

Supplemental information for:

Lignin monomer production integrated into the γ -valerolactone sugar platform

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Experimental

Biomass reaction and lignin recovery

Corn stover was obtained from the Great Lakes Bioenergy Research Center (GLBRC). Maple wood was obtained from Mascoma (Hanover, NH). Biomass was treated in batch mode with 200 g of dried biomass (5 wt% moisture) along with 800 g of 80 wt% γ -valerolactone (GVL, Sigma) and 20 wt% H₂O and either 150 mM (for corn stover) or 100 mM (Maple wood) H₂SO₄, all introduced into a 2 L high-pressure reactor (Parr) equipped with a custom high-solids impeller.³³ The reactor was heated to 393 K over ~30 min, and then held at this temperature for another 30 min. The reactor was then cooled by flowing water through the external heating jacket. Samples of the slurry were taken for analysis. The remainder was filtered and washed with hot GVL (350-370 K). The resulting filtrate was diluted 5 times with water to precipitate water-insoluble solids. The resulting aqueous solution was centrifuged, the supernatant discarded, and the precipitate re-

diluted with an equivalent amount of DI water. This operation was repeated five times to wash the insoluble solids. Following the final centrifugation and discarding of the supernatant, the wet solids were dried in a vacuum oven at 320 K for 3 days.

NMR characterization of lignin

Corn lignin from the GVL process (~30 mg) was dissolved in DMSO- d_6 /pyridine- d_5 (4:1, v/v, 600 μ L) and transferred into NMR sample tubes. Corn EL, described previously,²² was similarly prepared, and the whole corn stover material, after fine milling, was subjected to gel-NMR as previously described.²⁰⁻²² NMR spectra were acquired on a Bruker Biospin AVANCE 700 MHz spectrometer fitted with a cryogenically-cooled 5-mm TXI gradient probe with inverse geometry (proton coils closest to the sample). The central DMSO solvent peak was used as internal reference (δ_C , 49.5; δ_H , 3.49 ppm). Adiabatic HSQC experiments (hsqcetgpsisp2.2) were carried out using the parameters described previously.^{21,22} Processing used typical matched Gaussian apodization in F2 (LB = -0.5, GB = 0.001) and squared cosine-bell apodization and one level of linear prediction (32 coefficients) in F1. Volume integration of contours in HSQC spectra (processed using no linear prediction) used Bruker's TopSpin 3.1 (Mac) software with no correction factors; i.e., the data represent volume integrals only; endgroups (such as *p*-coumarate and triclin) are severely over-estimated by these methods due to their relaxation rate properties compared to the internal units of a chain. For quantitation of lignin aromatic distributions, only the carbon/proton-2 correlations from G and G' units and the carbon/proton-2/6 correlations from S and S' units were used, and the G and G' integrals were logically doubled; other aromatic integrals are reported relative to the total lignin aromatics (G + G' + S + S' = 100).

Catalyst preparation

Commercial catalysts Ru/C (5 wt% on carbon), Pt/C (10 wt% on carbon), Rh/C (5 wt% on carbon) and Pd/C (10wt% on carbon) were purchased from Sigma-Aldrich. A bimetallic Ru-Re/C catalyst was prepared by incipient wetness impregnation of the dried unreduced commercial Ru/C catalyst with an aqueous solution of HReO₄ (perrhenic acid, Sigma Aldrich). The concentration of HReO₄ was calculated to achieve a Ru-Re atomic ratio of 1:1. A bimetallic catalyst Rh-Re/C was prepared as previously described.²⁸ Briefly, the catalyst was prepared by wetness impregnation of Vulcan XC-72 carbon with aqueous solutions of RhCl₃ (Mitsubishi chemicals) and HReO₄ (perrhenic acid, Sigma Aldrich). In between the subsequent impregnations, the catalyst was dried in an oven at 383 K for 6 h. Precursor concentrations for both impregnations were calculated to have an Rh loading of 5 wt% with respect to the support, and a Rh-Re atomic ratio of 1:1. After preparation, both bimetallic catalysts were dried overnight in air using an oven at 383 K. All catalysts, both prepared and purchased, were reduced prior to use in flowing H₂ and passivated with flowing 2% O₂ in Argon. Reduction was conducted in a tube furnace connected to a variable power supply and PID temperature controller with a K-type thermocouple (Omega). A temperature-controlled program was used, which consisted of a 5 h linear temperature ramp to 723 K followed by a 2 h hold at that temperature before a cool-down.

