Supporting Information

Oxidative Catalytic Fractionation of Lignocellulosic Biomass Under Non-Alkaline Conditions

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1. General Considerations

All reagents were purchased and used as received without further purification unless otherwise noted. Acetone, acetonitrile, 1,4-dioxane, dimethyl carbonate, ethyl acetate, aniline, ammonium peroxydisulfate, $Co(OAc)_2 \cdot 4H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_2 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, Co_3O_4, Fe_2O_3, MnO, CuO, Pd/C (5 wt% metal loading), Pt/C (5 wt% metal loading), Ru/C (5 wt% metal loading), and DARCO KB-G active charcoal were purchased from Sigma Aldrich. Methanol was purchased from Fisher Scientific. Ethanol was purchased from Pharmco-Aaper. Phenanthroline was purchased from Oakwood Chemical. Carbon black (VXC72R) was purchased from Cabot Chemical. NE-19 (Populus nigra charkowiensis × P. nigra caudina) poplar was obtained from the Great Lakes Bionenergy Research Center in Madison, WI. This strain of poplar has been previously characterized and the yield of monomers from thioacidolysis was found to be 41%.[1] The poplar was ground to a particle size of <2 mm and washed in a Soxhlet extractor with subsequent 24 h ethanol, toluene, and 1,4 dioxane washes. Wiley milled (1 mm) lodgepole pine (Pinus contorta) samples were obtained from the USDA Forest Products Laboratory in Madison, WI. The miscanthus (miscanthus giganteus) sample obtained from the Great Lakes Bioenergy Research Center in Madison, WI, and was ground to a particle size of <5 mm.

Solid state NMR (ssNMR) spectra were obtained with Bruker Avance-500 MHz NMR spectrometer with a 1.2 mm magic-angle spinning ssNMR probe and chemical shifts are reported in parts per million (ppm). 2D NMR spectra were obtained with a Bruker Avance 600 MHz NMR spectrometer equipped with a TCI-F cryoprobe and chemical shifts are reported in parts per million (ppm).

Powder X-ray diffractograms (pXRD) were obtained using a Bruker D8 Advance diffractometer equipped with a Cu Kα conventional sealed X-ray tube and a Lynxeye detector.

HPLC/UV analysis on lignin-derived monomers and oligomers was obtained on a Shimadzu Prominence HPLC system equipped with a SPD-M20A diode array detector and a Restek Ultra C18 column (150 mm x 4.6 mm ID – 3 micron particle size) at 35 °C. Solvent A was 0.1% formic acid in Millipure water and solvent B was HPLC grade acetonitrile for the HPLC separations (flow rate 2 mL/min). Monomer yields were calculated based on a 1,4-dimethoxybenzene internal standard. The gradient of solvent B (acetonitrile) is shown in Figure S1. Semipreparative scale isolations of the lignin oligomers was done using a Restek Ultra C18 column (100 mm x 21.2 mm ID – 5 micron particle size) at 35 °C (flowrate 8 mL/min). The gradient profile for collecting the oligomers is shown in Figure S2.

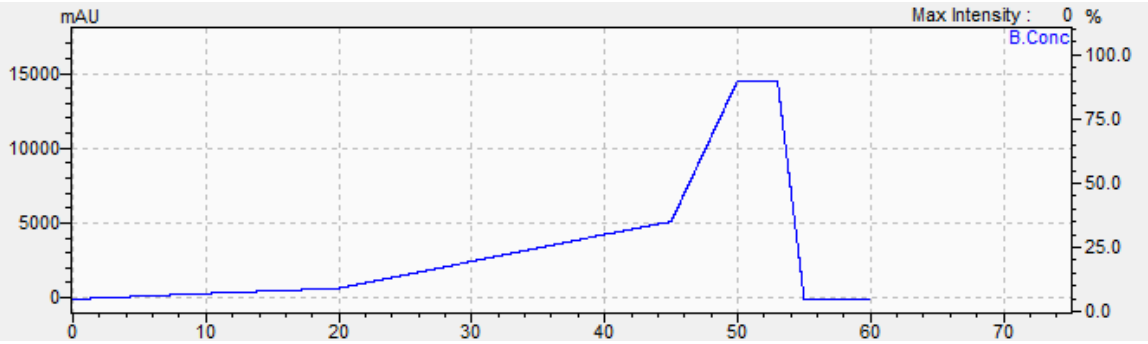

Figure S1. HPLC program showing the gradient of acetonitrile percentage (B.Conc) used to determine monomer yields. Solvent A was 0.1% formic acid in water.

