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A Synergistic Biorefinery Based on Catalytic Conversion of Lignin Prior to Cellulose Starting from Lignocellulosic Biomass

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Abstract

Current biomass utilization processes do not make use of lignin beyond its heat value. Here we report on a bimetallic Zn/Pd/C catalyst that converts lignin in intact lignocellulosic biomass directly into two methoxyphenol products, leaving behind the carbohydrates as a solid residue. Genetically modified poplar enhanced in syringyl (S) monomer content yields only a single product, dihydroeugenol. Lignin-derived methoxyphenols can be deoxygenated further to propylcyclohexane. The leftover carbohydrate residue is hydrolyzed by cellulases to give glucose in 95% yield, which is comparable to lignin-free cellulose (solka floc). New conversion pathways to useful fuels and chemicals are proposed based on the efficient conversion of lignin into intact hydrocarbons.

Keywords: Lignin, Biorefinery, Catalysis

Significance Statement

Renewable fuels are of great interest because of depleting fossil fuel reserves and climate change caused by increased CO_2 emissions. The component of biomass known as lignin hinders our ability to convert cellulose to ethanol and is currently wasted. Here we present a chemical method for converting lignin in two steps to fuels and chemicals while making the cellulosic carbohydrates more accessible. The described synergies should improve carbon utilization in the future biorefinery.

Introduction

Production of liquid fuels and chemicals from lignocellulosic biomass is an integral part of the solution to the energy grand challenge.[1] Biorefinery concepts for the production of liquid fuels and chemicals from biomass have been developed and some commercially implemented.[2–4] However, any renewable platform must provide both liquid fuels and commodity chemicals on a large scale. For example, in 2012 the U.S. consumed ~4.6 billion barrels of liquid fuels and produced greater than 90 Mton of organic commodity chemicals, respectively (including ~8 Mton of benzene).[5–7] Cellulosic conversion methods to ethanol and other liquid fuels make use of only the carbohydrate components of biomass (~50-60% by weight).[8–10] In comparison, the lignin component (20-30% by weight but accounting for ~37% of the carbon in biomass) inhibits the conversion of cellulose and constitutes a major waste stream that is burned for its heat value in most applications.[11] Therefore, lignin represents an opportunity for meeting the demand for a renewable platform of aromatic fuels and commodity chemicals (e.g. benzene, toluene, xylene (BTX), styrene, and cumene). As a result, methods for the selective conversion of lignin are important.[11]

The concept of lignin utilization to produce high-value products is not new.[12,13] However, actual reaction schemes to effectively convert lignin with high yield to useful end-products remains a significant challenge. There are processes that produce organosolv lignin separating it from hemicellulose and cellulose, but the resulting organosolv lignin fraction is an extremely complex mixture, which upgrading to a reasonable number of products in any significant yields is yet to be demonstrated.[14] Currently one of the few notable commercial processes utilizes lingo-sulfonate lignin derived from sulfite pulping to produce vanillin at a

maximum yield of only 7.5% by mass.[15] Even though new catalysts have been reported for the cleavage of ether C-O bonds and hydrodeoxygenation (HDO) of lignin model compounds, only limited successes have been reported with lignin or biomass.[16–23] Heterogeneous Ni catalysts have been used recently with lignosulfonate to give a mixture of phenolic compounds and dimeric lignin fragments with removal of the sulfur as H_2S.[22] Ford and co-workers have reported a catalytic method in supercritical methanol at 300-320 °C and 160-220 bar of H_2 that converts the lignified components of biomass to hydrogenated cyclic alcohols.[23] A recent report has appeared on the conversion of birch sawdust to phenolic compounds utilizing a Ni/C catalyst.[24,25] Previously we reported on a catalytic system that could cleave the β-O-4 linkages found in lignin dimeric and polymeric model compounds with high selectivity and yields.[26]

Here we present the use of a bimetallic catalyst based on Zn and nanoparticulate Pd in a selective conversion process compatible with diverse species of intact woody biomass. The catalyst produces a single lignin-derived product stream in high yields, leaving essentially all polysaccharide components of the biomass as a solid residue, which we have demonstrated undergoes enzymatic hydrolysis, resulting in high yields of glucose (Figure 1). In addition to several wild type species of poplar, conversion of genetically modified poplar that contain high S type lignin is descirbed.[27] This type of bioengineering offers a method to control the potential products from reactions involving biomass. Furthermore, methoxypropylphenols similar to those produced during this catalytic reduction of lignin can be converted quantitatively in a second step using a bifunctional Pt-Mo catalyst to hydrocarbon fuel or propylbenzene. The latter serves as platform for production of aromatic chemicals.

Selective catalytic conversion of lignin

Our biomass conversion process is accomplished via a bimetallic catalytic system composed of Zn^{II} sites and metallic Pd nanoparticles (3-4 nm) dispersed on a carbon support. This bimetallic system has been shown previously to have a synergistic effect that cleaves β-O-4 linkages found in model compounds more effectively then either component alone.[26] For this catalytic process the biomass was first milled to pass through a 40 mesh screen then washed consecutively with water and ethanol via soxhlet extraction. Three different types of pretreated wild-type (WT) poplar (species within the genus *Populus*) wood were reacted with the Zn/Pd/C catalyst in methanol (MeOH) at 225 °C and 500 psig of H_2 which resulted in 40-54% of the available lignin being converted to two products: 2-methoxy-4-propylphenol (dihydroeugenol) and 2,6-dimethoxy-4-propylphenol (Table 1, entries 1, 3, and 4, and Figure 2A). Based on our experimental results, Zn, Pd, and H_2 are all required for catalysis. Control reactions with poplar biomass using Zn alone gave minimal conversion to multiple oxygenated products and no products were generated in the absence of H_2. Reactions of poplar wood with Pd/C alone gave low yields of more highly oxygenated methoxypropylphenol products. To facilitate separation and recycling (shown in Table S1) of the Zn/Pd/C catalyst, we ran the reaction employing a microporous cage (325 mesh) to separate the Pd/C from the biomass. Such a cage allows the solvent and solute to access the catalyst and leaves behind a cellulosic biomass residue that is Pd/C free. This result is also consistent with the mechanism proposed in our previous study with model compounds where the Zn can be desorbed from the carbon surface and is free to pass in and out of the microporous cage.[26]

The described preparation/pretreatment of biomass is minimal and all the steps are scalable, an important prerequisite of any process for large-scale application in a biorefinery. The two products reflect guaiacyl (G) and syringyl (S) lignin components present in WT poplar and

illustrate the applicability of our catalysis to variants within the genus *Populus*. Following our single-step catalytic conversion, the starting biomass is fractionated into two forms, the first is a solid residue that is easily filtered and the second consists of products that are soluble in MeOH. The MeOH liquid-phase contains the methoxypropylphenol products shown in Table 1 and a small amount of soluble sugars that mostly originate from hemicellulose (Table S2 and Table S5). An additional phenolic product of methylparaben was detected and quantified from the reaction with the poplar species (Table S1). This product is extracted in various quantities from all reactions using poplar, even those without catalyst present, and its exact origin is unknown as the amounts of H lignin found in the poplar species is very low (Table S3). There is no evidence that the solvent, MeOH, is consumed during this reaction and its volatility makes it easy to separate from both the phenolic products and sugar residue. Upon removal of methanol, dihydroeugenol and 2,6-dimethoxypropylphenol can be extracted from the remaining residue using diethylether. NMR spectra of this extract confirm it consists of mainly two products with small amounts of unidentified impurities (Figure S2 and Figure S3). The non-ether soluble fraction was also analyzed via NMR and gave spectra with features consistent with sugars and aromatic lignin fragments suggesting that a portion of our unaccounted for lignin is present in the methanol solution (Figure S4). This fraction was then subjected to analysis for carbohydrates and found to contain a majority of xylans with smaller amounts of glucans and arabinans (Table S5).

In comparison to the Pd-Zn catalytic process described above for intact wood biomass, organosolv lignin contains hundreds of compounds,[15] rendering its conversion to a reasonable number of products extremely difficult (Figure S1c).

