Pyrolysis temperature and heating time affect rice hull biochar properties

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Abstract

Rice hulls are an abundant byproduct of rice production, and thus potentially useful as a feedstock in pyrolysis systems that generate biofuels and biochar. Pyrolysis temperatures affect the relative mass of biofuel and biochar, as well as their properties. The objective of this research was to determine the effect of pyrolysis temperature and exposure duration (time) on rice hull biochar properties, and subsequently, their effect on nursery and greenhouse substrates. Parboiled rice hulls were subjected to temperatures of 200, 400, or 600°C for 1, 2, or 4 h. Mass of rice hulls were reduced 12, 57, and 63% at temperatures of 200, 400, and 600°C, respectively. Elemental composition generally increased proportionally to the decrease in mass, as carbon, hydrogen, and oxygen were burned off and other macro- and micro-nutrients were concentrated in the resultant biochar (with the exception of sulfur). Phosphate and potassium release increased with temperature and time, and was greatest from biochar heated to 600°C. Calcium, magnesium, and micronutrient concentrations were low regardless of pyrolysis treatment.

Keywords: container production, greenhouse, nursery, nutrients, phosphorus, plant nutrition, potassium, potting mix, substrate

INTRODUCTION

Parboiled rice hulls (PBH, Riceland Foods, Inc., Stuttgart, AK) are dry rice husks removed from rice grains with steam or hot water. They are an abundant byproduct of rice production, and thus potentially useful as a feedstock in pyrolysis systems that generate biofuels and biochar. Gasified rice hull biochar, generated from the gasification of PBH, have been shown to be an effective amendment in soilless substrates for increasing water holding capacity and providing an abundant source of phosphorus (P) and potassium (K) (Altland and Locke, 2013a; Locke et al., 2013).

Most biochar research to date has been conducted on very specific biochar materials, making generalizations about biochar properties difficult. Properties of biochar are most affected by the starting feedstock and the pyrolysis regime (Spokas et al., 2012). The feedstock tends to be regional due to the expense of shipping or hauling biomass materials to the pyrolysis unit. Pyrolysis regime is also very specific and often implemented with the goal of extracting a specific range of thermally decomposed oils and gasses from the biomass, while the biochar component is largely considered a waste byproduct for disposal. The collective body of research on biochar applications to soilless substrates may show some consistent trends as reviewed by Altland et al. (2013b); however, a more systematic approach to how feedstock and pyrolysis regime affect the properties of biochar is warranted. The objective of this research was to determine the effect of pyrolysis temperature and exposure duration (time) on rice hull biochar chemical properties and their effect on nursery and greenhouse substrates.

MATERIALS AND METHODS

Biochar materials

Parboiled rice hulls (Riceland Foods, Inc., Stuttgart, AK) were subjected to temperatures of 200, 400, or 600°C for 1, 2, or 4 h in a muffle furnace (Isotemp 550, Thermo Fisher Scientific, Waltham, MA). Mass of the rice hulls and the resultant biochar was measured to determine percent reduction in mass. Rice hull and biochar materials were also analyzed for macronutrient and micronutrient concentrations (P, K, Ca, Mg, S, Cu, Fe, Mn, Mo, and Zn) using optical emission spectroscopy (iCAP 6000 Spectrophotometer, Thermo Fisher Scientific).

Water extractable nutrients

Water soluble nutrients readily available from rice hull biochar were determined by placing a 5 g sample inside a sealed nylon pouch, then submerging the pouch in 200 mL of reverse osmosis (RO) water in a glass jar. Starting 1 day after submersion, and every day thereafter for a total of 10 days, a 40-mL aliquot was removed from each jar for analysis. Immediately after, 40 mL of RO water was added back to each jar so that the volume remained 200 mL throughout the experiment. Samples were filtered through GF/F binder-free borosilicate glass fiber filter paper (Whatman Ltd., Kent, UK) to remove particles greater than 0.7 µm. A subsample of the filtrate was poured into 5 mL autosampler vials, capped, and analyzed with optical emission spectroscopy for concentration of P, K, Ca, Mg, and S. Nutrient concentrations were converted to cumulative mass released.

Column experiment

A standard commercial soilless medium composed of 85:15 sphagnum peat moss: perlite (v:v) (LB2, Sun Gro Hort., Vancouver, Canada) and containing no incorporated fertilizer was selected as the base substrate. The substrate was amended volumetrically with either 10% PBH (v/v) or 10% rice hull biochar generated at 200, 400, or 600°C for 2 h. A non-amended control was also included.

