University of Tennessee, Knoxville
Trace: Tennessee Research and Creative Exchange

Plant Sciences Publications and Other Works

Plant Sciences

11-2014

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

Amanda Joy Ashworth
University of Tennessee - Knoxville, aashwor2@utk.edu

Samy Sadaka
University of Arkansas, Little Rock, ssadaka@uaex.edu

Fred L. Allen
University of Tennessee, Knoxville, allenf@utk.edu

Mahmoud A. Sharara
University of Arkansas, Little Rock

Patrick D. Keyser
University of Tennessee, Knoxville

Follow this and additional works at: http://trace.tennessee.edu/utk_planpubs

Recommended Citation

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

Amanda J. Ashworth,[a*] Sammy S. Sadaka,[b] Fred L. Allen,[a] Mahmoud A. Sharara,[b] and Patrick D. Keyser [c]

Biochars form recalcitrant carbon and increase water and nutrient retention in soils; however, the magnitude is contingent upon production conditions and thermo-chemical conversion processes. Herein we aim at (i) characterizing switchgrass (*Panicum virgatum* L.)-biochar morphology, (ii) estimating water-holding capacity under increasing ratios of char: soil; and, (iii) determining nutrient profile variation as a function of pyrolysis conversion methodologies (*i.e.* continuous, auger pyrolysis system versus batch pyrolysis systems) for terminal use as a soil amendment. Auger system chars produced at 600°C had the greatest lignin portion by weight among the biochars produced from the continuous system. On the other hand, a batch pyrolysis system (400 °C – 3h) yielded biochar with 73.10% lignin (12 fold increases), indicating higher recalcitrance, whereas lower production temperatures (400 °C) yielded greater hemicellulose (*i.e.* greater mineralization promoting substrate). Under both pyrolysis methods, increasing biochar soil application rates resulted in linear decreases in bulk density (g cm^{-3}). Increases in auger-char (400 °C) applications increased soil water-holding capacities; however, application rates of >2 Mt ha^{-1} are required. Pyrolysis batch chars did not influence water-holding abilities (*P*>0.05). Biochar macro and micronutrients increased, as the pyrolysis temperature increased in the auger system from 400 to 600 °C, and the residence time increased in the batch pyrolysis system from 1 to 3 h. Conversely, nitrogen levels tended to decrease under the two previously mentioned conditions. Consequently, not all chars are inherently equal, in that varying operation systems, residence times, and production conditions greatly affect uses as a soil amendment and overall rate of efficacy.

Keywords: Switchgrass; Biochar production; Soil Amendment; Water-holding capacity; Nutrient profiles

*Contact information: a: Department of Plant Sciences, University of Tennessee, 2431 Joe Johnson Dr., 254 Ellington Plant Sciences, Knoxville, TN, USA; b: Department of Biological and Agricultural Engineering, University of Arkansas Division of Agriculture, 2301 S. University Ave. Little Rock, AR 72204, USA; c: Department of Forestry, Wildlife & Fisheries, University of Tennessee, 2431 Joe Johnson Dr., 274 Ellington Plant Sciences, Knoxville, TN 37996, USA; *Corresponding author: aashwor2@utk.edu*

INTRODUCTION

Biochar is a carbon (C)-rich, biomass-derived product generated through "thermal decomposition of organic material under a limited supply of oxygen (O$_2$), at relatively low temperatures (<700 °C)" (Lehmann and Joseph 2009). Pyrogenic carbon amendments have gained interest recently, as they may play a role in recalcitrant C formations, thus reducing positive greenhouse gas forcing, while enhancing plant growth. A multitude of studies have

indicated that not only the pyrolysis method, but also biochar production temperatures greatly influence chemical, physical, and biological properties of chars (Knoepp *et al*. 2005; Lehmann 2007; Chan and Xu 2009). The variable production conditions of biochar result in structural deviations (*i.e*., condensed aromatic C and higher levels of aliphatic C), which in turn impact varying soil-mineralization rates.

Biochar is generally thought to be highly recalcitrant, as well as able to adsorb ions due to its greater surface area and charge density compared to organic matter (Lehmann 2007; Clough *et al*. 2013). However, it should be noted that soil amendment characteristics of the final char are dependent on its production conditions (temperature and heating rate), as well as the nutrient profile of the initial feedstock. High temperatures (>500 °C) yield a more recalcitrant (aromatic) form of carbon when compared with low production temperatures. Similarly, high-lignin feedstocks (such as woody feedstocks) generally result in greater char yields, whereas high hemicellulose and cellulose feedstocks (such as switchgrass) generally yield more volatiles. Greater electrical conductivity (EC) and higher pH are also observed in chars when thermochemically decomposed at greater temperatures (>350 °C) (Keech *et al*. 2005).

Biochar composition and nutrient concentration level is dependent on the feedstock as well as operating conditions (Chan and Xu 2009). Biochar is low in nitrogen (N) relative to more stable C-bonded elements and therefore has a high C: N ratio. This is attributed to heating the feedstock, which causes volatilization of some nutrients, whereas other compounds become concentrated in the remaining biochar. Varying biochar-N concentration ranges have been reported from 1.8 to 56.4 g kg^{-1} and should be considered appropriately, as some nutrients in chars are not labile (Chan and Xu 2009; Clough and Condron 2010). On the other hand, concentration of biochar phosphorous (P) was found to increase with increasing biochar production temperatures, since P is typically bound to the inorganic fraction of the biomass (Knoepp *et al*. 2005; Hossain *et al*. 2011).