Lignin upgrading

In a typical experiment, 3 g of dried lignin was dissolved in 24 g of THF and 3 g of 85% H_3PO_4 in water. In cases where other acids or no acid was used, these 3 g were replaced by 3 g of the corresponding aqueous solution. This mixture was then added to a 50 mL high-pressure reactor (Parr) along with 1.5 g of catalyst. The reactor was stirred with a magnetic stir bar and heated with high-temperature heating tape (Omega) connected to a variable power supply controlled by a PID temperature controller (Omega) with a K-type thermocouple that measured the reaction temperature through a thermowell in the reactor. Once closed, the reactor was purged 3 times and then pressurized with 500 psi (3.45 MPa) of hydrogen. The reactor was heated to 423 K with a 30 min temperature ramp and then held at that temperature for 4 h before being cooled with an external flow of compressed air. Samples of the resulting liquid were taken for analysis and the remaining liquid was transferred to a rotary evaporator (Buchi) to remove the THF. The remaining mixture was transferred back to the 50 mL reactor, and a quantity of heptane corresponding to the amount of THF removed was added to the reactor. An amount of fresh catalyst corresponding to 5 wt% of the total liquid was added as well. The reactor was once again purged 3 times, and then pressurized with 500 psi (3.45 MPa) of hydrogen. The reactor was heated to 523 K with a 30 min temperature ramp, and then held at that temperature for 4 h before being cooled with an external flow of compressed air. After the reaction, the heptane phase was sampled for analysis.

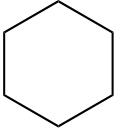
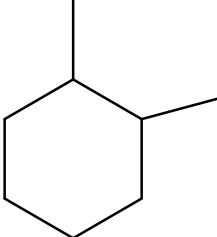
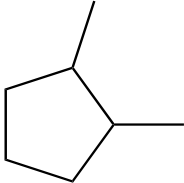
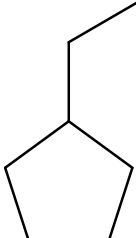
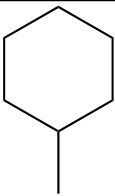
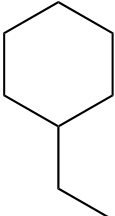
In cases where native lignin (i.e. whole corn stover) was treated, 1.5 g of corn stover was mixed with 24 g of THF, 0.25 g of H_3PO_4 of 85% H_3PO_4 in water and 0.25 g of catalyst in the 50 mL high-pressure reactor (Parr) to form a 5 wt% biomass solution. The amounts of acid and supported catalyst were reduced to keep the acid and metal catalyst to lignin ratios constant. The remaining treatment was performed as described above.

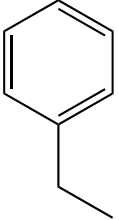
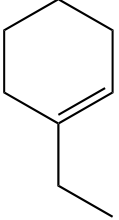
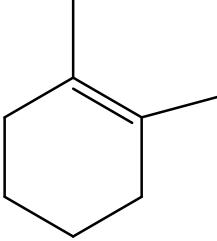
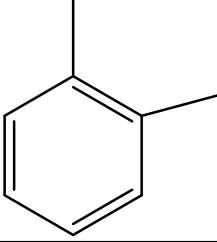
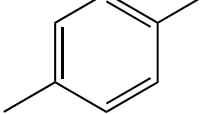
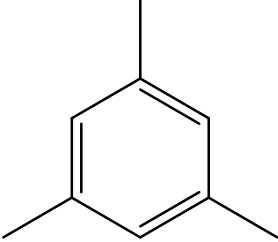
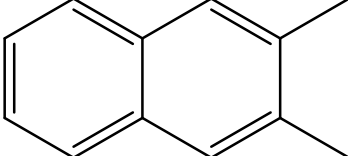
Product analysis