The experiment was conducted on a lab bench with three single-column replications per treatment. The glass columns were 4.5 cm i.d. and 38 cm long, with a volume of about 600 cm^3. They had a flat, false bottom above the stopcock to prevent compression and to control drainage. Each column was packed by adding approximately 200 cm^3 of substrate, gently packing with a wand, and repeating until the column was full and contained approximately 600 cm^3 substrate. On day 1, each column was saturated with 215 mL deionized (DI) water, enough to saturate the entire column of substrate, and let stand for 1 h. Each solution was drained through filter paper (Whatman #2 150 mm Qualitative Circular, Whatman Ltd., Kent, UK) into a 50 mL vial placed in an ice bath. After 30 min, the stopcocks were closed and the solutions were collected, stored in plastic vials, and frozen until analyzed. The following day 100 mL of DI water was added to each column. The stopcocks remained open for 30 min and about 45 mL of leachate was collected from each column. The leachate was filtered and chilled on ice, then frozen. Stopcocks were closed until the process was repeated the following day. This process was repeated daily, excluding weekends, for a total of 11 leaching events. At the time of analysis, samples were thawed and filtered through GF/F binder-free borosilicate glass fiber filter paper. The filtrate was then poured into 5 mL autosampler vials, capped, and analyzed with optical emission spectroscopy.

RESULTS AND DISCUSSION

Biochar materials

There was a significant interaction in percent mass reduction of PBH due to pyrolysis temperature and exposure time ($P=0.0163$) (Table 1). At 200°C, the 4 h exposure time resulted in greater mass reduction than 1 or 2 h. At 400 or 600°C, mass reduction was similar with respect to exposure time, and percent mass reduction was greatest at 600°C. It was hypothesized that mineral nutrient content would increase proportionally as C, H, and O thermally decomposed and volatilized during pyrolysis. Table 2 provides the actual nutrient concentration measured in PBH and biochar samples, along with the predicted nutrient concentration if each element were concentrated as a function of mass reduction. The slope and R^2 value for the relationship between actual and predicted values for each nutrient are shown.

Table 1. Reduction in mass of parboiled rice hulls heated in a muffle furnace at temperatures of 200, 400, or 600°C for 1, 2, or 4 h.

Temp. (°C)	Hour	Mass reduction (%)
200	1	9.7 d[1]
	2	11.0 d
	4	14.0 c
400	1	56.2 b
	2	56.7 b
	4	57.3 b
600	1	62.5 a
	2	62.4 a
	4	63.6 a

[1]Means with different letters are significantly different according to Fisher's protected least significant difference test (α=0.05).

Table 2. Macronutrient concentration of parboiled rice hulls (PBH, 0°C) and biochar generated from pyrolysis of the PBH at 200, 400, or 600°C for 1, 2, or 4 h. For each element, actual concentrations are provided along with predicted concentrations based on percent mass reduction of the biochar.

Temp.	Hours	P		K		Ca		Mg		S	
		Actual	Pred.	Actual	Pred.	Actual	Pred.	Actual	Pred.	Actual	Pred.
0	0	0.06	-	0.22	-	0.06	-	0.04	-	0.03	-
200	1	0.07	0.07	0.23	0.24	0.08	0.07	0.05	0.04	0.03	0.04
	2	0.06	0.07	0.22	0.25	0.08	0.07	0.05	0.04	0.03	0.04
	4	0.07	0.07	0.26	0.26	0.08	0.07	0.05	0.05	0.03	0.04
400	1	0.15	0.14	0.48	0.51	0.16	0.14	0.11	0.09	0.02	0.08
	2	0.13	0.14	0.48	0.51	0.16	0.14	0.11	0.09	0.02	0.08
	4	0.15	0.14	0.54	0.51	0.18	0.14	0.12	0.09	0.02	0.08
600	1	0.16	0.17	0.58	0.59	0.17	0.17	0.11	0.11	0.01	0.09
	2	0.14	0.17	0.54	0.59	0.16	0.17	0.10	0.11	0.01	0.09
	4	0.17	0.17	0.57	0.59	0.20	0.17	0.13	0.11	0.01	0.09
$LSD_{0.05}$[1]		0.02		0.02		0.01		0.01		0.01	
Main effects											
Temp.		0.0001		0.0001		0.0001		0.0001		0.0001	
Time		0.0004		0.0001		0.0001		0.0001		0.6951	
Temp.*time		0.4611		0.0157		0.0001		0.0001		0.0206	
Slope			0.96		1.02		0.83		0.78		-2.53
R^2			0.93		0.98		0.92		0.88		0.96

[1]Fisher's least significant difference (α=0.05).