Carbohydrate residue retains its value

To determine the composition of the leftover carbohydrate residue it was digested by acid hydrolysis, which produced mainly glucose (Table S6). This leftover carbohydrate residue was subjected to cellulase enzyme digestion, giving 95% of the theoretical glucose yield.[28] In comparison, intact poplar wood released only 11% of theoretical glucose from cellulase enzyme digestion over the same time period. These results are consistent with those reported in the literature showing that cellulose can be hydrolyzed by enzymes once lignin is removed, as lignin and deactivates cellulase enzymes.[29] The sugars from hydrolysis as well as the sugars present in the MeOH phase were analyzed allowing mass balance closure of 74% of the starting biomass weight in quantified products (Figure 3). Our results illustrate the positive impact of lignin conversion by the Zn/Pd/C catalyst on enhancing sugar yields from poplar. Furthermore, the released sugar can be upgraded by known biological and chemical catalytic conversion processes that have been developed independently for pure carbohydrates.[30,31]

The availability of the leftover carbohydrate residue for direct conversion was demonstrated by subjecting the sample to analytical fast pyrolysis in a pyroprobe/mass spectrometer developed previously for the determination of primary pyrolysis products.[32] The results obtained for pure cellulose and the leftover carbohydrate residue derived from woody biomass are compared in Figure 4, together with fast-pyrolysis products of raw woody biomass. The solid residue behaved similarly to pure cellulose, yielding a similar product distribution, the main product of which was cellobiosan. This result is in sharp contrast to the highly complex mixture obtained upon fast pyrolysis of the lignified raw biomass (Figure 4A).

Genetic variants control products

Lignin is made by radical polymerization of *p*-hydroxyphenyl (H), G, and S monomeric units to give various linkage types (Figure 1). The most ubiquitous linkage is the β-O-4. H, G, and S subunit abundance in lignin varies depending on the plant species, and the availability of different monomers can be manipulated genetically.[33,34] To evaluate whether such engineered lignins can be successfully converted using our process, we employed a genetically engineered line (717-F5H) with high-S lignin (Table 1, entry 2).[27,35] Unmodified WT-717 poplar gives a ~1:2 ratio of dihydroeugenol to 2,6-dimethoxy-4-propylphenol. In comparison the high-S line gives a greater yield of 2,6-dimethoxy-4-propylphenol with a final product distribution of 1:6 (Figure 2B). The results from this experiment demonstrate how tailoring biomass through genetic control can affect the product distribution.

Wood from other tree species, such as pine, white birch, and eucalyptus, can also be broken down by our catalyst (Table 1, entries 5-7). Pine contains exclusively G lignin and has very high lignin content (30% by weight). Pine gave exclusively dihydroeugenol as the phenolic product but with lower yield compared to poplar and birch, presumably due to the high degree of cross-linking in G lignins. Although the lignin content of white birch is only 16% by weight, it gave an impressive yield (52%) (Table 1, entry 6); whereas, the combination of high lignin content (24% by weight) and high yield 49% from eucalyptus produced the greatest overall yield of products from a mass standpoint (~12% of the total biomass converted to the two phenolic products).

Lignin-derived fuel and chemical platform

While the methoxypropylphenol products have value as chemicals, we have also developed novel catalysis for their conversion to the high-octane liquid fuel propylbenzene

(Figure 1). When dihydroeugenol; 2,6-dimethoxy-4-propylphenol; or a mixture of the two was reacted with H_2 over a Pt-Mo bimetallic catalyst at 300 °C and 342 psig H_2, propylcyclohexane and propylbenzene were obtained in >97% and ~0.7% yield, respectively (Table S8a). This is the highest reported yield of hydrocarbons from the continuous, vapor-phase reaction of lignin-derived methoxypropylphenols to date. The propylcyclohexane can be aromatized via a dehydrogenation reaction to give additional propylbenzene and return 3 equivalents of the H_2 used in the hydrogenation of methoxypropylphenols over the Pt-Mo catalyst.[36,37] Current work is aimed at the direct production of propylbenzene from methoxypropylphenols.

The effective lignin processing demonstrated here opens a new direction for biorefinery configurations and synergies. The catalytic depolymerization of lignin into methoxypropylphenols employs the lignin portion of biomass first, while simultaneously leaving behind an essentially intact solid-carbohydrate fraction that can be further processed via traditional biorefinery methods. Utilization of all components of lignocellulosic biomass feedstock (lignin, cellulose, and hemicellulose) is critical for maximizing fuel and chemical yield per acre. The selective production of two methoxypropylphenols and their further conversion to the hydrocarbon propylcyclohexane/propylbenzene platform reported here enables many options for the conversion of the natural aromatic structure of lignin into currently used aromatic chemicals that were previously not viable. In addition, we envision a biorefinery that encompasses multiple synergies (as opposed to conventional biorefineries involving only one processing method) designed to minimize chemical bond breaking by making products that exploit the natural structure of biomass.

The lignin-derived methoxypropylphenols can be used in the fragrance industry (i.e. dihydroeugenol), as well as be catalytically upgraded to a variety of fuels (e.g. propylbenzene,

toluene, etc.) and chemicals (e.g. propane, methanol, benzene, cumene, para-xylene, ethylbenzene, styrene, phenol, and acetone) as shown in Figure 5. We have demonstrated high-yield production of the hydrocarbon propylcyclohexane from lignin. Propylcyclohexane can be converted via dehydrogenation to propylbenzene, which can be hydrocracked subsequently to benzene and propane.[38] Benzene can be used as a chemical building block for production of fuels and chemicals via a variety of known and practiced conversions, such as: alkylation of benzene with co-produced propane (propylene after dehydrogenation) to form cumene, alkylation with co-produced MeOH to form toluene or xylenes, or alkylation with ethanol or ethylene to form ethylbenzene and styrene.[39,40] The propane produced can be dehydrogenated and employed for polymer production or converted further to acetone; which when reacted with phenol forms the polycarbonate monomer, bisphenol-A.[41]

The solid carbohydrate fraction can be further processed to fuels and chemicals by currently employed chemistries such as liquid-phase (catalytic) processing and biological conversion such as fermentation, or thermochemical processes such as fast hydropyrolysis or gasification followed by further catalytic upgrading.[42] Additionally, the waste from some steps, such as carbonaceous residue or char, can be utilized by feeding to a thermo-chemical unit (fast-pyrolysis or gasification) for conversion into a variety of intermediate products that can be upgraded.

New synergies emerge from integration of lignin and carbohydrate chemistries. For example, in Figure 5, we show alkylation of benzene with methanol to form para-xylene (an important chemical) or alkylbenzene molecules as fuels. The methanol can be sourced from cleavage of the methoxy groups of methoxypropylphenols or produced from the breakdown of the carbohydrate fraction. Additionally, methanol derived from the biomass itself can be used as

the solvent for the lignin depolymerization step with the aforementioned Zn/Pd/C catalyst. Styrene can be produced through an integrated pathway involving alkylation of benzene using ethylene or renewable ethanol produced from sugar fermentation.

In addition to the pathways discussed above, the development of new and more-direct pathways are immediately recognizable, utilizing the natural aromatic lignin structure (aromatic ring, alkyl and oxygen substituents) and minimizing the number of conversion steps to generate renewable commodities. For example, cumene could be synthesized directly from propylbenzene via isomerization of the propyl substituent, and hydrocracking of propylphenol could afford a direct route to phenol and propane. Some of these transformations present the need to develop new chemistries starting from a variety of different intermediate chemicals that go beyond "traditional" chemistry used in the petrochemical industry.

Conclusion

Catalytic conversion of lignin to discrete phenolic molecules was achieved with good yields utilizing a process that produces a clean carbohydrate residue. This was accomplished under reasonable conditions (225 °C, 500 psi H_2) using a synergistic Pd/C and Zn system that cleaves and deoxygenates the β-O-4 linkages in native lignin. These lignin-derived methoxypropylphenols can be further converted to a variety of valuable aromatic fuels and chemicals. This new approach to utilization of lignin enables the future biorefinery to obtain higher yields of fuels and chemicals. The newfound ability to utilize lignin-first for fuels and chemicals presents a new paradigm for biofuel production in which lignin is potentially more valuable than cellulose and provides opportunity for plant biologists to tailor biomass that

contains more lignin. Mapping of products based on the natural structure of lignin identifies new chemical transformations and catalysis that will stimulate target driven fundamental research.

Material and methods

Chemicals

Pd/C (5 wt%) was purchased from Strem Chemicals (Newburyport, MA). 4-Allyl-2,6-dimethoxyphenol (98% purity) was purchased from Alfa Aesar (Ward Hill, MA). Isoeugenol, eugenol, 2-methoxy-4-propylphenol (all >98% purity) and ammonium formate (>99% purity) were purchased from Sigma-Aldrich (St. Louis, MO). 2-Methoxy-4-methylphenol (98% purity) and methylparaben (>99% purity) were obtained from TCI America (Portland, OR). High-performance liquid chromatography−mass spectrometry (HPLC-MS) grade water and acetonitrile were purchased from Fisher Scientific (Pittsburgh, PA). All chemicals were used without further purification. A Zorbax SB-C18 column (4.6 × 250 mm, 5 μm particle size) was purchased from Agilent Technologies (Santa Clara, CA). 2,6-Dimethoxy-4-propylphenol was synthesized as outlined below.

