# 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 $0.65 \times 10^{-5}$ Torr, as read by an ion gauge, was maintained in the higher pressure LQIT vacuum manifold and $2.0 \times 10^{-10}$ 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.

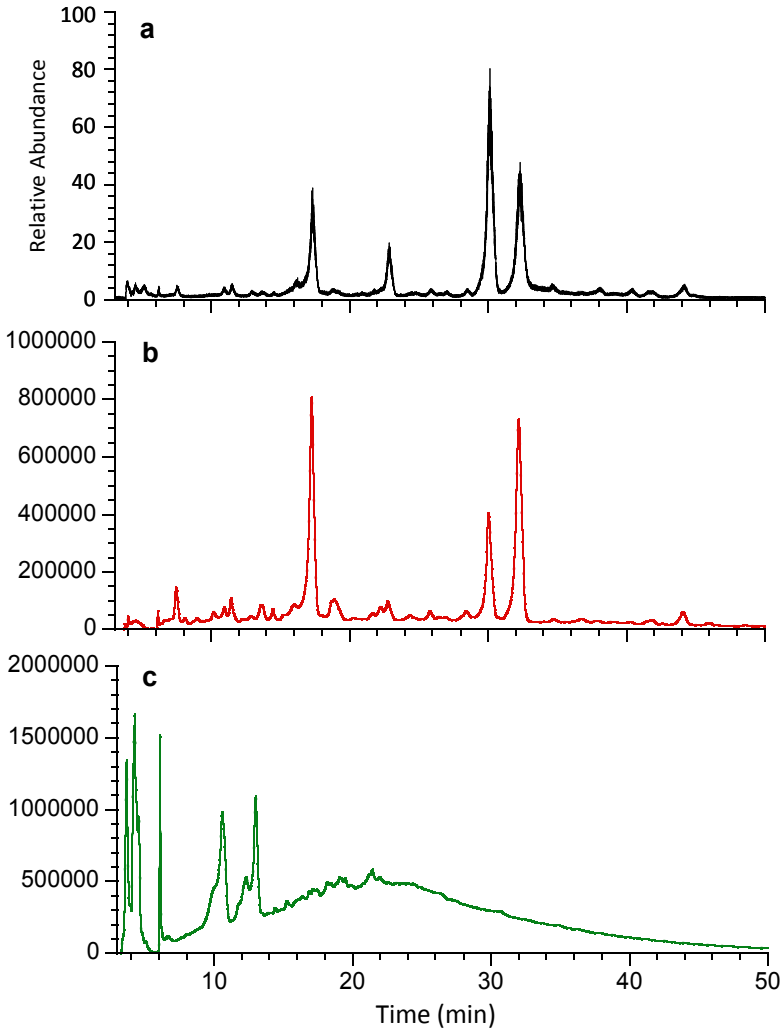


**Figure S1.** (a) HPLC/MS and (b) HPLC/UV spectra of poplar WT-LORRE @ 225 °C and 500 psig $H_2$ in MeOH for 12 hours (c) HPLC/UV spectra of organosolv poplar.

