Influence of Pyrolysis Temperature and Production Conditions on Switchgrass Biochar for Use as a Soil Amendment

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Introduction

Biochars may form recalcitrant carbon and increase water and nutrient retention in soils; however, the magnitude is contingent upon production conditions and thermo-chemical conversion processes. Discrepancies still exist among field applied biochar, as well as determinations of required char volumes for impacting soil characteristics. A considerable knowledge gap exists for understanding mechanisms and relative nutrient contributions from biochar based on residence time and temperature levels.

Objectives

(i) characterize switchgrass-biochar morphology, (ii) estimate water-holding capacity under increasing ratios of char: soil; and, (iii) determine nutrient profile variation as a function of pyrolysis conversion method, temperature level, and residence time.

Materials and Methods

Biochar Production Techniques

Batch, slow pyrolysis. Switchgrass (400 g) was loaded in a 3.78 L cylindrical metal containers, allowing only evolved volatiles to escape through vents (5, 3 mm diameter openings). Thereafter, containers were placed in a controllable muffle furnace (Neytech Vulcan furnace, Model 3-1750, Bloomfield, CT). As samples heated up, the released volatile organics increased the pressure inside the vessels thus displacing present air. Containers were sealed after retrieval from heated furnace at 400°C under residence times of 1, 2, and 3 h (Sadaka et al., 2014).

Continuous, externally heated auger system. Continuous pyrolysis was tested under three temperatures: 400, 500, and 600°C, at a constant residence time of 8 min. The system was purged with nitrogen (6 L min^{-1}) to sweep out evolved gases and to ensure the reactor was oxygen-free. Switchgrass particle size was the same as that in the batch slow pyrolysis tests, 2.5 cm. Biomass feeding was initiated after auger temperature reached test conditions. Thereafter, system ran for 3 h on steady state conditions.

Biochar characterization

Raw switchgrass and biochar was analyzed for: pH (SB70P, SympHny, VWR, Radnor, PA), elemental constituents (i.e., P, K, Ca, Mg, Na, Fe, Mn, Zn, Cu, N, and NO_3^-), as well as secondary cell wall composition [fiber (Acid and Neutral Detergent) and lignin [Official Methods of Analysis (2000)]. Nitrate was determined via the Potentiometric Method (986.31; Official Methods of Analysis, 1990). Inorganic, plant constituents (i.e. % ash; Official Methods of Analysis, 2000) were determined by muffle furnace combustion at 550°C for 4 h.

SEM Analysis of Biochar. Scanning electron microscopy analyses were performed for the auger-produced biochar at 400, 500, and 600°C, and the batch system produced biochar at 400°C for residence times of 1, 2, and 3 h. Samples were adsorbed to adhesive carbon tape on an aluminum stub by gold sputter coating. Biochar micro morphology images were taken using a scanning electron microscopy system FIB-SEM (Zeiss Auriga, Carl Zeiss NTS) at 250X magnification and 100 µm from the imaging sensor.

‡ $\theta g = Mw/Ms$ (1)

$\theta v = Vw/Vt = Vw/(Vs + Vf) = \theta g\,(Pb/Pw) = \theta g\,Psb$ (2)

$Db = Ms/Vt$ (3)

Materials and Methods

Water-Holding Capacity of Biochar-Amended Soils

Field experiment. On a Huntington silt loam soil (fine-silty, mixed, active, mesic Fluventic Hapludolls) field applications of switchgrass biochar (batch-slow pyrolysis at 400°C for 2 h) occurred late spring of 2012, at the rate of 2 Mt ha^{-1} on switchgrass. In 2013, five cores were collected at 0 to 15 cm depths and composited per plot with three replications. Samples were ground through a 2 mm sieve on a Wiley grinder (Thomas Scientific, Swedesboro, NJ), uniformly mixed, and any carbonaceous material removed. Samples were placed in PVC collars (83 cm^3). Control (no char) samples were taken in a similar manner.