Among macronutrients, P, K, Ca, and Mg were very close to predicted values, with slopes ranging from 0.78 to 1.02 and R^2 values ranging from 0.88 to 0.98 (Table 2). However, S was inversely correlated to predicted S concentration. This likely occurred because S is typically liberated from organic matter under pyrolysis conditions into a gaseous form of either carbonyl sulfide (COS) or hydrogen sulfide (H_2S) (Basu, 2010).

Phosphorus concentration was affected by pyrolysis temperature and time, but not their interaction (Table 2). It increased with increasing temperature. However, while pyrolysis time did affect P concentration (P=0.0004), there were relatively few and minor differences when averaged across temperature. Actual K, Ca, and Mg were all affected by an interaction between temperature and time. Temperature had the most pronounced effect, with nutrient concentrations nearly doubling from 200 to 400°C and smaller or no differences from 400 to 600°C. Similar to P, time within a temperature had relatively minor effects on nutrient concentration for K, Ca, and Mg relative to temperature. There was also a significant interaction between temperature and time on S concentration. Unlike the other macronutrients, S decreased with increasing temperature likely due to the aforementioned thermal decomposition of S compounds.

Micronutrient (Cu, Fe, Mn, Mo, and Zn) concentrations were similar to predicted values with slopes ranging from 0.72 to 1.10 and R^2 values ranging from 0.70 to 0.96 (data not shown). Pyrolysis temperature and time affected each nutrient, either as main effects or an interaction. Similar to K, Ca, and Mg, each of the micronutrient concentrations increased with increasing temperature and most distinctly from 200 to 400°C, while time had a less, albeit significant, effect.

Water-extractable nutrients

The mass of water-soluble P increased rapidly in the first few days, but leveled off between 4 and 6 days in all treatments (Figure 1). The mass of P released from biochar materials was greater for those heated at 200 and 600°C compared to 0 or 400°C. By day 11, the 0 and 400°C treatments released approximately 2.5 mg P while the 200 and 600°C treatments released approximately 3.4 mg P. Based on the percent P measured in each treatment (Table 2), the 5 g biochar sample released 74, 93, 36, and 43% of the P from PBH heated at 0, 200, 400, and 600°C, respectively. While the percent P of rice hull biochar increased predictably as a function of mass reduction (Table 2), release and availability of water-soluble P did not respond to temperature in any seemingly predictable manner.

Water-soluble K followed a trend similar to P, in that PBH heated to 600 and 200°C resulted in the greatest mass of K released, while those heated at 0 or 400°C released the least mass of K (Figure 1). The mass of K released represented 87, 100, 53, and 86% of the K contained within the PBH heated to 0, 200, 400, and 600°C, respectively, for 2 h. It is unclear why such high percentages of P and K were released from the biochar heated to 200°C compared to other treatments.

The masses of water-soluble Ca, Mg, and S released from the nylon pouches all followed a similar trend (Figure 1). Biochar heated at 0 or 200°C released a greater mass of each nutrient compared to biochar heated at 400 or 600°C. Kloss et al. (2012) observed a similar trend of decreased water soluble Ca, Mg, and S with increasing temperature in straw (*Triticum aestivum*), poplar (*Populus tremula*) wood, and spruce (*Picea abies*) wood biochar.

Column experiment

All PBH and biochar materials resulted in higher concentrations of P and K in column leachates for the first 4 days of the experiment, compared to the non-amended control (Figure 2). By leaching event 8 and 6, concentrations of P and K, respectively, from all amended treatments were similar to non-amended controls. Initially, the highest concentration of P resulted from biochar generated at 600°C, while those heated to 200 or 400°C were similar but greater than the PBH and non-amended controls. Similarly, the initial release of K was highest in substrate amended with biochar heated to 600°C, followed by those heated to 0 or 200°C, then biochar heated to 400°C, and finally the non-amended controls.

Concentrations of Ca, Mg, and S in column leachates were similar for all substrates regardless of amendment. This suggests while there are some measurable concentrations of Ca, Mg, and S from rice hull biochar, they are too low to be detectable against the background levels inherently found in a peatmoss:perlite substrate.

