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Quality variations of poultry litter biochar generated at different pyrolysis temperatures

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ABSTRACT

Producing biochar and biofuels from poultry litter (PL) through slow pyrolysis is a farm-based, value-added approach to recycle the organic waste. Experiments were conducted to examine the effect of pyrolysis temperature on the quality PL biochar and to identify the optimal pyrolysis temperature for converting PL to agricultural-use biochar. As peak pyrolysis temperature increased incrementally from 300 to 600 °C, biochar yield, total N content, organic carbon (OC) content, and cation exchange capacity (CEC) decreased while pH, ash content, OC stability, and BET surface area increased. The generated biochars showed yields 45.7–60.1% of feed mass, OC 325–380 g kg⁻¹, pH 9.5–11.5, BET surface area 2.0–3.2 m² g⁻¹, and CEC 21.6–36.3 cmol_c kg⁻¹. The maximal transformation of feed OC into biochar recalcitrant OC occurred at 500 °C, yet 81.2% of the feed N was lost in volatiles at this temperature. To produce agricultural-use PL biochar, 300 °C should be selected in pyrolysis; for carbon sequestration and other environmental applications, 500 °C is recommended.

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1. Introduction

Production of renewable energy and bioproducts from non-food biomass is a sustainable strategy to address the worldwide energy and climate change challenges [1]. Poultry litter (PL), a solid waste resulting from chicken rearing, is being explored as a feedstock for biofuels and industrial chemicals [2]. Physically, PL is a mixture of bedding materials (e.g., wood shavings, saw dust, and peanut hull), bird excreta, feather, feed spills, and chemical treatments (e.g., alum, sodium bisulphate, etc.). Through pyrolysis, a thermochemical conversion technology whereby organic materials are heated in the absence of oxygen, PL can be readily transformed into biochar, bio-oil, and syngas [3]. Biochar is the black solid remaining after biomass pyrolysis. It is porous, enriched with recalcitrant organic carbon (OC), and sorptive for water and nutrients, ideal as a soil amendment for carbon sequestration and soil fertility enhancement [4]. Bio-oil is the dark brown liquid condensate of pyrolysis volatiles at room temperature. It possesses a calorific value (~20 MJ/L) 50–60% to that of diesel on a volume basis and can be upgraded to a reasonable fuel used in furnaces and stationary engines for heating and electricity generation [5]. Syngas

is the uncondensable portion of pyrolysis vapors. It is a mixture of CO, H₂, CO₂, CH₄, C₂H₄, C₃H₆, and other hydrocarbon gases and is being used as a natural gas substitute for heating and electricity generation and as a source material in many chemical processes [6].

The annual generation of PL in the U.S. is 12 million dry tons, of which the majority is disposed of through land application as an organic fertilizer [7]. Production of biogas (mainly CH₄) from PL by anaerobic digestion has been practiced, yet the yield is low due to the high lignocellulosic content of the feedstock [8]. Thermochemical conversion of PL for biochar and biofuels through pyrolysis may be a value-added approach to reuse the organic waste. Especially for biochar, the material has been favored in cultivation agriculture as a long-functioning soil amendment [9]. Research has demonstrated that application of biochar to soils can result in long-term increases in soil OC content, soil quality, and crop production [4,10]. Novak et al. reported that biochar amendment at 2.0 wt% significantly improved the fertility of a sandy soil by decreasing soil acidity and increasing soil OC, P, Ca, K, and Mn contents [10].

The quality of biochar varies with feedstock, production conditions, and even storage [11]. Commonly measured quality parameters of biochar include bulk density, OC content, ash content, nutrient content, elemental composition, surface area, porosity, surface functional groups, cation exchange capacity, iodine number, and sorption properties [12]. To assess the quality of biochar used in crop production, at least seven properties should be measured: pH, volatile compound content, ash content,

Abbreviation: CEC, cation exchange capacity; EC, electrical conductivity; OC, organic carbon; PL, poultry litter; WHC, water holding capacity.

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water holding capacity, bulk density, pore volume, and specific surface area [13]. As an amendment for carbon sequestration and soil fertility enhancement, biochar should also be evaluated on carbon stability, plant-available nutrients, and nutrient release dynamics.

Slow pyrolysis is commonly used to generate agricultural-use biochar, with bio-oil and syngas as co-products. By this technology, organic residues are heated in batch reactors similar to 'charcoal kilns' or in continuous flow beds in the absence of air [14]. Slow pyrolysis is normally conducted at atmospheric pressure, with heat provided by partial combustion of the feed, by external heaters, or by hot gas recirculation. The typical yields of biochar, bio-oil, and syngas are 35%, 30%, and 35% of the dry feedstock (e.g., wood) biomass, respectively [14]. However, the heat flux, pyrolysis temperature, processing time, gas conditions, and feed (e.g., shredded wood) density and particle size influence biochar yield and characteristics [11]. Of these factors, the highest (peak) temperature during pyrolysis is critical in determining the yield and quality of biochar [11]. Pyrolysis of vegetative materials (carbonization) starts at temperature as low as 190 °C. At above 250 °C, carbohydrates lose mass at a significant rate with evolution of CO₂ and CO [11]. The yield of biochar decreased significantly with increasing the pyrolysis temperature, especially after the temperature exceeded 480 °C [15]. With elevating the peak temperature in the range of 300–800 °C, the yield and water sorption capacity of biochar decreased, whereas the OC content increased [11]. Biochar prepared at 400 °C had negligible BET surface area and a low iodine number (<50 mg g⁻¹). At higher pyrolysis temperature, the surface area, porosity, and iodine number of biochar were greater [16]. The oxygen-containing functional groups such as hydroxyl, carboxyl, carbonyl, ether, and lactone on biochar are also gradually lost as the peak temperature increases [17].