Feedstock

Poplar genotype NM-6 (*Populus nigra* x *P. maximowiczii*,WT- LORRE) was provided by Adam Wiese of the USDA Northern Research Station in Rhinelander, Wisconsin.[43] Hybrid aspen INRA 717-1B4 (*P. tremula* x *P. alba*, WT-717), Poplar (*P. nigra* x *P. maximowiczii*) WT-NM-6, the genetically engineered line 717-F5H and WT-White Birch (*Betula papyrifera*) were provided by Purdue University's Department of Forestry and Natural Resources Department. The WT

lodgepole pine (*Pinus contorta*) was provided by Mr. Jerry Warner (COL, U.S. Army Ret.), Managing Director of Defense LifeSciences, LLC (Alexandria, VA). The WT-Eucalyptus (*Eucalyptus grandis* x *E. urophylla*) was provided by William H. Rottman, ArborGen, Inc. (Ridgeville, SC).

Preparation of 2,6-dimethoxy-4-propylphenol. 2,6-Dimethoxy-4-propylphenol was synthesized through the hydrogenation of the side chain of 4-allyl-2,6-dimethoxyphenol. 4-Allyl-2,6-dimethoxyphenol was dissolved in a suspension of Pd/C (5 wt%, 105 mg) in 15 mL MeOH (1.945 g, 10.1 mmol). The reaction mixture was placed in a stainless steel Parr reactor, pressurized with 500 psig bar H_2 and heated at 60 °C for 3 hours. Pd/C was removed by filtration and methanol was removed *in vacuo* to yield 2,6-dimethoxy-4-propylphenol as a colorless oil. The reaction product was further purified on a silica-gel column with a mobile phase of 17% ethyl acetate and 83% hexanes. [^{1}H]NMR ($CDCl_3$) δ 0.93 (t, 3H, CH_3), 1.61 (s, 2H, CH_2), 2.50 (t, 2H, CH_2), 3.85 (s, 6H, OCH_3), 5.42 (s, 1H, OH), 6.39 (s, 2H, ArH).

Biomass Preparation

Biomass was first milled to pass through a 40 mesh screen using a Mini Wiley Mill (Thomas Scientific, Swedesboro, NJ). Biomass was washed consecutively with water and ethanol soxhlet using the LAP Determination of Extractives in Biomass procedure.[44] Following soxhlet extraction, the biomass was dried and evaluated using a moisture analyzer (Halogen model HB43-S, Mettler-Toledo LLC, Columbus, OH).

General *in situ* Generated Catalyst Reactions

In a typical experiment, 1.0 g of biomass, Pd/C (5 wt%), $ZnCl_2$ (5-10 wt%), methanol (30 mL), and glass stir bar were added to a stainless steel Parr reactor, which was subsequently sealed.

While stirring the mixture was purged with UHP grade H_2 for ~1 min, then pressurized with H_2 (500 psig, 34 bar). The mixture was heated to 225°C. This temperature was maintained for ca. 12 hours. The reaction was terminated by removing the heat and cooling the reactor to room temperature (WARNING! Use caution when handling and venting the reactor; Pd/C is pyrophoric). The reaction mixture was filtered to remove Pd/C and remaining solid biomass residue. This Pd/C/biomass mixture was washed with additional MeOH and the filtrate was collected and diluted in a volumetric flask. This solution was analyzed by GC-FID and HPLC/MS as described below to determine amounts of methoxypropylphenols.

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Author Contributions:

TP, SY, and JD performed experiments, analyzed data and wrote the paper. TJ, MH, and HIK designed and performed MS analyses. EG performed calculations for the synergistic biorefinery concept. IK, BH, and BS performed experiments and analyzed data. JIK performed ABSL and DFRC analyses. HC provided technical assistance on experiments with the PtMo catalysis. RM, CC, and NM supervised and provided technical knowledge on biomass handling and analyses. FR, WND, RA, and MMAO designed experiments, analyzed data, and wrote the paper. All authors provided comments on the paper.

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Conflict of Interest:

MMAO has equity interests with Spero Energy, Inc., a start up company focused on making specialty chemicals from renewable sources. NM acts as a consultant for Spero Energy. Activities with Spero Energy have been disclosed to Purdue University in accordance with Purdue Policy on Conflicts of Commitment and Reportable Outside Activities (www.purdue.edu/policies/ethics/iiib1.html).

Figure Legends

Figure 1. Selective depolymerization and hydrodeoxygenation (HDO) of lignin first from wood biomass to give a lignin-derived hydrocarbon platform and glucose from the carbohydrate residue.

Figure 2. Single ion monitoring ESI(-)/HPLC/MS of lignin products (m/z 165 and m/z 195) from (a) WT-717 poplar and (b) 717-F5H, a high-S transgenic line. CAD MS/MS of (c) deprotonated 2,6-dimethoxy-4-propyl phenol and (d) deprotonated dihydroeugenol derived from WT-717 poplar.

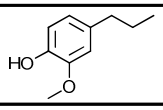
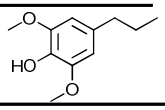
Figure 3. Mass balance after catalytic cleavage and HDO of WT poplar lignin over Zn/Pd/C catalyst. * Mass of phenolic products includes all quantified phenolics and also accounts for the loss of O into H_2O during HDO. Liquid Phase sugars were quantified by HPLC analysis. The solid phase residue was hydrolyzed with acid. Then glucose, arabinose, and xylose were quantified by HPLC analysis.

Figure 4. Positive mode ammonium attachment Atmospheric Pressure Chemical Ionization mass spectra measured for fast pyrolysis[32] products of (a) WT-LORRE poplar, (b) carbohydrate residue from WT poplar after our one-step catalytic conversion of lignin over Zn/Pd/C, and (c) pure crystalline cellulose.

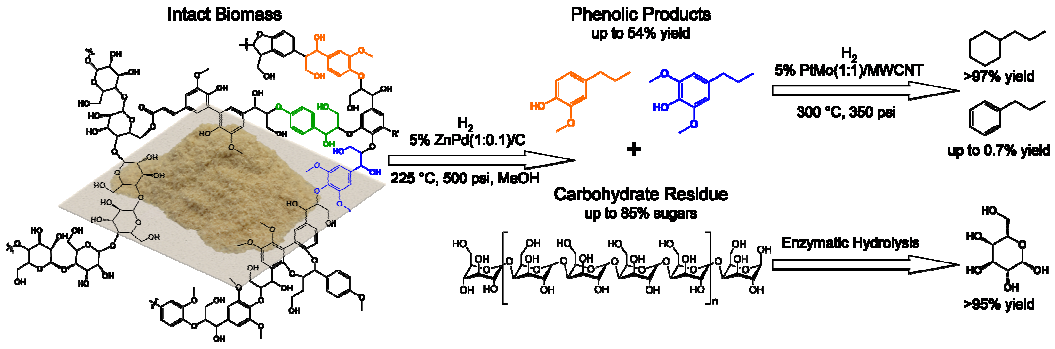
Figure 5. Pathways for the production of renewable fuels (in blue) and chemicals (in green) from the lignin portion of biomass. Methoxypropylphenols can be used as is for the fragrance industry (dihydroeugenol), or can be catalytically tailored to fuels (such as propylbenzene and toluene) or

used for the production of chemicals (such as propane, methanol, benzene, cumene, para-xylene, ethylbenzene, styrene, phenol, and acetone).

Table 1. Conversion of lignin starting with intact lignocellulosic biomass over Zn/Pd/C catalyst.

Biomass Type	%G Lignin[a]	%S Lignin[a]	% Lignin Content[b]	Selectivity 		Yield (wt%)[c]
Poplar WT-717	44	51	19	31	69	40
Poplar 717-F5H (High S Poplar)	20	73	20	17	83	36
Poplar WT-NM-6	40	55	18	28	72	44
Poplar WT-LORRE	49	47	19	45	55	54
WT-White Birch	44	49	16	31	69	52
WT-Eucalyptus	34	65	24	30	70	49
WT-Lodgepole Pine	100	0	31	100	NA	19

[a]Lignin composition as determined by DFRC (Derivatization Followed by Reductive Cleavage) analysis. [b]Lignin content as determined by ABSL (Acetyl Bromide-Soluble Lignin) lignin analysis. [c] Yield is calculated using the initial mass of lignin and the mass of the products, factoring in the loss of two atoms of oxygen for each mole of product produced.



