

Supplementary Information for

Kinetic and mechanistic insights into hydrogenolysis of lignin to monomers in a continuous flow reactor

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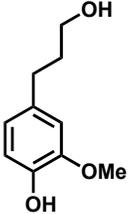
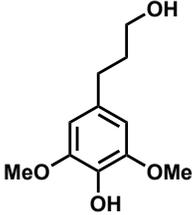
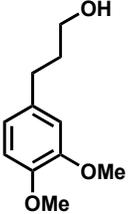
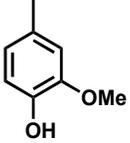
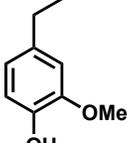
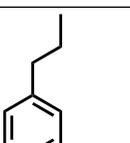
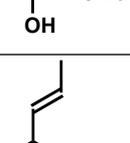
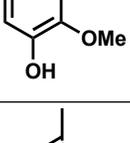
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Table S1. Chemical abbreviations.

Abbreviation	Chemical Name	Structure
GG	Guaiacylglycerol- β -guaiacyl ether	
VG	Veratrylglycerol- β -guaiacyl ether	
G	Guaiacol	
CA	Coniferyl alcohol	
SA	Sinapyl alcohol	
VA	Veratryl alcohol	

DCA	Dihydroconiferyl alcohol	
DSA	Dihydrosinapyl alcohol	
DVA	Dihydroveratryl alcohol	
MG	Methyl guaiacol	
EG	Ethyl guaiacol	
PG	Propyl guaiacol	
IE	Isoeugenol	
IE-OMe	Methyl isoeugenol	

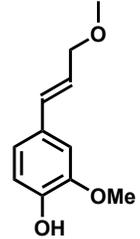
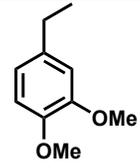
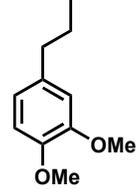
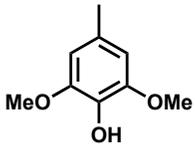
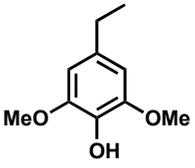
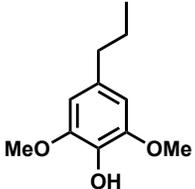
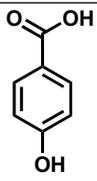
IE-γOMe	γ -O-Methyl isoeugenol	
EG-OMe	4-O-Methyl ethyl guaiacol	
PG-OMe	4-O-Methyl propyl guaiacol	
MS	Methyl syringol	
ES	Ethyl syringol	
PS	Propyl syringol	
pBA	p-Hydroxybenzoic acid	

Table S2. Compositional analysis of isolated lignins. Each sample was measured in duplicate with standard deviation calculation (n=2).

	Cu-AHP lignin	Mild acidolysis lignin	GVL lignin
Klason lignin (wt%)	82.1 ± 0.3	80.7 ± 0.7	84.2 ± 2.8
Acid-soluble lignin (wt%)	6.2 ± 0.1	3.9 ± 0.3	2.8 ± 0.5
Sugar content (wt%)	2.79 ± 0.13	2.93 ± 0.01	1.80 ± 0.05
Monosaccharide: Arabinose	0.19 ± 0.01	0.04 ± 0.00	0.04 ± 0.00
Monosaccharide: Galactose	0.58 ± 0.03	0.12 ± 0.01	0.04 ± 0.00
Monosaccharide: Glucose	0.20 ± 0.03	0.58 ± 0.00	0.12 ± 0.01
Monosaccharide: Xylose	1.66 ± 0.06	2.09 ± 0.02	1.60 ± 0.04
Monosaccharide: Mannose	0.17 ± 0.00	0.11 ± 0.01	0.00 ± 0.00
Ash	0.00	0.00	0.00

Table S3. Lignin β -ether content, theoretical and experimental monomer yields.

	Cu-AHP lignin	Mild acidolysis lignin	GVL lignin
β-O-4 (A) [mol %]	61.6	52.6	43.8
β-5 (B) [mol %]	1.6	1.3	1.9
β-β (C) [mol %]	2.2	2.9	2.5
Klason lignin content [%]	82.1	80.7	84.2
Theoretical monomer yield [mol %]	32.0	22.3	16.1
Monomer yield in batch reaction [mol %]	29.0	25.4	16.4
Monomer yield in flow reaction at 190 °C [mol %]	28.4	25.2	16.9

The monomer yields of the hydrogenolysis reaction both in batch and in flow reactions at 190 °C were close to the theoretical monomer yields for all three lignin streams. As we have discussed, the HSQC NMR and the GPC data, β -ethers were quantitatively cleaved (Fig. 3d, Fig. S1d, S3d). It should be noted that the theoretical monomer yield is an estimation of the maximum monomer yield; in the real case, the monomer yield could be slightly different. For example, in our overall monomer yields, the small amount of *p*-hydroxybenzoic acid (*p*BA) was taken into consideration, although it did not contribute to the β -ether content. Further studies on the behavior of the esters in lignin under the hydrogenolysis reaction need to be carried out in the future.

Table S4. Monomer yield from the hydrogenolysis of Cu-AHP lignin in the flow reactor. *The reaction was performed in a batch reactor at 200 °C as a control. The temperature of the reactor was set to 190 °C, changed to 160 °C at 220 min, and decreased to 140 °C at 360 min. The yield is in mole%. Major products selectivity is the sum of selectivities for **DCA**, **DSA**, and **pBA**.

Time (min)	DCA	DSA	PG	PS	EG	MG	MS	pBA	Total yield	Major products selectivity
180*	7.09%	16.35%	0.36%	1.68%	0.12%	0.24%	0.48%	2.65%	29.0%	90.0%
120	4.87%	14.74%	0.85%	2.31%	0.24%	0.49%	0.85%	2.31%	26.7%	82.2%
140	5.48%	15.23%	0.97%	2.44%	0.24%	0.61%	0.85%	2.44%	28.3%	81.9%
160	5.12%	14.25%	0.97%	2.31%	0.24%	0.49%	0.85%	2.44%	26.7%	81.7%
180	5.48%	15.10%	0.97%	2.56%	0.24%	0.61%	0.85%	2.56%	28.4%	81.5%
200	5.12%	14.13%	0.97%	2.44%	0.24%	0.49%	0.85%	2.31%	26.6%	81.2%
220	5.48%	14.86%	1.10%	2.44%	0.24%	0.61%	0.85%	2.44%	28.0%	81.3%
240	4.38%	12.18%	1.10%	2.07%	0.24%	0.49%	0.73%	2.31%	23.5%	80.3%
260	2.56%	7.67%	1.22%	0.97%	0.24%	0.24%	0.24%	1.58%	14.7%	80.2%
280	2.68%	7.55%	1.34%	0.97%	0.12%	0.24%	0.24%	1.58%	14.7%	80.2%
300	2.68%	7.55%	1.34%	0.97%	0.24%	0.24%	0.24%	1.58%	14.9%	79.5%
320	2.68%	7.92%	1.34%	0.97%	0.24%	0.24%	0.24%	1.58%	15.2%	80.0%
340	2.68%	7.55%	1.46%	0.97%	0.12%	0.24%	0.24%	1.58%	14.9%	79.5%
360	2.68%	7.92%	1.46%	0.97%	0.24%	0.24%	0.24%	1.58%	15.3%	79.4%
380	2.19%	6.33%	1.34%	0.85%	0.12%	0.12%	0.24%	1.46%	12.7%	78.8%
400	0.97%	3.05%	0.85%	0.85%	0.24%	0.00%	0.00%	0.85%	6.8%	71.4%
420	1.22%	3.29%	0.85%	0.85%	0.24%	0.00%	0.00%	0.85%	7.3%	73.3%
440	1.22%	3.41%	0.97%	0.85%	0.24%	0.00%	0.00%	0.85%	7.6%	72.6%
460	1.22%	3.41%	0.97%	0.85%	0.24%	0.00%	0.00%	0.85%	7.6%	72.6%
480	1.22%	3.41%	0.97%	0.85%	0.24%	0.00%	0.00%	0.85%	7.6%	72.6%
500	1.22%	3.53%	0.97%	0.85%	0.24%	0.00%	0.00%	0.85%	7.7%	73.0%

Table S5. Monomer yield from the hydrogenolysis of GVL lignin in the flow reactor. *The reaction was performed in a batch reactor at 200 °C as a control. The temperature of the reactor was set to 190 °C, changed to 160 °C at 220 min, and decreased to 140 °C at 360 min. The yield is in mole%. Major products selectivity is the sum of selectivities for **DCA**, **DSA**, and **pBA**.

Time (min)	DCA	DSA	PG	PS	EG	MG	MS	pBA	Total yield	Major products selectivity
180*	4.42%	6.17%	0.12%	1.86%	0.23%	0.00%	0.23%	3.38%	16.4%	85.1%
90	3.56%	5.70%	0.36%	2.73%	0.24%	0.24%	0.59%	3.21%	16.6%	75.0%
120	3.68%	5.46%	0.36%	2.61%	0.24%	0.24%	0.59%	3.33%	16.5%	75.5%
140	3.92%	5.58%	0.48%	2.73%	0.24%	0.24%	0.59%	3.09%	16.9%	74.6%
160	3.80%	5.34%	0.48%	2.61%	0.24%	0.24%	0.59%	2.97%	16.3%	74.5%
180	3.80%	5.34%	0.48%	2.61%	0.24%	0.24%	0.48%	3.09%	16.3%	75.2%
200	3.92%	5.46%	0.48%	2.73%	0.24%	0.24%	0.48%	3.09%	16.6%	75.0%
220	3.92%	5.34%	0.48%	2.61%	0.24%	0.24%	0.48%	2.97%	16.3%	75.2%
240	3.44%	4.75%	0.48%	2.26%	0.24%	0.24%	0.48%	2.97%	14.8%	75.2%
260	1.66%	2.26%	1.31%	0.95%	0.36%	0.00%	0.12%	1.78%	8.4%	67.6%
280	1.54%	2.26%	1.31%	0.83%	0.36%	0.00%	1.31%	1.43%	9.0%	57.9%
300	1.54%	2.26%	1.31%	0.83%	0.36%	0.00%	1.19%	1.78%	9.3%	60.3%
320	1.54%	2.26%	1.31%	0.83%	0.36%	0.00%	1.19%	1.66%	9.1%	59.7%
340	1.54%	2.14%	1.31%	0.83%	0.36%	0.00%	1.19%	1.78%	9.1%	59.7%
360	1.54%	2.14%	1.31%	0.83%	0.36%	0.00%	1.19%	1.54%	8.9%	58.7%
380	1.19%	1.78%	1.31%	0.59%	0.36%	0.00%	1.31%	1.31%	7.8%	54.5%
400	0.36%	0.71%	0.95%	0.24%	0.24%	0.00%	0.71%	0.59%	3.8%	43.8%
420	0.48%	0.71%	0.95%	0.24%	0.24%	0.00%	0.71%	0.48%	3.8%	43.8%
440	0.48%	0.71%	0.95%	0.24%	0.24%	0.00%	0.59%	0.48%	3.7%	45.2%
460	0.48%	0.71%	0.95%	0.24%	0.24%	0.00%	0.71%	0.59%	3.9%	45.5%
480	0.48%	0.71%	0.95%	0.24%	0.24%	0.00%	0.71%	0.48%	3.8%	43.8%
500	0.48%	0.71%	0.95%	0.24%	0.24%	0.00%	0.71%	0.59%	3.9%	45.5%

Table S6. Monomer yield from the hydrogenolysis of mild acidolysis lignin in the flow reactor. *The reaction was performed in a batch reactor at 200 °C as a control. The temperature of the reactor was set to 190 °C, changed to 160 °C at 220 min, and decreased to 140 °C at 360 min. The yield is in mole%. Major products selectivity is the sum of selectivities for **DCA**, **DSA**, and **pBA**.

Time (min)	DCA	DSA	PG	PS	EG	MG	MS	pBA	Total yield	Major products selectivity
180*	6.04%	12.20%	0.36%	2.90%	0.36%	0.24%	0.48%	2.78%	25.4%	82.9%
120	3.35%	8.43%	1.61%	5.33%	0.25%	0.50%	1.12%	2.97%	23.5%	62.6%
140	3.72%	9.29%	1.61%	5.20%	0.25%	0.50%	1.12%	3.47%	25.2%	65.5%
160	3.47%	8.55%	1.49%	4.71%	0.25%	0.50%	0.99%	2.85%	22.8%	65.2%
180	4.09%	9.42%	1.49%	4.71%	0.25%	0.50%	0.99%	3.59%	25.0%	68.3%
200	4.21%	9.67%	1.36%	4.58%	0.25%	0.50%	0.99%	3.35%	24.9%	69.2%
220	3.97%	9.05%	1.24%	4.09%	0.25%	0.50%	0.87%	2.85%	22.8%	69.6%
240	4.46%	9.91%	1.36%	3.97%	0.25%	0.50%	0.87%	3.47%	24.8%	72.0%
260	3.59%	7.68%	0.99%	2.23%	0.00%	0.37%	0.50%	2.48%	17.8%	77.1%
280	3.47%	7.43%	0.99%	2.23%	0.00%	0.37%	0.50%	2.35%	17.3%	76.4%
300	3.59%	7.56%	1.12%	2.35%	0.00%	0.37%	0.50%	2.11%	17.6%	75.4%
320	3.59%	7.56%	0.99%	2.23%	0.00%	0.37%	0.50%	2.23%	17.5%	76.6%
340	3.59%	7.68%	0.99%	2.23%	0.00%	0.37%	0.50%	2.48%	17.8%	77.1%
360	3.59%	7.43%	0.99%	2.23%	0.00%	0.37%	0.50%	1.86%	17.0%	75.9%
380	2.85%	5.82%	0.99%	1.73%	0.00%	0.25%	0.37%	1.61%	13.6%	75.5%
400	2.23%	4.46%	0.99%	1.61%	0.00%	0.25%	0.25%	1.49%	11.3%	72.5%
420	2.23%	4.34%	0.99%	1.61%	0.00%	0.25%	0.25%	1.49%	11.2%	72.2%
440	2.23%	4.09%	0.99%	1.49%	0.00%	0.25%	0.25%	1.36%	10.7%	72.1%
460	1.98%	3.84%	0.99%	1.49%	0.00%	0.25%	0.25%	1.49%	10.3%	71.1%

Table S7. Possible lignin oligomers retained after the hydrogenolysis reaction.

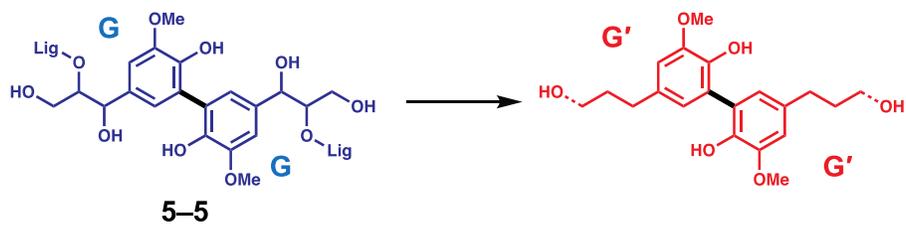
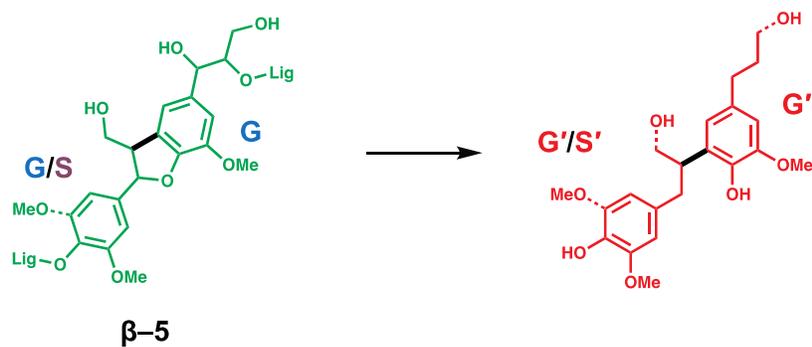
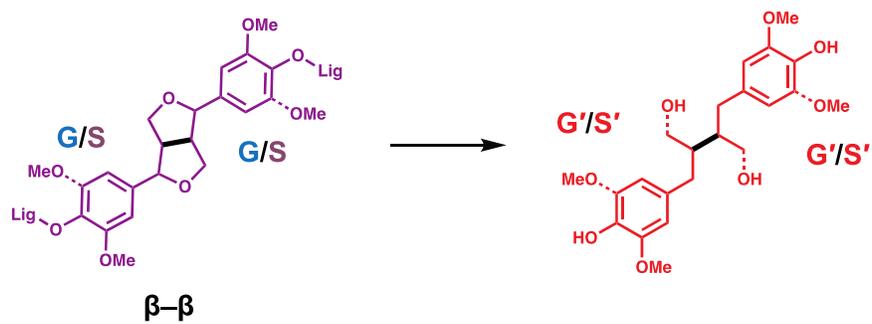


Table S8. Mass balance around the flow reactor for model compound hydrogenolysis reactions.

Exp No	Mass in (g)	Mass out (g)	Error (%)
1 (Fig. S6a)	11.69	11.70	0.07
2 (Fig. S6b)	9.98	10.21	2.32
3 (Fig. S7a)	12.33	12.02	2.47
4 (Fig. S7b)	5.83	6.02	3.37
5 (Fig. S9)	27.77	28.52	2.72
6 (Fig. S10)	22.59	23.67	4.77
7 (Fig. S11)	54.08	52.55	2.82
8 (Fig. S12)	8.04	8.24	2.50
9 (Fig. S13)	54.08	52.96	2.06
10 (Fig. S14)	54.08	51.97	3.89
11 (Fig. S15)	54.08	52.11	3.63
12 (Fig. S16)	54.08	52.41	3.08
13 (Fig. S17)	54.08	54.22	0.26
14 (Fig. S18)	46.77	46.56	0.45
15 (Fig. S19)	55.54	53.38	3.88
16 (Fig. S20)	27.77	27.96	0.68
17 (Fig. S21)	49.69	49.40	0.59
18 (Fig. S22)	51.15	50.68	0.92
19 (Fig. S23)	54.66	54.43	0.42
20 (Fig. S24)	54.08	53.32	1.40
21 (Fig. S25)	18.80	17.71	5.82
22 (Fig. S26)	54.08	52.49	2.93
23 (Fig. S27)	54.08	53.14	1.73
24 (Fig. S28)	30.69	30.67	0.09
25 (Fig. S29)	54.08	54.01	0.13
26 (Fig. S30)	54.08	53.27	1.50
27 (Fig. S31)	57.17	59.50	4.09
28 (Fig. S35)	70.50	70.30	2.55
29 (Fig. S36)	68.60	69.67	1.57
30 (Fig. 3)	64.79	66.24	2.25

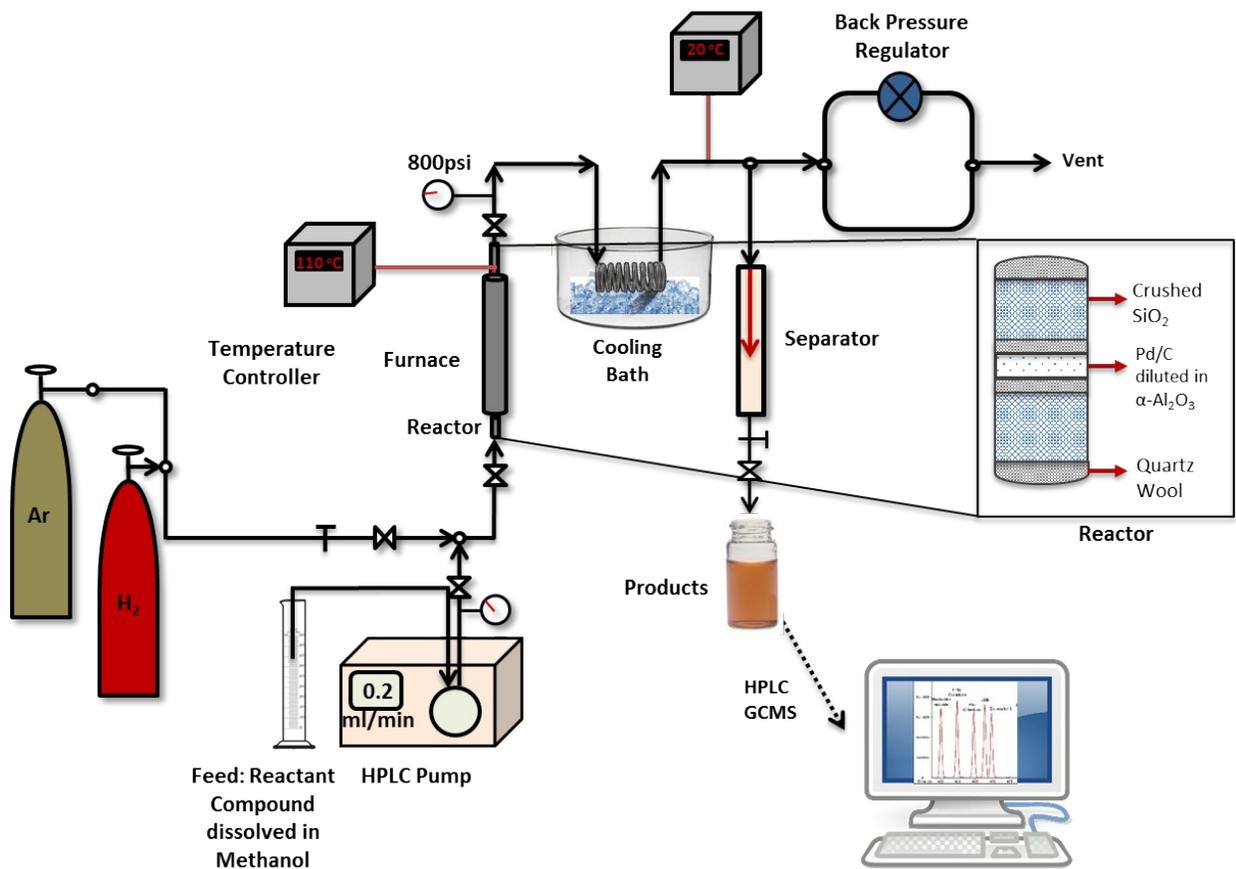


Figure S1. Flow-through reactor setup.

