Rapid Reductive Catalytic Fractionation for Holistic Valorization of Lignocellulose Through Precise Acid Tuning and Temporal Window Identification

Peidong Li [a,b], Wangyue Xie [a,b], Muhammad Fayyaz Farid [a,b], Tianyu Ren [b], Cheng Tung Chong [c], Zhuo He [a,b], Yuhe Liao [a,b], Yanbin Cui [a,b,*], Chenguang Wang [a,b,*]

[a] School of Energy Science and Engineering, University of Science and Technology of China, Hefei 230026, China

[b] Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China

[c] China-UK Low Carbon College, Shanghai Jiao Tong University, Shanghai 201306, China.

* Corresponding Author: cuiyb@ms.giec.ac.cn (Y. Cui), wangcg@ms.giec.ac.cn (C. Wang)

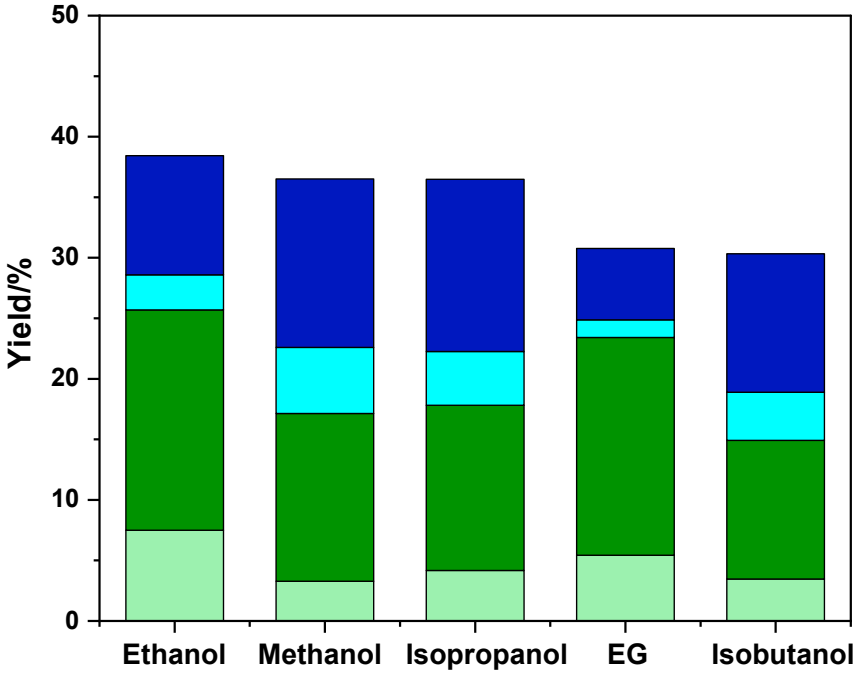

Figure S1 Monomer yield of the RCF using different alcohol-water mixtures at equal ratio