Slow pyrolysis is simple, robust, and low-cost, applicable to small-scale, farm-based biochar production. To produce agricultural-use biochar on farm from PL using slow pyrolysis, it is aspired to maximize the yield while ensure the quality (e.g., OC stability, nutrient content, and nutrient and water retention capacities) of the final product. Demirbas recommended a pyrolysis temperature of 450 °C to convert agricultural residues into biochar and bio-oil: at this temperature the yield and the OC content of biochar products were both acceptably high [15]. The aim of this study was to identify the optimal pyrolysis temperature for converting PL into biochar by comparing the quality characteristics of biochars from slow pyrolysis of PL at different temperatures.

2. Materials and methods

2.1. Poultry litter

Granular PL was obtained from Perdue AgriRecycle, LLC (Seaford, DE), who collects raw PL from local broiler farms and processes the material into a marketable organic fertilizer through pasteurizing (heating to 80–110 °C), milling, and pelletizing. The granular PL was <4 mm. It contained 7.7% of moisture. The dry mass consisted of 71.5% organic matter and 28.5% mineral ash. On the dry mass basis, the total OC, N, P, and K contents of the PL were 355.1, 30.7, 15.1, and 41.8 g kg⁻¹, respectively. Selected properties of the PL are listed in Table 1.

2.2. Pyrolysis of poultry litter

Pyrolysis of PL was performed using a benchtop slow pyrolysis unit that consisted of a pyrolysis canister, an electrical muffle furnace, a condenser, and a water washer [18]. The pyrolysis canister was an 11 cm i.d. by 13 cm height metal container, with a 5-mm hole in the lid. The furnace (Isotemp muffle furnace 36L, Thermo Fisher

Table 1

Chemical properties of poultry litter used for biochar generation. Values are means ± standard deviations of duplicate measurements on oven-dry mass basis.

Properties	Value	
Ash content (%)	28.53 ± 0.36	
Organic matter content (%)	71.47 ± 0.36	
Elemental composition	Total (g kg ⁻¹)	Water extractable ^a (g kg ⁻¹)
OC	355.1 ± 4.5	74.92 ± 1.51
N	30.66 ± 1.06	7.65 ± 0.63
P	15.14 ± 0.084	2.95 ± 0.020
S	16.16 ± 0.83	8.37 ± 0.08
K	41.77 ± 1.37	27.18 ± 0.01
Na	18.64 ± 0.79	2.89 ± 0.01
Ca	43.03 ± 1.86	1.53 ± 0.03
Mg	11.06 ± 1.13	1.34 ± 0.06
Fe	0.748 ± 0.012	0.051 ± 0.001
Mn	0.705 ± 0.003	0.018 ± 0.004
Cu	0.611 ± 0.014	0.159 ± 0.008
Pb	0.008 ± 0.003	ND
Zn	0.628 ± 0.018	0.048 ± 0.001
Cd	0.001 ± 0.000	ND
As	0.037 ± 0.003	0.030 ± 0.000
Se	0.002 ± 0.000	0.002 ± 0.000

^a Water extractable components were determined by extracting poultry litter with deionized water at a 1:10 solid/water ratio and room temperature under shaking for 24 h; ND = non-detectable.

Scientific, Inc., Suwanee, GA) could provide a constant temperature environment of 50–1100 °C at averagely 20 °C min⁻¹ temperature increase rate. There was a 4-cm vent in the top of the furnace, which was connected to the condenser through an iron tube. The condenser was three glass bottles sitting abreast in water baths. The PL (approximately 650 g) was packed loosely in the pyrolysis canister by pounding and was placed in the muffle furnace for heating. The furnace was set at a temperature ranging from 300 to 600 °C. Smoky vapors (pyrolysis volatiles) escaped from the canister through the hole in the lid as the furnace temperature reached above 250 °C and entered into the condenser from the furnace vent. At the set temperature, volatiles continuously escaped from the canister and were condensed as bio-oil in the condensation bottles. Uncondensable gases (syngas) were released into the atmosphere after passing through the water washer. An air-free environment was achieved inside the canister during pyrolysis, as the canister lid and the furnace door were air-tight and the continuous emission of pyrolysis volatiles from the canister prevented air from diffusing in through the hole in the lid. The pyrolysis temperature was maintained until no visible vapors entered into the condenser (indicating completion of pyrolysis). The reaction (pyrolysis) time between start and end of visible vapors from the furnace was recorded. The canister was then taken out of the furnace and cooled down to room temperature with immediately sealing the hole in the lid with a metal plug. The black biochar solids in the canister were transferred into a plastic bag and stored at room temperature for chemical characterization within 4 months.

2.3. Characterization of poultry litter biochar

2.3.1. Yield

The yield of biochar was calculated as the mass of biochar generated from a unit dry mass of PL following the equation:

$$\text{biochar yield (\%)} = \frac{\text{mass of biochar (g)}}{\text{oven dry mass of raw material (g)}} \times 100 \quad (1)$$

2.3.2. Apparent density

Apparent density is the mass of a material per unit volume it occupies in packing. It is a parameter essential to know when designing containers to hold the material and when procuring the

material to fill existing vessels. The apparent density of PL biochar was measured following the ASTM D-285 methods with slight modifications [19]. Samples were fed to a weight-known 100-mL graduated glass cylinder (i.d. 25.4 mm) to >50% of its capacity using an electric vibratory spatula through a funnel (outlet i.d. 20 mm). The vertical distance between the spatula and the cylinder was maintained constant during the feeding. The bulk volume of the sample in the cylinder was recorded. The sample mass was determined after the cylinder was weighed again. Apparent density (ρ_b) of the biochar was calculated as follows:

$$\rho_b \text{ (g cm}^{-3}\text{)} = \frac{m}{v} \quad (2)$$

where m is the oven-dry mass of biochar (g), v is the volume biochar occupies in the cylinder (cm^3).

