Supporting Information

An effective strategy to produce highly amenable cellulose and enhance lignin upgrading to aromatic and olefinic hydrocarbons

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Experimental Procedures

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1. Gas chromatography (GC-FID/MS) analysis

The filtered reaction product was analyzed using an Agilent 7890B GC-FID/MS, equipped with two identical Phenomenex ZB 1701 capillary columns connected to MS and FID detectors. The following temperature program was used for the analysis: the oven temperature was held at 40 °C for 3 min, then ramped to 280 °C at 4 °C/min, and held at 280 °C for 4 min. The yield of the monomers generated during the pretreatment was calculated relative to the mass of lignin initially loaded in the reactor as follows:

$$Yield\ of\ monomers\ (wt\%) = \frac{Concentration\ \left(\frac{mg}{mL}\right) * \left(Volume\ of\ solvent\ in\ reactor\ (mL)\right)}{Weight\ of\ lignin\ (mg)} \times 100$$

Derivatization followed by GC-FID/MS was also used to unambiguously identify the monomeric products using the procedure described previously.[1] For derivatization, the pretreated samples were redissolved in tetrahydrofuran (THF) and the reaction mixture was subjected to silylation at 50 °C for 15 min using bis(trimethylsilyl)trifluoroacetamide (>99%, Sigma Aldrich) and pyridine (>99.9%, Sigma Aldrich).

2. Gel permeation chromatography (GPC)

GPC was conducted using a Dionex/Thermo Scientific Ultimate 3000 Binary Semipreparative LC System (Sunnyvale, CA) equipped with two Agilent PLgel 3 µm 100 Å 300 × 7.5 mm columns, one Mesopore 300 × 7.5 mm column, and a diode array detector (DAD). THF was used as the mobile phase at a flow rate of 0.3 mL/min. The wavelengths used for analysis were 254 nm, 263 nm, and 280 nm.

3. Thermogravimetric analysis (TGA)

TGA was performed with a Mettler Toledo TGA-DSC system (TGA-DSC 1 STAR^e system, Mettler Toledo). Approximately 20 mg of lignin sample was placed in an alumina crucible, heated in a nitrogen environment (100 mL/min) up to 105 °C at 10 °C/min, and held for 40 min to determine moisture content. The sample was then further heated to 900 °C at 10 °C/min in the same nitrogen environment and held at the final temperature for 20 min to determine volatile content. Finally, air (100 mL/min) was introduced to combust the residue and to calculate the fixed carbon and ash content.

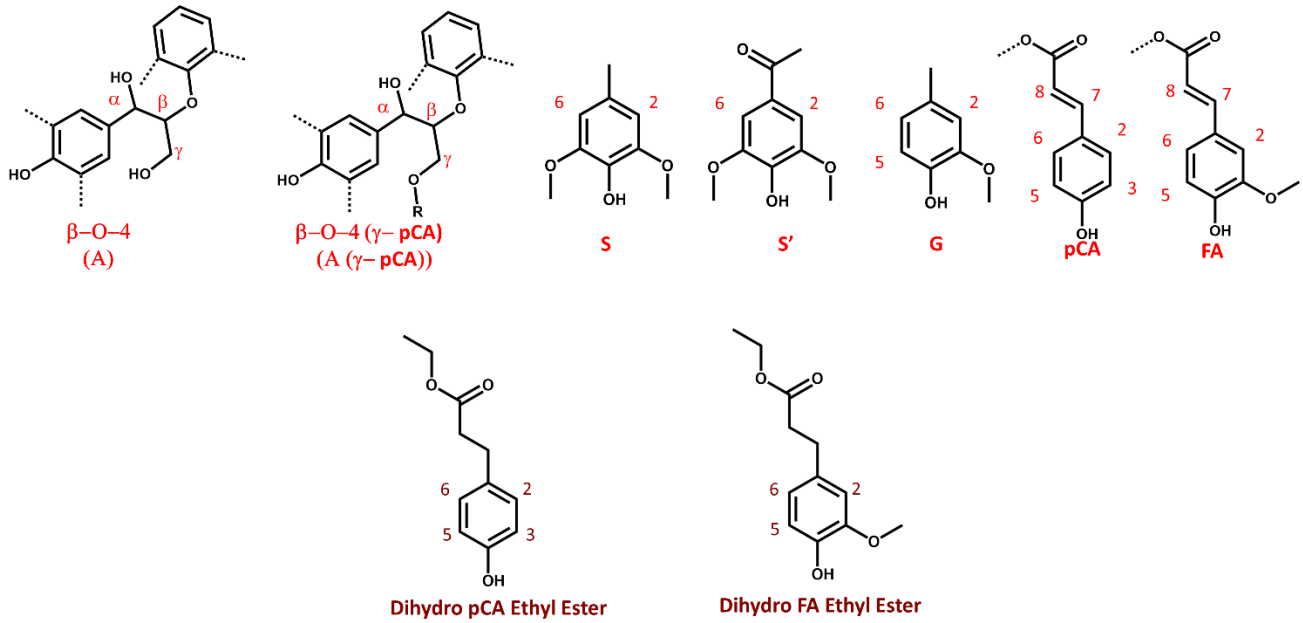
4. Elemental analysis (CHNS/O)

The C, H, N, S content was determined based on the dry ash-free mass and was measured in an elemental analyzer (Vario Micro Cube, Elementar, Germany) using approximately 5 mg of the sample for each run. The difference from 100% is assumed to be the oxygen content. The analysis was run in triplicate, and the average value from the trials was reported.

5. Heteronuclear single quantum coherence (HSQC NMR) analysis

Measurements were performed using 70 - 80 mg of parent lignin or pretreated lignin dissolved in 650–700 µL of a 4:1 v/v mixture of DMSO-d6 and pyridine-d5. The mixture was sonicated for 30 min to obtain a homogenous sample. The spectra were collected with a Bruker Avance III 600 MHz spectrometer using the pulse sequence 'hsqcetgpsisp2.2' at 25 °C, with the following parameters: interscan relaxation delay of 0.5 s, 32 scans with the total acquisition time of 3 h, a spectral width of 220 ppm in f1 and 12 ppm in f2, with centers around 90 ppm and 5 ppm, respectively. The DMSO solvent peak was used as an internal reference (δ_H/δ_c: 2.49/39.5). All data processing was carried out using MestReNova v12.0.1 software. The signals were assigned based on references[2-5] and ChemDraw predictions. The complete signal assignments are as follows:

Nature of Fragments	Assignment
-OCH3	55.6/3.73
A- γ	60.1/3.73 and 60.1/3.40
A-γ (γ- pCA)	63.3/4.42 and 63.3/3.94
A-G (α)	71.3/4.87
A-H (α)	71.3/4.87
A-S (α)	71.3/4.87
A-H/G (α)	84.4/4.39 and 83.9/4.45
S (2,6)	103.7/6.73
S'(2,6)	106.7/7.24
FA (2)	111.1/7.36
G (2)	110.8/7.02
G (5,6)	115.2/6.90
pCA(3,5)	115.8/6.84
pCA (2,6)	130.2/7.49
pCA and FCA (7)	144.9/7.53
Dihydro pCA Ethyl Ester (2,6)	128.3/6.97
Dihydro pCA Ethyl Ester (3,5)	115.9/6.77
Dihydro FA Ethyl Ester (2)	111.9/6.74
Dihydro FA Ethyl Ester (5)	114.8/6.58
Dihydro FA Ethyl Ester (6)	119.7/6.57



The integration ratio of the β-O-4 to aromatics was calculated according to the quantitative methods described in the following reference (**Equation S1**).[6] The percentage of end groups (such as coumarate and tricin) are severely over-estimated by this analysis due to their relaxation rate properties compared to the internal units of a chain and thus not included for the calculation of total pheylpropane units.[7]

Equation S1: *Formula for semiquantitative analysis of HSQC NMR results*

$$C_9 \text{ (Total Phenylpropane units)} = [I(S_{2,6}) + I(S'_{2,6})]/2 + [I(G_2)]$$

$$\beta\text{-O-4 \%} = [A(\alpha)]/C_9 \times 100$$

$$S/G = [I(S_{2,6}) + I(S'_{2,6})]/ [2*I(G_2)]]$$

6. CO chemisorption

A Micromeritics ASAP 2920 analyzer was used to estimate the metallic surface area per unit of mass of sample using CO chemisorption. The catalyst was first reduced in situ at 200 °C for 1 h using 10% hydrogen in argon, followed by a helium purge for 1 h prior to starting the CO chemisorption at 35 °C using

10% carbon monoxide in helium. A stoichiometric factor of 1 was considered for all metals for CO adsorption based on previous reports.[8-10]

7. Compositional analysis of biomass

The moisture content of the feedstocks was measured by drying the samples in an oven at 105 °C until a constant weight was achieved.[11] The compositional analyses of the parent biomass, pretreated pulp, and solvent-soluble products were conducted by Celignis Analytical, Limerick, Ireland (analysis package P9: https://www.celignis.com/package.php?value=13). Test methods were comparable to the National Renewable Energy Laboratory (NREL) TP-510-42618 "Determination of Structural Carbohydrates and Lignin in Biomass." All the samples were analyzed in duplicate, and the mean value was reported on a dry weight basis. The detailed analytical procedure is as follows:

Hydrolysis

A procedure similar to the Uppsala Method [12] was employed for the acid hydrolysis of the samples. Approximately 300 mg of the sample was added to a pressure tube containing 3 mL of 72% H_2SO_4. The sample and acid were then mixed thoroughly using a glass rod, and the pressure tube was transferred to a water bath, which was maintained at 30 °C for 1 h. The mixture was stirred every 10 min. Subsequently, 84 mL of water was added to the pressure tube to achieve a 4% acid concentration, and the tube was sealed. All the pressure tubes of an analytical batch were then transferred to an autoclave along with three pressure tubes containing 10 mL of a known sugar composition solution to which 348 µl of 72% H_2SO_4 was added. These additional tubes were referred to as the sugar recovery solutions and were used to determine the sugar losses associated with this secondary hydrolysis step (121 °C for 60 min). The pressure tubes were removed from the autoclave once the temperature fell below 80 °C and allowed to cool to room temperature. The hydrolysates were then filtered through crucibles of known weight, and the resulting filtrate was stored. Residual solids were washed from the tube using deionized water until all the residues were collected on the filter crucible. The solids were then dried overnight at 105 °C and weighed to determine the content of the Acid Insoluble Residue (AIR). The filter crucible was then ashed to determine the content of acid-insoluble ash (AIA). The Klason lignin content was determined as AIR minus AIA. The sum of Klason and acid-soluble lignin was referred to as the total lignin content present in the biomass.

Acid soluble lignin (ASL)

The hydrolysate was placed in a 1 cm path-length (3 mL volume) quartz cuvette and diluted with water until the UV-absorbance was within a linear region. The spectrum was collected in transmission mode

using an HP Agilent 8452A diode array spectrophotometer. The absorbance at 205 nm was used to determine the ASL content using an absorptivity constant of 110 M^{-1} cm^{-1}.[13]

Chromatography conditions

The hydrolysates were diluted 20x with a solution containing a known concentration of the internal standard melibiose. These diluted hydrolysates were then filtered using 0.2 µm Teflon syringe filters and transferred to vials for chromatographic analysis on a DIONEX ICS-3000 ion chromatography system comprising: an electrochemical detector (using Pulsed Amperometric Detection, PAD), a gradient pump, a temperature-controlled column, a detector enclosure, and an AS50 autosampler. The autosampler injected 10 µl of the diluted sample, and sugar separation was achieved via the use of Carbo-Pac PA1 guard and analytical columns connected in series. Sugar separation occurred in 16 min with deionized water as the eluent, a flow rate of 1.5 mL/min, and a column/detector temperature of 21 °C. The standard Dionex "Carbohydrates" waveform was used for detection (Dionex, 2000). After 16 min, the column was regenerated and re-equilibrated for the following sample. This involved a 2 min ramp to an eluent concentration of 400 mM NaOH. These conditions were held for 4 min after which there was a 2 min return to deionized water as the only eluent. This elution was maintained for 5 min prior to the injection of the next sample. PAD requires alkaline conditions for carbohydrate detection; thus, NaOH (300 mM) was added to the post-column eluent stream, using a Dionex DP pump, at a 0.3 mL/min flow rate. In a single injection, the chromatographic conditions allowed resolution between arabinose, galactose, rhamnose, glucose, xylose, mannose, and melibiose. Relative response factors were determined via sugar standard samples injected at regular intervals in the analytical sequence.

Enzymatic hydrolysis

Corn stover and the pulp obtained after one-pot fractionation and pretreatment of biomass were tested for enzymatic digestibility by Celignis Analytical, Limerick, Ireland (analysis package P121: https://www.celignis.com/package.php?value=67). Enzymatic hydrolysis tests were performed in 10 ml reaction vessels with a working volume of 3 ml, using Novozyme Cellic® CTec2 (30 mg protein/g glucan) enzyme at 50 °C for 72 h. Samples were collected at 12 h, 24 h, 48 h, and 72 h. The mass balances were calculated by accounting for solids and evaporation losses throughout the hydrolysis. Reaction vessel weights were recorded before and after collecting the sample at every sampling point to correct the sugar mg/ml data obtained for evaporation losses of liquid that may concentrate the sugars in the hydrolysate. The hydrolysis runs were performed in triplicate for each sample.

