POULTRY LITTER AND SWITCHGRASS BLENDING FOR BIOCHAR PRODUCTION

K. B. Cantrell, J. H. Martin II, J. M. Novak

ABSTRACT. *Biochars for both soil improvement and bioenergy applications are affected by the choice of both the parent feedstock and the pyrolysis temperature. As such, controlling these two variables may yield an ideal product with engineered properties—a "designer biochar." The potential for a designer biochar comes from its ability to combine the properties of manure-based biochars, which are nutrient-rich and alkaline, with lignocellulosic biochars, which are carbon-rich and neutral to acidic. In this study, two such feedstocks (poultry litter and switchgrass) were blended at different ratios (100%, 75%, 50%, 25%, and 0% litter), pelletized (6 mm diameter), and then subjected to slow pyrolysis at different temperatures (350°C, 500°C, and 700°C) to create test biochars. The biochars were tested for energy characteristics, pellet durability, and proximate composition. The results indicated that the blended biochars had lower pH, electrical conductivity, and ash contents than the pure poultry litter biochars. This suggests that a blended biochar is more appropriate for soil application. The blended biochars also had higher energy content (HHV), and the rate of mass loss during combustion was largely due to the increase of biochar carbon content. However, blending decreased the end temperature of combustion (compared to pure poultry litter biochars), suggesting that the blends contained more labile C. Structurally, the pure poultry litter pellets, regardless of pyrolysis temperature, were more durable, as indicated by less dust emitted, than the pure switchgrass pellets. Even though blended biochar pellets degrade more rapidly during handling and storage, blending manure and plant material for biochar production alleviates some of the other application issues when using pure manure-based biochars for soil improvement or energy conversion applications.*

Keywords. *Bioenergy, Manure management, Pyrolysis, Thermochemical conversion, Thermogravimetric analysis.*

Thermochemical conversion technologies are becoming popular processes for integration with current manure management strategies. They offer numerous advantages, including both the extraction of useful energy from a livestock operation's liability and production of value-added products (Cantrell et al., 2008). Slow pyrolysis of manure allows for the anoxic production of a black carbon material. This solid product when used as a soil amendment is often referred to as biochar (Lehmann and Joseph, 2009). Biochar has been thoroughly reviewed for its use as a soil amendment to improve crop yields and soil quality (Atkinson et al., 2010; Sohi et al., 2009; Spokas et al., 2012). Utilization of biochar also allows on-farm nutrient recycling (Cantrell et al., 2012b). Furthermore, when considered a charcoal, biochar may find utility for heat production (Beglinger and Locke, 1957; Novak et al., 2013).

Biochar behavior in a soil-plant system has been found to vary with both the parent feedstock and the pyrolytic temperature (Spokas et al., 2012). Biochar from a nutrient-rich feedstock, such as poultry litter, may have characteristics similar to a fertilizer (Cantrell et al., 2012a). However, poultry litter biochars at higher application rates are documented to greatly increase soil pH, thus influencing nutrient availability (Novak et al., 2009). These issues may be resolved by blending such feedstocks with a lignocellulosic feedstock, such as switchgrass. Plant-derived biochars have low plant nutrient contents concurrent with high carbon contents. These attributes are due to both the lignocellulosic feedstocks' low initial ash content (leading to a high remaining carbon content) and the composition of the ash, which is often high in components of lower nutrient value, i.e., SiO_2 and CaO (Bourke et al., 2007). Despite the decrease in nutrient content, plant-based biochars have been found to increase other soil characteristics, such as water retention (Novak et al., 2012; Novak et al., 2009). An additional benefit of blending manures with plant feedstocks includes a reduction in the pyrolysis heating requirement (Ro et al., 2010).

Similar to varying biochar soil behaviors, the combustion characteristics of biochars are dependent on the composition of the original biomass and the resulting char. Similar to the approach used in biomass combustion applications, blending of biochar with coal will be necessary if the effects of these differences are to be minimized in bio-

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char combustion applications. Gil et al. (2010) found that biomass-coal blends exhibited more suitable characteristics for industrial combustion systems. The appropriateness of these blends for combustion application can be further enhanced through densification. This is because densified materials (e.g., pelleting or briquetting) have improved handling, transportation, and utilization characteristics (Shaw et al., 2009; Sokhansanj et al., 2005). When compared to the original feedstock structure and characteristics, pelletizing generates a material with a more uniform shape and size along with an increased density and calorific value (per volume) (Kaliyan and Morey, 2009; Shaw et al., 2009). With regard to char applications (soil or energy conversion), pelletized chars have decreased dust concerns and may be easily adopted by transport and delivery systems. Accordingly, the concept of blending and pelletizing feedstocks along with controlling the pyrolysis temperature for char production may yield a customized product ideally suited for soil or energy conversion applications—a "designer biochar."

The designer biochar concept was tested and suggested by both Novak et al. (2009) and Steinbeiss et al. (2009) as a way to manipulate the feedstock and pyrolysis process (e.g., pyrolysis temperature and residence time) with the goal of engineering a biochar with the best possible characteristics matching a given soil type's selected needs. To advance the designer biochar concept, in this study, poultry litter and switchgrass combinations were blended, pelletized, and subsequently pyrolyzed to determine the effects of blend ratio and pyrolysis temperature on the energetic, structural, and compositional properties of the resulting biochar. The aim of this investigation was to compare the biochar pellets to determine if a biochar pellet could be produced with unique properties.

MATERIALS AND METHODS

MATERIALS

Poultry litter (PL; *Gallus domesticus*) was collected from an empty poultry house at a commercial facility in Orangeburg County, South Carolina, that used softwood shavings for bedding. The bedding received excrement from between 8 and 9 flocks (8.5 flocks per year), and the litter had an "as received" moisture content of 23.7 ±2.1 wt%.

Switchgrass (SG; *Panicum virgatum*) was harvested and round-baled from an established stand on a 7 ha field at the Clemson University Pee Dee Research and Education Center in Darlington County, South Carolina. The switchgrass was hammer milled (PPH1000D, Pellet Pro, Davenport, Iowa) to approximately 6 mm (0.25 in.) particle size, and the moisture content of the milled SG was determined to be 6.45 ±0.21 wt%. Moisture contents of the feedstocks were determined at 103°C according to ASABE Standard S358.2 (ASABE Standards, 2008).

Blends of PL and SG were created on a dry weight basis with PL at 0, 25, 50, 75, and 100 wt%. These blends were then brought to 30% total moisture content and pelletized using a pellet mill (PP220, Pellet Pros, Inc., Davenport, Iowa) equipped with a 6 mm (0.25 in.) flat die and roller set. This pellet mill had no accommodations for temperature or pressure control. The feedstocks were fed by hand, and the pellets were formed at atmospheric pressure as the roller compacted the biomass at each die hole to force out pelleted biomass. No oils or other lubricating agents were used in the pellet production process. The pellets were allowed to cure overnight before bagging and storage.

PYROLYSIS SYSTEM AND PROCESSING

Pyrolytic runs were performed at three temperatures: 350°C, 500°C, and 700°C. These temperatures were selected primarily to represent the spectrum of pyrolysis. For each run, 50 to 125 g of raw pelleted feedstock were loaded into a 200 mL ceramic evaporating dish. Initial weights varied due to feedstock density differences. Up to six dishes (one of each blend and one replicate as a check), placed on a stainless steel tray, were loaded into an electric box furnace equipped with a gas-tight retort (model 51662, Lindburg/MPH, Riverside, Mich.). This particular furnace-retort was specially modified with a stochastic state-space regulator (Cantrell and Martin, 2011) to ensure precision regulation of the final charring temperature. Within each temperature treatment, the placement of the sample dishes on the tray was randomized, and the temperature treatment runs were replicated in triplicate.

