# Supplementary Information

# Catalytic conversion of biomass using solvents derived from lignin

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## 1. Lignin Depolymerization

10 wt% Pd/C, 5 wt% Rh/C and Pt black were obtained from Sigma Aldrich. Poplar wood chips used in lignin depolymerization studies were obtained from the Forest Products National Laboratory (Madison, WI). The wood chips were crushed to mesh 20-40 prior to the experiments and used without drying. The moisture content of the wood was measured by drying the wood chips at 363 K for 24 hours and found to be 7 wt%.

A 300 ml autoclave (Parr Instruments) with magnetic stirring was used for lignin extraction and depolymerization. In a typical lignin conversion reaction, 10 g of wood powder and 0.5 g of catalyst were mixed in 100 ml water. The reactor was purged with hydrogen and pressurized to 500 psi. The reactor temperature was increased to 473 K using an external electrical heater and controlled with a type J thermocouple connected to a PID controller. After holding the temperature for the desired reaction time, the reactor was cooled to room temperature and depressurized. The reaction mixture was filtered to separate the liquid products from the wood residue and catalyst. The liquid phase was analyzed by GC (Shimadzu GC-2010 equipped with FID) and GC-MS (Shimadzu GCMS-QP2010S). The phenolic monomers (shown in Figure S.1) in the aqueous phase were extracted by contacting with 50 ml of diethyl ether (DEE) (Sigma Aldrich) and purified in a rotary evaporator.

Information on the phenolic monomers obtained from aqueous depolymerization of wood chips using Pd, Pt and Rh based catalysts are shown in Table S.2. These liquid mixtures were then contacted with water to extract the guaiacyl propanol and syringyl propanol to the aqueous phase to isolate propyl syringol and propyl guaiacol. The LDS used in this study was prepared according to the conditions of entry 1 in Table S.2, followed by extraction with DEE. After removal of DEE in a rotary evaporator, the organic phase was contacted with water to remove guaiacyl propanol and syringyl propanol. The remaining organic phase contained 20 wt% propyl guaiacol and 80 wt% propyl syringol. The boiling points of propyl guaiacol and propyl syringol are shown in Table S.1.

The phenylpropane monomers in lignin (i.e. $C_9$, $C_{10}$ and $C_{11}$) are connected to each other by $C_x$-O-$C_y$ (e.g. β-O-4, 4-O-5) and $C_x$-$C_y$ bonds (e.g. 5-5, β-5, β-1). Among the various lignin linkages, the β-O-4 linkage is the most dominant both in hardwood and softwood lignins, constituting about 60 and 50 percent of the total $C_x$ linkages respectively [1]. Also, the percentages of 5-5 linkages between $C_x$ monomers in hardwood and softwood are about 9 and 22%, respectively [2, 3].

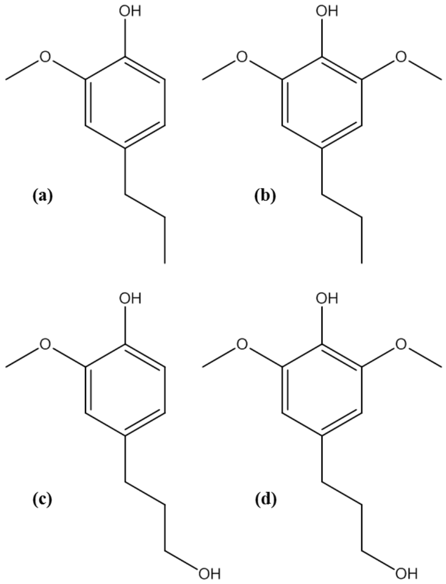

**Figure S.1.** Primary phenolic monomers obtained from catalytic hydrothermal depolymerization of lignin. a) propyl guaiacol, b) propyl syringol, c) guaiacyl propanol, d) syringyl propanol.

