Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Catalyst choice impacts aromatic monomer yields and selectivity in hydrogen-free reductive catalytic fractionation

Jacob K. Kenny, [a,b,c] David G. Brandner,[b,c] William E. Michener,[b] Yuriy, Román-Leshkov,[e] Gregg T. Beckham[b,c,*] and J. Will Medlin[a, *]

a. Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder 80303, CO US
b. Renewable Resources and Enabling Sciences Center, National Renewable Energy Laboratory, 15013 Denver W Pkwy, Golden, CO 80401, US
c. Center for Bioenergy Innovation, Oak Ridge National Laboratory (ORNL), Oak Ridge, TN 37831, US
d. Department of Chemical Engineering, Massachusetts Institute of Technology, 25 Ames Street, Cambridge, MA 02139, US
* Email: gregg.beckham@nrel.gov; will.medlin@colorado.edu

Materials and Methods:

Biomass substrate

The poplar is the same as used in our previous work.[1]

Batch RCF reactions

2 g of whole poplar biomass (with extractives), 100 mg of catalyst, 30 mL of MeOH (Sigma-Aldrich) were added to a 75 mL Parr reactor with a magnetic stir bar. The reactor was sealed, purged, and pressure-tested with He up to reaction pressure. For H_2-free reactions, the pressure of He was reduced to ~ 1 bar. For reactions with H_2, H_2 was loaded at a pressure of 30 bar. The stirring rate was set to 800 rpm, and reactor was heated to 225°C for the desired reaction time (for simplicity "reaction time" is defined to start 30 minutes after heating was initiated. Example: a reaction time of 6 hours corresponds to a total time of 6.5 hours. See **Figure S1** for temperature profile). For time course reactions, sacrificial reactors were used (1 reactor per sample) rather than sampling multiple points from one reactor. The reactors were quenched at the end of the reactions in an ice bath for 45 minutes. The headspace of H_2-free reactions was sampled with a gas bag. Liquid contents were filtered first through a tared qualitative glass filter and then through a 0.2 µm PES syringe filter, and the methanol solvent was evaporated in a rotary evaporator. Ethyl acetate (Sigma-Aldrich) (20 mL) and water (20 mL) were added to the crude RCF oil and separated in a separatory funnel. The aqueous layer was washed with an additional 20 mL ethyl acetate, and the organic layers were combined in a tared round bottom flask. The ethyl acetate was then removed via rotary evaporation, yielding an oil which was massed, and termed *lignin oil*. Solid residue, including catalyst, was massed by massing the qualitative filter.

Catalyst preparation of 5% Ni/C

A 5 wt% Ni/C catalyst was prepared similar to the preparation performed by Brandner *et al.*, except at a 5 wt% loading.[1] The other catalysts (Ru/C, Pd/C, Pt/C) were purchased from Sigma-Aldrich and used as received.

Model compound reactions

Model compound reactions were performed in a similar manner as RCF reactions. 60 mg of the selected model compound (coniferyl alcohol: Sigma-Aldrich; guaiacyl guaiacylglycerol-beta-guaiacyl ether, TCI America), or 30 mg of coniferyl aldehyde (Sigma-Aldrich) was added to a 75 mL Parr reactor along with 20 mg of catalyst and 30 mL of methanol. The reactor was then sealed, purged, and pressure-tested with He up to reaction pressure. For H_2-free reactions, the pressure of He was reduced to ~ 1 bar. For reactions with H_2, H_2 was loaded at a pressure of 30 bar. The stirring rate was set to 800 rpm, and reactor was heated to 225°C for 1 hour before cooling in an ice bath for 45 minutes. The reaction mixture was filtered through a 0.2 µm filter. Reaction products were analyzed with an Agilent 1290 Infinity II LC equipped with a Phenomenex Luna C18(2)-HST column. Monomer yields for model compound reactions are reported on a molar basis (as opposed to mass basis like poplar RCF yields).