2.3.3. Ash content

The ash content of PL biochar was measured following the standard ASTM D – 2866 methods [19]. Briefly, 5.0 g of oven-dry sample were weighed into a pre-ignited crucible and heated at 500 °C overnight (>8 h). The crucible was then cooled to room temperature in a desiccator and weighed again. The ash content was then calculated:

$$\text{ash content (\%)} = \frac{\text{weight of ash (g)}}{\text{dry mass of biochar (g)}} \times 100 \quad (3)$$

2.3.4. Organic carbon content

Total organic carbon (TOC) content of PL biochar was determined using a Shimadzu 5000A TC/TN analyzer equipped with an SSM-5000A solid sampling module (Shimadzu, Kyoto, Japan). Biochar was ground to pass a 0.15 mm sieve and 0.1 g was weighed into a sample boat. Oven-dried glucose (OC content 40%) was used as the calibration standard. Triplicate measurements were conducted for each sample.

2.3.5. Biochar carbon stability

The stability of biochar carbon against mineralization was evaluated using the dichromate oxidation method [20]. Briefly, 0.1 g of biochar (<0.15 mm) was weighed into a 500-mL conic flask, followed by addition of 10 mL 0.167 M $\text{K}_2\text{Cr}_2\text{O}_7$ and 20 mL concentrated H_2SO_4 . The mixture was settled on bench until the room temperature was reached. Deionized water was then added to bring the mixture to 250.0 mL. Precisely 100.0 mL of the supernatant were pipetted into a 250-mL conic flask and titrated with freshly standardized 0.5 M FeSO_4 to the endpoint using 1.5% phenanthroline aqueous solution as the indicator. Blanks without biochar addition were included as control. Unstable OC in biochar was calculated as:

$$\text{unstable OC (g kg}^{-1}\text{)} = \frac{(V_0 - V) \times C \times 7.5}{\text{dry mass of biochar (g)}} \quad (4)$$

where V_0 is the volume (mL) of FeSO_4 consumed in titrating the control, V is the volume (mL) of FeSO_4 consumed in titrating the biochar sample, and C is the concentration (mol/L) of the freshly standardized FeSO_4 solution. Stable/recalcitrant OC was calculated as the difference between the total OC and unstable OC contents of the biochar.

2.3.6. pH and electrical conductivity (EC)

Biochar (<2 mm) was soaked with deionized water at a 1:5 solid/water ratio for 24 h with occasional agitation. The slurry was then measured for pH using an Accumet AB15 pH meter with an Accumet 3-in-1 pH/ATC combination electrode (Fisher Scientific, Suwanee, GA) and for EC using an Oakton CON510 conductivity/TDS meter (Oakton Instruments, Vernon Hills, IL) with a CON510 conductance cell (cell constant = 1.0 cm^{-1}) and a built-in ATC probe to normalize the reading to 25 °C.

2.3.7. Total nutrient contents

Precisely 0.20 g of biochar (<0.15 mm) were weighed into a 45-mL Teflon cylinder, followed by addition of 5.0 mL concentrated HNO_3 and 5.0 mL deionized water. The cylinder was installed into a Parr acid digestion bomb (Parr Instrument Company, Moline, IL) and heated in a 1.2 kW microwave oven (General Electric, Inc., Louisville, KY) for 2.5 min at a 50% power level. After cooling to room temperature, the digest was transferred into a 100 mL volumetric flask, brought to volume with deionized water, and filtered through a 0.45- μm glass fiber membrane. The total phosphorus (TP) concentration of the digest was measured following the phosphomolybdate blue method of Murphy and Riley [21]. The total concentrations of K, Ca, Mg, and S were determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) techniques. Another batches of biochar were digested with a mixture of 2.0 mL concentrated H_2SO_4 , 2.0 mL H_2O_2 , and 8.0 mL deionized water. The filtered digests were analyzed for total nitrogen (TN) concentrations using the Shimadzu 5000A TC/TN analyzer.

2.3.8. Extractable nutrients

Aliquots (2.0 g) of PL biochars (<0.15 mm) were weighed into 50-mL HDPE centrifuge tubes, followed by addition of 40 mL of 0.01 M HCl or deionized water. The tubes were shaken for 72 h at room temperature. After centrifugation at 6,500 rpm for 20 min and filtration through 0.2- μm syringe filters, the extracts were analyzed for extractable nutrient concentrations. Extractable OC and extractable N contents were determined with a Shimadzu 5000A TC/TN analyzer. Extractable P contents were analyzed using the phosphomolybdate blue method after digesting the extracts with H_2SO_4 and potassium persulfate in an autoclave. Extractable Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , Na^+ , NH_4^+ , K^+ , Ca^{2+} , and Mg^{2+} were measured using a Metrohm 790 ion chromatography system (Metrohm Ltd., Herisau, Switzerland).

2.3.9. Water holding capacity

Water holding capacity (WHC) is an important parameter measuring the ability of biochar to retain water by adhesion and cohesion forces. To determine WHC, unground biochar (15 g oven dry mass equivalent) was pre-saturated by soaking the material in deionized water for 24 h. The mixture was then completely transferred into a Kontes flex glass column (2.5 cm i.d. $\times$ 10 cm, Kontes Glass Company, Inc., Vineland, NJ). Vacuum at 0.6 bar was applied to the column for 10 min to further drive away any air possibly trapped in biochar pores. The column was settled for another 24 h. Afterward the column was subject to 0.1 bar vacuum suction until no gravitational water drained out. The amount of water retained by biochar in the column was then determined by weighing. The WHC was calculated following the equation:

$$\text{water holding capacity (\%)} = \frac{\text{water retained (g)}}{\text{biochar mass (g)}} \times 100 \quad (5)$$

2.3.10. Cation exchange capacity

The cation exchange capacity (CEC) of biochar was measured by the ammonium acetate (NH_4OAC) extraction methods [22]. Briefly, 40 mL of 1 M NH_4OAC was added to 0.5 g of biochar in a 50-mL glass centrifuge tube. After shaking at room temperature for 20 minutes, the mixture was transferred onto a 0.45- μm glass fiber filter under vacuum. The biochar retained on the filter was further washed with two 20-mL portions of 1 M NH_4OAC , followed by three 30-mL portions of isopropanol. The biochar was then rinsed with four 50-mL portions of 1 M KCl. The rinsate collected in the vacuum flask was transferred to a 250 mL volumetric flask. After bring to the volume with deionized water, the rinsate was measured for NH_4^+ concentration using the phenate colorimetric methods. The CEC

($\text{cmol}_c \text{ kg}^{-1}$) of biochar was calculated by normalizing the amount of NH_4^+ in the rinsate with the biochar mass (0.5 g).