Applications of biochar have been shown to enhance soil quality and fertility, thereby building soil C and boosting nutrient retention; thus such application may increase crop yields either directly or indirectly (Mullen *et al*. 2010). Biochar applications may also promote C sequestration, and improve soil quality due to the vital role C plays in nutrient cycling. Studies have demonstrated that biochar enhances phosphorus (P) availability and cation exchange capacity (CEC) (Liang *et al*. 2006) and reduces nitrate leaching (Clough and Condron 2010). Furthermore, most of the labile nutrients in biochar are released slowly, and the material acts as a liming agent due to its high ash-content and alkaline macronutrients (Liang *et al*. 2006; Chan and Xu 2009; Laird *et al*. 2010). Additionally, utilization of biochar promotes a 'closed-loop' system, considering that the feedstock co-product is re-applied the following season.

Biochar application decreases the soil bulk density, which is one of the most important characteristics affecting porosity, aeration, and microbial respiration (Basso *et al*. 2013). Accordingly, it may have the potential to increase soil water-holding capacity, as biochar is absorbent due to a high particle surface charge density, which reacts with soil colloids. Such increases in exchange sites, depending on functional groups, may sustain biomass yields under extended drought periods. Novak *et al*. (2009a) found that additions of switchgrass-biochar (produced at 500 °C) on a sandy Ultisol increased the soil's water retention by 15.9%, relative to controls. Biochar tends to be hydrophobic (Basso *et al*. 2013); however, oxidation occurs after soil incorporation (Cheng *et al*. 2006; Liang *et al*. 2006a).

Chars are not equivalent, and little research has been performed to date on determining optimal production settings and their impact on morphology, as well as on validating or repudiating the agronomic benefits of utilizing switchgrass-based biochar as a soil amendment. Discrepancies still exist in field applied biochar, as well as determinations of required char volumes for actually impacting inherent soil characteristics. A considerable knowledge gap also still exists in terms of understanding the mechanisms and relative nutrient contributions from biochar based on residence time and temperature levels. Therefore, the objectives of this study were to: (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.

EXPERIMENTAL

Materials

The feedstock used in this study was a lowland switchgrass variety (cv. Alamo) grown near Pine Tree, Arkansas in 2011 and Vonore, Tennessee, for chars produced in 2012. Material utilized in 2011 was harvested in August 2011 and November for 2012. Switchgrass was field cured to <25% moisture, then re-dried at 49 ºC in a batch oven (Wisconsin Oven Corporation, East Troy, WI) for 48 to 72 h. Samples were then ground through a 2-mm sieve on a Wiley mill (Thomas Scientific, Swedesboro, NJ).

Biochar Production Techniques

Prepared switchgrass was placed in 3.78-liter cylindrical metal containers. Each container was loaded with 400 g of chopped switchgrass before tightly securing the lid, allowing only the evolved volatiles to escape through small vents (5, 3-mm diameter openings). Batch slow pyrolysis units were not purged prior to experiments. However, they were sufficiently packed with switchgrass as to leave only minimal interstitial voids. Following, the container was placed in a controllable muffle furnace (Neytech Vulcan furnace, Model 3-1750, Bloomfield, CT). As the samples heated up, the released volatile organics increased the pressure inside the vessels, thus displacing residual air. Observations of increased carbon contents after experiments, as described in an earlier study, confirmed that little to no oxidation took place during batch experiments. Containers were sealed immediately, after retrieval from heated furnace, with aluminum foil to prevent char oxidation and to allow for cooling. Biochar used in this study was produced using the same methodology at 400 ºC and under residence times of 1, 2, and 3 h (Sadaka *et al*. 2014).

Another set of slow pyrolysis experiments was carried out on switchgrass using a continuous, externally heated auger system (Sadaka 2013). Continuous pyrolysis was tested under three temperature levels of 400, 500, and 600 °C, at constant residence time of 8 min. The system was purged with nitrogen (6 L min^{-1}) throughout the experiments to sweep out the evolved gases and to ensure that the reactor was oxygen-free. The switchgrass particle size was the same as that in the batch slow pyrolysis tests, 2.5 cm. Biomass feeding was initiated after the auger temperature reached the test conditions. The system ran for 3 h on steady state conditions to produce the required amount of biochar. Subsequently, the tube furnace was turned off, and the feeding auger was stopped. After 4 h, the biochar collector was disconnected and emptied. The conversion mode in both

configurations, *i.e.*, batch, and continuous, is considered slow pyrolysis since heat transfer rates, and consequently biomass heating rate, are low in both cases.

