn^{II} coordination to the lignin model compound was studied using ¹H NMR spectroscopy. Lignin model compound **1** was dissolved in CD₃CN and characterized using ¹H NMR (Figure 2), and HMQC (Figure S8). CD₃CN was chosen in place of CD₃OD, as an aprotic NMR solvent was needed to avoid proton exchange between the OH protons of lignin model compound **1** and the NMR solvent. Addition of Zn(OTf)₂ to the NMR solution induced a downfield shift of the OH protons at the Cα and Cy positions of the lignin model compound (Figure 2). The observed shift is indicative of OH coordination to Zn^{II} and is rationalized through proposal of a six-membered ring complex of Zn^{II} coordinated to the oxygen atoms at Cα and Cy of the lignin model compound (Figure 2). HMQC spectrum of lignin model compound and Zn(OTf)₂ (1:1 molar ratio) is shown in Figure S9. Zn(OTf)₂ was the most suitable zinc salt for use in the NMR experiments as Zn(OAc)₂ and ZnCl₂ are insoluble in CD₃CN. Previous variation of zinc anion in the reaction of Pd/C with poplar biomass (Table 1, entry 2,10) has shown to have no significant impact on product yield or selectivity.

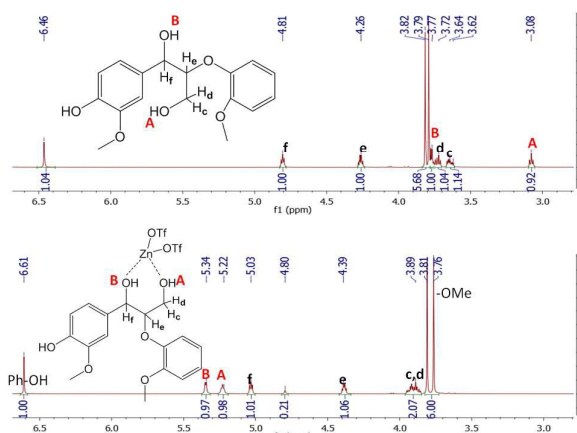


Figure 2: Top: ¹H NMR spectra of lignin model compound guaiacylglycerol-β-guaiacyl in CD₃CN. Bottom: ¹H NMR spectra of lignin model compound guaiacylglycerol-β-guaiacyl in CD₃CN, with 1 equivalent Zn(OTf)₂. ¹H NMR spectra collected at room temperature. Expanded spectra available in SI.

Addition of increasing equivalents of Zn(OTf)₂ to the solution of lignin model compound in CD₃CN, shifts the equilibrium in favor of the lignin-Zn^{II} complex as evidenced by the increasingly downfield shift of the OH protons (Figure 3). Upon addition of an excess of Zn(OTf)₂, the change in downfield shift of the hydroxyl protons plateaus (Figure 3), indicating that full ligation of Zn^{II} has been reached and the lignin-Zn^{II} complex is the major species.

As noted in Figure 3, significant downfield shift of the ¹H NMR signal for OH (A) and OH (B) of lignin model compound occurred upon addition of increasing Zn^{II} equivalents. As the ¹H NMR signal for each OH group showed only one signal, rather than an upfield

signal for free lignin model compound **1** and a downfield signal for the coordinated compound, it can be assumed that rapid exchange occurs.²² In this scenario, when concentration of lignin model compound **1** [L] is held constant and concentration of zinc(II) [Zn] is varied, Equation 1 can be derived to calculate the dissociation constant, K_d.²²

$$\Delta\delta_L = \Delta\delta_{L_0} [Zn] / ([Zn] + K_d) \quad (1)$$

Where $\Delta\delta_L$ = measured NMR shift. $\Delta\delta_{L_0} = \delta_{ML} - \delta_L$, where δ_{ML} = NMR shift for metal-ligand complex, and δ_L = NMR shift free ligand. It is assumed that $\Delta\delta_{L_0} = \delta_{ML} - \delta_L$ is a constant at high concentrations of metal, in this case when Zn:ligand = 3:1 (moles). In Figures S10 and S11, $\Delta\delta_L / \Delta\delta_{L_0}$ is plotted on the y-axis and can be considered a normalized chemical shift. From Equation 1, $\Delta\delta_L / \Delta\delta_{L_0}$ is plotted against [Zn], and fit to Equation 1 affords K_d, the dissociation constant for Zn^{II} coordination to compound **1**. The fits for both OH(A) and OH(B) of model lignin compound **1** afford K_d OH(A) = 0.040 ± 0.008 M, and K_d OH(B) = 0.049 ± 0.008 M.