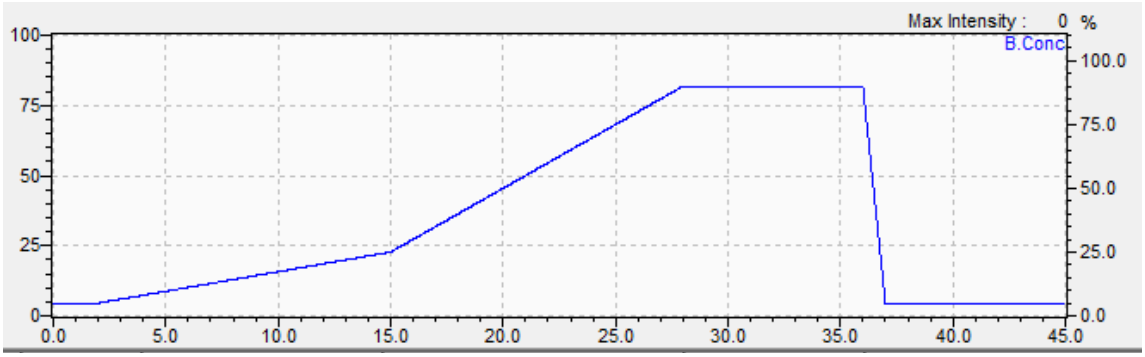

Figure S2. HPLC program showing the gradient of acetonitrile percentage (B.Conc) used to separate the lignin-derived oligomers. Solvent A was 0.1 formic acid in water.

Xylose and glucose were quantified by HPLC analysis using an Agilent 1260 Infinity HPLC system with an RID detector equipped with a Biorad Aminex HPX-87H column (300x7.8 mm) and Cation-H guard column. The mobile phase was 0.02 N H_2SO_4, with a flow rate of 0.500 mL/min and a column temperature of 50 °C. Reference standards were used to quantify the glucose and xylose concentrations.

Gel permeation chromatography (GPC) characterization of lignin-derived oligomers was conducted using a PSS PolarSil Linear S column with solution of 0.1 M lithium bromide (LiBr) in dimethyl formamide (DMF) as the mobile phase (flow rate of 0.3 mL/min). The sample concentrations were 1 mg/ml (dissolved in same solution as mobile phase) and the samples were sonicated for 1 h and filtered through a 0.2 um PTFE membrane prior to analysis.

A scaled down version of NREL/TP-510-42618[2] was used to quantify the glucan, xylan, and lignin amounts in the NE-19 poplar, as well as the lignin quantities in the pine, and miscanthus samples.

2. Experimental

M–N–C catalyst preparation.

Co–PANI–C and Fe–PANI–C catalysts were prepared according to a previous published report.[3] In specific, 2 g of carbon support (carbon black, either VXC72R from Cabot Chemical or DARCO KB-G activated carbon from Sigma Aldrich) was first treated in 45 mL concentrated HNO_3 solution at room temperature for 48 h to remove surface impurities. The carbon support was then filtered under vacuum followed by drying in a vacuum oven overnight. Aniline (2.0 mL) was then added to 0.4 g of acid-treated carbon support in 15 mL 0.5 N HCl solution. The suspension was stirred in an ice bath for ten minutes before the metal precursor and the oxidant (ammonium peroxydisulfate, APS, 4.4 g) were added. $Co(NO_3)_2{\cdot}6H_2O$ (1.024 g) and $FeCl_3{\cdot}6H_2O$ (0.570 g added in two portions) were used as precursors for Co–PANI–C and Fe–PANI–C catalysts, respectively. After stirring for 24 h, the suspension was filtered and the recovered solid was dried under vacuum. A first pyrolysis was performed at 850 ºC for 1 h in an inert nitrogen atmosphere flowing at a rate of 100 mL/min in a vertical Carbolite Gero MTF Model 12/38 tube furnace with a 3216 temperature controller. This "heat-treated" sample was then stirred in 0.5 M H_2SO_4 at 80 ºC for 8 h to remove any unstable and inactive species from the catalyst, and thoroughly washed with DI water. The acid treated sample was then filtered and dried before a second pyrolysis process under a nitrogen atmosphere at 850 ºC for 3 h.

The Co–phen–C catalyst was prepared in a similar previously reported method.[4] $Co(OAc_2){\cdot}4H_2O$ (508 mg), 720 mg of phenanthroline, and 2.7 g of acid-treated carbon support (same treatment as above) was added to 50 mL of ethanol. After stirring for 24 h at room temperature, the suspension was filtered and the

recovered solid was vacuum-dried. The sample was pyrolyzed at 800 ºC for 2 h in under inert nitrogen atmosphere.

Description of heterogeneous catalysts used in screening studies.
All catalysts were used at 10 wt% with respect to the biomass. The M–N–C catalysts feature metal loadings of 2.8 wt% Co (Co–phen–C), 3.1 wt% Co (Co–PANI–C), and 4.0 wt% Fe (Fe–PANI–C), based on ICP-OES analysis. The commercial noble metal catalysts feature 5 wt% metal loading. To achieve comparable composition for the metal oxide catalysts, the metal oxides (Co_3O_4, Fe_2O_3, MnO, and CuO) were mixed with carbon support as a diluent (carbon black VXC72R from Cabot chemical, treated with nitric acid for 48 h to remove surface impurities) to achieve a 5% metal loading in the mixture.