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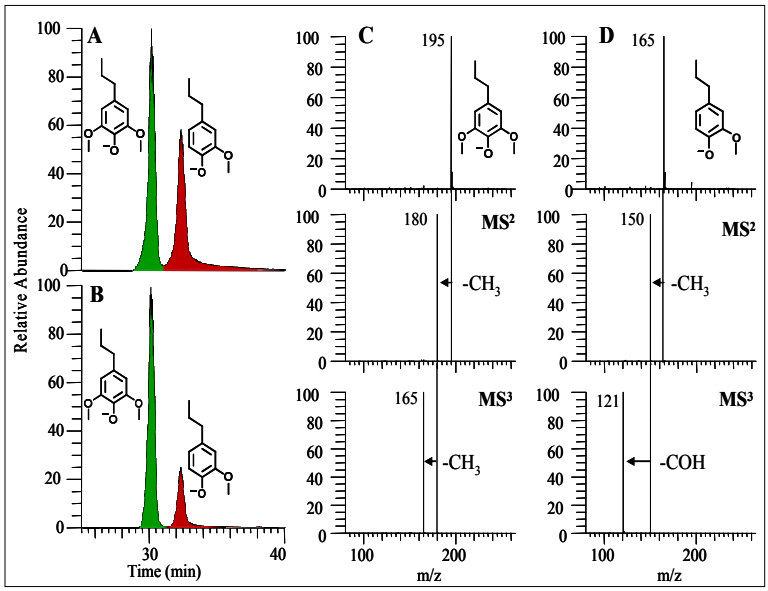

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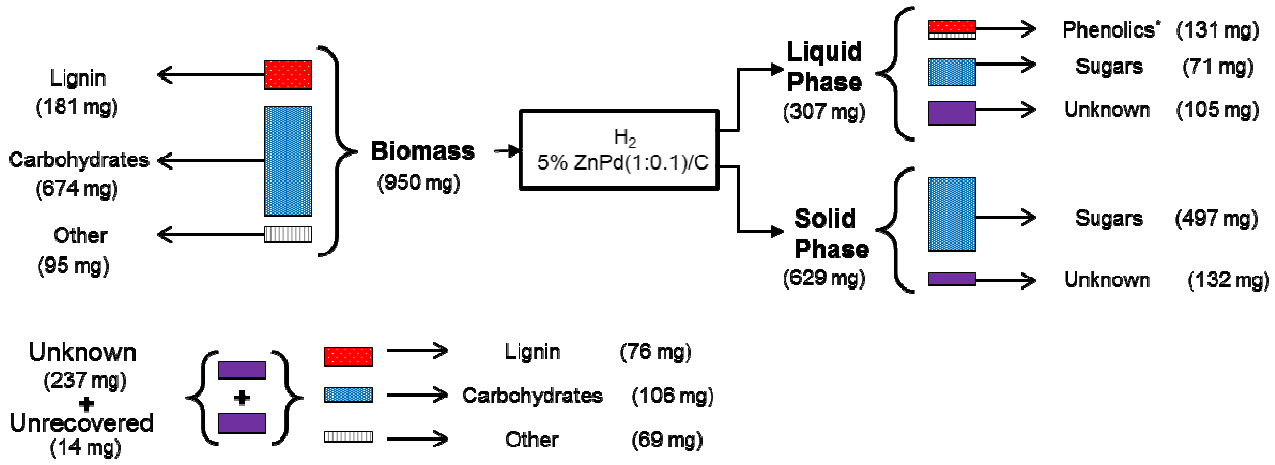

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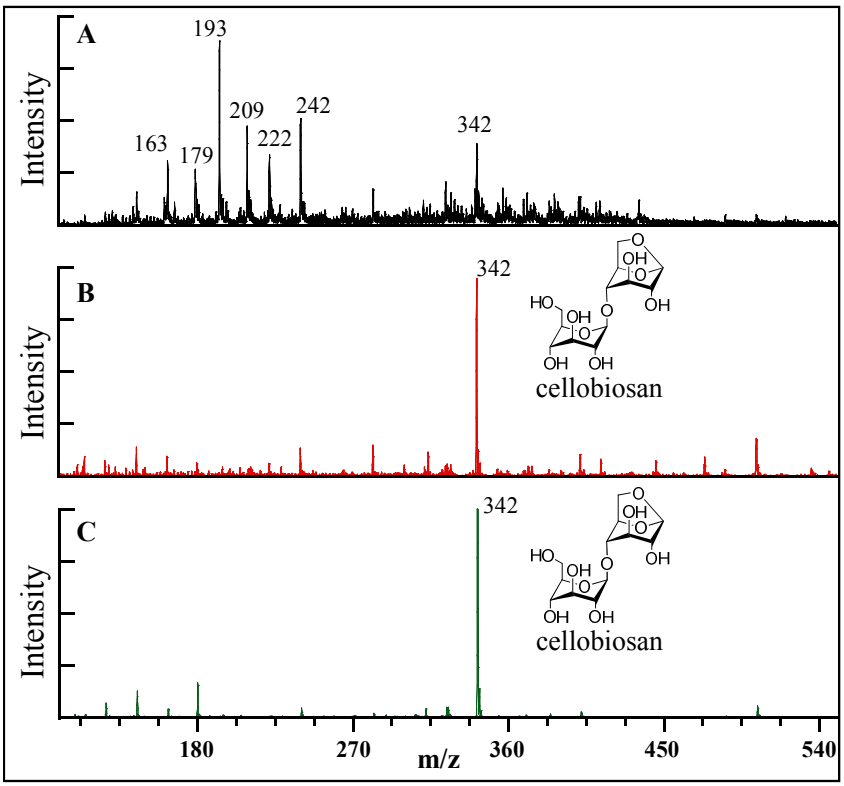

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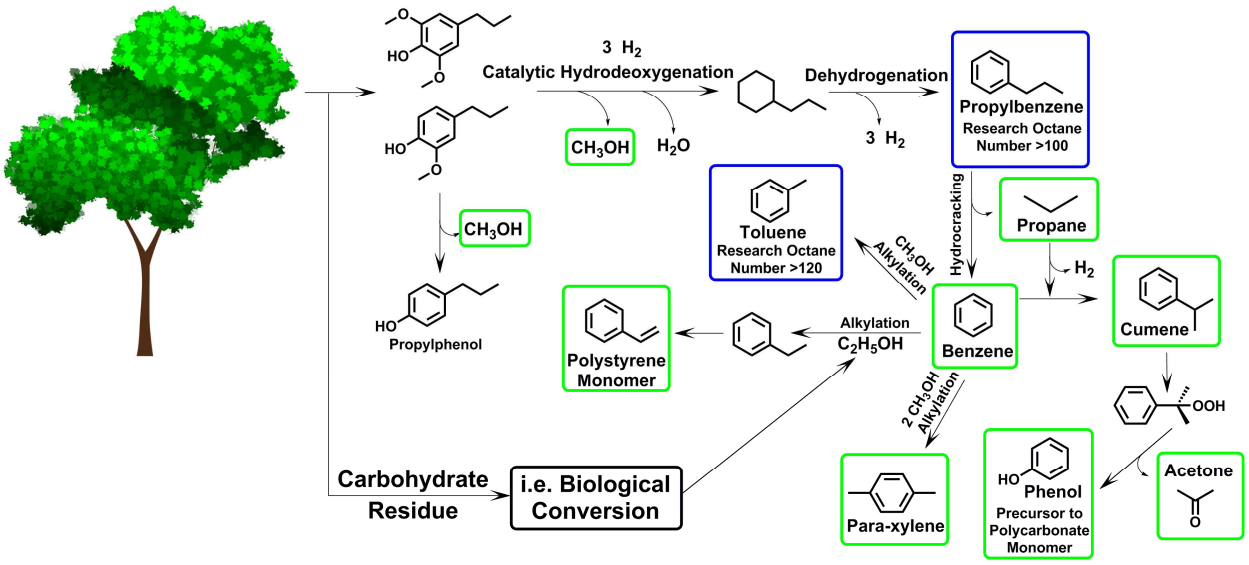

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Supplementary Information

HPLC/MS Analysis

Instrumentation. All analyses were performed using a Thermo Scientific linear quadrupole ion trap (LQIT)−Fourier transform ion cyclotron resonance (FT-ICR; 7 T magnet) mass spectrometer coupled with a Surveyor Plus HPLC. The HPLC system consisted of a quaternary pump, autosampler, thermostatted column compartment, and photodiode array (PDA) detector. The LQIT was equipped with an ESI source. HPLC eluent (flow rate of 500 μL/min) was mixed via a T connector with a 10 mg/mL sodium hydroxide water solution (flow rate of 0.1 μL/min) and connected to the ion source. This allows for efficient negative ion generation by ESI.[1] The LQIT-FT-ICR mass spectrometer was operated using the LTQ Tune Plus interface. Xcalibur 2.0 software was used for HPLC/MS data analysis. Automated gain control was used to ensure a stable ion signal. A nominal pressure of 0.65×10^{-5} Torr, as read by an ion gauge, was maintained in the higher pressure LQIT vacuum manifold and 2.0×10^{-10} Torr in the FT-ICR vacuum manifold, as read by an ion gauge.