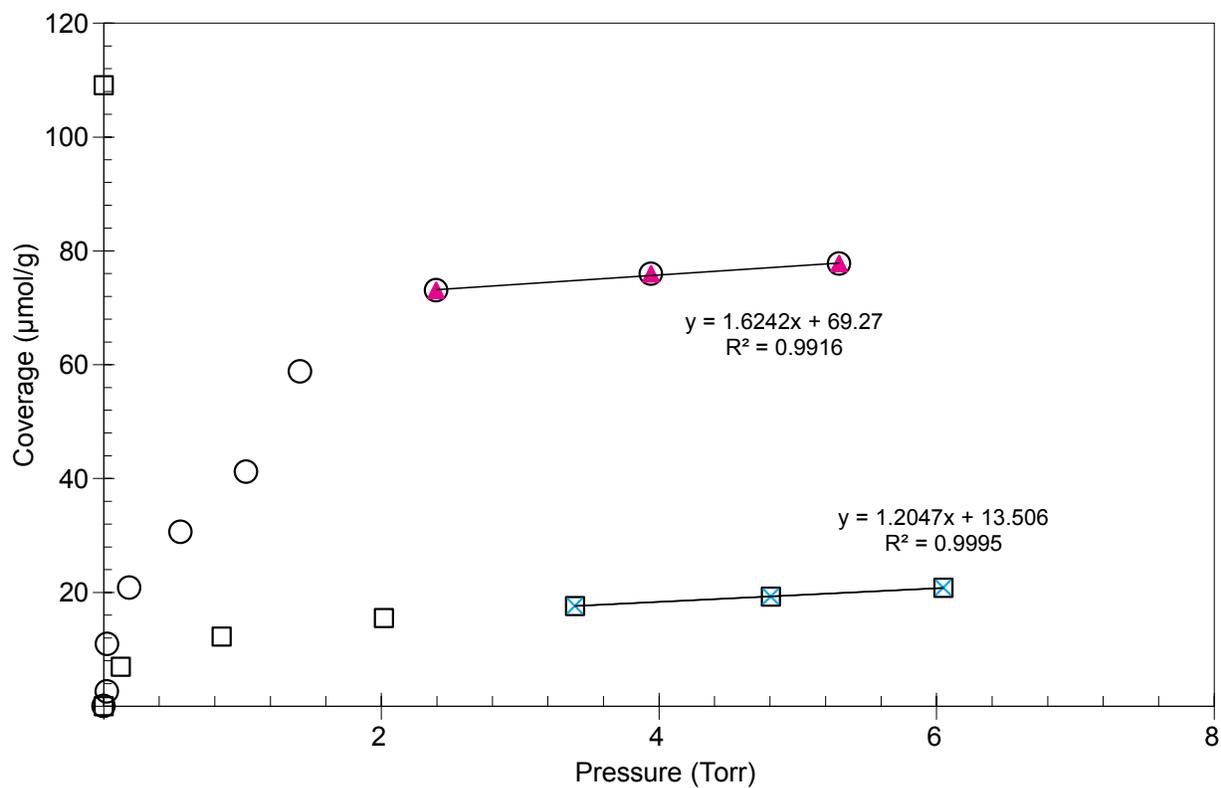


Figure S2. CO chemisorption of 5 wt% Pd/C. The circular and square data points correspond to the adsorption and desorption of CO on the catalyst surface, respectively.

Calculation of the fraction of liquid phase/gas phase via Aspen simulation.

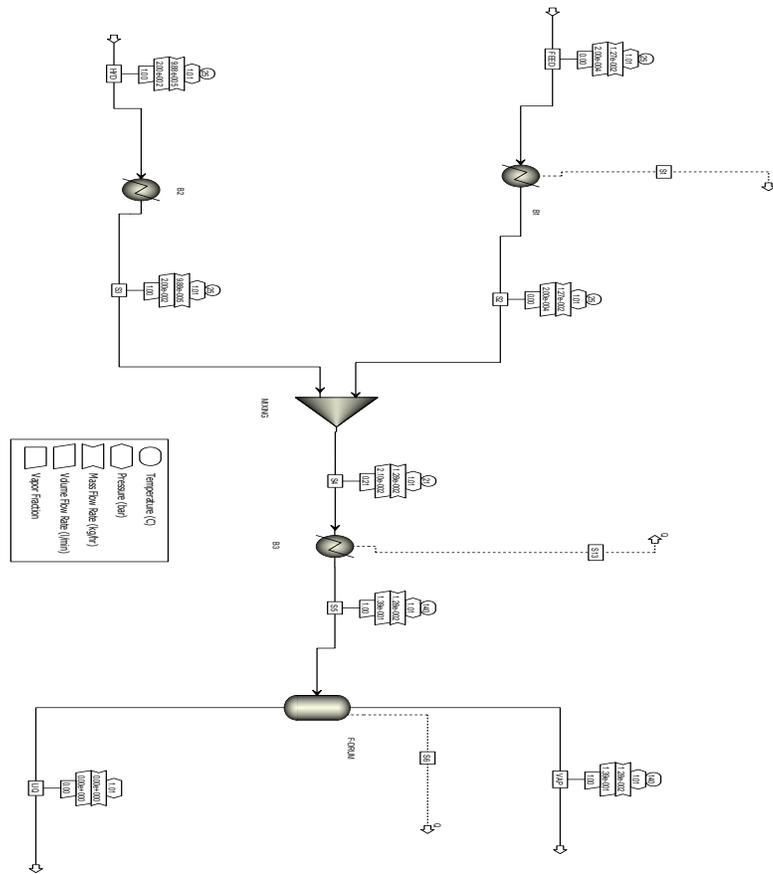


Figure S3. The flow chart of Aspen simulation for phase calculation. The flow chart shown in Fig. S7 is a representation of a process model, in which a liquid stream (Feed) and a gas stream (HYD) are heated (B1-B3), combined (MIXING) and fed to a flash drum (F-DRUM) to separate into gas (VAP) and liquid (LIQ) phases. The sensitivity analysis to calculate the liquid fraction of

the reaction medium (Fig. S8-S9) was obtained by changing the pressure of the system in the Aspen Plus simulation model.

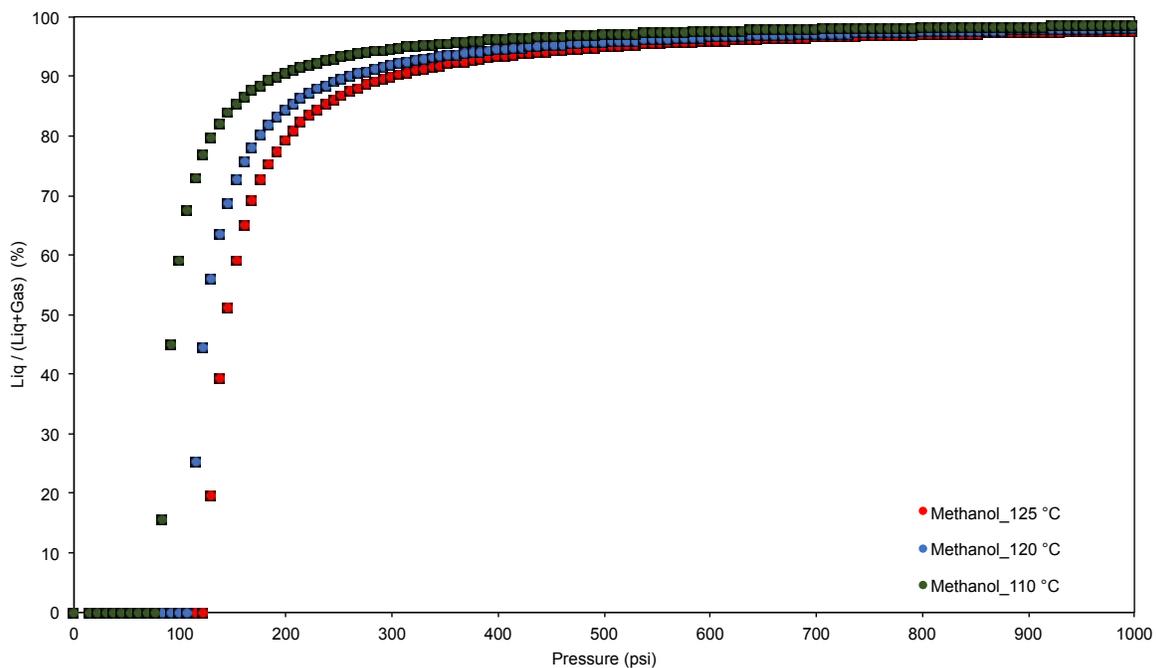


Figure S4. Liquid fraction of methanol in the reaction media (Aspen simulation results).
Reaction Conditions: 110-125 °C, 0.2 mL/min MeOH, 20 mL/min H₂.

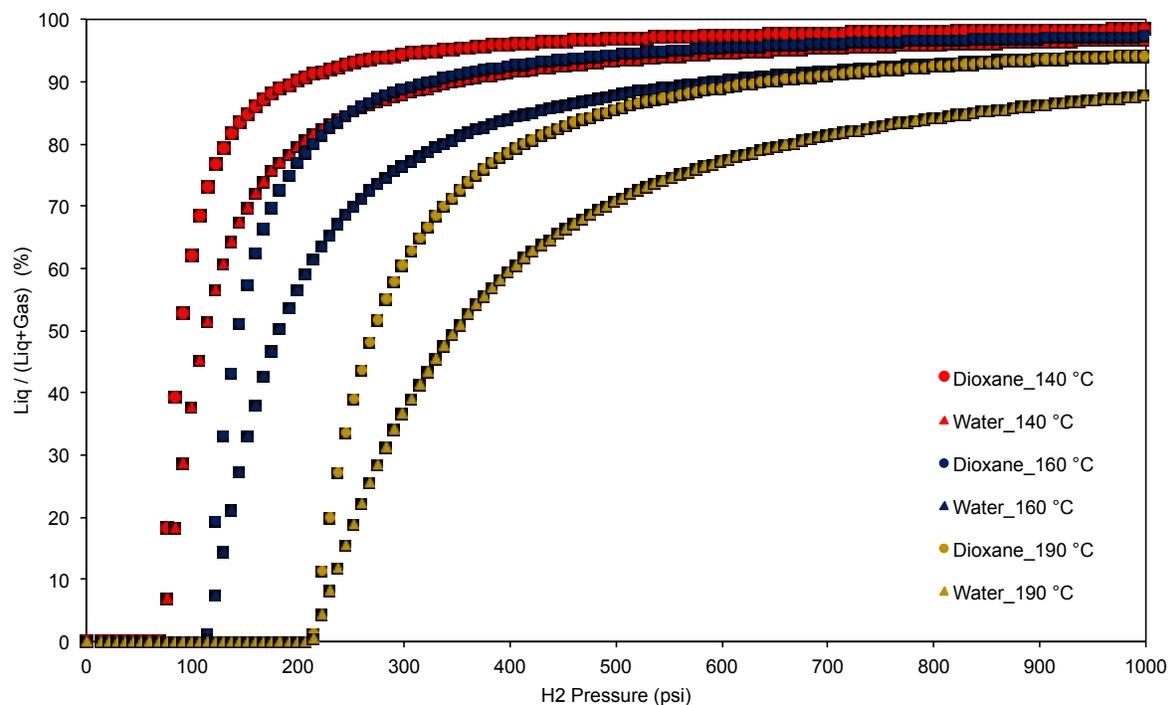


Figure S5. Liquid Fraction of 90% Dioxane:10% Water in the reaction media (Aspen simulation results). Reaction Conditions: 140-190 °C, 0.2 mL/min solvent, 20 mL/min H₂.

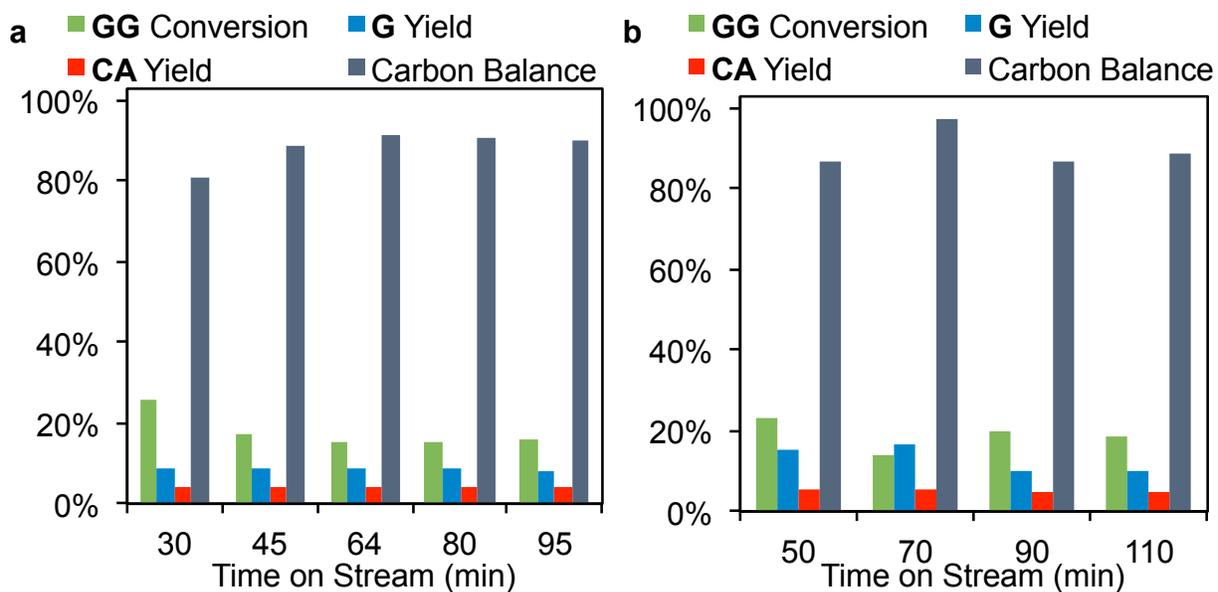


Figure S6. Reaction conversion and product distribution over time for homolysis of GG model compound a) in 80% methanol: 20% water and b) in methanol. Reaction Conditions: 160 °C, 800 psi Ar, 0.2 mL/min of a solution of model compound in methanol or 80% methanol (2 mg/mL GG), 20 mL/min Ar. The residence time of the reactor was 15 min. The reactor was packed with silica chips. There was no catalyst in the reactor.

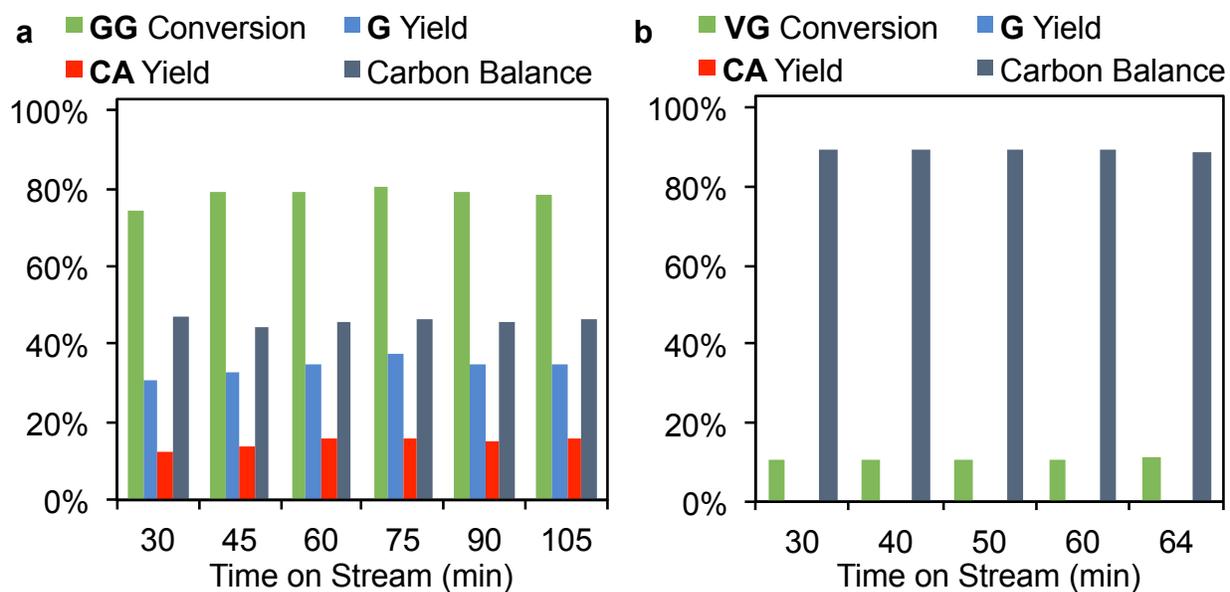


Figure S7. Reaction conversion and product distribution over time for homolysis of a) GG model compound and b) VG model compound in γ -valerolactone (GVL). Reaction Conditions: 200 °C, 800 psi Ar, 0.2 mL/min of a solution of model compound in GVL (2 mg/mL GG/VG), 20 mL/min Ar. The residence time of the reactor was 15 min. The reactor was packed with silica chips. There was no catalyst packed in the reactor.