Oxidative depolymerization of lignin in raw biomass
In a typical lignin depolymerization reaction of poplar, 0.1 g washed NE-19 poplar species, 10 wt% of heterogeneous catalyst, and 20 mL acetone were added to a Hastelloy C-276-steel Parr reactor. To measure the temperature in the reactor a K-type thermocouple was placed in a thermocouple well positioned in the middle of the reaction vessel. To facilitate good separation of catalyst and substrate, the heterogeneous catalyst was first loaded into a microporous cage (40 micron) which could be attached to the vessel head. The catalyst cage has the functionality to allow solvent as well as soluble solute to pass through and access the catalyst, while at the same time keep biomass substrate separate from the catalyst. The pressure vessels were sealed. The system was first purged with 6% O_2 balanced by N_2 for 3 times while stirring at 800 RPM with a magnetic stir bar, and then pressurized with 35 bar 6% O_2. The mixture was then heated at 190 ºC for 12 h. After 12 h, the Parr vessel would stop heating and return to room temperature. The reaction mixture was filtered to separate the liquid phase containing the aromatic products from the solid biomass residue. The residue was washed with additional acetone to remove the remaining phenolic products from the surface, and the liquid wash was combined with the filtrate. The combined liquid phase was condensed by rotary evaporation, diluted in a volumetric flask (5 mL), and then analyzed by HPLC/UV. The solid biomass residue was left to dry thoroughly under ambient conditions.

Note: *Special caution should be used when handling reactions performed in organic solvents at elevated temperature under oxygen atmosphere.*[5] *Oxygen diluted with an inert gas, such as N_2 or Ar, should be used to stay below the limiting oxygen concentration (LOC) of the organic solvent to prevent combustion.*

Quantification of lignin-, glucan-, and xylan-derived products
To fully characterize the reaction products post-OCF treatment, both the solid residue and the liquid phase were analyzed (see Figure 5 in the manuscript body for Sankey diagram containing results).

Solid residue: The solid residue obtained after filtration was air dried and weighed. The mass of the residue was 55.2 mg. A scaled down version of NREL/TP-510-42618 was used to quantify the glucans and xylans present in the solid residue. After acid hydrolysis, HPLC analysis showed that the residue composition consisted of 71.5% glucose and 8.1% xylose. These results correlate to 39.5 mg of glucans and 4.5 mg of xylans in the solid residue, accounting for 83% and 32% of the material from the raw biomass, respectively. Lignin was spectroscopically quantified following literature precedent.[6] UV-VIS analysis showed 11.7% of the residual solid was lignin corresponding to 6.3 mg of lignin accounting for 29.9% of the original lignin in raw biomass.

Liquid fraction: After solvent removal, the dried sample was dissolved in ethyl acetate and extracted with water. The aqueous phase was separated and dried. The solids from the aqueous extraction were hydrolyzed with 72 wt% sulfuric acid at 30 °C for 1 h, diluted to a sulfuric acid concentration of 4%, and heated at 121 °C for 1 h. The resultant solution was analyzed by HPLC to quantify the xylose and glucose. The results indicated that 1.3 mg of xylose and 0.8 mg glucose were present in this aqueous

fraction, corresponding to 9.4% and 1.7% of the xylans and glucans in the raw biomass, respectively. The ethyl acetate layer was analyzed by HPLC to quantify the monomers, and the results correspond to 3.2 mg of monomers, correlating to a 15% yield relative to the lignin in the raw biomass. The oligomers were separated using prep-HPLC and dried. The mass of oligomers was 12.1 mg, corresponding to 56% of the mass of the original lignin.

Overall, 101% of the lignin, 85% of the glucans, and 41% of the xylans were accounted for after OCF processing of raw poplar biomass.

Solvent recovery.
Solvent recovery was assessed after performing oxidative catalytic fraction in a 300 mL Hastelloy C-276-steel Parr reactor with 0.75g biomass, 0.075g of Co–PANI–C, 117g of acetone. The reactor was otherwise run as described above. After the reaction, ¼ inch tubing was fitted to the outlet and affixed to a round bottom chilled in a dry ice and acetone bath. 108 g of acetone was distilled from the reactor into the chilled collection flask corresponding to 92% recovery of the solvent. The remaining material in the reactor contained an unquantified amount of water, phorone, and isophorone.

3. Supplementary Tables and Figures

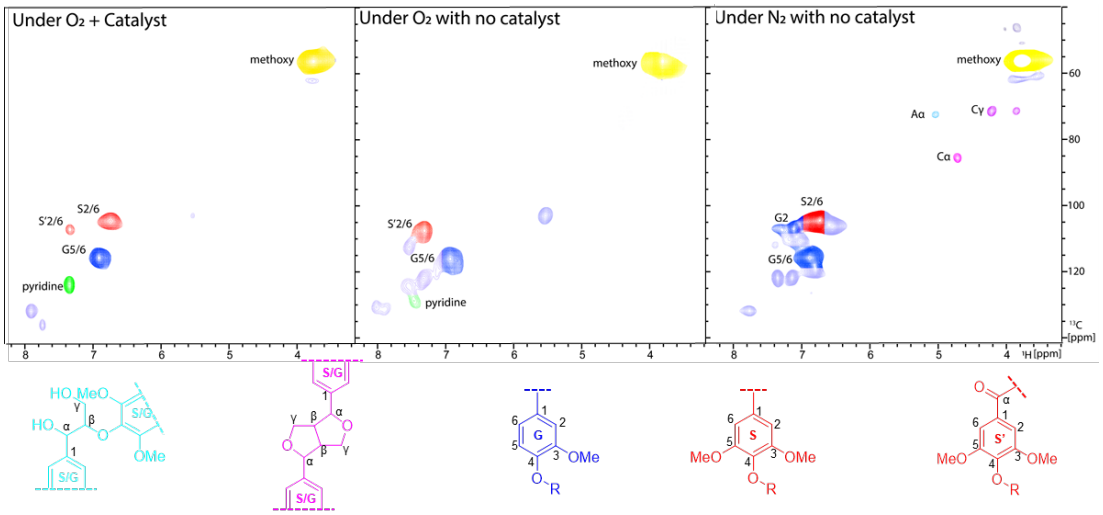

Figure S3. 2D HSQC NMR of acetone soluble fraction after oxidative catalytic fractionation. Conditions: 0.1 g poplar, 10 wt% Co–PANI–C catalyst, 20 mL of HPLC grade acetone, 190 ºC, 12 h, 35 bar 6% O_2 balance N_2 or N_2. Higher MW fraction isolated from monomer components using semi-preparative HPLC.