8. Method for carbon tracking

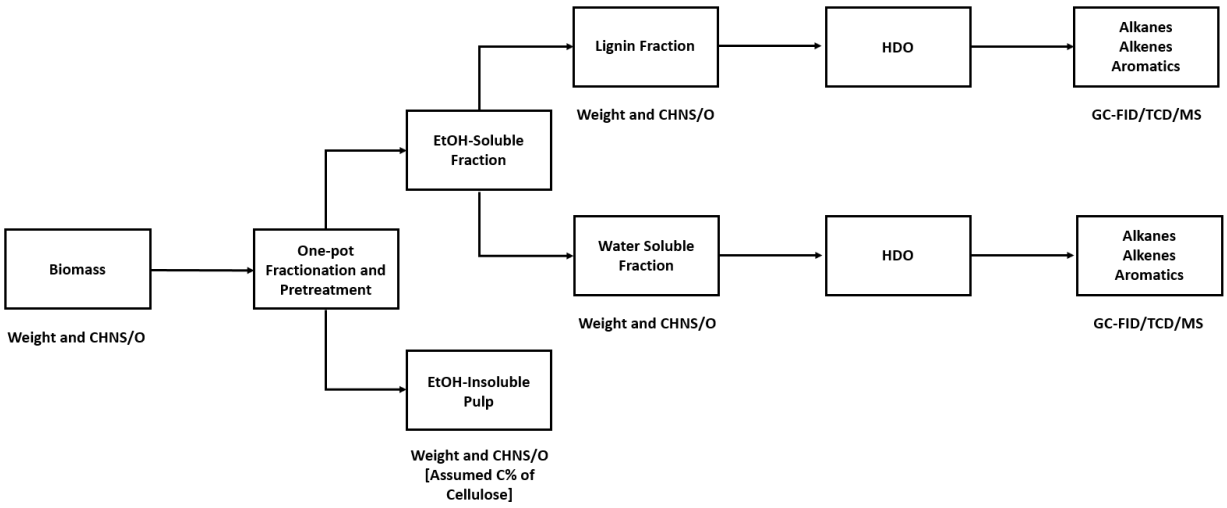
Accurate carbon tracking was achieved by following the procedure depicted in Scheme S1 and explained below:

1. Biomass was dried in an oven at 105 °C to desorb moisture until reaching a constant weight. At this point, the sample was allowed to return to room temperature and its exact weight was recorded using a freshly calibrated Mettler-Toledo balance with a ±0.1 mg precision. The elemental composition of the biomass (including its carbon content) was then determined using CHNS/O analysis.

2. The dried biomass sample was then transferred to a batch Parr reactor and subjected to the pretreatment in ethanol. After reaction, the reactor was allowed to cool down to room temperature and was depressurized. The solution, solid pulp, and solid catalyst were recovered, and the reactor was carefully rinsed to recover any products (monomers, oligomers, solid) that could stick to its walls. The solid residue (catalyst and EtOH-insoluble pulp) was recovered by filtering the reactor content using a 0.2 μm poly(ether sulfone) filter. The solid was then washed with 30 mL EtOH and dried in air. The catalyst was separated from the EtOH-insoluble pulp using a 75 μm sieve. Meanwhile, EtOH was evaporated from the EtOH-soluble products by drying the filtrate overnight at 40 °C in a vacuum oven. The weight of each fraction was then recorded, and their elemental compositions were determined by CHNS/O analysis.

3. To separate the soluble lignin- and carbohydrates-derived products present in the EtOH-soluble fraction, liquid-liquid extractions were successively performed three times with ethyl acetate and water. The lignin oil was mainly concentrated in the ethyl acetate phase, while the water phase contained the dissolved sugars. After separation, ethyl acetate and water were evaporated, and the samples were further dried in a vacuum oven overnight. The weight of each sample was recorded, and their elemental compositions were determined by CHNS/O analysis.

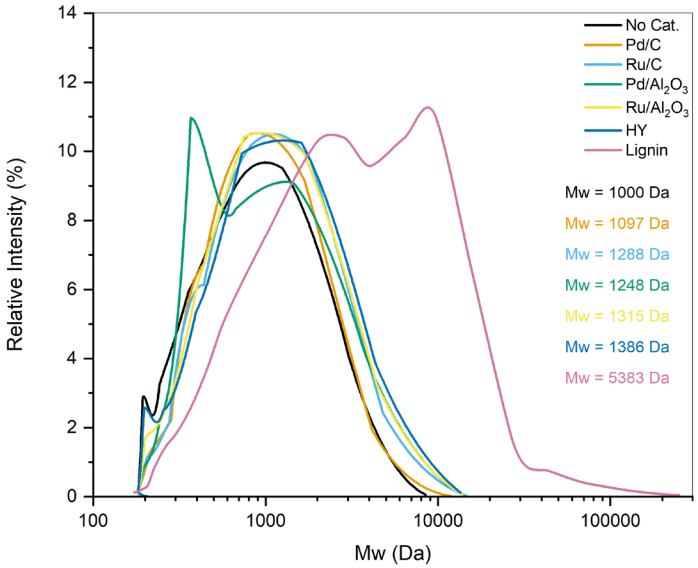
4. The recovered lignin fraction and water-soluble sugar-rich fraction were subjected to fast pyrolysis and hydrodeoxygenation. The obtained products such as alkanes, alkenes and aromatics were identified and quantified through online GC-FID/TCD/MS. The instrument was calibrated using relevant compounds, a list of which can be found in Table S6 (Supporting Information). All calibration curves were obtained using 5 calibration standards and a R^2 higher than 0.99 was achieved in each case. For compounds not commercially available, standard compounds with similar chemical structure were used instead.



Scheme S1. Schematic representation of the experimental process for carbon tracking from biomass feedstock to final products

Figures S1-S12

a)



b)

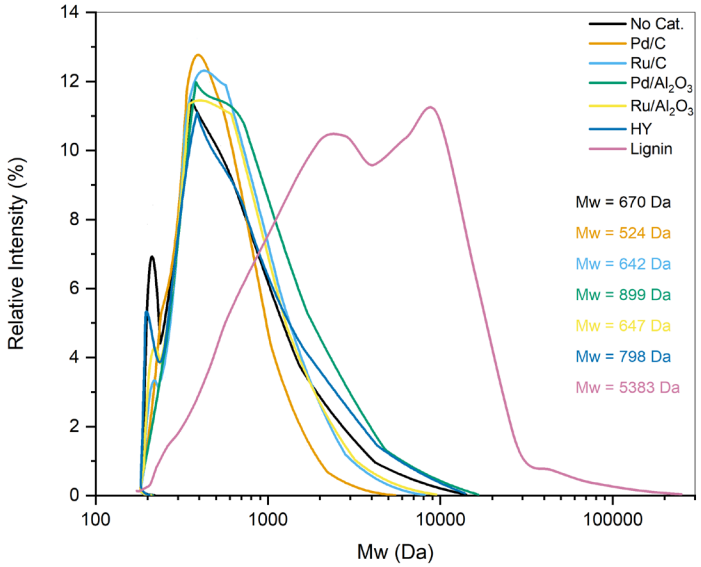
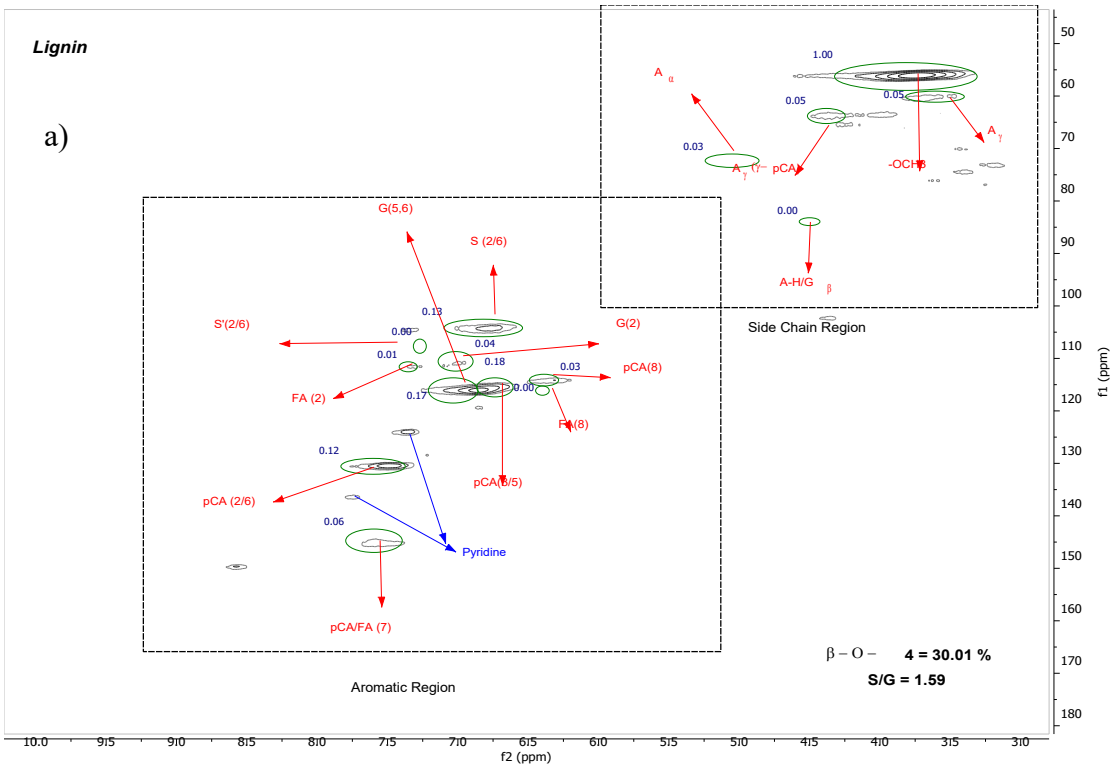
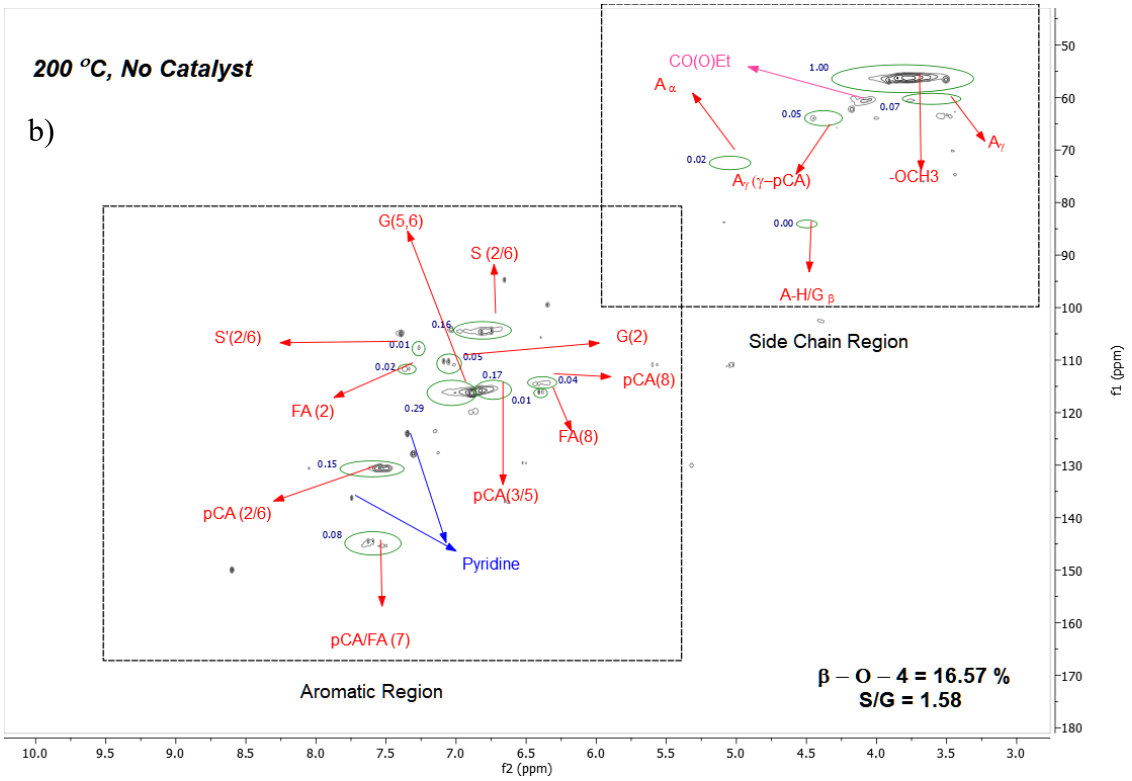
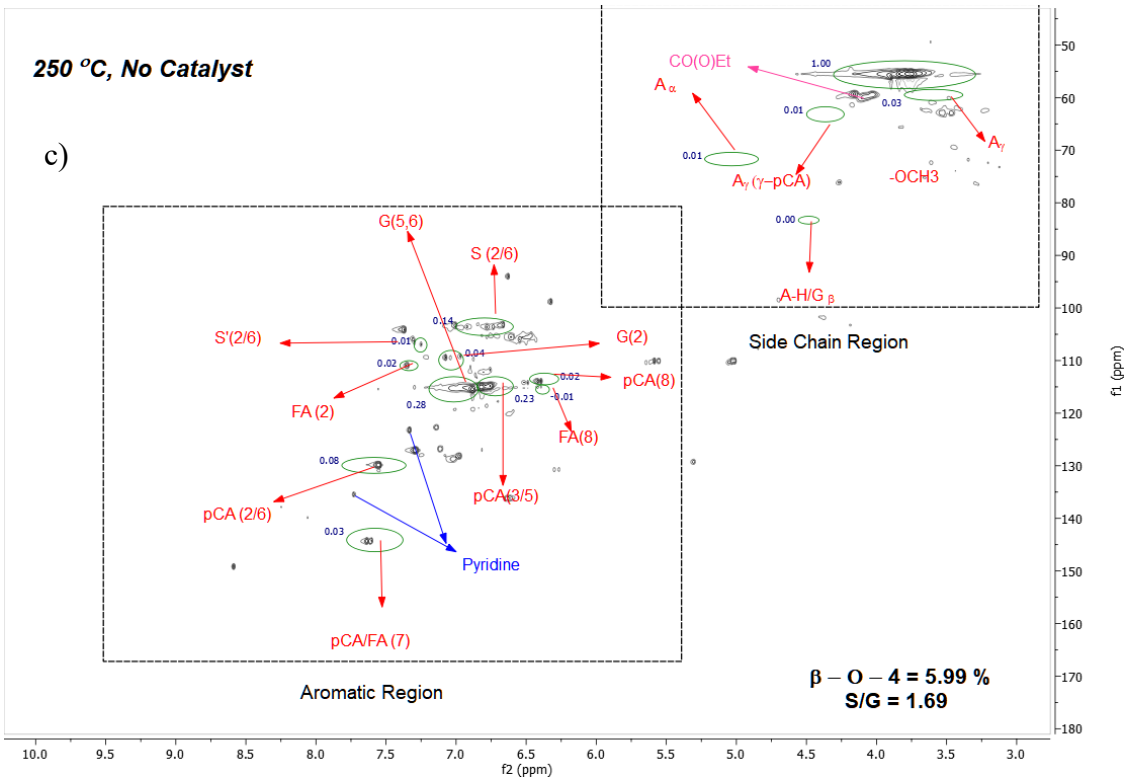
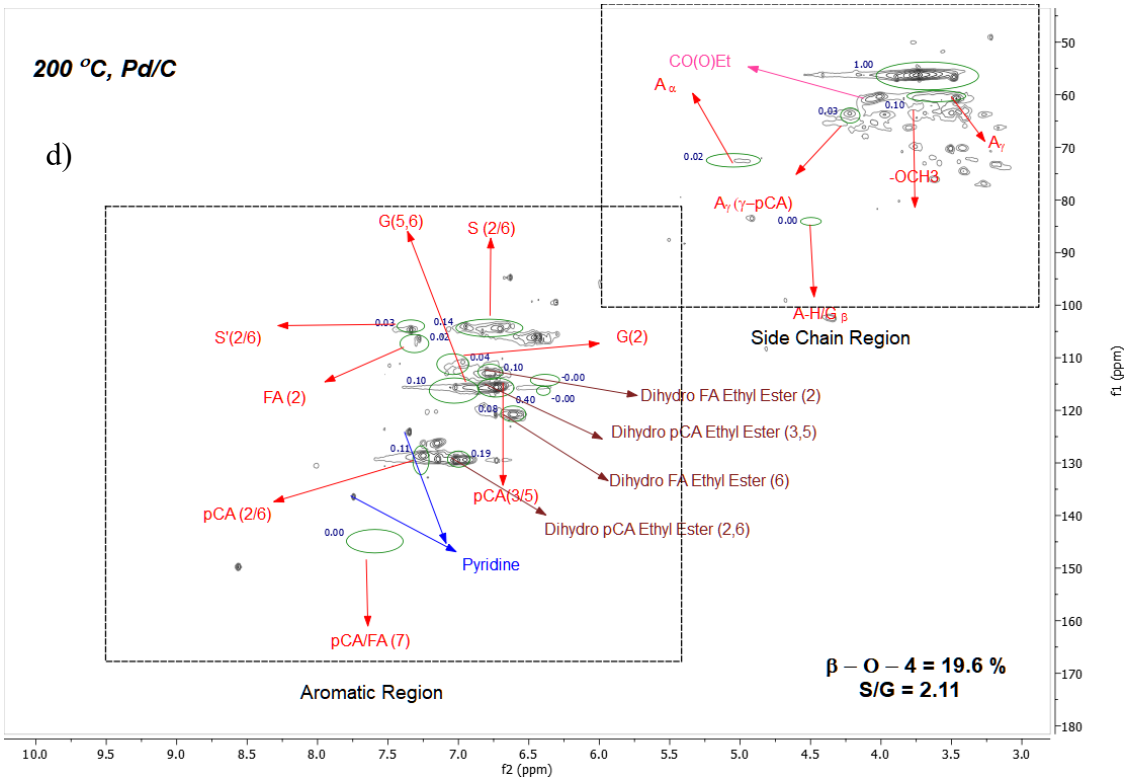