Samples were then dried at 49°C in a batch oven (Wisconsin Oven Corporation, East Troy, WI), and weighed, then later irrigated until saturated flow occurred, and re-weighed. Thereafter, samples were placed in a 1500F1 15 Bar Pressure Plate Extractor (Soilmoisture Equip. Corp., Santa Barbara, CA). Pressure was raised above atmospheric pressure until hydraulic gravity ceased (-33 kPa for 2 to 3 days). The higher pressure inside the chamber forced excess water through microscopic pores in the ceramic plate, simulating field capacity. Gravimetric and volumetric soil water content (GWC and VWC, respectively) at both saturated and field capacity conditions were determined, as well as bulk density (Eqs. 1, 2, & 3‡).

Lab experiments. Additional lab water-holding capacity experiments were conducted with biochars produced via two thermochemical systems (i.e., batch and continuous) and mixed under char: soil ratios. Soil samples were taken as described above and mixed with 5, 10, or 20% biochar by volume. Biochar produced in the auger system at 400°C constituted 'lab experiment 1.' Biochar utilized in 'lab experiment 2' was produced using the slow pyrolysis batch system described earlier at 400°C and 2 h of residence time. Samples were then prepared and analyzed for water-holding capacity as described for the field experiment.

Statistical Analysis. Each dependent variable was run separately and compared within 'experiment' under an ANOVA using Proc MIXED procedures of SAS (SAS, 2007), with biochar rate by volume or control as fixed effects, and soil collar and replication as random effects. Mean separation were performed with Fisher's Least Significant Difference with a Type I error rate of 5%.

Results

Table 1. Chemical composition of raw switchgrass and biochar produced from slow pyrolysis batch (2011) and auger pyrolysis (2012) conversion systems under various residence times (1-3 h) and pyrolysis temperatures.

Feedstock	pH	P	K	Ca	Mg	Na	Fe	Mn	N	NO_3^-	Cellulose	Hemi.	Ash	ADF[iii]	NDF[iv]	Lignin	Lignin : NDF	CEC[v]
		------mg kg^{-1}------									------% DM------							mmol$_c$kg^{-1}
Raw material																		
2011	.	1920	3800	5330	2600	2727	594	188	4.9	4.37	44. 0	31.4	7.8	55.1	86.4	11.1	12.8	47.3
2012	.	620	3620	3520	2123	3614	48	111	2.9	2.28	42.9	34.5	6.7	52.7	87.2	9.8	9.7	36.5
Conversion system																		
400-1[i]	.	2700	5100	7300	3600	510	485	227	1.7	0.02	22.8	3.0	8.8	78.6	81.6	55.8	68.3	64.8
400-2	.	2600	5300	7100	3400	440	415	210	1.4	0.03	21.9	6.0	9.3	77.8	83.8	56.9	55.6	62.9
400-3	.	3000	5600	7900	4000	490	349	244	1.4	0.02	11.5	2.3	9.4	84.6	86.9	73.1	84.1	71.0
400[ii]	6.7	5200	9900	12900	6300	820	1443	473	1.1	0.02	2.9	13.2	14.4	8.6	21.8	5.7	26.3	141.4
500	6.6	6000	10800	15500	7400	930	1577	531	1.0	0.02	4.7	18.5	18.1	10.8	29.3	6.1	20.7	169.6
600	7.4	7400	12400	23500	8100	1200	4017	1371	0.9	0.01	8.1	8.9	26.3	14.8	23.7	6.7	28.1	174.2

[i] Chars produced from batch system in 2012 at 400 °C and varying residence times (1, 2, and 3 h).
[ii] Chars produced from continuous auger system at 400, 500, and 600°C.
[iii] ADF is the Acid Detergent Fiber= Cellulose% + Lignin%
[iv] NDF is the Neutral Detergent Fiber= Cellulose% + Hemicellulose% + Lignin%
[v] CEC is the Cation Exchange Capacity