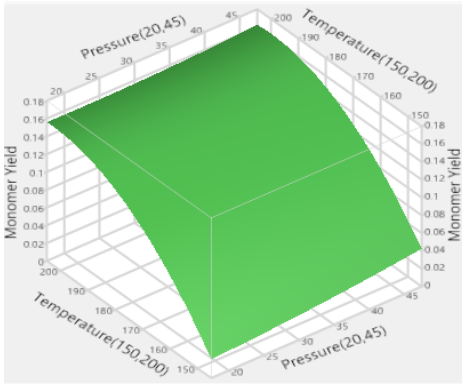

Figure S4. Design of Experiments (DOE) model used to optimize temperature and pressure. Reaction conditions. 0.1 g poplar biomass, 10 wt% catalyst, 20 mL acetone, 12 h, pressurized with 6% O_2 balance

nitrogen mixture. Model method REML with a Standard Least Squares personality. Model generated using JMP Pro

Table S1. Monomer yields from oxidative catalytic fractionation of raw poplar biomass using different solvents[a]

	Yields of major phenolic products (weight %)					
Solvent	PHBA[b]	Vanillic acid	Syringic acid	Vanillin	Syringaldehyde	Total (wt%)
Acetone	4.3	4.2	3.5	1.3	1.7	15.0
Ethyl acetate	2.9	1.0	1.1	0.7	1.3	2.9
Acetonitrile	3.0	4.0	2.4	1.6	2.6	13.6
1,4-Dioxane	1.6	0.0	0.0	0.2	0.3	2.1
H_2O	0.1	0.7	0.2	1.5	2.7	5.7

[a] Reaction conditions: 100 mg poplar, 10 wt% Co–PANI–C catalyst, 20 mL solvent, 190 ºC, 12 h, 35 bar 6% O_2. [b] PHBA = *p*-hydroxybenzoic acid

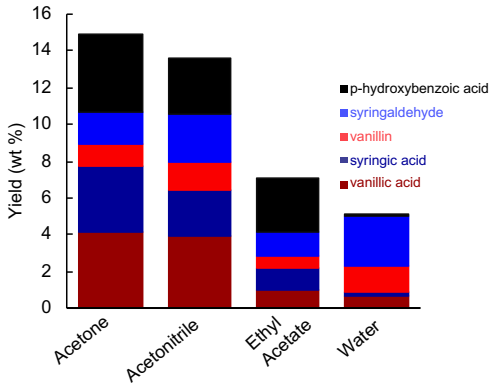

Figure S5. Monomer yields from oxidative catalytic fractionation of raw poplar biomass using different solvents. Conditions: 0.1 g poplar, 10 wt% Co–PANI–C catalyst, 20 mL solvent, 190 ˚C, 35 bar 6 % O_2 in N_2, 12 h.

Table S2. Monomer yields from oxidative catalytic fractionation of raw poplar using different catalysts[a]

	Yields of major phenolic products (weight %)					
Catalyst	PHBA[b]	Vanillic acid	Syringic acid	Vanillin	Syringaldehyde	Total (wt%)
Co–PANI–C	4.3	4.2	3.5	1.3	1.7	15.0
Fe–PANI–C	4.3	3.7	3.0	1.5	1.8	14.3
Co–Phen–C	4.2	4.7	3.2	1.4	1.5	15.0
Co_3O_4	4.2	4.3	3.3	1.3	1.6	14.7
Fe_2O_3	3.5	3.3	2.6	1.0	0.4	10.8
MnO	3.6	3.1	2.9	1.1	1.9	12.6
CuO	4.2	2.9	0.8	0.7	1.2	9.8
Dilute Co_3O_4	4.6	1.8	1.1	0.7	1.3	9.5

Dilute Fe_2O_3	4.0	1.3	1.0	0.9	0.7	7.9
Dilute MnO	4.2	1.8	1.3	0.5	0.6	8.4
Dilute CuO	4.0	1.6	1.2	1.3	1.0	9.1
Pd/C	2.9	1.4	1.1	0.3	1.0	6.7
Pt/C	2.5	1.7	1.8	0.5	0.6	7.1
Ru/C	2.7	2.7	3.0	1.3	1.8	11.5
No catalyst[c]	3.4	1.6	1.3	0.4	0.5	7.2
Inert atmosphere	1.5	0	0	0	0	1.5

[a] Reaction conditions: 100 mg poplar, 10 wt% heterogeneous catalyst, 20 mL acetone, 190 ºC, 12 h, 35 bar 6% O_2. [b] PHBA = *p*-hydroxybenzoic acid. [c] a Teflon liner was used to isolate the reactants from the Hastelloy-steel reactor.

