Supplementary Information

Phytic Acid as a Biorenewable Catalyst for Cellulose Pyrolysis to Produce Levoglucosenone

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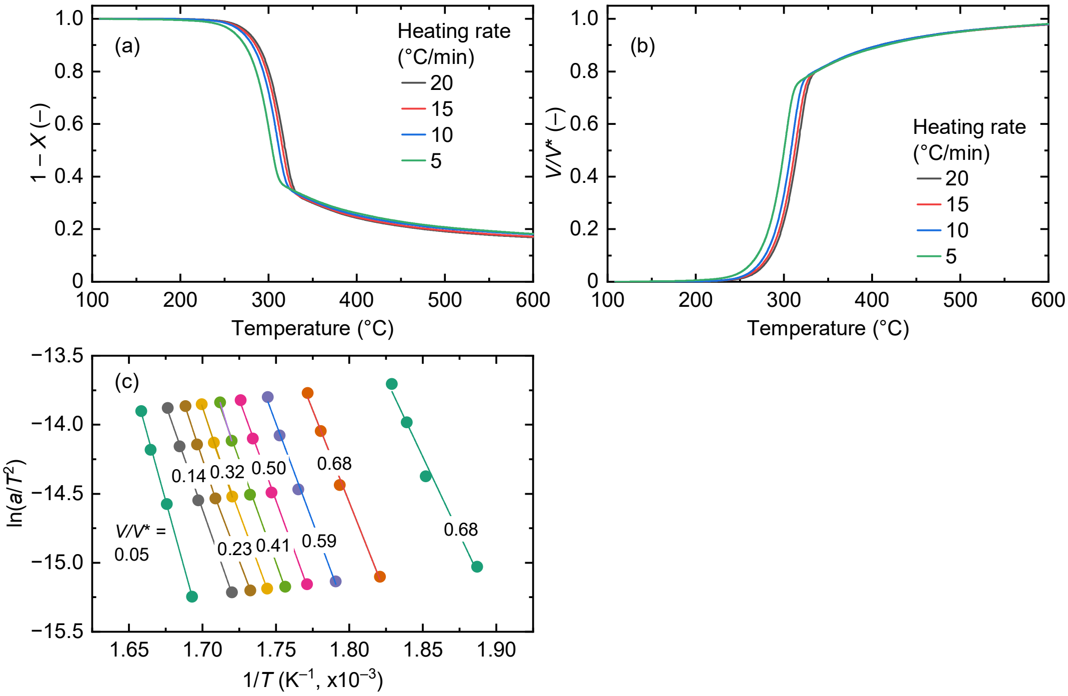

Figure S1. TGA of cellulose loaded with 0.3 wt% PA. A brief explanation for kinetic analysis with DAEM proposed by Miura et al.[35] using the result for cellulose loaded with 0.3 wt% PA as an example. (a) Pyrolysis curves were obtained from TGA experiments at different heating rates (a = 5, 10, 15, and 20 °C/min). The mass, measured during TGA, was transformed to relative mass with X as the conversion to volatiles on a dry mass basis. (b) The vertical axis was further converted to V/V^*, where V stands for the mass yield of volatiles released from the sample, and V^* stands for V at completion of volatiles release. In this work, V^* was defined as the yield of volatiles at 800°C during the measurement at 20 °C/min. V^* was 0.958 and 0.848 for cellulose and cellulose loaded with 0.3 wt% PA, respectively. (c) The employed DAEM uses equation below for calculating kinetic parameters at different conversion levels, where E, k_0, and R represent activation energy, frequency factor, and gas constant, respectively. From the data of V/V^*–T plot, $\ln(a/T^2)$ and $1/T$ at selected V/V^* were calculated and used for the Arrhenius plot, as shown in Figure S1 (c). The calculated values of E and k_0 are listed in Table S1. The value of V/V^* was set in increments of 0.03, ranging from 0.05 to 0.95 for cellulose and from 0.05 to 0.77 for cellulose loaded with 0.3 wt% PA. Outside the set range of V/V^*, differences in the values caused by heating rate were negligibly small, making the kinetic analysis difficult.

$$\ln\frac{a}{T^2} = \ln\frac{k_0 \mathrm{R}}{E} + 0.6075 - \frac{E}{\mathrm{R}T}$$

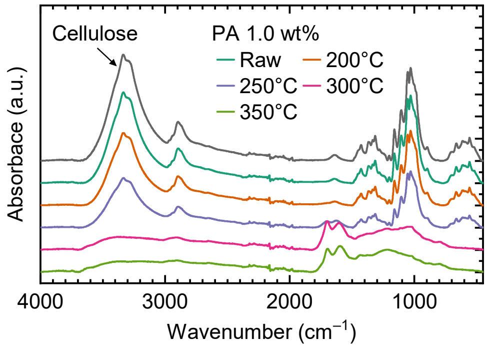

Figure S2. Fourier transform infrared spectroscopy (FT-IR) of cellulose loaded with 1.0 wt% PA after pyrolysis at different temperatures. FT-IR analysis was carried out in an attenuated total reflectance (ATR) mode on a PerkinElmer Spectrum two.