Biochar Characterization

A representative sample was collected, and physical, chemical, and thermo-chemical characteristics of raw and biochar switchgrass were determined. The pH values of raw switchgrass and biochar were determined using a pH electrode (SB70P, SympHony, VWR, Radnor, PA, USA). Dry, ground samples were diluted with deionized water, 10 mL per 1 g of sample, then vigorously stirred and allowed to stand for 1 h before pH measurement. Composite samples from each three replicates were mixed and stored individually. Switchgrass biochar samples as well as one raw switchgrass sample per experimental year were analyzed (Cumberland Valley Analytical Services, Hagerstown, MD) to determine 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 Detergent) and nutrients were determined by Official Methods of Analysis (2000) with modifications (Whatman 934-AH glass micro-fiber filters with 1.5 µm particle retention used in place of fritted glass crucible). Lignin was determined by methods outlined by Goering and Van Soest (1970), with fiber residues from acid detergent fiber (ADF) and neutral detergent fiber (NDF) fractions recovered with 1.5 µm-particle retention (7-cm Whatman Glass Fiber Filter in a California Buchner Funnel). Thereafter fiber residue and filter was transferred to a capped tube and 45 mL of 72% sulfuric acid was added. Tubes were then agitated for 2 h to insure that all fiber material was washed with acid. The contents of the tube after incubation was filtered onto a second filter, rinsed, dried, and weighed. Glass fiber filters and lignin residue were then ashed for 2 h at 550 °C to remove lignin and organic matter and then re-weighed to determine grams of lignin. Nitrate was determined via the Potentiometric Method (986.31; Official Methods of Analysis, 15th edition. 1990). Inorganic, non-combustible plant constituents (*i.e.* % ash; Official Methods of Analysis, 2000) were determined by muffle furnace combustion at 550 °C for 4 h. Percent N was determined via LECO elemental analyzer (ONH836 Oxygen/ Nitrogen/ Hydrogen Elemental Analyze) by combustion (Campbell 1992; LECO CN2000, St. Joseph, MI).

SEM Analysis of Biochar

Scanning electron microscopy analyses were performed for the auger-produced biochar at 400, 500, and 600 °C, as well as 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 samples micro morphology images were observed by using a scanning electron microscopy system FIB-SEM (Zeiss Auriga, Carl Zeiss NTS). Morphology images were taken at 250X magnification and 100 µm from the imaging sensor.

Water-Holding Capacity of Biochar-Amended Soils

Field experiment

The first water-holding capacity experiment in this study was conducted at the East Tennessee Research and Education Center (ETREC; Holston unit) in Knoxville, TN; on a Huntington silt loam soil (fine-silty, mixed, active, mesic Fluventic Hapludolls). This site has an annual temperature and precipitation of 14.5 °C and 142-mm, respectively, and was previously under hay management for three years prior to experimentation. Field

applications of switchgrass biochar (batch-slow pyrolysis at 400 °C for 2 h) occurred late spring of 2012, at the rate of 2 Metric tons per hectare (Mt ha^{-1}) on switchgrass plots under feedstock production. In the spring of 2013, five cores per plot were collected at 0 to 15 cm depths and composited per plot for the biochar and control plots. In total, three replications were taken. Samples were then ground through a 2-mm sieve on a Wiley mill (Thomas Scientific, Swedesboro, NJ). Samples were uniformly mixed, and any identifiable carbonaceous material (*e.g*., roots, residues, *etc*.) was removed. Mixed samples were placed in PVC collars (83 cm^3). Control (no char) samples were taken, composited, and analyzed 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 (Eq. 1) and volumetric (Eq. 2) soil water content (GWC and VWC, respectively) at both saturated and field capacity conditions were determined, as well as bulk density (Eq. 3).

$$\theta_g = M_w/M_s \tag{1}$$

$$\theta_v = V_w/V_t = V_w/(V_s + V_f) = \theta_g\,(P_b/P_w) = \theta_g\,P_{sb} \tag{2}$$

$$D_b = M_s/V_t \tag{3}$$

[In these equations, M_s is the mass of dry soil, M_w is the mass of wet soil, V_t is the bulk volume, and D_b is the bulk density.]

Lab experiments

Additional lab water-holding capacity experiments were conducted with switchgrass biochars produced via two thermochemical systems (*i.e*., batch and continuous) and mixed under various char: soil ratios. Soil samples were taken as described above from the field control plots and mixed with 5, 10, or 20% switchgrass biochar by volume. Biochar produced in the auger system at 400 °C was mixed to the aforementioned volume with composite soil samples and 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.

Water-holding capacity of soils amended with biochar data were analyzed under an ANOVA model using the 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 separations were performed with Fisher's Least Significant Difference (LSD) with a Type I error rate of 5%. Each dependent variable (*i.e*., gravimetric and volumetric water content for both saturated and field capacity conditions, as well as bulk density) was run separately and compared within 'experiment.'

RESULTS AND DISCUSSION

Pyrolysis Temperature and Production Conditions Impacts on Biochar Characteristics

Considering that switchgrass carbonization entails losing a fraction of the energy embedded in volatiles (*e.g*., hemicellulose, and cellulose), these losses were reflected in the biochar cell wall constituents as compared to the raw feedstock (Table 1). Devolatilization of switchgrass cell wall constituents becomes significant under various temperature ranges, *e.g*., hemicellulose (220 to 315 °C); cellulose between 315 to 400 °C; while lignin decomposition takes place mostly above 400 °C (Yang *et al*. 2006). Table 1 shows the decreases in concentration of each of these constituents with the increased severity of char production (temperature and/or residence time). Despite that, char production temperatures exceeded the nominal ranges of cellulose and hemicellulose devolatilization, and residual amounts of both were observed in all biochars. These amounts could be attributed to mass transfer limitations and particle size effects. The observed higher lignin contents at greater pyrolysis temperature suggests the formation of more recalcitrant forms of C compared to biochars produced at lower temperatures (Table 1), which is in agreement with previous studies (Bruun *et al*. 2011). In addition, differences in biochar carbon characterization from different years were likely attributable to phenotypic variation and date of harvest impacts on raw feedstock.