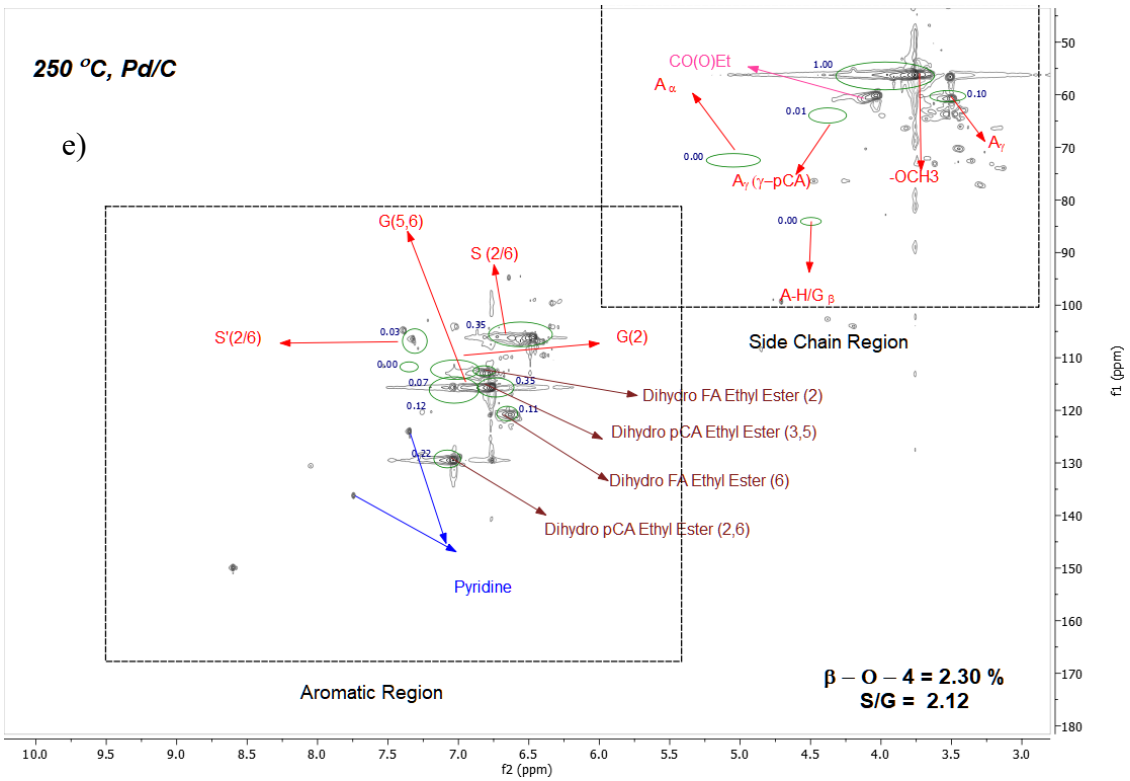
Figure S1. Molecular weight distributions for the samples pretreated at **a)** 200 ℃ and **b)** 250 ℃

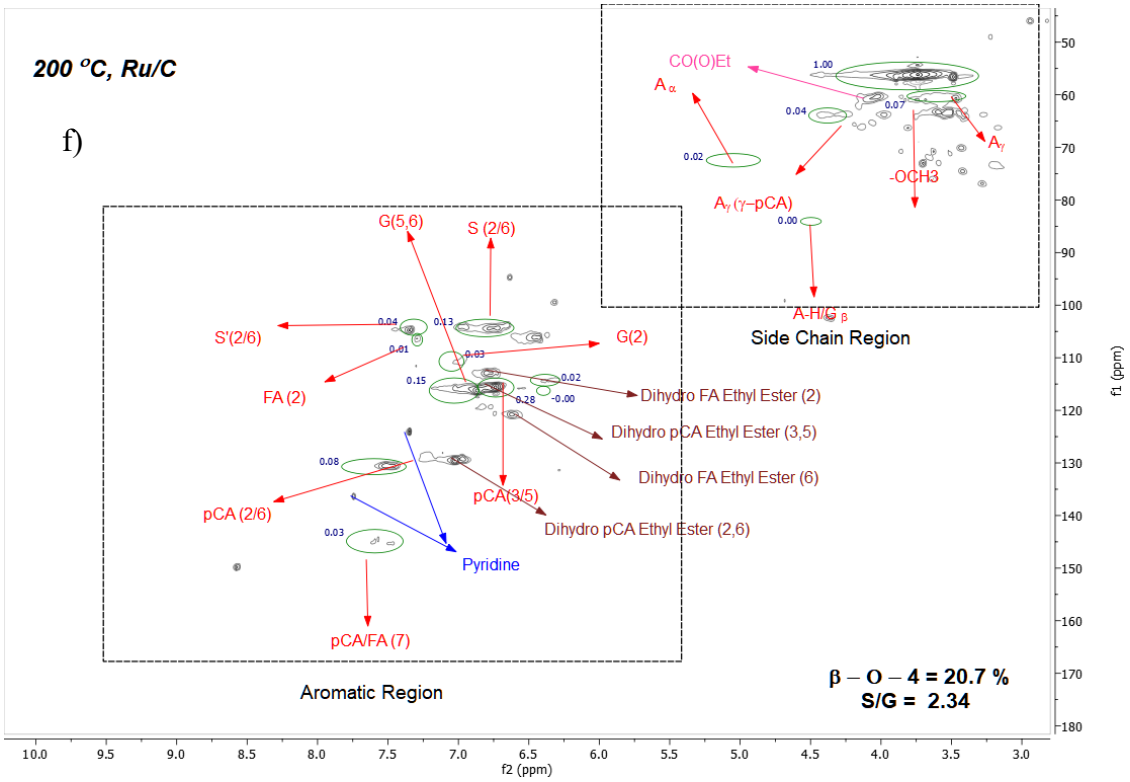

Lignin
a)
G(5,6)
S (2/6)
S'(2/6)
G(2)
FA (2)
pCA(8)
FA(8)
pCA(3/5)
pCA (2/6)
Pyridine
pCA/FA (7)
Aromatic Region
Side Chain Region
-OCH3
A-H/G β
β – O – 4 = 30.01 %
S/G = 1.59
f2 (ppm)
f1 (ppm)

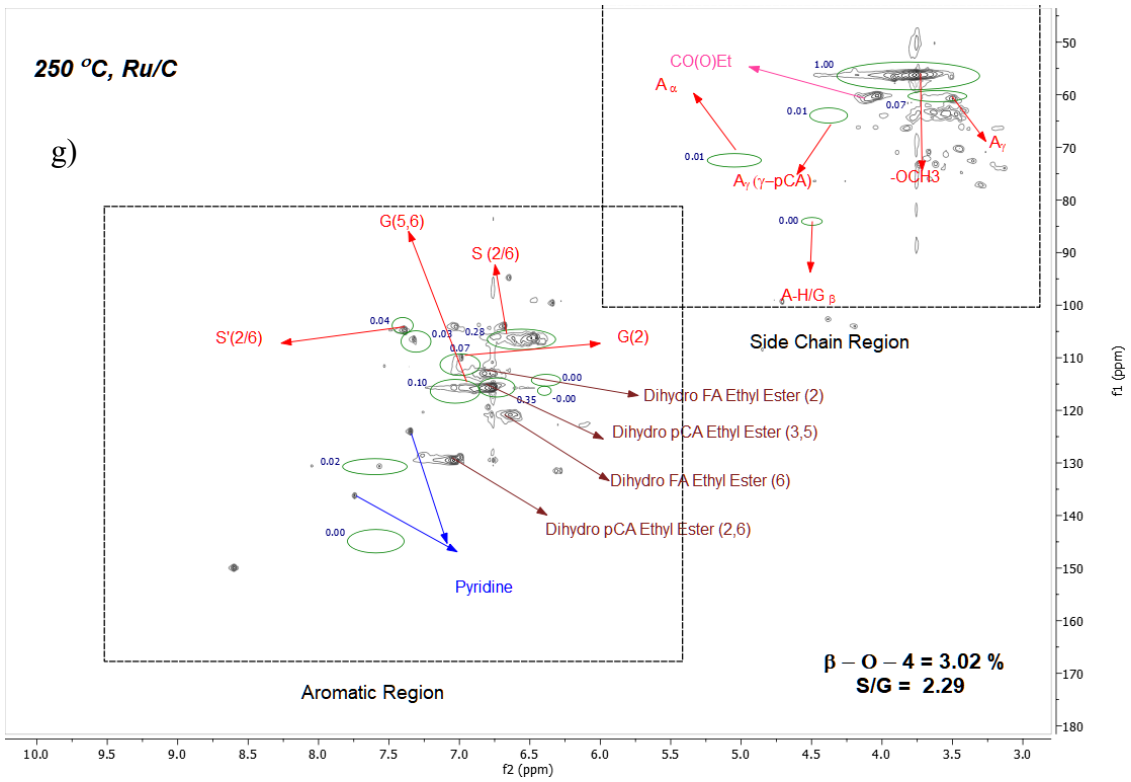

200 °C, No Catalyst
b)
CO(O)Et
Aγ (γ–pCA)
G(5,6)
S (2/6)
S'(2/6)
G(2)
FA (2)
pCA(8)
FA(8)
pCA(3/5)
pCA (2/6)
Pyridine
pCA/FA (7)
Aromatic Region
Side Chain Region
-OCH3
A-H/G β
β – O – 4 = 16.57 %
S/G = 1.58
f2 (ppm)
f1 (ppm)