2.3.11. BET surface area

The BET (Brunauer–Emmett–Teller) surface area of PL biochar was measured by N_2 adsorption at 77 K using a Micromeritics ASAP 2000 automated adsorption apparatus (Norcross, GA). Prior to the measurement, samples were degassed at 300 °C in a vacuum to 10^{-3} Torr [23].

2.3.12. Surface acidic groups

Acidic functional group contents of PL biochar was measured using the base titration methods [24]. Briefly, biochar was ground to <0.85 mm, further acid washed by mixing with 0.1 M HCl at a 1:50 carbon/solution ratio for 24 h, rinsed with deionized water until no residual Cl^- in the rinsate, and oven-dried at 105 °C. Aliquots (0.2 g) of the processed biochar were soaked with 20 mL of different base solutions (0.1 M NaOH, 0.1 M Na_2CO_3 , and 0.05 M NaHCO_3) for 24 h under shaking at room temperature. The solutions were passed through a 0.22 μm Millex GS filter unit (Millipore, Cork, Ireland). Precisely 10.00 mL of the solutions were pipetted into a 100-mL conic glass flask, followed by addition of 15 mL 0.1 M HCl, and back titrated with freshly standardized 0.1 M NaOH to endpoints using phenolphthalein as the indicator. The NaOH-titrable and NaHCO_3 -titrable acidities were treated as the total acidic surface functional groups and carboxyl groups, respectively; the difference between NaOH-titrable and Na_2CO_3 -titrable acidity was attributed to phenol groups; and the difference between Na_2CO_3 -titrable and NaHCO_3 -titrable acidity was attributed to lactone groups.

3. Results and discussion

3.1. Biochar yield and organic carbon content

The yield and OC content of PL biochars generated at different pyrolysis temperatures are given in Table 2. Reaction (carbonization) time is the time duration from start of pyrolysis (indicated by furnace temperature reaching above 250 °C and visible vapors entering the condenser) to completion of pyrolysis (indicated by termination of visible vapors entering the condenser). As the peak pyrolysis temperature increased, the required reaction time was reduced, while the biochar yield and the OC content of biochar decreased, and the ash content of the biochar products increased. At 300 °C, the pyrolysis was complete in 372 min, yielding 380 g OC kg^{-1} biochar 60.1% of the feed mass. At 600 °C, however, the pyrolysis time reduced to 130 min, and the biochar yield decreased to 45.7% while the OC to 325 g kg^{-1} (Table 2). The portion of the feedstock OC remaining in biochar after pyrolysis decreased as the pyrolysis temperature increased. At 300 °C pyrolysis temperature, 64.3% of the feed OC remained in biochar. When the pyrolysis temperature exceeded 450 °C, less than half (48.3%) of the feedstock OC remained and the majority was emitted as volatiles. At 600 °C, merely 41.8% remained (Table 2). Das et al. (2008) reported a biochar yield of 42.6% from pyrolyzing PL at 500 °C under a 2 L min^{-1} N_2 flow [18]. At 700 °C, the biochar yield decreased to 40.7% [25]. Relative to other organic feed materials, PL has generally higher ash contents (Table 1) and consequently yields more biochar through pyrolysis. In separate trials, slow pyrolysis of waste wood (0.73% ash), wheat straw (3.9% ash), and tree leaves (8.1% ash) at 400 °C using the same pyrolysis system as in the present study yielded biochar 32.2%, 36.2%, and 44.1% of the feed mass, respectively. Also due to the high ash content, PL biochar contained lower OC compared with other feedstock biochars. For example, the biochars derived from waste wood, wheat straw, and tree leaves

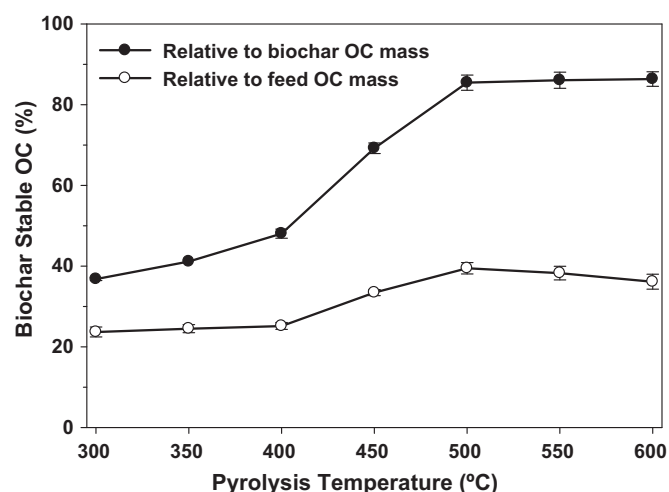


Fig. 1. Percentages of stable/recalcitrant organic carbon (OC) remaining in biochar from poultry litter at different pyrolysis temperatures. Error bars are standard deviations of triplicate measurements.

through pyrolysis at 400 °C demonstrated OC contents of 73.9%, 71.0%, and 64.2%, respectively (Measured following the same TOC analytical methods as in the present study).

