

## Supplementary information

### Phytic acid derivatized lignin as thermally stable and flame retardant material

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## Material

Softwood kraft lignin (KL) was obtained from FPIInnovations and produced via Lignoforce technology. Phytic acid sodium salt hydrate,  $C_6H_{18}O_{24}P_6$ , (PHA), sodium hydroxide (NaOH) ( $\geq 97\%$ ), sulfuric acid ( $H_2SO_4$ ) ( $\geq 98\%$ ), deuterium oxide ( $D_2O-d_6$ ) (99.9%), dimethyl sulfoxide- $d_6$  (DMSO- $d_6$ ) (99.8%), 3-(trimethylsilyl)propionic-2,2,3,3- $d_4$  acid sodium salt tetramethylsilane (TMSP) ( $\geq 98.5\%$ ), cyclohexanol (99%), 3-(2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (CDP) (95%), chromium(III) acetylacetonate (97%), sodium azide ( $NaN_3$ ) ( $\geq 99.5\%$ ), poly (diallyl dimethylammonium chloride) (PDADMAC) (100–200 kg/mol), nitric acid ( $HNO_3$ ), and hydrochloric acid (HCl) (37%) were all purchased from Millipore Sigma, Oakville, Canada. Filter paper with a porosity of Coarse, fast flow rate, and 15 cm diameter was purchased from Fisher. The 1000 g/mol cut-off dialysis membrane made of cellulose acetate was purchased from Spectrum Labs. Pinewood (untreated, ALEXANDRIA, made in Canada) was purchased from Canadian Tire Inc, Canada, Thunder Bay store, with two different sizes and barcodes and used for different analyses, i.e., 00010-3196C for limiting oxygen index analysis and 00015-30096C for smoke density analysis.

## Charge density, solubility, elemental analysis, and molecular weight measurements

To assess the charge density, PK samples with 1 wt.% concentration were stirred at 200 rpm for 24 h at 25°C. Then, the prepared suspensions were centrifuged at 1000 rpm for 5 min to separate soluble and insoluble parts. Afterward, 1 mL of the soluble portion of the samples was titrated against 0.005 mol/L PDADMAC solution to determine the charge density of the samples. Solubility analysis was conducted by adding 0.2 g of lignin derivatives to 19.8 mL of deionized water. The suspensions were shaken in a water bath (Innova 3100, Brunswick Scientific, Edison, NJ, USA) for 12 h at 200 rpm and 25°C. Organic elemental analysis was conducted for samples that were oven-dried at 60°C for 24 h, and then 0.02 g of them were transferred into the carousel chamber of the elemental analyzer. The sample's carbon, hydrogen, sulfur, and nitrogen contents were assessed by combusting the samples at 1200°C and analyzing the generated gases. Molecular weight measurement was investigated for samples that were prepared by dissolving 50 mg of sample in 10 mL of 0.1 M  $NaN_3$  for anionic samples. The prepared solutions were filtered using a 0.2  $\mu m$  filter and analyzed following a standard method.<sup>1</sup> The temperature of the column and detector were set at 35°C, and a flow rate of 0.7 mL/min was maintained. An RI detector used 70  $\mu L$  of each sample for analysis in this test.

## $^1H$ , HSQC, HMBC, and $^{31}P$ NMR analyses

$^1H$ , HSQC, and  $^1H$ - $^{31}P$  HMBC NMR samples were prepared by dissolving approximately 75–85 mg of KL in 1 mL of DMSO- $d_6$  and PK17 (i.e., the PK produced under the optimized conditions) in  $D_2O-d_6$  and stirred at 200 rpm for 24 hours, and then 5–6 mg of TMSP was added to the sample as the internal standard. Adjustments for  $^1H$  NMR were set to a total of 16 scans per sample, a 3.28 s acquisition time, with a 30° pulse, and 1.00 s of relaxation delay time. The  $^1H$ - $^{13}C$  HSQC assessment was performed under the conditions of a 90° pulse width of 48.17  $\mu s$ , a relaxation delay of 1.5 s, an acquisition time of 0.15 s, and 16 scans.  $^1H$ - $^{31}P$  HMBC was performed under the conditions of a relaxation delay of 7 s, a 90° pulse width of 13.5  $\mu s$ , 16 scans, an acquisition time of 0.36 s, and 25°C. In this analysis, 75–85 mg of PK17, as the optimized sample, was dissolved in  $D_2O-d_6$  and stirred at 200 rpm for 24 hours. The Top Spin 4.0.9 software was used to process NMR data points and spectra (2020 Bruker BioSpin GmbH).  $^{31}P$  NMR spectroscopic samples were prepared by dissolving 70 mg of the samples in 1 mL of pyridine/ $CDCl_3$  (1.6:1) mixture, then 200  $\mu L$  of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane was added to the mixture as the phosphorylation reagent in the presence of 70  $\mu L$  of cyclohexanol as the internal standard. The quantitative data of  $^{31}P$  NMR was collected at a pulse angle of 90°, room temperature, 0.65 acquisition time, and 25 s pulse delay with spectral parameters of a decoupling pulse sequence. The spectra were obtained using a nuclear magnetic resonance spectroscopy (AVANCE NEO-1.2 GHz, Bruker Corporation, USA) with 1024 scans per sample at 25°C, a 0.6 s acquisition time, a 90° pulse, and a 5 s relaxation delay time. Qualitative  $^{31}P$  NMR was conducted by dissolving 80 mg of KL in DMSO- $d_6$  and PK in  $D_2O-d_6$ . The spectra were collected at room temperature, with 256 scans, 0.72 s acquisition time, a 2 s pulse delay, a 30° pulse width, and a relaxation time of 2 s with spectral parameters of a decoupling pulse sequence.