Results presented in Table 1 indicate variation among biochars produced at different pyrolysis temperatures. Biochars produced at 600 °C showed the lowest hemicellulose concentrations. Chars produced at 600 °C had the greatest lignin portion by weight, indicating higher recalcitrant aromatics, whereas lower temperatures yielded a biochar with more 5 and 6 carbon sugars (*i.e*., greater hemicellulose composition), which would likely be readily consumed by microbes upon soil application, thereby promoting mineralization. Conversely, the more labile and prevalent 6 C sugar-containing secondary cell wall constituent (cellulose) tended to not decompose at higher temperatures (*e.g*. 2.8 to 8.1% by dry matter weight from 400 to 600 °C). This was likely attributable to the volatilization of hydrogen and oxygen at greater temperatures, resulting in less dilution of these two elements. Similarly, Demirbaş (2000) reported that the thermal decomposition of glucose, the main component of cellulose, yielded glucosan and water; consequently, moisture removal in carbonized feedstock may not have been complete at the lowest temperature. The moisture remaining in the biochar might be attributable, in part, to decomposition reactions. Accordingly, a portion of the evolved moisture was released via natural convection; however, the remaining portion was not removed from the carbonization reactor (Sadaka *et al*. 2014).

Increases in the calorific value of biochar, compared to the calorific value of the raw switchgrass, may be attributed to the decomposition of hemicellulose and cellulose, followed by greater associations of sequestered lignin (data not shown). Based on feedstock calorific values, lignin possesses the highest energy content per unit mass (23.3 to 27.0 MJ kg^{-1}), followed by cellulose (18.6 MJ kg^{-1}), and lastly hemicellulose (13.6 MJ kg^{-1}) (Sheng and Azevedo 2005). This was substantiated in the correlative increases in energy density with lignin values in this study (23.8 to 42.42 MJ kg^{-1} from 400 to 600 °C in auger batch system, data not shown).

Specifically, biochars produced via carbonization in the batch system at the same heating level but with increasing residence times all resulted in considerable increases in lignin levels (10 fold increases) compared to auger batch produced chars. This could potentially be due to these phenolic compounds concentrating under the carbonization system, whereas greater volatilization may have occurred in the auger system.

As switchgrass biochar pyrolysis temperature increased in batch systems, so did surface area, pH, and cation exchange capacity concurrently (*i.e.*, 141 to 174 $mmol_ckg^{-1}$). Such increases at higher pyrolyzing temperatures have been observed in other studies, where they were attributable to higher inorganic elements and aromatic constituents in pyrolyzed feedstock (Novak *et al*. 2009b; Kloss *et al*. 2012). Further, such increases in biochar aromaticity, biochar surface area and CEC, all likely effectuate C sequestration, which plays a role in climate change mitigation. The high ash content (26.3% by mass) of the 600 °C auger-produced char may be prohibitive as a thermal energy feedstock through further conversion due to the high slagging potential of ash elements in combustion chambers (Boateng *et al*. 2007). Biochar macro (P and K) and micro (Ca Mg, Na, Fe, Mn, Zn, and Cu) nutrients tended to become sequestered in char fractions, as the pyrolysis temperatures increased in the batch system from 400 to 600 °C (Table 1). However, nitrogen levels tended to minimally decrease, as it was assumedly converted into both gaseous and condensable products (*i.e.*, NH_3 and N_2O) at higher pyrolysis temperatures. This suggests that both switchgrass thermal-chemical production systems produce biochars with notably lower labile nitrate-nitrogen for use as a soil amendment.

SEM Analysis of Biochar at Various Pyrolysis Temperature and Production Conditions

Microscopic images revealed that the biochar samples were heterogeneous in form and tended to increase in amorphous structure when exposed to greater residence and higher pyrolyzing temperatures [conversion severity (Fig. 1)]. In addition, the images reveal that micro-pore spaces were present in all chars, but no noticeable differences in micro-porosity were readily distinguished in the SEM images. This suggests that, in general, the microstructure of biochars did not vary greatly between temperatures, 400 to 600 °C, or between production systems.

The micrographs suggest that as temperature was increased, so did thermal decomposition; however, secondary cell wall matrix remained generally identifiable (Fig. 1). The intermediate pyrolysis temperature (*i.e.* 500 °C) did not completely destroy the cellulosic structure of the original switchgrass (guard cells still visible, micrograph not shown); however, it did begin to destroy cell walls and affect morphology. Figures 1a and 1b show a relatively intact cell lumen, whereas Fig. 1c shows a more degraded, paracrystalline secondary cell wall.