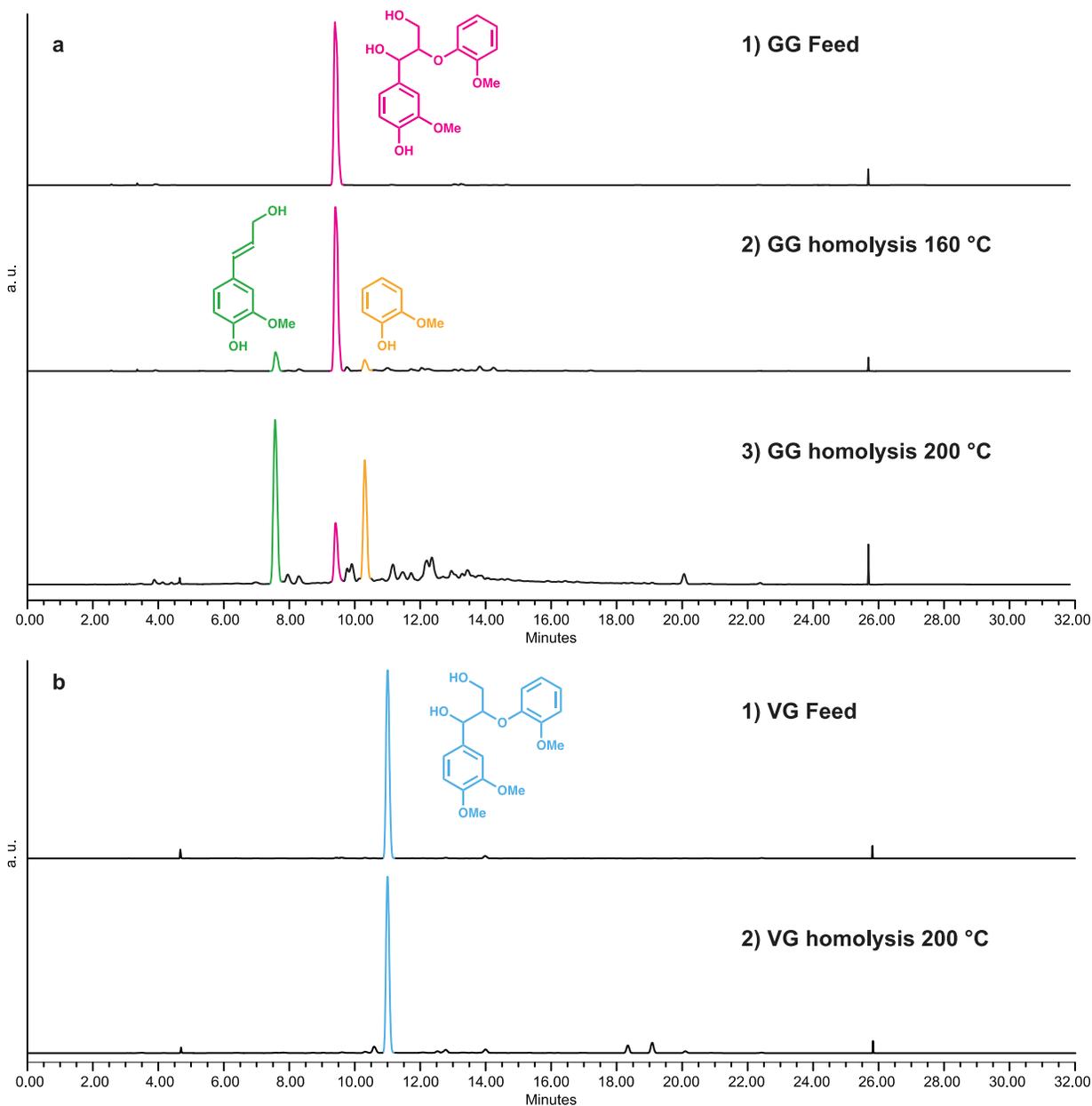


Fig S8. HPLC chromatogram from the homolysis reaction of GG (a) and VG (b). a-1) GG feed; a-2) Homolysis reaction of GG at 160 °C in MeOH; a-3) Homolysis reaction of GG at 200 °C in GVL/water (8:2, v/v); b-1) VG feed; b-2) Homolysis reaction of VG at 200 °C in GVL/water (8:2, v/v).

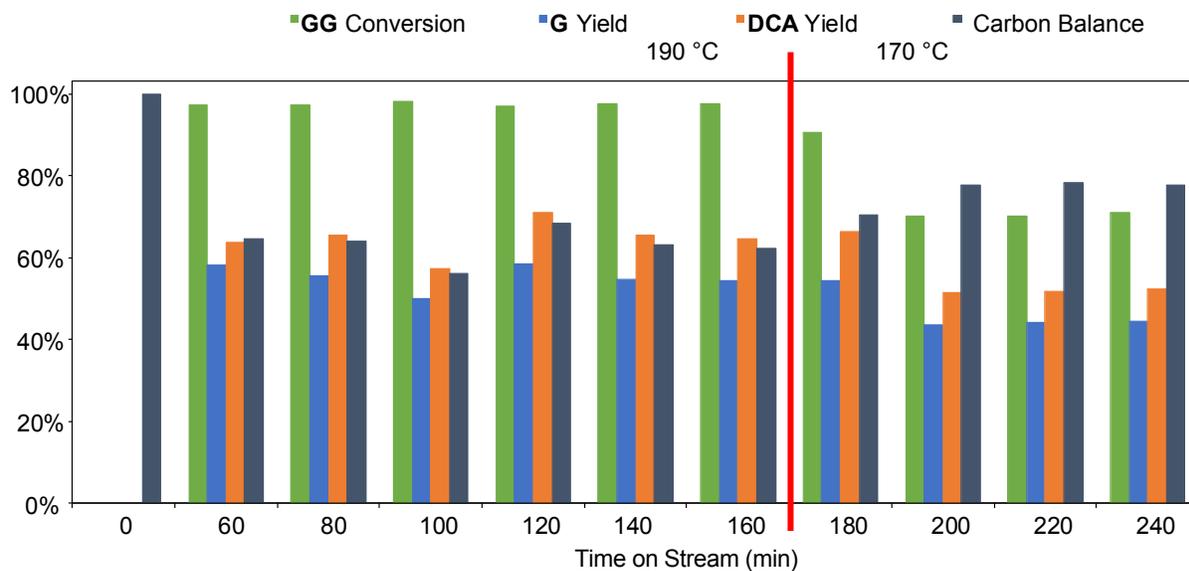


Figure S9. Reaction conversion and product distribution over time for hydrogenolysis of GG in methanol under H₂. Reaction Conditions: 190 °C and 170 °C, 800 psi H₂, 0.2 mL/min of a solution of GG in MeOH (2 mg/mL), 20 mL/min H₂, 50 mg 5% Pd/C.

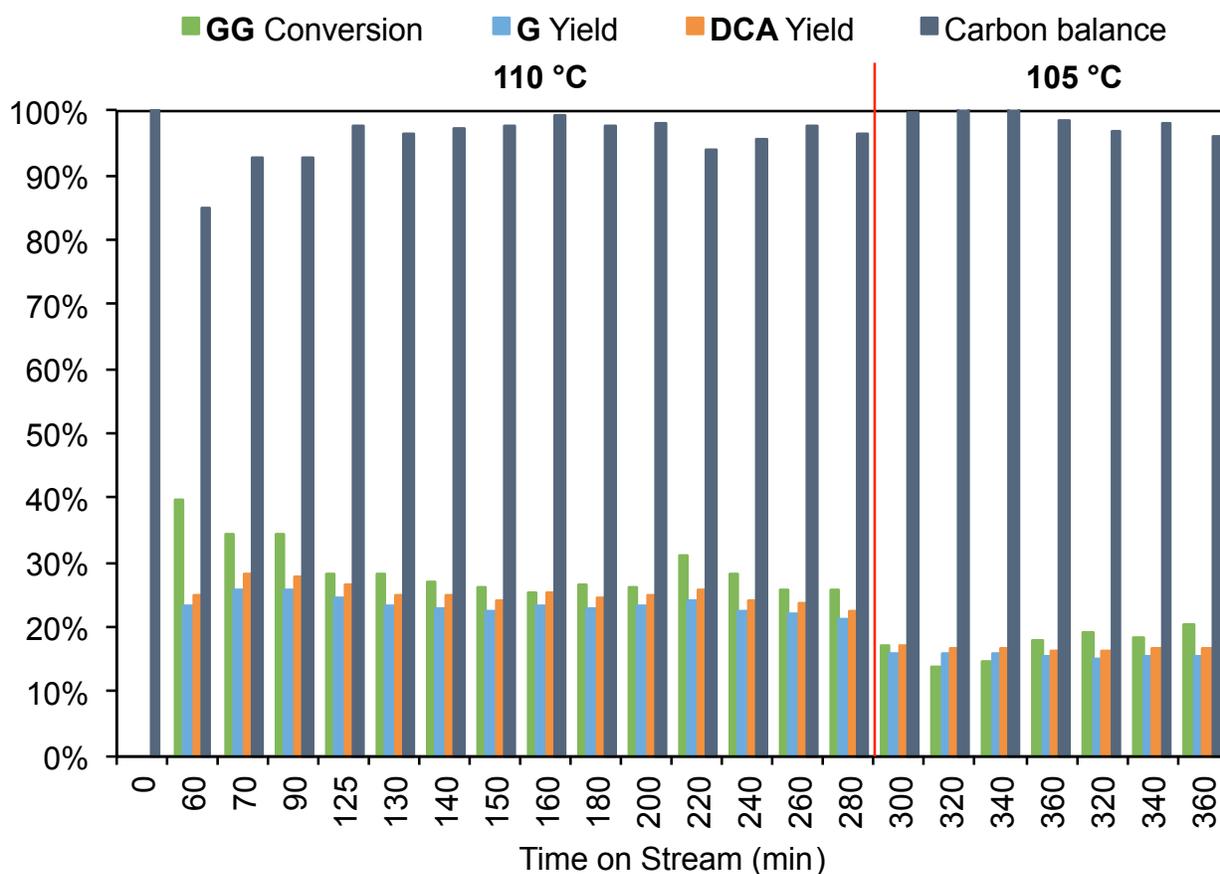


Figure S10. Reaction conversion and product distribution over time for catalytic reaction of GG in methanol under H₂ at 110-105 °C. Reaction Conditions: 110-105 °C, 600 psi H₂, 0.2 mL/min of a solution of 2 mg/mL GG in methanol, 20 mL/min H₂, 50 mg 5% Pd/C.

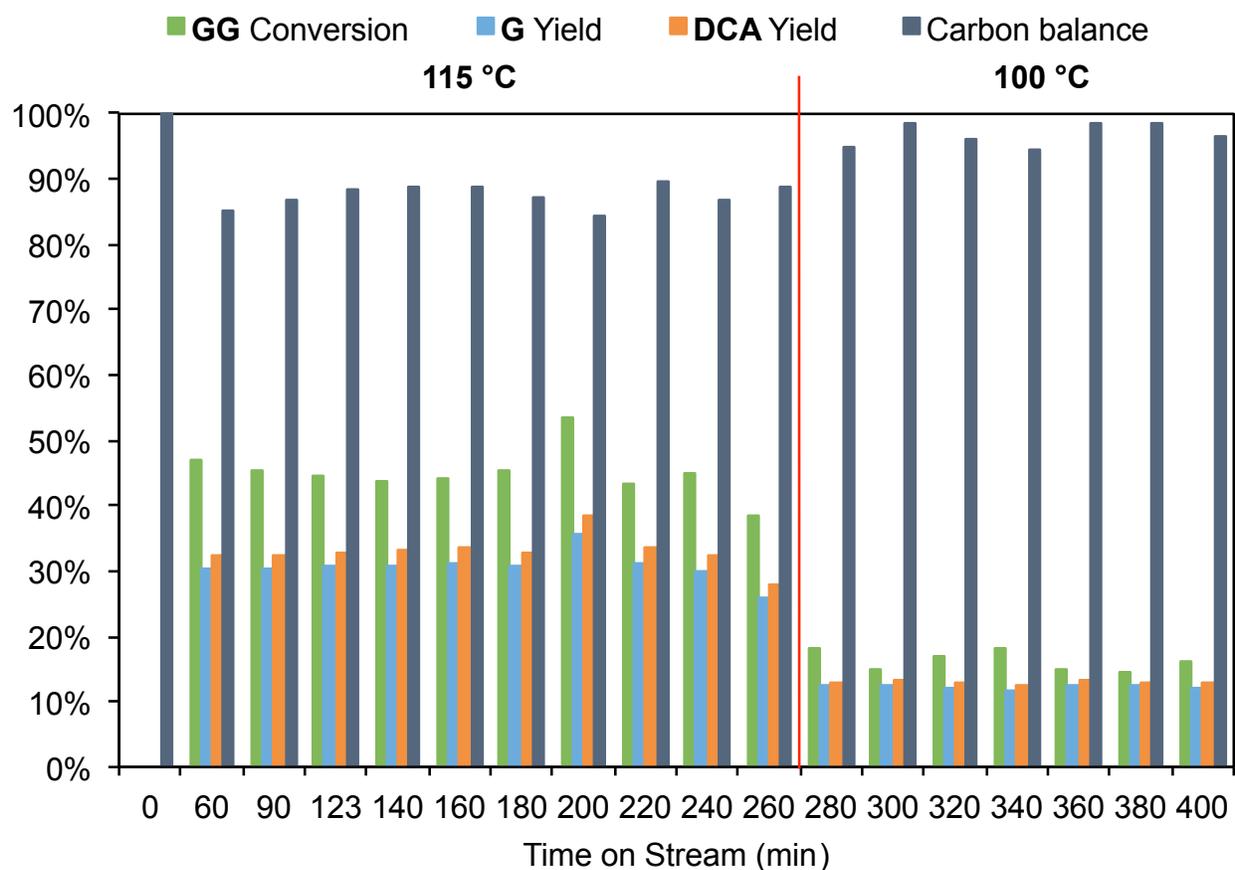


Figure S11. Reaction conversion and product distribution over time for catalytic reaction of GG in methanol under H₂ at 115-100 °C. Reaction Conditions: 115-100 °C, 600 psi H₂, 0.2 mL/min of a solution of 2 mg/mL GG in methanol, 20 mL/min H₂, 50 mg 5% Pd/C.

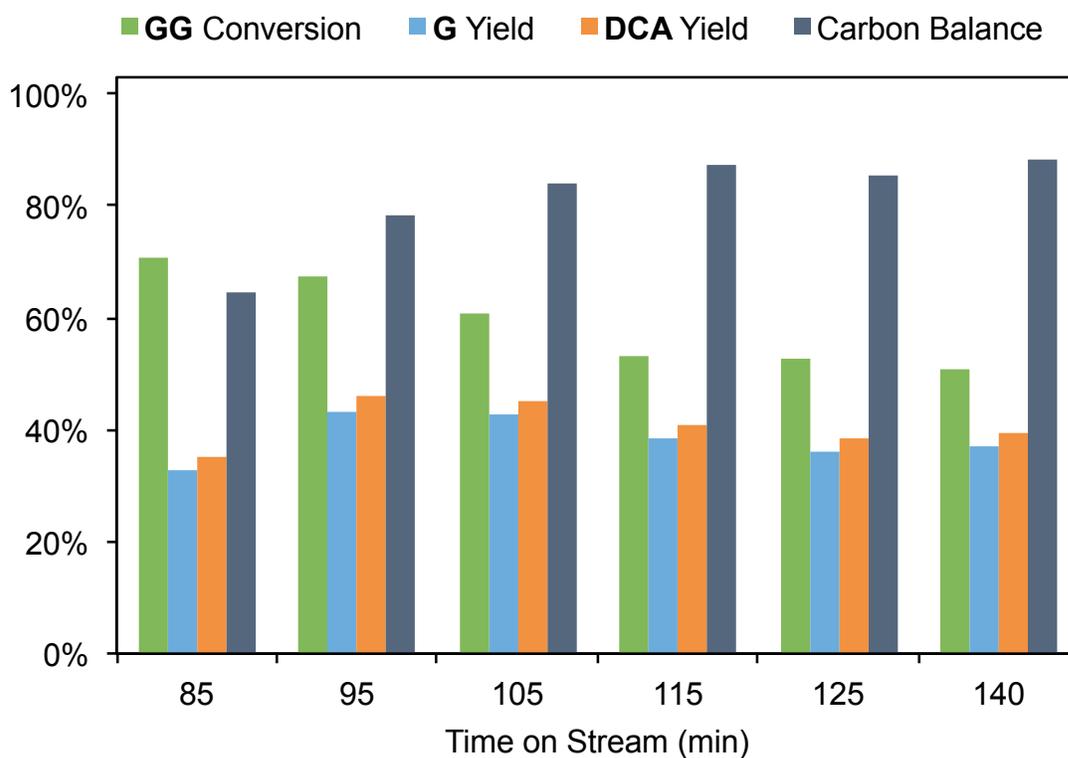


Figure S12. Reaction conversion and product distribution over time for catalytic reaction of GG in methanol under H₂ at 120 °C. Reaction Conditions: 120 °C, 600 psi H₂, 0.2 mL/min of a solution of 2 mg/mL GG in methanol, 20 mL/min H₂, 50 mg 5% Pd/C.

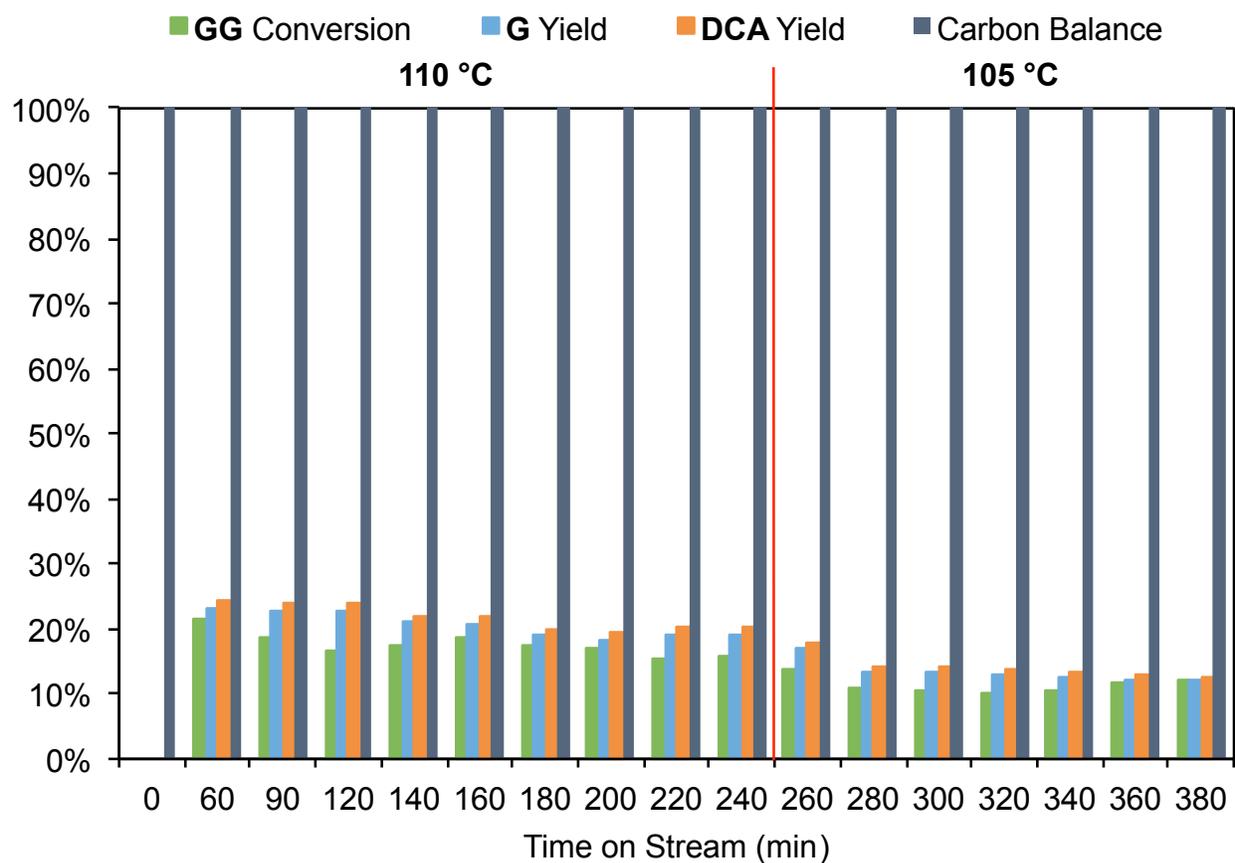


Figure S13. Reaction conversion and product distribution over time for catalytic reaction of 4 mg/mL GG in methanol under H₂. Reaction Conditions: 110-105 °C, 600 psi H₂, 0.2 mL/min of a solution of 4 mg/mL GG in methanol, 20 mL/min H₂, 50 mg 5% Pd/C.

