Supplementary Information (SI)

Glycerol-derived Ethers Enable Hydrogen-Free Reductive Catalytic Fractionation of Softwood Lignins into Functionalized Aromatic Monomers

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Section A: SI for properties of GDCs, biomass preparation, Klason test, and black liquor processing.

	μ (D)	MWt (g/mol)	ρ (g/cm³)	MVol (cm³/mol)	BPt (°C)	MPt (°C)	Tc (K)	P_c (MPa)	Vc (cm³/mol)	LogS	η (cP)
DMP	2.12	120.1	1.044	115.1	172.6	4.9	656.2	4.14	363.7	2.84	3.52
DEP	2.16	148.2	0.947	156.4	192	-59.7	617.8	2.9	474.2	2.26	3.93

Table S1. Physicochemical properties of DMP and DEP (Adapted from Szilvási et al.)[1]

μ - Dipole Moment
MWt – Molar weight
ρ – Density
MVol – Molar volume
BPt – Boiling point
MPt – Melting point
T_c – Critical temperature
P_c – Critical pressure
V_c – Critical volume
LogS - Water solubility
η – Dynamic Viscosity

Table S2. Biomass analysis relevant equations and results

	Equation	Result
Moisture (g/g)	$= \dfrac{mass\ of\ dried\ pine}{mass\ of\ undried\ pine}$	0.0403 ± 0.0001
Extractives (g/g)	$= \dfrac{mass\ of\ extractives\ oil}{mass\ of\ dried\ pine}$	0.0103 ± 0.0003
Ash	$= \dfrac{mass\ of\ ash}{mass\ of\ dried\ pine}$	0.0241 ± 0.0013
Lignin	$= \dfrac{mass\ of\ acid\ insoluble\ lignin}{mass\ of\ dried, extract\ free\ pine\ or\ residual\ p}$	0.2890 ± 0.0151
Holocellulose	$= 1 - lignin\ content$	0.7110 ± 0.0151

Table S3. Hansen Solubility Parameter (HSP) values for GDCs, lignin, and monolignols

Compound	δ_D (Mpa$^{0.5}$)	δ_P (Mpa$^{0.5}$)	δ_H (Mpa$^{0.5}$)	Ref
DMP	16.82	9.07	16.87	[1]
DEP	16.02	6.56	9.03	[1]
Lignin	21.9	14.1	16.9	[2]
p-Coumaryl alcohol	18.41	11.38	14.40	[3]
Coniferyl alcohol	18.41	12.15	14.43	[3]
Sinapyl alcohol	18.45	10.92	14.56	[3]

Determination of lignin content by the Klason method

In the first step of acid pre-hydrolysis, 30 mg of the sample (fresh DEFP or H_2-free RCF pulp) was measured and transferred into a 15 mL Ace glass tube reactor. Then, 0.300 mL (300 µL) of 72% (w/w) sulfuric acid was added to the reactor, which was then sealed. The sample was pre-hydrolyzed for 60 min at 30 °C in a water bath. Subsequently, the sample was diluted by adding 8.4 mL of deionized water, and the top of the Ace glass tube reactor was closed. The contents of the reactor were vortexed, ensuring that all solid samples were dispersed in the liquid solution. The filled reactors were then heated in an oil bath at 120 °C for 50 min. After the allotted time, the reactors were removed from the bath and allowed to cool to room temperature. On cooling, the reactors were opened, and the contents (solid residue and acidic liquid solution) were filtered using vacuum filtration. The solids were recovered and washed with 10-25 mL of ultrapure water. Finally, the solid residues were dried overnight in a drying oven at 105 °C, and their mass was measured, representing the acid insoluble lignin.

