Supporting Online Information

Temperature sensitivity of black carbon decomposition and oxidation

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Black C materials. The pyrolysis was performed by BEST Energies, Inc. (Daisy Reactor, WI, USA). The materials were then slightly ground to pass consecutive 2-mm and 0.5-mm sieves and particles remaining on the 0.5-mm sieve were collected for this study. Initial chemical properties of the BC materials are shown in Table S1. Water holding capacity determination, microbial inoculation, and nutrient solution preparation was performed as described by Nguyen and Lehmann (*1*).

Analyses of elemental contents of C, N, H, O and CECp (Potential Cation Exchange Capacity) were similar to those described in detail by Nguyen and Lehmann (*1*). In brief, C, N, and H concentrations of the BC-sand mixture were determined using dry combustion analysis. Black C ash and sand material in percent of the mixture were quantified by combusting 50 mg of ball ground BC-sand mixture at 630°C in a muffle furnace for 24 hours and O contents were calculated by difference from contents of C, N, H and ash-sand mixture and expressed as per carbon basic. Carbon loss was determined by the difference in C contents before and after one year.

CECp was quantified in duplicate by saturating 3.5 g of BC-sand mixture with 40 mL of 1N ammonium acetate at pH = 7. Black C particles slowly adsorbed ammonium from the solution presumably due to the large internal surface area. This depressed the apparent CECp of the mixture. To address this, we increased saturation time to 24 hours to allow complete ammonium adsorption and exchange. After ammonium acetate extraction, the mixture received 40 mL of 2N KCl to replace the adsorbed NH_4^+ cations. The extracted NH_4^+ was

determined using a continuous flow analyzer (Technicon Auto Analyzer, Chauncey, CT, USA) and calculated as CECp.

Incubation experiment. A completely randomized full factorial experiment with 8 replicates and 3 factors (2 biomass types, 2 charring temperatures and 6 incubation temperature levels) was set up. One gram of ground BC material was added to 30-mL bottles after mixing with 19 g of pure sand material. Beforehand, the sand had been heated at 550°C in a muffle furnace for 24 hours to remove any remaining organic matter. Each bottle received 2 mL of microbial nutrient solution (*1*). The BC-sand mixture was then moistened to 60% of water holding capacity which was kept constant over the one-year experiment. The bottles were placed in plastic trays positioned in one of 6 temperature-controlled chambers. The temperature was set to either 4, 10, 20, 30, 45 or 60°C.

The plastic trays were covered with aluminum foil to control water evaporation. Five small holes were created in the covered aluminum foil for gas exchange. Water was added to the tray to maintain a moist environment. The water content of the mixture in the bottle and water level in the plastic trays were monitored weekly by weighing and adding appropriate amounts of distilled water.

Direct polarization ^{13}C Nuclear Magnetic Resonance (DP-NMR). Approximately 60 mg of each BC powder was packed into a 4-mm (o.d.) zirconia rotor and sealed with a Kel-F cap. The ^{13}C NMR spectra were acquired at Rice University on a 200 MHz Bruker DSX

spectrometer (^{13}C frequency 50 MHz) equipped with a 4-mm magic angle spinning (MAS) probe.

Direct polarization magic angle spinning (DPMAS) spectra were acquired while spinning at 10 kHz by applying a 20-degree ^{13}C excitation pulse, continuous wave ^{1}H decoupling and 5 s recycle delay. DPMAS spectra with dipolar-dephasing were generated by inserting a 50 μs delay prior to decoupling and signal acquisition. The 5-s recycle delay was determined to be sufficient for complete T_1 relaxation since increasing the delay to 10 s generated no additional signal intensity. The DPMAS spectrum arising from the empty rotor and probe background was acquired under identical conditions, and this signal was subtracted from each of the charcoal spectra. Therefore, we interpret the peak areas obtained by DPMAS as quantitative measures of C functional groups present in the BC. Quantitative reliability was assessed by comparing the C-normalized signal intensity detected for each sample to the C-normalized signal intensity of an external standard, a procedure known as spin counting. A 50:50 mixture of glycine and cellulose (Sigma Aldrich) was used as the spin counting standard, following the convention of Smernik and Oades (*2*). For each sample, the percentage of C observed in the NMR spectrum (C_{obs}) was calculated using Eq. S1:

$$C_{obs}(\%) = 100 \times \frac{\text{signal intensity per unit carbon for sample}}{\text{signal intensity per unit carbon for glycine}} \qquad \text{(Eq. S1)}$$

The calculated observability was 91 – 110 (± 10) % of the BC (Table 1). Therefore, we interpret the peak areas obtained by DPMAS as quantitative measures of C functional groups present in the BC.