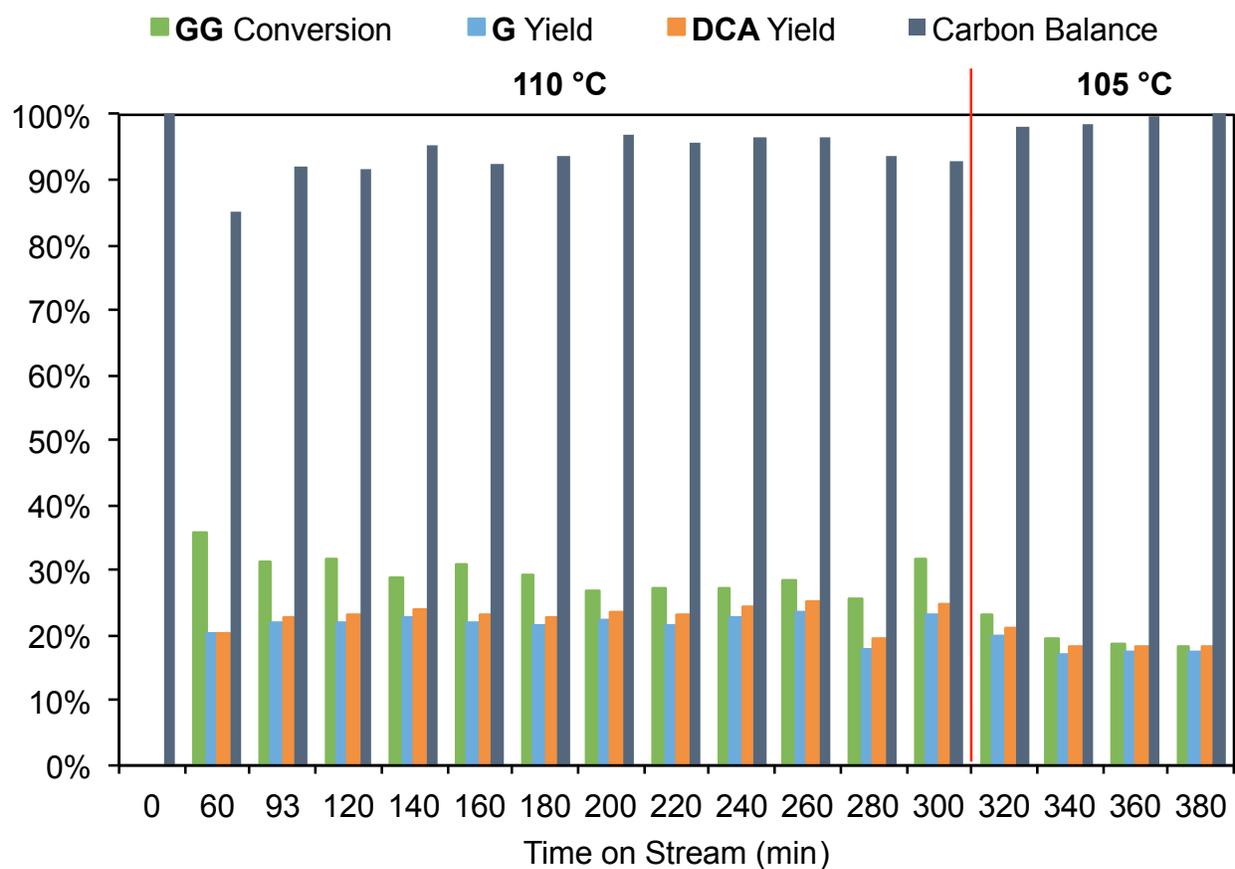


Figure S14. Reaction conversion and product distribution over time for catalytic reaction of 1 mg/mL GG in methanol under H₂. Reaction Conditions: 110-105 °C, 600 psi H₂, 0.2 mL/min of a solution of 1 mg/mL GG in methanol, 20 mL/min H₂, 50 mg 5% Pd/C.

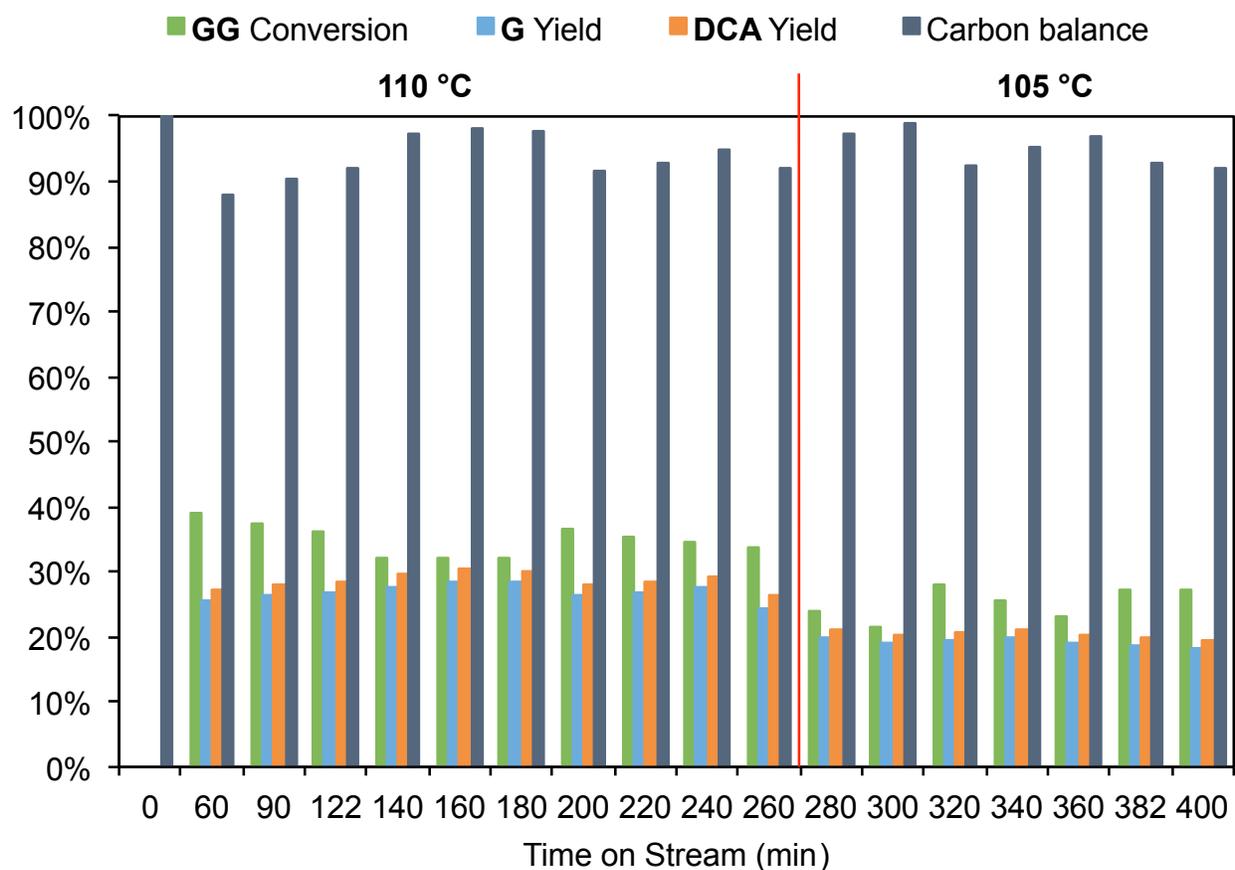


Figure S15. Reaction conversion and product distribution over time for catalytic reaction of GG in methanol under H₂ at 800 psi. Reaction Conditions: 110-105 °C, 800 psi H₂, 0.2 mL/min of a solution of 2 mg/mL GG in methanol, 20 mL/min H₂, 50 mg 5% Pd/C.

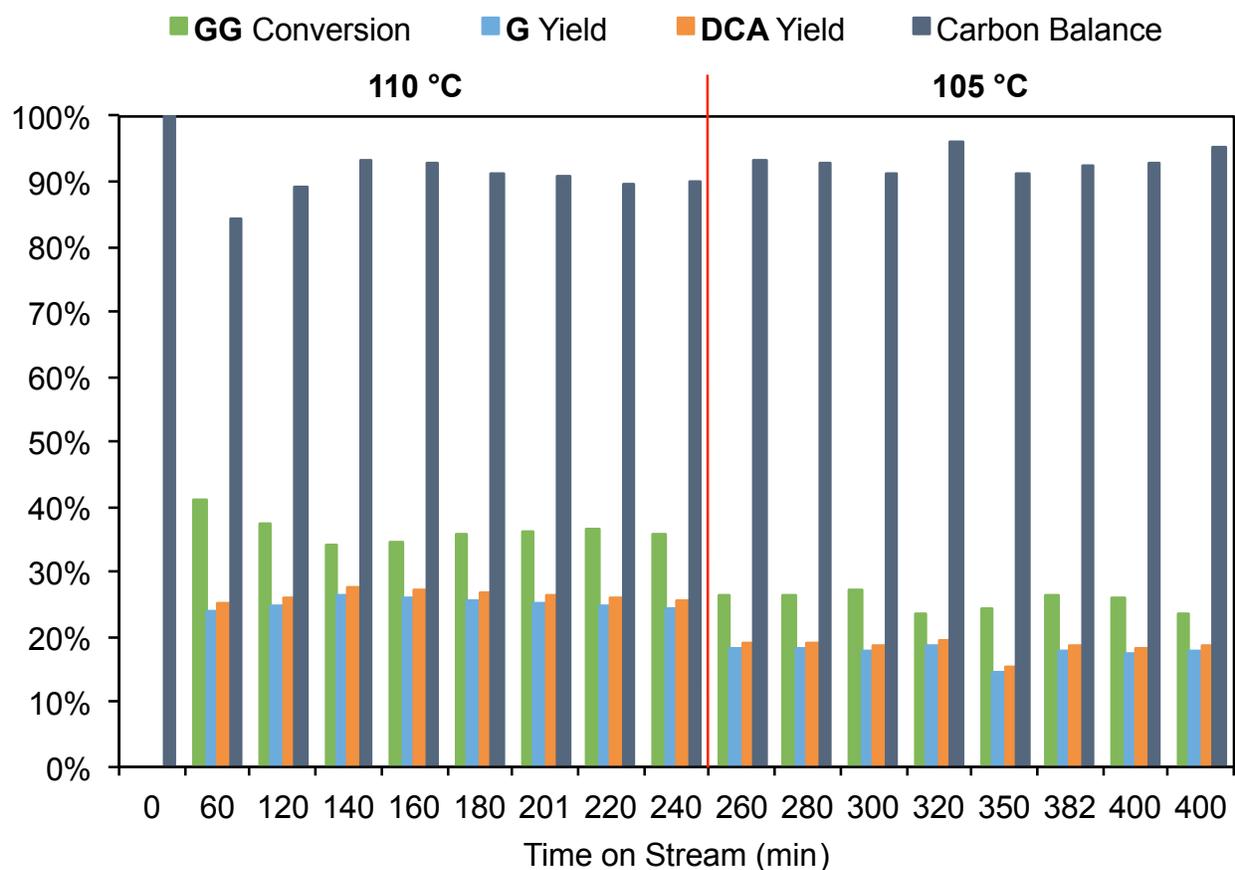


Figure S16. Reaction conversion and product distribution over time for catalytic reaction of GG in methanol under H₂ at 500 psi. Reaction Conditions: 110-105 °C, 500 psi H₂, 0.2 mL/min of a solution of 2 mg/mL GG in methanol, 20 mL/min H₂, 50 mg 5% Pd/C.

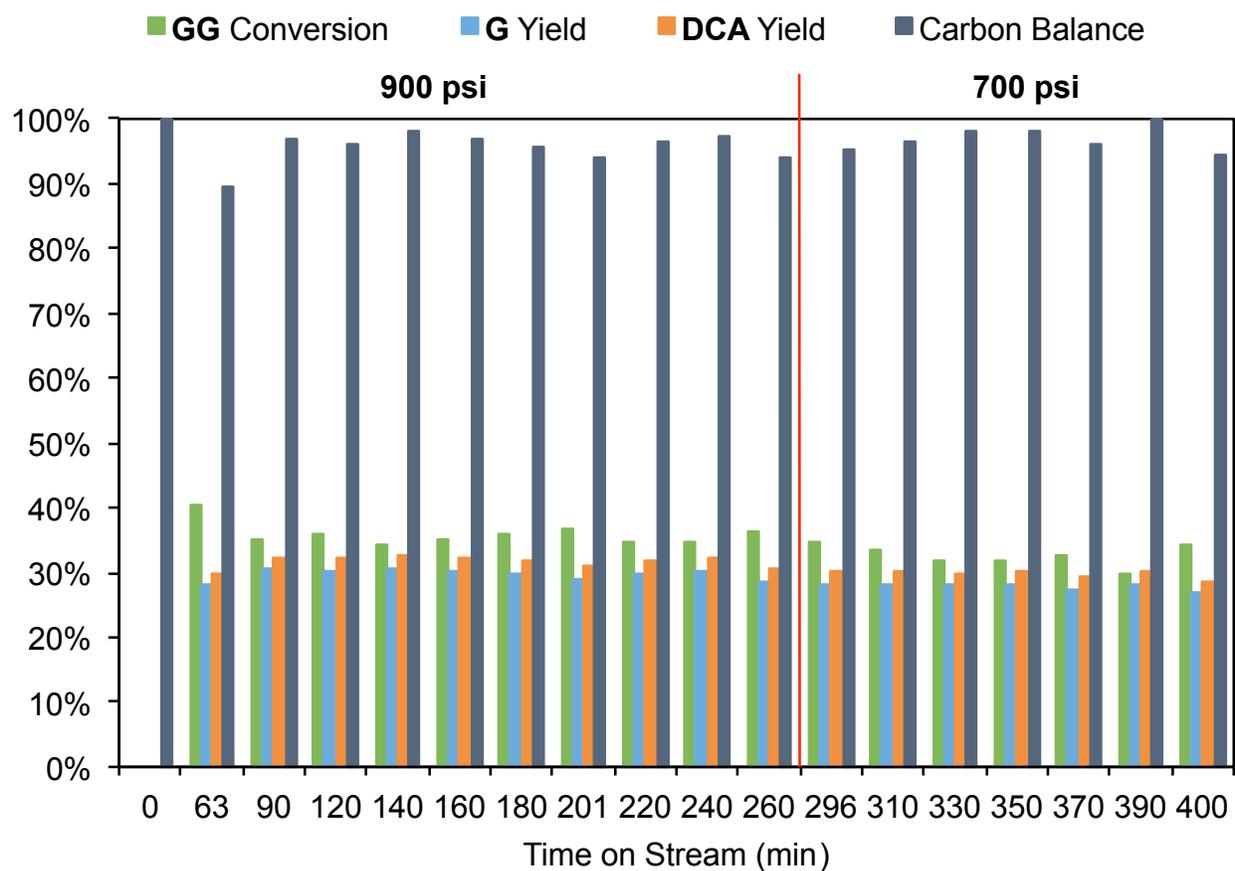


Figure S17. Reaction conversion and product distribution over time for catalytic reaction of GG in methanol under H₂ at 900-700 psi. Reaction Conditions: 110 °C, 900-700 psi H₂, 0.2 mL/min of a solution of 2 mg/mL GG in methanol, 20 mL/min H₂, 50 mg 5% Pd/C.

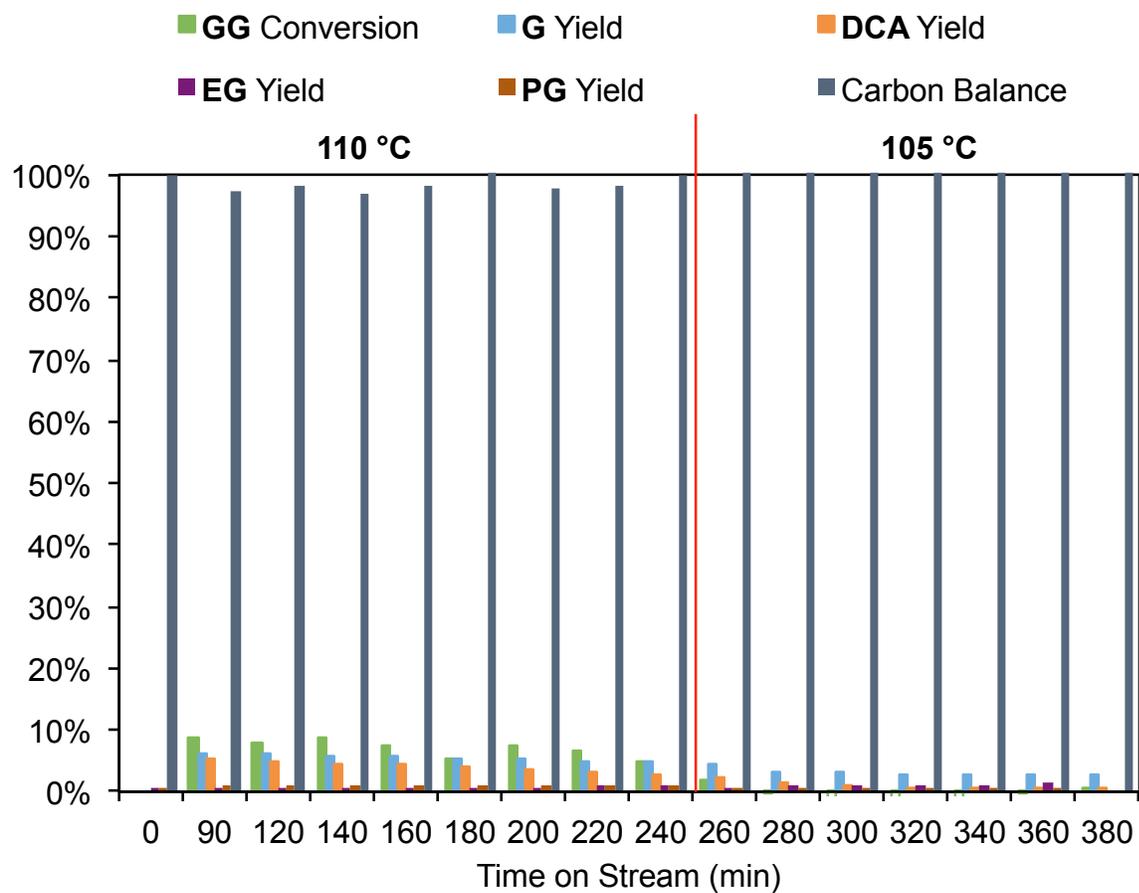


Figure S18. Reaction conversion and product distribution over time for catalytic reaction of GG in methanol under Ar at 110-105 °C. Reaction Conditions: 110-105 °C, 600 psi Ar, 0.2 mL/min of a solution of 2 mg/mL GG in methanol, 20 mL/min Ar, 50 mg 5% Pd/C.