Liquid-liquid extraction (LLE) and micro-distillation of black liquor (BL)

BL was added dropwise to 30 mL ultrapure water in a plastic centrifuge tube and the tube centrifuged at 5000 rpm for 8 min before decantation. The decanted liquid now free of any reserved solid was transferred to a separatory funnel and 8 mL dichloromethane (DCM) introduced. The closed separatory funnel was inverted 6-8 times to generate maximum interfacial contact, vented periodically (3 times after each set of inversions), and then held with a stand and clamps to allow layers to settle/separate. DCM being denser than water leads to the recovery of the organic layer from the bottom of the separatory funnel with the aqueous layer left in the separatory funnel. All organic layer recovered after 3 x 8 mL extractions was transferred to a round bottom flask that fits to the rotary evaporator (Rotovap) and DCM was evaporated and recovered as condensate under vacuum at 40 °C and slow rotation. The fraction left in the round bottom flask was then transferred to a micro-distillation unit with the distillation flask heated isothermally in an oil bath at 200 °C until further condensation of vaporized GDC into the condensate flask was not observed (typically took 5-6 mins). The concentrated liquid left in distillation flask is the desired lignin oil free of removable GDC.

Section B: SI for experimental and analytical results

Table S4. Monomer yield, pulp yield, and delignification with different catalysts and solvents. Reaction conditions: 730 mg DEFP (595 mg in experiment with recycled DMP), 7 mL solvent (5.7 mL recovered and used in DMP recycle experiment), 73 mg catalyst (59.5 mg for DMP recycle experiment), 200 °C, 7 h, 0.1 g/g catalyst dosage, 0.0096 mL/mg solvent-to-DEFP ratio, 1000 RPM.

	Monomer yield (wt% of initial lignin content)	Pulp yield (wt% of DEFP mass)	Delignification (wt% of initial lignin content)
Catalyst			
None	5.5	61.3	33.0
Ru/C	18.6	35.7	72.1
Pt/C	22.9	34.4	79.1
Solvent			
GLY/H$_2$O (1:1)		44.8	58.7
GLY/H$_2$O (1.5:1)		44.0	61.6
GLY/H$_2$O (2:1)		43.6	63.7
DEP	21.4	36.3	75.2
DMP	22.9	34.4	79.1
Recycled DMP	21.03	37.22	76.3

Table S5. Individual monomer yields with the screened catalysts. Reaction conditions: 730 mg DEFP, 7 mL solvent, 73 mg catalyst, 200 °C, 7 hr, 0.1 g/g catalyst dosage, 0.0096 mL/mg solvent-to-DEFP ratio, 1000 RPM.

|	4-Propyl guaiacol	4-Ethyl guaiacol	Conifer aldehyde	Eugenol	trans-Isoeugenol	Vanillin	Vanillic acid
Yields (wt% of initial lignin) with DMP							
None	0.14	0.01	1.14	0.02	0.32	3.85	0.01
Ru/C	1.71	0.47	2.65	0.37	9.16	4.05	0.17
Pt/C	1.94	0.75	6.67	0.97	8.82	3.44	0.26
Yields (wt% of initial lignin) with DMP (helium headspace)							
Pt/C	1.79	0.78	6.71	0.82	8.55	3.36	0.30
Yields (wt% of initial lignin) with DEP							
None	0.19	0.01	0.86	0.03	0.43	3.80	0.02
Ru/C	1.62	0.50	1.91	0.37	7.99	4.18	1.49
Pt/C	1.78	0.70	5.98	1.00	8.50	3.26	0.17

Table S6. Catalysts selectivity for the dominant monomeric species. Reaction conditions: 730 mg DEFP, 7 mL DMP, 73 mg catalyst, 200 °C, 7 hr, 0.1 g/g catalyst dosage, 0.0096 mL/mg solvent-to-DEFP ratio, 1000 RPM.