Monomer analysis with GC

The lignin oil was dissolved in 15 mL of acetone. ¼ mL of this oil/acetone solution was added to a vial, along with ¼ mL of pure acetone, and ½ mL of 2 g/L tri-tertbutyl benzene (Sigma-Aldrich) as an internal standard. Samples were injected on an Agilent 8890 gas chromatograph equipped with an FID detector utilizing an HP-5 column. Quantification was performed using calibration curves with authentic standards for all compounds. All commercially available standards were purchased from Sigma Aldrich. 4-

propenylsyringol was purchased from AKos GmbH. Ethyl syringol was purchased from AAblocks. Several standards, 4-(3-methoxy)propylguaiacol, 4-propylsyringol, 4-(3-methoxy)propylsyringol, and 4-propanolsyringol, were synthesized in house.[1]

$$monomer\ yield\ \% = \frac{\sum_1^i m_i}{\%\ lignin\ content * m_{poplar}}$$

where m_i is the mass of monomer i, %lignin content is the total lignin content measured from compositional analysis, and m_{poplar} is the mass of poplar loaded.

Headspace analysis

Gas from the headspace of H_2-free reactions was captured from the reactor with a gas bag and withdrawn from the gas bag into a syringe. The sample was injected onto an Agilent 7890A gas chromatograph equipped FID and TCD, with two Wasson columns (part numbers 2428, 2378) to measure the mole fraction of each component. Moles of components were calculated using the ideal gas law assuming a headspace volume of 45 mL.

Compositional analysis

Compositional analysis on the solids followed the NREL Laboratory Analytical Procedure (LAP).[2,3]

Supplemental Figures

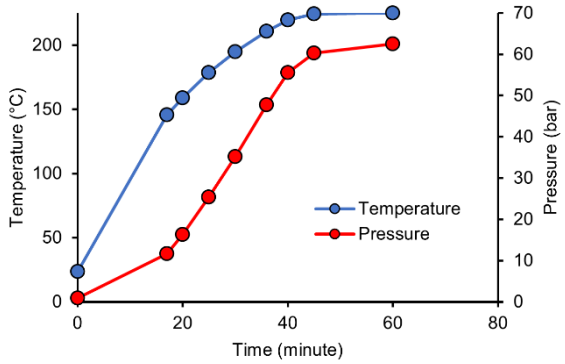

Figure S1. Heating and pressure profile of batch reactor heat-up during H_2-free RCF. Pressure during RCF with H_2 reached approximately 83 bar.

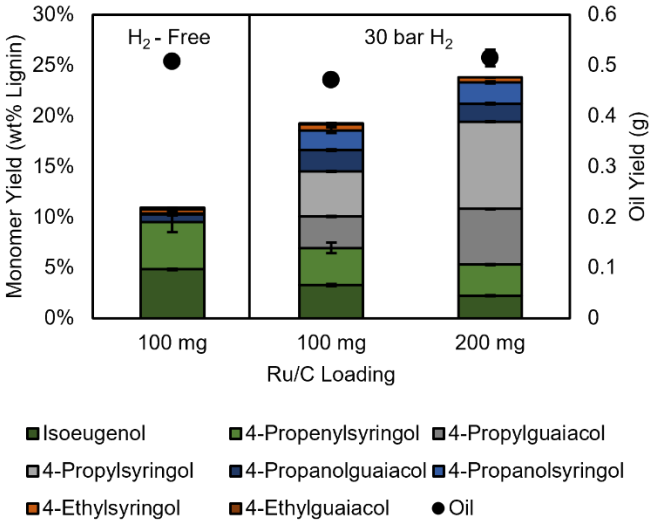

Figure S2. Comparison of monomer yields (not including methyl paraben or phenol as these presumably derive from para-hydroxy benzoate) with 100 and 200 mg Ru/C with 30 bar H_2, showing increased monomer yields for the higher catalyst loading, indicating that reactions with 100 mg Ru/C are limited by the rate of hydrogenolysis. Note, reactions with 200 mg Ru/C were performed in duplicate, and error bars show the range of two experiments. Conditions are the same as those in **Figure 2,** except catalyst loading is as specified here. Data presented in **Table S12.**