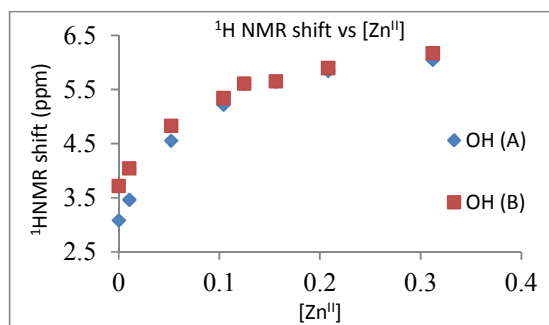
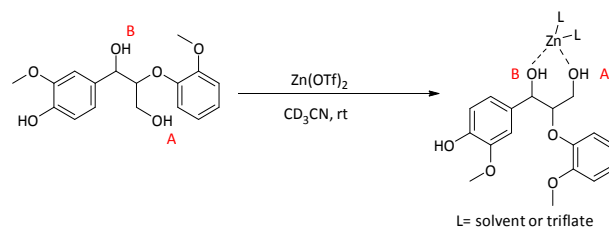
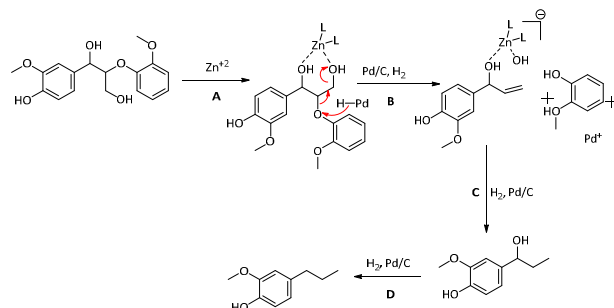


Figure 3: Lignin model compound **1** dissolved in CD₃CN. Proton shift of OH(A) and OH(B) monitored by ¹H NMR as increasing equivalents of Zn(OTf)₂ added to solution. Equivalents of Zn(OTf)₂ relative to concentration of lignin model compound **1**.

To further evaluate the interaction of OH(A) and OH(B) of lignin model compound with Zn^{II}, the ¹H NMR spectrum of a solution of lignin model compound and Zn(OTf)₂ in CD₃CN was studied at temperatures of 0–60°C. The shift of the hydroxyl protons OH(A) and OH(B) of model lignin compound in the presence of Zn(OTf)₂ was measured as a function of temperature and Equation 1 was used to calculate K_a of OH(A) and OH(B) binding to Zn^{II} at 10, 20, 30, and 60°C. A Van't Hoff plot (Figure S22, S23) shows the binding of Zn^{II} by OH(A) and OH(B) of model lignin compound to be exothermic with an average ΔH of $-8.7 \text{ kJ mol}^{-1} \pm 0.5$ and an average ΔS of $-11.1 \text{ J mol}^{-1} \text{ K}^{-1} \pm 0.7$.



Scheme 2: Proposed mechanism for cleavage and HDO of β -O-4 ether linkage using Pd/C and Zn^{II} catalyst, illuminating the role of Zn^{II} and synergy with palladium hydride HDO catalyst.

Discussion

Through chemical observations in conjunction with spectroscopic evidence of a lignin model compound coordination to Zn^{II} , a mechanism for the cleavage and HDO of the β -O-4 ether linkage of lignin via Pd/C and Zn^{II} catalyst is proposed (Scheme 2).

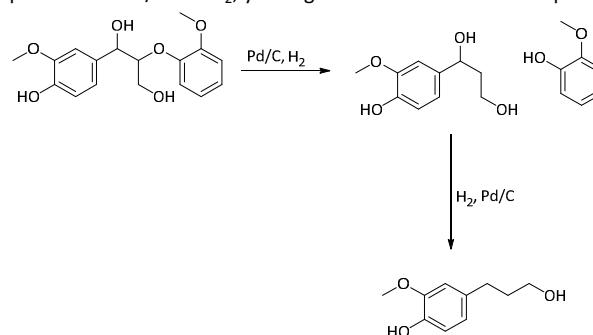
In Scheme 2, (Step A) a six-membered ring complex of Zn^{II} coordinated to the oxygen atoms at the C α and C γ positions of the lignin model compound is formed. Formation of such complex is supported by NMR spectroscopy (Figures 2 and 3). The reaction of PG-diol with Pd/C and Zn^{II} (Scheme 1B) shows that PG-diol is not an intermediate in the cleavage and HDO of the lignin model dimer, as PG-diol produces a mixture of PG-OH (63%) and propylguaiaicol (32%), whereas the lignin model dimer selectively produces propylguaiaicol (84%) (Table 2, entry 1). Therefore an initial mechanistic step cleaving the β -O-4 ether linkage and producing PG-diol cannot be a viable pathway in Scheme 2. Additionally, as PG-OH is unreactive with Pd/C and Zn^{II} (Scheme S2), it is proposed that the primary OH at C γ of the β -O-4 ether linkage must be removed first before the benzylic OH at C α .