Samples were pyrolyzed under the following temperature schedule: (1) hold for 60 min at 200°C for equilibration; (2) ramp up to the desired pyrolytic temperature within 60 min (2.5°C min^{-1} for 350°C runs, 5.0°C min^{-1} for 500°C runs, and 8.33°C min^{-1} for 700°C runs); (3) hold for 120 min at the desired temperature for equilibration; and (4) cool at 4.25°C min^{-1} to 100°C. During the initial 200°C hold, the retort was purged using industrial-grade N_2 gas flowing at 15 L min^{-1}. Nitrogen flow for the remaining steps was reduced to 1 L min^{-1} (equivalent to 0.6 and 0.04 retort chamber exchanges per min, respectively) to maintain anoxic conditions. After charring, the samples remained in an inert atmosphere, but they were allowed to cool to less than 60°C for subsequent removal from the retort.

RECOVERY YIELD

Biochar recovery yields were determined for each replication and expressed on a biochar weight basis. Biochar recovery yield (R_{BC}) was a dry basis percentage ratio of biochar mass to feedstock mass (M_B/M_F).

CHEMICAL AND PHYSICAL ANALYSES

Chemical analyses that were carried out for both feedstock and biochar samples included the following: pH, electrical conductivity (EC), proximate analysis, and energy content (higher heating value, HHV). Results were reported for single feedstock subsamples and as average values for triplicate pyrolyzed pelleted biochar samples. The pH and EC were measured in a 1% (w v^{-1}) suspension in deionized water prepared by shaking at 100 rpm for 2 h (Cantrell et al., 2012a). For the proximate analyses, the volatile matter (VM) and ash content were determined using a thermogravimetric analyzer (TGA/DSC1, Mettler Toledo International, Inc., Columbus, Ohio) following the method recommended by Cantrell et al. (2010b). The ash content of samples containing poultry litter was determined at 950°C on the TGA/DSC1 following the method recommended by Cantrell et al. (2010b); the ash content of samples containing only switchgrass was determined using the TGA/DSC1 at 575°C (Cantrell et al., 2010c). The fixed carbon (FC) content was determined following ASTM method D3172 as the sum of VM and ash subtracted from 100% (ASTM, 2006). The HHV was determined using an isoperibol calorimeter (AC500, Leco Corp., St. Joseph, Mich.) following ASTM method D5865 (ASTM, 2006). Single feedstock and composite char subsamples (of the triplicate replications) were also assessed for ultimate analysis (C, H, N, and S; oven-dry ash basis) by Hazen Research, Inc. (Golden, Colo.) following ASTM method D3176 (ASTM, 2006). Oxygen was determined by difference including the ash content (i.e., 100% – sum(CHNS) – ash).

Physical analyses of the biochar pellets included measurements of attrition and the amount of fines in the pellets following ASTM method D1508 (ASTM, 2010). Due to the initial small sample size, 15 to 25 g of pelleted biochar was placed on a 250 μm sieve. The biochar fines were determined from the mass retained after shaking for 5 min at 3600 vibrations per minute. The attrition was determined from the retained mass after an additional shaking of 15 min. These values were determined in duplicate for fresh biochar samples. Individual biochar pellets were also assessed for their hardness ($n = 9$) following ASTM method D3313-05a. The device used for measuring this attribute was an in-house benchtop penetrometer. This unit consisted of the following: (1) a 3 mm diameter stainless steel flat-tipped probe; (2) a force transducer (MDB-10, Transducer Techniques, Temecula, Cal.); (3) an analog-to-digital converter (1608FS, Measurement Computing, Norton, Mass.); (4) a motor controller (Microlynx 4, Schneider Electric, Marlborough, Conn.); and (5) a linear driver (Haydon Switch and Instrument Co., Waterbury, Conn.). Driving the probe, logging the force data, and returning the probe to its starting position were controlled by software (written in Labview 2012, National Instruments, Austin, Tex.). When the penetrometer was initialized, the 3 mm probe contacted the pellet surface. The probe was driven by the motor controller connected to the linear driver with a constant downward velocity of 1 mm s^{-1}. This speed was also used by Colley et al. (2006). The software's data output was imported into a spreadsheet programmed to obtain a force-strain diagram (ordinate = g-force; abscissa = % of pellet diameter deformed) for every pellet. From this diagram, one pair of *x-y* coordinates was selected for treatment comparisons. The *x-y* coordinates associated with permanent deformation of the pellet were considered the breaking point, and this point was selected as the first break in the force-strain diagram.

SEM IMAGING

Scanning electron microscopy (SEM) images were taken of selected biochar pellets to their show macro-scale and micro-scale internal morphology. Imaging was provided by the Iowa State University Microscopy and NanoImaging Facility (www.microscopy.biotech.iastate.edu). SEM images were taken on cross-sections of the pellets (i.e., the fractured surface after breaking the pellet). Specimens were mounted on aluminum stubs using double-stick tape, and they were later sputter coated with a 10 nm layer of palladium:gold (80:20) using a Desk II cold sputter/etch unit (Denton Vacuum, Inc., Moorestown, N.J.). The coated specimens were placed in a JSM 5800 LV scanning electron microscope (Japanese Electron Optical Limited, Peabody, Mass.) at high vacuum and viewed at acceleration voltages of 10 kV. Digital images (.tif format) were captured at a scan rate of 115 s each and stored for later processing and viewing. SEM observations were between magnifications of 100× and 5000× (see bar scales in fig. 3 for comparison).

THERMAL ANALYSIS

Thermal analyses of both feedstock and biochar samples were conducted in triplicate using a thermogravimetric analyzer (TGA/DSC1, Mettler Toledo International, Inc., Columbus, Ohio) calibrated with the melting points of Id, Al, and Au to record mass loss (thermogravimetry, TG) and temperature changes (differential thermal analysis, DTA) simultaneously. The rate of mass loss was determined as the first derivative of TG (DTG). All samples were placed in 70 μL alumina crucibles and oxidized using zero-grade air (21.5% O_2, 78.5% N_2; <1 ppm total hydrocarbons) at a flow rate of 60 mL min^{-1} within a temperature range from 40°C to 950°C at a constant heating rate of 10°C min^{-1}. Immediately prior to each run on the TGA/DSC1, the samples underwent a 15 min isothermal 105°C drying step to allow later analyses on a dry basis.

Characteristic zones and temperatures defined on the TG, DTA, and DTG (rate of mass loss, derivative of TG) curves were based on previous work (Biagini et al., 2006; Bridgeman et al., 2008; Cantrell et al., 2010a; Munir et al., 2009): T_{Start} was the temperature associated with 2.5% of the total weight loss; T_i and DTG_i were, respectively, the temperature and rate of mass loss associated with the maximum rate of mass loss during the active (volatile) combustion zone (i = V) and the char combustion zone (i = C). The final characteristic temperature was T_{End}, which represented the temperature associated with the intersection of lines tangent to the ending baseline and slope of the final DTG curve passing through the maxima.

RESULTS AND DISCUSSION

RECOVERY YIELD

For single-component biochars, the biochar recoveries (fig. 1) were within the range of published literature values (Cantrell et al., 2012a; Novak et al., 2013). Within all blends, R_{BC} decreased with increasing pyrolysis tempera-

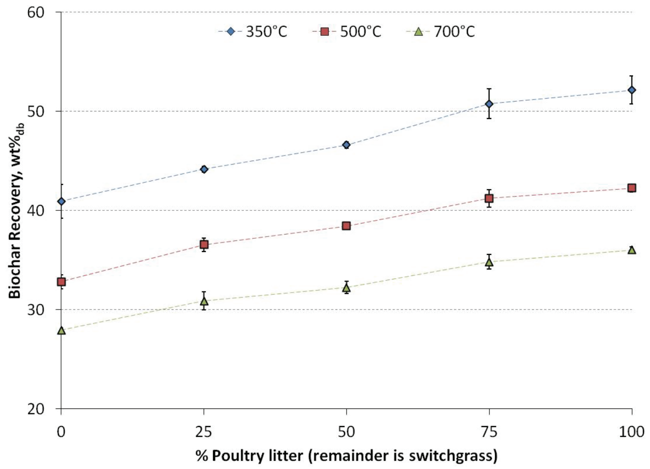


Figure 1. Recovery yields of poultry litter and switchgrass blended biochar pellets (0% poultry litter = 100% switchgrass). Error bars are standard deviations of three pyrolytic runs.

ture (fig. 1). The opposite trend occurred with increasing poultry litter contributions; recovery yields increased with increasing poultry litter composition. This was not unexpected, as the ash content of poultry litter was significantly greater than the ash content of switchgrass (14.0 vs. 0.94 wt%$_{db}$ ash; table 1).