**Table S.1.** Boiling points of selected chemical species.

| Compound | Boiling Point (K) |
|---|---|
| Furfural | 435 |
| γ-Valerolactone | 481 |
| Levulinic Acid | 519 |
| Propyl Guaiacol | 537[a] |
| Propyl Syringol | 574[a] |

[a] Boiling point shown is a predicted value. Boiling point has been measured to be 401-403 K at 0.020 bar for propyl guaiacol and 388 K at 0.0005 bar for propyl syringol.[4, 5]

Hardwood lignin contains almost equal amounts of coniferyl and sinapyl alcohols, whereas softwood lignin is primarily made of coniferyl alcohol [2, 3]. The selective catalytic hydrogenolysis of $C_x$-O-$C_y$ linkages results in the formation of phenylpropane monomers and dimers and small quantities of higher oligomers [6]. Given the ratio between $C_x$-O-$C_y$ to $C_x$-$C_y$ linkages, it is possible to calculate the theoretical yields of monomers and dimers. For example, in case of a hardwood with 70% $C_x$-O-$C_y$ and 30% $C_x$-$C_y$ linkages, the maximum theoretical yields of monomers and dimers obtainable upon selective cleavage of $C_x$-O-$C_y$ bonds are 49 wt% and 29 wt% of the protolignin, respectively, where larger oligomers account for the balance.

**Table S.2.** Phenolic monomers [(a) propyl guaiacol, (b) propyl syringol, (c) guaiacyl propanol, (d) syringyl propanol] obtained from aqueous phase depolymerization of wood lignin. The boiling points of the mixtures were estimated based on the boiling points of their constituents. Pd, Pt and Rh refer to 10 wt% Pd/C, Pt black and 5 wt% Rh/C, respectively.

| Entry | Catalyst | Wood (g) | T (K) | Time (h) | Monomer selectivity (%) | | | | Boiling point (K) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | (a) | (b) | (c) | (d) | |
| 1 | Pd | 10 | 473 | 1 | 9.4 | 37.1 | 37.2 | 16.3 | 594 |
| 2 | Pd | 10 | 473 | 4 | 4.2 | 1.8 | 90.4 | 3.5 | 610 |
| 3 | Pt | 10 | 473 | 1 | 17.4 | 44.7 | 20.6 | 17.3 | 587 |
| 4 | Pt | 10 | 473 | 4 | 42.1 | 5.4 | 51.1 | 1.3 | 589 |
| 5 | Rh | 10 | 473 | 1 | 23.2 | 62.4 | 11.8 | 2.6 | 576 |
| 6 | Rh | 10 | 473 | 4 | 50.5 | 10.7 | 37.6 | 1.2 | 583 |

## 2. Liquid-Liquid Extractions

Liquid-liquid extractions of furfural (FuAL), furfuryl alcohol (FuOH), 5-hydroxymethylfurfural (HMF) and levulinic acid (LA) were carried out in batch systems starting with different concentrations (in the aqueous phase) using propyl guaiacol (PG) and lignin derived solvent (LDS) in a 1:1 mass ratio with the aqueous phase at room temperature. In addition to the extractions demonstrated in Table 1, equimolar amounts of levulinic and formic acids in 0.5 M sulfuric acid were prepared to represent the products of cellulose deconstruction. The levulinic and formic acids were then extracted from this aqueous mixture using PG or LDS with a 1:1 mass ratio. These results along with the extraction results of GVL are shown in Table S.3.