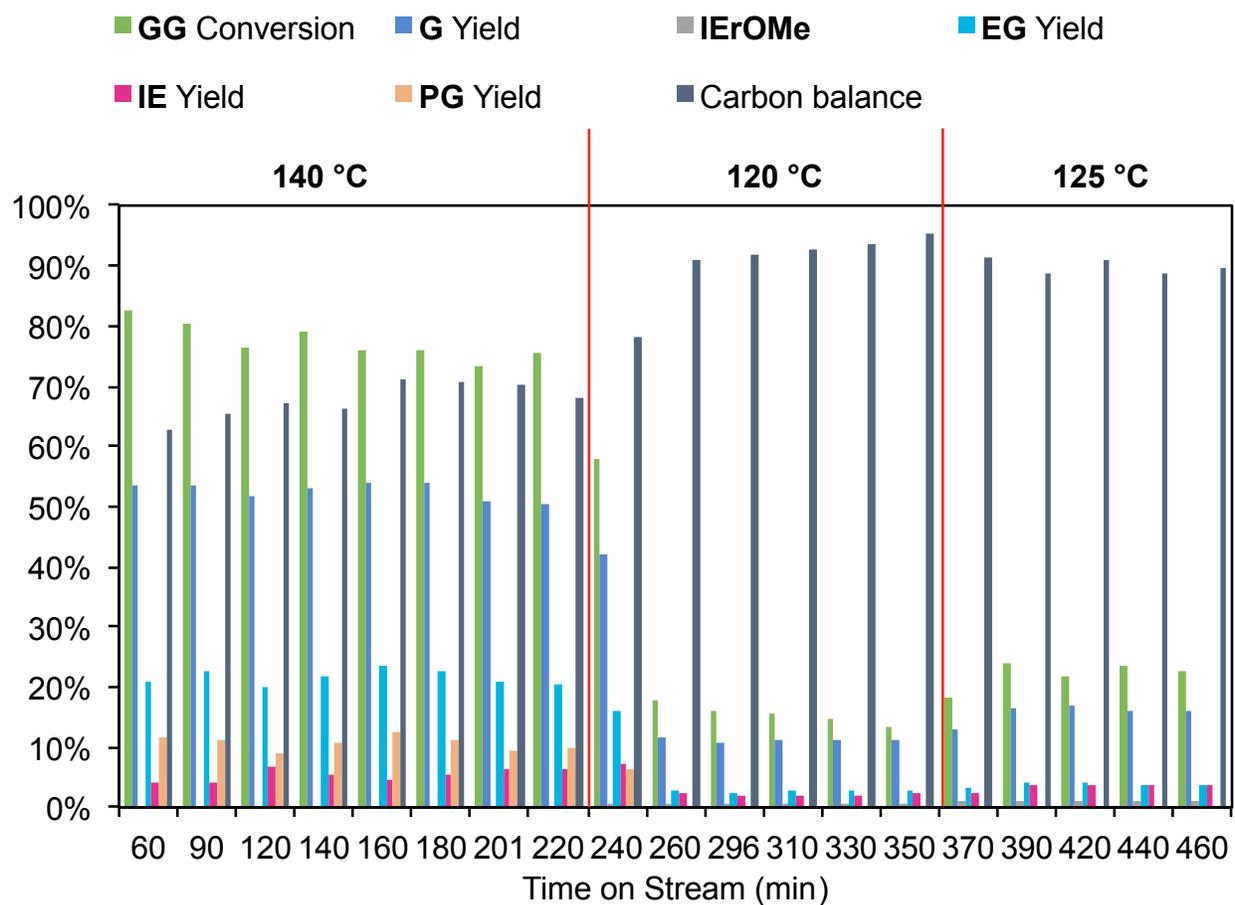


Figure S19. Reaction conversion and product distribution over time for catalytic reaction of GG in methanol under Ar at 140-120 °C. Reaction Conditions: 140-120 °C, 600 psi Ar, 0.2 mL/min of a solution of 2 mg/mL GG in methanol, 20 mL/min Ar, 50 mg 5% Pd/C.

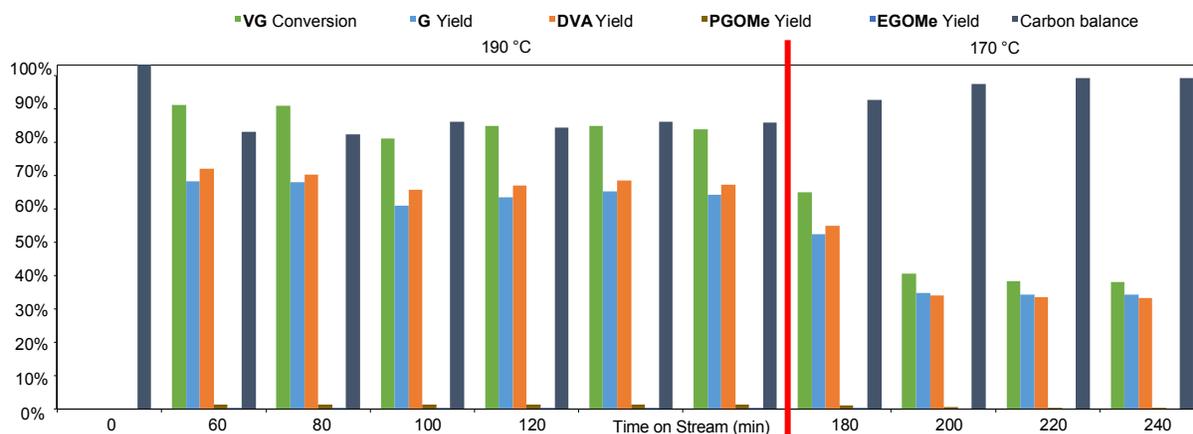


Figure S20. Reaction conversion and product distribution over time for a) catalytic reaction of VG in methanol under H₂. Reaction Conditions: 190 °C and 170 °C, 800 psi H₂, 0.2 mL/min of a solution of VG in MeOH (2 mg/mL), 20 mL/min H₂, 50 mg 5% Pd/C.

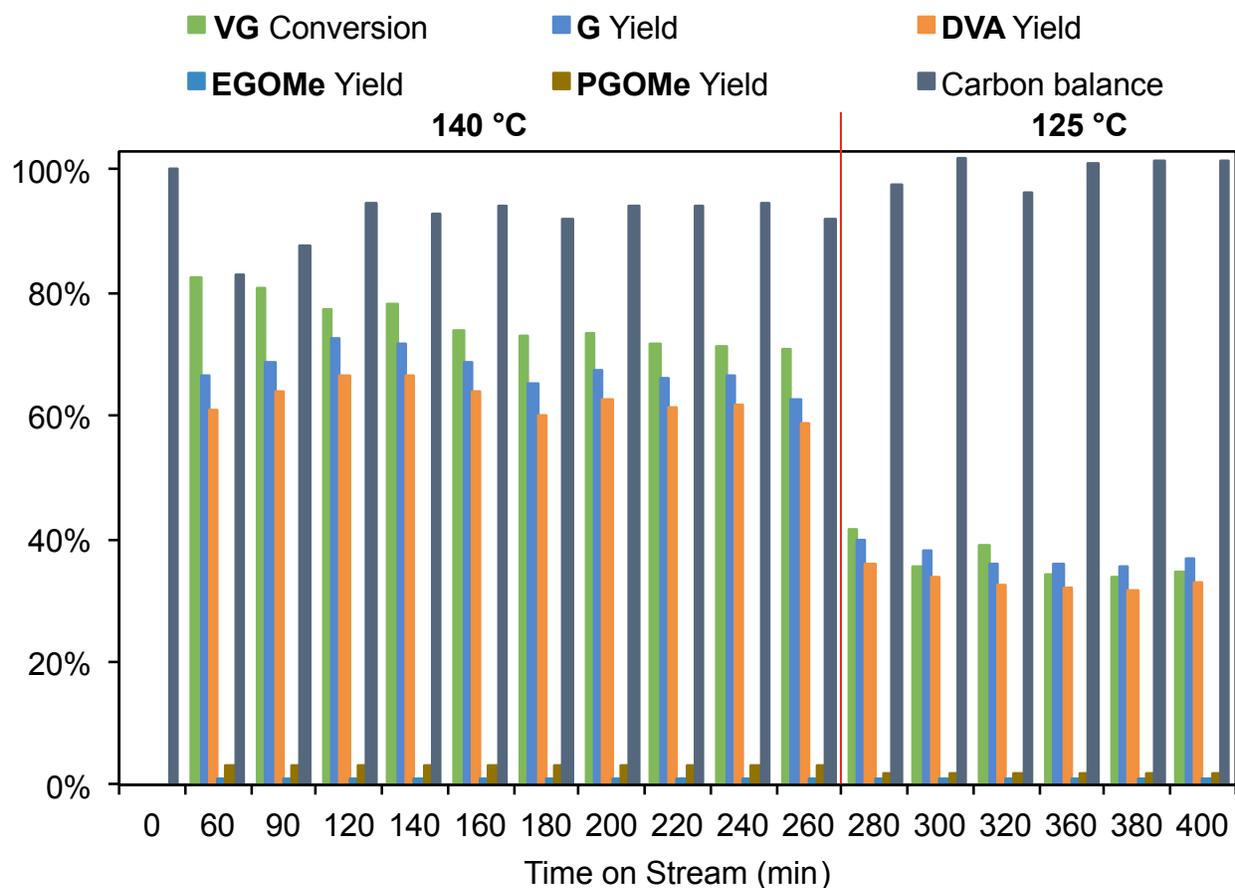


Figure S21. Reaction conversion and product distribution over time for catalytic reaction of VG in methanol under H₂ at 140-125 °C. Reaction Conditions: 140-125 °C, 800 psi H₂, 0.2 mL/min of a solution of 2 mg/mL VG in methanol, 20 mL/min H₂, 50 mg 5% Pd/C.

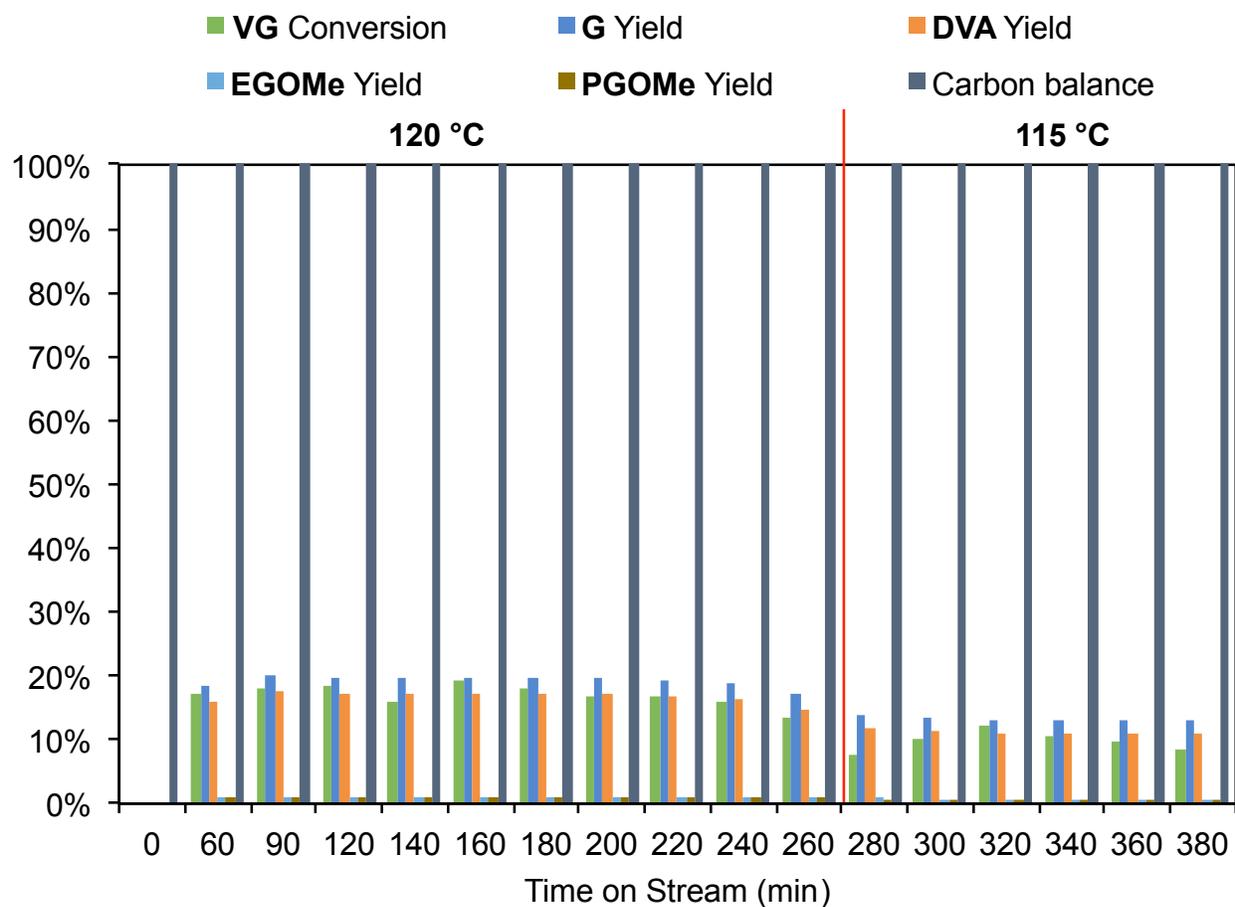


Figure S22. Reaction conversion and product distribution over time for catalytic reaction of VG in methanol under H₂ at 120-115 °C. Reaction Conditions: 120-115 °C, 600 psi H₂, 0.2 mL/min of a solution of 2 mg/mL VG in methanol, 20 mL/min H₂, 50 mg 5% Pd/C.

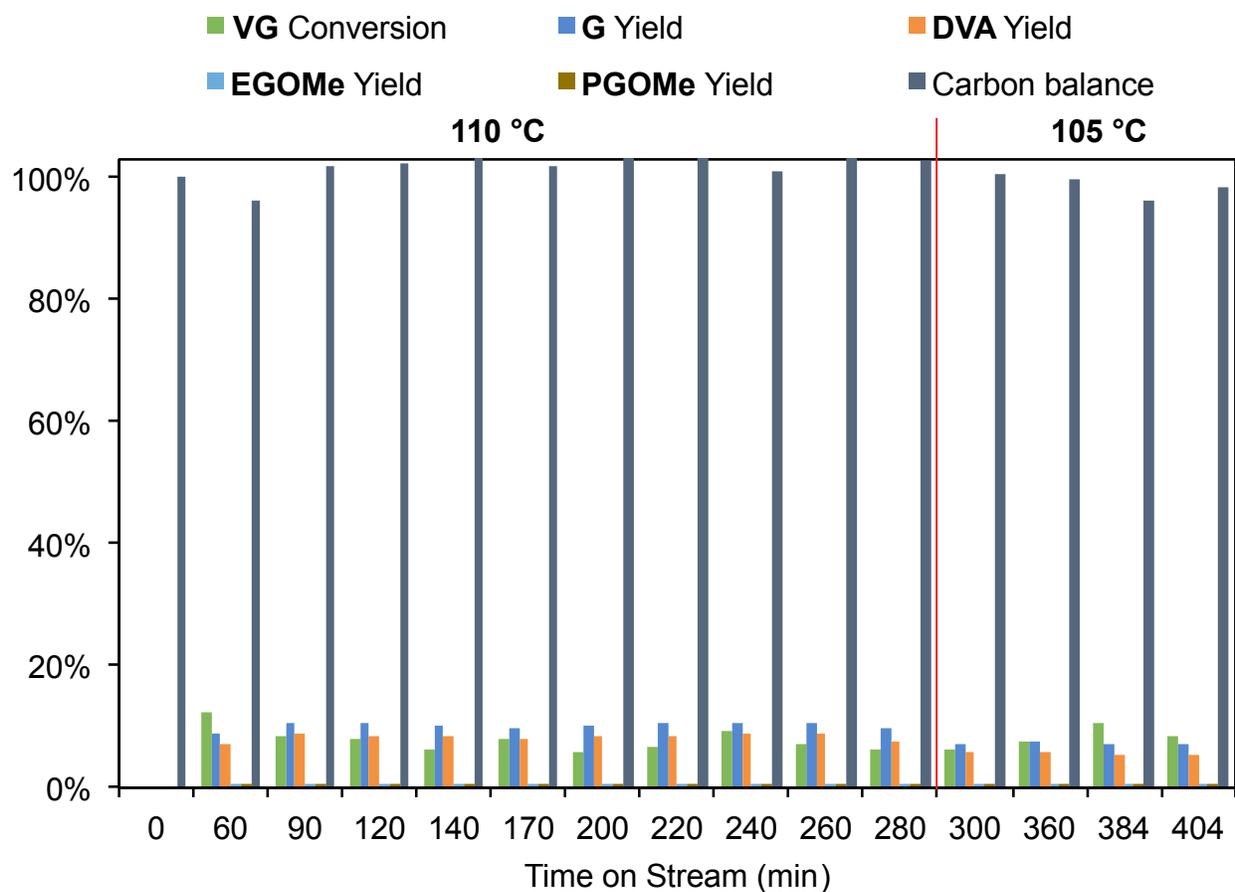


Figure S23. Reaction conversion and product distribution over time for catalytic reaction of VG in methanol under H₂ at 110-105 °C. Reaction Conditions: 110-105 °C, 600 psi H₂, 0.2 mL/min of a solution of 2 mg/mL VG in methanol, 20 mL/min H₂, 50 mg 5% Pd/C.

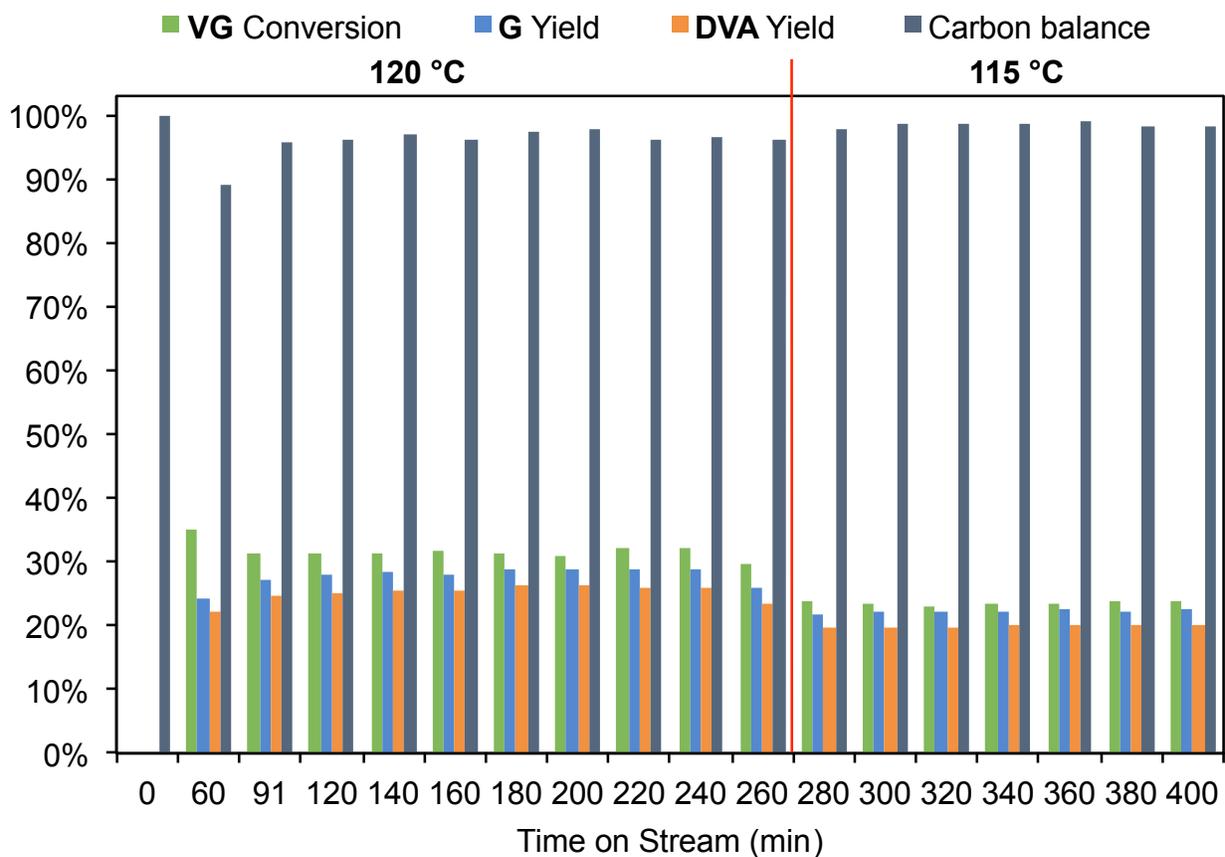


Figure S24. Reaction conversion and product distribution over time for catalytic reaction of 1 mg/mL VG in methanol under H₂. Reaction Conditions: 120-115 °C, 600 psi H₂, 0.2 mL/min of a solution of 1 mg/mL VG in methanol, 20 mL/min H₂, 50 mg 5% Pd/C.