Within each temperature treatment, the percentage of poultry litter in a blend had a strong linear relationship with the recovery yield ($R^2 > 0.967$). This suggested opportunities for predicting blended biochar recoveries from single-component feedstock recoveries. The strong linear relationships also did not give an indication of any interactive effects of blending components on the final biochar recovery. However, when the blends were pyrolyzed at increasing temperatures, the change in biochar recovery across the % poultry litter (i.e., the slopes in fig. 1) began to decline. This suggested that blending had less of an effect on biochar recoveries than an increase in pyrolysis temperature.

CHEMICAL AND PHYSICAL CHARACTERISTICS

Certain characteristics of biochar blending and pyrolysis temperature were observed in the results of the proximate analysis (table 1). More volatile matter (VM) was removed with increasing pyrolysis temperature, resulting in a stable material with large amounts of fixed carbon (FC). This conformed to well known progressions between pyrolysis temperature and both VM and FC (Antal and Grønli, 2003). For instance, the contribution of FC to (FC + VM) for the 50:50 blend was initially 20%; for the 700°C biochar, this ratio increased to more than 80%. Regardless of pyrolysis temperature, ash content increased (along with decreases in FC content) with increases in the blend's poultry litter content. This was not surprising, since ash content was significantly greater for the poultry litter compared to the switchgrass (table 1). Despite less VM in the poultry litter versus the switchgrass feedstocks, VM was greater in the pure poultry litter biochars, in some instances (700°C chars) up to 57% greater. This suggested that the poultry litter feedstock was composed of less labile, easily volatized or carbonizable components.

Pyrolyzing all of the raw feedstocks and blends increased their pH and generated alkaline biochars (table 1). Biochars at 350°C had a heightened pH; however, additional increases in pyrolysis temperature did not appear to have as great an effect on pH. Furthermore, regardless of temperature treatment, the biochar created from any blend with poultry litter did not have significant differences in pH. This was in contrast to the blends of raw feedstock, which varied from 5.5 to 7.6. With alkaline pH values as high as 10.5 for the 700°C biochars, manure-based biochar additions to soils have been reported to have negative consequences on the chemistry of sandy soils with low buffer capacity (Novak et al., 2009). As such, blending the poultry litter with switchgrass did not significantly alter the pH from pure poultry litter pH values; thus, the impact could

Table 1. Effects of blending and pyrolysis temperature on pH, electrical conductivity, and proximate analysis (volatile matter, fixed carbon, and ash) of poultry litter and switchgrass biochar pellets (standard deviations shown in parentheses, r = 3).

Pyrolysis Temperature (°C)	Poultry Litter Content[a] (%)	pH	Electrical Conductivity (µS cm^{-1})	Proximate Analysis Volatile Matter (wt%$_{db}$)	 Fixed Carbon (wt%$_{db}$)	 Ash (wt%$_{db}$)
Raw	0	5.5	101	87.8	11.3	0.9
	25	6.7	448	75.8	17.8	6.4
	50	6.9	810	73.6	18.5	7.9
	75	7.0	1160	70.9	17.1	12.0
	100	7.6	1465	67.8	18.2	14.0
350	0	8.0	81 (6)	34.0 (2.66)	61.1 (2.51)	4.9 (0.24)
	25	9.4	356 (55)	32.9 (3.06)	53.1 (2.50)	14.0 (0.56)
	50	9.5	730 (48)	34.3 (2.61)	48.0 (1.26)	17.7 (1.35)
	75	9.6	1185 (107)	35.1 (3.24)	41.4 (2.00)	23.6 (2.35)
	100	9.6	1595 (122)	35.8 (1.56)	37.7 (1.08)	26.6 (0.52)
500	0	9.9	175 (18)	16.9 (1.51)	76.9 (1.47)	6.2 (0.07)
	25	10.1	459 (28)	15.6 (1.75)	66.1 (2.00)	18.3 (0.74)
	50	10.0	926 (30)	17.1 (0.18)	60.8 (0.78)	22.1 (0.72)
	75	10.0	1223 (50)	18.3 (0.09)	52.4 (1.55)	29.3 (1.64)
	100	10.0	1747 (46)	21.6 (0.50)	45.6 (0.34)	32.8 (0.38)
700	0	9.6	265 (13)	6.6 (0.25)	86.0 (0.32)	7.4 (0.09)
	25	10.5	757 (20)	8.3 (0.31)	71.6 (1.05)	20.2 (1.31)
	50	10.3	1317 (35)	11.3 (0.74)	63.4 (1.00)	25.3 (0.97)
	75	10.4	1813 (78)	13.6 (0.08)	54.7 (0.89)	31.7 (0.92)
	100	10.4	2538 (26)	15.3 (0.08)	36.9 (0.52)	47.8 (0.59)

[a] Poultry litter content of 0 is 100% switchgrass.

be controlled through overall application rates. This would be especially important in low buffer capacity soils, where large pH swings due to biochar applications can lead to changes in available nutrients. Fortunately, Novak et al. (2014) demonstrated a balancing of soil fertility characteristics through biochar applications using 80:20 pine chip: poultry litter blend. With these same biochar concentrations, they were also able to balance soil-available and plant-available phosphorus. The biochar's EC values were characterized to determine if these biochars would potentially create unwanted salt effects in soils, especially at high application rates (Cantrell et al., 2012a; Lehmann and Joseph, 2009). Poultry litter is typically high in EC because of unassimilated elements in the manure. For the feedstocks, blending the high-EC poultry litter (1465 μS cm^{-1}; table 1) with low-EC switchgrass (101 μS cm^{-1}; table 1) mediated potential EC effects. This mediation remained consistent for chars pyrolyzed at the same temperature. Increasing the pyrolysis temperature increased the EC for both the single-component and blend biochars. This was in line with other literature (Cantrell et al., 2012a; Novak et al., 2009).

Following the progressions of blending poultry litter with switchgrass feedstocks with regard to VM and ash, greater amounts of poultry litter in the feedstocks reduced both the C and H contents (table 2). These coincided with diminished O contents. These reductions were likely due to the carbohydrate structure of switchgrass. Additionally, the poultry litter feedstock was rich in N and S, and switchgrass blending was able to mitigate these N and S concentrations. High S content in poultry litter and biochar can be a concern, since S can contribute to fouling issues in downstream processing equipment (Cantrell et al., 2008; Ro et al., 2010). Thus, blending may benefit energy generation processes and reduce wear on equipment when using manure-based charcoal.

By pyrolyzing the blends, the C concentration increased significantly for the biochars (table 2). For reasons well known (Antal and Grønli, 2003), the C content changes occurred concurrently with the H and O losses. Despite the increase in C content of the biochars, the C recovery when pyrolyzing the feedstocks gradually decreased from 60.7 ±3.2 wt% for the 350°C biochars to 44.6 ±3.4 wt% for the 700°C biochars. Within a temperature treatment, C recoveries generally peaked with blending, and pyrolyzing pure switchgrass recovered more carbon than poultry litter. For low concentrations of poultry litter in the blend, continual increases in pyrolysis temperature actually increased the biochar's carbon content. When the poultry litter concentration was greater than 50 wt% in the feedstock, the 700°C pyrolysis temperature yielded biochars with lower C contents. A possible explanation is that the ash components reached an influential concentration at poultry litter concentrations greater than 50% and acted as catalysts in the complex degradation reactions.