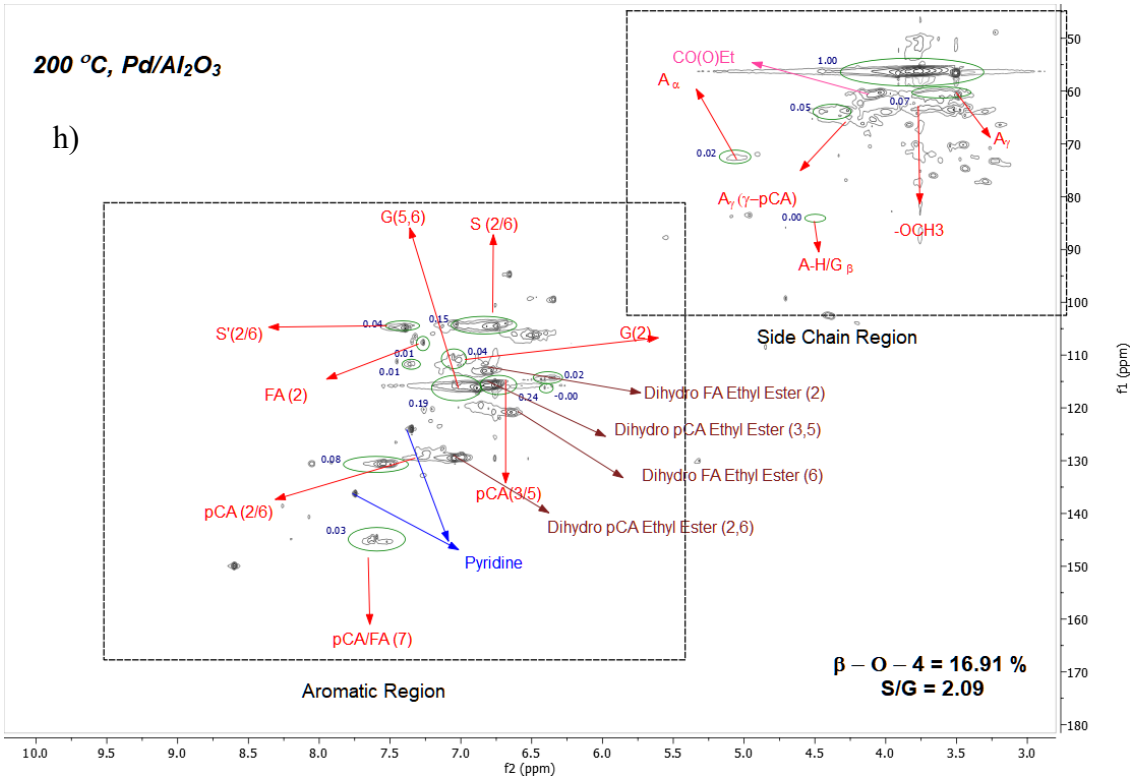

250 °C, No Catalyst
c)
CO(O)Et
A α
A γ
A γ (γ–pCA)
-OCH3
A-H/G β
Side Chain Region
G(5,6)
S (2/6)
S'(2/6)
G(2)
pCA(8)
FA (2)
FA(8)
pCA(3/5)
pCA (2/6)
Pyridine
pCA/FA (7)
Aromatic Region
β – O – 4 = 5.99 %
S/G = 1.69
f2 (ppm)
f1 (ppm)

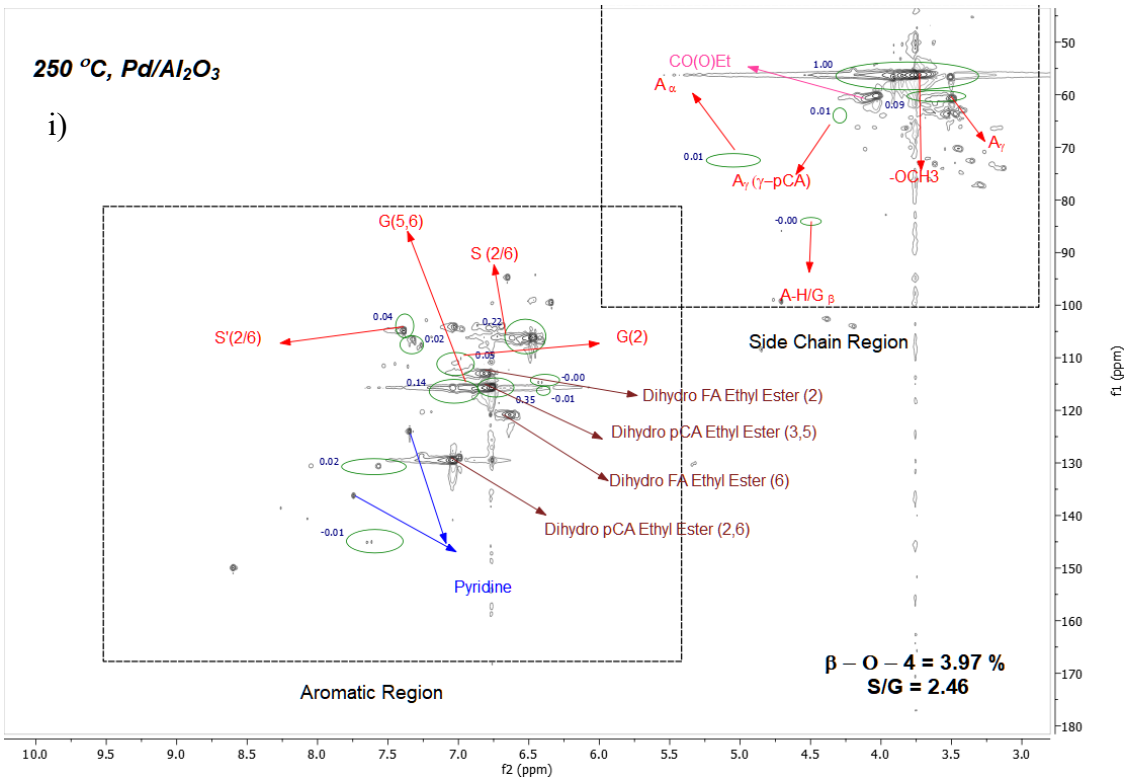

200 °C, Pd/C
d)
CO(O)Et
A α
A γ
A γ (γ–pCA)
-OCH3
A-H/G β
Side Chain Region
G(5,6)
S (2/6)
S'(2/6)
G(2)
FA (2)
Dihydro FA Ethyl Ester (2)
Dihydro pCA Ethyl Ester (3,5)
Dihydro FA Ethyl Ester (6)
pCA(3/5)
pCA (2/6)
Dihydro pCA Ethyl Ester (2,6)
Pyridine
pCA/FA (7)
Aromatic Region
β – O – 4 = 19.6 %
S/G = 2.11
f2 (ppm)
f1 (ppm)

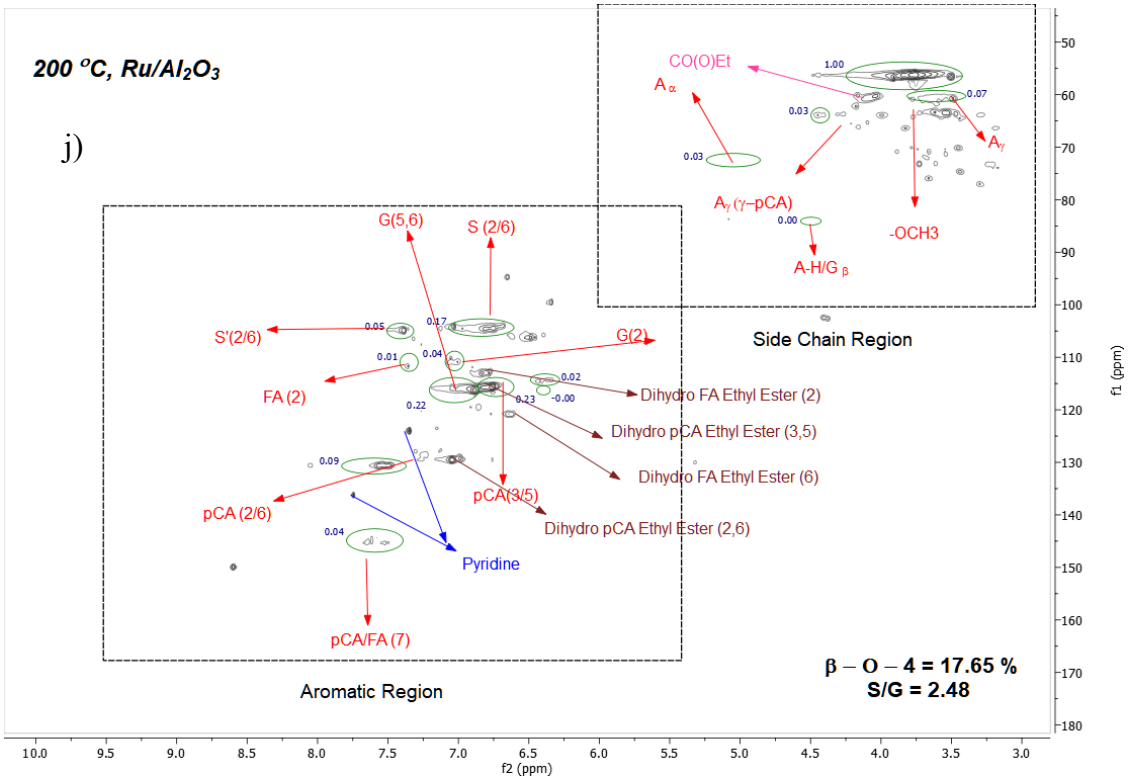

250 °C, Pd/C
e)
CO(O)Et
A α
A γ (γ–pCA)
-OCH3
A γ
A-H/G β
Side Chain Region
G(5,6)
S (2/6)
S'(2/6)
G(2)
Dihydro FA Ethyl Ester (2)
Dihydro pCA Ethyl Ester (3,5)
Dihydro FA Ethyl Ester (6)
Dihydro pCA Ethyl Ester (2,6)
Pyridine
Aromatic Region
β – O – 4 = 2.30 %
S/G = 2.12
f2 (ppm)
f1 (ppm)

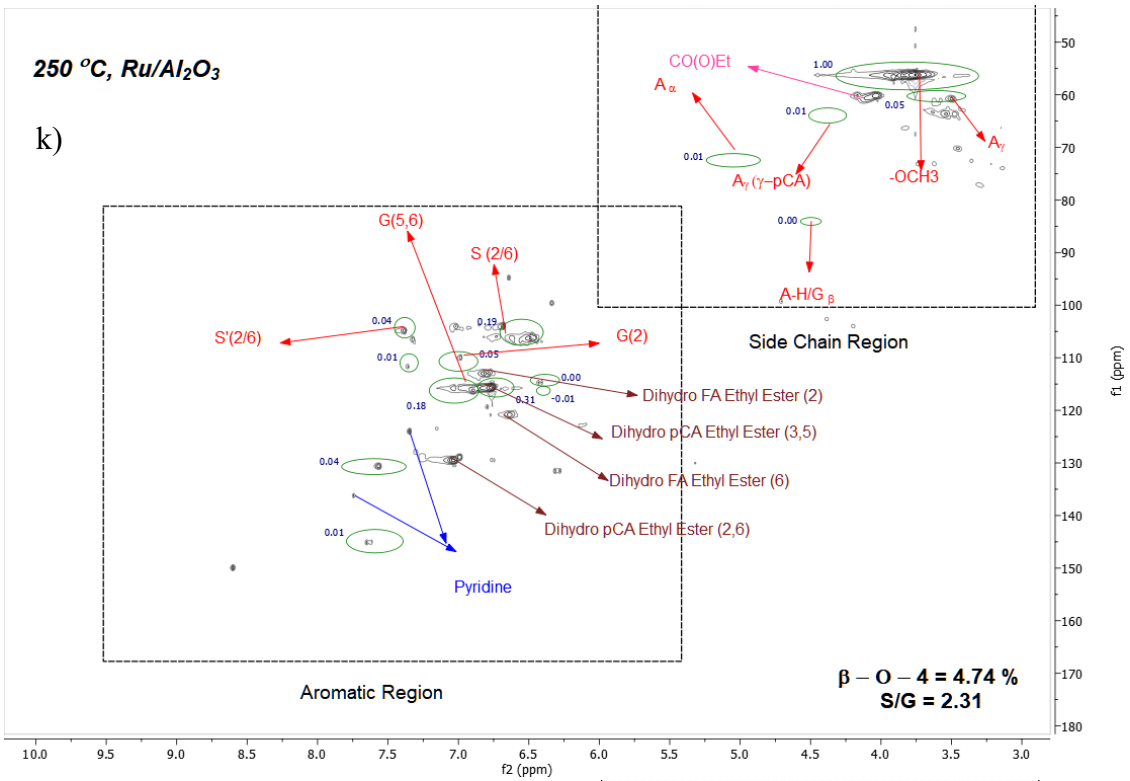

200 °C, Ru/C
f)
CO(O)Et
A α
A γ (γ–pCA)
-OCH3
A γ
A-H/G β
Side Chain Region
G(5,6)
S (2/6)
S'(2/6)
G(2)
FA (2)
Dihydro FA Ethyl Ester (2)
Dihydro pCA Ethyl Ester (3,5)
Dihydro FA Ethyl Ester (6)
pCA (2/6)
pCA(3/5)
Dihydro pCA Ethyl Ester (2,6)
Pyridine
pCA/FA (7)
Aromatic Region
β – O – 4 = 20.7 %
S/G = 2.34
f2 (ppm)
f1 (ppm)


250 °C, Ru/C
g)
CO(O)Et
A α
A γ (γ–pCA)
A γ
-OCH3
A-H/G β
Side Chain Region
G(5,6)
S (2/6)
S'(2/6)
G(2)
Dihydro FA Ethyl Ester (2)
Dihydro pCA Ethyl Ester (3,5)
Dihydro FA Ethyl Ester (6)
Dihydro pCA Ethyl Ester (2,6)
Pyridine
Aromatic Region
β – O – 4 = 3.02 %
S/G = 2.29
f2 (ppm)
f1 (ppm)