Table S3. Lignin oxidative depolymerization of select biomass sources[a]

	Yields% of major phenolic products							
Biomass	PHBA[b]	Vanillic acid	Syringic acid	Vanillin	Sa[c]	*p*-Coumaric acid	Ferulic acid	Total (wt%)
Poplar	4.3	4.3	3.5	1.3	1.7	-	-	15.0
Pine [d]	-	5.5	-	1.8	-	-	-	7.3
Miscanthus[e]	2.4	5.4	1.2	1.1	1.2	0.5	0.3	12.1

[a] Reaction conditions: 100 mg biomass, 10 wt% Co–PANI–C, 20 mL acetone, 190 ºC, 12 h, 35 bar 6% O_2. [b] PHBA = *p*-hydroxybenzoic acid. [c] Sa = syringaldehyde. [d] lignin content = 22%. [e] lignin content = 20%.

Table S4. Monomer yields from oxidative catalytic fractionation of raw poplar biomass over while reusing the catalyst[a]

	Yields of major phenolic products (weight %)					
	PHBA[b]	Vanillic acid	Syringic acid	Vanillin	Syringaldehyde	Total (wt%)
Initial	4.3	5.2	2.4	1.3	1.3	14.5
1st recycle	4.3	4.6	2.4	1.4	1.2	13.9
2nd Recycle	4.2	4.8	2.4	1.3	1.3	14.0
3rd Recycle	4.3	4.8	2.3	1.3	1.2	13.9
4th Recycle	4.3	4.8	2.0	1.2	0.8	13.1

[a] Reaction conditions: 100 mg biomass, 10 wt% Co–PANI–C, 20 mL acetone, 190 ºC, 12 h, 35 bar 6% O_2. [b] PHBA = *p*-hydroxybenzoic acid.

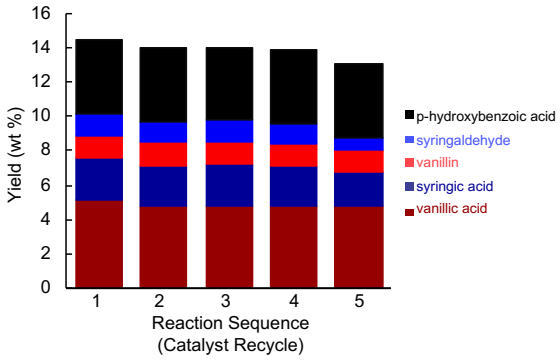

Figure S6. Monomer yields from oxidative catalytic fractionation of raw poplar while recycling the catalyst over 4 recycles. Conditions: 0.1 g poplar, 10 wt% Co–PANI–C catalyst initially, 20 mL solvent, 190 ˚C, 35 bar 6 % O_2 in N_2, 12 h.

Table S5. Monomer yields from oxidative catalytic fractionation in a pressure vessel equipped with overhead stirring with high mass loadings of raw poplar biomass

	Yields of major phenolic products (weight %)					
	PHBA[a]	Vanillic acid	Syringic acid	Vanillin	Syringaldehyde	Total (wt%)
0.5wt% loading[b]	4.3	4.2	3.5	1.3	1.7	15.0
3wt% loading[c]	4.8	3.9	4.3	1.2	1.7	15.9

[a] PHBA = *p*-hydroxybenzoic acid.[b] Reaction conditions: 100 mg biomass, 10 wt% Co–PANI–C, 20 mL acetone, 190 ºC, 12 h, 35 bar 6% O_2.[c] Reaction conditions: 300 mg biomass, 10 wt% Co–PANI–C, 10 mL acetone, 190 ºC, 12 h, 35 bar 6% O_2

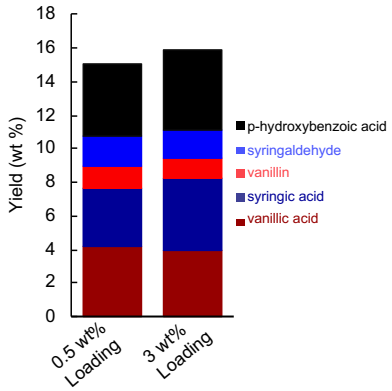

Figure S7. Monomer yields from oxidative catalytic fractionation of raw poplar biomass using different solvents. Conditions: 0.1 g poplar (0.5 wt% loading) and 0.3 g poplar (3 wt% loading), 10 wt% Co–PANI–C catalyst, 20 mL solvent (0.5 wt% loading) or 10 mL solvent (3 wt% loading), 190 ˚C, 35 bar 6 % O_2 in N_2, 12 h.