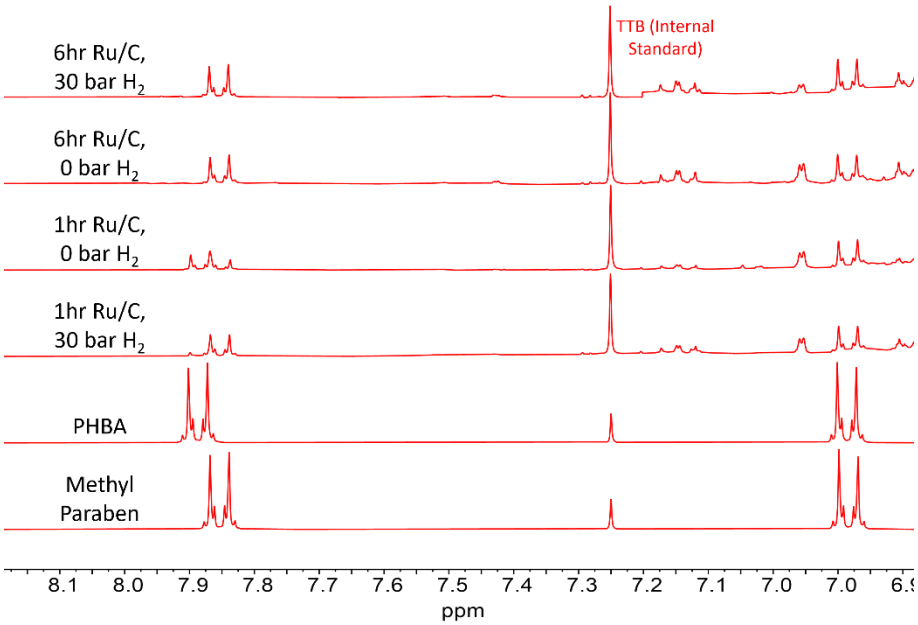

Figure S3. ^{1}H spectrum of para-hydroxy benzoate (PHBA), methyl paraben, and RCF oils from reactions with and without H_2. Solvent: d_6-acetone, approximately 15 mg/mL lignin oil.

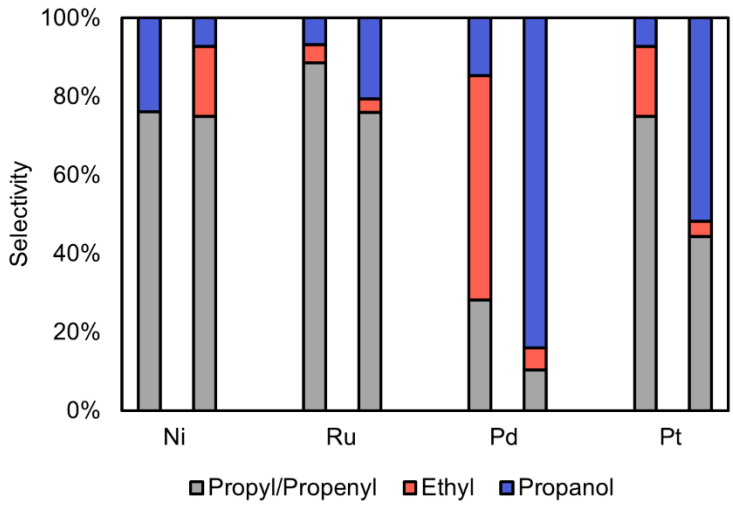

Figure S4. Selectivity to ethyl, propyl/propenyl, and propanol products calculated from **Figure S2**, normalized to 100%, showing that high selectivity to ethyl products consistently coincided with low selectivity to propanol products. Left bars are for reactions in H_2-free conditions, and right bars are for reactions with 30 bars H_2. For Ni and Ru, selectivity to propyl/propenyl products remains consistent even when external H_2 is added. For Pd and Pt, external H_2 has a large impact on selectivity.