200 °C, Pd/Al2O3
h)
CO(O)Et
A α
A γ (γ–pCA)
A γ
-OCH3
A-H/G β
Side Chain Region
G(5,6)
S (2/6)
S'(2/6)
G(2)
FA (2)
Dihydro FA Ethyl Ester (2)
Dihydro pCA Ethyl Ester (3,5)
Dihydro FA Ethyl Ester (6)
pCA(3/5)
pCA (2/6)
Dihydro pCA Ethyl Ester (2,6)
Pyridine
pCA/FA (7)
Aromatic Region
β – O – 4 = 16.91 %
S/G = 2.09
f2 (ppm)
f1 (ppm)


250 °C, Pd/Al2O3
i)
CO(O)Et
Aα
Aγ (γ–pCA)
-OCH3
Aγ
A-H/Gβ
Side Chain Region
G(5,6)
S (2/6)
S'(2/6)
G(2)
Dihydro FA Ethyl Ester (2)
Dihydro pCA Ethyl Ester (3,5)
Dihydro FA Ethyl Ester (6)
Dihydro pCA Ethyl Ester (2,6)
Pyridine
Aromatic Region
β – O – 4 = 3.97 %
S/G = 2.46
f2 (ppm)
f1 (ppm)


200 °C, Ru/Al2O3
j)
CO(O)Et
Aα
Aγ (γ–pCA)
-OCH3
Aγ
A-H/Gβ
Side Chain Region
G(5,6)
S (2/6)
S'(2/6)
G(2)
FA (2)
Dihydro FA Ethyl Ester (2)
Dihydro pCA Ethyl Ester (3,5)
Dihydro FA Ethyl Ester (6)
pCA(3/5)
pCA (2/6)
Dihydro pCA Ethyl Ester (2,6)
Pyridine
pCA/FA (7)
Aromatic Region
β – O – 4 = 17.65 %
S/G = 2.48
f2 (ppm)
f1 (ppm)


250 °C, Ru/Al2O3
k)
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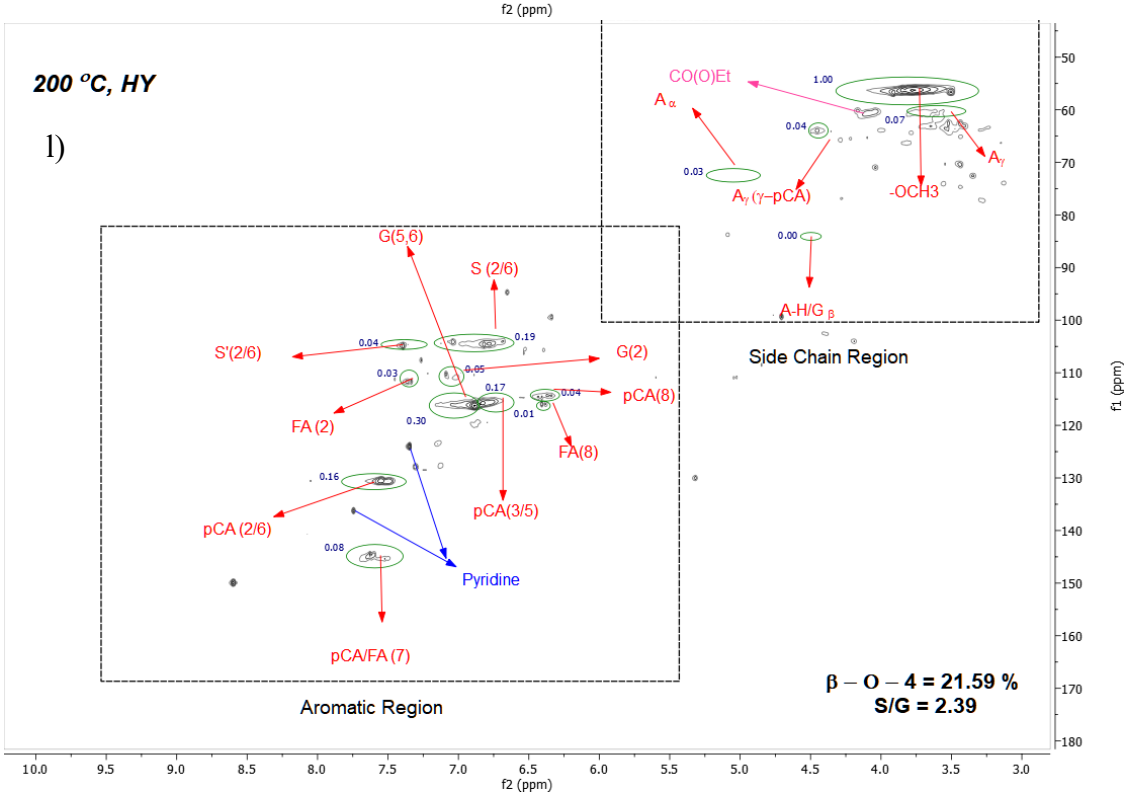
G(2)
Dihydro FA Ethyl Ester (2)
Dihydro pCA Ethyl Ester (3,5)
Dihydro FA Ethyl Ester (6)
Dihydro pCA Ethyl Ester (2,6)
Pyridine
Aromatic Region
β – O – 4 = 4.74 %
S/G = 2.31
f2 (ppm)
f1 (ppm)


200 °C, HY
l)
CO(O)Et
Aα
Aγ (γ–pCA)
-OCH3
Aγ
A-H/Gβ
Side Chain Region
G(5,6)
S (2/6)
S'(2/6)
G(2)
FA (2)
pCA(8)
FA(8)
pCA(3/5)
pCA (2/6)
Pyridine
pCA/FA (7)
Aromatic Region
β – O – 4 = 21.59 %
S/G = 2.39
f2 (ppm)
f1 (ppm)

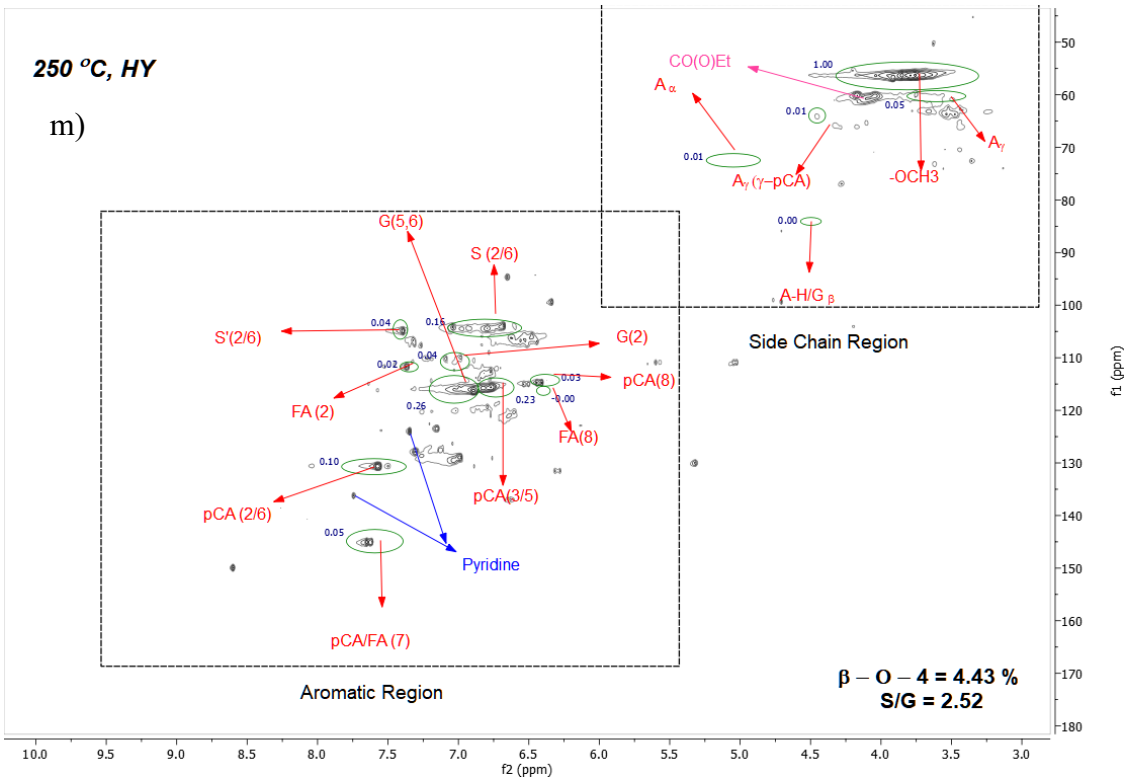


Figure S2. HSQC NMR spectra of **a)** the parent lignin, and the pretreated samples obtained at **b)** 200 °C, no catalyst, **c)** 250 °C, no catalyst, **d)** 200 °C, Pd/C, **e)** 250 °C, Pd/C, **f)** 200 °C, Ru/C, **g)** 250 °C, Ru/C, **h)** 200 °C, Pd/Al_2O_3, **i)** 250 °C, Pd/Al_2O_3, **j)** 200 °C, Ru/Al_2O_3, **k)** 250 °C, Ru/Al_2O_3, **l)** 200 °C, HY, **m)** 250 °C, HY along with their relative integrals. The signal assignments are provided in Section 5 of the Supplementary Experimental Procedures.

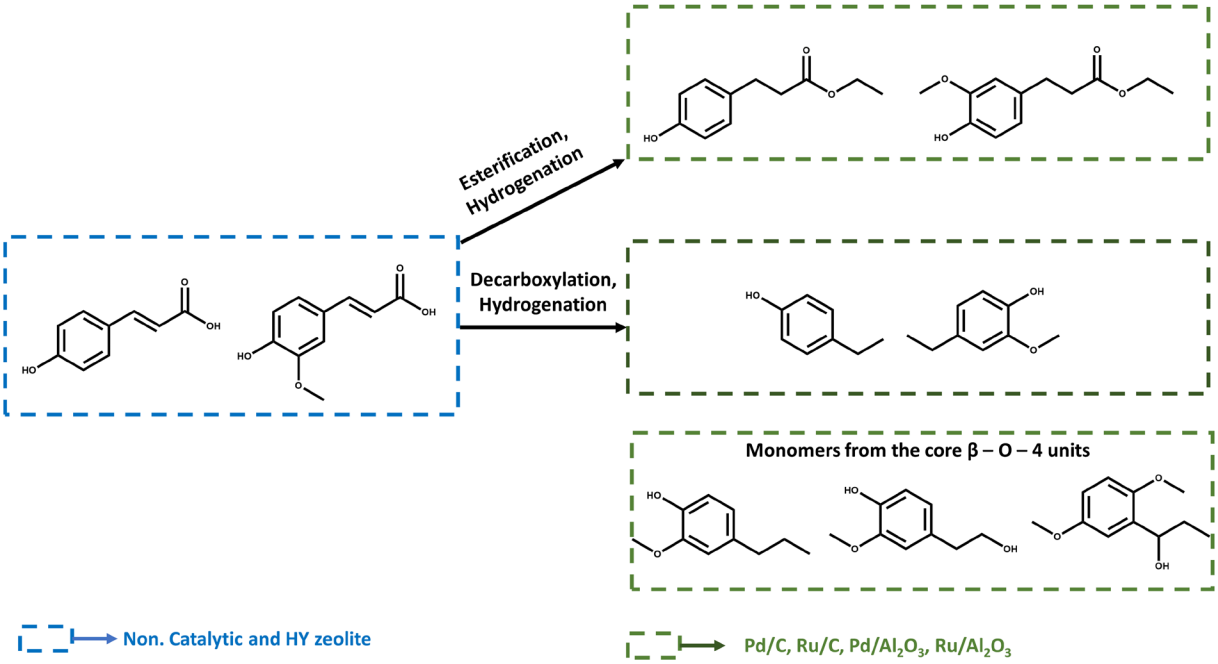


Figure S3. Mechanistic insights obtained from the pretreatment of organosolv lignin in EtOH by combining information from elemental analysis (**Figure 2**), GC-FID/MS analysis of the phenolic monomers obtained under various conditions (**Figure 3**), and HSQC NMR analysis of the pretreated samples and parent corn stover organosolv lignin (**Figure S2**).