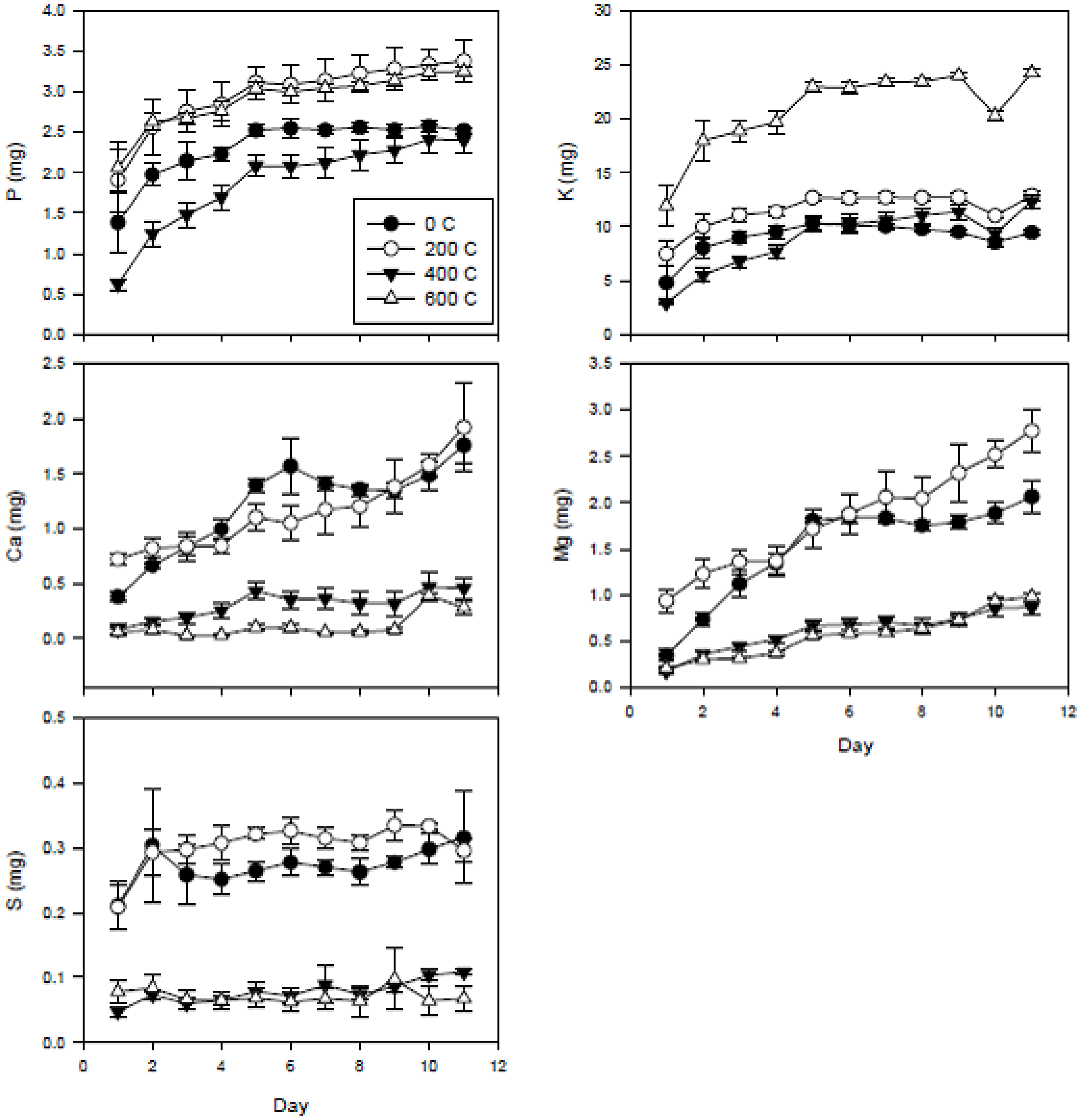

Figure 1. Release of P, K, Ca, Mg, and S from parboiled rice hulls heated at 0, 200, 400, or 600°C for 2 h. Approximately 5 g of each biochar material was sealed in a nylon pouch placed in 200 mL of water. Samples of the water solution were collected daily for 11 days to determine mass of each nutrient released.