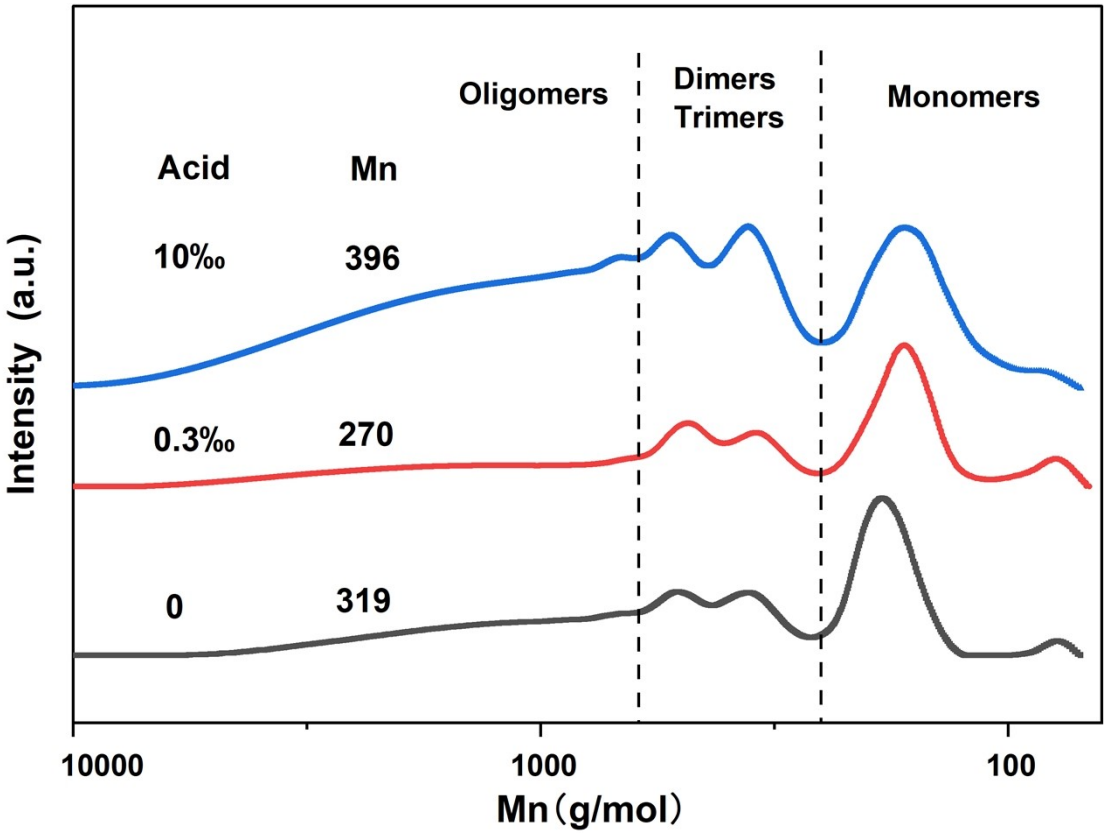

Figure S2 GPC analysis of lignin samples from RCF process with varied acid ratio at 190℃