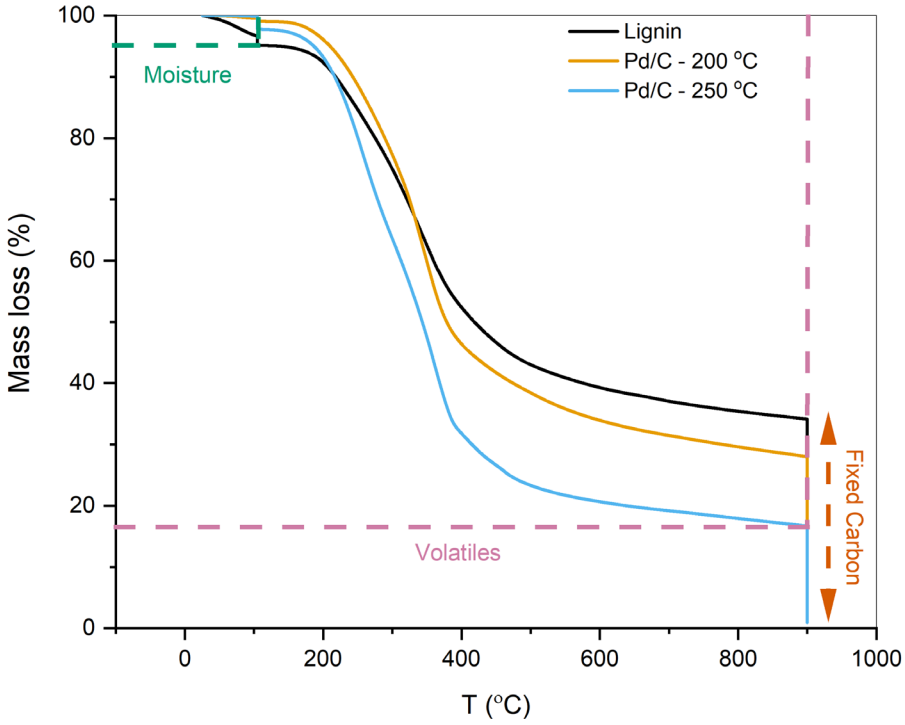
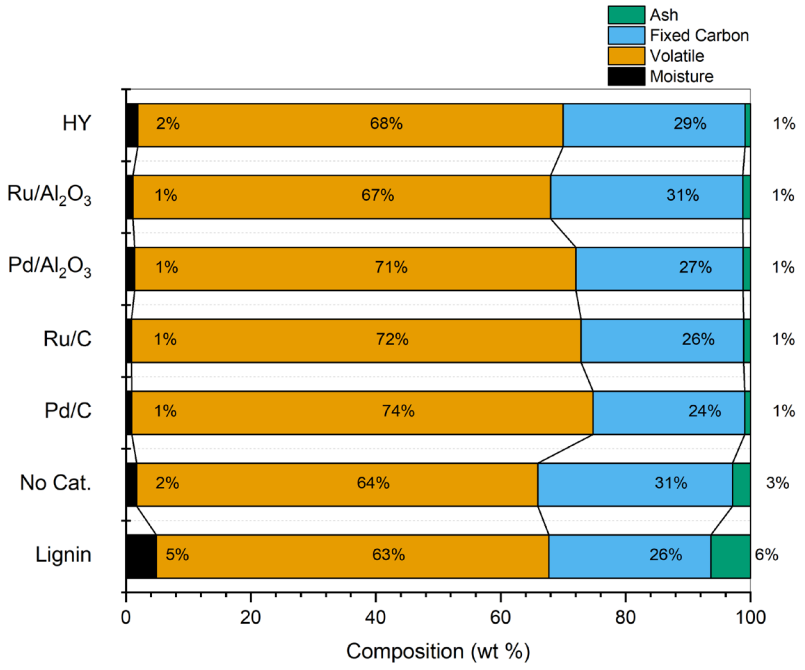


Figure S4. TGA curves of lignin and representative pretreated samples. The moisture content, volatiles, fixed carbon content and ash derived from TGA of all samples are presented in form of proximate analysis in **Figure S5**.

a)



b)

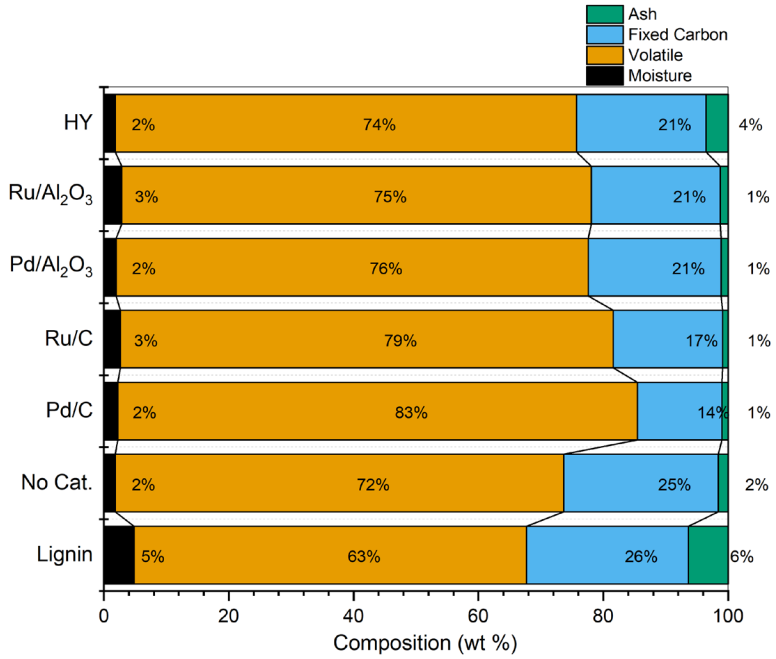


Figure S5. Proximate analysis (wt%) of pretreated samples at **a)** 200 ℃ and **b)** 250 ℃.

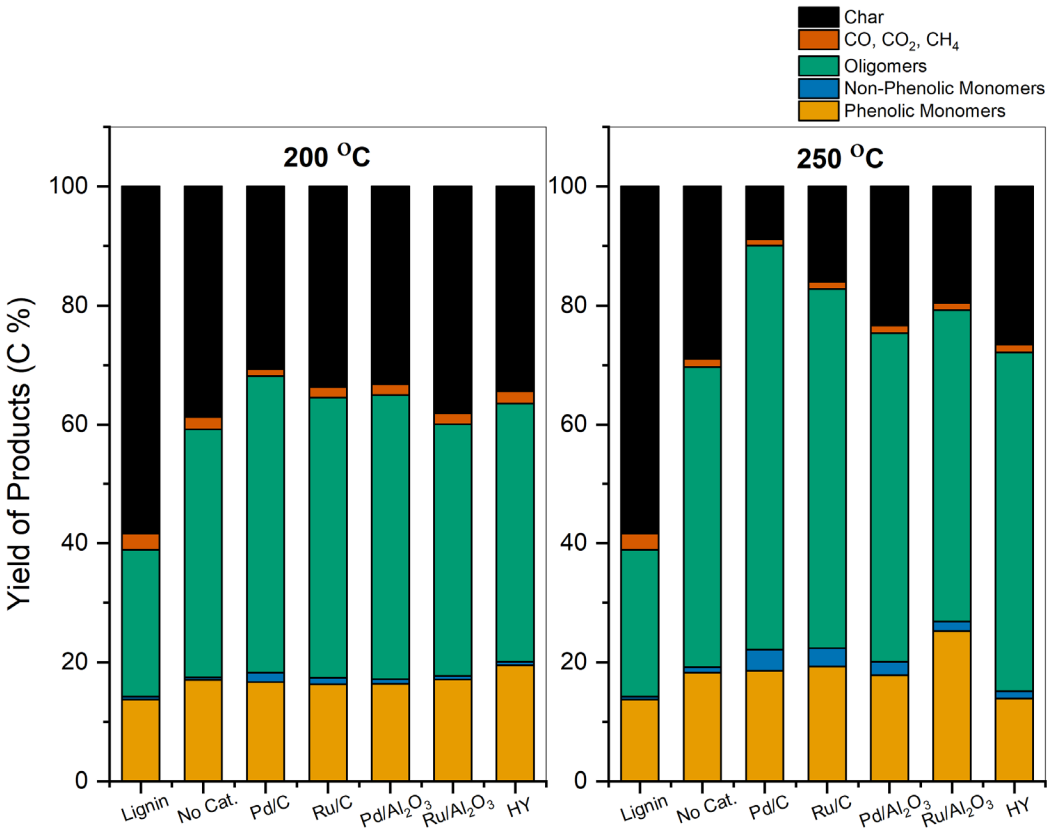


Figure S6. Products obtained for the fast pyrolysis at 500 °C of the parent lignin and of the samples pretreated in EtOH at 200 and 250 °C in the presence of various catalysts. The yields of the phenolic monomers, non-phenolic monomers, and light gases (CO, CO_2, CH_4) were calculated based on online GC-FID/TCD/MS analysis and quantification of these products (C%). The char yield was calculated from the mass of solid residue recovered after fast pyrolysis. The oligomers were calculated using the following formula: Oligomers (C%) = 100 – Σ (Other Quantified Products (C%). It should be noted that this artificial closing of the carbon balance introduces errors in the calculated values. Therefore, the values reported here for the oligomers are qualitative.

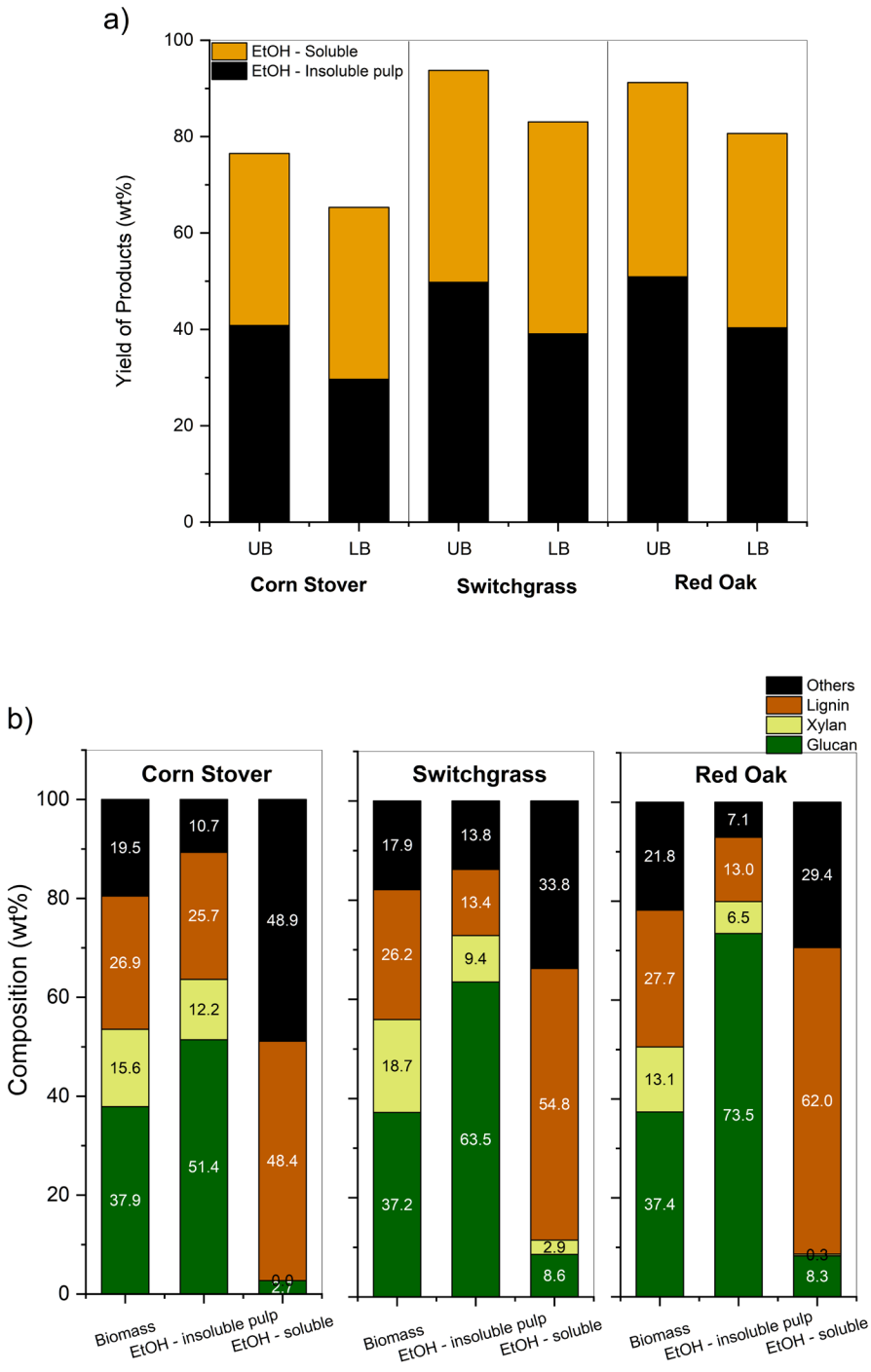


Figure S7. a) Mass balance and **b)** composition analysis of products obtained from one-pot fractionation and pretreatment of biomass (UB: upper bound and LB: lower bound).

