Supporting Information

A new method for solid acid catalyst evaluation for cellulose hydrolysis

Table S1. Acid site density of the catalysts used in the current study measured by solid state Boehm titration.

Catalyst	Acid Site Density (mmol/g)
CMP-SO$_3$H-0.3	0.90 ± 0.01
AMB-15	4.80 ± 0.01
SZ	1.310 ± 0.002
SAC	0.56 ± 0.01
SH	1.78 ± 0.01
HZSM-5	0.80 ± 0.01

Table S2. Comparison of the yields (%) of most abundant soluble products generated by solid acid and leached homogeneous acid catalyzed cellulose hydrolysis.

Sample	Glucose	Levulinic Acid	Formic Acid	HMF
Solid	12 ± 3	27 ± 4	36 ± 5	trace

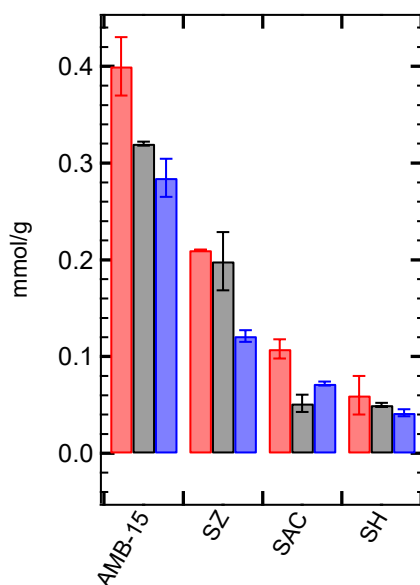|					
CMP-SO₃H-0.3	**Leachate**	1 ± 1	57.0 ± 0.3	60 ± 1	trace
AMB-15	**Solid**	9 ± 1	13 ± 4	17 ± 4	0.1
	Leachate	18 ± 3	11 ± 4	16 ± 4	0.5
SZ	**Solid**	1.0 ± 0.1	3 ± 1	5 ± 2	1
	Leachate	8 ± 1	1.0 ± 0.4	5.0 ± 0.3	0.3
SAC	**Solid**	3 ± 1	0.1 ± 0.1	5 ± 2	trace
	Leachate	6 ± 1	1.4 ± 0.4	6.0 ± 0.5	1
SH	**Solid**	2.4 ± 1	1.0 ± 0.2	4 ± 1	trace
	Leachate	3.0 ± 0.2	0.2 ± 0.1	4 ± 1	0.2
HZSM-5	**Solid**	1.0 ± 0.2	trace	3.6 ± 1	trace
	Leachate	1.0 ± 0.4	trace	1.0 ± 0.5	0.1
Water		1.0 ± 0.1	trace	0.5 ± 0.1	trace