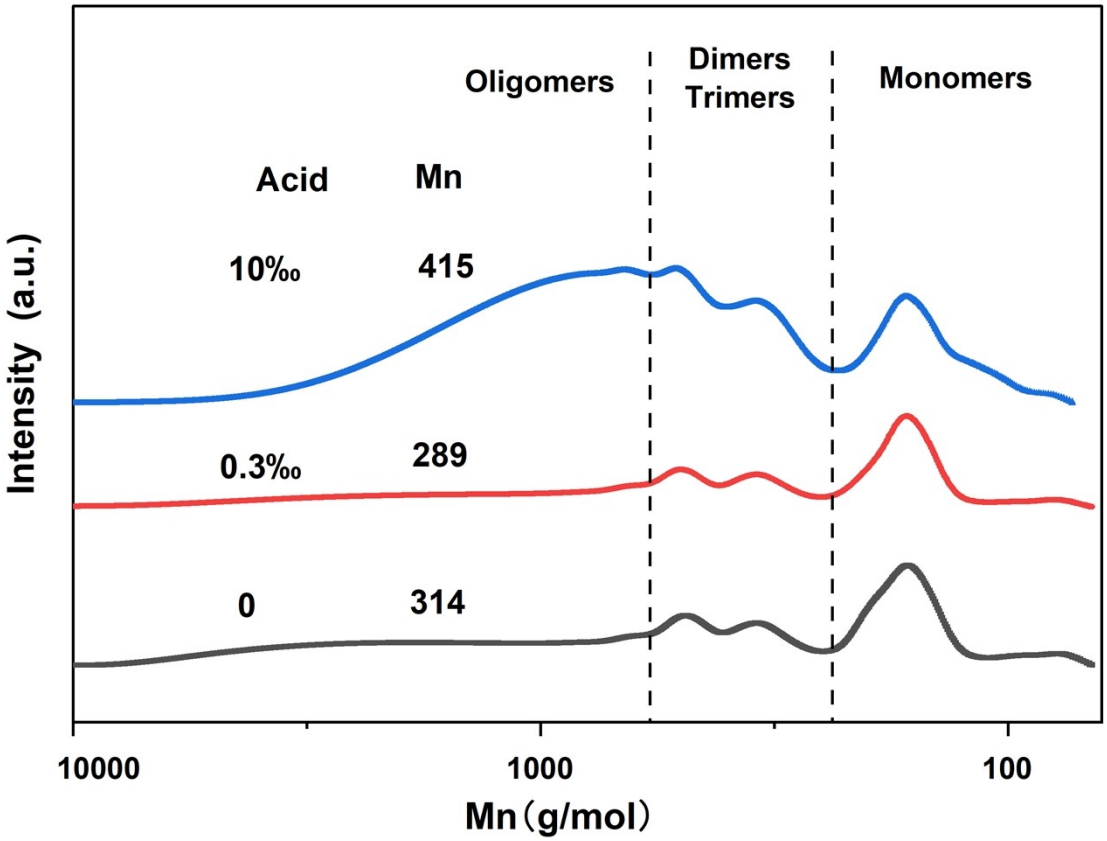

Figure S3 GPC analysis of lignin samples from RCF process with varied acid ratio at 210℃

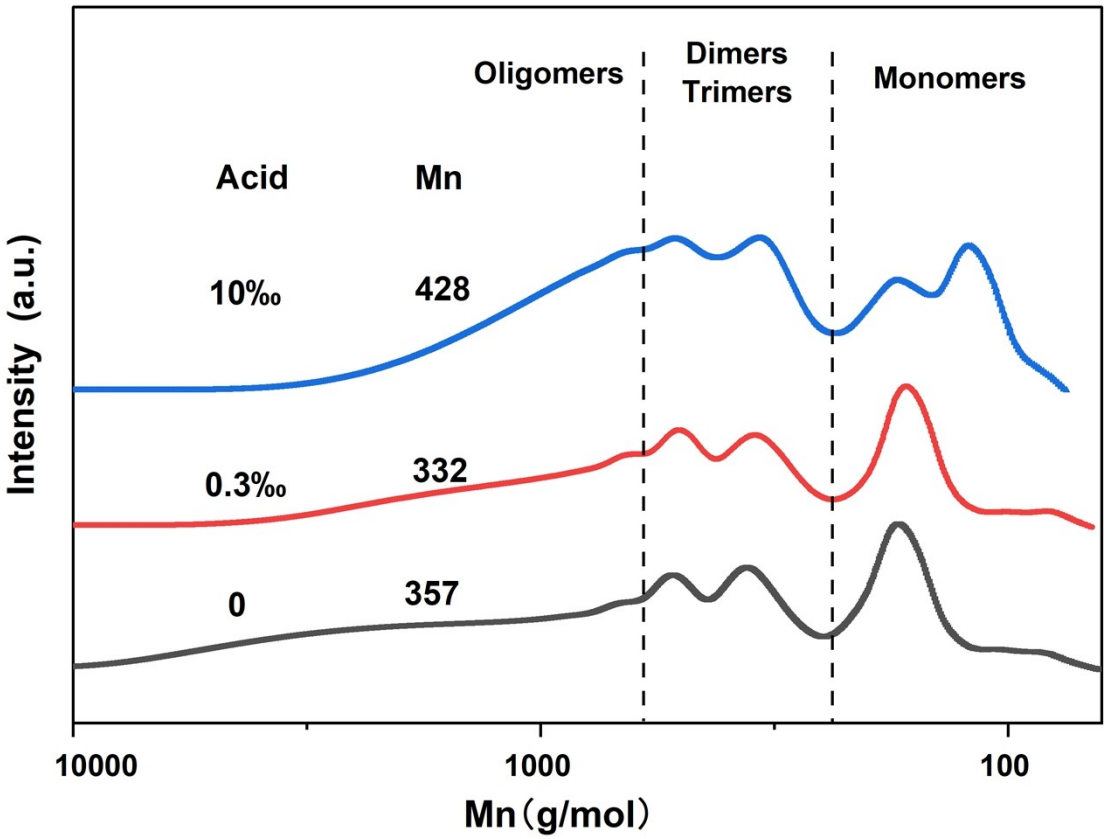

Figure S4 GPC analysis of lignin samples from RCF process with varied acid ratio at 230℃