Aromatic substrates have been shown to adsorb with the benzene ring positioned flat atop the palladium metal surface forming a π -complex with the metal d-orbitals.²³ This π -interaction (Scheme 2, step B) brings Pd-H into close proximity to the β -O-4 ether linkage. Hydride transfer from Pd-H to the β -O-4 oxygen initiates C-O cleavage concurrently with a concerted removal of the OH group at the C γ position (Scheme 2, Step B). Transfer of a hydride from Pd-H to the ether linkage (Scheme 2, step B) would result in formation of a Pd^+ on the surface, and a $[\text{Zn}^{\text{II}}\text{-OH}]^-$ anion. Coordination of Zn^{II} makes the OH a better leaving group. Catalyst regeneration is envisaged to take place by reaction of Pd^+ with H_2 to form Pd-H and solvated $[\text{H}^+]$. The latter protonates $[\text{Zn}^{\text{II}}\text{-OH}]^-$ anion to give H_2O and a Zn^{II} complex that can bind another lignin molecule. This step is in agreement with previously reported EXAFS

data showing the active catalyst to be comprised of Zn^{II} sites and metallic Pd^0 nanoparticles under catalyst operating conditions.⁴

Under the reducing conditions studied, the terminal C=C bond in Scheme 2, step C, is readily hydrogenated by Pd/C. Experiments without Zn^{II} (Scheme 1) have shown Pd/C to be effective in the hydrogenolysis of the benzylic OH at C α , as proposed in Scheme 2, Step D.

A proposed reaction mechanism for the cleavage and HDO of the β -O-4 ether linkage of lignin model compound **1** via Pd/C without added Zn^{II} is outlined in Scheme 3. As shown in Table 2, entry 2, reaction of lignin model compound **1** with Pd/C in the absence of Zn^{II} removes the benzylic OH group at C α , leaving the OH group at C γ intact to selectively produce PG-OH and guaiacol. It is proposed that C-O cleavage in the lignin dimer could be initiated by hydride transfer from Pd-H to the β -O-4 oxygen, producing PG-Diol as an intermediate. As demonstrated in Scheme 1, reaction A, HDO of the benzylic OH group in PG-Diol occurs readily in the presence of Pd/C and H_2 , yielding PG-OH as a final reaction product.



Scheme 3: Proposed mechanism for cleavage and HDO of β -O-4 ether linkage using Pd/C without Zn^{II} catalyst, yielding G and PG-OH.

Experimental

Materials and Methods

2-Methoxy-4-propylguaiaicol (PG), ZnCl_2 , $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and NiCl_2 were purchased from Aldrich. Guaiacylglycerol- β -guaiaicyl ether and (4-(3-hydroxypropyl)-2-methoxyphenol) were purchased from TCI. 2,6-Dimethoxy-4-propylphenol (PS) was synthesized from 4-allyl-2,6-dimethoxyphenol as previously reported.⁴ Poplar (*P. tremula* x *P. alba*, WT-717) and the genetically engineered line 717-F5H was provided by Purdue University's Department of Forestry and Natural Resources Department.

General Reaction Procedures

In a typical experiment, substrate, 5-10 wt% Pd/C (5 wt%), 0-10 wt % co-catalyst ($\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, or NiCl_2) methanol (25 ml), and glass stir bar were added to a stainless steel Parr reactor and sealed. While stirring, the mixture was purged with UHP grade H_2 4-6 times to expel air, then pressurized with 300-500 psig H_2 . Reactions were conducted at 150-225 °C at a stirring speed of 600 rpm. Reaction temperature was maintained for 8-12

hours, then cooled to room temperature. Upon cooling, the reaction mixture was filtered to remove Pd/C, and rinsed with additional methanol. In reactions containing intact biomass, a solid carbohydrate residue was removed by filtration with extensive characterisation of the carbohydrate residue appearing in previous work.⁴ The filtrate was collected and diluted in a volumetric flask for analysis by GC-FID and/or HPLC/MS.