In general, smaller particle size was observed, as greater magnification was required to scan microfibrils in 600 °C samples, suggesting thermal recalcitrance. Generally, as residence time was increased, identifiable plant constituents decreased (Fig. 1d and 1f), resulting in a more ash appearance. As mentioned earlier, this increase in ash content was measured in batch system (8.9 to 9.4 % ash) with increases in pyrolysis residence time.

bioresources.com

Table 1. pH and 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	Zn	Cu	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	60	11	4.92	17.37	44. 00	31.39	7.75	55.06	86.44	11.05	12.78	47.23
2012 Conversion system	.	620	3620	3520	2123	3614	48	111	16	2	2.91	2.28	42.94	34.49	6.78	52.72	87.21	9.76	9.76	36.54
400-1[i]	.	2700	5100	7300	3600	510	485	227	66	9	1.69	0.02	22.85	3.0	8.87	78.6	81.6	55.75	68.32	64.75
400-2	.	2600	5300	7100	3400	440	415	210	66	8	1.41	0.03	21.94	6.0	9.31	77.8	83.8	56.86	55.66	62.97
400-3	.	3000	5600	7900	4000	490	349	244	67	9	1.39	0.02	11.5	2.3	9.36	84.6	86.9	73.1	84.12	71.02
400 [ii]	6.7	5200	9900	12900	6300	820	1443	473	118	16	1.13	0.02	2.86	13.2	14.4	8.6	21.8	5.74	26.3	141.40
500	6.6	6000	10800	15500	7400	930	1577	531	116	17	1.05	0.02	4.72	18.5	18.1	10.8	29.3	6.08	20.7	169.57
600	7.4	7400	12400	23500	8100	1200	4017	1371	137	30	0.92	0.01	8.13	8.9	26.3	14.8	23.7	6.67	28.1	174.23

[i] Chars produced from batch system in 2012 at 400 °C and varying residence times (1, 2, and 3 hours).
[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
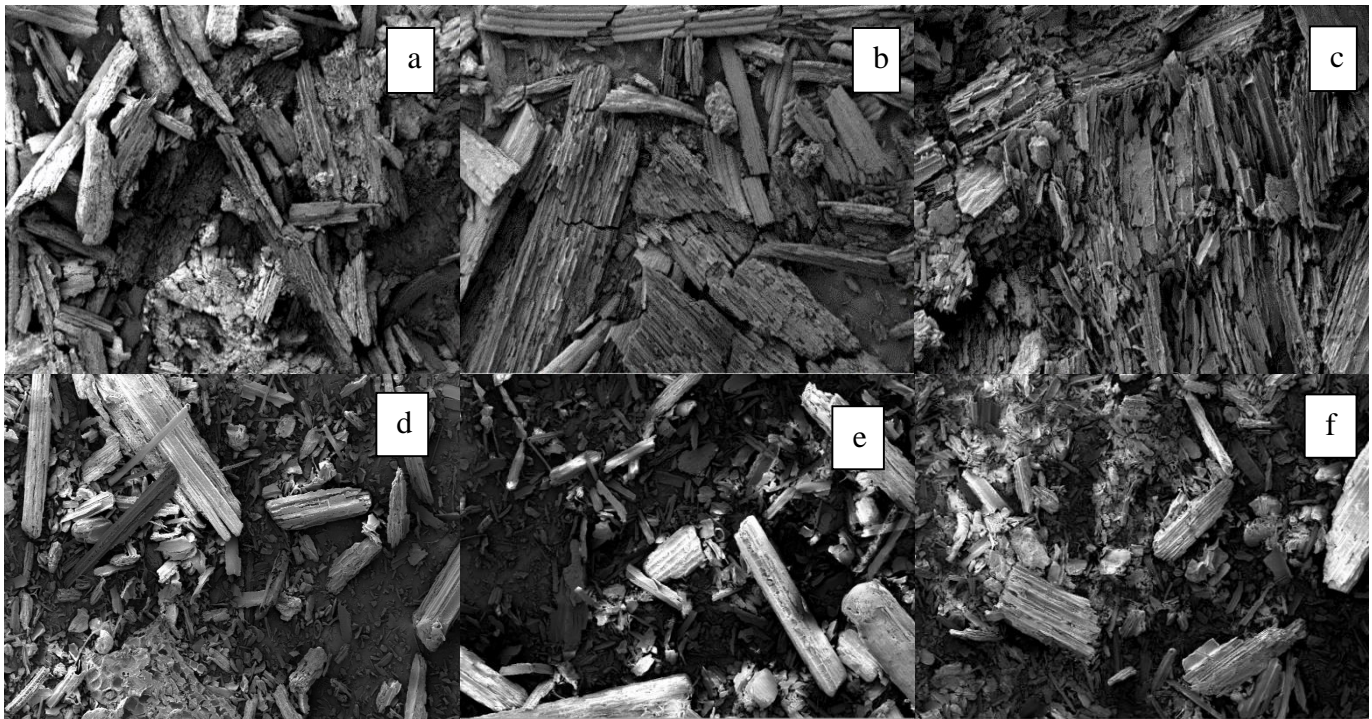
Fig. 1. Scanning electron microscope images of biochar particles taken at 250X magnification and 100 µm. Material was pyrolyzed under externally-heated auger system at various temperatures, *i.e.*, 400 (a), 500 (b), and 600°C (c), respectively; and, under a carbonized batch system at various residence times, *i.e.*, 1h (d), 2 h (e), and 3 h (f).