These C changes coincided with changes in the other measured elements, N and S (table 2). The N and S changes were not always linear with respect to blending. For S, increasing poultry litter concentrations increased the S content; however, there was a marked decrease in S content between the pure poultry litter biochars and the biochars with 25% switchgrass and 75% poultry litter. Nitrogen was found to increase with poultry litter concentration for the raw feedstocks; however, for the biochars, there was a decrease in N content when comparing the 25% switchgrass and 75% poultry litter biochar to pure poultry litter. For both the 350°C and 700°C temperature treatments, the N content peaked in the 75% poultry litter char. This suggested some interactive effects of blending during pyrolysis on the final composition of the biochar.

Regarding temperature effects, S in the pure poultry litter was somewhat resistant to volatilization, with an average value for feedstock and all biochars of 0.603 ±0.022

Table 2. Blending and pyrolysis temperature effects on elemental composition of poultry litter (PL) and switchgrass blended biochar pellets.

Pyrolysis Temperature (°C)	Poultry Litter Content[a] (%)	Elemental Composition					Atomic Ratios	
		C ($wt\%_{db}$)	H ($wt\%_{db}$)	N ($wt\%_{db}$)	S ($wt\%_{db}$)	O[b] ($wt\%_{db}$)	H/C	O/C
Raw	0	55.03	6.17	0.26	0.044	37.3	1.35	0.51
	25	46.81	5.44	1.21	0.24	39.9	1.39	0.64
	50	45.27	5.34	2.33	0.38	38.8	1.42	0.64
	75	42.85	5.16	3.30	0.61	36.1	1.45	0.63
	100	42.15	5.23	3.67	0.58	34.4	1.49	0.61
350	0	75.87	4.57	0.51	0.034	14.1	0.72	0.14
	25	64.37	3.96	2.25	0.28	15.1	0.74	0.18
	50	60.16	3.48	3.30	0.40	15.0	0.69	0.19
	75	54.20	3.59	4.78	0.74	13.1	0.79	0.18
	100	51.07	3.79	4.45	0.61	13.5	0.89	0.20
500	0	84.78	3.21	0.97	0.060	4.8	0.45	0.04
	25	69.18	2.44	2.15	0.30	7.6	0.42	0.08
	50	66.62	2.38	3.14	0.61	5.5	0.43	0.06
	75	58.43	2.00	3.50	0.91	6.2	0.41	0.08
	100	51.68	1.90	4.25	0.59	8.5	0.44	0.12
700	0	88.49	0.92	0.90	0.12	2.2	0.12	0.02
	25	73.62	0.83	1.37	0.39	3.6	0.14	0.04
	50	64.04	0.64	1.96	0.68	7.4	0.12	0.09
	75	55.18	0.49	2.46	0.85	9.3	0.11	0.13
	100	45.91	0.76	2.16	0.63	2.73	0.20	0.04

[a] Poultry litter content of 0 is 100% switchgrass.

[b] O determined as 100% – sum(CHNS) – ash.

wt%. While this phenomenon was consistent with batch runs performed in similar pyrolysis units (Cantrell et al., 2012a; Lima and Marshall, 2005b), a concentration increase of S in the biochar from the feedstock was seen in a pilot-scale system (Ro et al., 2010). In this study, a similar increase was seen in all blended biochars (table 2).

The total N content in all biochars increased initially with pyrolysis (from the feedstock to 350°C). After this temperature, the poultry litter biochars (pure and blended) exhibited similar or decreased N content (table 2). This phenomenon was also noted for other manure-based biochars (Cantrell et al., 2012a). The initial increases and persistence of N may be related to recalcitrant N occurring in heterocyclic compounds; this was reported by Kazi et al. (2011). Continuous increases in pyrolysis temperature decreased N contents to less than those of feedstocks containing more than 50% poultry litter. These losses may be attributed to breakdown of amide bonds and pyridine rings (Cantrell et al., 2012a; Das et al., 2009).

Atomic ratios, because of dissimilar O and H losses, varied as a function of feedstock and pyrolysis temperature (table 2). Comparing just the raw poultry litter and switchgrass feedstocks, poultry litter had greater O/C ratios, suggesting a greater degree of oxygenated structures. All molar ratios demonstrated a decreasing trend with increasing pyrolysis temperature. This was characteristic of the carbonization process leading to more recalcitrant aromatic structures (Chen et al., 2008; Lehmann and Joseph, 2009; Uchimiya et al., 2010). While most ratios were unique, there was some overlap in the blended biochars pyrolyzed at 500°C.

When the HHV of the char was compared to its respective raw feedstock, pyrolysis increased the HHV for all biochars (fig. 2) except for pure poultry litter at 700°C, which exhibited similar HHV to its feedstock, i.e., 16.2 MJ kg^{-1}_{db} (average). The increases in HHV were largely attributed to the loss of light low-energy-content volatile matter and the formation of energy-dense aromatic ring structures. This was supported by the decreasing H/C ratios (table 2).

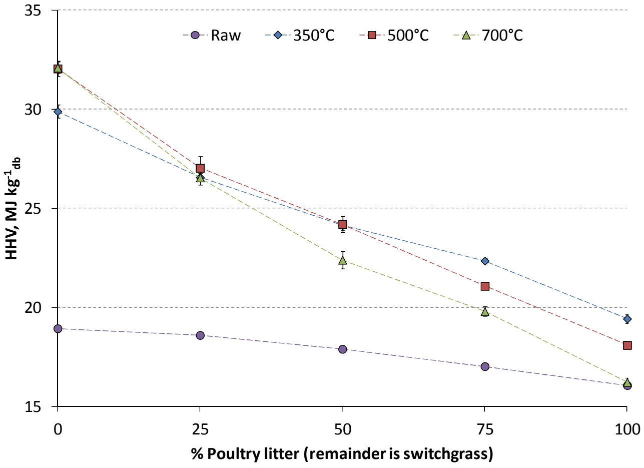


Figure 2. Energy content (HHV) of poultry litter and switchgrass blended feedstocks and biochars (0% poultry litter = 100% switchgrass). Error bars are standard deviations for three samples.

One interesting HHV trend observed with blending was the effect of pyrolysis temperature. The absolute value of the slope of the linear relationship between HHV and blend increased with increases in pyrolysis temperature. For pure switchgrass, low-temperature pyrolysis (350°C), compared to 500°C and 700°C pyrolysis, generated a biochar with lower HHV. As the blend of poultry litter increased beyond 25%, lower-temperature pyrolysis favored higher HHV. The 25% poultry litter blend generated biochars with similar HHV (21.1 ±1.3 MJ kg^{-1}_{db}) regardless of pyrolysis temperature (fig. 2).