## FTIR analysis

FTIR analysis was conducted with the 50 mg powder sample, which had previously been dried at 60°C. Samples were analyzed at the resolution of 4  $cm^{-1}$  with spectral width ranging between 4000 to 500  $cm^{-1}$  and 32 scans in an adsorbent mode.

### ICP-AES and XPS analyses

The phosphorous content of samples was measured with ICP-AES by digesting 500 mg of sample from a homogenous and grind solid in nitric and hydrochloric acids at  $180\pm 5^{\circ}\text{C}$  with a CEM Mars Xpress microwave oven using I-CHEM glass vessels. Once the digestion was complete, the samples were diluted to 40 mL according to EPA Method 3051A. The ICP-AES Varian (Agilent) Vista Pro Radial CETAC ASX-510 analyzed the digested samples. The surface chemical composition was analyzed by Xray Photoelectron Spectroscopy (XPS) with a monochromatic Al K $\alpha$  X-ray source (1486.7 eV) operating at 15 kV (90 W) in a FAT mode (fixed analyzer transmission) when 10 mg of a dried sample was tested at  $60^{\circ}\text{C}$ . The energy pass amount was 40 eV for the ROI region and 80 eV for the Survey region. A voltage of 284.6 eV was used to calibrate the C 1s binding energy. Full-spectrum, narrow high-energy resolution spectra, elemental composition, and functional groups were assessed using ESCape software for fitting graphs, elemental composition, functional groups binding energy, and mass concentration of bonds.

### Thermal analysis

Thermogravimetric analysis (TGA) was investigated with samples that were dried in a  $60^{\circ}\text{C}$  oven for 24 hours. Then, 78 mg of the samples were analyzed under a nitrogen gas atmosphere in a thermal analyzer (TGA i1000, Instrument Specialists Inc.) with a gas flow rate of 20–30 psi and 15 mL/min in the temperature range of  $25\text{--}800^{\circ}\text{C}$  at the rate of  $10^{\circ}\text{C}/\text{min}$ . In another set of experiments, the samples were collected from the TGA instrument when heated at different temperatures of  $220^{\circ}\text{C}$ ,  $320^{\circ}\text{C}$ ,  $600^{\circ}\text{C}$ , and  $800^{\circ}\text{C}$  for their elemental analysis by XPS. Differential scanning calorimetry (DSC) analysis was carried out by placing 10 to 12 mg of dried samples in hermetic Tzero<sup>®</sup> aluminum pans. It loaded to a differential scanning calorimeter (DSC Q2000, TA Instruments, DE, USA) with a nitrogen gas flow rate of  $50^{\circ}\text{C}/\text{min}$ . This experiment was performed in two heating and one cooling cycle. In the first cycle, to erase the thermal history, the temperature was raised from  $20^{\circ}\text{C}$  to  $230^{\circ}\text{C}$ , then cooled from  $230^{\circ}\text{C}$  to  $20^{\circ}\text{C}$  at  $5.0^{\circ}\text{C}/\text{min}$ . In the second cycle, a heating cycle was performed from  $20^{\circ}\text{C}$  to  $230^{\circ}\text{C}$  at  $10.0^{\circ}\text{C}/\text{min}$  for the  $T_g$  determination. This analysis was conducted twice; the standard deviations and average values were reported.

### Flame retardant analysis

The fire resistance behavior of coated wood samples was measured by the limiting oxygen index (LOI) with the sample size of (140mm  $\times$  20 mm  $\times$  10 mm) at room temperature, and samples were marked 50 mm from the wood top to the bottom. Coated samples were placed in a vertical glass column of the instrument with a flow rate of 40 mm/s of oxygen and nitrogen gas. The length of the flame was adjusted to 20 mm. The minimum amount of oxygen needed to ignite the sample was recorded as an LOI.

For smoke density analysis, the propane gas pressure was adjusted to 42 psi. The coated sample with the dimension of (4.5 mm  $\times$  4.5 mm  $\times$  1 mm) was placed on the square metal screen for burning, and the propane burner exposed the sample. The smoke density apparatus software was used for analysis, and data was collected based on the smoke density rate and light adsorption percentage.

**Table S1** The effect of different parameters on the reaction

Sample ID	Ratio KL/PHA (mol: mol)	Time (min)	Temperature (°C)	Solvent	pH adjustment strategy <sup>a</sup>	Solubility (%)	Charge density (mmol/g)
PK1	1:0.02	240	80	DI Water	1	97	-1.8
PK2	1:0.06	240	80	DI Water	1	93	-2.3
PK3	1:0.16	240	80	DI Water	1	94	-2.9
PK4	1:0.2	240	80	DI Water	1	98	-2.8
PK5	1:0.3	240	80	DI Water	1	97	-3.1
PK6	1:0.4	240	80	DI Water	1	72	-4.3
PK7	1:0.4	240	80	DI Water	2	97	-4
PK8	1:0.4	240	80	Urea	2	97	-3.8
PK9	1:0.4	240	100	Urea	2	98	-4
PK10	1:0.4	240	120	Urea	2	98	-3.9
PK11	1:0.4	20	80	DI Water	2	97	-4.2
PK12	1:0.4	40	80	DI Water	2	97	-3.8
PK13	1:0.4	60	80	DI Water	2	95	-3.5
PK14	1:0.4	120	80	DI Water	2	98	-3.4
PK15	1:0.4	180	80	DI Water	2	98	-3.7
PK16	1:0.4	240	80	DI Water	2	97	-4
PK17	1:0.4	20	20	DI Water	2	97	-4.2
PK18	1:0.4	20	40	DI Water	2	93	-4
PK19	1:0.4	20	60	DI Water	2	96	-4
CK		240	80	DI Water	2	93	-0.8

<sup>a</sup>the strategies explained in section: (1) after adding the reagent, the reaction was exploited without pH adjustment, and the samples were neutralized and dialyzed after the reaction; (2) after adding the reagent, the pH of the reaction was adjusted to 11, and the reaction ran at pH 11. Afterward, the reaction medium was neutralized and dialyzed.