3.2. Carbon stability of poultry litter biochar

Although PL biochar generated at lower pyrolysis temperature had higher OC content (Table 2), the OC was unstable and the majority was subject to oxidation. Nearly 63.2% of the OC in PL biochar generated at 300 °C pyrolysis temperature was unstable (oxidizable by dichromate to CO_2) (Fig. 1). The percentage decreased to 14.5% for the product from 500 °C pyrolysis and further to 13.6% for the 600 °C product (Fig. 1). In general, the recalcitrant portion of PL biochar OC (resistant to oxidation by acidic dichromate) increased as the pyrolysis temperature was elevated (Fig. 1). On the contrary, the yield and OC content of PL biochar decreased (Table 2). Overall, the portion of OC in the raw feed material that was transformed into recalcitrant carbon in biochar maximized at 500 °C (39.5%, Fig. 1). Since pyrolyzing PL at 500 °C engendered the highest portion of stable/recalcitrant OC from the feedstock, if carbon sequestration is highlighted, a peak pyrolysis temperature of 500 °C should be employed to convert PL into biochar.

3.3. Quality characteristics of poultry litter biochar

The apparent density of PL biochar ranged from 0.52 to 0.56 g cm^{-3} and was independent of the pyrolysis temperature (data not shown). The apparent density was lower than that of the raw poultry litter (0.67 g cm^{-3}), but higher than that of commercial activated carbon (0.45–0.49 g cm^{-3}) [23]. The typical bulk density of cultivated field soils is 1.4 g cm^{-3} . Consequently, PL biochar amendment would decrease soil bulk density.

The WHC of PL biochar ranged from 0.88 to 1.10 g g^{-1} (88% to 110%, Fig. 2). The biochar generated at 450 °C had the highest WHC. The WHC of a soil is primarily determined by its texture and organic matter content. For sandy loam, loam, and clay soils, the typical values are 21%, 30%, and 38%, respectively [26]. The WHCs of dairy and poultry manures may be high up to 243% and 173%, respectively [27]. Plant available water is stored in soil micro- and meso-pores. Biochar improves soil WHC by increasing its porosity and pore continuity.

Cation exchange capacity indicates the ability of biochar to adsorb cation nutrients. The CEC value of PL biochar ranged from 29.2 to 51.1 $\text{cmol}_c \text{ kg}^{-1}$, decreasing with increasing the pyrolysis

Table 2Production of biochar from poultry litter through pyrolysis at different temperatures. Values are means $\pm$ standard deviations of triplicate measurements.

Pyrolysis temperature ($^{\circ}\text{C}$)	Reaction time min	Yield (%) ^a	Biochar ash (%) ^b	Biochar OC ^c (%) ^b	Feed OC retention (%)
300	372 $\pm$ 10	60.13 $\pm$ 0.26	47.87 $\pm$ 0.12	37.99 $\pm$ 0.50	64.32 $\pm$ 0.76
350	271 $\pm$ 8	56.17 $\pm$ 0.25	51.29 $\pm$ 0.40	37.65 $\pm$ 0.15	59.56 $\pm$ 0.40
400	225 $\pm$ 5	51.52 $\pm$ 0.07	56.62 $\pm$ 0.31	36.10 $\pm$ 0.54	52.38 $\pm$ 0.61
450	200 $\pm$ 7	48.69 $\pm$ 0.04	58.66 $\pm$ 0.46	35.22 $\pm$ 0.51	48.30 $\pm$ 0.55
500	175 $\pm$ 3	47.57 $\pm$ 0.13	60.58 $\pm$ 0.09	34.47 $\pm$ 0.49	46.18 $\pm$ 0.62
550	150 $\pm$ 8	46.62 $\pm$ 0.08	60.65 $\pm$ 0.07	33.88 $\pm$ 0.42	44.47 $\pm$ 0.50
600	130 $\pm$ 5	45.71 $\pm$ 0.14	60.78 $\pm$ 0.16	32.52 $\pm$ 0.33	41.85 $\pm$ 0.47

^a % of dry feed mass.^b % of biochar mass.^c OC: organic carbon content.

temperature (Fig. 2). The biochar produced at 400 $^{\circ}\text{C}$ possessed CEC of 41.7 $\text{cmol}_c \text{kg}^{-1}$. Biochars from pyrolyzing and steam activating PL, peanut hulls, and pine chips at 400 $^{\circ}\text{C}$ demonstrated CEC values of 57.4, 11.7, and 6.0 $\text{cmol}_c \text{kg}^{-1}$, respectively; and the values decreased to 37.0, 4.5, and 6.0, respectively, as the pyrolysis temperature was elevated to 500 $^{\circ}\text{C}$ [28]. Poultry litter has a high content of ash (Table 1). It is postulated that K, Na, Ca, Mg, and P in the feed biomass would promote formation of O-containing functional groups on biochar surface during pyrolysis and thus, result in higher CEC [29]. Mineral soils generally have CEC less than 15 $\text{cmol}_c \text{kg}^{-1}$. Humic substances, however, may have CEC greater than 100 $\text{cmol}_c \text{kg}^{-1}$ [26]. Soils with high CEC values will be able to retain cationic nutrient fertilizers (e.g., K^+ and NH_4^+) in the root zone and prevent the nutrients from deep leaching. It is evident that PL biochar amendment will improve soil nutrient retention.

The BET surface area of raw PL was 0.90 $\text{m}^2 \text{g}^{-1}$. After pyrolysis, it increased less than one order of magnitude in PL biochar (Fig. 2). The PL biochar generated at 400 $^{\circ}\text{C}$ had BET surface area 3.94 $\text{m}^2 \text{g}^{-1}$, a level slightly higher than that of typical soil organic matter [30]. The effect of pyrolysis temperature was fairly moderate: the BET surface area of PL biochar was elevated from 2.68 to 5.79 $\text{m}^2 \text{g}^{-1}$ as the