## 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.

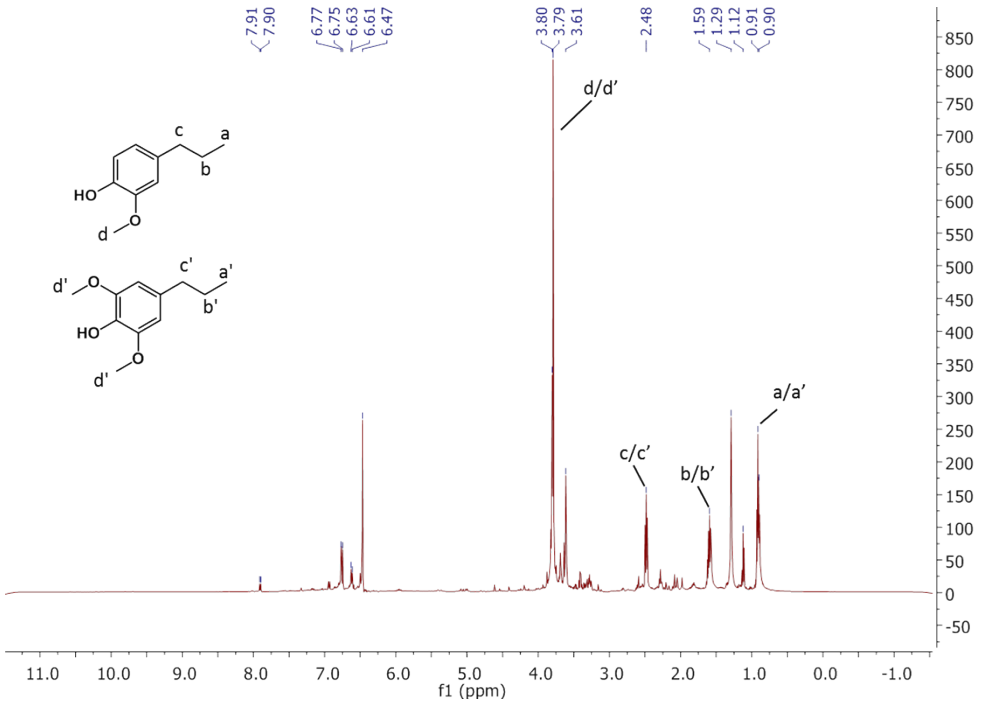


**Figure S2.** $^{1}$H NMR spectrum of extracted phenolic products from poplar WT-717 treated with Pd/C and $Zn^{2+}$ @ 225 °C and 500 psig $H_2$ in MeOH for 12 hours.

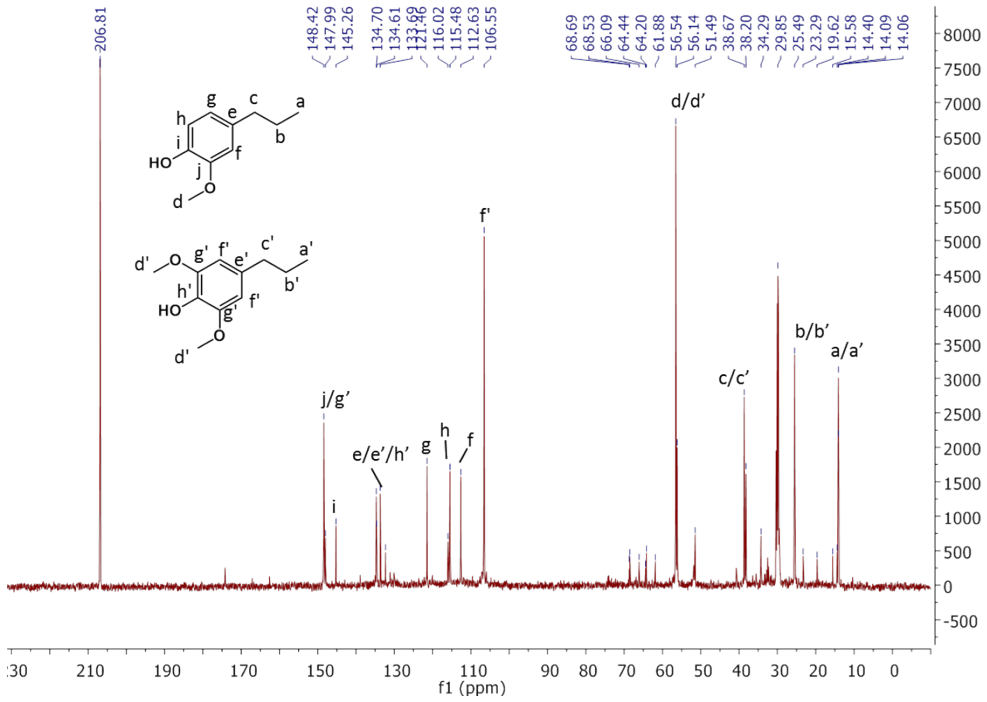


**Figure S3.** $^{13}$C NMR spectrum of extracted phenolic products from poplar WT-717 treated with Pd/C and $Zn^{2+}$ @ 225 °C and 500 psig $H_2$ in MeOH for 12 hours.