Sample ID	Organic elements				ICP-AES	XPS	M <sub>w</sub>	M <sub>n</sub>	Table S2 Elem
Label	δC / δH (ppm)			Assignment					
OCH <sub>3</sub>	C (%)	H (%)	N (%)	S (%)	P (%)	C-H in -OCH <sub>3</sub> (methoxy)	(g/mol)	(g/mol)	
PK1	54.64	55/3.2	6.49	0	1.17	C <sub>β</sub> -H <sub>β</sub> in phenyl coumarane units	3900	2543	
PK2	52.11	55.2/3	5.59	0	1.15	C <sub>β</sub> -H <sub>β</sub> in resinol units	4380	3779	
PK3	48.25	62/3.4	5.92	0	1.07	C <sub>v</sub> -H <sub>v</sub> in β-O-4' linkage	4561	4194	
PK4	47	64/3.7	5.92	0	1.02	C <sub>v</sub> -H <sub>v</sub> in phenyl coumarane	4577	4161	
PK5	45.46	63.3/4.1	5.92	0	1.02	C <sub>v</sub> -H <sub>v</sub> in p-hydroxycinnamyl alcohol end groups	4528	4139	
PK6	43.21	72.8/4.7	4.99	0	0.84	C <sub>v</sub> -H <sub>v</sub> in resinol units	4560	4233	
PK7	44.42	5.6	0	0.01	7	C <sub>α</sub> -H <sub>α</sub> in β-O-4' linkage	4668	4412	ental analy sis of CHNS , ICP- AES, and XPS
PK8	44.27	5.6	0	0.01	7	–	4747	4482	
PK9	51.07	6.81	0	0.01	7	–	4778	4641	
PK10	49.44	6.35	0	0.01	6	–	4781	4642	
PK11	39.23	5.22	0	0.72	7.2	–	4671	4383	
PK12	41.47	5.37	0	0.82	7.1	–	4659	4378	
PK13	41.47	5.65	0	0.83	6.7	–	4664	4382	
PK14	43.15	5.74	0	0.84	6.2	–	4670	4429	
PK15	40.31	5.56	0	0.76	6.7	–	4652	4240	
PK16	42.63	5.69	0	0.82	7.4	–	4668	4412	
PK17	40.29	5.66	0	0.84	7.2	7	4800	4624	
PK18	41.16	5.66	0	0.86	7.1	–	4784	4589	
PK19	41.27	5.63	0	0.84	7.6	–	4811	4640	
CK	60.53	6.64	0	1.3	<2	0	3268	1690	Table S3 The assign ment s of the
KL	62.71	6.82	0	1.6	0	0	-	-	

<sup>13</sup>C–<sup>1</sup>H cross signals obtained from HSQC NMR spectra

$A_{\beta}$	85.6/4.3	$C_{\beta}$ - $H_{\beta}$ in $\beta$ -O-4 linked to G units
$B_{\alpha}$	86.9/4.6	$C_{\alpha}$ - $H_{\alpha}$ in resinol units
$C_{\alpha}$	88.6/5.5	$C_{\alpha}$ - $H_{\alpha}$ in phenylcoumaran substructures
$G_2$	111/6.9	$C_2$ - $H_2$ in guaiacyl units
$G'_2$	112.5/7.5	$C_2$ - $H_2$ in oxidized ( $C_{\alpha}$ =O) guaiacyl units
$G_5$	116/6.6	$C_5$ - $H_5$ in guaiacyl units
$G_6$	121.5/6.7	$C_6$ - $H_6$ in guaiacyl units
$G'_6$	124.6/7.4	$C_6$ - $H_6$ in oxidized ( $C_{\alpha}$ =O) guaiacyl units
$D_{\beta}$	128.6/6.8	$C_{\beta}$ - $H_{\beta}$ in cinnamaldehyde end groups
$H_{2,6}$	127.7/7.2	$C_{2,6}$ - $H_{2,6}$ in p-hydroxybenzoate units

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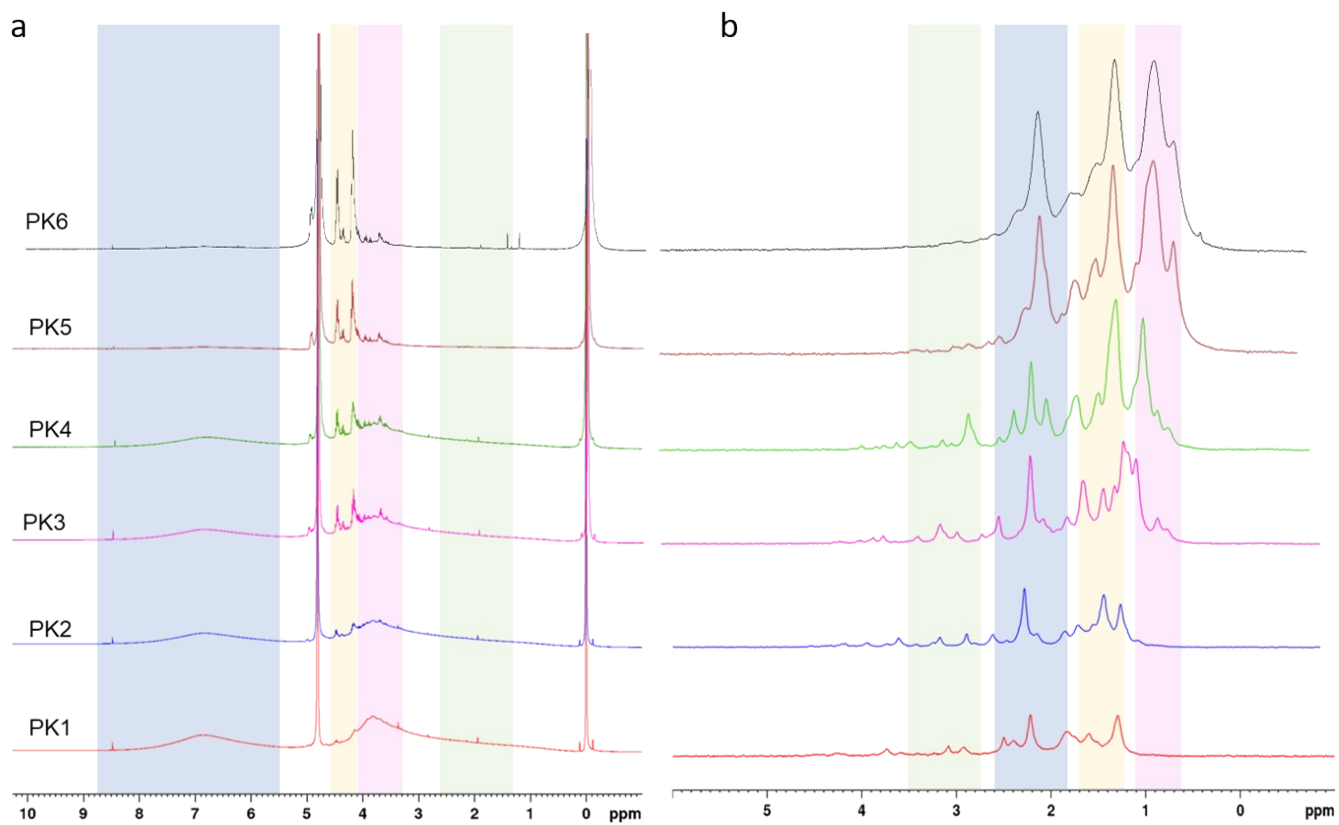