pyrolysis temperature increased from 300 to 600 $^{\circ}\text{C}$ (Fig. 2). Likely, the inorganic ash materials at high contents (Table 2) have filled or blocked access to the micropores in the PL biochar, resulting in relatively low surface area [31]. Commercial activated carbon has BET surface area in the range of 500–1000 $\text{m}^2 \text{g}^{-1}$ [23]. Clearly, higher pyrolysis temperature (e.g., >700 $^{\circ}\text{C}$) and additional activation are needed to yield biochar products with high BET surface area. The BET surface area may be elevated to >400 $\text{m}^2 \text{g}^{-1}$ if PL biochar pyrolyzed at 700 $^{\circ}\text{C}$ is further activated with steam [23]. By pyrolyzing broiler litter at 350 and 700 $^{\circ}\text{C}$ for 1 h under a 0.1 $\text{m}^3 \text{h}^{-1}$ N_2 flow, Uchimiya et al. found the biochar products after 0.1 M HCl washing had BET surface area 60 and 94 $\text{m}^2 \text{g}^{-1}$, respectively; and the surface area increased to 335 $\text{m}^2 \text{g}^{-1}$ for both products after activation with 3 mL min^{-1} steam at 800 $^{\circ}\text{C}$ for 45 min [32]. The same authors also reported that cottonseed hull biochars generated at 350, 500, 600, and 800 $^{\circ}\text{C}$ pyrolysis temperatures demonstrated BET surface areas 4.7, 0, 34, and 322 $\text{m}^2 \text{g}^{-1}$, respectively [32]. The measurements may not be adequately accurate, as the BET surface area of a biochar cannot be 0.

Oxygen-containing functional groups such as hydroxyl, carboxyl, carbonyl, ether, and lactone are developed on biochar

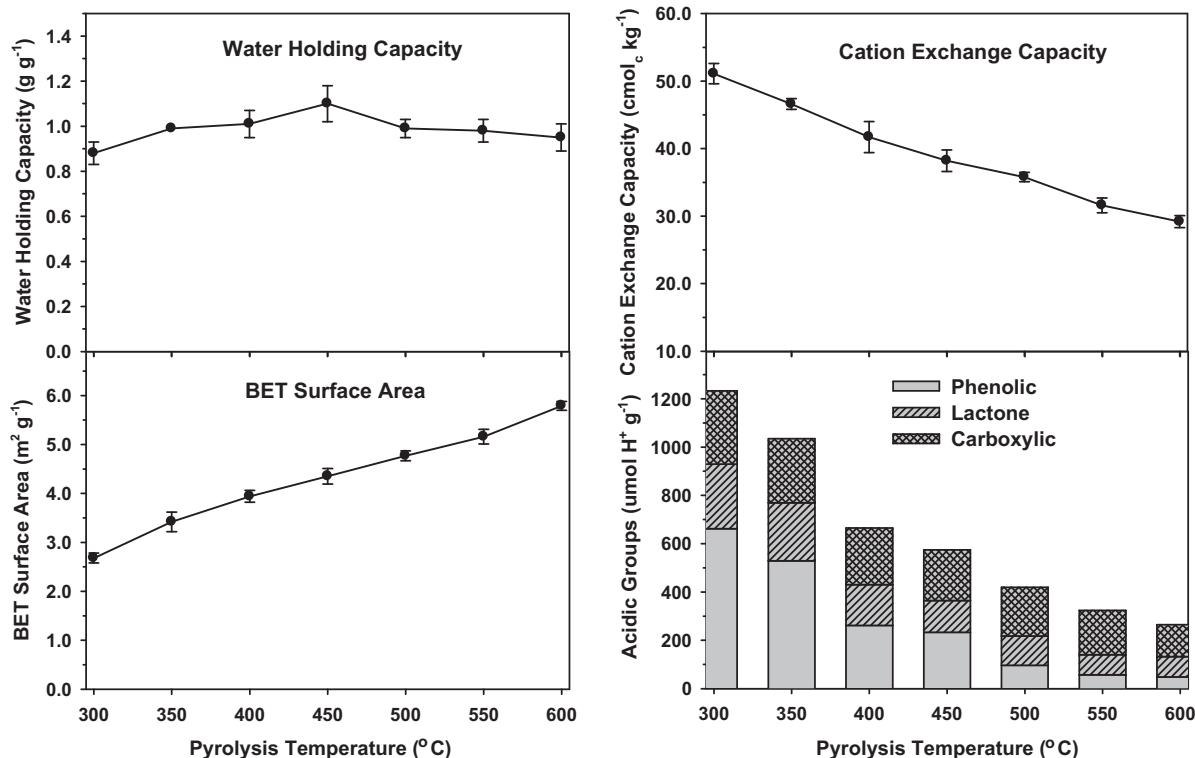


Fig. 2. Water holding capacity (WHC), BET surface area, cation exchange capacity (CEC), and acidic functional groups of poultry litter biochars generated at different pyrolysis temperatures. Error bars are standard deviations of triplicate measurements.

during pyrolysis [16]. These functional groups largely determine the sorptive capacity of biochar for ionic solutes. The PL biochars had 265–1233 $\mu\text{mol H}^+ \text{g}^{-1}$ of acidic surface functional groups, decreasing readily as the pyrolysis temperature increased (Fig. 2). In pyrolyzing nutshells for charcoal, Varhegyi et al. also found that the products decreased in acidic surface functional groups with elevating the pyrolysis temperature [16]. Poultry litter-based activated carbon produced through 700 °C carbonization and steam activation demonstrated acidic surface functional groups >3000 $\mu\text{mol H}^+ \text{g}^{-1}$, even higher than commercial activated carbon (>700 $\mu\text{mol H}^+ \text{g}^{-1}$) [33]. Of the acidic functional groups in the PL biochar, carboxylic groups accounted for 24.6–56.5%, phenol groups 13.5–53.7%, and lactone groups 21.7–38.5% (Fig. 2). Furthermore, the percentage of carboxylic groups in the total acidic surface groups largely increased whereas that of phenol groups decreased as the pyrolysis temperature was raised in the range of 300–600 °C (Fig. 2). The CEC of biochar is mainly a result of these acidic surface functional groups. After incorporation into soil, biochar is subject to biotic and abiotic oxidation of its unstable OC (Fig. 1) and in turn, increases its acidic functional groups and CEC [34].