The DPMAS spectra with C-H dipolar dephasing were used to quantify the protonated, oxygen-substituted, alkyl-substituted, and bridgehead aromatic C in the BC. Using the algorithms derived by Solum et al. (*3*), we estimated the average size of aromatic domains with in the BC structure (i.e. the number of aromatic C atoms fused together in a cluster). We also estimated the average number of oxygen atoms and alkyl side chains attached to each cluster (*3*). Finally, we estimated the average length of the side chains attached to each C cluster using Eq. (S2):

$$\text{alkyl C per side chain} = \frac{\text{total alkyl C, } f_{al}}{\text{alkyl substituted aromatic C, } f_a^S} \qquad \text{(Eq. S2).}$$

Calculations. Carbon contents remaining after incubation were determined by calculating the ratio of the percentage of C concentration (%) after incubation to C concentration (%) before the experiment using C contents determined by elemental C analyses, following Eq. S3:

$$\text{Re}\,maining C(\%) = \frac{C_{after}}{C_{before}} * 100 \qquad \text{(Eq. S3).}$$

Carbon mineralization, oxidation and CECp as a function of incubation temperature were quantified, based on a first order kinetic model (*4*, *5*) with 3 parameters (Eq. S4):

$$f = Y_0 + ae^{-bT} \text{ or } f = Y_0 + a(1 - e^{-bT}) \qquad \text{(Eq. S4),}$$

where the dependent variable is the exponential decay or rise pattern, respectively, f is the content (remaining C, O/C or CECp) at incubation temperature T (°C), Y_o is the initial content, a is a constant and b is a reaction rate constant. A linear model was also used for any

observed parameters that were linearly dependent on the incubation temperature. The temperature coefficient (Q_{10}) was calculated using Eq. S5:

$$Q_{10} = \left[\frac{R_2}{R_1}\right]^{\left(\frac{10}{T2-T1}\right)} \quad \text{(Eq. S5)},$$

where R_1 and R_2 are C losses (% of initial C concentration) at 2 temperatures, T1 and T2, of an interval, respectively (*6*).

References

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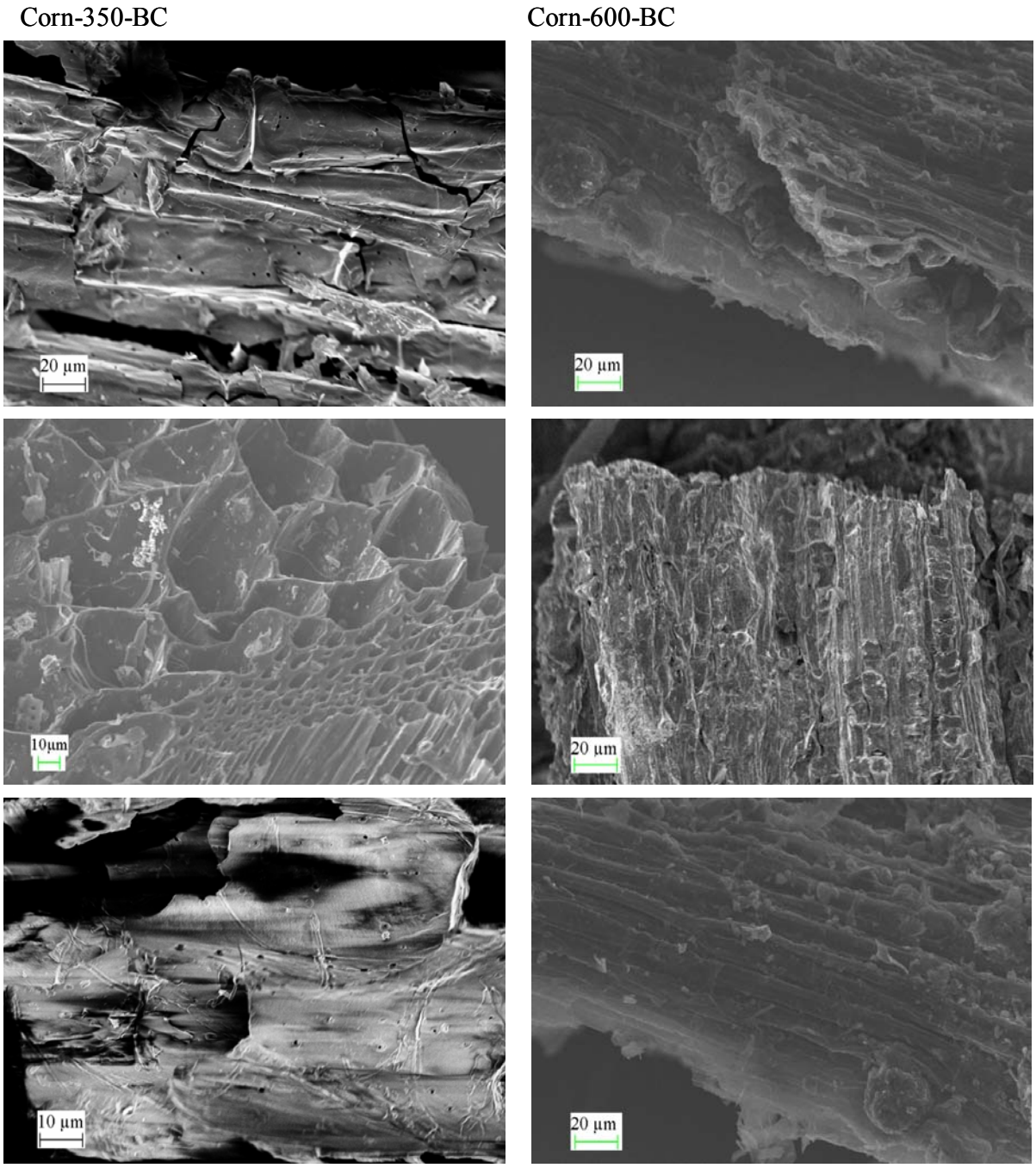