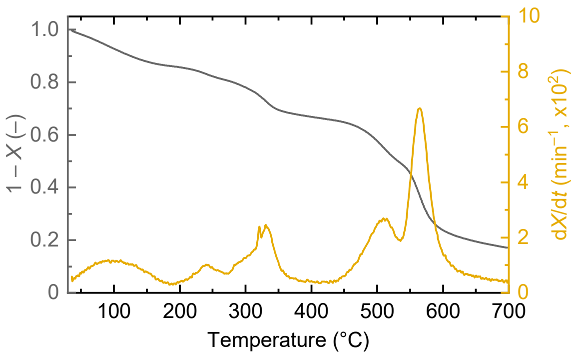

Figure S3. TGA of PA under a flow of N_2 at 10 °C/min. PA contained about 20 wt% of water, which was lost below 200°C.

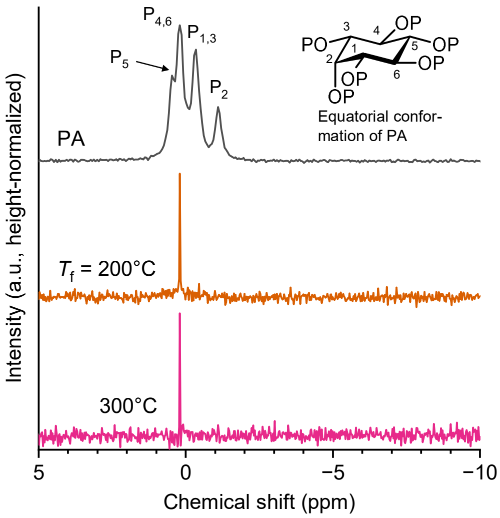

Figure S4. ^{31}P solution NMR spectrum of PA (aqueous standard solution) and aqueous extracts from char after pyrolysis of cellulose loaded with 1.0 wt% PA at 200°C and 300°C. P = $–PO_3H_2$, $–PO_3H^–$, or $–PO_3^{2–}$, depending on pH.[50]

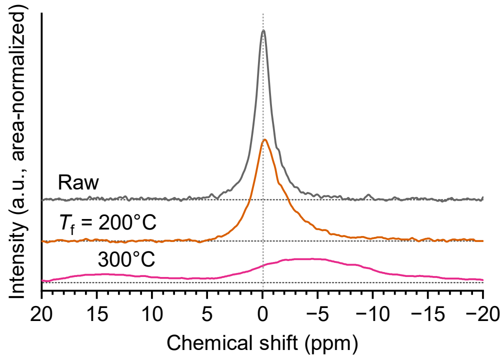

Figure S5. ^{31}P solid-state NMR spectrum of chars prepared by pyrolysis of cellulose loaded with 1.0 wt% phosphoric acid at different temperatures.

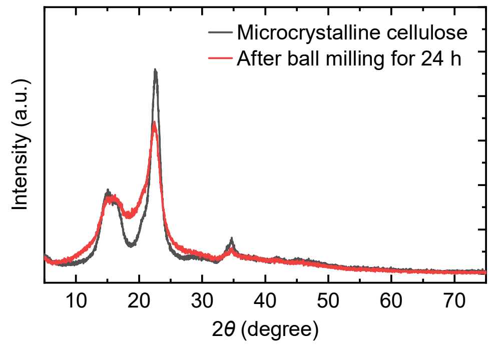

Figure S6. XRD patterns of cellulose before and after ball-milling. CrI decreased from 85.6% to 60.0% with the ball-milling.

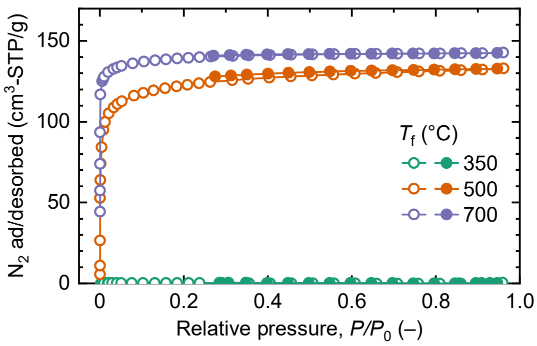

Figure S7. N_2 ad/desorption isotherms of chars prepared at different T_f. BET surface area calculated from the isotherms were 1.0, 472, and 550 m^2/g for chars prepared at 350, 500, and 700°C, respectively.