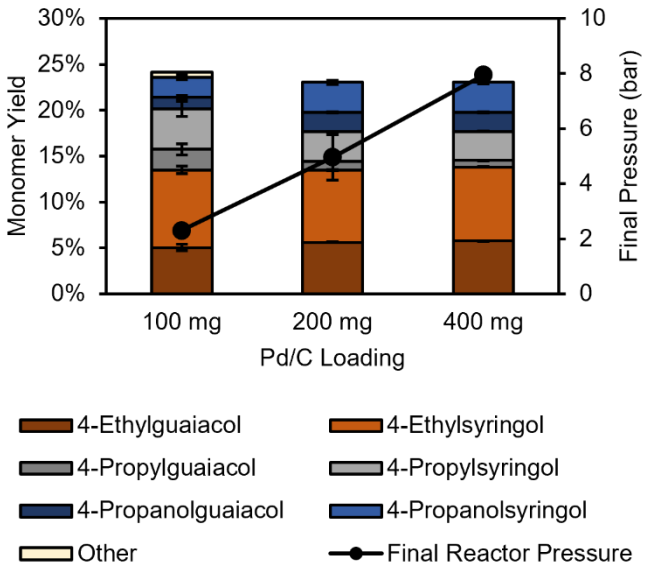

Figure S5. Lignin derived monomer yields (not including methyl paraben or phenol as these presumably derive from para-hydroxy benzoate) for H_2-free reactions with different amounts of Pd/C catalyst, showing that ethyl selectivity remains constant. Isoeugenol and propenyl syringol were not detected and are not included in the legend. Final reactor pressure refers to the pressure of the reactor post reaction after it had cooled down to room temperature. Conditions are the same as those in **Figure 2,** except catalyst loading is as specified here. Oil yields are not shown, but are included in the data table presented in **Table S13.**

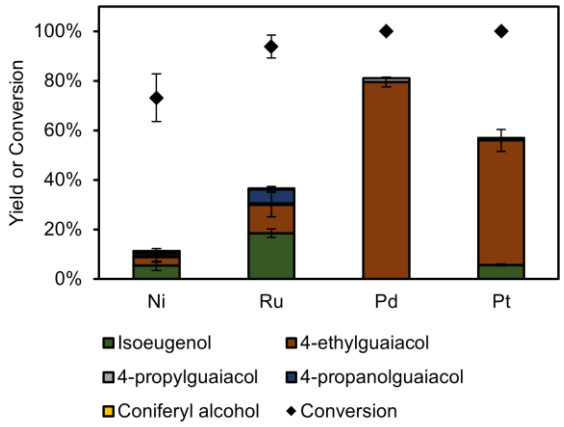

Figure S6. Monomer yields and conversions from coniferyl aldehyde. Conditions: 30 mg coniferyl aldehyde, 1 hour reaction after 30 minute heat-up, 20 mg catalyst, 30 mL methanol, 0 bar H_2, 225°C

Data Tables: Note – error indicates the standard deviation of the monomer yield.

Table S1. Composition of biomass substrate used in RCF reactions.

Substrate	Ash	Extractives	Lignin	Glucan	Xylan	Galactan	Arabinan	Mannan	Acetyl	Total
OP-367 (*P. deltoides x P. nigra*)	0.69	3.54	25.95	45.31	13.24	1.34	0.14	2.79	3.84	97.43

Table S2. Monomer yields for time course RCF reactions of poplar using Ru/C with and without 30 bar external H_2

H_2 (bar)	Time (hour)	EG	ES	P(ene) G	P(ene) S	PG	PS	P(OH) G	P(OH)S	Other	Phenol	MP/*p* HBA	Total	Error +/-
0	1	0.0%	0.0 %	4.0%	4.2%	0.0 %	0.0 %	0.5%	0.0%	0.0%	1.0%	2.3%	12.1 %	0.6%
	3	0.1%	0.4 %	4.8%	4.7%	0.0 %	0.0 %	0.7%	0.1%	0.0%	1.4%	2.4%	14.7 %	1.4%
	6	0.4%	0.7 %	4.7%	6.0%	0.4 %	0.4 %	1.0%	0.4%	0.0%	1.5%	3.2%	18.6 %	0.3%
30	1	0.0%	0.3 %	3.6%	4.7%	1.7 %	2.3 %	1.9%	1.7%	0.2%	1.0%	2.2%	19.7 %	0.1%
	3	0.1%	0.6 %	3.3%	3.7%	3.1 %	4.5 %	2.1%	2.0%	0.0%	1.4%	2.4%	23.0 %	0.5%
	6	0.4%	0.9 %	2.3%	2.9%	4.1 %	6.7 %	2.2%	2.6%	0.0%	1.5%	3.4%	27.0 %	0.3%

continued:

	Time (hour)	Oil (g)	Error +/-
0	1	0.371	0.005
	3	0.508	0.007
	6	0.546	0.007
30	1	0.409	0.013
	3	0.471	0.004
	6	0.537	0.016

Table S3. H_2 and CO gas yields during time course H_2-free RCF with Ru/C corresponding **Figure S4**. Errors are the standard deviation of triplicate measurements of the total monomer yield.

Time (hour)	H_2 (mmol)	Error +/-	CO (mmol)	Error +/-	CO_2 (mmol)	Error +/-
1	1.34	0.26	0.90	0.15	0.11	0.03
3	3.63	0.39	2.45	0.14	0.23	0.05
6	7.09	0.21	3.86	0.03	0.31	0.02

Table S4. Monomer yields for RCF of poplar with and without 30 bar external H_2. Errors are the standard deviation of triplicate measurements of the total monomer yield.

H_2 (bar)		EG	ES	P(ene)G	P(ene)S	PG	PS	P(OH)G	P(OH)S	Other	Phenol	MP/*p*HBA	Total	Error +/-
0	Ni	0.0%	0.0%	1.5%	0.5%	0.0%	0.0%	0.3%	0.3%	0.0%	1.1%	2.2%	6.0%	1.1%
	Ru	0.1%	0.4%	4.8%	4.7%	0.0%	0.0%	0.7%	0.1%	0.0%	1.4%	2.4%	14.7%	0.6%
	Pd	5.0%	8.5%	0.0%	0.0%	2.2%	4.4%	1.3%	2.2%	0.8%	1.5%	2.2%	28.1%	1.5%
	Pt	1.3%	2.6%	5.0%	7.1%	1.0%	3.6%	1.1%	0.5%	0.6%	1.6%	2.4%	26.8%	1.6%
30	Ni	0.1%	0.5%	3.5%	3.2%	2.5%	3.1%	1.5%	1.4%	0.3%	1.4%	2.7%	19.9%	1.4%
	Ru	0.1%	0.6%	3.3%	3.7%	3.1%	4.5%	2.1%	2.0%	0.0%	1.4%	2.4%	23.0%	0.5%
	Pd	0.4%	0.9%	0.0%	0.0%	0.4%	2.1%	9.0%	11.2%	0.4%	1.3%	2.5%	28.4%	1.3%
	Pt	0.3%	0.7%	0.6%	0.3%	2.9%	7.0%	5.7%	6.9%	0.9%	1.7%	2.7%	29.8%	1.7%

ES: ethyl syringol, EG: ethyl guaiacol, P(ene)G: isoeugenol, P(ene)S: 4-propenyl syringol, PG: 4-propyl guaiacol, PS: 4-propyl syringol, P(OH)G: 4-(3-hydroxyl propyl) guaiacol, P(OH)S: 4-(3-hydroxyl propyl) syringol, other refers to the sum of 4-(3-methoxy propyl) guaiacol and 4-(3-methoxy propyl) syringol

Table S5. H_2 gas yields from control and H_2-free RCF reactions. Data are provided in units of mmol. Errors are the standard deviation of triplicate measurements of the total monomer yield.

Catalyst	Control	Error +/-	RCF	Error +/-
Ni/C	15.7	2.1	0.02	0.04
Ru/C	17.9	1.0	3.6	0.4
Pd/C	10.3	1.3	1.5	0.2
Pt/C	4.6	0.9	4.0	0.30

Table S6. Monomer yields from H_2-free reactions with coniferyl alcohol. Errors are the standard deviation of triplicate measurements of the total monomer yield.