	Vanillin	Trans-isoeugenol	Conifer aldehyde	4-Propyl guaiacol
None	0.117	0.010	0.035	0.004
Ru/C	0.056	0.127	0.037	0.024
Pt/C	0.044	0.112	0.084	0.025
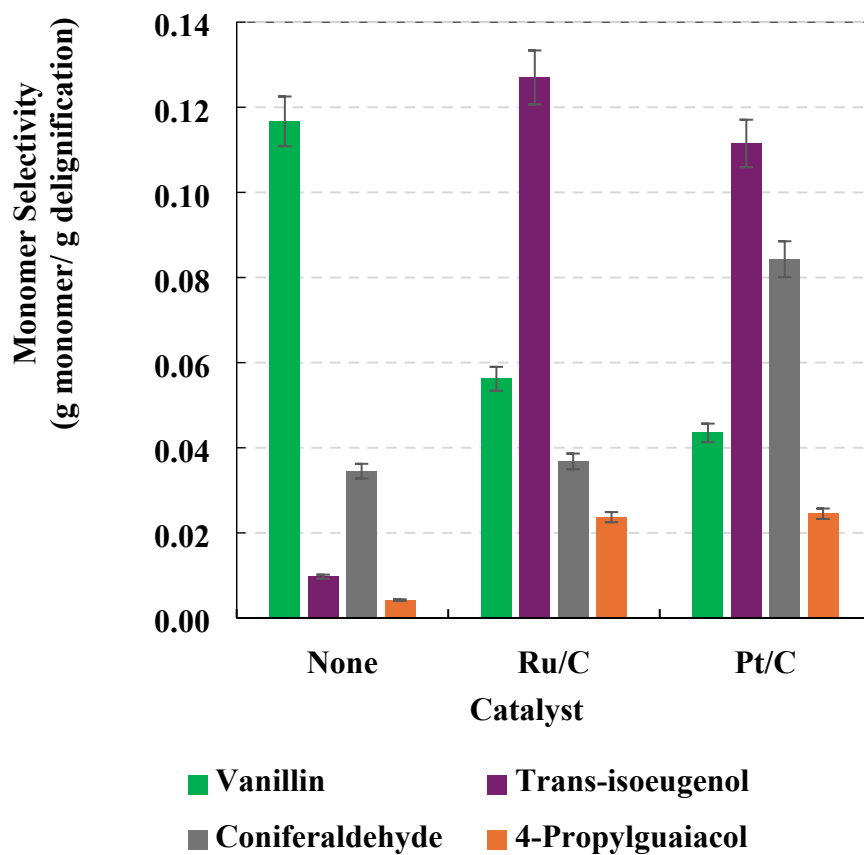
Fig. S1. Catalysts selectivity for the dominant monomeric species. Reaction conditions: 730 mg DEFP, 7 mL DMP, 73 mg catalyst, 200 °C, 7 hr, 0.1 g/g catalyst dosage, 0.0096 mL/mg solvent-to-DEFP ratio, 1000 RPM.

Table S7. Monomer yield, pulp yield, and delignification at different temperatures, times, catalyst dosages, and solvent-to-DEFP ratios. Reaction conditions: 730 mg DEFP, 7 mL DMP, 73 mg 5 wt% Pt/C, 200 °C , 4 hr, 0.1 g/g catalyst dosage, 0.0096 mL/mg solvent-to-DEFP ratio, 1000 RPM.

Temperature (°C)	Monomer yield (wt%)	Pulp yield (wt%)	Delignification (wt%)
160	16.1	39.5	67.9
180	17.8	37.8	70.4
200	20.3	37.2	73.4
230	20.7	37.1	74.1
250	21.2	37.0	74.3
Time (hr)			
1	15.3	51.3	63.7
2.5	17.6	44.8	68.2
4	20.3	37.2	73.4
5.5	21.8	35.6	76.5
7	22.9	34.4	79.1
Catalyst dosage (g cat./g biomass)			
0.1	20.3	37.2	73.4
0.2	22.9	35.4	79.0
0.3	23.3	35.0	81.7
Solvent-to-DEFP ratio (mL/mg)			
0.0068	17.8	40.2	68.5
0.0096	20.3	37.2	73.4
0.0137	20.4	36.3	74.7
0.0205	20.5	35.8	74.5

Table S8. Monomer selectivity variation with delignification. Reaction conditions: 730 mg DEFP, 7 mL DMP, 4 hr time for temperature-associated values, 200 °C temperature for time-associated values, 73 mg 5 wt% Pt/C, 0.1 g/g catalyst dosage, 0.0096 mL/mg solvent-to-DEFP ratio, 1000 RPM.

