



Oxidation resistance of biochars as a function of feedstock and pyrolysis condition



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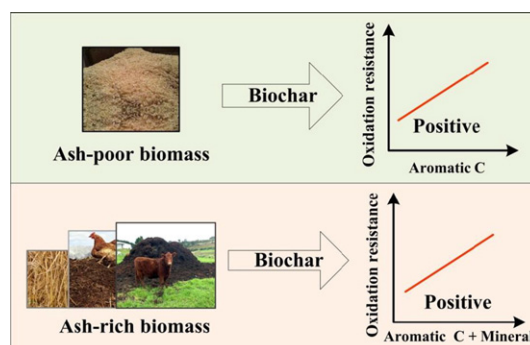
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HIGHLIGHTS

- Oxidation resistance of biochar was studied using H₂O₂ with varying concentrations.
- Hydrochar showed higher oxidation resistance than low temperature pyrochar.
- Impact of temperature upon oxidation resistance of pyrochar depended on feedstock.
- Oxidation resistance of ash-poor biochar was mainly regulated by aromaticity.
- Oxidation resistance of ash-rich biochar was also affected by mineral encapsulation.

GRAPHICAL ABSTRACT



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ABSTRACT

Assessing biochar's ability to resist oxidation is fundamental to understanding its potential to sequester carbon. Chemical oxidation exhibits good performance in estimating the oxidation resistance of biochar. Herein, oxidation resistance of 14 types of biochars produced from four feedstocks at different pyrolysis conditions (hydrothermal versus thermal carbonization) was investigated via hydrogen peroxide oxidation with varying concentrations. The oxidation resistance of organic carbon (C) of hydrochars was relatively higher than that of 250 °C pyrochars (P250) but was comparable to that of 450 °C pyrochars (P450). Both hydrochars and P450 from ash-rich feedstocks contained at least three different C pools (5.9–18.3% labile, 43.2–56.5% semi-labile and 26.9–45.9% stable C). Part (<33%) of aromatic C within 600 °C pyrochars (P600) was easily oxidizable, which consisted of amorphous C. The influence of pyrolysis temperature upon oxidation resistance of biochars depended on the feedstock. For ash-rich feedstock (rice straw, swine manure and poultry litter), the oxidation resistance of biochars was determined by both aromaticity and mineral components, and mineral protection was regulated by pyrolysis conditions. The amorphous silicon within hydrochars and P450 could interact with C, preventing C from being oxidized, to some extent. Nevertheless, this type of protection did not occur for P250 and P600.

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1. Introduction

There has been growing interest in the use of biomass waste to produce biochar because of its wide range of applications in carbon (C) sequestration, soil quality improvement, water treatment and environmental remediation (Lehmann et al., 2006; Kizito et al., 2015; Naisse et al., 2015). Extensive research has shown that biochar application can reduce greenhouse gas emissions and increase the stable C content in soils (Keith et al., 2011; Singh et al., 2012). The organic C within biochar is generally treated as an inert C pool, with mean residence times (MRTs) of several centuries to millennia (Singh et al., 2012; Wang et al., 2016). The existence of old, biochar-abundant Terra Preta in the Amazon (Glaser et al., 2001) and similar biochar-rich soils elsewhere in the world (Downie et al., 2011) further provides examples of the long-term C sequestration potential of biochar in soils. However, MRTs of decadal to century time scales have also been observed for laboratory-produced and natural biochar in soils (Ascough et al., 2008; Cheng et al., 2008; Hilscher and Knicker, 2011).

The inconsistency in the reported C sequestration potential of biochar in soils may be due to the different processing conditions of the biochar production under investigation (Han et al., 2016a; Singh et al., 2012; Crombie et al., 2013). For example, Singh et al. (2012) investigated the stability of 11 biochars made from five biomass feedstocks (*Eucalyptus saligna* wood and leaves, papermill sludge, poultry litter, cow manure) at 400 and 550 °C, and found that C in manure-based biochars mineralized faster than that in plant-based biochars, and C in 400 °C biochars mineralized faster than that in corresponding 550 °C biochars. Biochar contains several types of organic structures, including water-soluble organics, high molecular weight aliphatics and insoluble aromatic structures (Mcbeath and Smernik, 2009; Keiluweit et al., 2010). In general, soluble and low molecular weight organics are mineralized faster than aliphatics and condensed aromatics (Kuzyakov et al., 2009). The proportion of these different organic components and the degree of condensation of aromatic C within biochars varied depending on the feedstock sources (e.g., wood, grass, and manure) with pyrolysis conditions (e.g., heating treatment temperatures (HTTs), hydrothermal or thermal carbonization) (Sun et al., 2011; Crombie et al., 2013; Domene et al., 2015). Consequently, the resultant biochars may be oxidized at different rates to different degrees, and their susceptibility to oxidative attack possibly results from different mechanisms. However, the impact of pyrolysis condition and feedstock source upon the oxidation resistance of biochar is still relatively poorly understood. Especially for the biochar produced by hydrothermal carbonization (HTC) process (referred to as hydrochar), its structure was found to differ considerably