FIGURE S1a. SEM images of corn-BC formed at 350 and 600°C

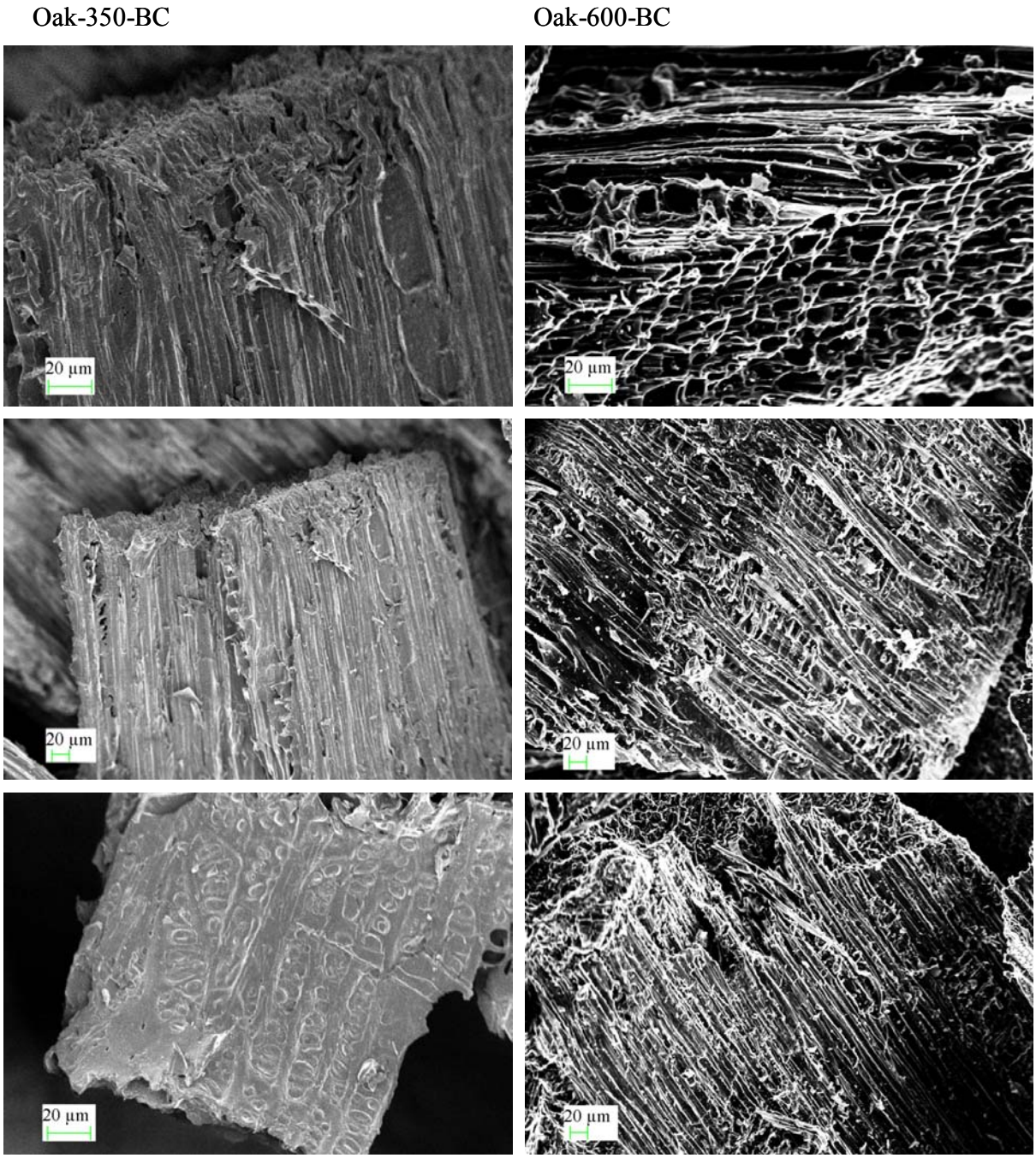


FIGURE S1b. SEM images of oak-BC formed at 350 and 600°C

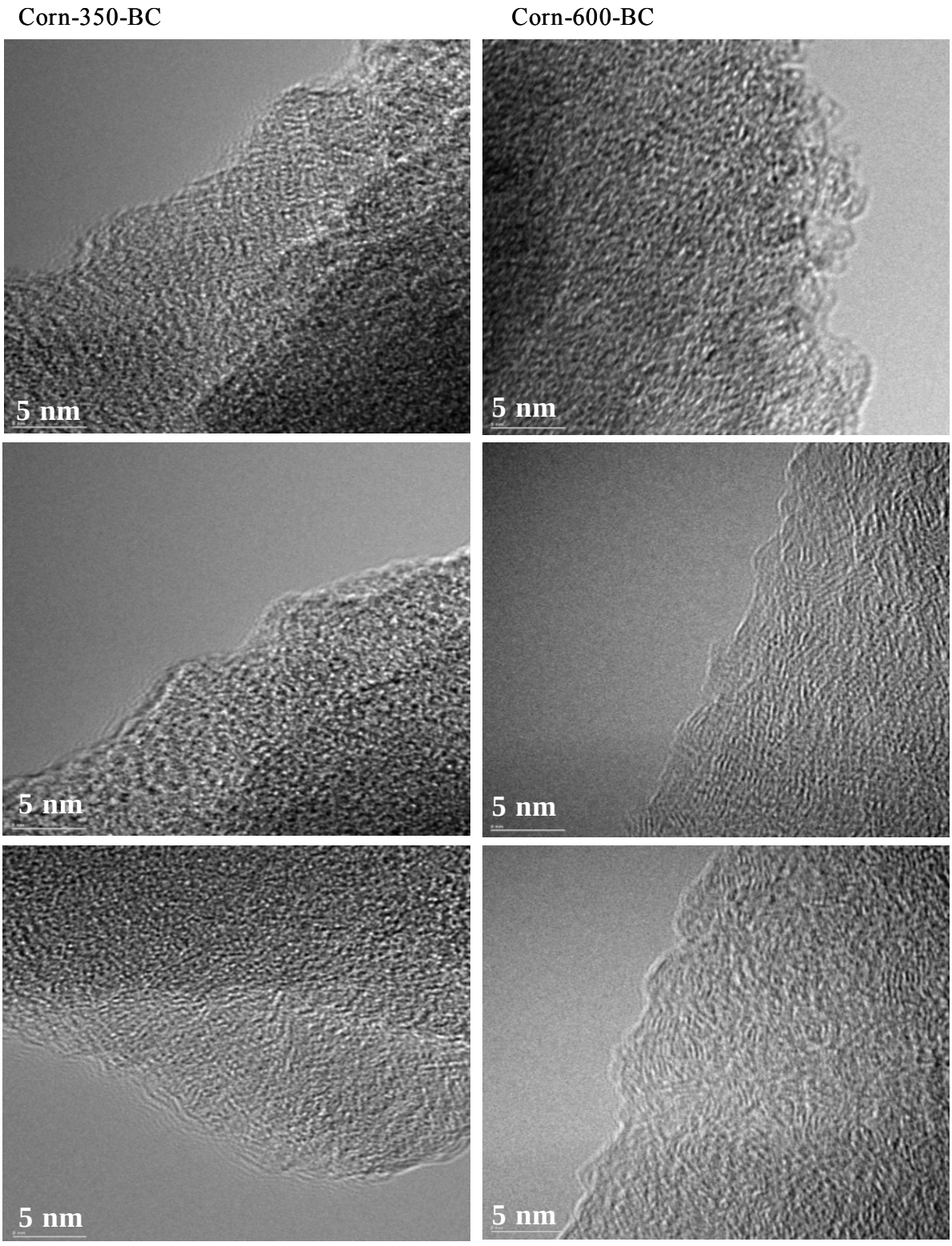