Analyte	Ni	Ru	Pd	Pt	None
Isoeugenol	30.3%	48.4%	0.0%	39.9%	0.8%
Ethyl Guaiacol	0.4%	0.7%	39.9%	13.7%	0.0%
Propyl Guaiacol	1.6%	0.6%	36.0%	8.6%	0.0%
Propanol Guaiacol	0.2%	1.6%	2.6%	1.8%	0.0%
Conversion	98.2%	98.9%	100.0%	99.6%	85.8%
Total Monomer Yield	32.4%	51.2%	78.5%	64.1%	0.8%
Error +/-	3.6%	6.4%	4.9%	7.4%	0.1%

Table S7. Monomer yields from 30 bar H_2 reactions with coniferyl alcohol. Errors are the standard deviation of triplicate measurements of the total monomer yield.

Analyte	Ni	Ru	Pd	Pt	None
Isoeugenol	0.0%	0.0%	0.0%	0.0%	6.8%
Ethyl Guaiacol	0.0%	2.3%	0.1%	0.1%	0.1%
Propyl Guaiacol	26.9%	3.6%	2.5%	16.1%	0.5%
Propanol Guaiacol	47.2%	57.1%	73.9%	66.7%	0.0%
Conversion	100.0%	100.0%	100.0%	100.0%	95.6%
Total Monomer yield	74.0%	63.0%	76.5%	82.8%	7.4%
Error +/-	3.0%	1.9%	8.6%	2.5%	8.4%

Table S8. Monomer yields from H_2-free reactions with GGE. Errors are the standard deviation of triplicate measurements of the total monomer yield.

Analyte	Ni	Ru	Pd	Pt	None
Isoeugenol	3.8%	57.6%	0.0%	39.1%	0.5%
Ethyl Guaiacol	2.9%	1.4%	29.9%	16.7%	1.2%
Propyl Guaiacol	0.2%	2.4%	5.6%	14.3%	0.0%
Propanol Guaiacol	0.0%	0.7%	0.3%	2.4%	0.0%
Acetovanillone	0.0%	0.0%	23.8%	0.0%	0.0%
1-Propanone, 1-(4-hydroxy-3-methoxyphenyl)	0.0%	0.0%	9.5%	0.0%	0.0%
Coniferyl alcohol*	9.6%	0.3%	0.0%	1.3%	17.4%
Conversion	92.2%	100.0%	100.0%	93.0%	86.3%
Guaiacol	71.5%	91.7%	72.7%	85.2%	67.9%
Total Monomer Yield	6.9%	62.1%	35.9%	72.6%	1.6%
Error +/-	1.0%	2.9%	3.6%	1.7%	0.5%

*coniferyl alcohol is not included in total monomer yield.

Table S9. Monomer yields from 30 bar H_2 reactions with GGE. Errors are the standard deviation of triplicate measurements of the total monomer yield.

Analyte	Ni	Ru	Pd	Pt	None
Isoeugenol	0.0%	0.0%	0.0%	1.6%	8.5%
Ethyl Guaiacol	0.0%	2.5%	0.6%	0.5%	0.8%
Propyl Guaiacol	45.0%	10.8%	3.5%	23.0%	0.9%
Propanol Guaiacol	41.0%	48.9%	55.5%	54.7%	2.8%
Coniferyl alcohol*	0.0%	0.0%	0.0%	0.3%	19.2%
Conversion	100.0%	100.0%	100.0%	93.0%	89.1%
Guaiacol	90.0%	54.8%	58.3%	83.1%	72.1%
Total Monomer Yield	86.0%	62.2%	59.5%	79.9%	13.0%
Error +/-	1.1%	1.0%	2.4%	2.8%	12.0%

*coniferyl alcohol is not included in total monomer yield.

Table S10. Monomer yields from H_2-free reactions with coniferyl aldehyde. Errors are the standard deviation of triplicate measurements of the total monomer yield.

