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CHARACTERIZATION OF DESIGNER BIOCHAR PRODUCED AT DIFFERENT TEMPERATURES AND THEIR EFFECTS ON A LOAMY SAND

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ABSTRACT

Biochar additions to degraded soils have the potential to improve crop yield and soil quality. We hypothesize that the biochar production process can be tailored to form designer biochars that have specific chemical characteristics matched to selective chemical and/or physical issues of a degraded soil. We produced biochars from peanut hulls, pecan shells, poultry litter, and switchgrass at temperatures ranging from 250ºC to 700ºC. Biochars were characterized by % mass recovery and by their physical and chemical distinctiveness. These were mixed at 2% w/w with a Norfolk loamy sand (fine-loamy, kaolinitic, thermic Typic Kandiudults) and were laboratory incubated to examine changes in the Norfolk's soil properties. Higher pyrolysis temperatures resulted in lower biochar mass recovery, greater surface areas, elevated pHs, higher ash contents, and minimal total surface charge. Removal of volatile compounds at the higher pyrolysis temperatures also caused biochars to have higher percentages of carbon (C) but much lower hydrogen (H) and oxygen (O) contents. ^{13}C NMR spectral analyses confirmed that aliphatic structure losses occurred at the higher pyrolysis temperatures, causing the remaining structures to be composed mostly of poly-condensed aromatic moieties. Biochars produced at higher pyrolysis temperatures increased soil pH values, while biochar made from poultry litter feedstock grossly increased Mehlich-1 extractable phosphorus (P) and sodium (Na) concentrations. Water-holding capacity varied after biochar incorporation. Biochars produced from different feedstocks and under different pyrolysis conditions influenced soil physical and chemical properties in different ways; consequently, biochars may be designed to selectively improve soil chemical and physical properties by altering feedstocks and pyrolysis conditions.

***Keywords*:** Designer biochar, pyrolysis, feedstock, soil improvement; GRACEnet

1. INTRODUCTION

Biochar addition to soils has attracted widespread attention as a method to increase soil C sequestration while also reducing atmospheric CO_2 concentrations [1,2]. Increased soil C sequestration also can improve soil quality because of the vital role that C plays in chemical, biological, and physical soil processes and many interfacial interactions [3,4]. Biochar is a byproduct of the pyrolysis processing of organic feedstocks [5]. Varied technological designs for pyrolysis can covert feedstocks like grasses, nutshells, forestry products and animal manures into biochar [5]. Pyrolysis is the heating of biomass in an oxygen-limited atmosphere, causing release of volatile C structures, hydrogen (H), methane (CH_4) and carbon monoxide (CO). The volatile C structures (alcohols, oils, tars, acids, etc.) can be re-condensed as bio-oil [5]. The biochar that remains consists mainly of C, and contains some O, H, N, and ash [calcium (Ca), potassium (K), etc.].

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Over a long period of time, inhabitants of the Amazonia region known as “Terra Preta de Indio” applied large quantities of biochar plus other organic debris and refuse to the infertile Oxisols [6]. Elements such as Ca, K, and P entrained within the biochar, bones, and other refuse materials increase soil nutrient levels and promote plant growth [6]. Recent efforts to replicate the “Terra Preta” conditions using biochars made from present pyrolysis methods have shown that biochars can sequester C [7,8], improve soil fertility, [6,9,10] and sometimes increase crop yields [11,12].

The ability of biochar to store C and improve soil fertility will depend on its physical and chemical properties, which can be varied in the pyrolysis process or through the choice of feedstock. Because degraded soils in different regions around the world have specific quality issues, it follows that one biochar type will not solve all soil quality problems. For example, biochars with a highly aromatic composition may best be suited for long-term C sequestration because of their recalcitrant nature [6,10]. Biochars with large amounts of C in poly-condensed aromatic structures are obtained by pyrolyzing organic feedstocks at high temperatures (400 to 700ºC) [6,13-15], but also have fewer ion exchange functional groups due to dehydration and decarboxylation [6,13, 15], potentially limiting its usefulness in retaining soil nutrients. On the other hand, biochars produced at lower temperatures (250 to 400ºC) have higher yield recoveries and contain more C=O and C-H functional groups that can serve as nutrient exchange sites after oxidation [6]. Moreover, biochars produced at these lower pyrolysis temperatures have more diversified organic character, including aliphatic and cellulose-type structures. These may be good substrates for mineralization by bacteria and fungi [16], which have an integral role in nutrient turnover processes and aggregate formation [3]. Feedstock selection also has a significant influence on biochar surface properties [17] and its elemental composition [18,19]. Because both feedstock and pyrolysis conditions affect physical [17] and chemical [18] properties, biochar producers may wish to consider the goals for the biochar amendment, and adjust their feedstock and pyrolysis protocol to create a designer biochar that is tailored to remedy a specific soil issue.