Water-holding Capacity of Biochar-amended Soils

In-field experiment: Influence of biochar field applications on soil characteristics

Field applications of biochar had no effect on soil characteristics, as bulk density (P=0.19), volumetric water content [saturated; (P=0.15)], gravimetric water content [saturated; (P=1.00)], volumetric water content [field capacity; (P=0.56)], gravimetric water content [field capacity; (P=0.96)] were not different from that of the control [$P \geq 0.05$ (Table 2)]. This indicates that either an application rate greater than 2 Mt ha^{-1}, or more cumulative application years are required to affect water-holding capacity, density, and porosity of our tested silt loam soil.

Lab experiment 1: Water holding capacity by volume under an auger system

Percent biochar by volume (produced by auger system at 400 ℃) impacted porosity and bulk density dynamics in a silt loam soil ($P \leq 0.0001$). Particularly, as biochar volume increased, bulk density decreased, which was expected due to the high pore-size distribution and nano-porosity of biochar (Table 2). These results suggest further indirect effects including greater rooting depth, less greenhouse gas flux, and greater germination, all due to overall lower bulk density and higher porosity (Novak *et al*. 2009a; Lin *et al*. 2012; Basso *et al*. 2013). Based on the first field experiment, a greater application rate than 2 Mt ha^{-1} is required to increase water-holding capacity and decrease bulk density. Levels upward of 10% in 0 to 15 cm layers must be applied in order to obtain such results; however, such field-level applications (*i.e.* $\geq$16 Mt ha^{-1}) are likely unrealistic. Therefore, while biochar applications may enhance soils water-holding capacities *ex situ*, required

rates are not feasible either due to required production restraints or due to producer feasibility. Cumulative rates over years (>2 yrs) may reach targeted concentrations in the soil. However, results suggest that auger-produced biochar applications of 5% or more (*i.e.*, 8.04 Mt ha^{-1}) in the upper 15-cm have the potential to decrease (*P*=0.05) bulk density levels in soils.

Biochar proportions positively influenced GWC distributions for both saturated and field capacity conditions [(*P*=0.05; *P*≤0.0001), respectively]. In general, as biochar contents increased, GWC increased, particularly at greater composition rates (20%; 32.10 Mt ha^{-1}). Greater biochar levels have shown increases in GWC in other experiments as well (Laird *et al*. 2010; Novak *et al*. 2009a; Tryon 1948). However, VWC did not show consistent trends for both saturated and field capacity water contents in our study [(*P*=0.62; *P*≤0.0001), respectively], as this measurement is a function of bulk density, and bulk densities were reduced by greater biochar proportions. Volumetric water content at greater application rates was not different from biochar controls (0%) under saturated conditions (*P*>0.05), whereas variation was observed between the 5 and 20% compositions at field capacity.

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 g cm^{-3}	VWC[i] (θ_v) Saturated cm^3 cm^{-3}	GWC[ii] (θ_g) Saturated g g^{-1}	VWC (θ_v) FC[iii] cm^3 cm^{-3}	GWC (θ_g) FC[iv] g g^{-1}
In-Field Experiment					
Biochar amended[v]	1.10±0.04 (a)[vii]	0.57± 0.01 (a)	0.51± 0.02(a)	0.24± 0.02(a)	0.22± 0.03 (a)
Control	1.14± 0.02 (a)	0.59± 0.02 (a)	0.51 ± 0.01(a)	0.25± 0.02 (a)	0.22± 0.02(a)
Lab Experiment 1[vi]					
0% biochar	0.94±0.05 (a)	0.76±0.03 (a)	0.81±0.16 (b)	0.52±0.06 (a)	0.55±0.06 (b)
5% biochar	0.82±0.02 (b)	0.61± 0.20(a)	0.74±0.27 (b)	0.35±0.06 (c)	0.43±0.08 (b)
10% biochar	0.67±0.08 (c)	0.67±0.14 (a)	1.01± 0.22 (b)	0.38±0.05 (bc)	0.58± 0.13 (b)
20% biochar	0.41±0.01 (d)	0.67±0.14 (a)	1.64± 0.31(a)	0.46± 0.02(ab)	1.12± 0.07 (a)
Lab Experiment 2[vi]					
0% biochar	0.95± 0.04 (a)	0.55± 0.12 (a)	0.58± 0.14 (b)	0.19± 0.09 (a)	0.20±0.10 (a)
5% biochar	0.91±0.02 (ab)	0.58± 0.03 (a)	0.64± 0.04 (ab)	0.20± 0.17 (a)	0.22± 0.01(a)
10% biochar	0.87± 0.04 (b)	0.55±0.060 (a)	0.63± 0.06 (ab)	0.19± 0.02 (a)	0.22± 0.02(a)
20% biochar	0.79± 0.03 (c)	0.54± 0.02(a)	0.78± 0.04 (b)	0.19± 0.01 (a)	0.24±0.01 (a)

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

Lab experiment 2: Water-holding capacity by volume under a batch system

Similar to lab experiment 1, increases in biochar (produced at 400 ºC and 2 h residence time) by volume from soils in the 'in field experiment' positively increased gravimetric water content saturation, albeit not significantly (*P*=0.071) (see Table 2).

bioresources.*com*

Further, none of the other water-holding capacity measurements taken on the batch system were impacted by increases in char presence ($P>0.05$). The only impactful metric from increases in char composition was bulk density ($P=0.002$). This suggests that the slow pyrolysis severity in the batch system may not allow for amphiphilic particle formation compared to the auger system (Table 2).