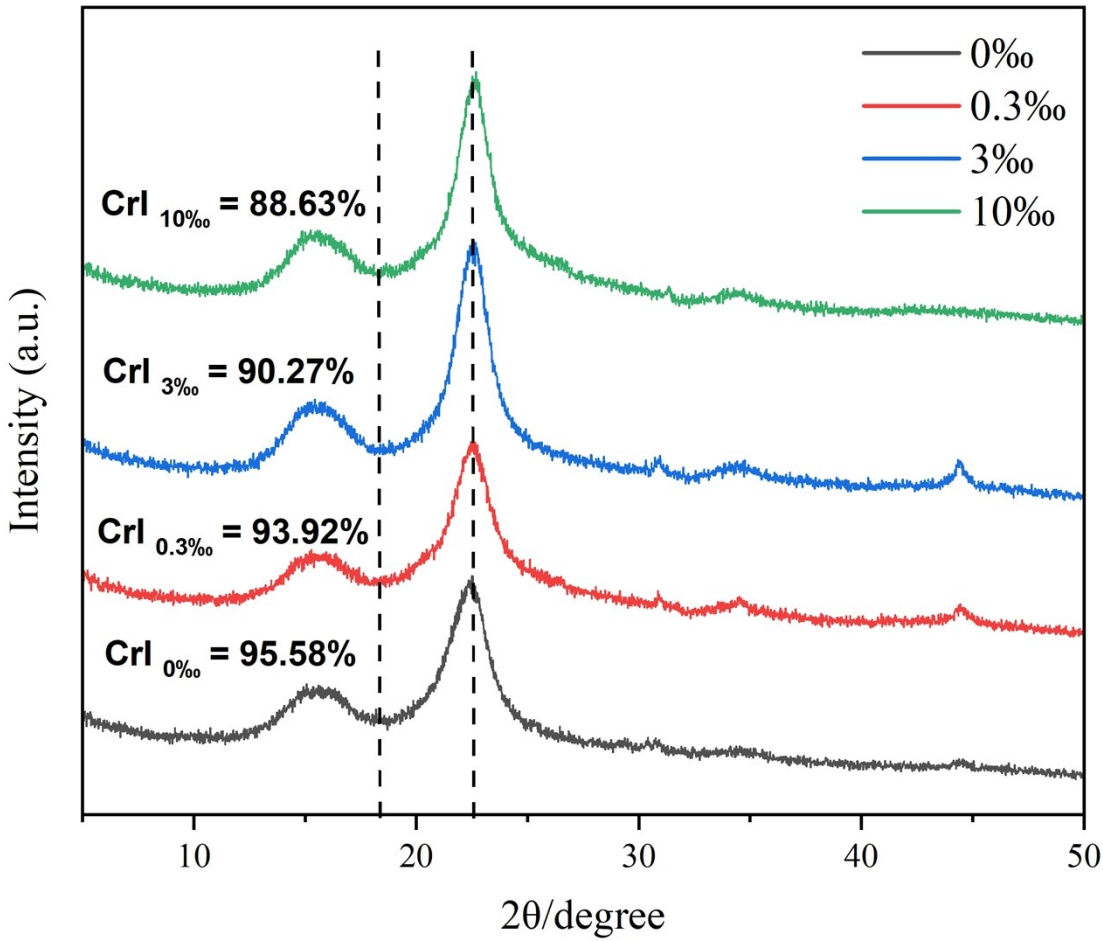

Figure S5 X-ray diffraction spectra of recovered pulp from RCF with varied acid concentration