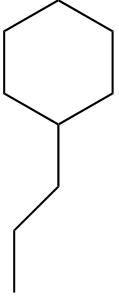
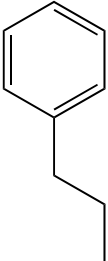
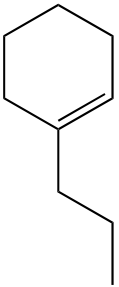
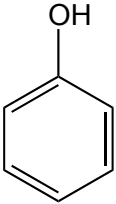
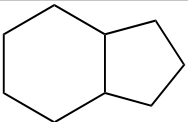
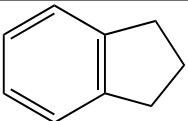
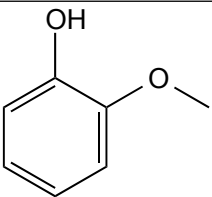
The slurry produced by batch treatment of biomass was diluted 10 times with water and analyzed for glucose, xylose, levulinic acid, GVL, 5-HMF and furfural using a Waters 2695 HPLC system with an Aminex HPX-87H column (Bio-Rad) and a 5 mM H_2SO_4 aqueous mobile phase flowing at 0.6 mL/min. Concentrations of sugars were measured using the RI detector, whereas concentrations of 5-HMF and furfural were measured using the PDA detector at 230 nm. Oligomers were measured according to the procedure published by the National Renewable Energy Laboratory,³⁴ using unstirred 10 mL thick-walled glass reactors (Grace-Davison) placed in an oil bath set to 393 K for heating. Lignin upgrading products were identified and quantified by injecting undiluted samples (both in THF and/or heptane) into a GC-MS (GCMS-QP2010) and GC-FID (GC-2010, Shimadzu), respectively. All components were identified by spectra available in the NIST 05 spectral library except for three syringyl derivatives (methyl-, ethyl- and propyl-syringol) which were identified by comparison with previously published MS-spectra.³⁵ The various components were quantified using GC-FID by using external propylguaiacol and propyl cyclohexane standards. The FID weight-based sensitivities (area/g) of propyl-

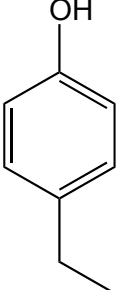
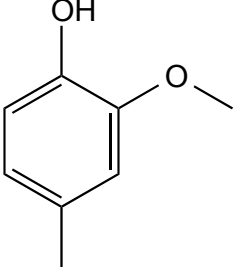
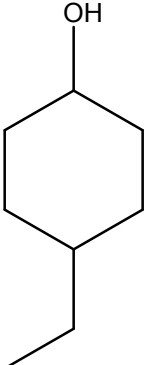
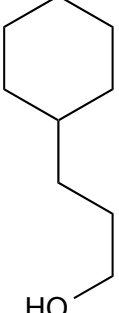
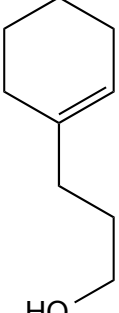
guaiacol and propyl cyclohexane were within 8% of each other. Based on this result, deoxygenated compounds (alkanes, olefins and aromatic compounds) were assumed to have the same sensitivity as propyl cyclohexane, syringyl and guaiacyl derivatives were assumed to have the same sensitivity as propylguaiacol, and all other compounds were assumed to have a sensitivity corresponding to the average of the two (see details in Table S1). We contend that this ensures that the error in our calculation of the total carbon yield that will be below 5%.