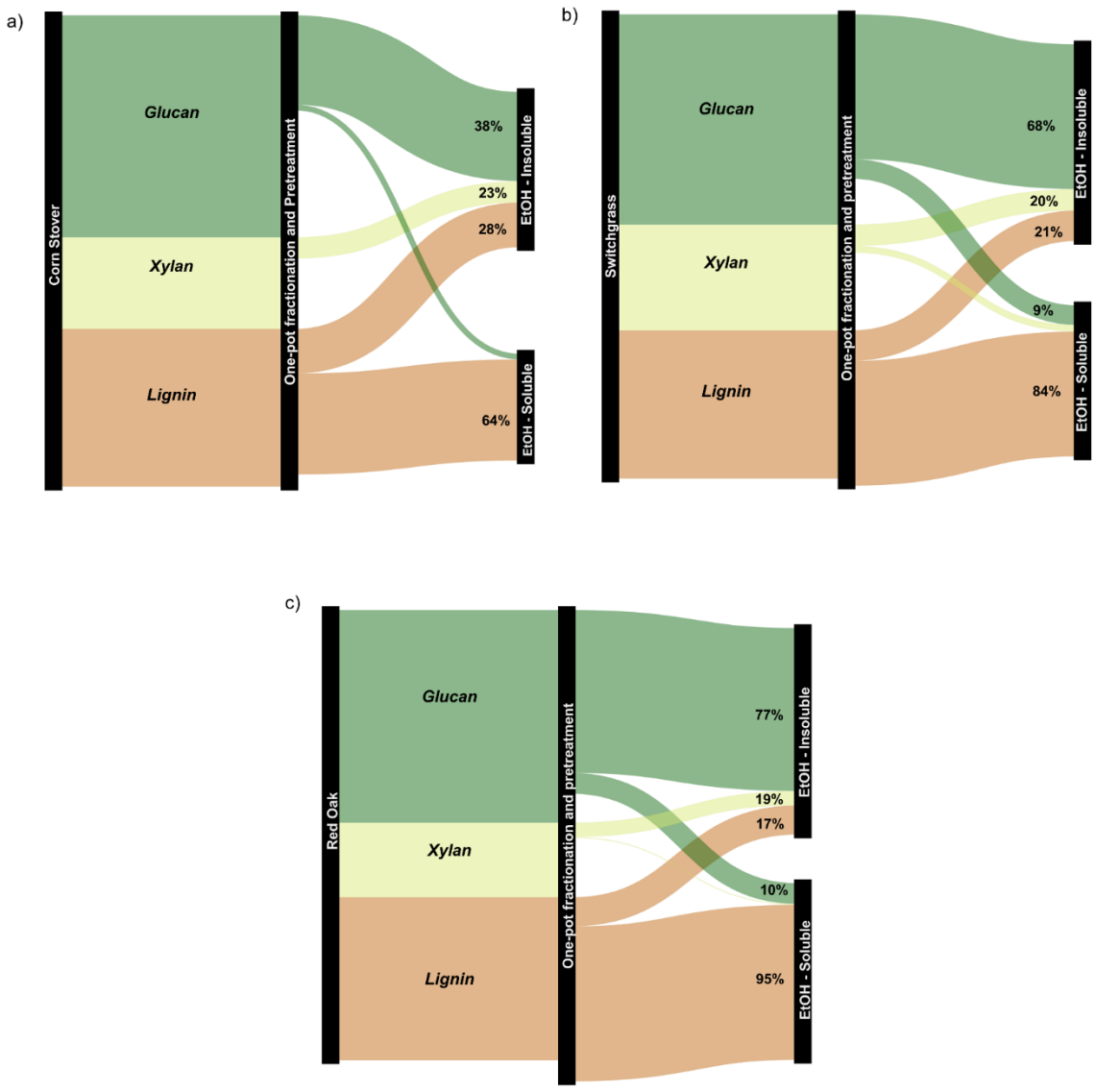


Figure S8. Component balance (lower bound values) for the products obtained from the one-pot fractionation and pretreatment of biomass for **a)** corn stover, **b)** switchgrass, and **c)** red oak.

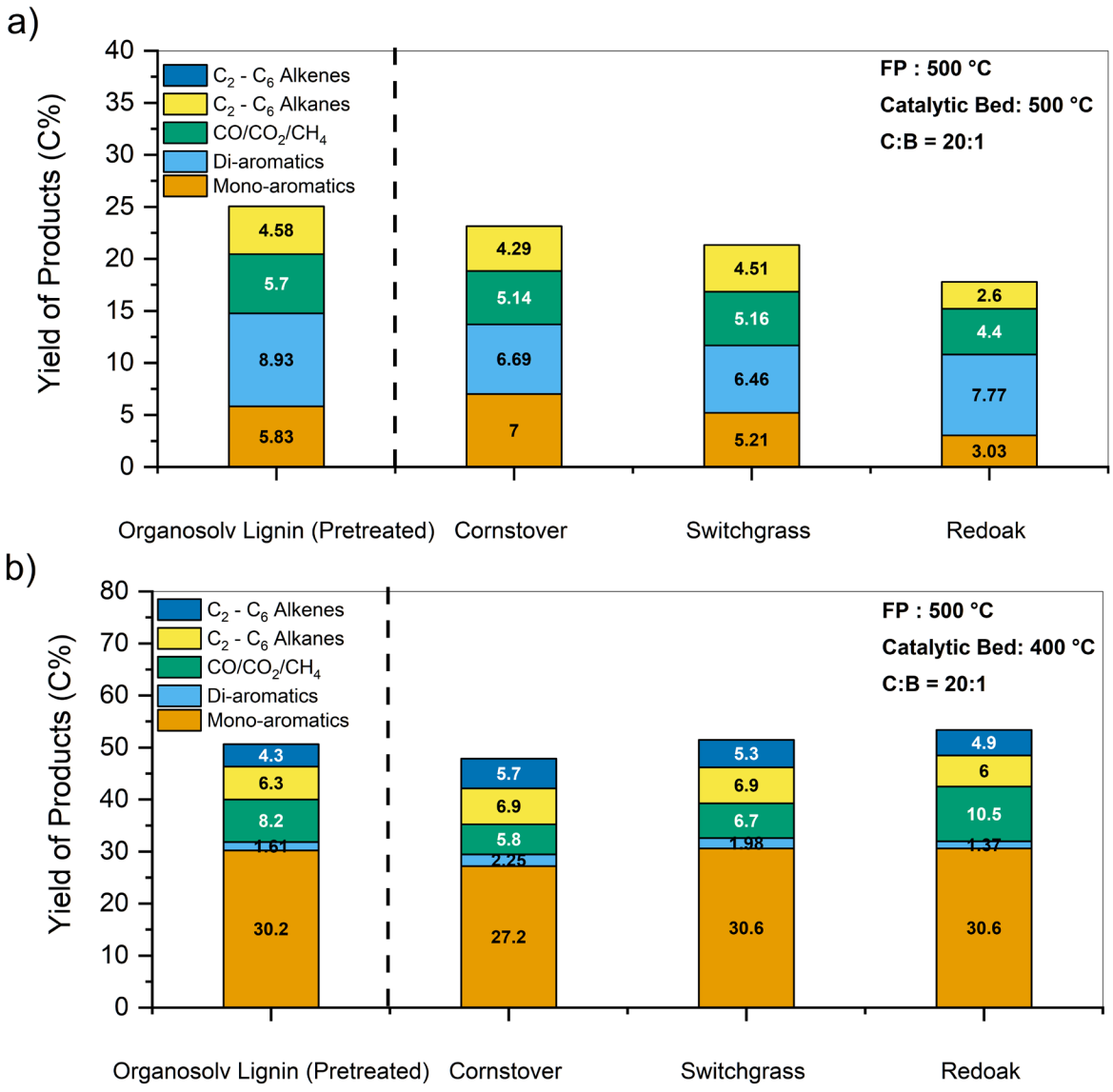


Figure S9. Carbon yields of products obtained from **a)** CFP and **b)** HDO of lignin oil obtained from one-pot fractionation and pretreatment of biomass at 250 ℃, EtOH over Pd/C catalyst. Reaction conditions for CFP: ZSM-5 (Si/Al = 15) catalyst, fast pyrolysis temperature (FP): 500 ℃, catalytic bed temperature: 500 ℃, catalyst: biomass = 20:1; reaction conditions for HDO: MoO_3 catalyst, fast pyrolysis temperature (FP): 500 ℃, catalytic bed temperature: 500 ℃, catalyst: biomass = 20:1. The results for organosolv lignin pretreated at 250 ℃ in EtOH over Pd/C are also provided for reference.

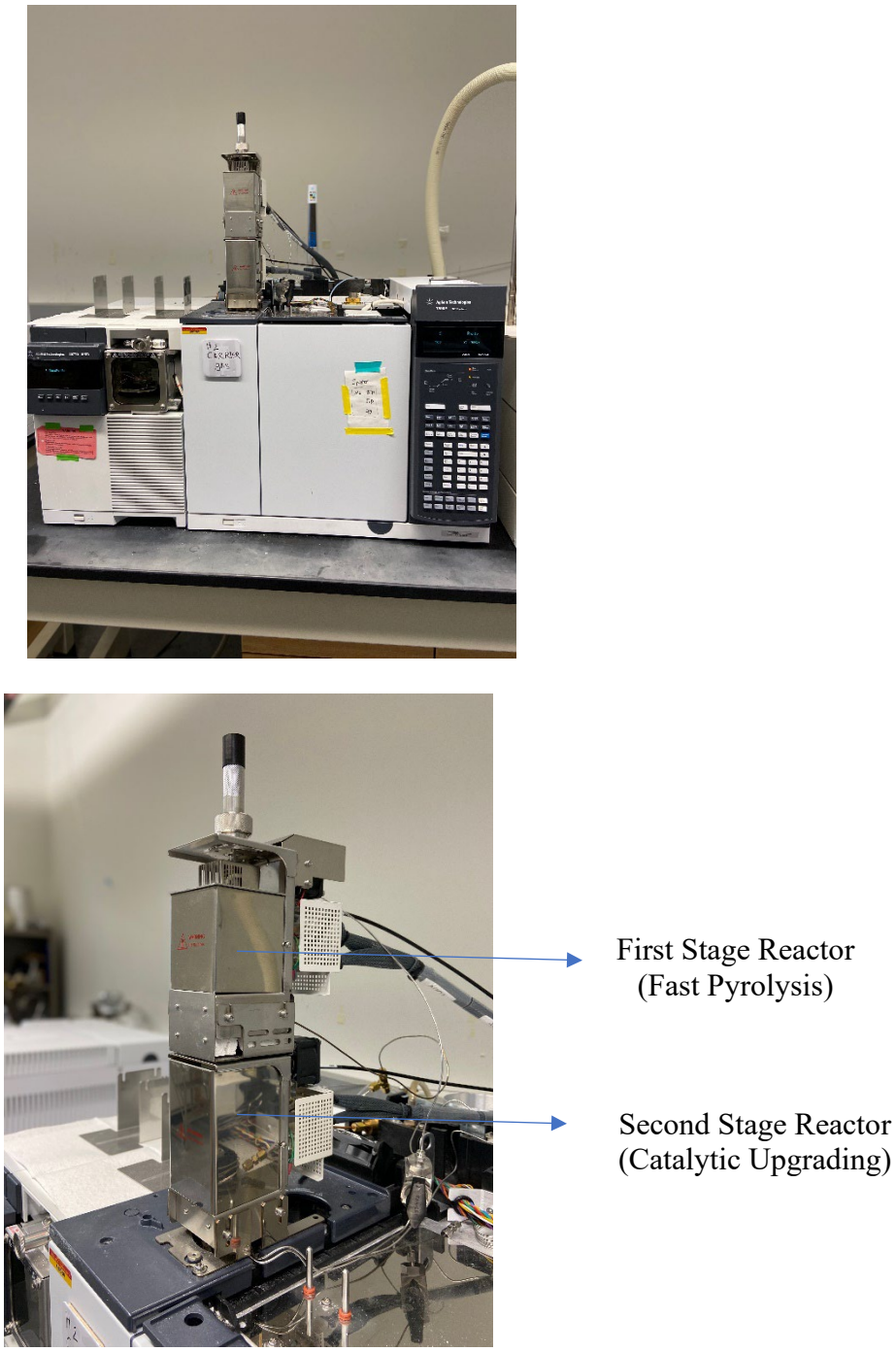


Figure S10. Picture of the single-shot tandem micro-pyrolyzer reactor used for fast pyrolysis, catalytic fast pyrolysis, and hydrodeoxygenation experiments. The first image shows the complete system setup along with the online GC-FID/TCD/MS. The second image shows the reactor setup (top: fast pyrolysis, bottom: catalytic reactor).

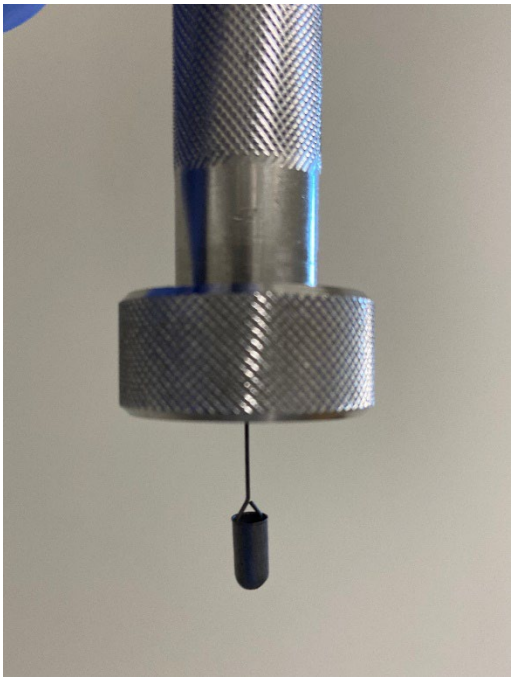


Figure S11: Picture of the sample cup where lignin/pretreated samples are placed for fast pyrolysis or CFP/HDO experiments. The sample is dropped into the reactor setup where it undergoes fast pyrolysis in the first stage reactor, and the produced volatiles are carried to the second stage reactor for catalytic upgrading. Char measurements are undertaken by measuring the difference in weights of sample cups before and after the reaction.

a)

b)

Figure S12. Pictures of the catalytic bed used for CFP and HDO experiments **a)** before reaction, **b)** after four reactions.

Tables S1-S6

Table S1. Metallic surface areas measured by CO chemisorption.

Catalyst	**Metallic Surface Area (m^2/g-sample)**
5 wt% Pd/C	3.39
5 wt% Ru/C	3.04
5 wt% Pd/Al_2O_3	4.52
5 wt% Ru/Al_2O_3	4.63
HY	NA

Table S2. Detailed product yields for the HDO of the recovered lignin oils.