Temperature (°C)	Delignification (g lig./g lig. Initial)	Monomer Selectivity (g monomer/ g delignification)	Time (hr)	Delignification (g lig./g lig. Initial)	Monomer Selectivity (g monomer/ g delignification)
160	0.679	0.237	1	0.637	0.240
180	0.704	0.253	2.5	0.682	0.258
200	0.734	0.277	4	0.734	0.277
230	0.741	0.280	5.5	0.765	0.285
250	0.743	0.286	7	0.800	0.289

Table S9. Delignification selectivity variation with dissolved DEFP. Reaction conditions: 730 mg DEFP, 7 mL DMP, 4 hr time for temperature associated values, 200 °C temperature for time associated values, 73 mg 5 wt% Pt/C, 0.1 g/g catalyst dosage, 0.0096 mL/mg solvent-to-DEFP ratio, 1000 RPM.

Temperature (°C)	Dissolved DEFP (mg DEFP dissolved/ mg DEFP)	Delignification Selectivity (g lig. removed/ g DEFP dissolved	Time (hr)	Dissolved DEFP (mg DEFP dissolved/ mg DEFP)	Delignification Selectivity (g lig. removed/ g DEFP dissolved)
160	0.605	0.324	1	0.585	0.314
180	0.622	0.327	2.5	0.603	0.327
200	0.628	0.338	4	0.628	0.338
230	0.629	0.340	5.5	0.644	0.343
250	0.630	0.341	7	0.656	0.348

Table S10. Monomer yield, monomer selectivity, pulp yield, delignification, and monomer selectivity for different loadings of acetic acid. Reaction conditions: 730 mg DEFP, 7 mL DMP, 73 mg 5 wt% Pt/C, 200 °C, 4 hr (bars not hatched), 7 hr (hatched bars), 0.1 g/g catalyst dosage, 0.0096 mL/mg solvent-to-DEFP ratio, 1000 RPM.

Acetic acid (AA) loading (mg AA/ mg DEFP)	Time (hr)	Monomer yield (wt%)	Monomer selectivity (g monomer/ g delignification)	Pulp yield (wt%)	Delignification (wt%)
0	7	22.9	0.289	34.4	79.1
0.5	4	24.3	0.291	34.8	83.5
0.6	4	24.7	0.292	34.3	84.7
0.7	4	24.8	0.292	34.1	84.9
0.7	7	24.9	0.289	32.0	86.4

Table S11. Monomer yield, pulp yield, and delignification for DMP, water and acetic acid solvent formulations.