Biomass Preparation

Biomass was milled to pass through a 40 mesh screen using a Mini Wiley Mill (Thomas Scientific, Swedesboro, NJ). Biomass was washed with water, followed by ethanol using a soxhlet apparatus using the NREL LAP Determination of Extractives in Biomass procedure.²⁴ Following soxhlet extraction, biomass samples were dried at 45 °C and water content evaluated with a moisture analyzer (Halogen model HB43-S, Mettler-Toledo LLC, Columbus, OH).

GC-FID Analysis

Gas chromatography was performed using an Agilent Technologies 6890N Network GC System equipped with a FID detector, auto-sampler, and DB-5 capillary column of dimension 0.25 mm ID × 0.25 μm × 30 m. injection volume 1.0 μL, inlet temperature 275 °C, detector temperature 275 °C and a split ratio 1:10. Initial column temperature was 50 °C (1 min) with a temperature rise at 10 °C/min up to 250 °C and then at 25 °C/min to the final temperature of 300 °C. GC peaks for all lignin derived products (PG, PS, PG-OH, PS-OH, G) were identified by retention time in comparison with authentic samples. Each peak of GC chromatogram was properly integrated and the actual concentration of each product was obtained from the pre-calibrated plot of peak area against concentrations of authentic samples.

NMR Spectroscopy

NMR spectra were recorded on a Bruker DRX-500 NMR spectrometer equipped with a TBI probe using a BB coil. BrukerTopSpin software (version 1.3) was used for data acquisition and MestReNova (version 8) was used in processing spectra. All spectra obtained were referenced to residual solvent peaks.

Conclusions

We have shown that the β-O-4 ether linkage can be selectively cleaved in both lignocellulosic biomass (Table 1, entry 6) and lignin model compounds (Table 2, entry 2) with Pd/C alone in methanol, at elevated temperatures, under H₂ pressure. In both cases the primary OH at the C_γ position of the β-O-4 ether linkage remains intact, yielding PG-OH (as well as PS-OH in the case of lignocellulosic biomass). This contrasts the reaction of lignocellulosic biomass

(Table 1, entries 1-4) and lignin model compounds (Table 2, entry 1) with Pd/C and Zn^{II} which cleaves both the benzylic OH at C_α, and the primary OH at C_γ yielding mainly propylguaicol, as well as propylsyringol in the case of lignocellulosic biomass. It has been demonstrated herein that the key difference in reactivity lies in the ability of Zn^{II} to activate and facilitate removal of the OH group at the C_γ position of the β-O-4 ether linkage.

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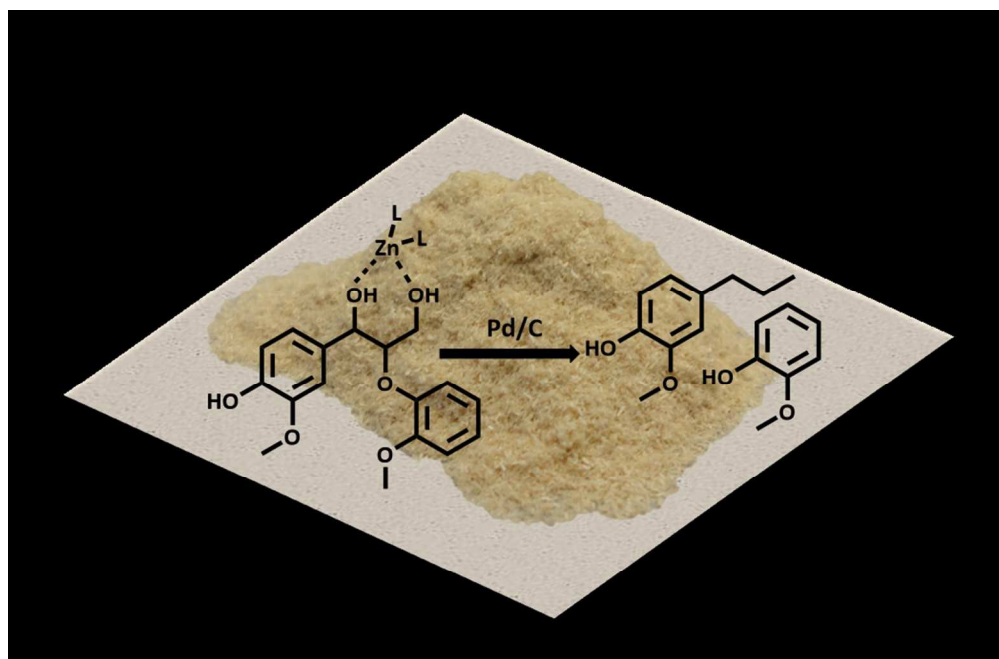
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