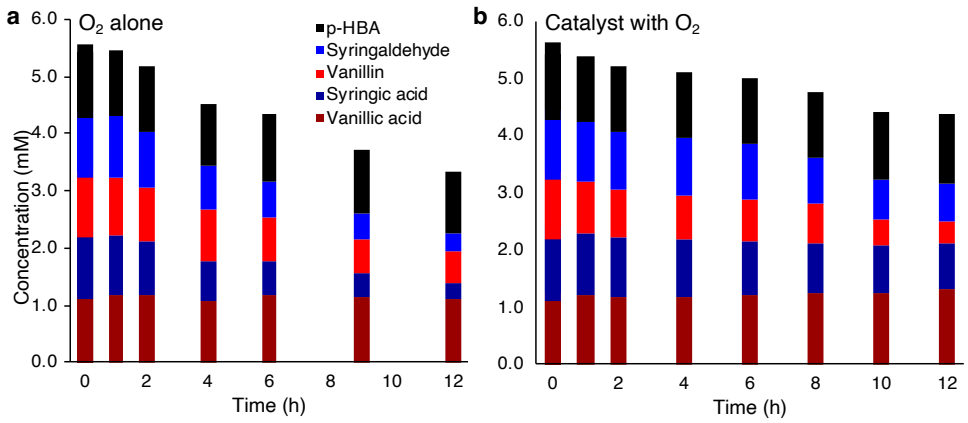

Figure S8. Decomposition of the 5 aromatic monomers in the presence of O_2 alone (a) and in the presence of catalyst with O_2 (b). Conditions 1 mM *p*-hydroxybenzoic acid, vanillic acid, syringic acid, vanillin, syringaldehyde in 100 mL of acetone, 190 ˚C, 35 bar 6% O_2 in N_2. 1 mL aliquots taken using a Parr 4878 Automated Liquid Sampler.

Table S6. Compositional analysis of NE 19 and solid residue after reaction

	Weight percent of major Components of Biomass				
	Cellulose	Hemicellulose	Lignin	Water	Mass Balance
washed NE-19	45.1	13.2	21.4	5.6	14.7
post-OCF residue[a]	67.6	7.7	11.3	5.6	7.8

[a] Reaction conditions: 100 mg poplar, 10 wt% Co–PANI–C, 20 mL acetone, 190 ºC, 12 h, 35 bar 6% O_2.

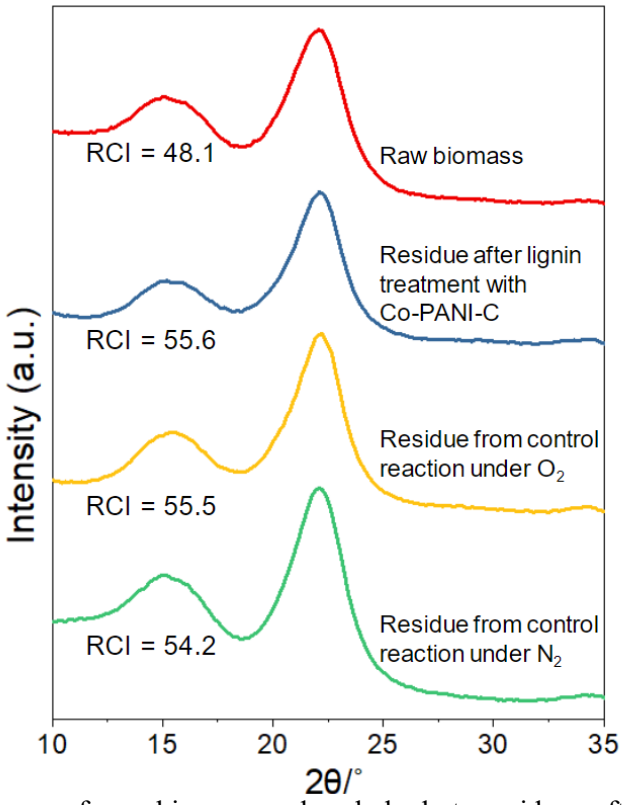

Figure S9. pXRD diffractogram of raw biomass and carbohydrate residues after different treatments. Relative Crystallinity Index calculated using the equation from Holtzapple.[7]

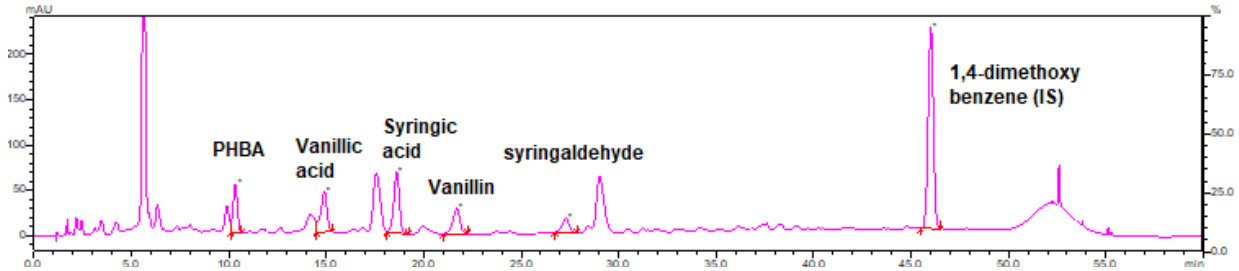

Figure S10. HPLC chromatogram showing identity of monomers from OCF of poplar lignin. Monomers were detected by measuring the optical absorbance at 280 nm. The yields of monomers were quantified based on an internal standard, 1,4-dimethoxybenzene. Reaction conditions: 100 mg poplar, 10 wt% Co–PANI–C, 20 mL acetone, 190 ºC, 12 h, 35 bar 6% O_2.