FIGURE S2a. TEM images of corn-BC formed at 350 and 600 °C

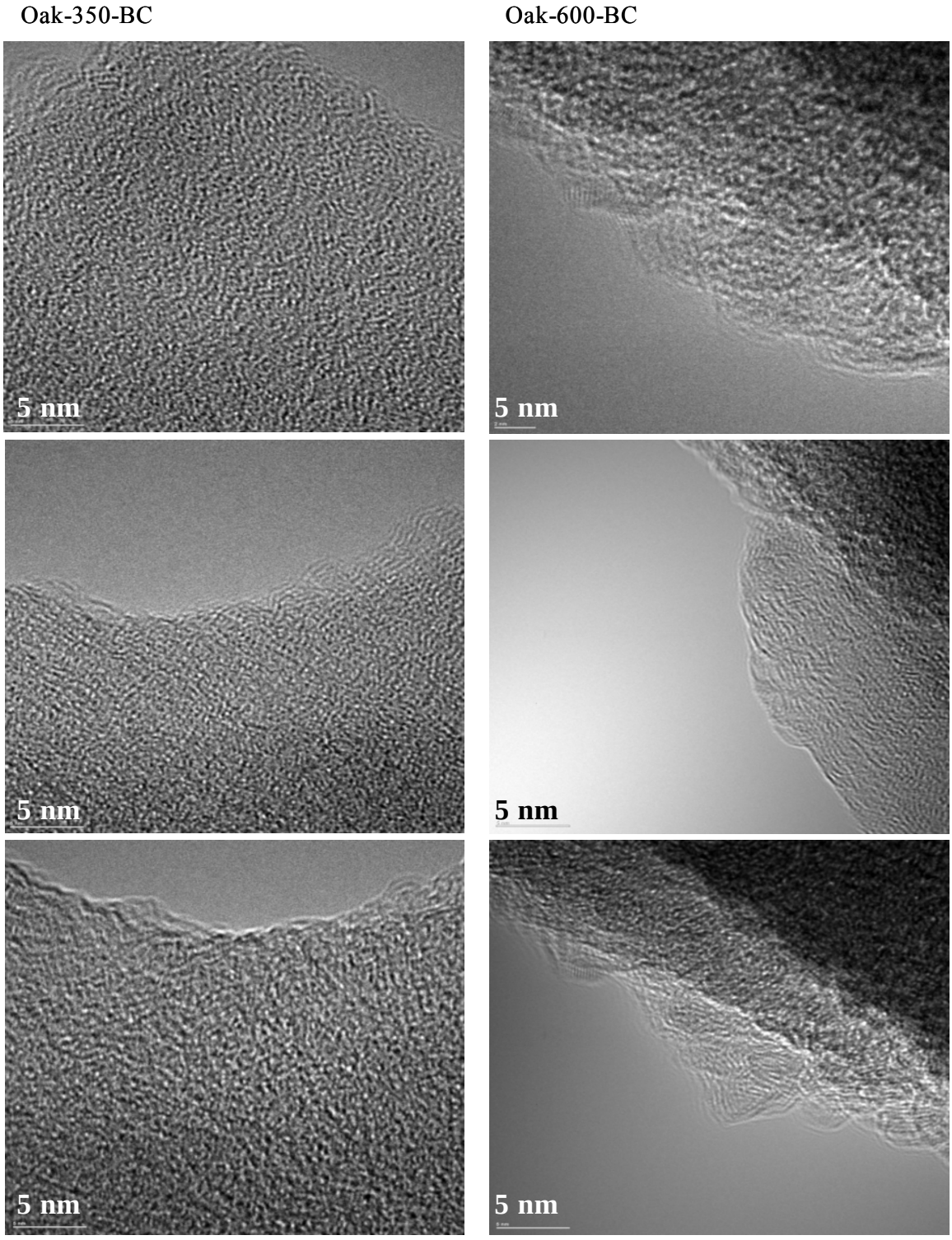


FIGURE S2b. TEM images of oak-BC formed at 350 and 600 °C

