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Supercritical Methanol Depolymerization and Hydrodeoxygenation of Lignin and Biomass over Reduced Copper Porous Metal Oxides

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Supplementary Information

Table S1. Lignin fraction carbon yields of 15 and 30 min from SCM-DHDO experiments with maple wood and GVL extracted lignin. Dimer and trimer yields were estimated for the 15 min time-point using a high-temperature GC-FID.

	Carbon yield from lignin fraction (%)						
Feed	Maple Wood	GVL extracted lignin	Maple Wood	GVL extracted lignin			
By compound	15 min	15 min	30 min	30 min			
Guaiacol	0.8	0.1	0.9	0.2			
4-Ethylphenol	1.5	0.1	1.4	1 0.3			
4-Methylguaiacol	1.5	0.2	1.4	1 0.5			
4-Ethylguaiacol	1.4	0.5	1.2	0.9			
4-Propylphenol	1.4	0.0	1.2	0.0			
4-Propylguaiacol	6.3	0.8	5.7	7 1.3			
4-Methylsyringol	0.8	0.2	0.8	0.4			
4-Ethylsyringol	0.8	0.3	0.9	0.5			
4-Propylsyringol	0.8	1.1	1.3	3 0.9			
By type							
Syringols	2.4	1.6	3.1	1.8			
Guaiacols	10.1	1.7	9.2	2 3.0			
Phenols	2.9	0.1	2.6	6 0.3			
By alkyl tail length							
No tail (C_0)	0.8	0.1	0.9	0.2			

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2.3	0.4	2.2	0.9	
3.7	1.0	3.6	1.7	
8.6	1.9	8.2	2.2	
0	0.6	0	3.0	
0	0.0	0	0.0	
15.4	4.1	15.0	8.1	
1.0/4.2/1.2	1.0/1.0/0.1	1.0/2.9/0.8	1.0/1.6/0.2	
0.1/0.3/0.4/1.0	0.1/0.2/0.5/1.0	0.1/0.3/0.4/1.0	0.1/0.4/0.8/1.0	
0.0	2.3	Not measured	Not measured	
0.0	0.0	Not measured	Not measured	
	3.7 8.6 0 0 15.4 1.0/4.2/1.2 0.1/0.3/0.4/1.0 0.0	3.7 1.0 8.6 1.9 0 0.6 0 0.0 15.4 4.1 1.0/4.2/1.2 1.0/1.0/0.1 0.1/0.3/0.4/1.0 0.1/0.2/0.5/1.0 0.0 2.3	3.7 1.0 3.6 8.6 1.9 8.2 0 0.6 0 0 0.0 0 15.4 4.1 15.0 1.0/4.2/1.2 1.0/1.0/0.1 1.0/2.9/0.8 0.1/0.3/0.4/1.0 0.1/0.2/0.5/1.0 0.1/0.3/0.4/1.0 0.0 2.3 Not measured	

Table S2. Carbon yields from 4 h SCM-DHDO experiments with various feedstocks. Base reaction conditions: 100 mg feed, 100 mg CuMgAlOx catalyst, 2.4 g MeOH, 5 psig initial He pressure, 300°C reaction temperature, and 4 h reaction time. *PA products are not deconvoluted from the lignin products.

Lignin Fraction Carbon Yields (%)										
Feed:	100 mg GVL extracted lignin (unreduced catalyst)	100 mg GVL extracted lignin	100 mg Maple Wood	25 mg GVL extracted lignin	100 mg GVL extracted lignin (150 mg catalyst)	25 mg GVL extracted lignin + 75 mg Cellulose	100 mg GVL extracted lignin + 100 mg PA*	100 mg GVL extracted lignin + 25 mg PA*	100 mg Maple Enzyme Lignin (EL)	100 mg MeOH insoluble GVL extracted lignin
4-Ethylcyclohexanol	0.9 (0.03)	1.6 (0.13)	2.8	1.4 (0.12)	1.5 (0.16)	3.3 (0.08)	2.3 (0.04)	1.9 (0.15)	1.6 (0.03)	1.3
4-Propylcyclohexanol	1.5 (0.06)	2.7 (0.32)	9.3	1.8 (0.14)	2.3 (0.13)	2.6 (0.15)	3.2 (0.01)	2.7 (0.18)	4.8 (0.07)	2.2
4-Propylphenol	1.1 (0.04)	0.7 (0.08)	ND	0.3 (0.05)	0.4 (0.03)	ND	0.7 (0.04)	0.6 (0.04)	0.7 (0.01)	0.6
Unidentified Aromatics	10.9 (0.74)	7.7 (1.18)	12.7	7.5 (1.46)	6.5 (1.33)	4.8 (1.06)	11.3 (1.68)	9.3 (1.32)	7.0 (0.71)	5.8
Unidentified Cyclohexanols	6.3 (0.40)	7.6 (0.42)	18.5	10.6 (0.87)	8.4 (1.50)	7.0 (0.39)	10.3 (0.96)	8.3 (0.91)	10.3 (0.33)	6.8
Total aromatics	11.9 (0.78)	8.4 (1.24)	12.7	7.9 (1.51)	6.9 (1.36)	4.8 (1.06)	12.1 (1.72)	9.8 (1.36)	7.7 (0.70)	6.4
Total cyclohexanols	8.7 (0.49)	11.9 (0.59)	30.5	13.8 (1.12)	12.2 (1.79)	12.9 (0.61)	15.8 (1.00)	13.0 (1.24)	16.7 (0.23)	10.4
Total monomer yield	20.7 (1.27)	20.3 (1.81)	43.1	21.7 (2.63)	19.1 (3.16)	17.7 (1.68)	27.8 (2.73)	22.8 (2.60)	24.4 (0.47)	16.8
Aromatic/cyclohexanol ratio (A/C ratio)	1.37	0.70	0.42	0.57	0.56	0.37	0.77	0.75	0.46	0.62
Estimated dimer yield	Not measured	57	54	Not measured	Not measured	Not measured	Not measured	Not measured	Not measured	Not measured
Estimated trimer yield	Not measured	7	6	Not measured	Not measured	Not measured	Not measured	Not measured	Not measured	Not measured