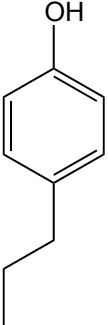
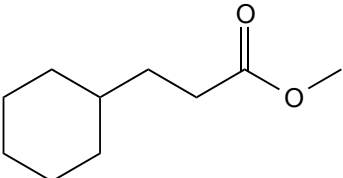
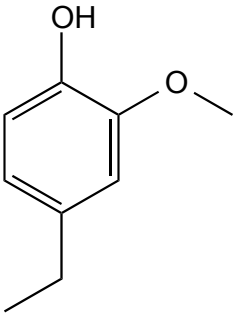
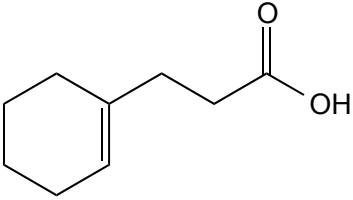
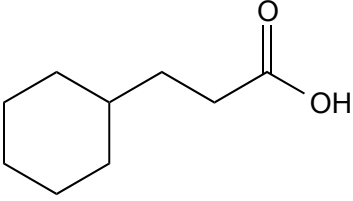
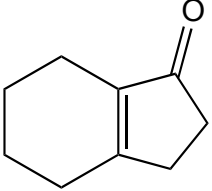
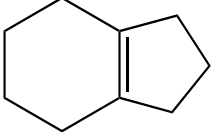
Table S1 Identified (but not unambiguously authenticated) lignin products, the standard used for their quantification by GC-FID, and their classification by category used for total yield breakdown (see Fig. 2 and S1).

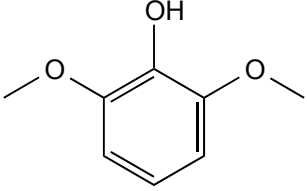
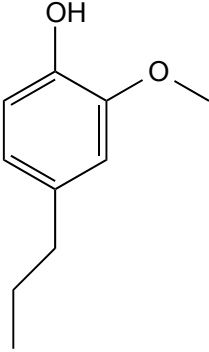
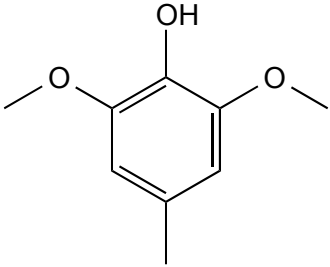
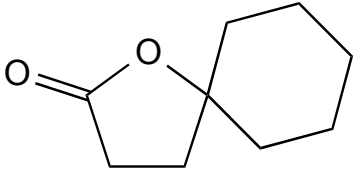
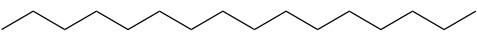
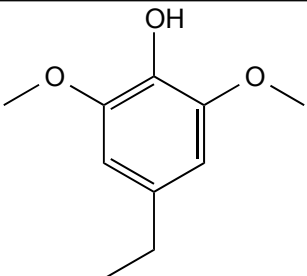
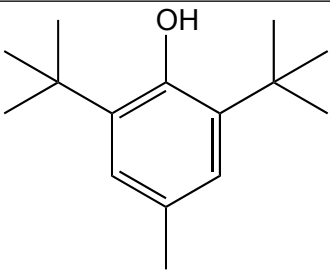
Molecule	Name	Standard used for GC-FID quantification	Category
	Cyclohexane	Propyl-cyclohexane	Alkanes
	Dimethyl cyclohexane	Propyl-cyclohexane	Alkanes
	Dimethyl cyclopentane	Propyl-cyclohexane	Alkanes
	Ethyl cyclopentane	Propyl-cyclohexane	Alkanes
	Methyl-cyclohexane	Propyl-cyclohexane	Alkanes
	Ethyl cyclohexane	Propyl-cyclohexane	Alkanes