**Table S.3.** Extraction of biomass-derived compounds from an aqueous phase containing 0.5 M $H_2SO_4$ using 1:1 solvent mass ratio at 298 K.

| Entry | Solvent | Compound | Concentration (M) | % Mole in Organic Phase |
|---|---|---|---|---|
| 1 | PG | LA/FA | 0.7/0.7 | 41/7±1 |
| 2 | PG | LA/FA | 2.0/2.0 | 42/9±2 |
| 3 | PG | GVL | 0.7 | 86±3 |
| 4 | PG | GVL | 2.0 | 91±2 |
| 5 | LDS | LA/FA | 0.7/0.7 | 40/11±1 |
| 6 | LDS | LA/FA | 2.0/2.0 | 39/12±2 |
| 7 | LDS | GVL | 0.7 | 72±2 |
| 8 | LDS | GVL | 2.0 | 74±2 |

## 3. Biphasic Reactions

Glucose, xylose, HMF and FuOH were obtained from Sigma Aldrich and used directly. The biphasic reactions of these components (i.e., dehydration of glucose and xylose, hydrolysis of HMF and FuOH) were carried out in batch systems utilizing mineral acids as catalysts in the aqueous phase. Table S.4 lists the reaction conditions for each of the cases. The experiments were carried out in 10 mL glass reactors kept at constant temperature in a pre-heated oil bath using magnetic stirring (1200 rpm). To end the reactions, the glass reactors were taken out from the oil bath and cooled in an ethylene glycol bath kept at freezing temperature with dry ice. The reactor was then placed in a centrifuge for 2 min at 3000 rpm to accelerate phase separation. The two phases were then separated and analyzed to quantify reactants/products using GC (Shimadzu GC 2060, equipped with a DB-5 column (Restek) and an FID) and HPLC (Waters 2695 instrument equipped with a 996 PDA UV detector and Zorbax SB-C18 reverse phase column (Agilent), operating at a temperature of 308 K using an acetonitrile:water gradient at a flow rate of 1 ml min$^{-1}$) for organic phase samples and HPLC (Waters 2695 system with a Bio-Rad Aminex HPX-

87H column with a differential refractometer (Waters 410) and a photodiode array detector (Waters 996)) for aqueous phase samples.

**Table S.4.** Reaction conditions for biphasic reaction systems. Solvent to aqueous phase ratio is given by weight.

| Biphasic System | Temperature (K) | Time (min) | Aqueous Phase Composition | Organic Phase Composition | Organic:Aqueous (mass ratio) |
|---|---|---|---|---|---|
| Glucose to HMF | 443 | 35 | 5 wt% glucose, 0.005 M $AlCl_3$, 0.1 M HCl in saturated NaCl solution | PG/LDS | 2:1 |
| HMF to Levulinic Acid | 423 | 30 | 1 M HCl in saturated NaCl solution | 1 wt% HMF in PG/LDS | 3:1 |
| Xylose to Furfural | 443 | 20 | 1.5 wt% xylose, 0.1 M HCl in saturated NaCl solution | PG/LDS | 1:6.7 |
| Furfuryl Alcohol to Levulinic Acid | 398 | 45 | 1 M $H_2SO_4$ | 1 wt% Furfuryl Alcohol in PG/LDS | 2:1 |