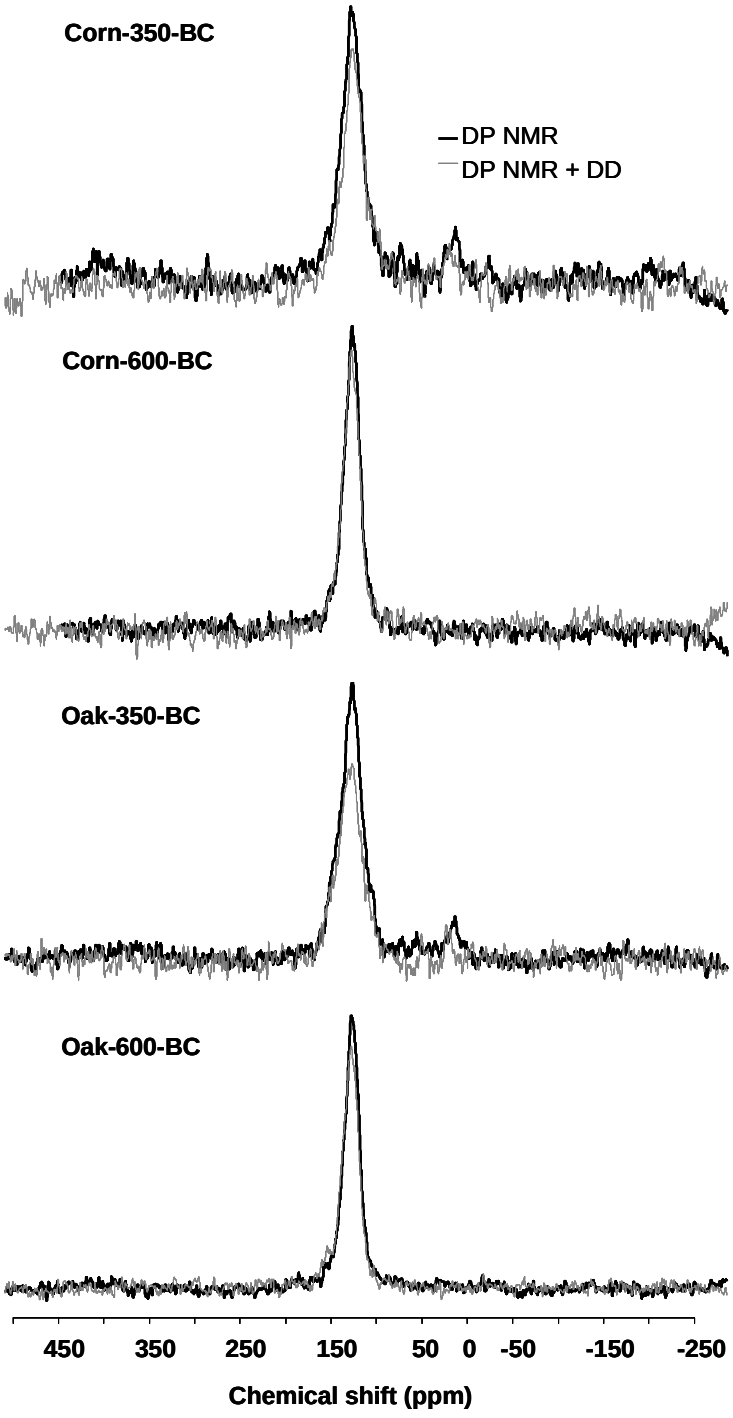
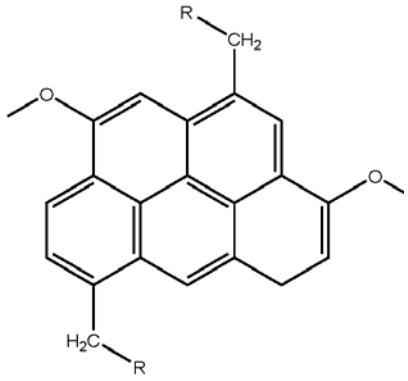


FIGURE S3. Functional group chemistry of the BC materials determined by direct polarization ^{13}C NMR

Corn-350-BC



Corn-600-BC

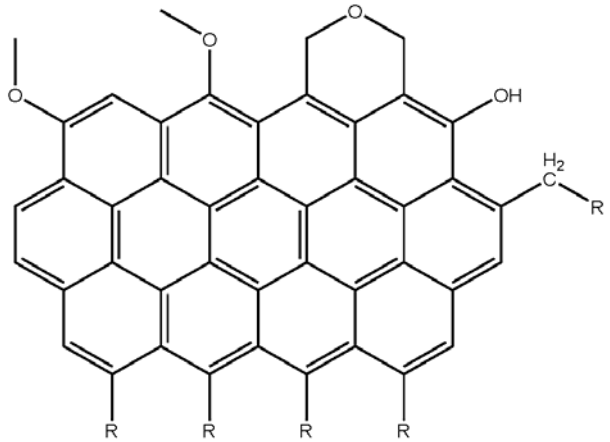


FIGURE S4. Calculated proposed structure of a structure of an aromatic cluster determined by direct polarization ^{13}C NMR