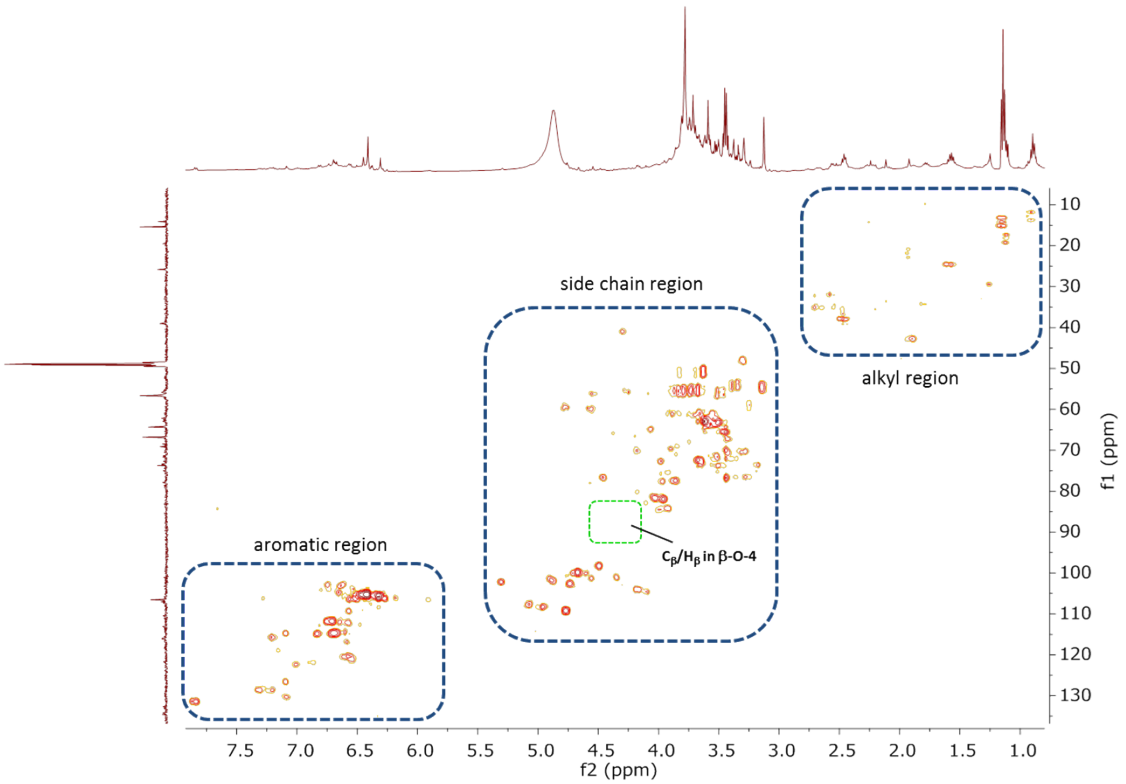


**Figure S4.** HMQC NMR spectrum of non-ether soluble residue from poplar WT-717 treated with Pd/C and $Zn^{2+}$ @ 225 °C and 500 psig $H_2$ in MeOH for 12 hours.

## 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 $^{o}$C 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 ($[M-H]^-$).