*trace indicates yields less than 0.05%

Figure S1. Comparison of the leached homogeneous acid concentration per gram of catalyst (red bars), the decrease of acid sites of the catalysts post hydrothermal treatment (grey bars), and the concentration of the leached bisulfate species per gram of catalyst (blue bars). CMP-SO$_3$H-0.3 is not included in this analysis since it leaches chloride and solid state titration would not capture this change. HZSM-5 was not analyzed due to very low leaching of homogeneous acid.
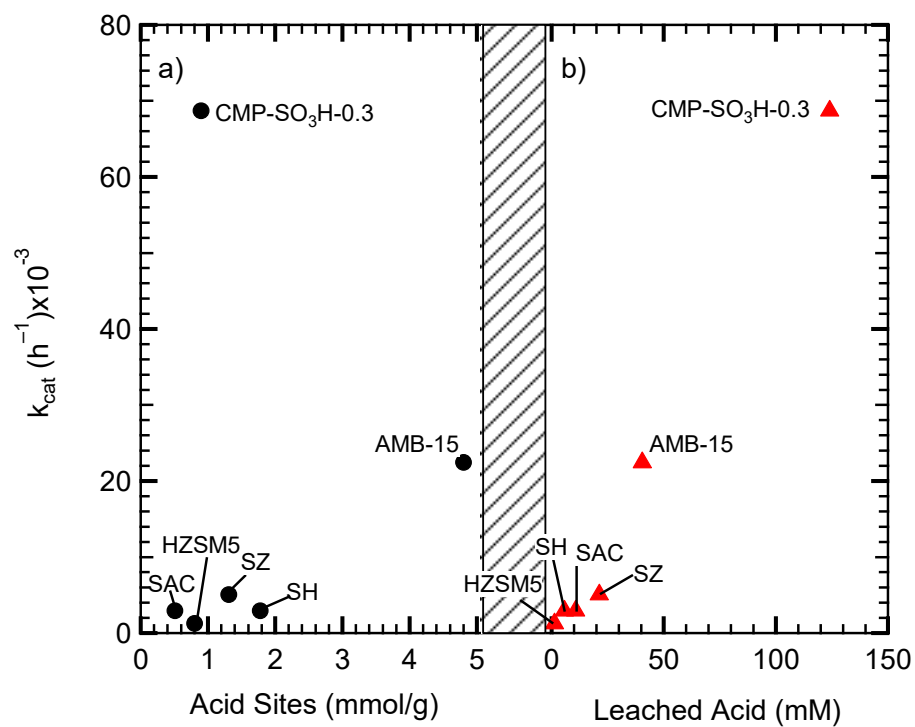
Figure S2. Correlation between first order catalytic hydrolysis rate constant k_{cat} of cellulose hydrolysis using fresh solid acid catalyst and amount of acid sites in a) and concentration of leached homogeneous acid in b). Error bars are omitted for clarity.
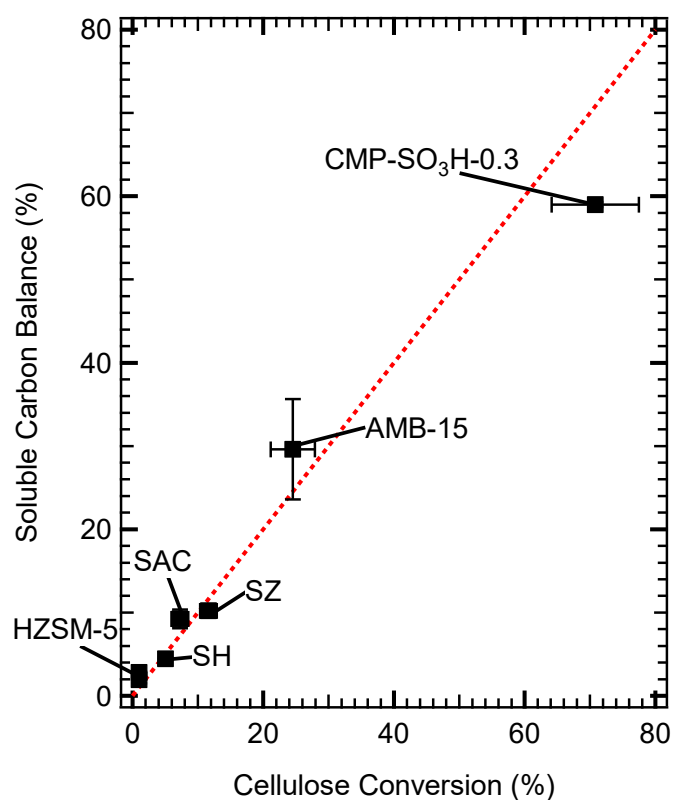
Figure S3. Parity plot of measured soluble carbon balance versus predicted cellulose conversion by Saeman's homogeneous acid hydrolysis model. The dotted red line represents parity between the two metrics. The black squares datapoints represent the results obtained from acid hydrolysis with the supernatants of each catalyst, where the acid concentration remains constant throughout the reaction.
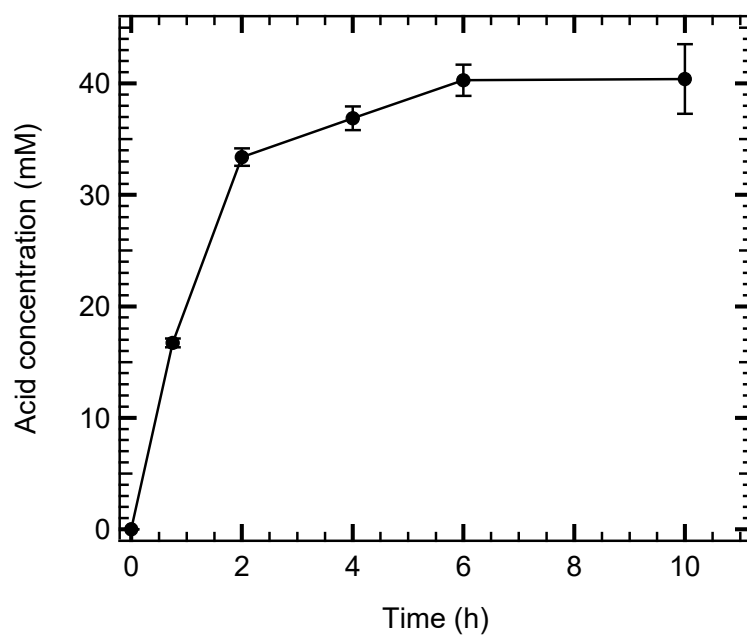
Figure S4. Concentration of the leached homogeneous acid for Amberlyst-15 as a function of treatment time at 150 °C.
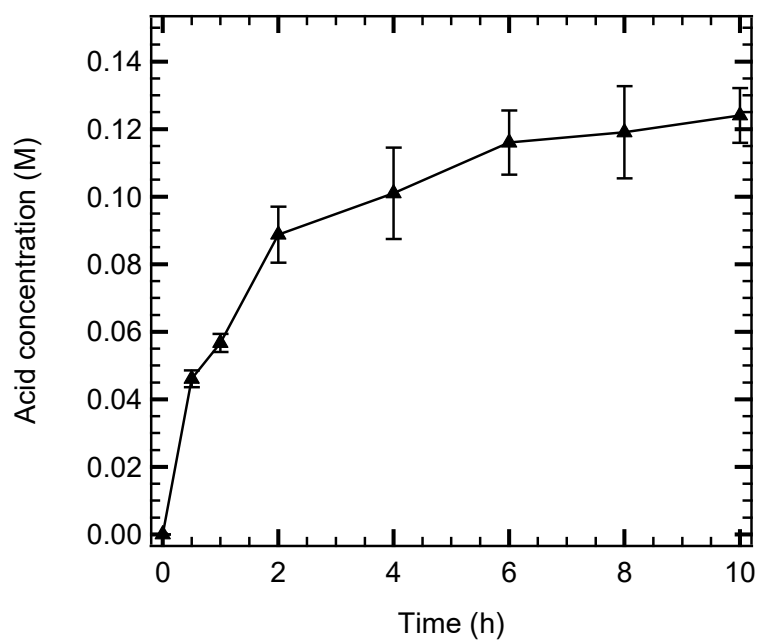

