Physico-Chemical Characteristics of Carbonized Biomass Prepared by Different Methods

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Abstract

Twelve black carbon samples prepared from various source materials by fast pyrolysis, slow pyrolysis, and hydrothermal conversion methods and three samples isolated from coal or wood fly ashes were characterized for their cation and anion exchange capacities, pH, moisture holding capacity, specific surface, crystallinity, and microscopic morphologies. A wide range in properties was observed, and were largely correlated with method of preparation rather than source material. These results indicate that careful consideration needs to be given to the specific properties of each black carbon before using it as a soil amendment. In general, black carbon produced by slow pyrolysis and hydrothermal conversion was suitable for soil amendment. For black carbon produced by most fast pyrolysis methods, additional processing to increase cation exchange capacity and lower pH is recommended before application to soil.

Materials and Methods

Biochar	Process	Biomass	Source
OKEB	Slow	Oak	Eprida
PBEB	Slow	Pine Bark	Eprida
PCEB	Slow	Pine Wood	Eprida
PCNS	Slow	Pine Wood	Eprida
HYT	Hydrothermal	Glucose	Max Planck Institute
HW	Fast	Hardwood (Oak)	NREL
WS	Fast	Wheat Straw	NREL
CSA	Fast	Corn Stover	NREL
CSB	Fast	Corn Stover	NREL
PNNL-M	Fast	Maple Wood	PNNL
PNNL-P	Fast	Pine Wood	PNNL
CCOB	Flash	Corn Cob	Univ. of Hawaii
POPL	Combustion	Hybrid Poplar Wood	Boise Cascade

Analysis	Method
pH	200 mg in 1.25 mL H_2O or 2 M KCl, 1h equilibration
CEC	800 mg, saturation w/1 M NH_4OAc (pH 7), KCl exchange, 1 week equilibration
AEC	Cl- saturation, SO4 exchange
Boehm Titration	200 mg, saturation w/ 10 mL 0.05 M $NaHCO_3$, Na_2CO_3, NaOH, or HCl for 24 h, backtitrate
Specific Surface	BET N_2 adsorption
Moisture Capacity	200 mg, gravimetric H_2O retention on filter membrane
XRD	cavity powder mount, 5-70 °2θ, Cu-Kα
SEM	Field-emision SEM, 2-20 keV

Results

Chemical Properties

Sample	pH: H_2O	pH: 2M KCl	CEC	AEC	Boehm Titrations: $NaHCO_3$	Boehm Titrations: Na_2CO_3	Boehm Titrations: NaOH	Boehm Titrations: HCl
			mmol$_c$ kg^{-1}					
OKEB	6.3	5.4	360	0.041	140	580	1630	300
PBEB	5.2	4.0	520	0.037	260	870	1950	75
PCEB	5.8	4.5	240	0.047	71	400	1140	24
PCN	5.1	4.4	210	0.034	53	220	1050	-20
HYT	--	--	460	--	--	--	--	--
HW	9.7	9.5	86	0.05	-70	69	32	420
WS	12.0	11.4	120	0.044	-510	-320	-140	1060
CSA	10.0	9.5	330	0.035	-560	57	340	1280
CSB	11.8	10.3	184	0.044	-820	-400	-250	1760
PNNL-M	--	--	--	--	320	420	1040	470
PNNL-P	--	--	--	--	76	300	1290	52
CCOB	--	--	67	--	--	--	--	--
POPL	--	--	77	--	--	--	--	--

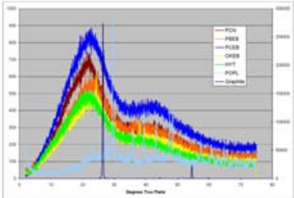
Physical Properties

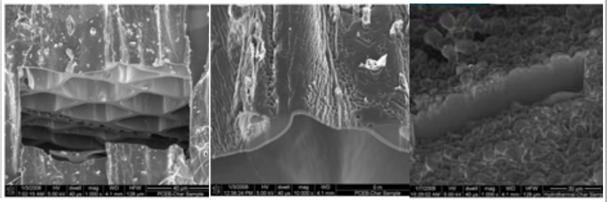
Sample	BET Data: Specific Surface	BET Data: Mean Desorption Pore Size	H_2O Holding Capacity: As received	H_2O Holding Capacity: After MeOH extraction
	m^2 g^{-1}	nm	g g^{-1}	g g^{-1}
OKEB	2.6	20	0.4	--
PBEB	2.0	153	0.4	--
PCEB	1.5	40	0.5	1.2
PCN	1.5	29	0.8	--
HYT	0.6	50	0.3	0.8
HW	34.0	--	0.7	--
WS	7.4	15	0.8	--
CSA	5.0	19	0.9	1.0
CSB	62.0	3	0.8	--
PNNL-M	1.9	36	0.8	1.0
PNNL-P	1.2	26	0.6	1.1
CCOB	6.6	10	1.1	--
POPL	86.0	4	1.2	--

X-ray Diffraction

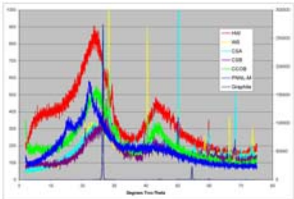
Focused Ion Beam Scanning Electron Microscopy

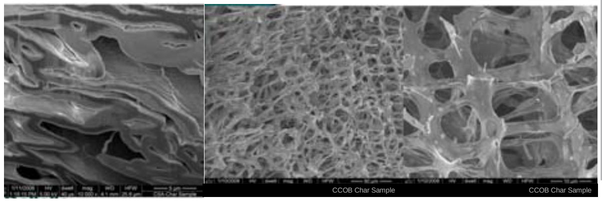
Slow Pyrolysis and Combustion





Fast and Flash Pyrolysis





Discussion

In terms of their chemical properties, the slow pyrolysis and hydrothermal conversion chars are very similar. They typically have slightly acidic pHs, high CECs, and high titratable acidic functional groups. Their XRD patterns show a very low degree of crystallinity, and are similar regardless of their biomass source. However, their microscopic structures can be quite different (e.g., PCEB and HYT FIB-SEM cross sections), and this seems to be the only effect of biomass type on their properties. These chars also seem to have lower H_2O holding capacities (MHC) than the fast pyrolysis chars, probably due to a combination of larger pore sizes and the presence of entrained bio-oils. Treatment with methanol increases their MHC significantly.

The fast pyrolysis and flash pyrolysis chars, on the other hand present a more heterogeneous group, probably due to the wide variety of fast pyrolysis conditions encountered in the separate processes. They typically have highly alkaline pHs, relatively low to moderate CECs,and high titratable basic functional groups. Their specific surfaces vary significantly and pore sizes tend to be smaller than for the slow pyrolysis chars. Their MHCs are larger than for the slow pyrolysis chars, and show little change with methanol extraction, suggesting lower quantities of entrained bio-oil. As with the slow pyrolysis chars, however, their microscopic structures reflect the source biomass.

The combustion char is similar in some respects to the fast-pyrolysis chars, in that it has a high specific surface, small pore size, and high MHC. It differs from all the pyrolysis chars, however, in having a relatively low C content, as seen in the XRD pattern where entrained mineral phases are prominent and the amorphous C peaks are relatively minor features.

From the standpoint of suitability as soil amendments, the slow pyrolysis chars generally seem well-suited due to their high CECs and moderate pHs. Relatively poor moisture retention may be an issue, however. Post-pyrolysis treatment of the fast-pyrolysis chars may be needed, except for acidic soils where liming is desired.

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