PELLET CHARACTERISTICS

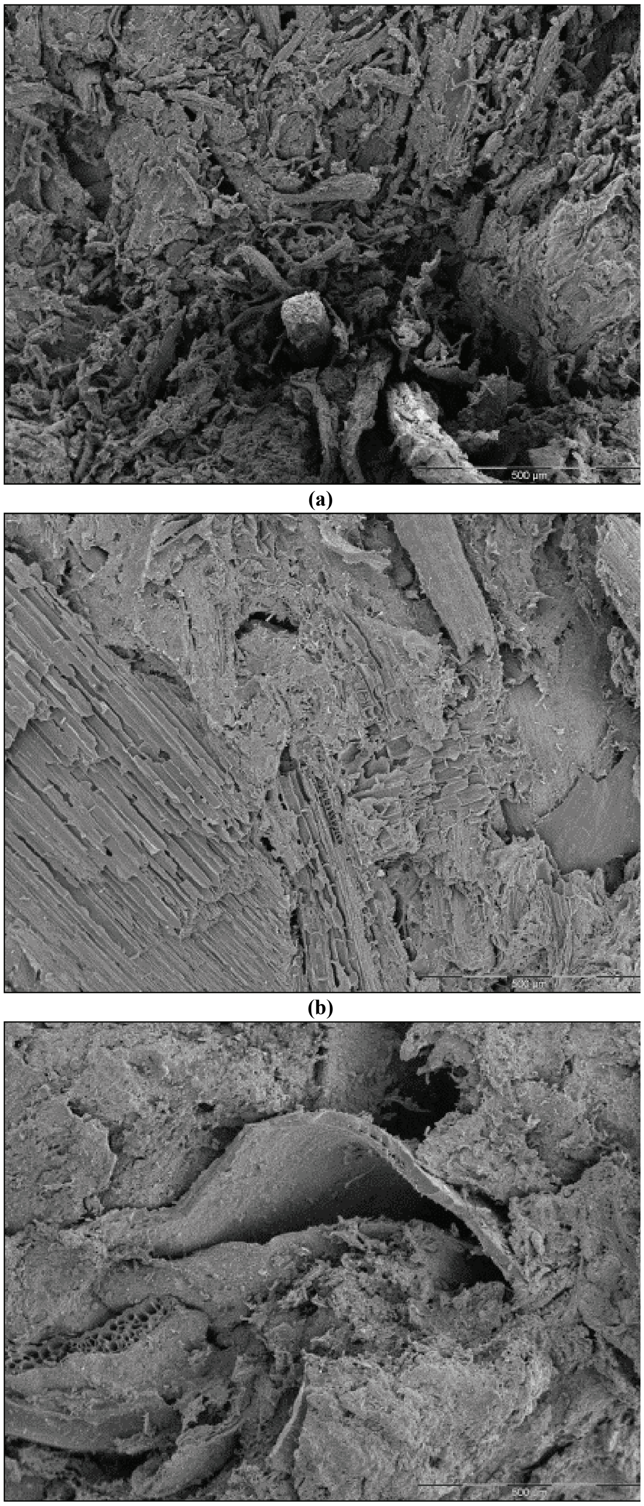
The attrition of pellets was used to evaluate their durability, or abrasive resistance, as well as to understand the biochar pellets' relative loss during transportation and handling. Measuring the fines allowed comparison of the relative dustiness of the material: the greater the attrition and fines values, the greater the pellet degradation and dust. Both attrition and fines values were low to moderate (table 3). The attrition values obtained in this study were moderately less than those reported for granular activated carbon from broiler litter, which ranged from 17.9% to 20.7% (Lima and Marshall, 2005a). Some of the difference may be due to the attrition measurement. Lima and Marshall (2005a) added glass beads to their carbon samples prior to dry agitation; they also determined attrition using a small sample size (3 g) and reduced the size of the pellets to between 0.42 and 1.0 mm. Consequently, attrition was determined for samples greater than 0.425 mm.

Attrition and fines differed significantly across all temperatures for both types of single-component pellets. Across the three temperatures, pure poultry litter pellets were more durable than pure switchgrass pellets (table 3). However, for the pure switchgrass pellets, increasing the pyrolysis temperature increased attrition and fines; thus, greater pyrolysis temperatures produced dustier and less structurally sound switchgrass pellets. When blending the

Table 3. Dependence of biochar pellet attrition and fines (standard deviations shown in parentheses) on poultry litter content and pyrolysis temperature.

Pyrolysis Temp. (°C)	Poultry Litter Content[a] (%)	Attrition (wt%)	Fines (wt%)	Breaking Force Characteristics % Pellet Diameter	 Force (g-force)
350	0	11.3 (3.7)	3.4 (1.1)	16.3	775
	25	11.0 (3.7)	1.2 (0.4)	6.6	450
	50	10.7 (4.1)	2.8 (0.3)	5.7	198
	75	3.1 (1.5)	2.6 (1.9)	4.3	682
	100	2.3 (0.2)	1.2 (0.1)	3.3	513
500	0	13.7 (0.8)	3.0 (0.6)	15.8	510
	25	19.0 (3.1)	1.8 (0.3)	6.3	350
	50	6.1 (0.4)	1.4 (0.3)	5.9	354
	75	4.8 (1.7)	2.6 (0.6)	4.9	638
	100	1.6 (0.4)	0.7 (0.2)	3.1	231
700	0	24.4 (5.8)	12.4 (5.8)	12.3	524
	25	15.8 (2.8)	3.9 (0.5)	8.9	449
	50	6.2 (0.9)	1.9 (1.0)	5.9	413
	75	4.8 (1.3)	2.0 (0.5)	4.3	649
	100	2.7 (1.4)	0.7 (0.1)	2.6	251

[a] Poultry litter content of 0 is 100% switchgrass.



(a)

(b)

(c)

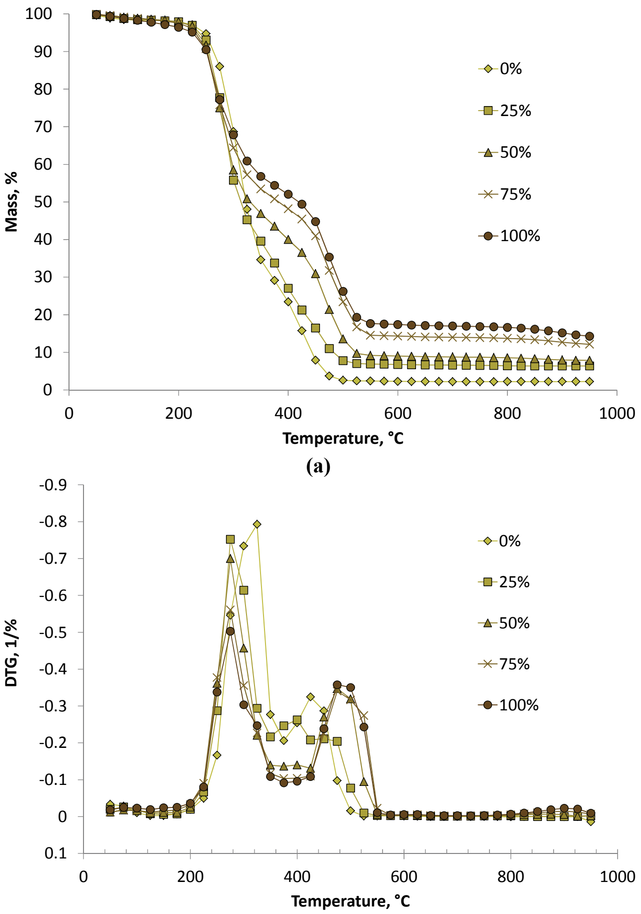
Figure 3. SEM images (100× magnification, bar = 500 µm) along axial view of 350°C biochar pellets for (a) pure switchgrass, (b) 50:50 blended poultry litter and switchgrass, and (c) pure poultry litter.

two components, attrition gradually decreased with each interval increase of poultry litter. Blending the two components altered the structure of the biochar pellets. To observe these changes, SEM images were taken along the axial view of the pellets. SEM images of pure switchgrass pellets clearly showed void spaces (fig. 3a). As the biochar composition shifted to pure poultry litter pellets (figs. 3b and 3c), these void spaces and fissures became less apparent. This may be due to the increased ash content of the poultry litter (table 1) allowing metal bridging and covalence bonding. This would also allow “cementing” of the C components, creating more durable pellets that are less subject to breakage. Kaliyan and Morey (2010) identified solid bridging during pelletizing and briquetting of raw corn stover and switchgrass. While compacting raw feedstocks caused solid bridging, pyrolytic temperature would also impact solid bridging, with increased processing temperature promoting molecular diffusion across individual feedstock particles. Further studies are necessary to relate attrition and fines to ash composition, such as Ca/Si ratios or other components that may influence the attraction forces between particles. Additional studies could also investigate relationships with blending and the pressure forces during the pelletizing process.