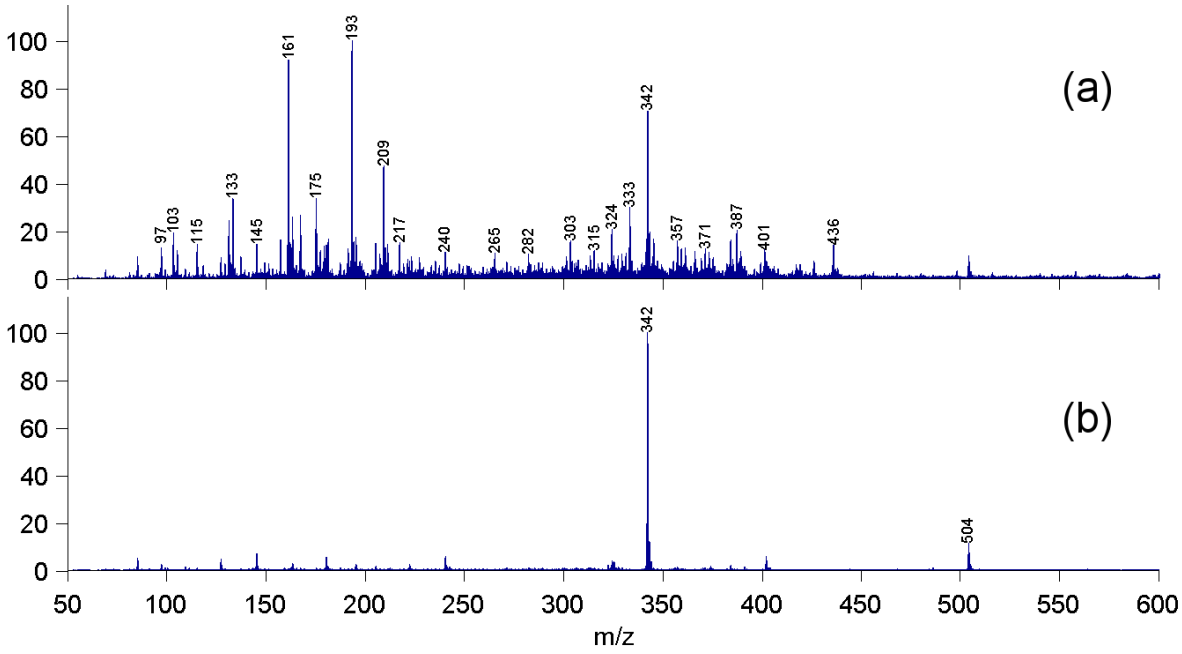


**Figure S5.** Pyrolysis of unreacted raw eucalyptus WT (a) and eucalyptus WT residue (b) in Ammonium Positive Attachment mode.

## 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 |

**References for Supplementary Material:**


1. L. J. Haupert, B. C. Owen, C. L. Marcum, T. M. Jarrell, C. J. Pulliam, L. M. Amundson, P. Narra, M. S. Aqueel, T. H. Parsell, M. M. Abu-Omar and H. I. Kenttämaa, *Fuel*, 2012, **95**, 634–641.
2. L. L. Lopez, P. R. Tiller, M. W. Senko and J. C. Schwartz, *Rapid Commun. Mass Spectrom.*, 1999, **13**, 663–668.
3. F. Lu and J. Ralph, *J. Agric. Food Chem.*, 1997, **45**, 2590–2592.
4. X. Li, N. D. Bonawitz, J.-K. Weng and C. Chapple, *Plant Cell Online*, 2010, **22**, 1620–1632.
5. R. S. Fukushima and R. D. Hatfield, *J. Agric. Food Chem.*, 2001, **49**, 3133–3139.
6. A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter and D. Templeton, *Determination of sugars, byproducts, and degradation products in liquid fraction process samples: Issue Date, 12/08/2006*, National Renewable Energy Laboratory, 2006.
7. A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton and D. Crocker, *Determination of structural carbohydrates and lignin in biomass: Issue Date, 7/8/2011*, National Renewable Energy Laboratory, 2008.