## 4. Selective Hydrogenation of LA to GVL

Levulinic acid, formic acid and 0.5 M $H_2SO_4$ were obtained from Sigma Aldrich. The selective hydrogenation of levulinic acid to GVL was carried out in a down-flow fixed bed reactor over 5 wt% Ru/C (Sigma-Aldrich). The $RuSn_4/C$ samples were prepared by incipient wetness impregnation of 5 wt% Ru/C (Sigma-Aldrich) with an aqueous solution of $SnCl_2 \cdot 2H_2O$, followed by heating in air at 353 K for 2 h. The feed was prepared by extracting LA and FA from an aqueous solution (2 M LA, 2 M FA, 0.5 M $H_2SO_4$) with PG (as shown in Table S.3, entry 2). The catalyst was loaded in a stainless steel tube with ¼" OD and 10 cm length. In a typical experiment, 0.1 g of catalyst was mixed with crushed silica granules to fill the reactor volume. Two plugs of quartz wool were utilized to keep the catalyst bed in place. The reactor was heated with an aluminum block that was heated externally by a heating tape and wrapped with fiber glass insulation. Type-K thermocouples (Omega) were used to measure the reaction temperature, which was controlled by a PID controller (Love controls) connected to a variable transformer (Tesco). Mass flow controllers (Brooks 5850E) were used to regulate the flow of $H_2$ during the experiments. A back-pressure regulator (GO model BP-60) was used to control the total pressure, which was measured by two gauges at the entrance and the exit of the bed. A gas-liquid separator at room temperature was used to collect the liquid effluent phase for analysis. Prior to reactions in fixed bed reactors, catalyst samples were reduced in-situ for 3 h at 723 K (1 K $min^{-1}$). After the reduction was completed, the temperature and pressure (13.8 bars of $H_2$) were adjusted, and the reactants were introduced into the reactor using a Syringe pump (Harvard Apparatus PHD 2000). The weight hourly space velocity (WHSV) was calculated for experiments using the mass flow rate of levulinic acid into the reactor and the mass of the catalyst used. The liquid effluent was separated from the hydrogen in a separator at room temperature and analyzed with Shimadzu GC 2060, equipped with a DB-5 column (Restek) and an FID and a Shimadzu 2060 GC/MS with a NIST library of spectra.

Figure S.2 shows reaction pathways involved in the production of GVL in the presence of alkylphenol solvents. Levulinic acid can be hydrogenated over Ru/C to form GVL. In a subsequent step, GVL can undergo hydrogenation to form methyltetrahydrofuran (MTHF). Although MTHF has a high energy density and can be blended with gasoline to high extents, production of MTHF lies outside of the strategy outlined in this work. Furthermore, hydrogenation of the alkylphenol solvent results in the removal of oxygen functional groups (e.g., methoxy and hydroxyl) and reduction of the benzene ring.

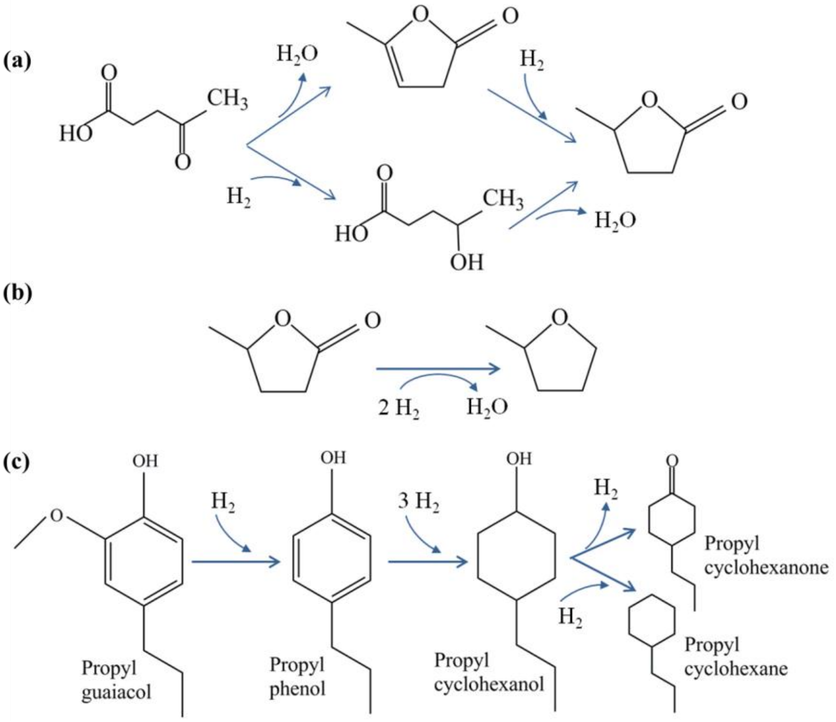

**Figure S.2.** Reactions for conversion of (a) LA to GVL, (b) GVL to MTHF and (c) hydrogenation of PG.

## References

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