Fig. S1  $^1\text{H}$  NMR spectra for PK samples (a) and  $^{31}\text{P}$  NMR spectra for PK samples to study the effect of molar ratio (b)

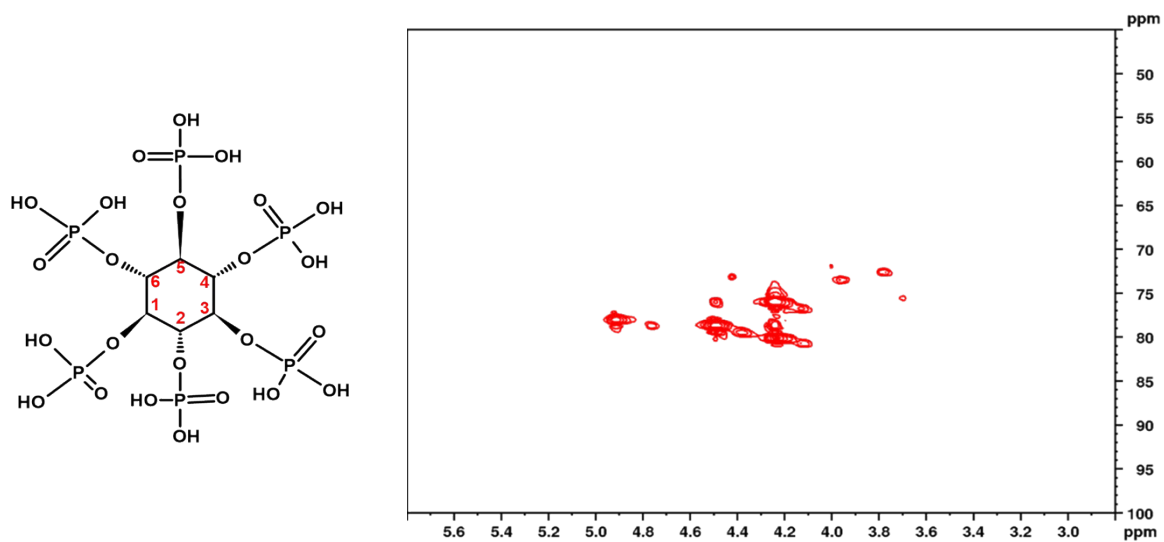


Fig. S2 HSQC of Phytic acid.