	Monomer yield (wt%)	Pulp yield (wt%)	Delignification (wt%)
DMP/H$_2$O	16.2	29.97	89.2
DMP	22.85	34.4	79.1
DMP/H$_2$O-0.6	23.53	27.59	90.7
DMP-0.6	24.74	34.26	84.7
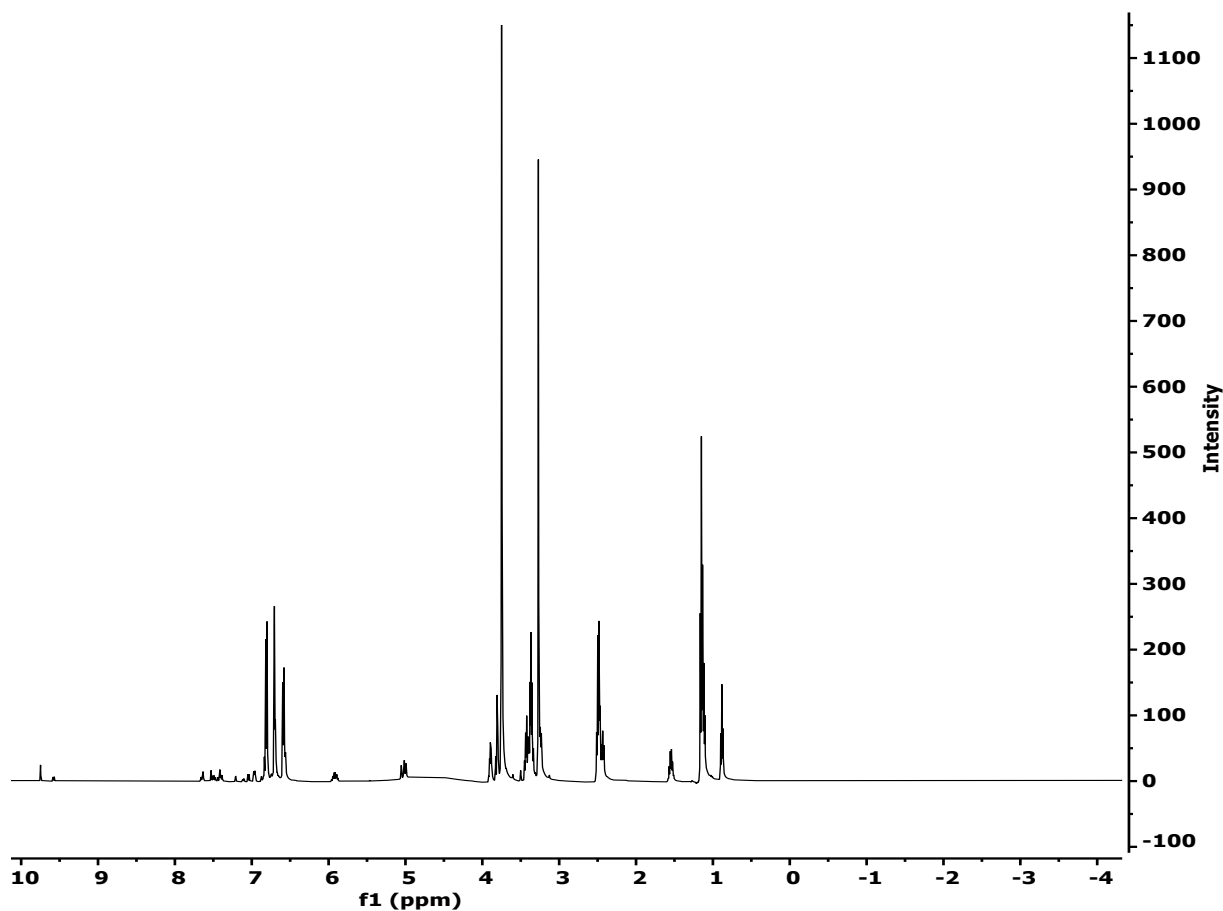
Fig. S2 ^{1}H NMR Spectrum of lignin oil from H$_2$-free RCF. Reaction conditions: 730 mg DEFP, 7 mL DMP, 