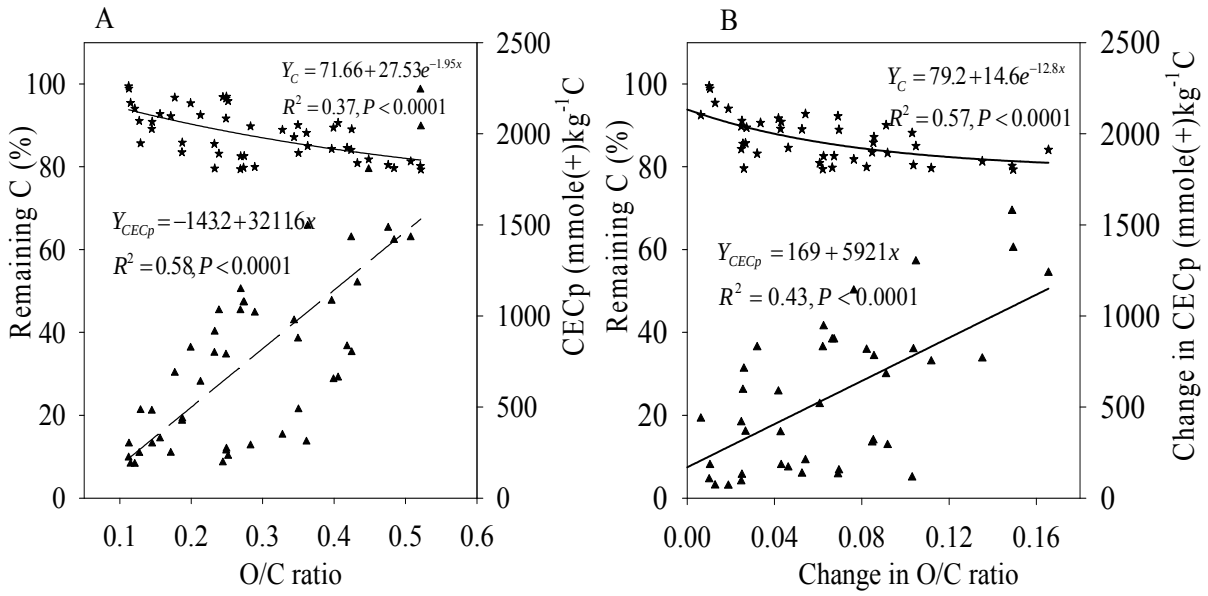


FIGURE S5. Remaining C (Y_c) and CECp (Y_{CECp}) as a function of O/C ratios (A) and change in O/C ratios (B).

TABLE S1. Initial properties of BC materials

Biomass types	Charring temp. (°C)	pH[b]	CECp[a]	C	N	O	H	C/N	O/C	H/C
				(%)	(%)	(%)	(%)			
Corn residue	350	5.88	610	67.5	0.9	25.1	4.74	73	0.37	0.07
	600	6.71	215	79.0	0.92	16.3	2.52	86	0.21	0.03
Oak wood	350	4.84	131	75.9	0.10	19.6	4.27	759	0.26	0.06
	600	4.91	89	88.4	0.12	9.0	2.13	737	0.10	0.02

[a]CECp = Potential Cation Exchange Capacity in mmole(+)kg^{-1}C

[b]pH in 1:20 w:v water

TABLE S2. Parameters of the fitted model, $f = Y_0 + ae^{-bT}$, of remaining C as a function of incubation temperature, shown in main manuscript Figs. 3A and B

BC materials	Y_o	a	b	R^2	P
Overall mean	82.67	16.27	0.061	0.99	0.008
Corn-350-BC	80.26	12.63	0.078	0.84	0.050
Corn-600-BC	79.86	21.35	0.071	0.90	0.031
Oak-350-BC	84.94	16.04	0.057	0.87	0.048
Oak-600-BC	84.15	16.57	0.036	0.90	0.030

TABLE S3. Remaining C (%) of 24 cross combinations after a 1-year incubation. Values followed by the same letter were not significantly different (means and standard deviation-SD, N=8)