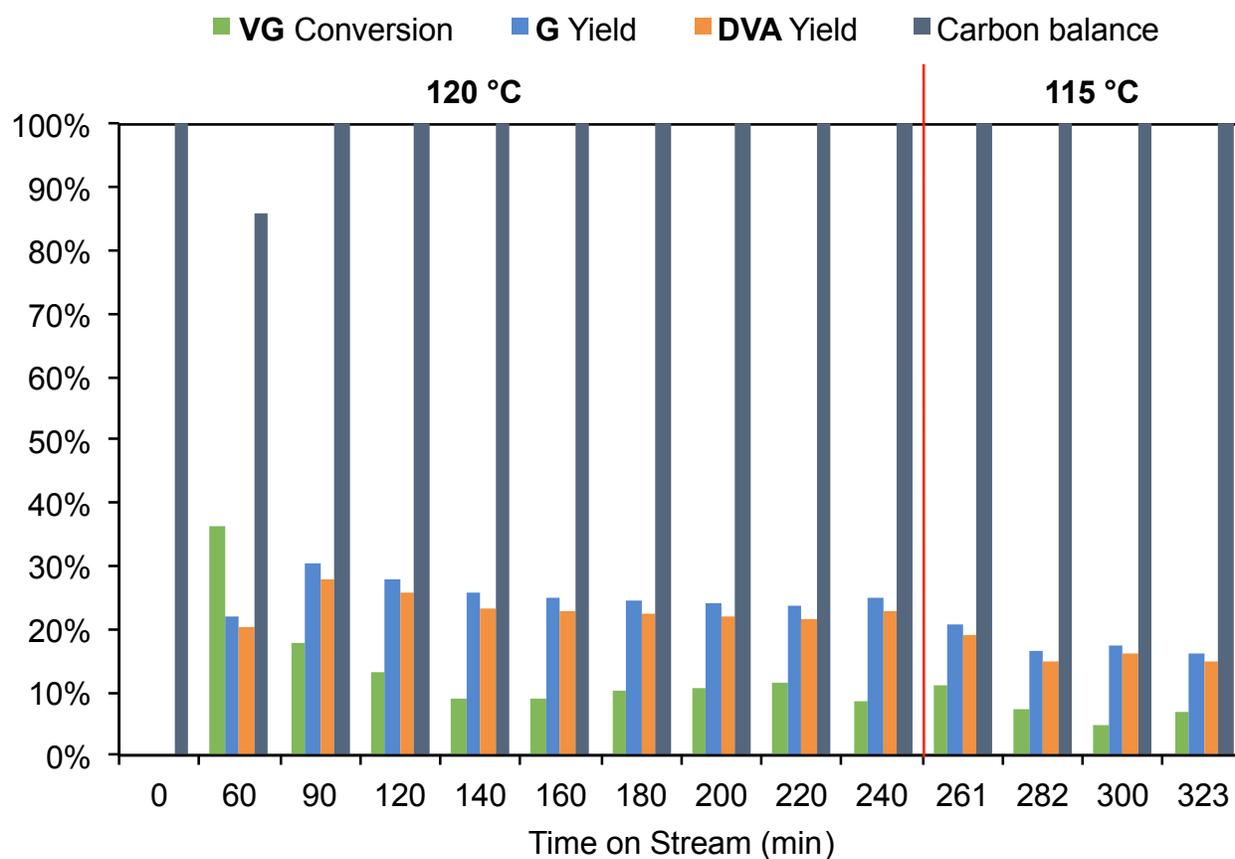


Figure S25. Reaction conversion and product distribution over time for catalytic reaction of 4 mg/mL VG in methanol under H₂. Reaction Conditions: 120-115 °C, 600 psi H₂, 0.2 mL/min of a solution of 4 mg/mL VG in methanol, 20 mL/min H₂, 50 mg 5% Pd/C.

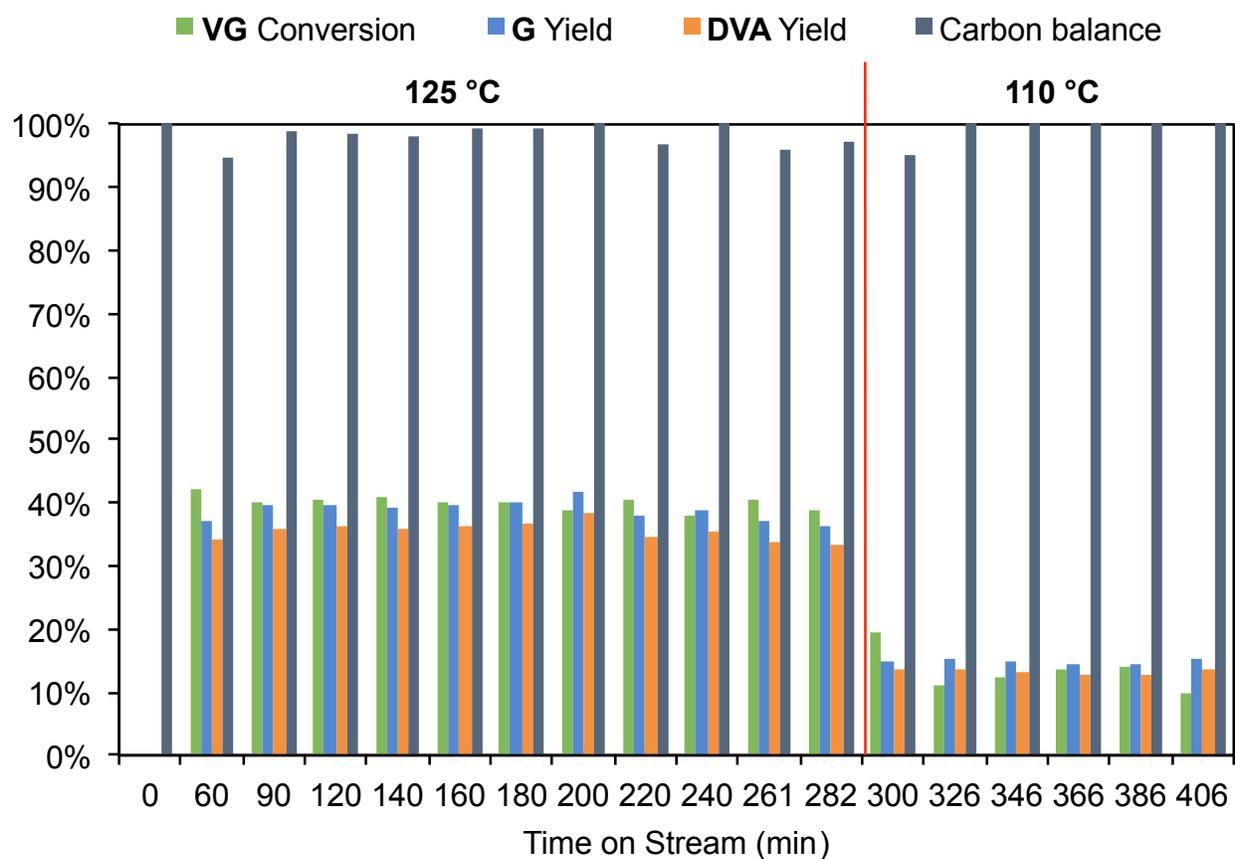


Figure S26. Reaction conversion and product distribution over time for catalytic reaction of VG in methanol under H₂ at 800 psi. Reaction Conditions: 125-110 °C, 800 psi H₂, 0.2 mL/min of a solution of 2 mg/mL VG in methanol, 20 mL/min H₂, 50 mg 5% Pd/C.

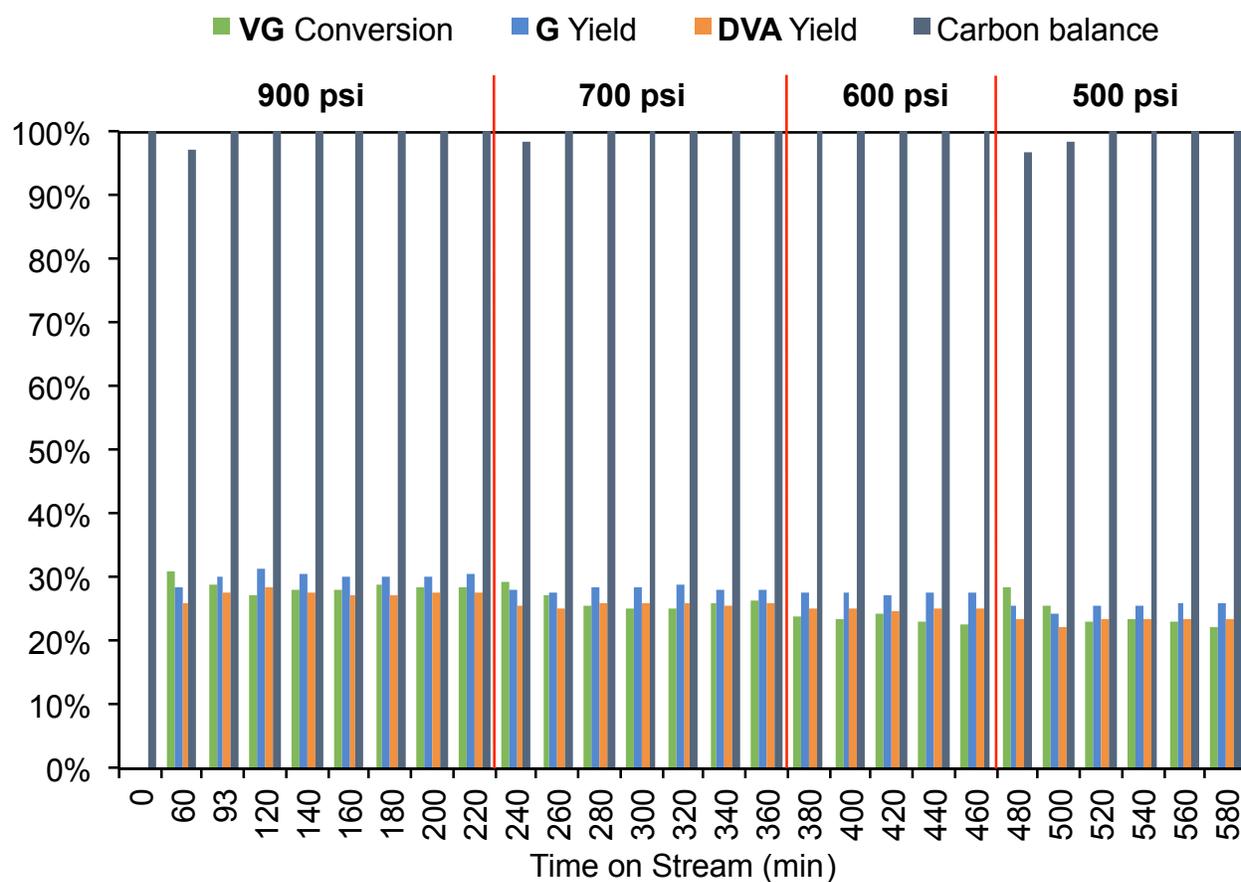


Figure S27. Reaction conversion and product distribution over time for catalytic reaction of VG in methanol under H₂ at 900-500 psi. Reaction Conditions: 120 °C, 900-500 psi H₂, 0.2 mL/min of a solution of 2 mg/mL VG in methanol, 20 mL/min H₂, 50 mg 5% Pd/C.

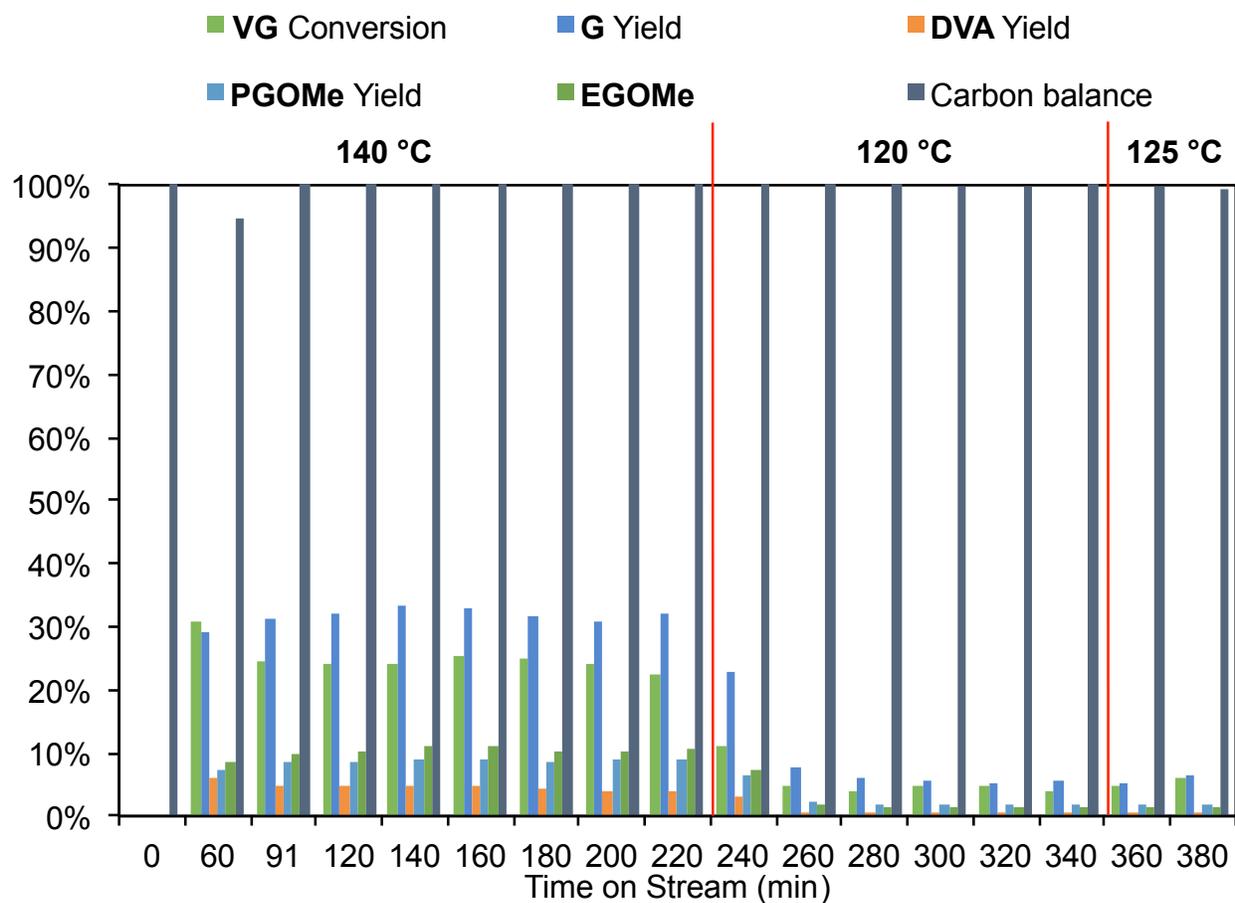


Figure S28. Reaction conversion and product distribution over time for catalytic reaction of VG in methanol under Ar at 140-120 °C. Reaction Conditions: 140-120 °C, 600 psi Ar, 0.2 mL/min of a solution of 2 mg/mL VG in methanol, 20 mL/min Ar, 50 mg 5% Pd/C.

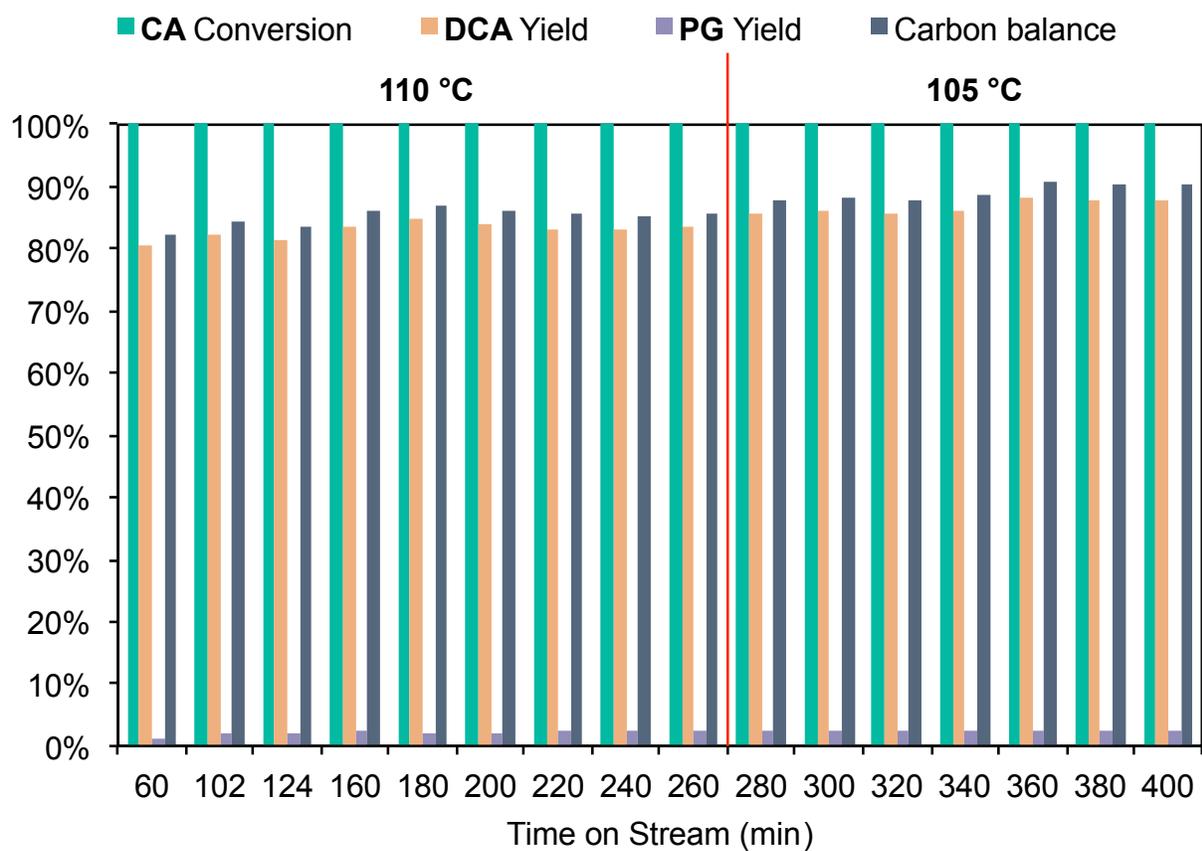


Figure S29. Reaction conversion and product distribution over time for hydrogenolysis of CA under H₂. Reaction Conditions: 110-105 °C, 600 psi H₂, 0.2 mL/min of a solution of CA in MeOH (2 mg/mL), 20 mL/min H₂, 50 mg 5% Pd/C.