73 mg 5 wt% Pt/C, 200 °C, 7 h, 0.1 g/g catalyst dosage, 0.0096 mL/mg solvent-to-DEFP ratio, 1000 RPM.
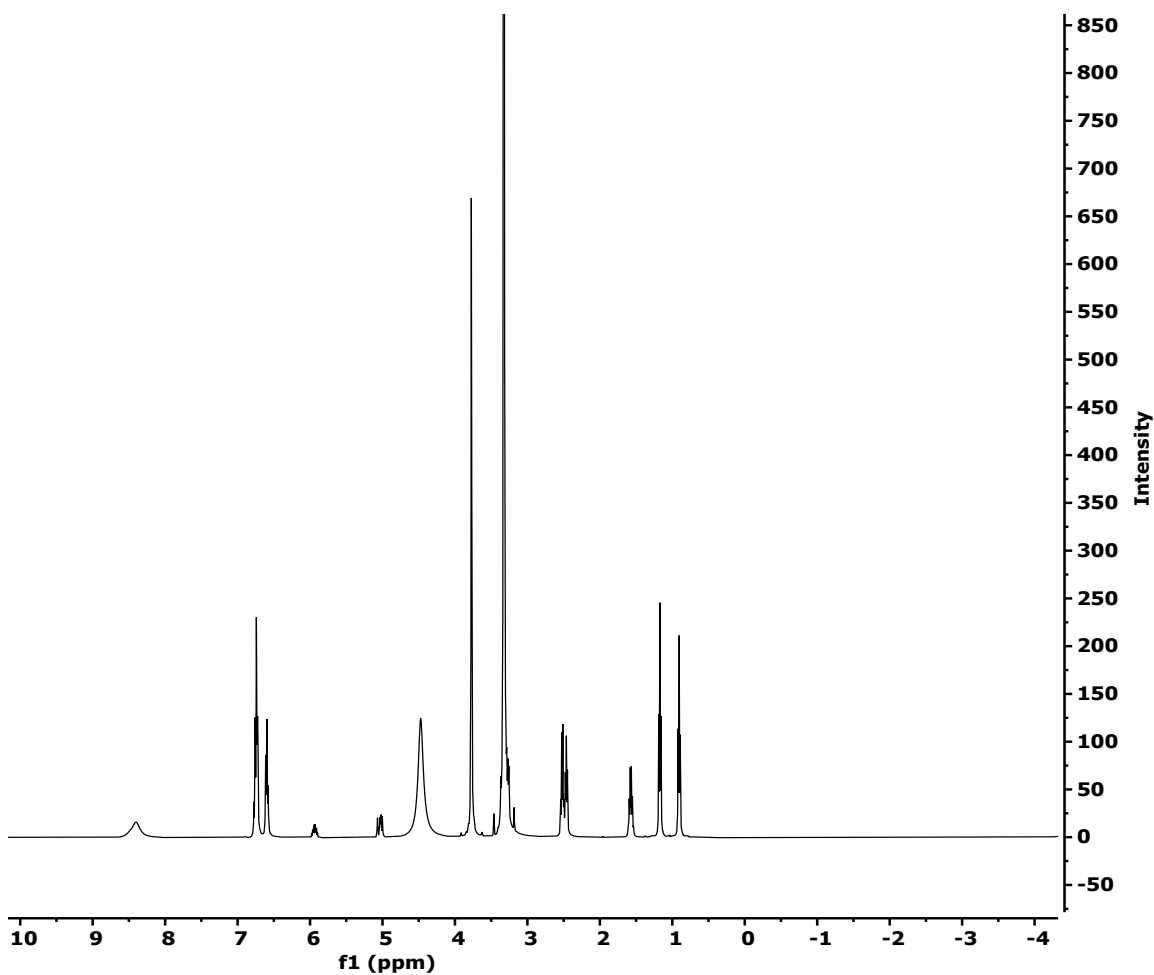
Fig. S3 ^{1}H NMR Spectrum of lignin oil from neat solvolysis. Reaction conditions: 730 mg DEFP, 7 mL DMP, 200 °C, 7 h, 0.0096 mL/mg solvent-to-DEFP ratio, 1000 RPM.