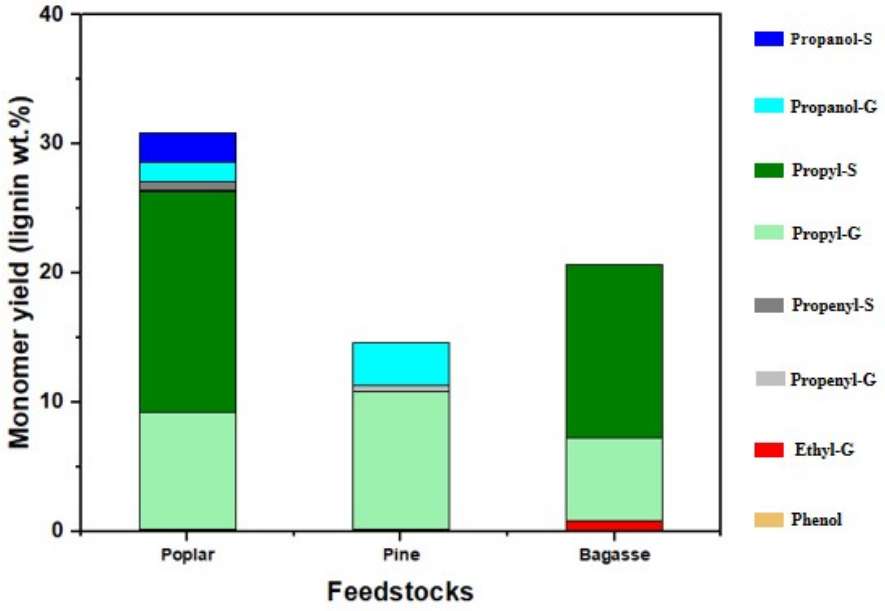

Figure S6 Comparison of monomer production from different lignocellulosic feedstocks.

Reaction condition: 0.8 g biomass, 0.16 g 10% Ni/C, 20 mL ethanol:H_2O=1:1, 2 MPa H_2, 0.3‰ acid concentration, 210 ℃, 0 h.