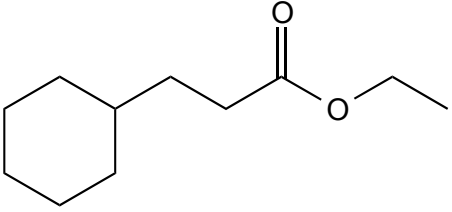
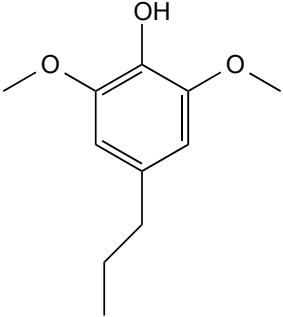
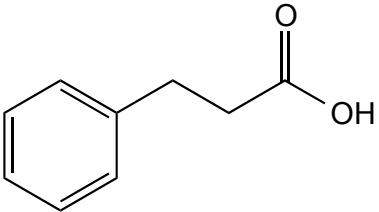
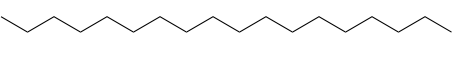
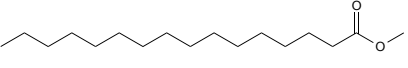
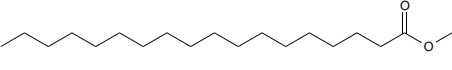
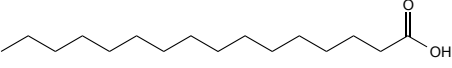
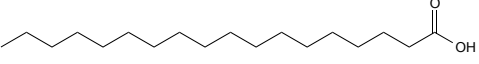
	Ethylbenzene	Propyl-cyclohexane	Other
	Ethylcyclohexene	Propyl-cyclohexane	Olefins
	Dimethylcyclohexene	Propyl-cyclohexane	Olefins
	o-Xylene	Propyl-cyclohexane	Other
	p-Xylene	Propyl-cyclohexane	Other
	Trimethyl Benzene	Propyl-cyclohexane	Other
	Dimethylnaphthalene	Propyl-cyclohexane	Other

	Propyl- cyclohexane	Propyl- cyclohexane	Alkanes
	Propylbenzene (Phenylpropane)	Propyl- cyclohexane	Other
	Propyl- cyclohexene	Propyl- cyclohexane	Olefins
	Phenol	Average	Alcohols
	Hexahydroindane	Propyl- cyclohexane	Alkanes
	Indane	Propyl- cyclohexane	Other
	Guaiacol	Propyl- guaiacol	Guaiacyl-R

	Ethylphenol	Average	Alcohols
	Methylguaiacol	Propyl-guaiacol	Guaiacyl-R
	4-Ethyl cyclohexanol	Average	Alcohols
	Cyclohexane propanol	Average	Alcohols
	Propyl cyclohexene	Average	Alcohols

	4-Propylphenol	Average	Alcohols
	Cyclohexane propanoic acid methyl ester	Average	Cyclohexane propanoic acid methyl ester
	Ethylguaiacol	Propyl-guaiacol	Guaiacyl-R
	Cyclohexene propanoic acid	Average	Unsaturated cyclohexane propanoic acids
	Cyclohexane propanoic acid	Average	Cyclohexane propanoic acid
	2,3,4,5,6,7-hexahydro-inden-1-one	Average	2,3,4,5,6,7-hexahydro inden-1-one
	hexahydroindene	Propyl-cyclohexane	Olefins

	Syringol	Propyl-guaiacol	Syringyl-R
	Propylguaiacol	Propyl-guaiacol	Guaiacyl-R
	Methylsyringol	Propyl-guaiacol	Syringyl-R
	1-Oxaspiro(4,5)decan-2-one	Average	1-Oxaspiro(4,5)decan-2-one
	Hexadecane	Propyl-cyclohexane	Alkanes
	Ethylsyringol	Propyl-guaiacol	Syringyl-R
	Butylated hydroxyl-toluene	Average	Other