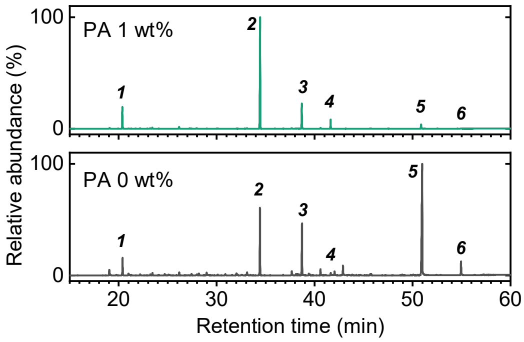

Figure S8. GC/MS chromatogram of liquid product from slow pyrolysis of cellulose loaded with 1.0 wt% PA and without PA: 1) furfural, 2) LGO, 3) DGP, 4) ADGH, 5) LGA, and 6) AGF.

Table S1. Kinetic parameters obtained from DAEM analysis of pyrolysis curves for cellulose and cellulose loaded with 0.3 wt% PA.

Cellulose					Cellulose loaded with 0.3 wt% PA				
V/V^* (–)	X (–)	E (kJ/mol)	k_0 (s^{-1})	R^2	V/V^* (–)	X (–)	E (kJ/mol)	k_0 (s^{-1})	R^2
0.05	0.048	209	1.67×10^{16}	0.9977	0.05	0.042	187	1.02×10^{16}	0.9871
0.08	0.076	203	3.80×10^{15}	0.9989	0.08	0.067	203	1.82×10^{17}	0.9920
0.11	0.105	200	1.45×10^{15}	0.9994	0.11	0.093	216	1.87×10^{18}	0.9939
0.14	0.133	199	1.08×10^{15}	0.9994	0.14	0.118	223	6.55×10^{18}	0.9960
0.17	0.162	198	6.90×10^{14}	0.9994	0.17	0.143	232	3.37×10^{19}	0.9958
0.20	0.190	197	5.33×10^{14}	0.9997	0.20	0.168	235	5.33×10^{19}	0.9960
0.23	0.219	196	3.97×10^{14}	0.9998	0.23	0.194	238	6.87×10^{19}	0.9967
0.26	0.247	195	2.97×10^{14}	0.9998	0.26	0.219	240	9.04×10^{19}	0.9965
0.29	0.276	194	2.07×10^{14}	0.9996	0.29	0.244	242	1.25×10^{20}	0.9969
0.32	0.304	193	1.53×10^{14}	0.9993	0.32	0.269	243	1.38×10^{20}	0.9980
0.35	0.333	191	9.86×10^{13}	0.9995	0.35	0.294	245	1.75×10^{20}	0.9979
0.38	0.361	192	1.19×10^{13}	0.9996	0.38	0.320	246	1.58×10^{20}	0.9988
0.41	0.390	189	6.60×10^{13}	0.9995	0.41	0.345	247	2.07×10^{20}	0.9976
0.44	0.418	189	5.90×10^{13}	0.9997	0.44	0.370	246	1.43×10^{20}	0.9982
0.47	0.447	188	4.27×10^{13}	0.9996	0.47	0.395	247	1.54×10^{20}	0.9980
0.50	0.475	186	2.82×10^{13}	0.9996	0.50	0.421	247	1.30×10^{20}	0.9985
0.53	0.504	186	2.48×10^{13}	0.9996	0.53	0.446	248	1.53×10^{20}	0.9980
0.56	0.533	185	2.04×10^{13}	0.9996	0.56	0.471	248	1.17×10^{20}	0.9986
0.59	0.561	185	1.76×10^{13}	0.9999	0.59	0.496	249	1.33×10^{20}	0.9981
0.62	0.590	182	9.53×10^{12}	0.9995	0.62	0.522	250	1.42×10^{20}	0.9983
0.65	0.618	182	8.26×10^{12}	0.9996	0.65	0.547	250	1.41×10^{20}	0.9985
0.68	0.647	181	7.32×10^{12}	0.9998	0.68	0.572	252	1.78×10^{20}	0.9989
0.71	0.675	179	4.00×10^{12}	0.9996	0.71	0.597	257	4.66×10^{20}	0.9994
0.74	0.704	179	3.88×10^{12}	0.9998	0.74	0.623	278	2.52×10^{22}	0.9994
0.77	0.732	177	2.78×10^{12}	0.9998	0.77	0.648	320	1.05×10^{26}	0.9990
0.80	0.761	177	2.21×10^{12}	0.9997					
0.83	0.789	175	1.37×10^{12}	0.9998					
0.86	0.818	173	9.20×10^{11}	0.9998					
0.89	0.846	172	6.42×10^{11}	0.9996					
0.92	0.875	173	7.19×10^{11}	0.9994					
0.95	0.903	172	4.56×10^{11}	0.9987					