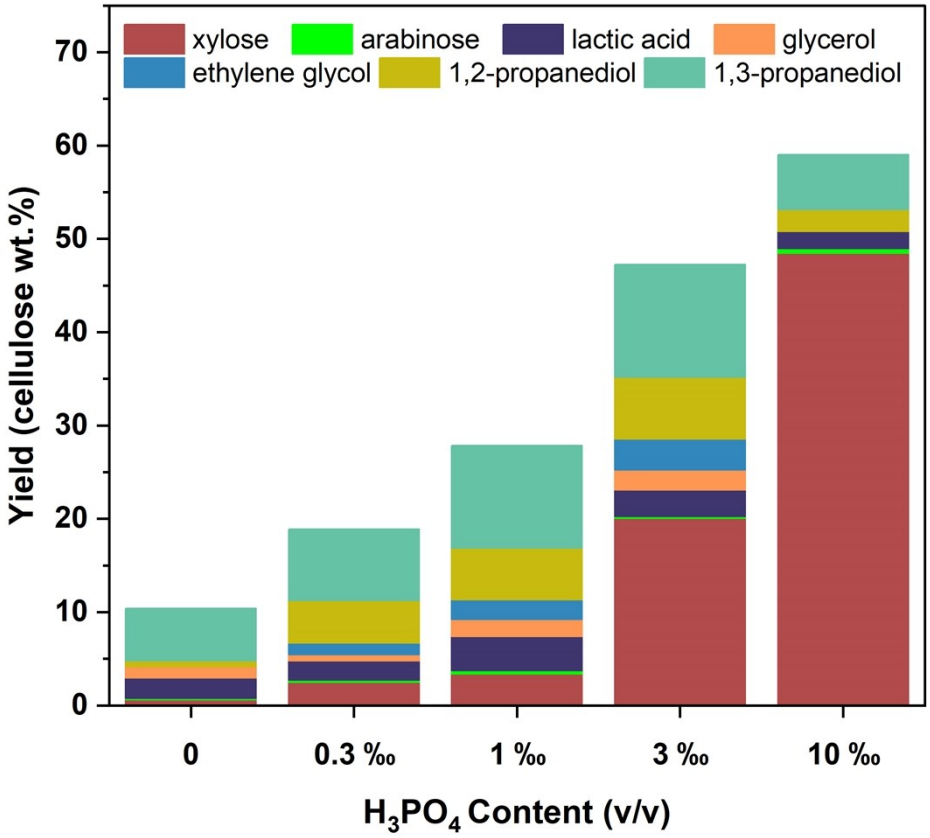

Figure S7 Carbohydrate decomposed products in liquid phase detected via UPLC

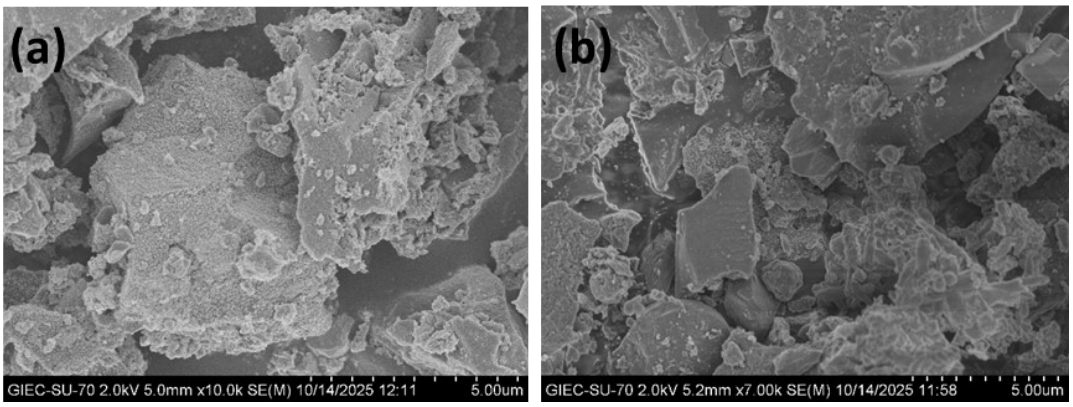

Figure S8 SEM image of (a) origin and (b) recovered catalyst

Table S1 The ratio of propyl-, propenyl, propanol-substituted aromatic monomers under different solvent compositions

Solvent composition	Ratio	Propyl-	Propenyl-	Propanol-
Ethanol: Water [a]	0:100	0.889	0.000	0.111
	10:90	0.799	0.000	0.201
	30:70	0.810	0.000	0.190
	50:50	0.669	0.000	0.331
	70:30	0.618	0.000	0.382
	90:10	0.608	0.000	0.392
	100:0	0.792	0.000	0.208
Ethanol: Water [b]	0:100	1.000	0.000	0.000
	10:90	1.000	0.000	0.000
	30:70	0.890	0.000	0.110
	50:50	0.644	0.000	0.356
	70:30	0.622	0.000	0.378
	90:10	0.612	0.000	0.388
	100:0	0.838	0.000	0.162

[a] Reaction conditions: 20 mL of solvent mixture, 0.8 g of poplar woodmeal, 0.16 g of Ni/C, 210°C, 2 MPa H_2, 3h

[b] Reaction conditions: 20 mL of solvent mixture, 0.8 g of poplar woodmeal, 0.16 g of Ni/C, 210°C, 2 MPa H_2, 0h

Table S2 The ratio of propyl-, propenyl, propanol-substituted aromatic monomers under different reaction temperatures and acid concentrations

Reaction temperature	Acid concentration	Propyl-	Propenyl-	Propanol-
190°C	0‰	0.600	0.000	0.400
	0.1‰	0.895	0.000	0.105
	0.3‰	0.764	0.013	0.223
	1‰	0.798	0.028	0.173
	3‰	0.606	0.024	0.371
	10‰	0.597	0.383	0.019
210°C	0‰	0.584	0.000	0.416
	0.1‰	0.923	0.000	0.077
	0.3‰	0.848	0.023	0.124
	1‰	0.866	0.089	0.037
	3‰	0.730	0.222	0.030