Considering that neither volumetric nor gravimetric water-holding measurements (saturated or field capacity situations) differed ($P>0.05$) with increasing char: soil ratios compared to lab experiment 1, biochar characteristics were greatly affected by conversion methods (*i.e*., auger *vs.* batch). The fact that the auger biochars were produced under continuous purging of evolved volatiles, compared to only passive, convective flow in batch system, biochar conversion method is responsible for the observed differences. Therefore, results suggest that under batch systems, water-holding capacities would not likely increase with increasing application rates. Lack of attenuating trends could be resultant from both shrinkage and attrition of pyrolyzed material and binding of soil exchange sites. Further, these analyses reinforce the principle that char's composition and final use as a soil amendment is greatly dictated by feedstock conversion systems.

CONCLUSIONS

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

1. Applications of biochar may be a valuable tool for enhancing soil quality and fertility. Further, biochar as a soil amendment can decrease bulk density due to its porous internal structure.

2. Although both conversion systems can decrease bulk density, not all conversion systems may increase soils' water-holding capacity. Additions of auger-produced chars in a silt loam soil can increase gravity-drained water content, relative to controls.

3. 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.

4. Biochars produced at 600 °C had the greatest lignin portion by weight compared with biochar produced at 400 °C. Additionally, biochar produced from the batch system (400 °C-3) showed 73.10% lignin content (12 fold increase from the maximum lignin produced from the continuous system).

5. Thermal decomposition processes affected final biochar nutrient profiles, and subsequently their final use as a soil amendment.

6. Micrographs suggest that as temperature increases, so does thermal decomposition; however, the intermediate pyrolysis temperatures and residence times did not result in complete destruction of raw cellulosic structure. Further, secondary cell wall decomposition occurred at 600 °C in the auger system, resulting in more paracrystalline formations.

7. Based on NO₃- values, little variation was detected for all pyrolysis temperatures, due to the volatility of nitrogen in plant tissue. Values of pH were positively affected by pyrolysis temperatures and residence time; therefore, more acidic soils would favor chars produced at higher temperatures and longer residence times.

8. With increased pyrolysis temperature, biochar aromaticity, biochar surface area and CEC increased, resulting in greater cation-nutrient adsorption and retention due to amphiphilic properties.

9. 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.

ACKNOWLEDGMENTS

REFERENCES CITED

Basso, A. S., Miguez, F. E., Laird, D. A., Horton, R., and Westgate, M. (2013). "Assessing potential of biochar for increasing water-holding capacity of sandy soils," *GCB Bioenergy* 5(2), 132-143. DOI: 10.1111/gcbb.12026

Boateng, A. A., Daugaard, D. E., Goldberg, N. M., and Hicks K. B. (2007). "Bench-scale fluidized-bed pyrolysis of switchgrass for bio-oil production," *Ind. Eng. Chem. Res.* 46 (7), 1891-1897. DOI: 10.1021/ie0614529

Bruun, E. W., Hauggaard-Nielsen, H., Ibrahim, N., Egsgaard, H., Ambus, P., Jensen, P.A., and Dam-Johansen, K. (2011). "Influence of fast pyrolysis temperature on biochar labile fraction and short-term carbon loss in a loamy soil," *Biomass and Bioenergy* 35(3), 1182-1189. DOI: 10.1016/j.biombioe.2010.12.008

Campbell, C. R. (1992). "Determination of total nitrogen in plant tissue by combustion," in: *Plant Analysis Reference Procedures for the Southern U.S. Southern Coop. Ser. Bull,* C. Owen Plank (ed.) Univ. of Georgia, Athens. (http://www.ncagr.gov/agronomi/pdffiles/sera368.pdf)

Chan, K. Y., and Xu, Z. H. (2009). "Nutrient properties and their enhancement," in: *Biochar for Environmental Management: Science and Technology,* J. Lehmann and S. Joseph (eds). Earthscan. London, UK.

Cheng, C., Lehmann, J., Thies, J. Burton, S., and Engelhard, M. (2006). "Oxidation of black carbon by biotic and abiotic processes," *Organic Geochemistry* 37(11), 1477-1488. DOI: 10.1016/j.orggeochem.2006.06.022

Clough, T. J., Condron, L. M., Kammann, C., and Müller, C.A. (2013). "Review of biochar and soil nitrogen dynamics," *Agronomy* (3), 275-293. DOI:10.3390/agronomy3020275.