High-performance liquid chromatography/high-resolution tandem mass spectrometry. All samples were introduced into the HPLC/MS via an autosampler as a full-loop injection volume (25 μL) for high reproducibility. 1 mg/L ammonium formate in water (A) and 1 mg/mL ammonium formate in acetonitrile (B) were used as the mobile-phase solvents. Ammonium formate was used to encourage negative ion production. A nonlinear, two-slope gradient was used (35% A and 65% B at 30.0 min to 5% A and 95% B at 55.0 min). The column was placed in a thermostatted column compartment that maintained the column at a temperature of 30 °C to increase the reproducibility of the retention times and peak widths. The PDA detector for HPLC was set at 280 nm. The exact conditions used for ionization of the analytes and injection of the ions into the mass spectrometer were optimized using a stock solution of 2-methoxy-4-propylphenol in a 0.15 mg/mL NaOH 50:50 acetonitrile/water solution. All ion optics were optimized using the automated tuning features of the LTQ Tune Plus interface. The ESI probe position was optimized manually for optimal signal. The following ESI conditions were used: sheath gas pressure 60 (arbitrary units), auxiliary gas pressure 30 (arbitrary units), sweep gas pressure 0 (arbitrary units), and spray voltage 3.50 kV. For the analysis of lignin conversion products, data-dependent scans were used. Data-dependent scanning involves the instrument automatically selecting the most abundant ions from the ion source, one after another, for further experiments. This allows for separate MS acquisitions to be performed simultaneously for the same ions in the two different mass analyzers of the LQIT-FT-ICR wherein the higher duty-cycle LQIT performs tandem mass spectral acquisitions for the selected ions, while the lower duty-cycle FT-ICR carries out high-resolution measurements for elemental composition determination for the same ions. A resolving power of 400,000 at m/z 400 was used in the FT-ICR. The MS^2 experiments involve the isolation (using a mass/charge ratio window of 2 Th) and fragmentation of selected ions formed upon negative ion-mode ESI spiked with NaOH. The ions were kinetically excited and allowed to undergo collisions with helium target gas for 30 ms at a q value of 0.25 and at normalized collision energy[2] of 40%. The most abundant product ion formed

in the MS^2 experiments was subjected to a further stage of ion isolation and fragmentation (MS^3).

Quantitation of aromatic products from lignin conversion (S1). Standard solutions, each containing, dihydroeugenol, 2,6-dimethoxy-4-propylphenol, and methylparaben, were made from 1.0 mM stock solutions and diluted to a final volume of 1.0 mL with the following final concentrations: 0.005, 0.010, 0.050, 0.10, and 0.15 mM. Vanillyl alcohol was used as the internal standard (0.1 mM) and was added into each of the five standard solutions. A full-loop injection was performed for each standard solution; thus, a total volume of 25 μL was injected onto the column. After separation, selected ion chromatograms for deprotonated dihydroeugenol, 2,6-dimethoxy-4-propylphenol, methylparaben, and vanillyl alcohol were extracted from measured mass spectrometric data by Thermo Xcalibur Quan Browser software and used to create calibration curves.

Table S1. HPLC/MS quantitation of all soluble aromatic/phenolic products from lignin conversion and HDO over Zn/Pd/C catalyst in MeOH.*

Biomass Type	Methylparaben (mg)†	2,6-Dimethoxy-4-propylphenol (mg)	Dihydroeugenol (mg)	Removed Oxygen (mg)‡
Poplar WT-717	5.4	49.4	21.9	2.3
Poplar WT-717 Microporus Cage	9.0	41.6	29.2	2.3
-Recycled Cage Reaction 1	3.5	47.1	23.3	2.3
-Recycled Cage Reaction 2	2.3	29.6	15.0	1.4
-Recycled Cage Reaction 3	2.3	22.0	11.6	1.0
Poplar NM-6	6.7	62.5	30.5	3.0
Poplar WT-LORRE	26.2	56.1	46.0	3.3
Poplar 717-F5H (High S Poplar)	3.2	59.4	12.1	2.3
Lodgepole Pine WT	n/a	n/a	56.5	1.8
White Birch WT	n/a	54.0	26.3	2.6
Eucalyptus WT	n/a	80.0	34.5	3.7
Poplar WT-LORRE no $ZnCl_2$	6.8	8.3	6.6	0.5
Poplar WT-LORRE no Pd/C	15.2	0	0	0
Poplar WT-LORRE no H_2	8.4	1.4	3.7	0.15

* Based on 1,000 mg of starting intact biomass. † Methylparaben is a quantifiable aromatic product that is extracted during catalysis. ‡ Calculated using the number of moles of products generated based on the fact that two atoms of O are removed for every mole of product.

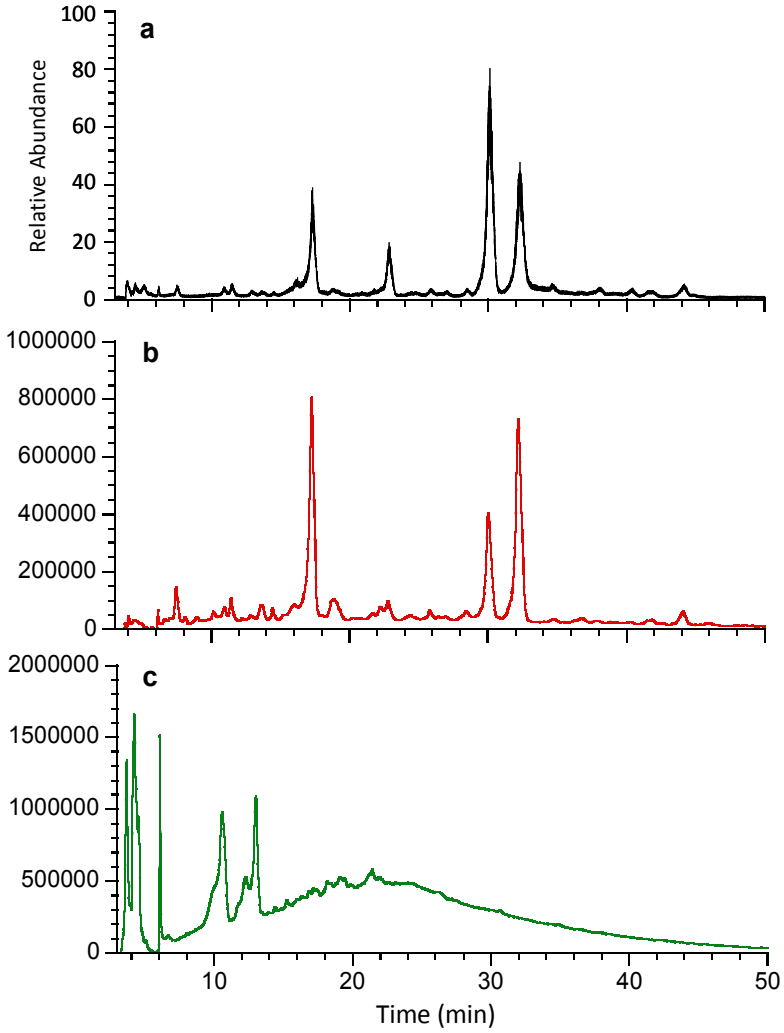

Figure S1. (a) HPLC/MS and (b) HPLC/UV spectra of poplar WT-LORRE @ 225 °C and 500 psig H_2 in MeOH for 12 hours (c) HPLC/UV spectra of organosolv poplar.

NMR Analysis

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 processing of spectra. All spectra obtained were referenced to residual solvent peaks accordingly.