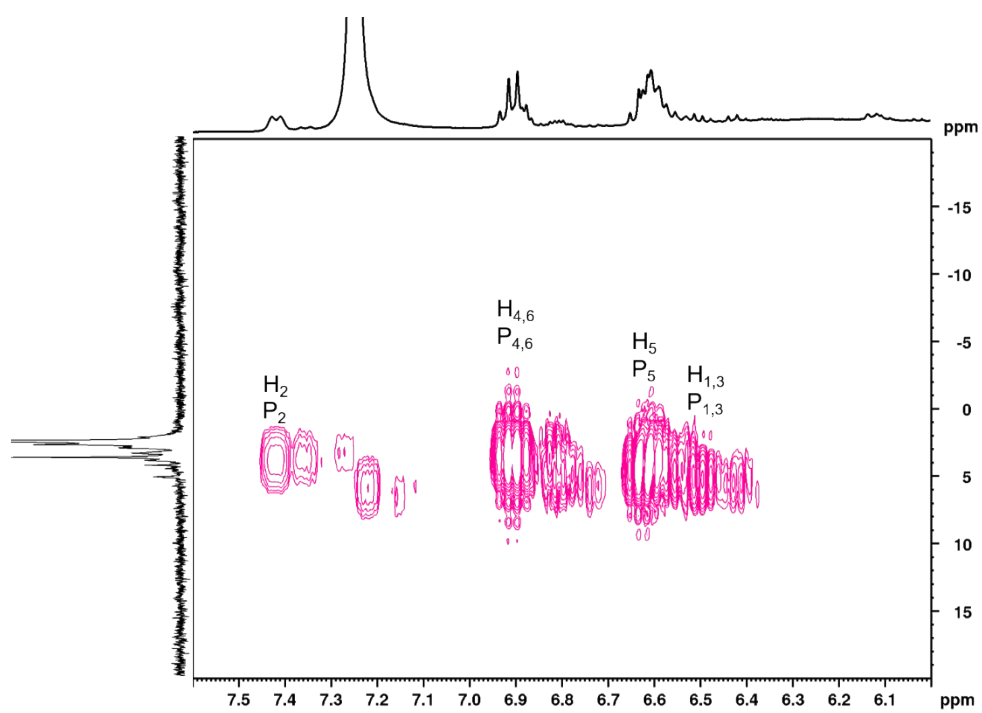
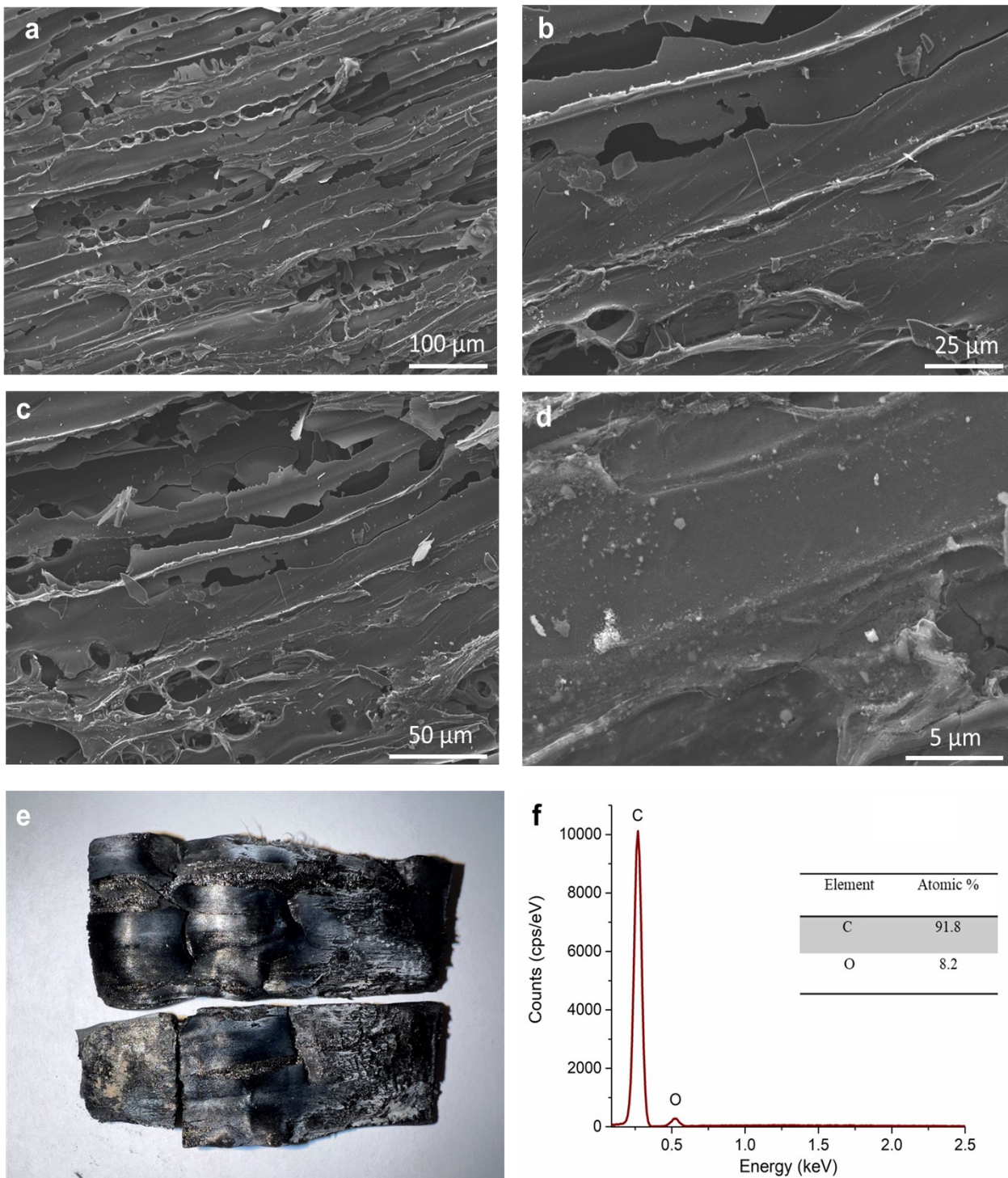
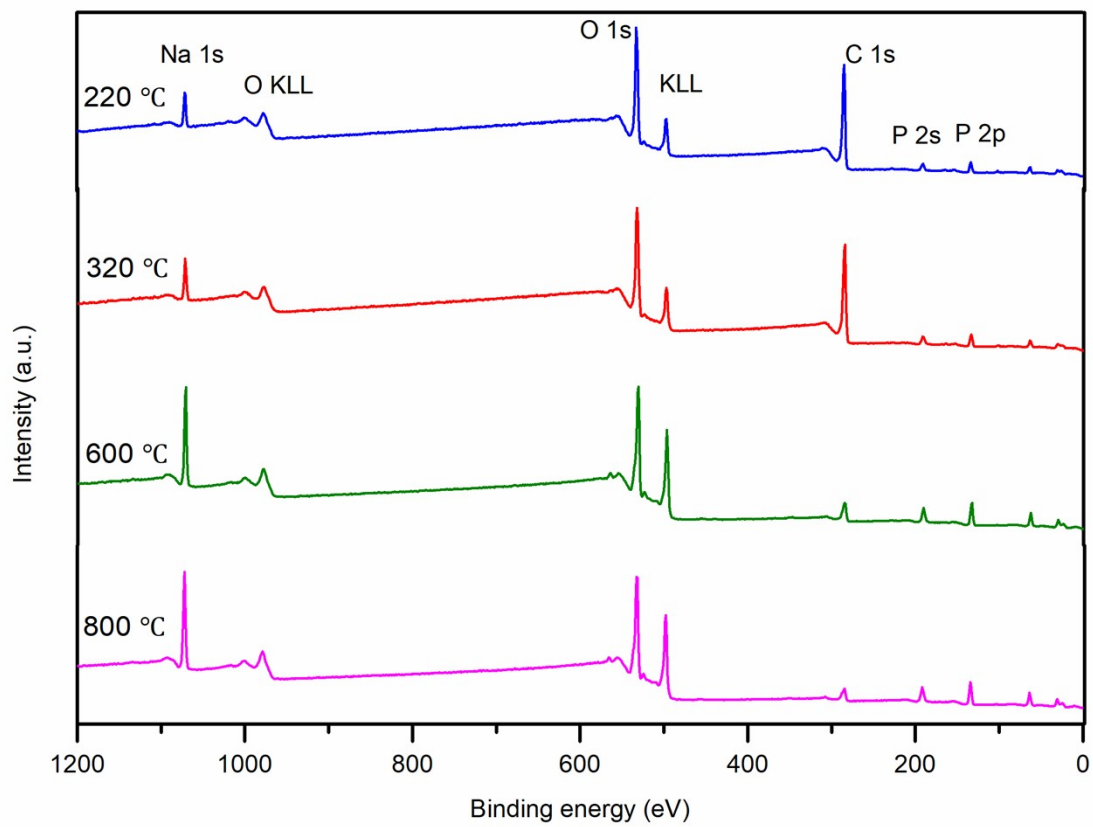