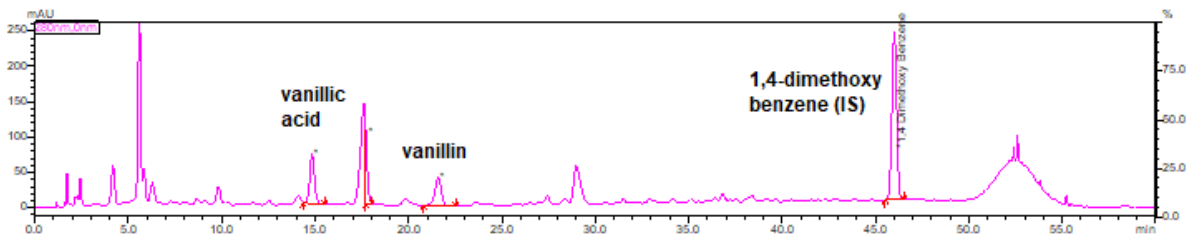

Figure S11. HPLC chromatogram showing identity of monomers from OCF of pine lignin. Monomers were detected by measuring the optical absorbance at 280 nm. The yields of monomers were quantified

based on an internal standard, 1,4-dimethoxybenzene. Reaction conditions: 100 mg pine, 10 wt% Co–PANI–C, 20 mL acetone, 190 ºC, 12 h, 35 bar 6% O_2.

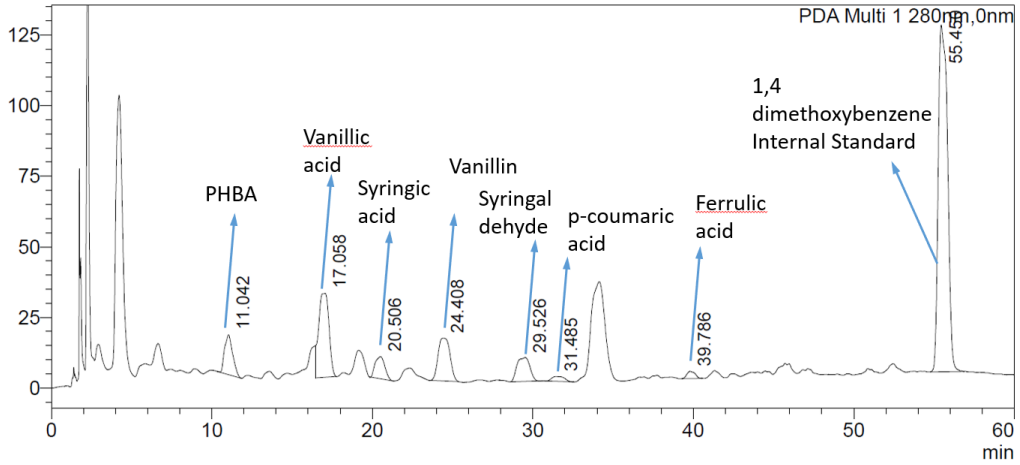

Figure S12. HPLC chromatogram showing identity of monomers from OCF of miscanthus lignin. Monomers were detected by measuring the optical absorbance at 280 nm. The yields of monomers were quantified based on an internal standard, 1,4-dimethoxybenzene. Reaction conditions: 100 mg miscanthus, 10 wt% Co–PANI–C, 20 mL acetone, 190 ºC, 12 h, 35 bar 6% O_2.

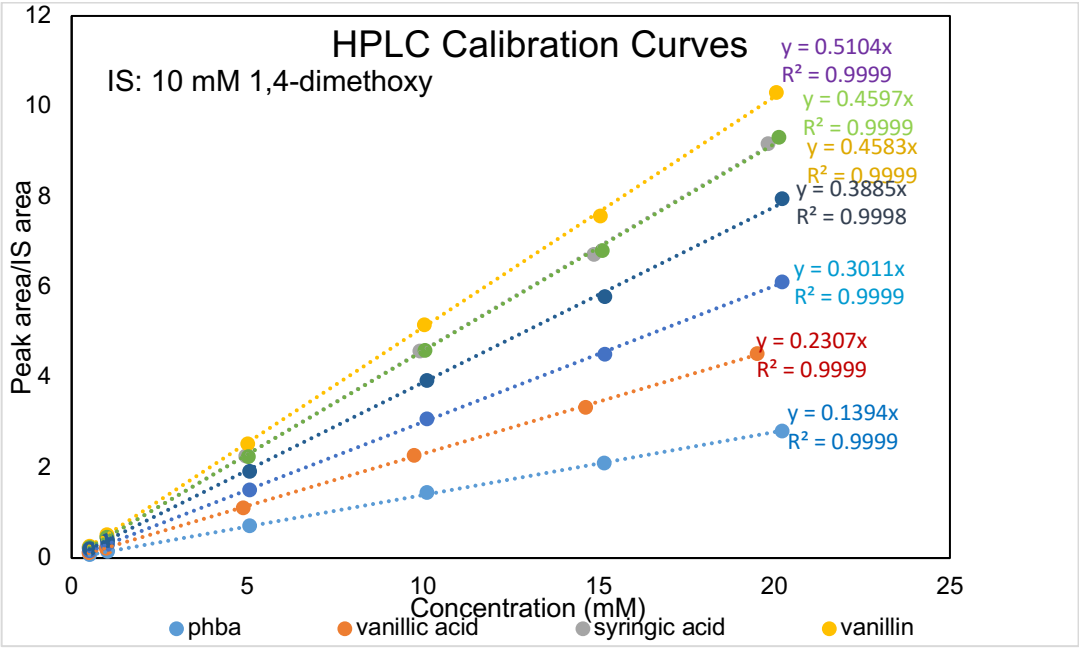

Figure S13. HPLC Photodiode array calibration curve for identified monomers at 280 nm.