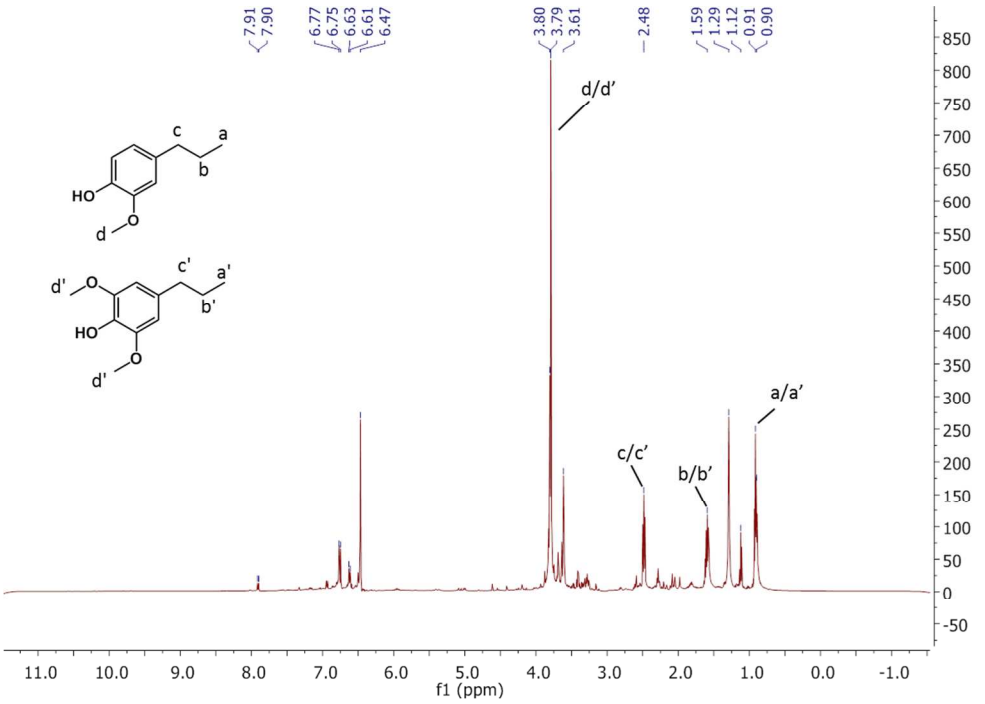

Figure S2. ^{1}H NMR spectrum of extracted phenolic products from poplar WT-717 treated with Pd/C and Zn^{2+} @ 225 °C and 500 psig H_2 in MeOH for 12 hours.

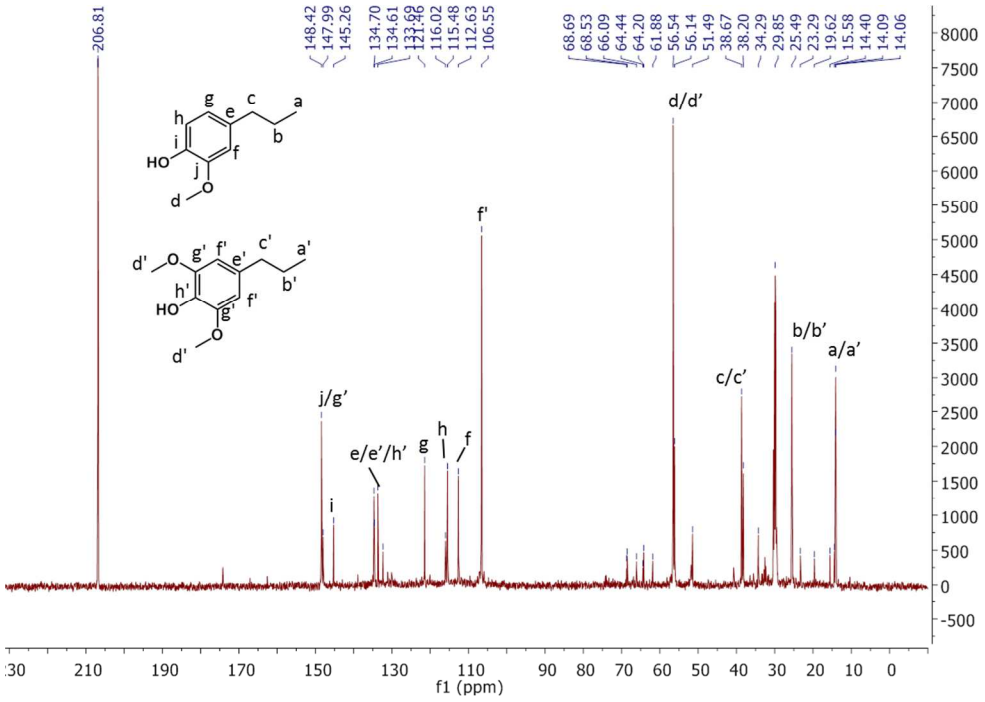

Figure S3. ^{13}C NMR spectrum of extracted phenolic products from poplar WT-717 treated with Pd/C and Zn^{2+} @ 225 °C and 500 psig H_2 in MeOH for 12 hours.

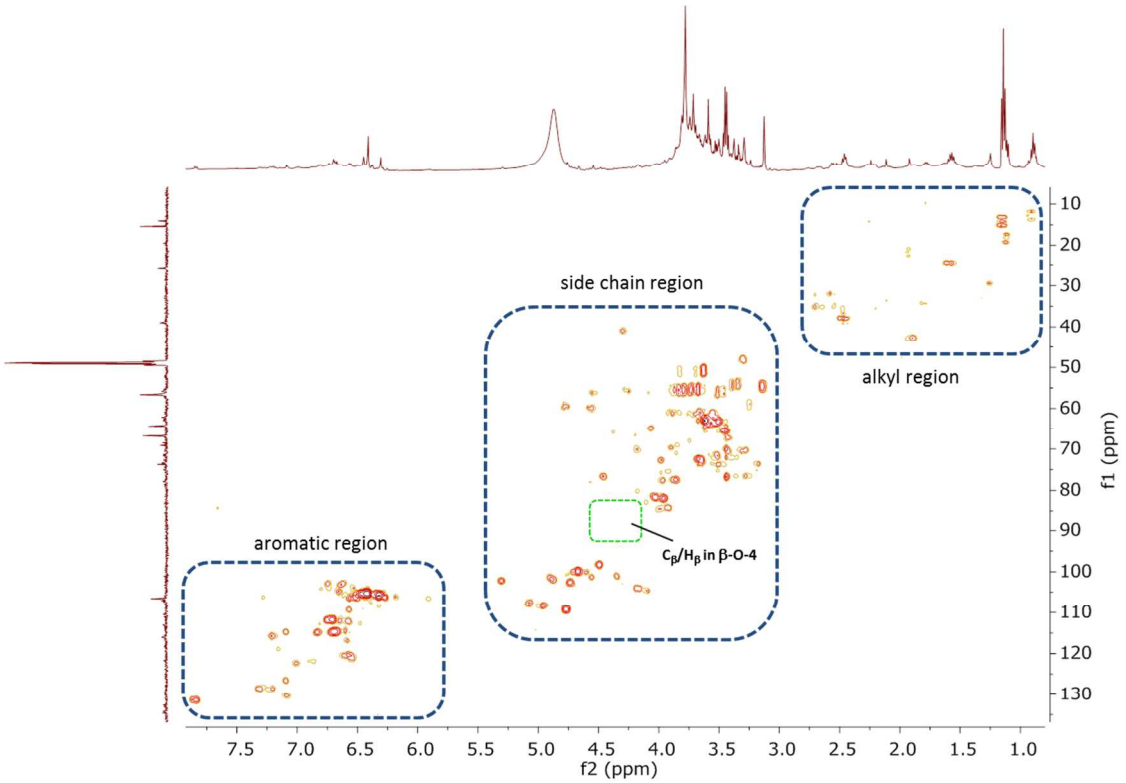

Figure S4. HMQC NMR spectrum of non-ether soluble residue from poplar WT-717 treated with Pd/C and Zn^{2+} @ 225 °C and 500 psig H_2 in MeOH for 12 hours.

Mass Balance for WT-LORRE Poplar by Wt. %

Table S2. Reaction mass balance after catalytic cleavage and HDO of WT poplar lignin over Zn/Pd/C catalyst.*

Organic Liquid Phase	
Ether soluble	
dihydroeugenol	4.9%
2,6-dimethoxy-4-propylphenol	6.0%
methylparaben	2.8%
unknown	11%
Water soluble	
glucose	1.3%
xylose	5.8%
arabinose	0.4%
Solid Residue	
glucan	46%
xylan	6.0%
arabinan	0.4%
unknown	13.9%
TOTAL	98.5%

* Mass of phenolic products includes all phenolics quantified via HPLC/UV and HPLC/MS spectroscopy and accounts for the loss of O into H_2O during HDO. All sugars were extracted from the organic layer and quantified by HPLC analysis. Cellulosic solid residue was hydrolyzed with acid. Then glucose, arabinose, and xylose were quantified by HPLC analysis.

Determination of Lignin Content in Washed Biomass

DFRC (Derivatization Followed by Reductive Cleavage). Composition of lignin was determined by DFRC analysis as previously reported.[3] Briefly, 15 mg of cell-wall samples were resuspended in 20% acetyl bromide solution, containing 4,4'-ethylidenebisphenol dissolved in acetic acid as an internal standard. The dissolved lignin solution was dried down, dissolved in 2 mL of dioxane/acetic acid/ water (5/4/1, v/v/v) and reacted with 50 mg of Zn dust for 25 minutes. The reaction products were purified with C-18 SPE columns (Supelco), and acetylated with pyridine/acetic anhydride (2/3, v/v). The lignin derivatives were analyzed by gas chromatography/flame ionization detection (GC-FID) (Model 7890A, Agilent Technologies, Santa Clara, CA) using response factors relative to the internal standard of 0.80 for *p*-coumaryl alcohol peracetate, 0.82 for coniferyl alcohol peracetate, and 0.74 for sinapyl alcohol peracetate (see Table S3).