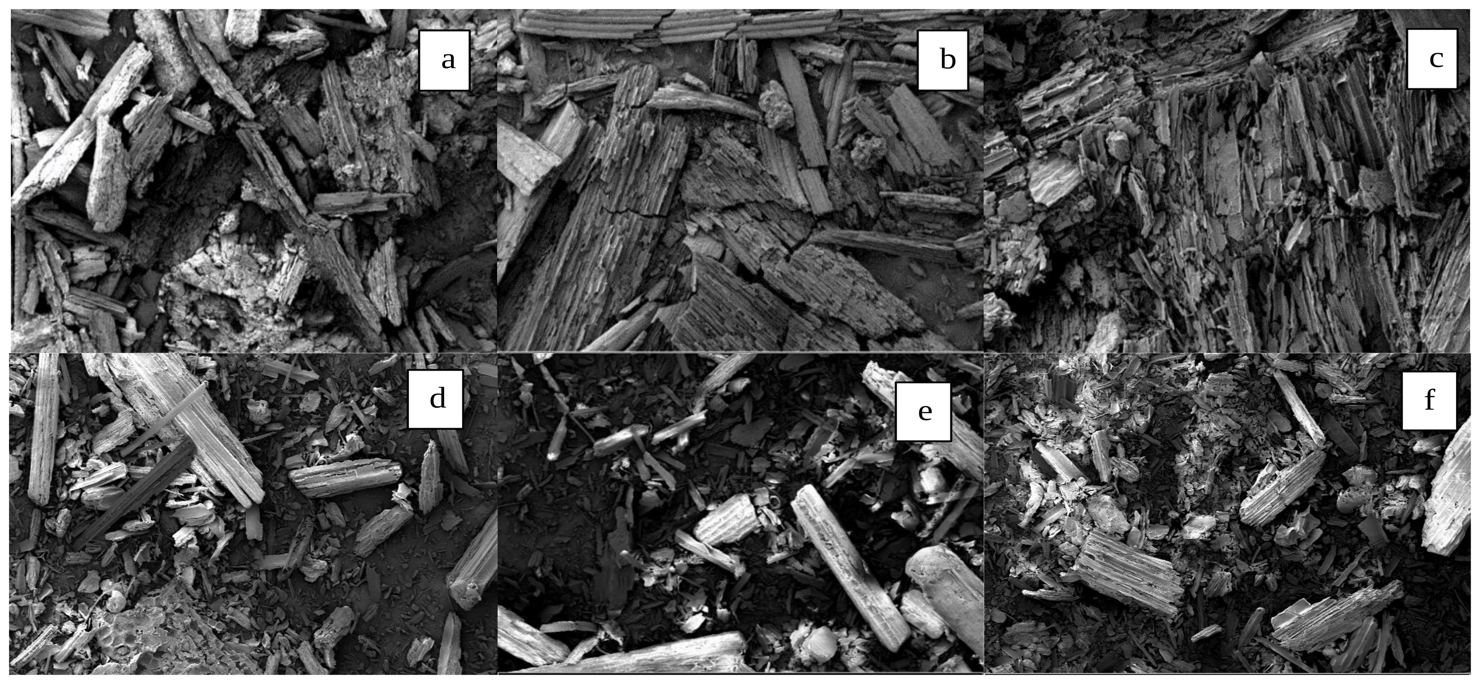

Fig. 1. Scanning electron microscope images of biochar particles taken at 250X magnification and 100 µm. Material was pyrolyzed under externally-heated auger system at various temperatures, *i.e.*, 400 (a), 500 (b), and 600°C (c), respectively; and, under a carbonized batch system at various residence times, *i.e.*, 1 hr (d), 2 hr (e), and 3 hr (f).

Results

Table 2. Switchgrass biochar effects on water-holding capacity and soil characteristics on a Huntington silt loam soil at the East Tennessee Research and Education Center, Knoxville, TN.