Incubation	Corn residue				Oak wood			
Temp. (°C)	350°C		600°C		350°C		600°C	
	%	SD	%	SD	%	SD	%	SD
4	90.1^{cdef}	4.80	94.6^{abc}	7.61	96.7^{ab}	3.29	99.2^{a}	0.81
10	84.5^{ghijk}	2.95	93.5^{bcd}	5.76	96.4^{ab}	3.89	94.7^{abc}	2.92
20	85.0^{ghi}	6.83	82.6^{hijk}	4.67	89.0^{defg}	4.00	91.0^{cde}	6.30
30	80.1^{ijk}	4.99	82.6^{hijk}	1.77	86.2^{efjh}	5.94	92.5^{abc}	6.41
45	81.6^{hijk}	2.42	79.6^{k}	3.62	88.6^{defg}	7.50	85.8^{fgh}	6.32
60	79.8^{jk}	3.86	81.6^{hijk}	5.42	84.6^{ghij}	5.87	86.4^{efgh}	4.23

TABLE S4. ANOVA of remaining C

Source	DF	Sum of Squares	F ratio	Prob > F	
Incubation Temp.	5	1509	12.10	<.0001	*
Biomass type	1	1094	43.85	<.0001	*
Incubation Temp. * Biomass type	5	155	1.24	0.2915	ns
Charring Temp.	1	157	6.30	0.0130	*
Incubation Temp.*Charring Temp.	5	280	2.24	0.0522	ns
Biomass types*Charring Temp.	1	10	0.40	0.5286	ns
Incubation Temp.*Biomass type*Charring Temp.	5	297	2.38	0.0407	*
Error	168	4190			

TABLE S5. O/C ratios of 24 cross combinations after 1-year incubation. Values followed by the same letter were not significantly different (means and standard deviation –SD, N=8)

Incubation	Corn residue				Oak wood			
Temp. (°C)	350°C		600°C		350°C		600°C	
	O/C	SD	O/C	SD	O/C	SD	O/C	SD
4	0.40^{bcd}	0.07	0.19^{ijk}	0.06	0.25^{hi}	0.05	0.11^{l}	0.04
10	0.41^{bcd}	0.08	0.22^{ij}	0.05	0.25^{hi}	0.05	0.12^{l}	0.04
20	0.43^{bc}	0.03	0.23^{ij}	0.09	0.32^{efgh}	0.08	0.14^{kl}	0.03
30	0.48^{ab}	0.15	0.27^{fghi}	0.10	0.34^{defg}	0.07	0.16^{jkl}	0.08
45	0.48^{ab}	0.12	0.27^{fghi}	0.08	0.35^{def}	0.10	0.16^{jkl}	0.09
60	0.52^{a}	0.08	0.26^{ghi}	0.05	0.39^{cde}	0.10	0.17^{jkl}	0.05

TABLE S6. ANOVA of O/C ratios

Source	DF	Sum of Squares	F ratio	Prob > F	
Incubation Temp.	5	0.21	7.01	<.0001	*
Biomass type	1	0.44	73.34	<.0001	*
Incubation Temp. * Biomass type	5	0.01	0.28	0.924	ns
Charring Temp.	1	1.77	291.77	<.0001	*
Incubation Temp.*Charring Temp.	5	0.03	1.13	0.349	ns
Biomass types*Charring Temp.	1	0.02	2.60	0.109	ns
Incubation Temp.*Biomass type*Charring Temp.	5	0.01	0.19	0.966	ns
Error	168	1.02			

TABLE S7. CECp (mmole(+)kg^{-1}C) of 24 cross combinations after incubation. Values followed by the same letter were not significantly different (means and standard deviation-SD, N=8)

Incubation	Corn residue				Oak wood			
Temp. (°C)	350°C		600°C		350°C		600°C	
	CECp	SD	CECp	SD	CECp	SD	CECp	SD
4	656^{ef}	129	662^{ef}	181	265^{gh}	180	260^{gh}	159
10	957^{cd}	209	805^{de}	121	212^{gh}	92	187^{h}	85
20	990^{cd}	255	855^{cde}	248	298^{gh}	60	273^{gh}	94
30	1449^{b}	211	1109^{c}	269	416^{fgh}	176	287^{gh}	136
45	1618^{b}	401	1052^{cd}	162	925^{cd}	259	459^{fg}	155
60	2140^{a}	679	1023^{cd}	186	1462^{b}	580	451^{fg}	157

TABLE S8. ANOVA of CECp

Source	DF	Sum of Squares	F ratio	Prob > F	
Incubation Temp.	5	20713061	61.37	<.0001	*
Biomass type	1	11934931	176.80	<.0001	*
Incubation Temp. * Biomass type	5	833310	2.47	0.0346	*
Charring Temp.	1	5239188	77.61	<.0001	*
Incubation Temp.*Charring Temp.	5	6498700	19.25	<.0001	*
Biomass types*Charring Temp.	1	137499	2.04	0.1554	ns
Incubation Temp.*Biomass type*Charring Temp.	5	50034	0.15	0.9803	ns
Error	168	11340991			