Table S3. DFRC analysis of lignin composition for each of the biomass samples.

Lignin Type	Poplar WT-717	Poplar WT-NM-6	Poplar WT-LORRE	Poplar 717-F5H	WT-Lodgepole Pine	WT-White Birch	WT-Eucalyptus
H (mg)	9.64	8.98	7.34	17.80	5.17	12.58	2.51
G (mg)	80.15	84.20	90.93	48.65	118.99	75.66	117.71
S (mg)	92.88	115.41	86.72	182.38	0.00	84.44	225.99

ABSL. Lignin content was determined by the acetyl bromide method.[4,5] The dried samples (between 2 and 5 mg) were added to a 10-mL glass tube with 2.5 mL of 25% acetyl bromide in acetic acid. The tubes were tightly sealed with Teflon lined caps. Tubes were stirred overnight at room temperature until the wall tissue completely dissolved. The samples were transferred to a 50-mL volumetric flasks containing 2 mL 2 M NaOH. The tubes were rinsed with acetic acid to complete the transfer. 0.35 mL of 0.5 M freshly prepared hydroxylamine hydrochloride was added to the volumetric flasks which were then made up to 50 mL with acetic acid and inverted several times. The absorbance of the solutions was recorded at 280 nm with UV/Vis spectrophotometer (Model DU730, Beckman Coulter, Brea, CA). (see Table S4)

Table S4. Acetyl bromide soluble lignin content analysis (ABSL).

Biomass Type	mg ABSL/g CW	% ABSL
Poplar WT-717	160	19
Poplar NM-6	159	18
Poplar WT-LORRE	172	19
Poplar 717-F5H (High S Poplar)	174	20
Lodgepole Pine WT	283	31
White Birch WT	136	16
Eucalyptus WT	215	24

Determination of Carbohydrates

Liquid fraction (Table S5). To determine sugar content in the methanol fraction, 20 mL of H_2O was added to 10 mL methanol and the resulting solution extracted 3 times with 20 mL of Et_2O in each extraction to remove small organic fragments and aromatics. The methanol was then removed under reduced pressure. The carbohydrates in the water layer were quantified by HPLC following the sulfuric acid digestion using a method previously developed by Sluiter et al.[6]

Table S5. Sugar content of the MeOH fraction after extraction of phenolic products from lignin.

Biomass Type	Glucans (mg)	Xylans (mg)	Arabinans (mg)	Total Sugar (mg)
Poplar WT-717	17	52	8	77
Poplar NM-6	23	78	5	106
Poplar WT-LORRE	12	55	4	71
Poplar 717-F5H (High S Poplar)	16	68	5	89
Lodgepole Pine WT	30	85	5	118
White Birch WT	24	42	4	70
Eucalyptus WT	38	44	3	85

Solid residue (Table S6). The remaining cellulosic residue for each biomass was collected on filter paper then dried. The moisture content of each sample was measured and the carbohydrates in the samples were quantified via HPLC after sulfuric acid digestion following the method previously developed by Sluiter et al.[7] HPLC analysis was performed using an Aminex® HPX-87H 300 x 7.8 mm column (Bio-Rad Laboratories, Hercules, CA) with a refractive index detector (model 2414, Waters Corporation, Milford, MA) in an Alliance Waters 2695 Separations Module (Waters Corporation, Milford, MA). Column temperature was maintained at 65 °C. The mobile phase was 5 mM H_2SO_4 at a flow rate of 0.6 mL/min.

Table S6. Sugar content of the remaining cellulosic solid residue after lignin conversion over Zn/Pd/C as determined via acid hydrolysis with HPLC analysis.

Biomass Type	Residue Mass (mg)*	Glucan (mg)	Xylan (mg)	Arabinan (mg)	Total Sugars (mg)	Total Sugar %
Poplar WT-717	555	383	29	4	416	75
Poplar WT-LORRE	627	433	57	4	494	79
Poplar 717-F5H (High-S Poplar)	572	430	49	4	483	84
Poplar WT-NM-6	477	261	21	4	286	60
Lodgepole Pine WT	546	398	22	4	424	78
White Birch WT	475	365	0	4	369	78
Eucalyptus WT	506	429	0	4	433	86

* Mass of the residue excluding Pd/C catalyst and moisture.

Enzymatic Hydrolysis

Pd/C free solid residue (Table S7). Using compositional analysis data, biomass samples equal to the equivalent of 0.1g cellulose were added to plastic vials. Added to each vial was 5.0 ml of citrate buffer (0.1 M, pH 4.8, containing 2% NaN_3). CTEC cellulase was added to the vials at a concentration of 60 fpu (filter paper units), and the total volume was brought to 10 ml with distilled water. Reaction controls for the biomass contained buffer, water, and the identical amount of biomass in 10 ml volume. Cellulase controls were prepared with CTEC cellulase, buffer, and water in 10 ml volume. Samples were sealed and agitated 50 ^oC for 76 hours. After 76 hours, the glucose concentration in each sample was analyzed by HPLC. The low concentrations of glucose detected in control reactions were subtracted from the yields of the corresponding biomass reactions.

Table S7. Enzymatic Hydrolysis of Pd/C free biomass residue after reaction under catalytic HDO conditions.

Biomass	Dry Residue Mass (g)	Cellulose Mass (g)	Cellulose by mass (%)	Glucose Yield at 76 hours (%)	Avg.	Std. Dev.
WT-717 Poplar	0.2310	0.0952	41	12.67		
WT-717 Poplar	0.2292	0.0944	41	8.82	10.75	2.72
Wt-717 Poplar Residue	.1201	0.0940	78	94.55		
WT-717 Poplar Residue	.1224	0.0958	78	96.38	95.47	1.29

Pyrolysis of the Cellulosic Solid Residue from the Biomass (see example in Figure S5).

Pyrolysis experiments were performed using a Pyroprobe 5200 HP supplied by CDS Analytical (Oxford, PA). The pyroprobe is equipped with a resistively heated platinum coil surrounding a quartz tube capable of heating at up to 20,000°C/s. Sample was loaded on the inside of the quartz tube and then pyrolyzed with a heating rate of 1,000°C/s at a temperature of 600°C for 3 seconds. The pyrolysis was performed inside the atmospheric chemical ionization (APCI) source of a Thermo Scientific (Waltham, MA) LTQ linear quadrupole ion trap (LQIT). The pyrolysis products evaporating from the probe were immediately quenched in a 100°C region where they were ionized via either positive or negative mode APCI. The corona discharge was operated at 3,000 V with a discharge current of 4 μA. Ionization of pyrolysis products was achieved with the aid of dopants infused into the APCI source through the APCI probe. In both positive and negative mode APCI, a 50:50 (v/v) solution of ammonium hydroxide:water was co-fed through a T connector with a 50:50 (v/v) solution of methanol:water. In positive mode APCI, the flow rates were 3 μL/min for the ammonium hydroxide:methanol solution and 300 μL/min for the methanol:water solution. With positive mode APCI, analytes were ionized either by protonation ($[M+H^+]$) or ammoniation ($[M+NH_4^+]$). In negative mode APCI, the flow rates were 1 μL/min for the ammonium hydroxide:methanol solution and 300 μL/min for the methanol:water solution. With negative mode APCI, the analytes are deprotonated ($[M-H]^-$).