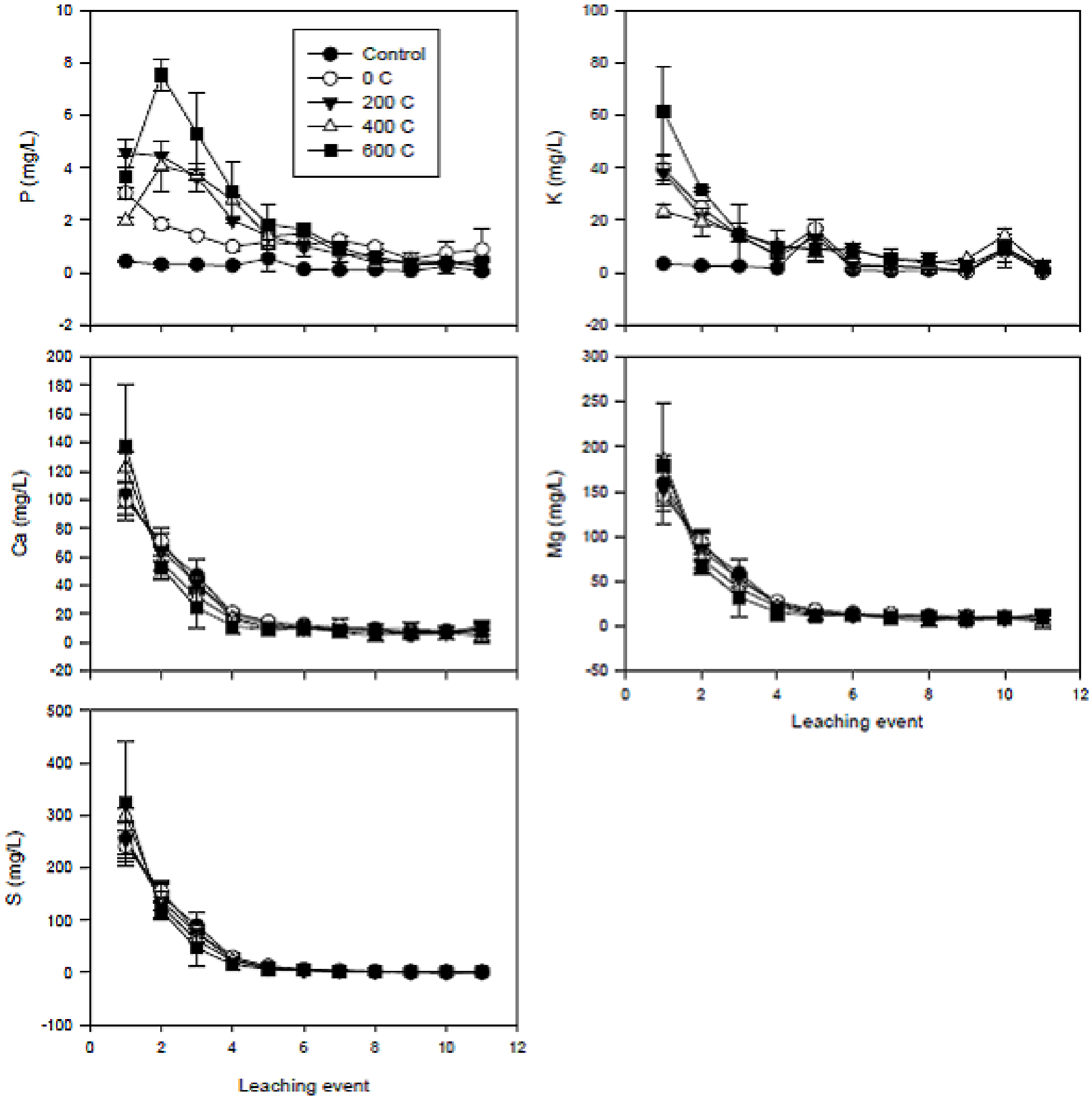

Figure 2. Leachate concentrations of P, K, Ca, Mg, and S from columns containing an 85 sphagnum peatmoss:25 perlite (by vol.) substrate amended 10% (by vol.) with parboiled rice hulls that had been heated at 0, 200, 400 or 600°C. A non-amended control substrate was also included. Leachates were collected daily for 11 leaching days.

CONCLUSIONS

Biochar derived from rice hulls contained a measurable amount of macronutrients and micronutrients. With the exception of S, all nutrients discussed herein increased in concentration proportionally with the reduction in mass caused by thermal decomposition of the C, H, and O. Of the total P and K in rice hull biochar, a high percentage (36 to 100%) was water soluble and thus readily available for plant uptake. Unfortunately, no clear trend in how pyrolysis temperature affects water solubility can be ascertained from these data. Phosphorus and K concentrations in biochar heated to 600°C were high enough to be detectable in leachates of a typical greenhouse substrate. This has also been observed in other rice hull biochars heated to over 815°C (Altland and Locke, 2013b). The objective of this research was to determine the effect of pyrolysis temperature and exposure duration on rice hull biochar chemical properties. Not one of the rice hull or biochar treatments can be labeled as 'ideal'. If biochar usage increases in the future, these data can be used to inform pyrolysis engineers about the properties of biochar materials over a range temperature and exposure duration, and how this will affect nutrient availability when the biochar is used in soilless substrates.

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