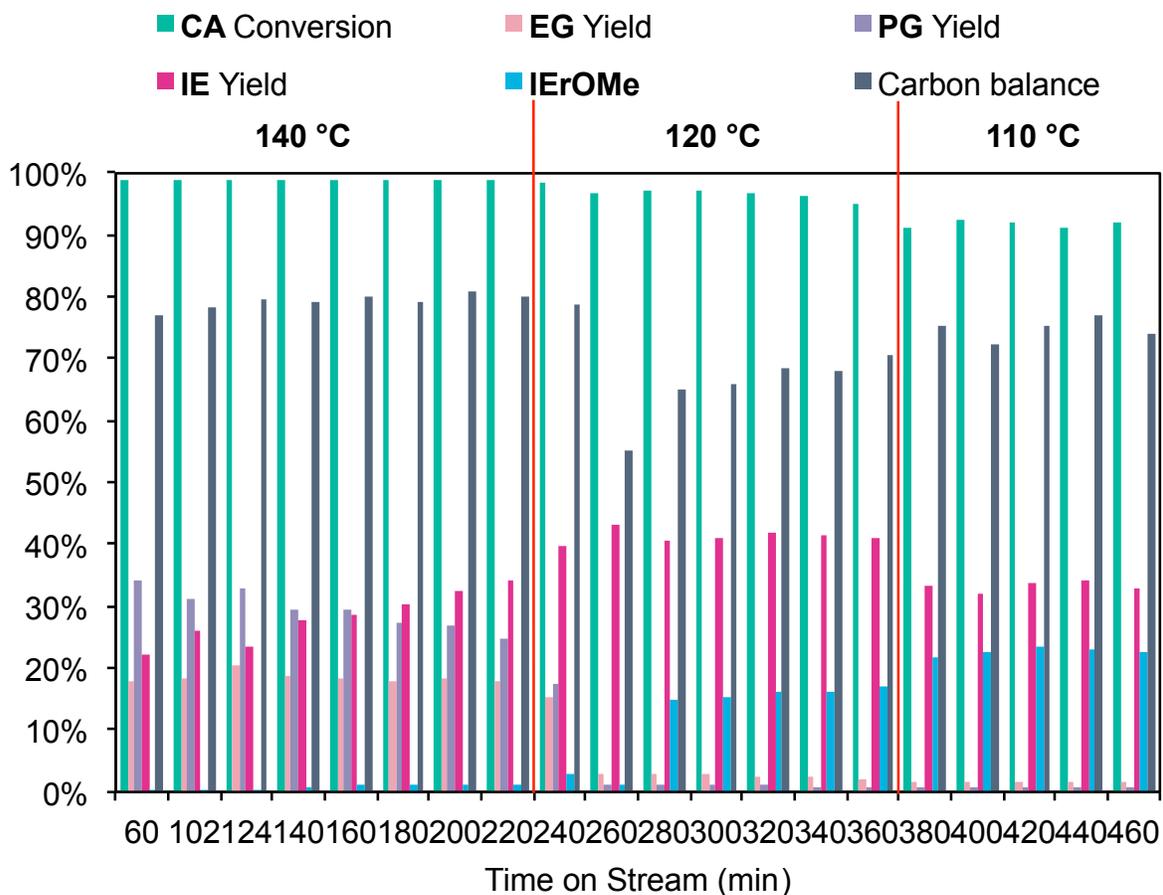


Figure S30. Reaction conversion and product distribution over time for catalytic reaction of CA under Ar at 140-110 °C. Reaction Conditions: 140-110 °C, 600 psi Ar, 0.2 mL/min of a solution of CA in MeOH (2 mg/mL), 20 mL/min Ar, 50 mg 5% Pd/C.

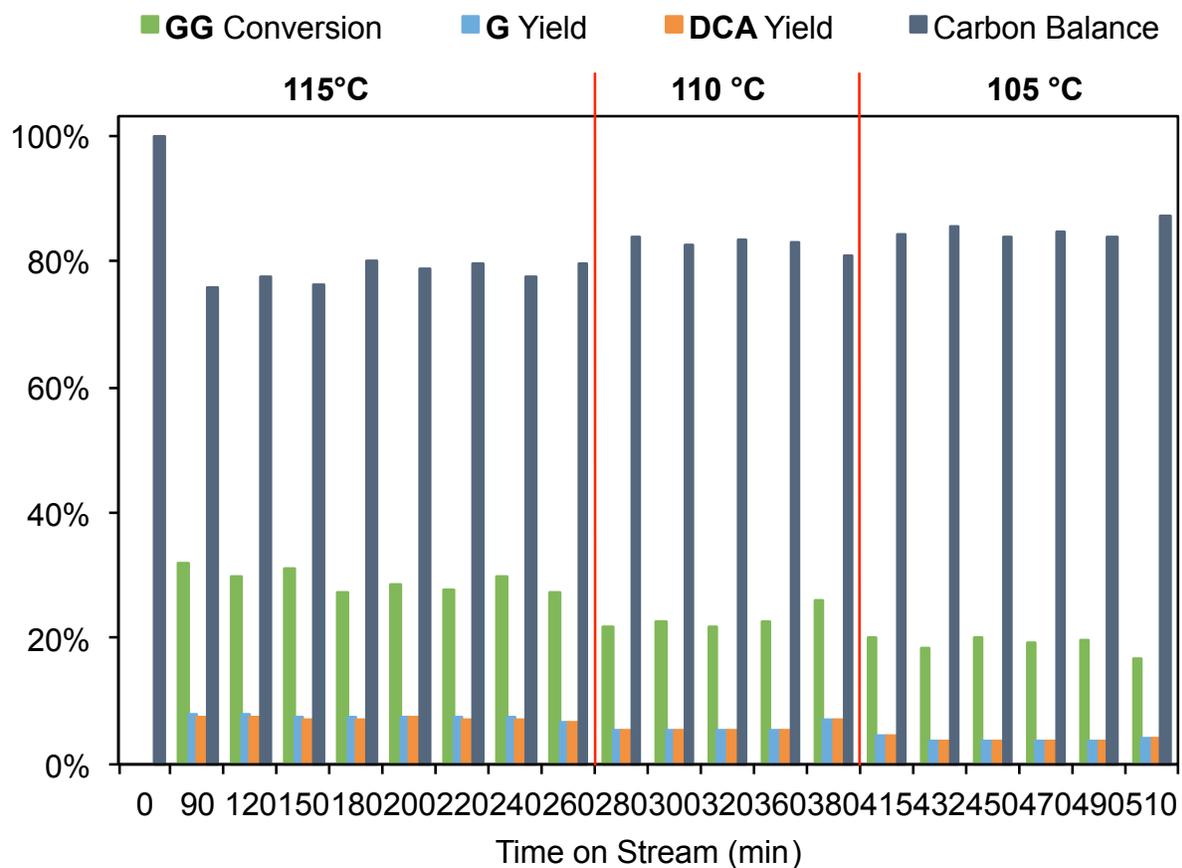


Figure S31. Reaction conversion and product distribution over time for catalytic reaction of GG in dioxane/water under H₂ at 115-105 °C. Reaction Conditions: 115-105 °C, 600 psi H₂, 0.2 mL/min of a solution of 2 mg/mL GG in dioxane/water (9:1, v/v), 20 mL/min H₂, 50 mg 5% Pd/C.

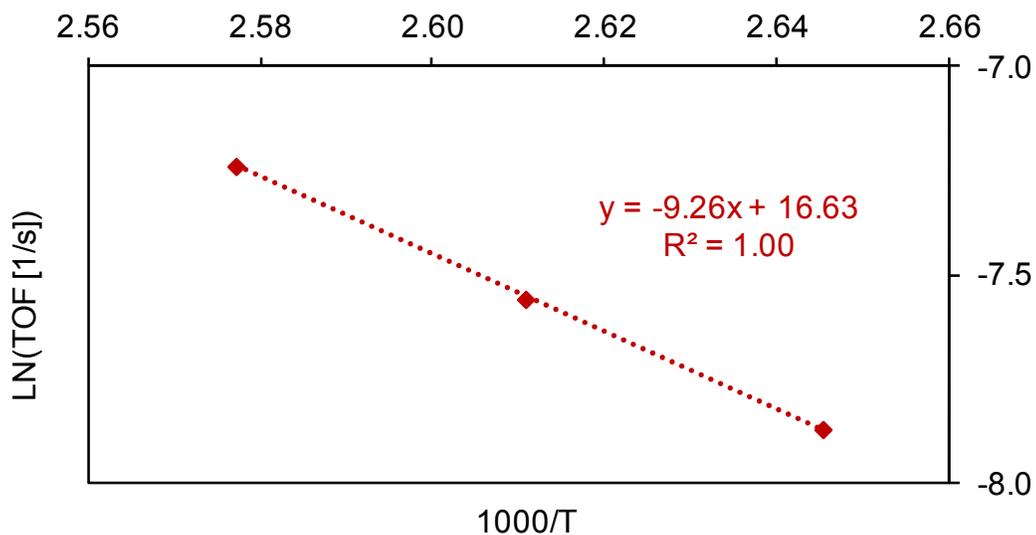


Figure S32. Arrhenius plot for GG model compound hydrogenolysis from 105 °C to 115 °C under 20 mL/min H₂ flow at 600 psi, 50 mg 5 wt% Pd/C. The activation energy was calculated as 76 kJ/mol.

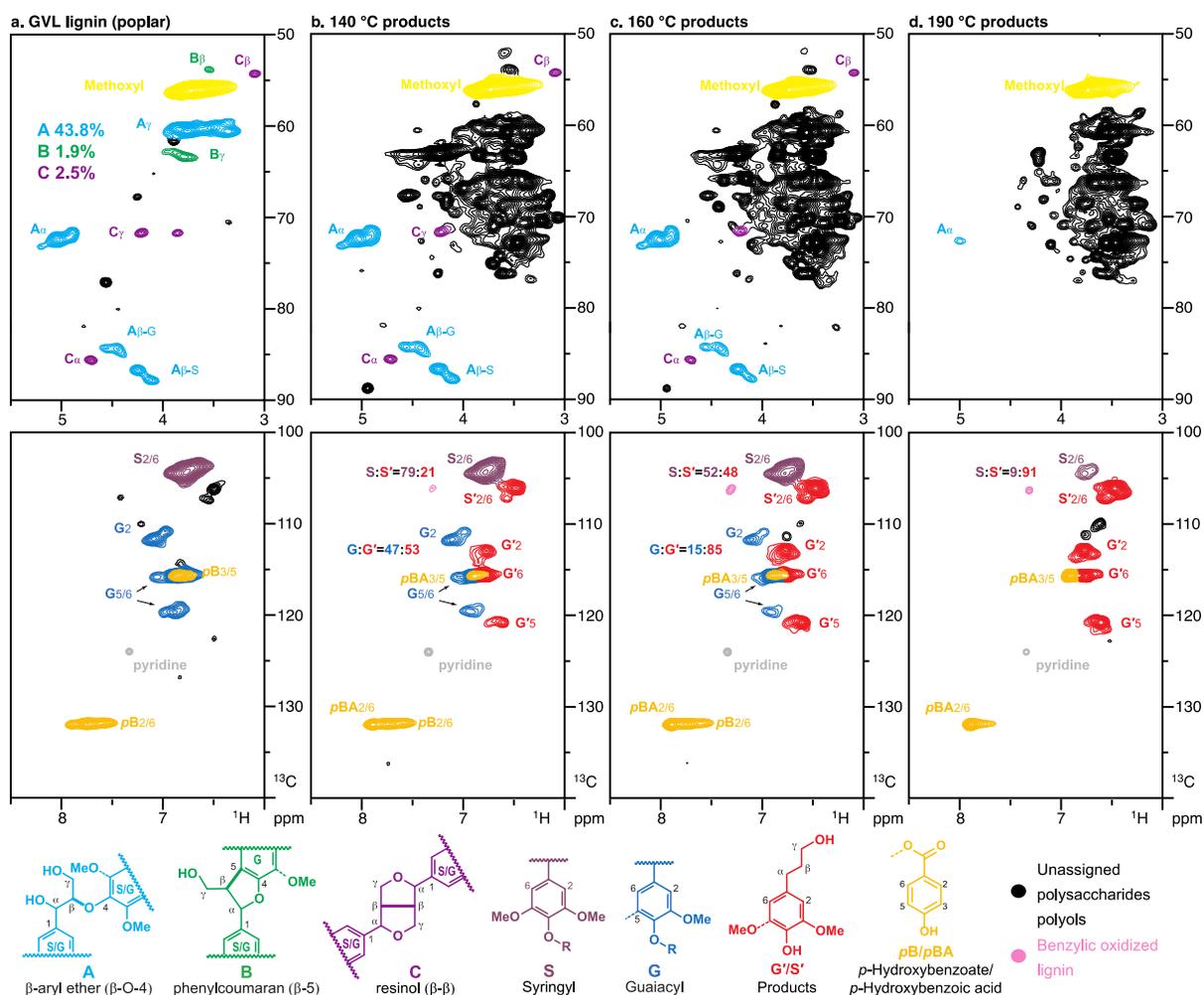


Figure S33. Partial 2D HSQC NMR spectra of a) GVL lignin obtained from poplar; GVL lignin hydrolysis products after flow-tube reaction: b) at 140 °C; c) at 160 °C; d) at 190 °C. The top four spectra: Lignin sidechain fingerprint region (δ_H 3.0-5.5 ppm, δ_C 50-90 ppm); The bottom four spectra: Aromatic region (δ_H 6.0-8.5 ppm, δ_C 100-140 ppm). The possible lignin oligomers retained are summarized in Table S7.

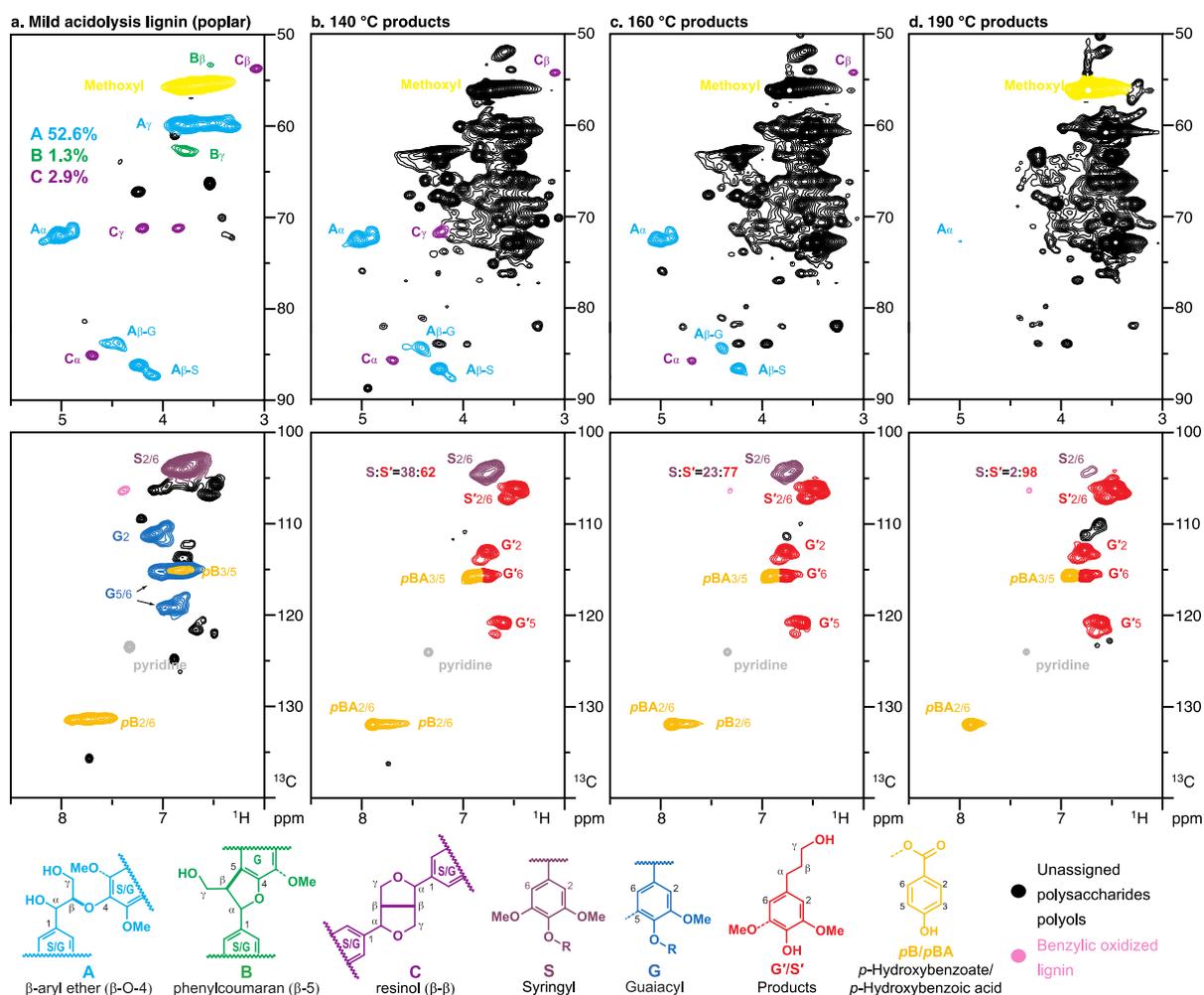


Figure S34. Partial 2D HSQC NMR spectra of a) Mild-acidolysis lignin obtained from poplar; Mild-acidolysis lignin hydrogenolysis products after flow-tube reaction b) at 140 °C; c) at 160 °C; d) at 190 °C. The top four spectra: Lignin sidechain fingerprint region (δ_H 3.0-5.5 ppm, δ_C 50-90 ppm); The bottom four spectra: Aromatic region (δ_H 6.0-8.5 ppm, δ_C 100-140 ppm). The possible lignin oligomers retained are summarized in Table S7.