3.4. Nutrient contents of poultry litter biochar

The PL biochar had pH in the range of 9.5–11.5, increasing with the pyrolysis temperature (Fig. 3a). The high pH reflected the major ash components K^+ , Na^+ , Ca^{2+} , Mg^{2+} , HCO_3^- , and CO_3^{2-} in PL biochar (Table 3). Biochars are generally alkaline. Gaskin et al. (2008) reported that biochars generated from PL, peanut hulls, and pine chips through 400 °C pyrolysis had pH 10.1, 10.5, and 7.6, respectively [28].

The EC of PL biochar (1:5 solid/water extract) ranged from 22.8 to 31.0 dS m^{-1} (Fig. 3b), lower than raw PL (50.2 dS m^{-1}) [35]. Consistent with the ash content increase (Table 2), the PL biochar EC also increased gradually with the pyrolysis temperature (Fig. 3b). Considering its high salinity, PL biochar should be applied to soil at controlled rates to avoid potential toxicity on crop seeds and seedlings.

The raw PL contained 30.7, 15.1, 41.8, 43.0, 11.1, and 16.2 g kg^{-1} of N, P, K, Ca, Mg, and S, respectively (Table 1). After pyrolysis, these nutrients except for N became enriched in PL biochar and the total contents increased with elevating the pyrolysis temperature (Table 3). The TN content of PL biochar decreased as the pyrolysis temperature increased (Table 3). Compared with the raw PL, biochars generated at lower pyrolysis temperatures (≤ 350 °C) had higher while those generated at higher pyrolysis temperatures (≥ 400 °C) had lower TN content (Table 3). Accounting for the biochar yield (Table 2), overall loss of N from the PL feed during pyrolysis was significant and the loss was greater at higher pyrolysis temperature (Fig. 3c). At 300, 400, 500, and 600 °C, remaining N in biochar accounted for 81.8, 44.2, 4.7, and 1.8% of the feed N (30.7 g kg^{-1} , Table 1), respectively (Fig. 3c). As the pyrolysis temperature exceeded 400 °C, the majority (>56%) of the feed N was lost as volatiles (e.g., N_2O , NO, NO_2 , and low molecular weight organic N) in bio-oil and syngas. It is evident that biochar production from animal manures should be conducted at low pyrolysis temperature (e.g., 300 °C) to conserve the feed N.

Nitrogen existed in PL biochar predominantly as nonextractable, organic forms. Water or 0.01 M HCl extractable N accounted for less than 11.8% of the total N (Table 3). Organic N dominated (>95%) in water extractable N, with insignificant (<5%) NO_3^- -N and NH_4^+ -N present. Compared with the 7.65 g kg^{-1} water extractable N in the raw PL (Table 1), pyrolysis had significantly reduced the water extractable N content in biochar, to 4.91 g kg^{-1} in the 300 °C product and 0.12 g kg^{-1} in the 500 °C product (Table 3). It is true that PL biochar generated at lower pyrolysis temperatures (≤ 350 °C) would add more TN to soil than the raw PL if both were applied at

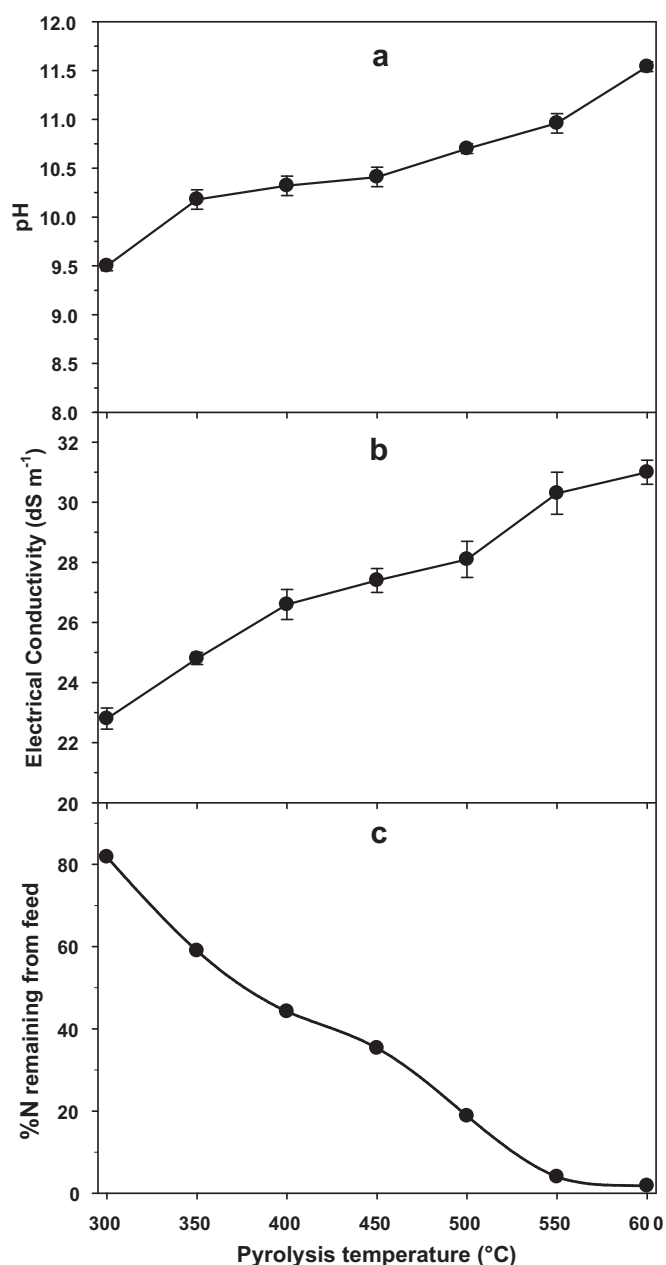


Fig. 3. (a) pH (1:5 solid/water extracts), (b) electrical conductivity (1:5 solid/water extracts), and (c) nitrogen (N) remaining from the feed in poultry litter biochars generated at different pyrolysis temperatures. Error bars are standard deviations of triplicate measurements.

the same mass rate (Table 2), yet the biochar would furnish much less water-extractable N to crops (Table 3). Pyrolysis also converted a significant portion of PL phosphorus into water non-extractable forms. In raw PL, water extractable P accounted for 19.5% of the total P (Table 1); in PL biochar, it was less than 7.0% (Table 3). At pyrolysis temperature ≤ 350 °C, more than 55% of the total P in PL biochar was HCl extractable. With increasing the pyrolysis temperature to ≥ 500 °C, HCl-extractable P decreased to <16% of the total P in biochar (Table 3). Since nutrient release kinetics of an organic fertilizer are largely determined by its nutrient water extractability [35], PL biochar may serve as a slow-release nutrient amendment in crop production and consequently, reduce the risk of nutrient runoff losses following land application.