While poultry litter additions created more durable pellets that were more likely to maintain their structure during transportation and handling, the hardness of the pellets might influence their usefulness in end applications. For example, the harder a pellet is in animal feed, the lower the animal’s intake of that feed becomes (Ford, 1977); likewise, a harder, denser pellet may incur increased energy for complete combustion because of mass transfer limitations. For strength characteristics, increasing the poultry litter concentration in the biochar pellets caused the characteristic length (% pellet diameter; table 3) to show a downward trend. For pure poultry litter biochar pellets, the initial yield point began to deform at an average 3.0% of the pellet diameter across all temperatures. At a 50:50 blend, this yield almost doubled to 5.8% of the pellet diameter. While adding switchgrass caused an increasing trend in the characteristic length, this action varied for the associated force. At every temperature, the breaking force demonstrated a decreasing trend from the 510 to 775 g-force for the 100% switchgrass biochar pellets. An anomaly was noted for every sample with 75% poultry litter content; at this content, the biochar pellets required a significantly greater breaking force than at 50% poultry litter content (table 3). This may have been due to the increase in lignin and carbohydrates from the switchgrass providing a complex structure for a mixture of bond types (e.g., covalent, polar, hydrogen, ionic) that could include the ash in the poultry litter. Furthermore, it is speculated that the finer ash portion of the poultry litter filled the voids created by the switchgrass and allowed increased solid bridging.

THERMOGRAVIMETRIC ANALYSIS

Thermal degradation assessment of the raw feedstocks demonstrated two combustion macro-steps: (1) an active combustion segment with the release and immediate combustion of volatiles, and (2) a transition into a char combustion step (Cantrell et al., 2010a; Munir et al., 2009; Novak et al., 2013) (fig. 4). Thus, two peaks occurred in the differential thermogravimetric analysis (DTG) curves whose maxima (T_{Vmax} and T_{Cmax}) are identified in table 4. Losses in these regions can be attributed to cellulose decomposi-



(a)

(b)

Figure 4. Characteristic shifts in (a) combustion thermogravimetric (TG) curves and (b) differential thermogravimetric (DTG) curves of poultry litter (PL) and switchgrass (SG) feedstocks with increasing PL content (0% PL = 100% SG).

tion and release of labile aliphatic compounds (Cantrell et al., 2010a). In the char oxidation phase (the second step), the partially carbonized residue from the initial combustion phase and the original fixed carbon showed a slow and continuous weight loss until T_{End} was achieved.

For combustion of the feedstocks, blending poultry litter at increasing concentrations was found to decrease T_{Start} and T_{Vmax}. This coincided with the decrease in VM of the original blend. In addition, the rate of mass loss during the volatile combustion stage (DTG_{Vmax}) decreased along with the absolute mass loss (ML_V). The opposite was observed during the char combustion stage: increases in poultry litter increased characteristic TGA parameters associated with the char combustion stage. The maximum char combustion temperature (T_{Cmax}) increased as well as T_{End}.

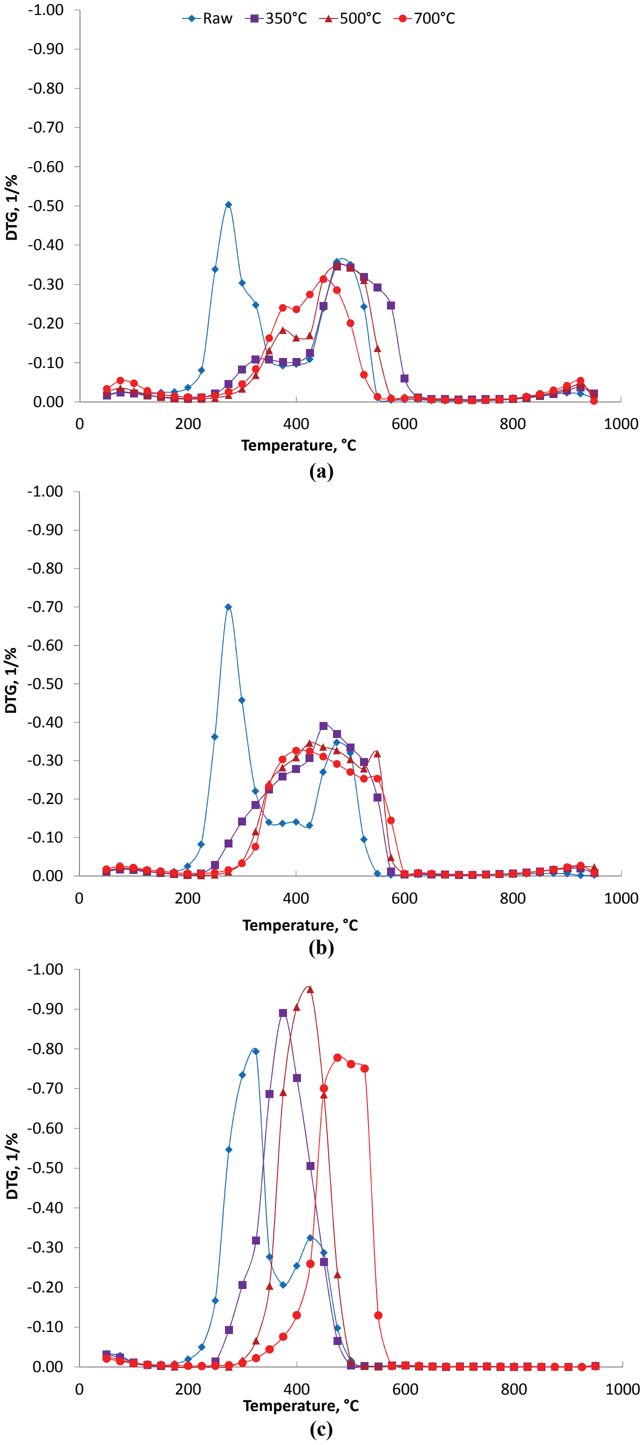
As feedstock blends were pyrolyzed at higher temperatures, the DTG curves slowly shifted from prominent dual-peak curves to single-peak maxima occurring at higher temperatures with a higher T_{End} (fig. 5, and the lack of DTG T_{Vmax} values in table 4). This intense char combustion peak indicated both a higher fixed carbon content (than the feedstock) and a product with a more uniform carbon structure. Pyrolysis also shifted the T_{Start} values. The blending trends varied: for pyrolysis at 350°C, increasing poultry litter concentrations increased T_{Start} (fig. 6). However, additional pyrolysis exhibited a reverse trend, with T_{Start} decreasing as much as 105°C between pure switchgrass and pure poultry litter biochars. For blends predominately containing poultry litter (i.e., greater than 50% PL), there were identifiable volatile combustion zones, particularly for the 350°C biochars. This volatile combustion zone was also identified for the pure poultry litter pellets pyrolyzed at 500°C. These phenomena may be explained by heavier organic compounds (e.g., proteins, fats, oils, etc.) in the VM associated with the poultry litter, compared to the switchgrass, and requiring more energy to volatilize and remove during the pyrolysis process.

A char combustion zone was identifiable for all the examined blends. However, as the poultry litter concentration increased in the biochar, the DTG_{Cmax} values generally de-

Table 4. TGA combustion characteristics of blended poultry litter and switchgrass biochar pellets.