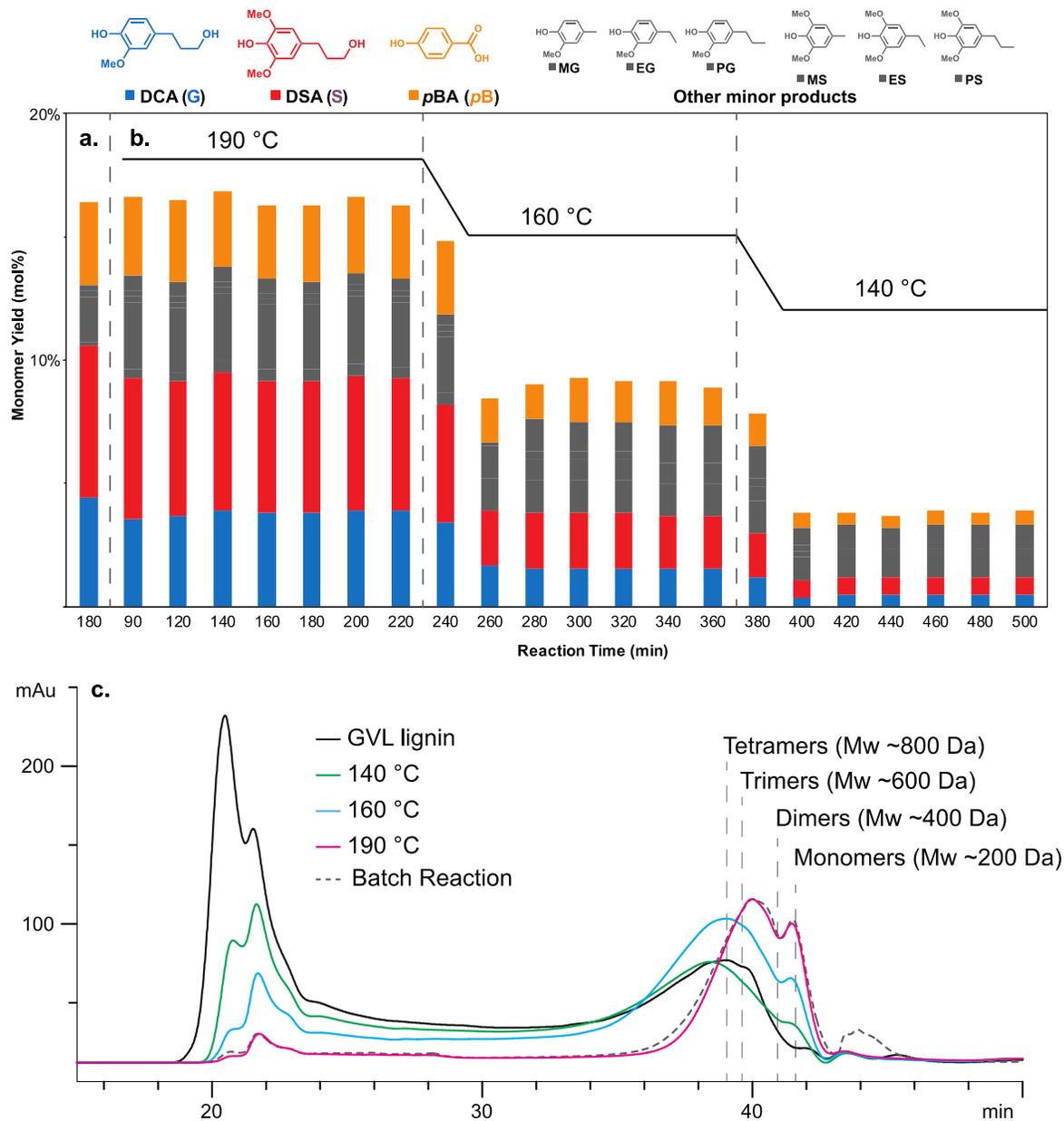


Figure S35. Monomer yields for lignin hydrogenolysis. **a)** The GVL lignin hydrogenolysis products in the batch reactor: 100 mg GVL lignin, 30 mL dioxane/water (9:1, v/v), 50 mg 5% Pd/C, 3 h, 450 psi H₂ (STP), 200 °C.; **b)** The GVL lignin hydrogenolysis products in the flow-reactor: 1 mg/mL GVL lignin dissolved in dioxane/water (9:1, v/v), 50 mg 5% Pd/C, 800 psi H₂ (STP). The temperature of the reactor was set to 190 °C, changed to 160 °C at 220 min, and decreased to 140 °C at 360 min. **c)** GPC Chromatogram for GVL lignin and hydrogenolysis products of GVL lignin in a flow reactor at 140-190 °C and in a batch reactor at 200 °C. The x-

axis is the elution time, and the y-axis is the UV absorbance at 280 nm. Monomer yields are reported in Table S5.

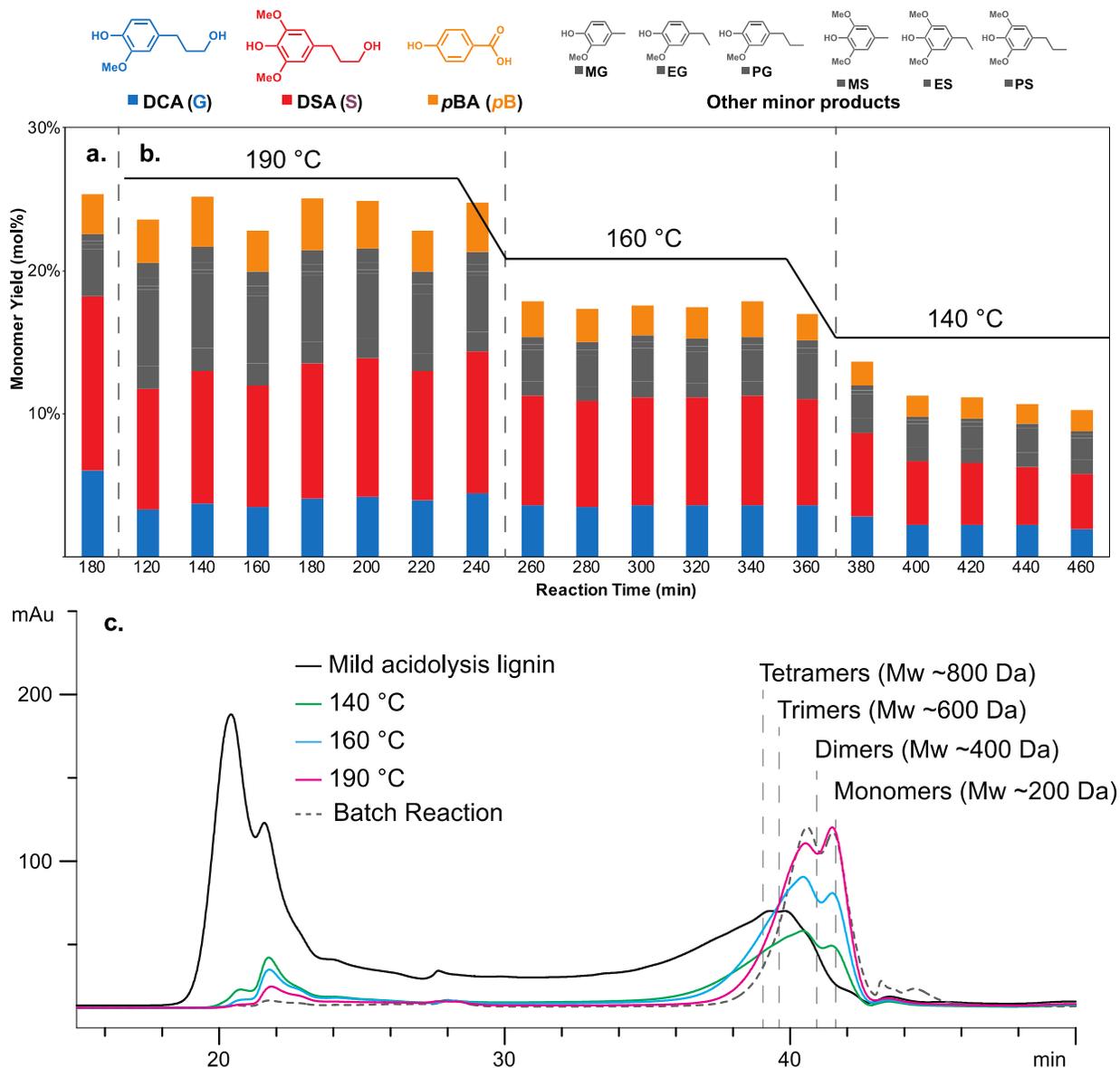


Figure S36. Monomer yields for lignin hydrogenolysis. **a)** The mild-acidolysis lignin hydrogenolysis products in the batch reactor: 100 mg mild-acidolysis lignin, 30 mL dioxane/water (9:1, v/v), 50 mg 5% Pd/C, 3 h, 450 psi H₂ (STP), 200 °C.; **b)** The GVL lignin hydrogenolysis products in the flow-reactor: 1 mg/mL GVL lignin dissolved in dioxane/water (9:1, v/v), 50 mg 5% Pd/C, 800 psi H₂ (STP). The temperature of the reactor was set to 190 °C, changed to 160 °C at 220 min, and decreased to 140 °C at 360 min. **c)** GPC Chromatogram for GVL lignin and hydrogenolysis products of GVL lignin in a flow reactor at 140-190 °C and in a batch reactor at

200 °C. The x-axis is the elution time, and the y-axis is the UV absorbance at 280 nm. Monomer yields are reported in Table S6.

Synthetic model compounds for GPC analysis of the lignin depolymerization products

Lignin model compounds with different molecular weight was used for calibrating the depolymerization products (Fig. S6). The model compounds were synthesized and characterized as previously reported.^{1,2}

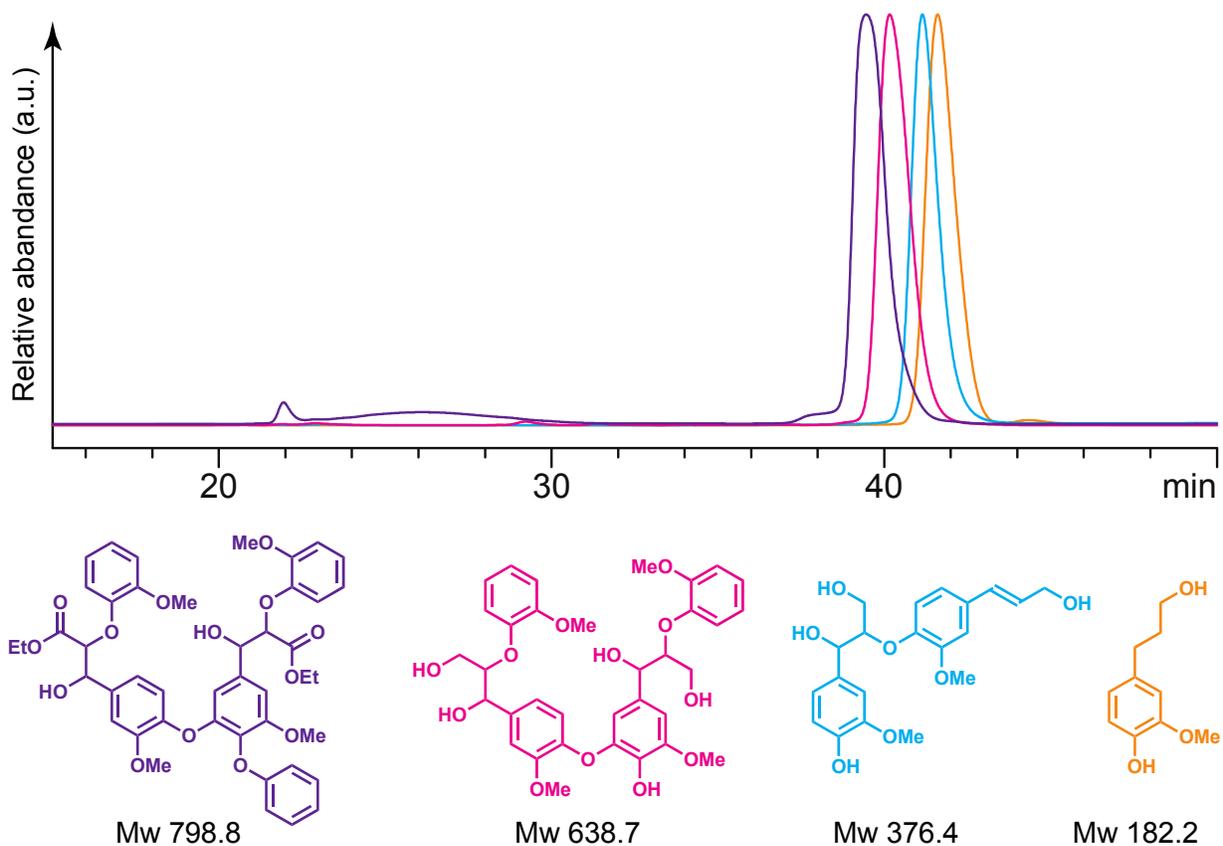


Figure S37. GPC calibration curves from synthetic model compounds. The x axis is the elution time. The y axis is the response of a UV-light detector (at 280 nm) normalized to the most abundant signal in each chromatogram. a.u., arbitrary unit

Lignin hydrogenolysis reaction under Ar

The lignin solution (1 mg/mL) was continuously fed to the flow-through reactor with Pd/C catalyst under Ar flow [20 cm³ (STP)/min]. Essentially no products were detected from lignin homolysis or other cleavage reactions under Ar. After the reaction, some polymeric components were seen to have precipitated in the reactor as a dark brown powder. A recent study showed that, when there is insufficient H₂ during lignin hydrogenolysis, the main products were **CA**-type and **IE**-type compounds, which is consistent with our model compound study.³ Another study reported that, in the two-stage flow-through reactor, a modest amount of the homolysis/solvolysis products were obtained at the first lignin extraction stage.⁴ We contend that the addition of an acid catalyst, such as phosphoric acid or biomass-derived acetic acid, can facilitate the homolysis/solvolysis reaction but these acid-catalyzed reactions easily lead to condensation. In our process, under neutral conditions and short residence time, the unwanted reaction pathways were hindered.

General synthetic procedures

General procedure for NaBH₄ reduction

NaBH₄ (5 eq.) was suspended in EtOH in a round-bottom flask and cooled in an ice-water bath. Aldehyde or ester (1 eq. in EtOH) was added into the NaBH₄ suspension slowly through a dropping funnel. The reaction was gradually warmed to room temperature and monitored by thin-layer chromatograph (TLC) for 4 h. EtOAc was added, then DI-water and sat. NH₄Cl solution was added slowly using a dropping funnel. The aqueous layer was washed with EtOAc, the combined organic layer was washed with brine, dried over MgSO₄, and evaporated *in vacuo*. The crude product was purified by flash-chromatography.

General procedure for double-bond saturation or benzyl group removal using H₂-Pd/C

The alkene was dissolved in MeOH in round-bottom flask fitted with a magnetic stirrer. Pd/C (5 wt%) was then suspended in the solution. The gas in the solvent and flask was removed *in vacuo*, and the flask was then fitted with a hydrogen-filled balloon. The reaction suspension was stirred at room temperature for 2 h, then filtered through Celite. Reaction solvent was removed *in vacuo* and the crude product was redissolved in a small amount of EtOAc then purified by flash-chromatography.

General procedure for methylation

Phenolic compound (1 eq.), K₂CO₃ (1.5 eq.), and iodomethane (4 eq.) were suspended in acetone in a round-bottom flask. The reaction was stirred at room temperature for 15 h. The completion of the reaction was confirmed by GC-MS, after which time the product was filtered through Celite. Reaction solvent was removed *in vacuo*. The crude product was redissolved in EtOAc, washed with sat. NH₄Cl, brine, then dried over MgSO₄. The combined organic layer was evaporated *in vacuo*, redissolved in a small amount of EtOAc, then purified by flash-chromatography.

The synthesis of guaiacylglycerol- β -guaiacyl ether (**GG**) model compound was essentially as previously⁵. NMR profiles were in well agreements as previously reported.^{5,6}

Compound 1: benzyl vanillin

Vanillin (15.2 g, 0.1 mol) was dissolved in 40 mL DMF in a 250 mL round bottom flask. K₂CO₃ (20.7 g, 0.15 mol) and KI (1 g) was added into the flask. BnBr (18.8 g, 0.11 mol) was added at room temperature while stirring vigorously with a magnetic stirrer. The reaction suspension was heated at 50 °C overnight (~15 h). The suspension was filtered and the precipitate was washed with EtOAc (3 \times 50 mL). The combined filtrate was washed with DI-water (2 \times 50 mL), brine (50 mL), dried over MgSO₄, then evaporated *in vacuo* to give a pale yellow oil. The crude product was crystallized from ethanol (20 mL) and hexane (80 mL) in a freezer at -20 °C. Benzyl vanillin was obtained as a white crystalline solid (90% yield).

Compound 2: ethyl 2-methoxyphenoxyacetate

Ethyl chloroacetate (26.9 g 0.22 mol), guaiacol (24.8 g, 0.2 mol) were dissolved in 300 mL acetone. K₂CO₃ (41.5 g, 0.3 mol) and KI (1 g) were added while stirring vigorously with a magnetic stirrer. The reaction was heated at 50 °C, refluxing for 3 h. The suspension was filtered and the precipitate was washed with EtOAc (3 \times 50 mL). The combined filtrate was washed with DI-water (2 \times 50 mL), brine (50 mL), dried over MgSO₄, then evaporated *in vacuo* to give a pale yellow oil. The crude product was purified by distillation under reduced pressure. Compound **2** was obtained as a colorless oil (85% yield).

Compound 3: β -hydroxy ester

Diisopropylamine (6.1 g, 0.06 mol) was dissolved in anhydrous THF (50 mL) in a 500 mL three-necked flask equipped with a 100 mL dropping funnel, a drying tube containing Drierite (CaSO₄, Sigma), and connected to a dried nitrogen gas flow. The flask was cooled in a dry ice/isopropanol bath (-78 °C). To this, 24 mL of n-BuLi (2.5 M in hexanes) was added dropwise from the dropping funnel. Compound **2** (10.5 g, 0.05 mol) was dissolved in anhydrous THF (50 mL) and added dropwise into the freshly prepared LDA. After stirring for an additional 15 min, benzyl vanillin dissolved in anhydrous THF (50 mL) was added dropwise into the reaction solution. The reaction was followed by TLC while keeping at -78 °C for 1 h. The reaction mixture was then quenched by adding EtOAc (200 mL) and sat. NH₄Cl. After the reaction warming to room temperature, the organic layer was washed with sat. NH₄Cl and brine (until the washings became neutral), then dried over MgSO₄ and evaporated *in vacuo* to give a yellow syrup. The crude product was purified by flash-chromatography. Compound **3** was obtained as a yellow syrup (≥90% yield).

Compound 4: benzyl-protected GG β-O-4 dimer (4-O-benzyl-GG)

Synthesized from compound **3** (9.05g, 0.02 mol) via general synthetic procedure sodium borohydride reduction as described above. Compound **4** was obtained as a pale yellow oil (86% yield) after flash-chromatographic purification.

Compound 5: phenolic GG β-O-4 dimer (GG)

Synthesized from compound **4** (6.15 g, 0.015 mol) via hydrogenation to remove the benzyl group, as described above. Compound **5** was obtained as a colorless oil (99% yield) after flash-chromatography purification. (After a few days, white crystals of the *erythro* diastereomer formed).

Compound 6: 4-O-methyl GG β-O-4 dimer (VG)

Synthesized from compound **5** (1.60 g, 0.005 mol) via methylation as above. Compound **6** was obtained as a colorless oil (99% yield) after flash-chromatographic purification.

Compound 7: coniferyl alcohol (CA)

Synthesized from coniferaldehyde (3.56 g, 0.02 mol, Sigma) via sodium borohydride reduction as described above. Compound **7** was obtained as a white crystalline solid (98% yield) after flash-chromatographic purification.

Compound 8: dihydroconiferyl alcohol (DCA)

Synthesized from compound **7** (1.80 g, 0.01 mol) by hydrogenation of the double bond as described above. Compound **8** was obtained as a colorless oil (99% yield) after flash-chromatographic purification.

Compound 9: dihydroveratryl alcohol (DVA)

Synthesized from compound **8** (0.364 g, 0.002 mol) via methylation as described above. Compound **9** was obtained as a colorless oil (99% yield) after flash-chromatographic purification.

Compound 10: methylated ethyl guaiacol (EG-OMe)

Synthesized from ethyl guaiacol (2.0 g, 0.0131 mol, Sigma) via methylation as described above. Compound **10** was obtained as colorless oil (99% yield) after flash-chromatographic purification.

Compound 11: methylated propyl guaiacol (PG-OMe)

Synthesized from eugenol (2.0 g, 0.0112 mol, Sigma) via methylation and double-bond hydrogenation as described above. Compound **11** was obtained as colorless oil (99% yield) after flash-chromatographic purification.

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