	10‰	0.576	0.330	0.034
230°C	0‰	0.596	0.039	0.342
	0.1‰	0.790	0.133	0.040
	0.3‰	0.732	0.196	0.033
	1‰	0.683	0.231	0.036
	3‰	0.627	0.290	0.000
	10‰	0.512	0.388	0.000

Reaction conditions: 20 mL ethanol: H_2O = 1:1, 0.8 g of poplar wood 0.16 g of Ni/C, and 2 MPa H_2, 0 h

Table S3 The ratio of propyl-, propenyl, propanol-substituted aromatic monomers under 0‰ H_3PO_4 addition

Reaction time(min)	Propyl-	Propenyl-	Propanol-
170℃	-	-	-
180℃	-	-	-
190℃	-	-	-
200℃	1.000	0.000	0.000
205℃	0.692	0.000	0.308
0min	0.629	0.000	0.371
10min	0.597	0.000	0.403
30min	0.569	0.000	0.431
50min	0.560	0.000	0.440
90min	0.524	0.000	0.476
120min	0.506	0.000	0.494
180min	0.487	0.000	0.513
240min	0.488	0.000	0.512

Reaction conditions: 6 g poplar biomass, 1.2 g 10% Ni/C, 150 mL ethanol: H_2O=1:1, 210℃, 2 MPa H_2, 0‰ H_3PO_4

Table S4 The ratio of propyl-, propenyl, propanol-substituted aromatic monomers under 0.3‰ H_3PO_4 addition

Reaction time(min)	Propyl-	Propenyl-	Propanol-
170℃	0.604	0.171	0.188
180℃	0.618	0.172	0.184
190℃	0.638	0.172	0.174
200℃	0.666	0.155	0.166
205℃	0.707	0.117	0.161
0min	0.747	0.086	0.153
10min	0.758	0.066	0.161
30min	0.798	0.029	0.151

50min	0.819	0.012	0.141
90min	0.814	0.006	0.137
120min	0.810	0.005	0.140
180min	0.820	0.004	0.121
240min	0.864	0.002	0.095

Reaction conditions: 6 g poplar biomass, 1.2 g 10% Ni/C, 150 mL ethanol: H_2O=1:1, 210℃, 2 MPa H_2, 0.3‰ H_3PO_4

Table S5 The ratio of propyl-, propenyl, propanol-substituted aromatic monomers under 10‰ H_3PO_4 addition

Reaction time(min)	Propyl-	Propenyl-	Propanol-
170℃	0.249	0.706	0.034
180℃	0.207	0.750	0.033
190℃	0.201	0.755	0.035
200℃	0.225	0.727	0.036
205℃	0.250	0.697	0.038
0min	0.276	0.655	0.045
10min	0.337	0.585	0.043
30min	0.381	0.527	0.043
50min	0.466	0.411	0.038
90min	0.524	0.338	0.032
120min	0.576	0.267	0.025
180min	0.614	0.206	0.021
240min	0.654	0.140	0.019

Reaction conditions: 6 g poplar biomass, 1.2 g 10% Ni/C, 150 mL ethanol: H_2O=1:1, 210℃, 2 MPa H_2, 10‰ H_3PO_4

Table S6 Acid insoluble matter analysis of cellulose submitted to RCF process with varied acid concentration

H_3PO_4 fraction	Cellulose input	Acid insoluble matter (wt.%)	Cellulose recovery (wt.%)	Acid insoluble matter (wt.%)
0	0.8	0.0	75.5	0.0
0.1‰	0.8	0.0	70.9	0.0
0.3‰	0.8	0.0	64.3	0.0
1.0‰	0.8	0.0	53.0	4.7
3.0‰	0.8	0.0	52.5	7.2
10‰	0.8	0.0	57.7	14.4

[a] Reaction conditions: 0.8 cellulose, 0.16g Ni/C, 20 mL ethanol: H_2O=1:1, 210 °C, 2 MPa H_2, reaction time 0 h.\