Pyrolysis Temperature (°C)	Poultry Litter Content[a] (%)	T_{Start} (°C)	Volatile Combustion T_{Vmax} (°C)	Volatile Combustion DTG_{Vmax} (%/°C)	Volatile Combustion ML_V ($\%_{db}$)	Char Combustion T_{Cmax} (°C)	Char Combustion DTG_{Cmax} (%/°C)	Char Combustion ML_C ($\%_{db}$)	T_{End} (°C)
Raw	0	240	288	0.975	70.1	422	0.336	27.4	500
	25	232	286	0.803	58.9	396	0.269	32.3	514
	50	230	269	0.763	51.5	472	0.357	37.9	537
	75	224	264	0.685	47.8	482	0.349	32.0	542
	100	211	266	0.674	44.5	487	0.362	31.1	548
350	0	280	267	0.227	5.3	373	0.776	90.3	486
	25	279	-	-	-	406	0.384	83.2	560
	50	281	405	0.319	36.8	473	0.456	39.3	554
	75	289	395	0.169	18.9	473	0.352	52.6	613
	100	290	332	0.111	7.7	478	0.311	49.7	622
500	0	332	-	-	-	430	0.783	91.9	503
	25	320	-	-	-	444	0.460	78.5	531
	50	323	-	-	-	440	0.372	71.5	568
	75	314	-	-	-	463	0.304	63.2	614
	100	311	388	0.185	17.8	491	0.354	39.3	561
700	0	364	-	-	-	481	0.759	92.2	552
	25	337	-	-	-	468	0.416	75.0	593
	50	304	-	-	-	427	0.287	67.4	614
	75	294	-	-	-	471	0.245	58.5	630
	100	260	-	-	-	458	0.223	49.8	597

[a] Poultry litter content of 0 is 100% switchgrass.



(a)

(b)

(c)

Figure 5. Characteristic shifts in combustion differential thermogravimetric (DTG) curves of (a) poultry litter, (b) 50:50 blend of poultry litter and switchgrass, and (c) switchgrass with increasing pyrolysis temperature.

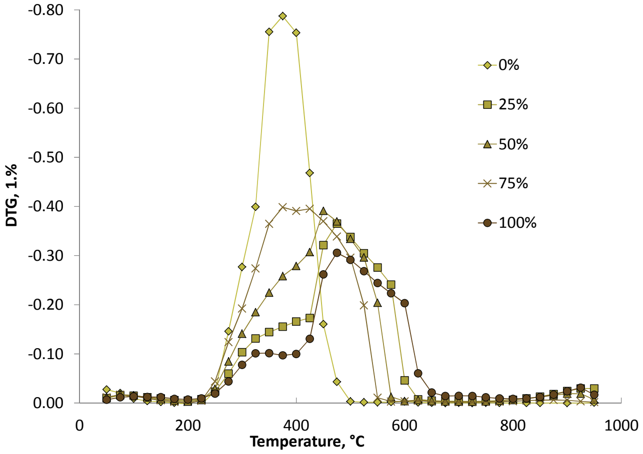


Figure 6. Characteristic shifts in combustion differential thermogravimetric (DTG) curves of poultry litter (PL) and switchgrass (SG) 350°C biochars with increasing PL content (0% PL = 100% SG).

creased. In addition, pure switchgrass biochars exhibited greater DTG_{Cmax} values than pure poultry litter biochars; this was in addition to greater ML_C values for the switchgrass. This may be largely due to the increased ash content of the poultry litter (table 1) as well as the increased fixed carbon content of the switchgrass biochars. Despite the slower rate of weight loss during this phase at greater poultry litter concentrations, the T_{Cmax} values were greater for greater poultry litter concentrations, suggesting more energetically demanding chars. The increase in T_{End} values also indicates that the poultry litter created a biochar that required more energy to begin the combustion process (of the biochar), but this material sustained a burn for a longer period of time.

CONCLUSION

Biochar characteristics for both soil and energy applications have been documented to be affected by both the parent feedstock and the pyrolysis production temperature. Controlling these two variables may yield a unique product with engineered properties—a designer biochar. Manure-based biochars are known to be extremely alkaline with high ash contents, while lignocellulosic biochars are known to be carbon-rich with pH values closer to neutral. Poultry litter and switchgrass feedstocks were blended at different ratios (25%, 50%, and 75% poultry litter), pelletized, and then subjected to slow pyrolysis at different temperatures (350°C, 500°C, and 700°C) to determine the effect that blend ratio and pyrolysis temperature had on the final biochar's energetic, pellet durability, and proximate composition characteristics.

Pyrolysis of single-component feedstocks followed the literature, with increases in temperature removing more C, H, N, and S and increasing the pH, EC, and ash contents. Furthermore, these values were unique to the pure biochars. In comparing pure poultry litter biochars to the blended poultry litter and switchgrass biochars, the high EC and ash contents were mediated, suggesting a more appropriate biochar for soil application. However, blending poultry litter with switchgrass did not impact pH; therefore, mediation may need to be achieved by managing soil application rates. In observing biochar recoveries, blending poultry litter and switchgrass had no interactive effects on biochar recoveries. However, increases in poultry litter resulted in greater biochar recoveries, largely due to the increase in the feedstock's ash content. Interestingly, as the pure poultry litter and its blends were pyrolyzed at increasing temperatures, blending had less of an effect on biochar recovery.

With respect to combustion characteristics, blending poultry litter with switchgrass increased both the gross energy content (HHV) and the rate of mass loss, largely due to the increase of biochar C, but blending decreased the end temperature of combustion, suggesting more labile C (compared to pure poultry litter biochars).

Structurally, the pure poultry litter pellets, regardless of pyrolysis temperature, were more resistant to degradation and less dusty than the pure switchgrass pellets. Blending switchgrass allowed for some elasticity in the biochar pellets, meaning that they were able to deform more without breaking under an applied force, and an increase in their compressive strength. Even though the blended biochar pellets become more prone to degradation with constant handling, manure-plant blended pellets alleviate some of the other application issues when using pure manure-based biochars.

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REFERENCES

Antal, M. J., & Grønli, M. (2003). The art, science, and technology of charcoal production. *Ind. Eng. Chem. Res., 42*(8), 1619-1640. http://dx.doi.org/10.1021/ie0207919.

ASABE Standards. (2008). S358.2: Moisture measurement—Forages. St. Joseph, Michigan: ASABE.

ASTM. (2006). Volume 05.06: Gaseous fuels; Coal and coke; Bioenergy and industrial chemicals from biomass. In *Annual Book of ASTM Standards*. West Conshohocken, Pa.: ASTM.

ASTM. (2010). Volume 09.01: Rubber, natural and synthetic—General test methods; Carbon black. In *Annual Book of ASTM Standards*. West Conshohocken, Pa.: ASTM.

Atkinson, C. J., Fitzgerald, J. D., & Hipps, N. A. (2010). Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: A review. *Plant Soil, 337*(1-2), 1-18. http://dx.doi.org/10.1007/s11104-010-0464-5.

Beglinger, E., & Locke, E. G. (1957). Charcoal: Its manufacture and use. *Econ. Bot., 11*(2), 160-173. http://dx.doi.org/10.1007/BF02985305.

Biagini, E., Barontini, F., & Tognotti, L. (2006). Devolatilization of biomass fuels and biomass components studied by TG/FTIR technique. *Ind. Eng. Chem. Res., 45*(13), 4486-4493. http://dx.doi.org/10.1021/ie0514049.

Bourke, J., Manley-Harris, M., Fushimi, C., Dowaki, K., Nunoura, T., & Antal, M. J. (2007). Do all carbonized charcoals have the same chemical structure? 2. A model of the chemical structure of carbonized charcoal. *Ind. Eng. Chem. Res., 46*(18), 5954-5967. http://dx.doi.org/10.1021/ie070415u.

Bridgeman, T. G., Jones, J. M., Shield, I., & Williams, P. T. (2008). Torrefaction of reed canary grass, wheat straw, and willow to enhance solid fuel qualities and combustion properties. *Fuel, 87*(6), 844-856. http://dx.doi.org/10.1016/j.fuel.2007.05.041.

Cantrell, K. B., & Martin, J. H. (2011). State-space temperature regulation development of biochar production: Part II. Application to manure processing via pyrolysis. *J. Sci. Food Agric., 92*(3), 490-495. http://dx.doi.org/10.1002/jsfa.4617.

Cantrell, K. B., Ducey, T., Ro, K. S., & Hunt, P. G. (2008). Livestock waste-to-bioenergy generation opportunities. *Bioresource Tech., 99*(17), 7941-7953. http://dx.doi.org/10.1016/j.biortech.2008.02.061.