Experiment	Bulk Density	VWC (θ_v) Saturated	GWC (θ_g) Saturated	VWC (θ_v) FC[i]	GWC (θ_g) FC[ii]
	g cm^{-3}	cm^3 cm^{-3}	g g^{-1}	cm^3 cm^{-3}	g g^{-1}
In-Field Experiment					
Biochar amended[iii]	1.1±0.1 (a)[v]	0.57± 0.1 (a)	0.51± 0.2(a)	0.24± 0.0(a)	0.22± 0.0 (a)
Control	1.14± 0.02 (a)	0.59± 0.2 (a)	0.51 ± 0.1(a)	0.25± 0.0 (a)	0.22± 0.0(a)
Lab Experiment 1[iv]					
0% biochar	0.94±0.1 (a)	0.76±0.3 (a)	0.81±0.2 (b)	0.52±0.1 (a)	0.55±0.1 (b)
5% biochar	0.82±0.2 (b)	0.61± 0.2(a)	0.74±0.3 (b)	0.35±0.1 (c)	0.43±0.1 (b)
10% biochar	0.67±0.1 (c)	0.67±0.1 (a)	1.01± 0.2 (b)	0.38±0.1 (bc)	0.58± 0.1 (b)
20% biochar	0.41±0.1 (d)	0.67±0.2 (a)	1.64± 0.3 (a)	0.46± 0.0(ab)	1.12± 0.1 (a)
Lab Experiment 2[iii]					
0% biochar	0.95± 0.1 (a)	0.55± 0.1 (a)	0.58± 0.1 (b)	0.19± 0.1 (a)	0.20±0.1 (a)
5% biochar	0.91±0.2 (ab)	0.58± 0.3 (a)	0.64± 0.1 (ab)	0.20± 0.2 (a)	0.22± 0.0 (a)
10% biochar	0.87± 0.1 (b)	0.55±0.1 (a)	0.63± 0.2 (ab)	0.19± 0.0 (a)	0.22± 0.0 (a)
20% biochar	0.79± 0.3 (c)	0.54± 0.1(a)	0.78± 0.1 (a)	0.19± 0.0 (a)	0.24±0.0 (a)

[i] Volumetric water content at field capacity (VWC FC; -33 kPa)
[ii] Gravimetric water content at field capacity (FC; -33 kPa)
[iii] Biochar produced from the batch system, at 400ºC and 2h residence time
[iv] Biochar produced from the auger system at 400ºC
[v] Different letters indicate a significant difference within a given experiment at *P*<0.05, (± standard error).

Conclusions

Switchgrass compositional changes took place under varying pyrolysis residence time (batch system) and temperatures (auger system), which resulted in biochemical and physical biochar transformations (Table 1; Ashworth et al., 2014). Further conclusions are as follows:

- Although both conversion systems decreased bulk density, not all conversion system biochars may increase soils' water-holding capacity. Additions of auger-produced chars in a silt loam soil increased gravity-drained water content, relative to controls (Table 2).
- Neither volumetric nor gravimetric water-holding measurements (saturated or field capacity situations) differed under batch-produced chars. Therefore, under batch systems, water-holding capacities would not likely increase with increasing application rates (Table 2).
- Biochars produced at 600°C had the greatest lignin portion by weight compared with biochars produced at 400ºC. Additionally, biochar produced from batch systems (400ºC-3h) had 73.1% lignin [12 fold increase from the maximum lignin produced from continuous system (Table 1)].
- Thermal decomposition processes affected final biochar nutrient profiles, and subsequently their final use as a soil amendment (Table 1).
- Micrographs suggest that as temperature increases, so does thermal decomposition. Further secondary cell wall decomposition occurred at 600°C in auger systems, resulting in more paracrystalline formations (Fig. 1).
- Based on NO_3^- values, little variation was detected for pyrolysis temperatures, due to volatility of nitrogen in plant tissue. Values of pH were positively affected by pyrolysis temperatures and residence time (Table 1); therefore, more acidic soils would benefit from chars produced at higher temperatures and longer residence times.
- With increased pyrolysis temperature, biochar aromaticity, biochar surface area and CEC increased, resulting in greater cation-nutrient adsorption and retention perhaps due to amphiphilic properties and particle charge.

It cannot be assumed that all chars will increase soil water-holding capacities, nutrient retention, and improve soil tilth based on the rates and chars tested herein. Therefore the observed diversity in biochar characteristics within a given production system per feedstock requires considerations for biochar usage as a soil amendment.

References

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