Clough, T. J., and Condron, L. M. (2010). "Biochar and the nitrogen cycle: Introduction," *J. Environ. Qual*. 39, 1218-1223. DOI:10.2134/jeq2010.020

Demirbaş, A. (2000). "Mechanisms of liquefaction and pyrolysis reactions of biomass," *Energy Conversion and Management* 41, 633-646. DOI: 10.1016/S0196-8904(99)00130-2

Goering, H. K., and Van Soest., P. J. (1970). "Forage fiber analysis," USDA Agricultural Research Service. Handbook number 379. U.S. Dept. of Agriculture. Superintendent of Documents, US Government Printing Office, Washington, D.C. 20402. (http://naldc.nal.usda.gov/download/CAT87209099/PDF)

Hossain, M. K., Strezov, V., Chan, K. Y., Ziolkowski, A., and Nelson, P. F. (2011). "Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar," *Journal of Environmental Management* 92(1), 223-228.

Keech, O., Carcaillet, C., and Nilsson, M. C. (2005). "Adsorption of allelopathic compounds by wood–derived charcoal: The role of wood porosity," *Plant and Soil* 272, 291–300. DOI: 10.1007/s11104-004-5485-5

Kloss, S., Zehetner, F., Dellantonio, A., Hamid, R., Ottner, F., Liedtke, V., Schwanninger, M., Gerzabek, M. H., and Soja, G. (2012). "Characterization of slow pyrolysis biochars: Effects of feedstocks and pyrolysis temperature on biochar properties," *J. Environ. Qual.* 41, 990-1000. DOI: 10.2134/jeq2011.0070.

Knoepp, J. D., DeBano, L. F., and Neary, D.G. (2005). *Soil Chemistry*, RMRS-GTR 42-4, U.S. Department of Agriculture, Forest Service, Rocky Mountain Research Station, Ogden, UT

Laird, D., Fleming, P., Davis, D. D., Horton, R., Wang, B., and Karlen, D. L. (2010). "Impact of biochar amendments on the quality of a typical Midwestern agricultural soil," *Geoderma* 158, 443-449. DOI: 10.1016/j.geoderma.2010.05.013

Lehmann, J. (2007). "Bio-energy in the black," *Front. Ecol. Environ* 5, 381–387. (http://dx.doi.org/10.1890/1540-9295(2007)5[381:BITB]2.0.CO;2)

Lehmann, J. (2006). "Bio-char sequestration in terrestrial ecosystems: A review," *Mitig. Adapt. Strategies Glob. Change* 11, 403-427. DOI: 10.1007/s11027-005-9006-5

Lehmann, J., and Joseph, S. (2009). "Biochar for environmental management: An introduction," in: *Biochar for Environmental Management Science and Technology*, J. Lehmann and S. Joseph (eds), Earthscan, London, UK. (http://www.biochar-international.org/images/Biochar_book_Chapter_1.pdf)

Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B. Skjemstad J. O., Thies, J. F., Luizao, J., Petersen, J., and Neves, E. G. (2006). "Black carbon increases cation exchange capacity in soils," *Soil Sci. Society America Journal* 70, 1719-1730. DOI: 10.2136/sssaj2005.0383

Lin, Y., Munroe, P., Joseph, S., Henderson, R., and Ziolkowski, A. (2012). "Water extractable organic carbon in untreated and chemical treated biochars," *Chemosphere*. 87, 151-157. DOI: 10.1016/j.chemosphere.2011.12.007

Mullen, C. A., Boateng, A. A., Goldberg, N. M., Lima, I. M., Laird, D. A., and Hicks, K. B. (2010). "Bio-oil and biochar production from corn cobs and stover by fast pyrolysis," *Biomass and Bioenergy* 34, 67-74. DOI: 10.1016/j.biombioe.2009.09.012

Novak J. M., Busscher, W. J., Laird, D., Ahmedna, M., Watts, D. W., and Niandou, M. A. S. (2009a). "Impact of biochar amendment on fertility of a southeastern coastal plain soil," *Soil Sci. Society America Journal* 174, 105-112. DOI: 10.1097/SS.0b013e3181981d9a

Novak, J. M., Lima, I., Xing, B., Gaskin, J. W., Steiner, C., Das, K. C., and Schomberg, H. (2009b). "Characterization of designer biochar produced at different temperatures and their effects on a loamy sand." *Annals of Environmental Science* 3(1), 2.

Sadaka, S. S. (2013). "Gasification of raw and torrefied cotton gin wastes in an auger system," *Applied Engineering in Agriculture* 29(3), 405-414.

Sadaka, S., Sharara, M. A., Ashworth, A. J., Keyser, P., Allen, F., and Wright, A. (2014). "Characterization of biochar from switchgrass carbonization," *Energies* 7(2), 548-567. DOI: 10.3390/en7020548

SAS Institute. (2007). SAS/STAT 9.3 User's guide. SAS Inst., Cary, NC.

Sheng, C., and Azevedo, J. (2005). "Estimating the higher heating value of biomass fuels from basic analysis data," *Biomass and Bioenergy* 28, 499-507. DOI: 10.1016/j.biombioe.2004.11.008

Tryon, E. H. (1948). "Effect of charcoal on certain physical, chemical, and biological properties of forest soils," Ecological Monographs - *Ecological Society of America* 18, 81-115. DOI: 10.2307/1948629

Yang, H., Yan, R., Chen, H., Zheng, C., Lee, D. H., and Liang, D.T. (2006). "In-depth investigation of biomass pyrolysis based on three major components: hemicellulose, cellulose and lignin," *Energy Fuels* 20, 388-393. DOI: 10.1021/ef0580117