Analyte	Ni	Ru	Pd	Pt
Isoeugenol	5.3%	18.5%	0.0%	5.6%
4-ethylguaiacol	3.5%	11.6%	79.5%	50.3%
4-propylguaiacol	0.3%	0.5%	1.5%	0.9%
4-propanolguaiacol	1.1%	5.8%	0.0%	0.0%
Coniferyl alcohol*	1.0%	0.3%	0.0%	0.0%
Conversion	73.1%	93.8%	100.0%	100.0%
Total Monomer Yield	10.3%	36.3%	81.0%	56.8%
Error +/-	4.6%	4.6%	2.0%	4.7%

*coniferyl alcohol is not included in total monomer yield.

Table S11. Lignin product monomer yields from H_2-free reactions with Pd/C and Pt/C with varying amounts of water from **Figure 2.**

		EG	ES	P(ene)G	P(ene)S	PG	PS	P(OH)G	P(OH)S	Other	Oil (g)	Total	Error
Pd/C	MeOH	5.0%	8.5%	0.0%	0.0%	2.2%	4.4%	1.3%	2.2%	0.8%	0.472	24.4%	1.5%
	0.25	2.0%	3.8%	0.2%	0.0%	5.5%	9.6%	0.2%	0.2%	0.0%	0.538	21.6%	0.3%
	0.5	0.9%	1.0%	0.4%	3.1%	4.1%	7.1%	0.4%	0.0%	0.2%	0.639	17.1%	0.3%
Pt/C	MeOH	1.3%	2.6%	5.0%	7.1%	1.0%	3.6%	1.1%	0.5%	0.6%	0.482	22.9%	1.7%
	0.25	1.7%	3.6%	0.2%	0.0%	6.5%	11.7%	0.2%	0.3%	0.0%	0.499	24.3%	0.2%
	0.5	0.9%	1.0%	0.6%	1.6%	5.6%	11.2%	0.3%	0.0%	0.1%	0.562	21.2%	0.4%

Table S12. Monomer yields from RCF reactions with 200 mg Ru/C from **Figure S2.**

	EG	ES	P(ene)G	P(ene)S	PG	PS	P(OH)G	P(OH)S	Other	Oil (g)	Total	Range
200 mg Ru/C	0.0%	0.5%	2.2%	3.1%	5.5%	8.6%	1.8%	2.1%	0.0%	0.515	23.8%	0.0%

Table S13. Lignin product monomer yields from RCF reactions with 100 mg, 200 mg, and 400 mg Pd/C from **Figure S5.**

	EG	ES	P(ene)G	P(ene)S	PG	PS	P(OH)G	P(OH)S	Other	Oil (g)	Total	Error
100 mg	5.0%	8.5%	0.0%	0.0%	2.2%	4.4%	1.3%	2.2%	0.6%	0.472	24.1%	1.5%
200 mg	5.6%	7.9%	0.0%	0.0%	1.0%	3.2%	2.1%	3.3%	0.0%	0.428	23.0%	0.3%
400 mg	5.8%	8.1%	0.0%	0.0%	0.7%	3.2%	2.1%	3.3%	0.0%	0.389	23.1%	0.3%

References

1 D. G. Brandner, J. S. Kruger, N. E. Thornburg, G. G. Facas, J. K. Kenny, R. J. Dreiling, A. R. C. Morais, T. Renders, N. S. Cleveland, R. M. Happs, R. Katahira, T. B. Vinzant, D. G. Wilcox, Y. Román-Leshkov and G. T. Beckham, *Green Chem.*, 2021, **23**, 5437–5441.

2 A. Sluiter, B. Hames, R. O. Ruiz, C. Scarlata, J. Sluiter, D. Templeton and D. of Energy, *Biomass Anal. Technol. Team Lab. Anal. Proced.*, 2004, 1–14.

3 M. M. Abu-Omar, K. Barta, G. T. Beckham, J. S. Luterbacher, J. Ralph, R. Rinaldi, Y. Román-Leshkov, J. S. M. Samec, B. F. Sels and F. Wang, *Energy Environ. Sci.*, 2021, **14**, 262–292.