Figure S5. Concentration of the leached homogeneous acid for CMP-SO$_3$H-0.3 as a function of treatment time at 150 °C.
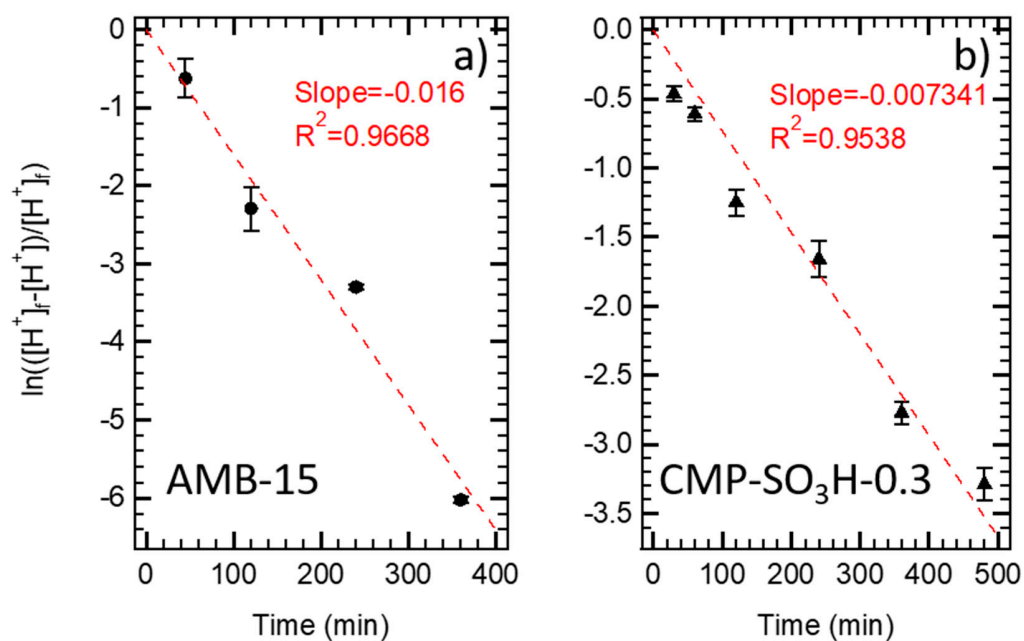
Figure S6. Kinetic analysis of homogeneous acid leaching from AMB-15 in a) and CMP-SO$_3$H-0.3 in b) assuming the leaching obeys first order kinetics. The slope, indicative of the leaching rate constant, is used in the kinetic modeling for cellulose hydrolysis catalyzed by time dependent acid concentration.