Fig. S3  $^1\text{H}$ - $^{31}\text{P}$  HMBC spectra of the PK18 in  $\text{D}_2\text{O}$ .





**Fig. S4** SEM images (a-d), digital picture (e), and EDX graph (f) of char residue after burning UW in smoke density analysis.



**Fig. S5** XPS wide spectra of PK17 after burning in different temperatures

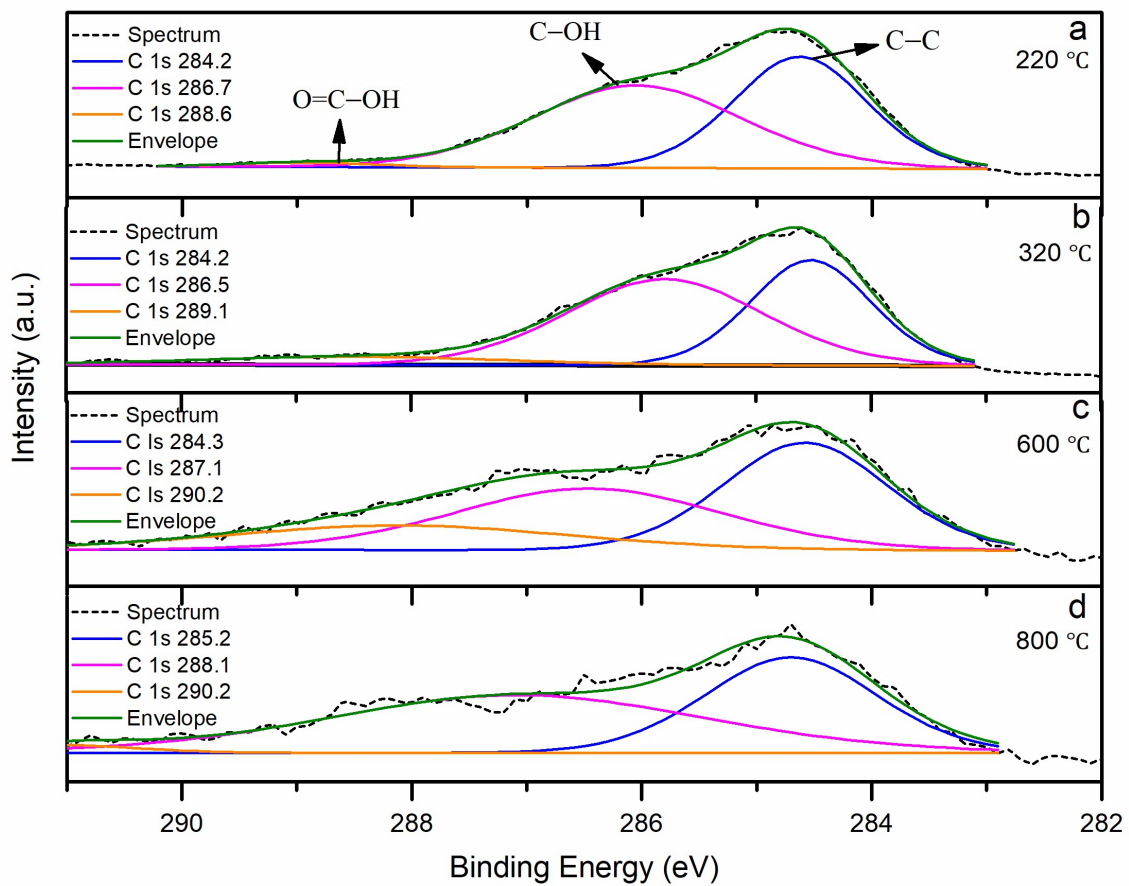


Fig. S6 XPS spectra of C 1s for PK17 after burning in different temperatures: (a) 220°C, (b) 320°C, (c) 600 °C, and (d) 800°C.