Table S12. Yields of furan derivatives in neat solvolysis and H_2-free RCF. Reaction conditions: 730 mg DEFP, 7 mL DMP, 73 mg catalyst, 200 °C, 7 hr, 0.1 g/g catalyst dosage, 0.0096 mL/mg solvent-to-DEFP ratio, 1000 RPM.

	Yields (wt% of holocellulose)				
	2-Furaldehyde	**Furan-2,5-dicarboxylic acid**	**Tetrahydro furan**	**Levulinic acid**	**5-Hydroxy methylfurfural**
None	3.33	1.30	0.60	0.38	2.44
Ru/C	2.05	0.55	0.17	0.07	1.89
Pt/C	1.93	0.41	0.08	0.05	1.74

Table S13. (a) Comparison of DEFP mass-based monomer and furan derivatives yields for neat solvolysis and H_2-free RCF (b) Comparison of DEFP mass-based monomer and furan derivatives yields for the screened GDCs. Reaction conditions: 730 mg DEFP, 7 mL DMP (for catalyst part), 73 mg 5 wt% Pt/C (for solvent part), 200 °C, 7 hr, 0.1 g/g catalyst dosage, 0.0096 mL/mg solvent-to-DEFP ratio, 1000 RPM.

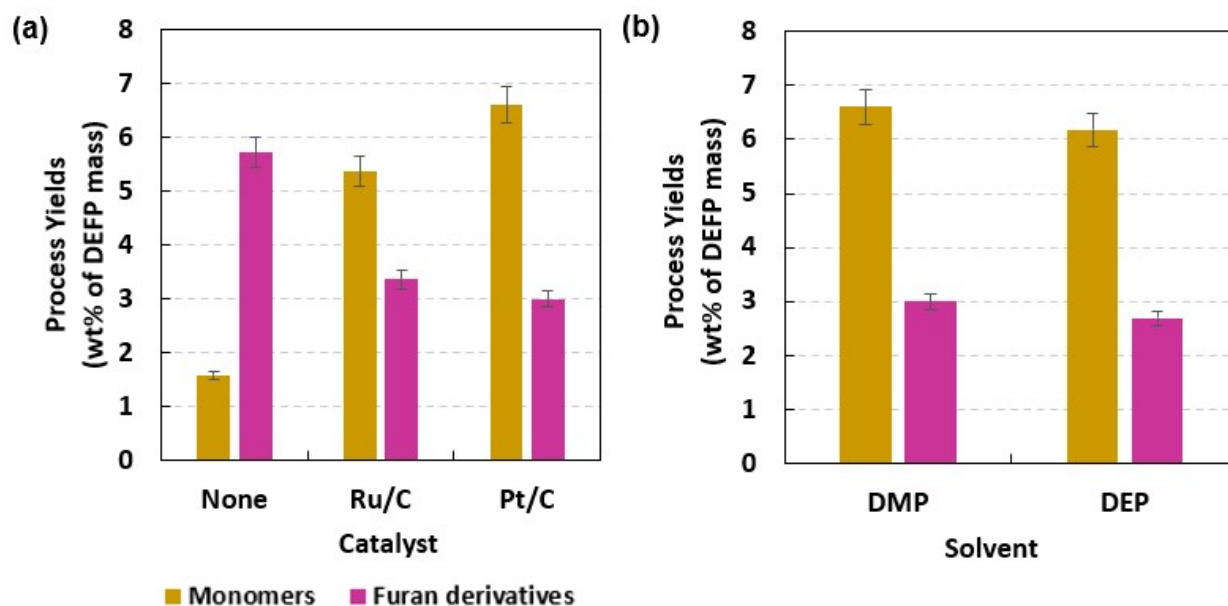|	Monomers	Furan derivatives
Catalyst		
None	1.6	5.7
Ru/C	5.4	3.4
Pt/C	6.6	3.0
Solvent		
DMP	6.6	3.0
DEP	6.2	2.7

Fig. S4 (a) Comparison of DEFP mass-based monomer and furan derivatives yields for neat and H_2-free RCF (b) Comparison of DEFP mass-based monomer and furan derivatives yields for the screened GDCs. Reaction conditions: 730 mg DEFP, 7 mL DMP, 73 mg catalyst (Pt/C for (b)), 200 °C, 7 hr, 0.1 g/g catalyst dosage, 0.0096 mL/mg solvent-to-DEFP ratio, 1000 RPM.

Calculation of the crystallinity index of DEFP and pulps according to Segal's method [4]

$$CI\ (\%) = \left(\frac{I_{002} - I_{am}}{I_{002}}\right) X\ 100$$

Where $CI\ (\%)$ is the crystallinity index, I_{002} is the intensity of the crystalline peak at $2\theta = 22.6°$, and I_{am} is the intensity of the amorphous peak at $2\theta = 18°$.

Considering Fig. 11a (XRD)

XRD of DEFP (Blue):

$$CI\ (\%) = \left(\frac{10414 - 4991}{10414}\right) X\ 100 = 52.1\%$$

XRD of pulp produced from DMP RCF conducted at 160 °C, 4 h, 10 wt% Pt/C catalyst dosage (yellow):

$$CI\ (\%) = \left(\frac{7360 - 4685}{7360}\right) X\ 100 = 36.3\%$$

XRD of pulp produced from DEP RCF conducted at 200 °C, 7 h, 10 wt% Pt/C catalyst dosage (red):

$$CI\ (\%) = \left(\frac{6413 - 4118}{6413}\right) X\ 100 = 35.8\%$$

XRD of pulp produced from DMP RCF conducted at 200 °C, 7 h, 10 wt% Pt/C catalyst dosage (green):

$$CI\ (\%) = \left(\frac{5719 - 3922}{5719}\right) X\ 100 = 31.4\%$$

References

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