Cantrell, K. B., Hunt, P. G., Ro, K. S., Stone, K. C., Vanotti, M. B., & Burns, J. C. (2010a). Thermogravimetric characterization of irrigated bermudagrass as a combustion feedstock. *Trans. ASABE, 53*(2), 413-420. http://dx.doi.org/10.13031/2013.29581.

Cantrell, K. B., Martin II, J. H., & Ro., K. S. (2010b). Application of thermogravimetric analysis for the proximate analysis of livestock wastes. *J. ASTM Intl., 7*(3), Paper ID JAI102583.

Cantrell, K. B., Watts, D. W., & Gunter, D. H. (2010c). Prospects of winter wheat straw for energy production. ASABE Paper No. 1010070. St. Joseph, Mich.: ASABE.

Cantrell, K. B., Hunt, P. G., Uchimiya, M., Novak, J. M., & Ro, K. S. (2012a). Impact of pyrolysis temperature and manure source on physicohemical characteristics of biochar. *Bioresource Tech., 107*, 419-428. http://dx.doi.org/10.1016/j.biortech.2011.11.084.

Cantrell, K. B., Ro, K. S., Szogi, A. A., Vanotti, M. B., Smith, M. C., & Hunt, P. G. (2012b). Green farming systems for the southeast USA using manure-to-energy conversion platforms. *J. Renewable Sustainable Energy, 4*(4), 041401. http://dx.doi.org/10.1063/1.3663846.

Chen, B., Zhou, D., & Zhu, L. (2008). Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. *Environ. Sci. Tech., 42*(14), 5137-5143. http://dx.doi.org/10.1021/es8002684.

Colley, Z., Fasina, O. O., Bransby, D., & Lee, Y. Y. (2006). Moisture effect on physical characterization of switchgrass pellets. *Trans. ASABE, 49*(6), 1845-1851. http://dx.doi.org/10.13031/2013.22271.

Das, D. D., Schnitzer, M. I., Monreal, C. M., & Mayer, P. (2009). Chemical composition of acid-base fractions separated from biooil derived by fast pyrolysis of chicken manure. *Bioresource Tech., 100*(24), 6524-6532. http://dx.doi.org/10.1016/j.biortech.2009.06.104.

Ford, D. J. (1977). Influence of diet pellet hardness and particle size on food utilization by mice, rats, and hamsters. *Lab. Animals, 11* (4), 241-246. http://dx.doi.org/10.1258/002367777780936486.

Gil, M. V., Oulego, P., Casal, M. D., Pevida, C., Pis, J. J., & Rubiera, F. (2010). Mechanical durability and combustion characteristics of pellets from biomass blends. *Bioresource Tech., 101*(22), 8859-8867. http://dx.doi.org/10.1016/j.biortech.2010.06.062.

Kaliyan, N., & Morey, R. V. (2009). Densification characteristics of corn stover and switchgrass. *Trans. ASABE, 52*(3), 907-920. http://dx.doi.org/10.13031/2013.27380.

Kaliyan, N., & Morey, R. V. (2010). Natural binders and solid bridge type binding mechanisms in briquettes and pellets made from corn stover and switchgrass. *Bioresource Tech., 101*(3), 1082-1090. http://dx.doi.org/10.1016/j.biortech.2009.08.064.

Kazi, Z. H., Schnitzer, M. I., Monreal, C., & Mayer, P. (2011). Separation and identification of heterocyclic nitrogen compounds in biooil derived by fast pyrolysis of chicken manure. *J. Environ. Sci. Health B, 46*(4), 51-61.

Lehmann, J., & Joseph, S. (2009). *Biochar for Environmental Management: Science and Technology.* Sterling, Va.: Earthscan.

Lima, I. M., & Marshall, W. E. (2005). Adsorption of selected environmentally important metals by poultry manure-based granular activated carbons. *J. Chem. Tech. Biotech., 80*(9), 1054-1061. http://dx.doi.org/10.1002/jctb.1283.

Lima, I. M., & Marshall, W. E. (2005). Granular activated carbons from broiler manure: Physical, chemical, and adsorptive properties. *Bioresource Tech., 96*(6), 699-706. http://dx.doi.org/10.1016/j.biortech.2004.06.021.

Munir, S., Daood, S. S., Nimmo, W., Cunliffe, A. M., & Gibbs, B. M. (2009). Thermal analysis and devolatilization kinetics of cotton stalk, sugar cane bagasse, and shea meal under nitrogen and air atmospheres. *Bioresource Tech., 100*(3), 1413-1418. http://dx.doi.org/10.1016/j.biortech.2008.07.065.

Novak, J. M., Lima, I., Baoshan, X., Gaskin, J. W., Steiner, C., Das, K. C., Watts, D. W., Busscher, W. J., & Schomberg, H. (2009). Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. *Ann. Environ. Sci., 3*, 195-206.

Novak, J. M., Busscher, W. J., Watts, D. W., Amonette, J. E., Ippolito, J. A., Lima, I. M., Gaskin, J., Das, K. C., Steiner, C., Ahmedna, M., Rehrah, D.; Schomberg, H. (2012). Biochars impact on soil-moisture storage in an Ultisol and two Aridisols. *Soil Sci., 177*(5), 310-320. http://dx.doi.org/10.1097/SS.0b013e31824e5593.

Novak, J. M., Cantrell, K. B., & Watts, D. W. (2013). Compositional and thermal evaluation of lignocellulosic and poultry litter chars via high and low temperature pyrolysis. *BioEnergy Res., 6*(1), 114-130. http://dx.doi.org/10.1007/s12155-012-9228-9.

Novak, J. M., Cantrell, K. B., Watts, D. W., Busscher, W. J., & Johnson, M. G. (2014). Designing relevant biochars as soil amendments using lignocellulosic-based and manure-based feedstocks. *J. Soils Sediments, 14*(2), 330-343. http://dx.doi.org/10.1007/s11368-013-0680-8.

Ro, K. S., Cantrell, K. B., & Hunt, P. G. (2010). High-temperature pyrolysis of blended animal manures for producing renewable energy and value-added biochar. *Ind. Eng. Chem. Res., 49*(20), 10125-10131. http://dx.doi.org/10.1021/ie101155m.

Shaw, M. D., Karunakaran, C., & Tabil, L. G. (2009). Physicochemical characteristics of densified untreated and steam-exploded poplar wood and wheat straw grinds. *Biosystems Eng., 103*(2), 198-207. http://dx.doi.org/10.1016/j.biosystemseng.2009.02.012.

Sohi, S., Lopez-Capel, E., Krull, E., & Bol, R. (2009). *Biochar, Climate Change, and Soil: A Review to Guide Future Research.* Acton, Australia: CSIRO Land and Water.

Sokhansanj, S., Mani, S., Bi, X., Zaini, P., & Tabil, L. (2005). Binderless pelletization of biomass. ASAE Paper No. 056061. St. Joseph, Mich.: ASAE.

Spokas, K. A., Cantrell, K. B., Novak, J. M., Archer, D. W., Ippolito, J. A., Collins, H. P., Boateng, A. A., Lima, I. M., Lamb, M. C., McAloon, A. J., Lentz, R. D, & Nichols, K. A. (2012). Biochar: A synthesis of its agronomic impact beyond carbon sequestration. *J. Environ. Quality, 41*(1), 973-989. http://dx.doi.org/10.2134/jeq2011.0069.

Steinbeiss, S., Gleixner, G., & Antonietti, M. (2009). Effect of biochar amendment on soil carbon balance and soil microbial activity. *Soil Biol. Biochem., 41*(6), 1301-1310. http://dx.doi.org/10.1016/j.soilbio.2009.03.016.

Uchimiya, M., Lima, I. M., Klasson, K. T., Chang, S., Wartelle, L. H., & Rodgers, J. E. (2010). Immobilization of heavy metal ions (CuII, CdII, NiII, and PbII) by broiler litter-derived biochars in water and soil. *J. Agric. Food Chem., 58*(9), 5538-5544. http://dx.doi.org/10.1021/jf9044217.