Pyrolysis further decreased the water extractability of K from 65.1% in the feed (Table 1) to approximately 46.6% in biochar

Table 3
Total and extractable nutrient contents of poultry litter biochar generated through pyrolysis at different temperatures. Values are means of triplicate measurements with coefficients of variation less than 2%.

Nutrient content (g kg ⁻¹)		Pyrolysis temperature (°C)						
		300	350	400	450	500	550	600
N	Total	41.71	32.22	26.30	22.25	12.14	3.11	1.18
	HCl extractable	2.07	1.50	0.834	0.138	0.119	0.239	0.312
	Water extractable	4.91	3.49	1.46	0.154	0.124	0.252	0.331
P	Total	22.73	24.02	26.29	26.59	27.87	29.84	30.54
	HCl extractable	16.59	13.33	7.00	5.07	4.44	4.15	2.82
	Water extractable	0.343	0.138	0.172	0.725	0.916	2.045	1.916
K	Total	69.28	74.55	81.16	85.70	87.92	89.69	91.51
	HCl extractable	40.09	43.07	48.25	50.20	51.35	52.19	53.34
	Water extractable	32.01	34.18	36.67	39.17	40.40	43.89	44.61
Ca	Total	71.75	76.42	83.44	87.85	90.46	93.04	94.01
	HCl extractable	23.88	22.57	13.08	9.56	9.18	8.54	8.24
	Water extractable	0.238	0.199	0.152	0.065	0.051	0.043	0.038
Mg	Total	18.61	19.74	21.47	22.83	23.28	23.75	24.23
	HCl extractable	9.59	9.93	11.16	12.11	11.39	11.15	10.78
	Water extractable	0.278	0.128	0.065	0.056	0.050	0.048	0.046
S	Total	26.95	28.84	31.15	33.21	34.02	34.96	35.30
	HCl extractable	11.23	11.86	13.01	14.61	14.33	13.87	12.18
	Water extractable	12.30	12.96	13.91	14.74	15.28	16.14	14.44

(Table 3). The HCl-extractable K was roughly 58.4% of the total K in all the PL biochars generated at different pyrolysis temperatures (Table 3). The Ca water extractability was decreased from nearly 3.6% in the feed (Table 1) to <0.3% in biochar. The HCl extractable Ca, on the other hand, decreased from 33.3% to 8.8% of total Ca in PL biochar as the pyrolysis temperature increased from 300 °C to 600 °C (Table 3). Similar scenarios occurred for Mg; yet more Mg in PL biochar (44.4–53.0%) was HCl-extractable (Table 3). In raw PL, 51.8% of the S was water extractable (Table 1). In PL biochar, 40.9–46.2% of the S was water extractable and 34.5–44.0% HCl-extractable as SO₄²⁻ (Table 3).

The richness in N, P, K, S, Ca, Mg, and other plant nutrients of PL biochar generated at low pyrolysis temperature (e.g., 300 °C) may provide immediate fertility improvement if the material is land-applied as a soil amendment. Kimetu et al. reported that the corn yield was nearly doubled in Western Kenya when soil was amended with wood biochar [36]. In addition to the introduced nutrients, enhanced fertilizer use efficiency through biochar amendment was also responsible for the crop productivity improvement. Compared with chemical fertilization alone, biochar in combination with chemical fertilizers significantly improved production of radish, corn, cowpea, and peanut [4,37]. Due to its relatively higher CEC value (Fig. 2), PL biochar is anticipated to retain more nutrients in soil and decrease nutrient leaching. Consequently, soil nutrient cycling may be enhanced.

3.5. Optimal pyrolysis temperature for converting poultry litter into biochar

Elevating the pyrolysis temperature in 300–600 °C remarkably decreased the yield, OC content, N content, and CEC while increased the carbon stability and BET surface area of the biochar product (Table 2, Table 3, Fig. 2). To achieve best quality of biochar with acceptable yield from slow pyrolysis of PL, a reasonably low pyrolysis temperature should be selected. In addition to ensuring the biochar yield, a lower temperature environment is more efficient to achieve and maintain. Demirbas recommended a pyrolysis temperature of 450 °C to convert agricultural residues into biochar and bio-oil [15]. Our results suggest that over the 300–600 °C temperature range, 300 °C is the optimal pyrolysis temperature to convert PL into biochar for agricultural uses. However, if pyrolysis of PL

aims predominantly at carbon sequestration and energy production, 500 °C should be adopted to convert the highest portion of feedstock OC as recalcitrant OC in biochar while yielding more bio-oil and syngas. Indeed, a peak temperature in the range of 300–500 °C should be employed to convert PL into biochar through slow pyrolysis.

4. Conclusions

Pyrolysis temperature is the key factor determining the yield and quality of biochar from slow pyrolysis of PL. The yield, total N content, OC content, and CEC value of PL biochar decreased with elevating the pyrolysis temperature in the range of 300–600 °C, while the carbon stability, BET surface area, pH, and EC increased. The PL biochar produced at 300 °C showed the highest yield, N content, and CEC value, while the products generated at 500 °C had the greatest recalcitrant OC mass. To produce agricultural-use PL biochar, a low pyrolysis temperature within 300–500 °C should be adopted.

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