from that of pyrochar produced by dry pyrolysis (Libra et al., 2011; Titirici et al., 2012). Recently, Sun et al. (2011) and Han et al. (2016b) identified that hydrochar could sorb a wider spectrum of both polar and non-polar organic contaminants in comparison to pyrochars, suggesting a high potential of hydrochar as a sorbent for agricultural and environmental applications. Unfortunately, the benefits of hydrochar would be affected in extent and duration if it could be rapidly oxidized in the environment (Lehmann and Joseph, 2009). Very few studies have investigated the oxidation resistance of hydrochar (Kammann et al., 2012; Malghani et al., 2013; Schimmelpfennig et al., 2014; Malghani et al., 2015; Schulze et al., 2016). Moreover, the results of these available studies were somewhat inconsistent. For example, by laboratory incubation study of 200 °C hydrochar and 550–600 °C pyrochar produced from *Miscanthus × giganteus*, Schimmelpfennig et al. (2014) found that the materials would be degraded in the order of feedstock > hydrochar > pyrochar. Kammann et al. (2012) have reported that CO₂ emission from oxidation was significantly larger in the hydrochar-soil mixtures than in the control. By contrast, Malghani et al. (2015) observed that the oxidation rates for roughly two thirds of hydrochars were very low. These unknowns or debates on the oxidation resistance of biochar may hinder the successful design of biochar systems to sequester C.

To date, various tests have been employed to assess the ability of biochars to resist oxidation of biochars, ranging from long-term soil incubations (Singh et al., 2012; Kuzyakov et al., 2014) to simulate realistic environmental conditions to quicker tests such as hydrogen pyrolysis (Meredith et al., 2012; McBeath et al., 2015) and oxidation by chemical agents (e.g., H₂O₂, H₂SO₄ and HNO₃) (Xue et al., 2012; Mašek et al., 2013) or chemical oxygen demand (COD) and biochemical oxygen demand (BOD) (Cao et al., 2013). Mia et al. (2017) reviewed several accelerated methods of biochar oxidation, and observed the similar evolution of C structure of biochar after natural oxidation and artificial chemical oxidation, showing the potential of chemical oxidation to reveal the oxidation-resistance of biochar in natural soils. Among various chemical oxidation agents, Cross and Sohi (2013) demonstrated that H₂O₂ oxidation allows the identification of C forms of varying stability in biochar and screen its susceptibility to oxidative attack.

The main objective of this study was therefore to examine the impact of pyrolysis conditions (hydrothermal or thermal carbonization) and feedstocks on the oxidation resistance of C within biochars by using H₂O₂ oxidation and to uncover the potential mechanisms responsible for their oxidation resistance. To achieve our goals, ash-poor (pine wood) and ash-rich feedstocks (rice straw, swine solids and poultry litter) were considered. Moreover, in order to more precisely distinguish

Table 1
Bulk and surface elemental compositions of original biochars.

Samples	Bulk elemental composition (elemental analysis)							Surface elemental composition (XPS)						
	C (%)	H (%)	N (%)	O (%)	H/C	(O + N) /C	Ash (%)	C (%)	O (%)	N (%)	Si (%)	P (%)	Ca (%)	(O + N) /C
PRS250	53.20	3.85	1.12	24.18	0.87	0.36	17.64	65.97	26.37	2.09	5.58	UL ^a	UL	0.64
PRS450	57.03	2.59	1.18	15.57	0.54	0.22	23.63	67.68	23.42	2.07	6.83	UL	UL	0.29
PRS600	60.36	1.71	1.06	8.94	0.34	0.13	27.93	63.81	22.80	1.63	11.77	UL	UL	0.29
PPW250	64.70	4.77	0.04	28.60	0.88	0.33	1.90	73.91	25.00	0.79	0.30	UL	UL	0.26
PPW450	73.09	2.79	0.07	20.10	0.46	0.21	3.94	79.82	19.70	0.23	0.24	UL	UL	0.19
PPW600	81.44	2.33	0.05	11.73	0.34	0.11	4.45	84.03	14.73	0.69	0.55	UL	UL	0.14
HSS250	54.02	5.69	2.67	12.51	1.26	0.22	25.11	79.08	17.04	3.11	0.78	0.56	0.33	0.20
PSS250	50.92	5.55	3.30	20.22	1.31	0.35	20.01	77.74	19.08	2.69	0.49	0.93	0.88	0.47
PSS450	42.29	2.38	3.25	10.58	0.68	0.25	41.50	64.47	30.74	3.37	1.42	3.29	3.00	0.21
PSS600	44.62	1.37	2.82	7.92	0.37	0.19	43.29	71.66	24.46	3.40	0.48	13.24	10.02	0.40
HPL250	39.13	3.06	3.09	8.95	0.94	0.24	45.77	57.26	30.08	4.77	7.88	4.73	4.69	0.30
PPL250	40.81	3.93	3.40	25.60	1.16	0.54	26.26	54.01	36.36	7.84	1.80	2.29	1.98	0.63
PPL450	37.44	1.79	2.86	10.44	0.57	0.27	47.46	64.56	28.99	3.68	2.77	4.62	4.33	0.39
PPL600	38.80	1.10	2.26	8.36	0.34	0.21	49.49	62.42	31.01	2.27	4.30	10.12	8.93	0.40

^a Below the detection limit. Note: the polarity index ((O + N) / C) of samples in the bulk and at the surface was calculated from the atomic ratio of (O + N) and C. Note that the first capital H or P denotes hydrochar or pyrochar; SS, RS, PL and PW indicate the biochar feedstock (swine solids, rice straw, poultry litter and pine wood); 250, 450 and 600 refer to the heating treatment temperatures.

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