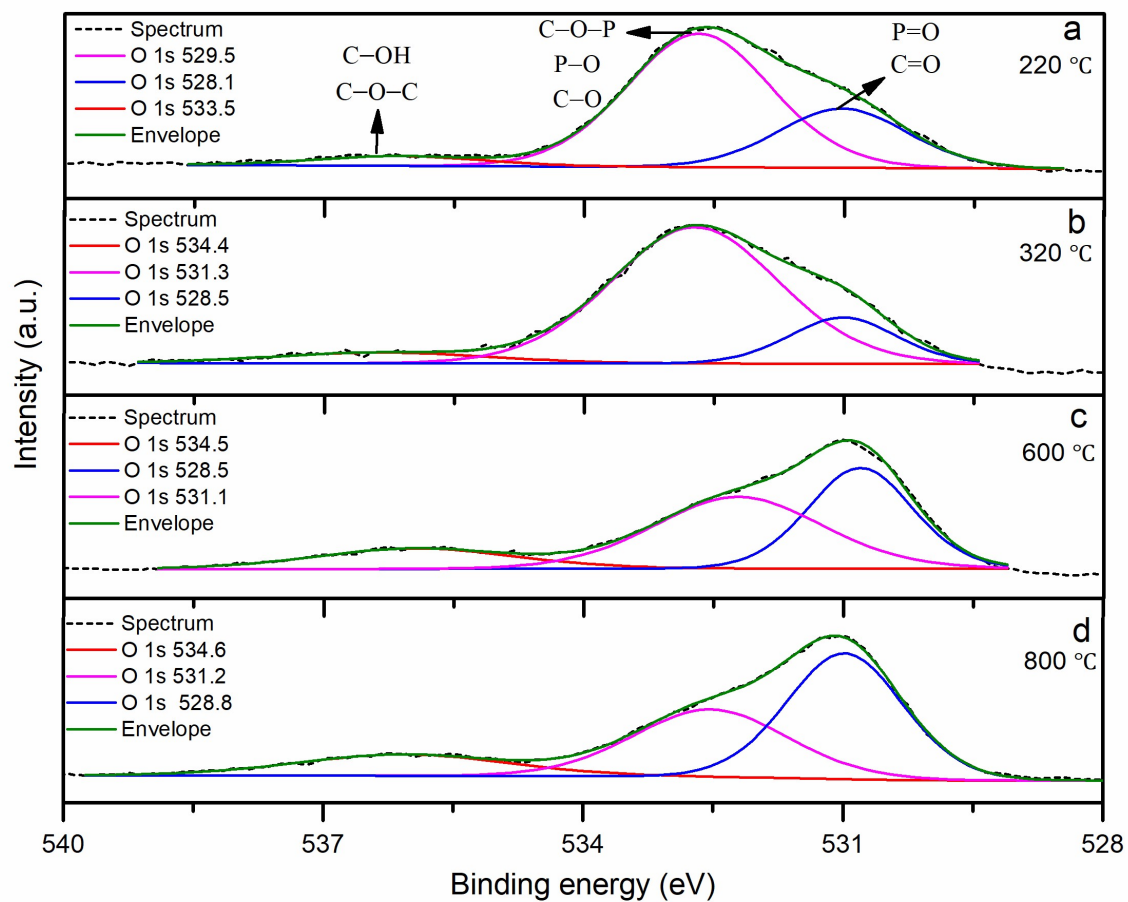


Fig. S7 XPS spectra of O 1s for PK17 after burning in different temperatures: (a) 220°C, (b) 320°C, (c) 600°C, and (d) 800°C.

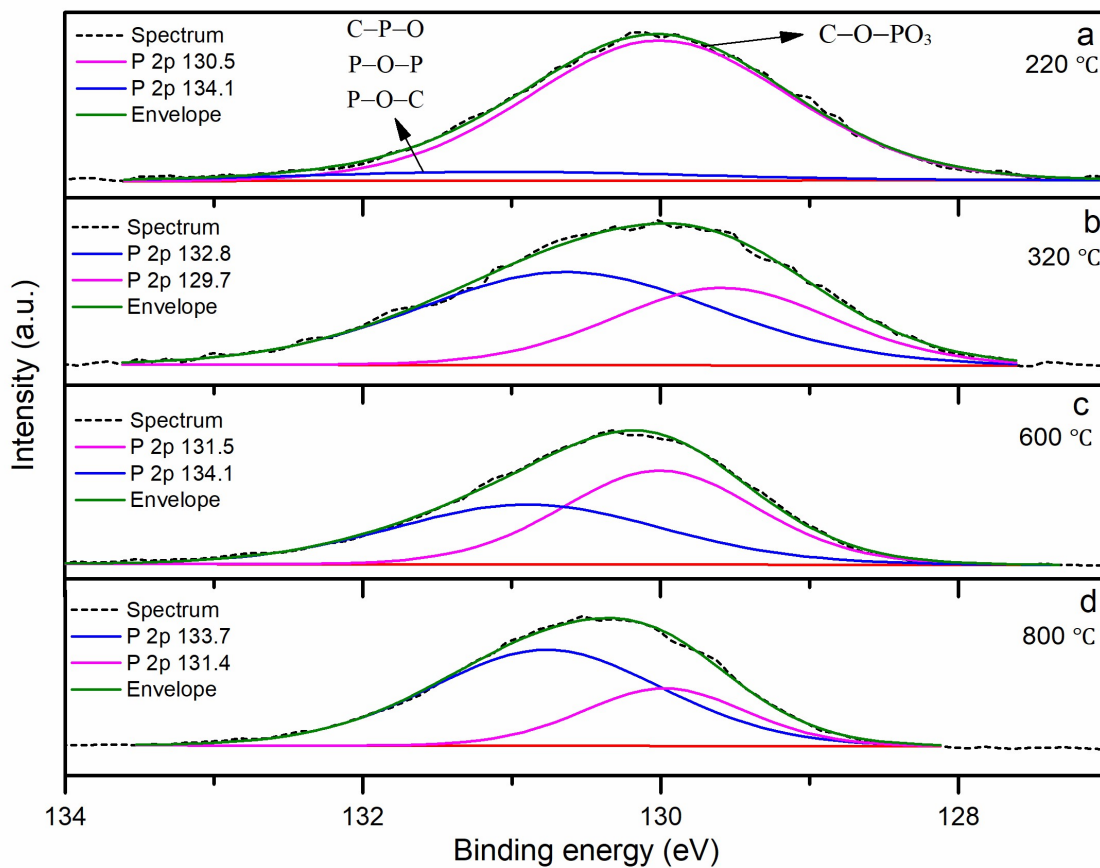


Fig. S8 XPS spectra of P 2p for PK17 after burning in different temperatures: (a) 220°C, (b) 320°C, (c) 600°C, and (d) 800°C.