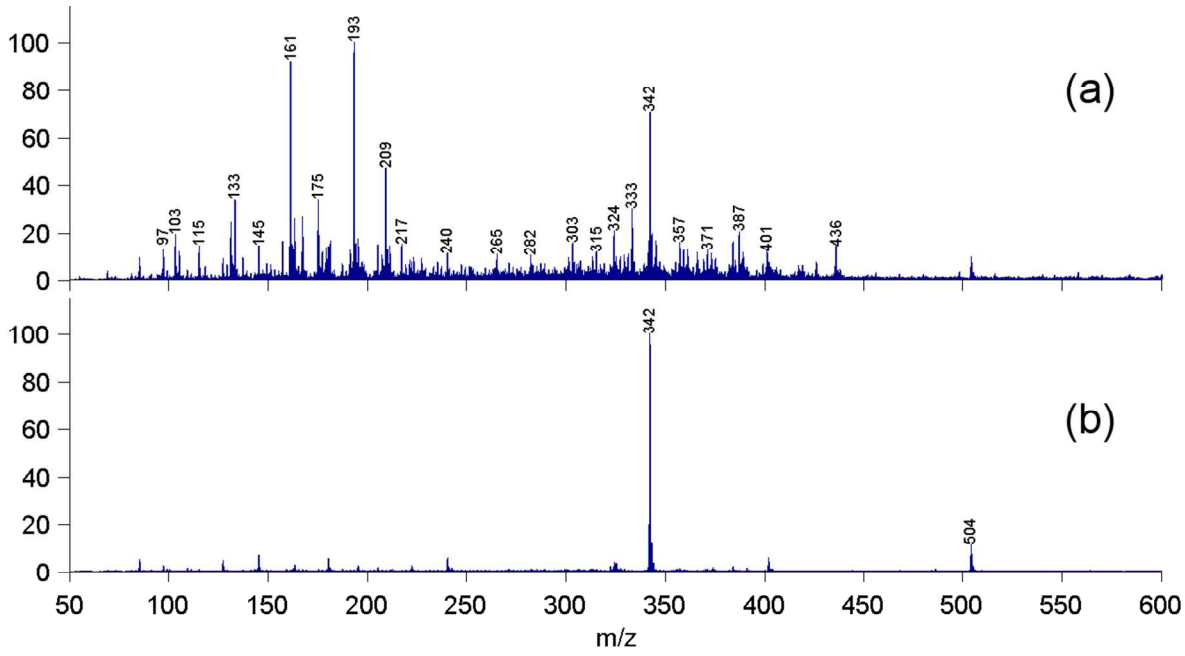

Figure S5. Pyrolysis of unreacted raw eucalyptus WT (a) and eucalyptus WT residue (b) in Ammonium Positive Attachment mode.

Calculating % Yield

The % yield of products is based on the total mass of the products and removed O divided by the mass of the lignin content of each sample as shown in the following equation.

$$\%\ \text{yield} = \frac{\text{dihydroeugenol (mg)} + \text{2,6-dimethoxy-4-propyl phenol (mg)} + \text{removed O (mg)}}{\text{initial weight of biomass (mg)} \times \textit{ABSL}\ \text{lignin}\ \%} \times 100$$

Hydrodeoxygenation Reaction of Dihydroeugenol to Hydrocarbons, Propylcyclohexane and Propylbenzene – Continuous Vapor-Phase Reactor

The hydrodeoxygenation reaction of 2-methoxy-4-propylphenol (dihydroeugenol) was conducted in a high-pressure, vapor-phase, fixed-bed, plug-flow, continuous, stainless-steel reactor at 300°C and a total pressure of 350 psig. During reaction, the hydrogen (Praxair UHP) partial pressure was 342.4 psig, 2-methoxy-4-propylphenol (Sigma-Aldrich >99%) partial pressure was 1.1 psig, and Argon (used as an internal standard, 99.997%) partial pressure was 6.5 psig. The weight hourly space velocity (WHSV, gram dihydroeugenol·gram catalyst^{-1}·h^{-1}) was 5.1.

The catalyst used was a bimetallic PtMo with a 5 wt% Pt loading and a 1:1 atomic Pt:Mo ratio using multi-walled carbon nanotubes (MWCNT) (Cheaptubes, Inc.) as the support. The catalyst was prepared via sequential incipient wetness impregnation of the MWCNT support. First, an

aqueous solution of tetraammineplatinum(II) nitrate ($Pt(NH_3)_4(NO_3)_2$, Sigma-Aldrich) was added and the 5%Pt/MWCNT was dried overnight at 60°C in air. Then, an aqueous solution of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$), Sigma-Aldrich) was added, and the 5%PtMo(1:1)/MWCNT catalyst was dried overnight at 120°C in air. The catalyst was reduced at 200 psig *in situ* in 50 sccm H_2 and 75 sccm He at 450°C for 2 hours. The catalyst loading in the reactor was 110 mg, with the catalyst bed diluted with quartz powder in a 10:1 quartz to catalyst ratio.

All gas- and vapor-phase products were analyzed with an online Agilent 6890N gas chromatograph with a Carboxen-1000 column connected to a thermal conductivity detector and a SPB-1 capillary column connected to an Agilent Deans Switch 3-way splitter which split the flow to a Flame Ionization Detector and Agilent 5973N Mass Spectrometer. Mass balances closed to 100% ± 5%.

Under these conditions, the product propylcyclohexane was produced in >97% yield, as can be seen in S10a. Yield is defined as:

$$\frac{Moles\ of\ Ring\ Product}{Moles\ of\ Dihydroeugenol\ Converted} \times Conversion\ of\ Dihydroeugenol$$

Ring products include all compounds that contain a ring structure (i.e., all products except methanol, methane, and water that are produced from removal of the oxygenated ring substituents).

Hydrodeoxygenation Reaction of Dihydroeugenol and 2,6-Dimethoxy-4-propylphenol to Hydrocarbons, Propylcyclohexane and Propylbenzene – Micro-Scale Pulse Reactor

The hydrodeoxygenation reaction of 2-methoxy-4-propylphenol (dihydroeugenol) and 2,6-dimethoxy-4-propylphenol was conducted in a pulsed, high-pressure, fixed-bed reactor at 300 °C and a total pressure of 350 psig (24 bar). The pulse reactor used is a modified Pyroprobe 5200 HP, manufactured by CDS Analytical, Inc. A known amount of reactant was loaded in the quartz tube and placed in a chamber at 350 psig pressure of hydrogen. The quartz tube was heated using the Pt coil to vaporize the reactant, which was carried to the fixed-bed reactor as a pulse by the flowing hydrogen gas. During reaction, a pulse of the reactant (dihydroeugenol (Sigma-Aldrich >99%) and/or 2,6-dimethoxy-4-propylphenol) in hydrogen (Praxair UHP) at a pressure of 350 psig was passed over a catalyst and analyzed using a downstream GC-FID-MS detector.

The catalyst used was a bimetallic PtMo with a 5 wt% Pt loading and a 1:1 atomic Pt:Mo ratio using multiwalled carbon nanotubes (MWCNT) as the support. The preparation and reduction procedure has been described in the earlier section of the document.

All gas- and vapor-phase products were analyzed with an online Agilent 7890N gas chromatograph with a DB1701 column connected to an Agilent Deans Switch 3-way splitter which split the flow to a Flame Ionization Detector and an Agilent 5975C Mass Spectrometer. Mass balances closed to 100% ± 5%.

Under these conditions, the product propylcyclohexane was produced in >97% yield, as can be seen in S10b. Yield is defined as:

$$\frac{Moles\ of\ Ring\ Product}{Moles\ of\ Dihydroeugenol\ Converted} \times Conversion\ of\ Dihydroeugenol$$

Ring products include all compounds that contain a ring structure (i.e., all products except methanol, methane and water which are produced from removal of the oxygenated ring substituents). Table S.7 shows the comparison of the product yields in the micro-scale pulse reactor and the continuous reactor. Table S.7 shows that >97% yield is obtained for the product propylcyclohexane with either reactant dihydroeugenol or 2,6-dimethoxy-4-propylphenol, or with a 50:50 (V:V) mixture of dihydroeugenol and 2,6-dimethoxy-4-propylphenol.

Table S8. (**a**) Product yields of the high-pressure, vapor-phase hydrodeoxygenation reaction of 2-methoxy-4-propylphenol (dihydroeugenol) at 100% conversion in the continuous reactor. (**b**) Comparison of product yields of the high-pressure, vapor-phase hydrodeoxygenation reaction of dihydroeugenol, 2,6-dimethoxy-4-propylphenol and a 50:50 mixture at 100% conversion in the micro-scale pulse reactor and the continuous reactor.

a

Product	Yield at 100% conversion of Dihydroeugenol
Propylcyclohexane	97.8
Propylbenzene	0.2
Propylcyclopentane	0.7
Methyl-propylcyclopentane	0.5
Other Products	0.8
Reaction Conditions: 300 °C, 350 psi, 0.06 mL/min dihydroeugnol, 2.65 L/min H_2, 50 ml/min Ar, 110 mg 5% PtMo(1:1)/MWCNT catalyst	

b

Product	Yield at 100% Conversion			
	Micro-scale pulse reactor			Continuous reactor
	Dihydroeugenol	2,6-dimethoxy-4-propylphenol	50:50 mixture	Dihydroeugenol
Propylcyclohexane	97.8	97.5	98.0	97.8
Propylbenzene	0.5	0.7	0.6	0.2
Propylcyclopentane	0.6	0.6	0.5	0.7
Methyl-propylcyclopentane	0.1	0.0	0.0	0.6
Other Products	1.0	1.2	0.9	0.8

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