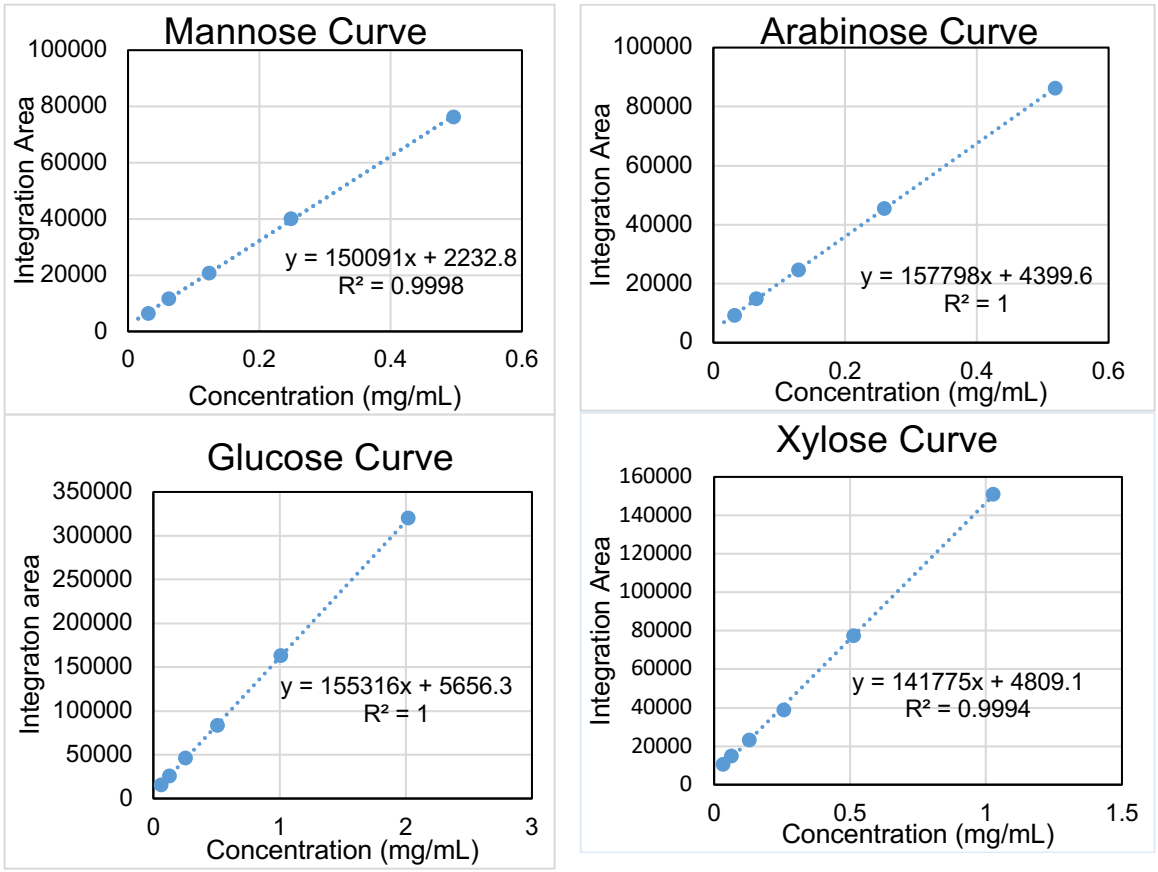

Figure S14. HPLC Refractive index detector calibration curves for common carbohydrate residues.

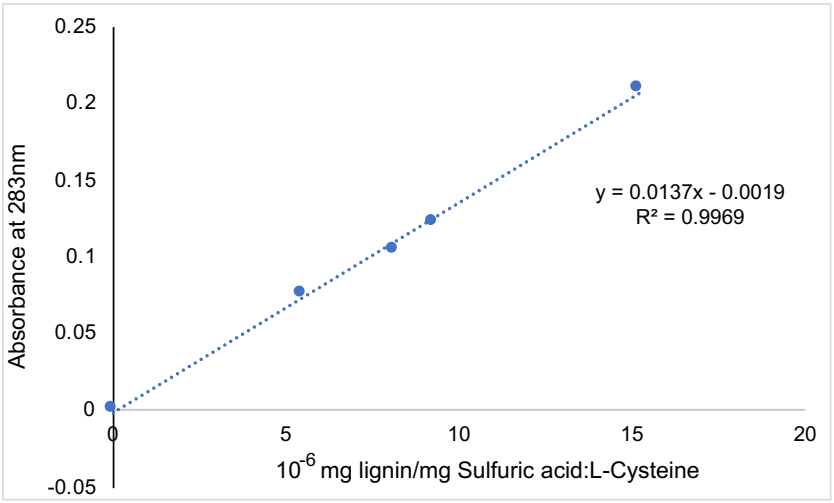

Figure S15. UV-VIS calibration curves for lignin content in NE-19 Poplar

4. References

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