Compound	Product Yield (C%) *Corn Stover*	Product Yield (C%) *Switchgrass*	Product Yield (C%) *Red Oak*
Benzene	4.62	5.51	6.26
Toluene	7.50	9.07	10.83
Ethylbenzene	4.52	4.78	3.51
m-Xylene	2.69	3.37	3.73
o/p-Xylene	0.98	1.19	1.66
n-Propylbenzene	4.91	4.76	4.86
1-Ethyl-3-methylbenzene	1.71	1.61	1.49
1-Ethyl-4-methylbenzene	0.28	0.21	0.22
Mesitylene	0.76	0.79	0.75
1,2,3-Trimethylbenzene	0.11	0.09	0.56
1,3-Diethylbenzene	0.16	0.04	0.05
2-Propenylbenzene	2.42	1.92	1.50
1,4-Diethylbenzene	0.48	0.26	1.35
1,2-Diethylbenzene	0.15	-	0.30
Indene	0.15	0.05	0.20
Sum of aromatics	***34.16***	***34.55***	***39.25***
Ethane	5.03	5.51	3.85
Propane	2.63	3.38	3.56
i-Butane	0.57	0.68	0.35
n-Butane	2.02	2.06	1.24
n-Pentane	1.11	1.51	1.08
Hexane	-	0.61	0.37
Sum of $C_2 - C_6$ alkanes	***11.36***	***13.75***	***10.87***
Ethylene	1.57	1.88	1.33
Propylene	0.72	0.71	0.72
1-Butene	0.12	0.12	0.06
trans-2-Butene	0.27	0.19	0.09
cis-2-Butene	0.16	0.12	0.07

1-Pentene	-	1.43	1.13
trans-2-Pentene	0.4	0.33	0.28
1-Hexene	-	0.69	0.5
3-Hexene	1.00	0.84	0.88
Sum of $C_2 - C_6$ alkenes	***4.68***	***6.31***	***5.06***

Table S3. Detailed product yields for the HDO of recovered water-soluble fractions.

Compound	**Product yield (C%)** ***Corn Stover***	**Product yield (C%)** ***Switchgrass***	**Product yield (C%)** ***Red Oak***
Benzene	1.41	2.72	4.94
Toluene	2.85	3.83	4.09
Ethylbenzene	0.15	0.78	1.07
m-Xylene	1.12	-	0.00
o/p-Xylene	0.40	1.91	1.72
n-Propylbenzene	0.66	0.79	0.72
1-Ethyl-3-methylbenzene	0.60	0.19	0.60
1-Ethyl-4-methylbenzene	0.13	0.60	0.58
Mesitylene	0.45	0.0076	0.07
1,2,3-Trimethylbenzene	0.09	0.63	0.52
1,3-Diethylbenzene	0.03	0.09	0.06
2-Propenylbenzene	0.48	-	0.00
1,4-Diethylbenzene	0.16	0.09	0.25
1,2-Diethylbenzene	0.08	0.06	0.08
Sum of aromatics	***10.20***	***11.76***	***14.70***
Ethane	4.02	13.46	9.79
Propane	3.08	5.44	5.57
i-Butane	0.63	1.27	1.30
n-Butane	3.27	4.18	4.66
n-Pentane	2.27	4.51	3.73
Hexane	0.78	1.68	2.49
Cyclohexane	0.93	1.82	2.86
Sum of C_2 – C_6 alkanes	***14.98***	***33.00***	***30.40***
Ethylene	2.75	7.81	8.13
Propylene	2.17	2.80	2.33
1-Butene	0.73	0.42	0.34
trans-2-Butene	0.99	0.93	0.78
cis-2-Butene	0.66	0.57	0.5
1-Pentene	3.43	6.21	4.86

trans-2-Pentene	1.1	0.48	0.56
1-Hexene	-	1.91	2.94
Cyclopentene	1.65	8.08	2.83
Sum of C_2 – C_6 alkenes	***14.90***	***29.21***	***25.60***

Table S4. Sugar release yields obtained through enzymatic hydrolysis of corn stover and EtOH-insoluble pulp obtained from corn stover after one pot fractionation and pretreatement.

Sample	**Glucose Yields (mg/g of biomass/pulp)**	**Xylose Yields (mg/g of biomass/pulp)**
Corn Stover	94.38 ± 4.8	31.33 ± 0.87
EtOH Insoluble Pulp (Corn Stover)	345.96 ± 2.06	108.69 ± 1.39

Table S5. State-of-the-art results published to date for the lignin-first fractionation and upgrading of lignocellulosic biomass. The results obtained in the present work for corn stover, switchgrass, and red oak are provided for comparison

Lignocellulose Source	**Fractionation Conditions**	**Upgrading Conditions**	**Yield (wt% reference to lignin content)**	**Yield (wt% reference to initial weight of biomass)**
Birch Wood[14]	Temperature = 235 ºC Solvent = Methanol Catalyst = 5 wt% Ru/C Pressure = 30 bar H_2 (RT) Time = 3 h Ratio of LB:C = 10 (wt/wt) Volume of solvent: Mass of LB = 0.1875 g/ mL	*Step 1: Hydro-processing* (Gas phase) Temperature = 305 ºC Catalyst = 64 wt% Ni/SiO_2 WHSV = 6 $hour^{-1}$ *Step 2: D*ealkylation Temperature = 410 ºC Catalyst = Z140-H WHSV = 2.8 $hour^{-1}$	Phenol: 19.8 wt% Propylene: 9.3 wt% Cresols, benzenes, and others:4.2 wt%	Phenol: 7.1 wt% Propylene: 3.7 wt% Cresols, benzenes, and others:2.0 wt%
Pine Wood[14]	Temperature = 235 ºC Solvent = Methanol Catalyst = 5 wt% Ru/C Pressure = 30 bar H_2 (RT) Time = 3 h Ratio of LB:C = 10 (wt/wt) Volume of solvent: Mass of LB = 0.1875 g/ mL	*Step 1: Hydro-processing (Gas phase)* Temperature = 285 ºC Catalyst = 64 wt% Ni/SiO_2 WHSV = 4.4 $hour^{-1}$ *Step 2: Dealkylation* Temperature = 410 ºC Catalyst = Z140-H WHSV = 3.7 $hour^{-1}$	Phenol: 6.39 wt% Propylene: 2.87 wt% Cresols, benzenes, and others:1.0 wt%	Phenol: 1.8 wt% Propylene: 0.8 wt% Cresols, benzenes, and others: 0.3 wt%
Poplar or Spruce[15]	Temperature = 180 ºC Solvent = 2- Propanol: Water (7:3 v/v) Catalyst = Raney Ni Time = 3 h Ratio of LB:C = 1.5 (wt/wt) Volume of solvent: Mass of LB = 0.1 g/ mL	*Hydrodeoxygenation* Temperature = 300 ºC Catalyst = Phosphidated–Ni/SiO_2 Lignin bio-oil = 100 mg Mass of Catalyst = 200 mg Time = 20 h Pressure = 50 bar H_2 (RT)	Aliphatic C_6-C_{10} and C_{14}-C_{20} : 40 – 45 wt%	Aliphatic C_6-C_{10} and C_{14}-C_{20} : 10 wt%

Poplar or Spruce[15]	Temperature = 180 ºC Solvent = 2- propanol: water (7:3 v/v) Catalyst = Raney Ni Time = 3 h Ratio of LB:C = 1.5 (wt/wt) Volume of solvent: Mass of LB = 0.1 g/ mL	*Hydrodeoxygenation* Temperature = 350 ºC Catalyst = Phosphidated – Ni/SiO_2 Lignin bio-oil = 100 mg Mass of Catalyst = 200 mg Time = 20 h Pressure = 5 bar H_2 (RT)	Aromatic C_6-C_{10} and C_{14}-C_{20} : 30 – 33.8 wt% Aliphatic C_6-C_{10} and C_{14}-C_{20} : 10 – 11.3 wt%	Aromatic C_6-C_{10} and C_{14}-C_{20} : 7.5 wt% Aliphatic C_6-C_{10} and C_{14}-C_{20} : 2.5 wt%
Apple Wood[16]	Temperature = 250 ºC Solvent = Methanol Catalyst = 5 wt% Ru/SiC Pressure = 10 bar H_2 (RT) Time = 3 h Ratio of LB:C = 6.67 (wt/wt) Volume of solvent: Mass of LB = 0.05 g/ mL	*Hydrodeoxygenation* Temperature = 350 ºC Catalyst = MoO_3 Mass of catalyst = 5 g Solvent = Hexane Lignin oil flow-rate = 0.2 mL/min H_2 flow-rate = 500 mL/min		Aromatic C_7-C_{12} products = 6.9 wt%
Pinewood Sawdust[17]	Temperature = 230 ºC Solvent = Methanol: Water (1.12:1 v/v) Catalyst = 5 wt% Pt/C Pressure = 30 bar H_2 (RT) Time = 3 h Ratio of LB:C = 20 (wt/wt) Volume of solvent: Mass of LB = 0.05 g/ mL	*Demethoxylation + Transalkylation* Temperature = 350 ºC Catalyst = HZSM-5 + MoP/SiO_2 (1:1 w/w) Mass of catalyst = 200 mg Lignin oil flow-rate = 0.15 mL/min (0.5 mol% in benzene) H_2 flow-rate = 30 mL/min Pressure = 90 bar	Phenol = 5.1 wt%	Phenol = 1.3 wt%
Birch Wood[9]	Temperature = 225 ºC Solvent = Methanol: Catalyst = 5 wt% Pd/C Pressure = 30 bar H_2 (RT) Time = 6 h Ratio of LB:C = 10 (wt/wt) Volume of solvent: Mass of LB = 0.1 g/ mL	*Dehydrogenative-Decarbonylation + Hydrodeoxygenation* Temperature = 300 ºC Catalyst = 2 wt% $RuFe/Nb_2O_5$ Mass of catalyst = 20 mg Mass of lignin oil = 100 mg Time = 15 h	Ethylbenzene = 8.2 wt%	

Corn Stover ***(This work)***	Temperature = 250 ºC Solvent = Ethanol: Catalyst = 5 wt% Pd/C Pressure = 30 bar H_2 (RT) Time = 3 h Ratio of LB:C = 10 (wt/wt) Volume of solvent: Mass of LB = 0.025 g/ mL	*Fast pyrolysis* Temperature = 500 ºC *Hydrodeoxygenation* Temperature = 400 ºC Mass of catalyst = 10 mg Mass of lignin-oil = 500 µg H_2 flow-rate: 120sccm	Aromatics = 24.7 wt% Alkenes = 3.5 wt% Alkanes = 10.4 wt%	Aromatics = 6.1 wt% Alkenes = 2 wt% Alkanes = 3.5 wt%
Switchgrass ***(This work)***	Temperature = 250 ºC Solvent = Ethanol: Catalyst = 5 wt% Pd/C Pressure = 30 bar H_2 (RT) Time = 3 h Ratio of LB:C = 10 (wt/wt) Volume of solvent: Mass of LB = 0.025 g/ mL	*Fast pyrolysis* Temperature = 500 ºC *Hydrodeoxygenation* Temperature = 400 ºC Mass of catalyst = 10 mg Mass of lignin-oil = 500 µg H_2 flow-rate: 120sccm	Aromatics = 24.1 wt% Alkenes = 4.0 wt% Alkanes = 5.9 wt%	Aromatics = 7.1 wt% Alkenes = 4.1 wt% Alkanes = 3.0 wt%
Red Oak ***(This work)***	Temperature = 250 ºC Solvent = Ethanol: Catalyst = 5 wt% Pd/C Pressure = 30 bar H_2 (RT) Time = 3 h Ratio of LB:C = 10 (wt/wt) Volume of solvent: Mass of LB = 0.025 g/ mL	*Fast pyrolysis* Temperature = 500 ºC *Hydrodeoxygenation* Temperature = 400 ºC Mass of catalyst = 10 mg Mass of lignin-oil = 500 µg H_2 flow-rate: 120sccm	Aromatics = 28.8 wt% Alkenes = 4.0 wt% Alkanes = 8.7 wt%	Aromatics = 9.5 wt% Alkenes = 3.3 wt% Alkanes = 5.2 wt%

Table S6. List of calibration standards used for monomer quantification after pretreatment, fast pyrolysis, CFP, and HDO along with vendor and purity.

Calibration Standards for Monomer Quantification	Calibration Standards for Fast Pyrolysis	Calibration Standards for CFP and HDO
2-Ethyl Phenol (Sigma Aldrich, >99%)	CO (Airgas)	Ethane (Airgas, Mixture 2 mole% in He)
Propylguaiacol (Sigma Aldrich, >99%)	CH_4 (Airgas)	Ethylene (Airgas, Mixture 2 mole% in He)
3-(3,4-Dimethoxyphenyl)-1-propanol (Sigma Aldrich, >99%)	$CO\ (Airgas)_2$	Propane (Airgas, Mixture 2 mole% in He)
Ethyl 3-(4-hydroxyphenyl)propanoate (Fischer Scientific, >95%)	Phenol (Sigma Aldrich, >99%)	Propylene (Airgas, Mixture 2 mole% in He)
p-coumaric acid (MP Biomedicals Inc, >99%)	Guaiacol (ACROS Organics, >99%)	Benzene (Sigma Aldrich, >99%)
	o-Cresol (Sigma Aldrich, >99%)	Toluene (Fisher Scientific, >99%)
	p-Cresol (ACROS Organics, >99%)	m-Xylene (Fisher Scientific, >99%)
	p-Methylguaiacol (Sigma Aldrich, >98%)	1,4 Diethyl Benzene (Alfa Aesar, >98%)
	4-Ethylphenol (Sigma Aldrich, >99%)	Propyl Benzene (Sigma Aldrich, >98%)
	4-Ethylguaiacol (Alfa Aesar, >98%)	Mesitylene (Sigma Aldrich, >98%)
	4-Vinyl Phenol (ACROS Organics,95%, 10% solution in propylene glycol)	Naphthalene (ACROS Organics, >99%)
	4-Vinyl Guaiacol (Frontier Scientific, 98%)	
	Eugenol (Sigma Aldrich, 99%)	
	Isoeugenol (ACROS Organics, 98% (cis+trans))	
	1,3,5-Trimethoxybenzene (Sigma Aldrich, >99%)	
	Vanillin (Sigma Aldrich, >99%)	
	3',5'-Dimethoxyacetophenone (Alfa Aesar, 97%)	
	2,6-Dimethoxy-4-allylphenol (Sigma Aldrich, > 95%)l	

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