	Cyclohexane propanoic acid ethyl ester	Average	Other
	Propylsyringol	Propyl- guaiacol	Syringyl-R
	Phenylpropanoic acid	Average	Unsaturated cyclohexane propanoic acids
	Octadecane	Propyl cyclohexane	Alkane
	Hexadecanoic acid methyl ester	Average	FAMEs
	Octadecanoic acid methyl ester	Average	FAMEs
	Hexadecanoic acid	Average	Fatty acid
	Octadecanoic acid	Average	Fatty acid

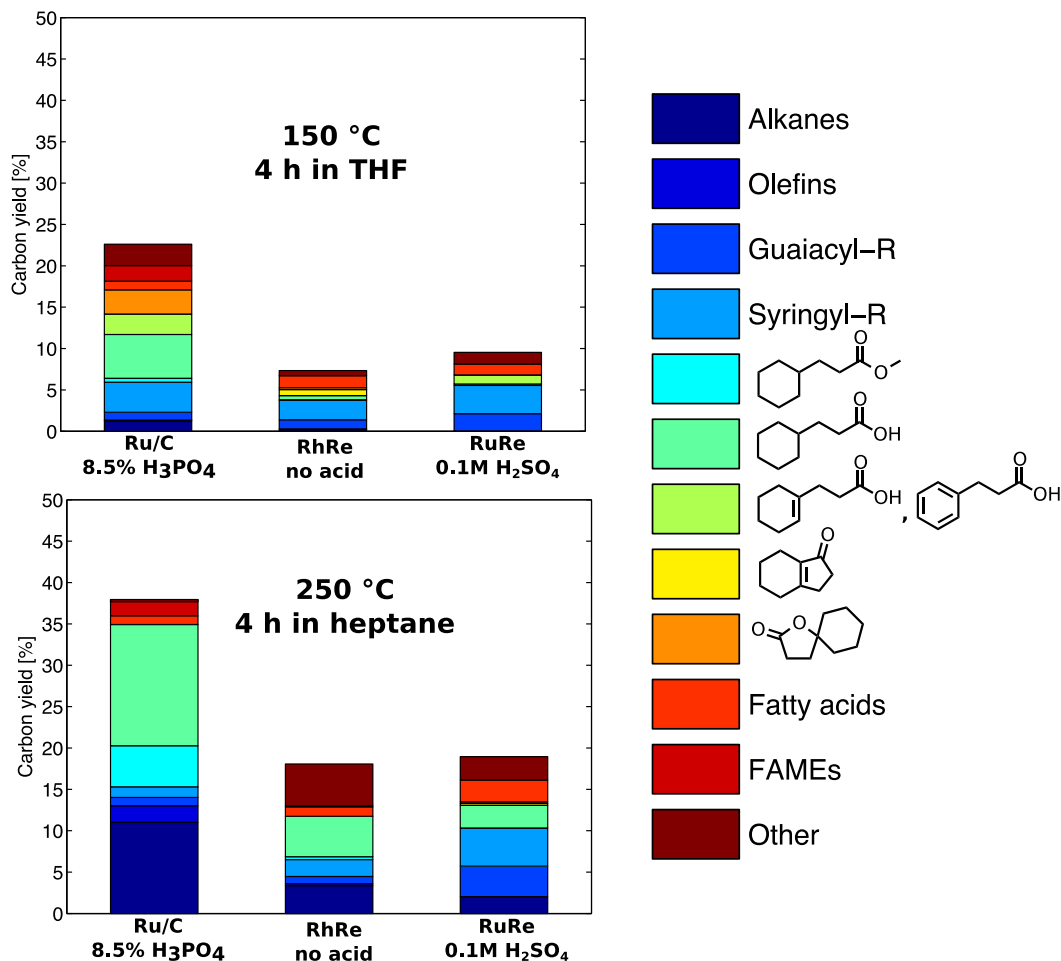


Fig. S1 Effect of using bimetallic alloys as catalysts. Guaiacyl- and Syringyl-R designates guaiacyl and syringyl monomers with an R = methyl, ethyl or propyl. FAMEs stands for fatty acid methyl ester.