**Table S4** Mass percentage concentration of major elements for KL, PK18, and burned PK17 from TGA in different temperatures

Samples	Mass concentration (%)		
	C 1s	O 1s	P 2p
KL 25 °C	74	24.25	0
PK17 25 °C	60	32.26	7
PK17 220 °C	59.78	32.95	7.27
PK17 320 °C	57.93	33.57	8.50
PK17 600 °C	21.39	54.85	23.75
PK17 800 °C	15.12	58.02	26.86

**Table S5** Mass percentage concentration of C 1s for KL, PK18, and burned PK17 from TGA in different temperatures

Samples	Mass concentration (%)		
	C 1s		
	C–C	C–OH	O=C–OH
KL25 °C	42.44	55.21	2.35
PK17 25 °C	48.41	51.04	0.55
PK17 220 °C	45.28	52.82	1.9
PK17 320 °C	39.56	52.70	7.74
PK17 600 °C	41.23	41.94	16.83
PK17 800 °C	41.93	55.40	2.67

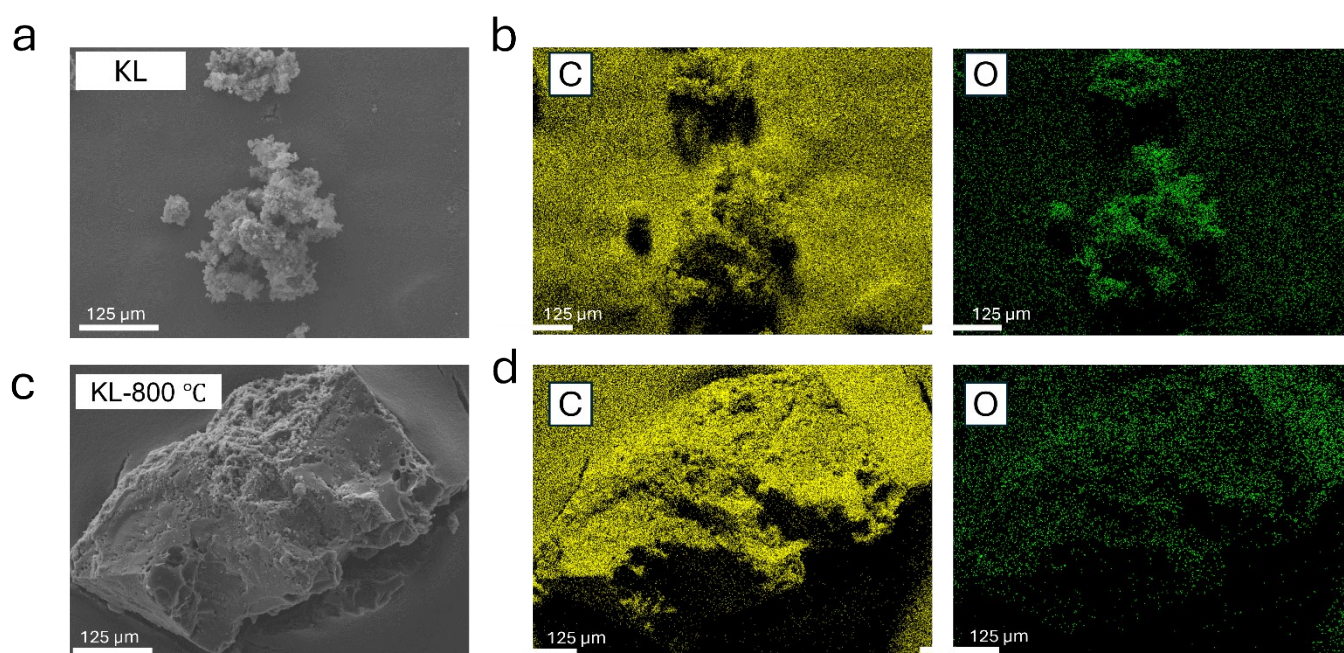
**Table S6** Mass percentage concentration of O 1s for KL, PK18, and burned PK17 from TGA in different temperatures

Samples	Mass concentration (%)		
	O 1s		
	C-OH C-O-C	C-O-P P-O C-O	P=O C=O
KL	96.49	–	3.51
PK17 25 °C	81.31	10.76	7.93
PK17 220 °C	5.77	67.40	26.83
PK17 320 °C	7.78	75.81	16.41
PK17 600 °C	15.42	45.16	39.42
PK17 800 °C	15.22	35.30	49.49

**Table S7** Mass percentage concentration of P 2p for KL, PK17, and burned PK18 from TGA in different temperatures

Samples	Mass concentration (%)	
	P 2p	
	C-O-PO <sub>3</sub>	C-P-O P-O-P
KL	–	–
PK17 25 °C	95.64	4.36
PK17 220 °C	91.34	8.66
PK17 320 °C	38.01	61.99
PK17 600 °C	53.09	46.91
PK17 800 °C	29.67	70.33





**Fig. S9** The SEM images (a and c) and the EDS elemental mapping (b and d) of KL before and after combustion.

#### References

- 1 F. Kong, S. Wang, J. T. Price, M. K. R. Konduri and P. Fatehi, *Green Chemistry*, 2015, **17**, 4355–4366.