Biochar produced from pecan shells (*Carya illinoensis)* was recently reported to significantly improve the fertility of a sandy Coastal Plain soil [10]. In that study, only one high temperature (700ºC) pyrolyzed biochar was used. While fertility improvements were obtained [10], another serious issue of sandy soils--low water holding capacities--was not investigated. It is common for crops grown in soils of the Coastal Plain region of South Carolina to experience severe water deficits because the sandy soil textures have low water holding capacities [20]. These sandy soils only hold about 0.08 m of water per meter of soil depth [21], which is insufficient to sustain crop growth especially through frequent 5 to 20 day periods of drought [22].

Past studies have demonstrated water retention increases in sandy soils treated with biochar supplements [23,24]; however, these increases were obtained after adding 4 to 45% biochar. This is a large amount of biochar to apply to soil (80 to 900 t ha^{-1}) and may not be practical in some geographic regions with limited feedstock reserves or in environmentally sensitive areas. Therefore, it may be possible to design a biochar to obtain improvements in soil water holding capacities while using lower biochar application rates, and in turn also improve soil fertility. There is limited information, however, concerning how biochar quality can influence soil properties. We hypothesize that the biochar chemical production process and feedstock choice can be planned to create designer biochar that has specific chemical characteristics allowing for more soil C sequestration and improvement of selective chemical and/or physical issues of degraded soils. The objectives of this study were to physically and chemically characterize biochars produced from four different feedstocks pyrolyzed under two different temperature regimes and to examine the effects of these different biochars on altering the fertility and water-holding capacity of a Norfolk loamy sand.

2. MATERIALS AND METHODS

2.1. Production of Biochars

The raw feedstocks used in this study were obtained from The University of Georgia (peanut hulls; *Archis hypogaea*); the North Carolina Agricultural and Technical State University (pecan shells); USDA-ARS-New Orleans location (poultry litter; *Gallus domesticus*), and Clemson University, Pee Dee Research and Education Service (switch grass; *Panicum virgatum* L.). These feedstocks are commonly produced as agricultural byproducts and are obtainable in large quantities in North and South Carolina, Georgia, and Louisiana.

The raw feedstocks were initially air-dried and ground or milled to pass a 1 or 2-mm sieve. All biochars were produced over a 1 to 3 h period using a slow pyrolysis process. Peanut hull biochars were produced in a batch pyrolysis unit in two groups, one at 400 and then at 500ºC with N_2 as a carrier gas. Pecan shell biochar was made using a †Lindberg box programmable furnace equipped with a retort (model 5116HR; Lindberg, Watertown, WI) under an N_2 atmosphere at 350ºC and then at 500ºC [10]. Biochar from pelletized poultry litter (4.75-mm-diameter pellets) was made in two batches at 350ºC and 700ºC under N_2 gas also in a Lindberg box programmable furnace equipped with a retort. Biochar from switch grass was made in two batches at 250ºC and 500ºC using similar procedures as for the pecan shell biochar. The lower temperature (250ºC) range for this feedstock was arbitrarily chosen to have at least one sample pyrolyzed below 300-400ºC, a threshold temperature range where cellulose and hemi-cellulose structural degradation occurs [5]. In these processes, the biochar mass recovery was calculated as a percentage of the mass of feedstock input (dry wt. DW) and biochar mass output (biochar mass DW/feedstock mass DW). Additionally, the C recovery efficiency after each pyrolytic process was calculated on an oven-dry wt basis as biochar C mass/feedstock C mass. Afterwards, all eight biochars were ground to pass through a 0.25-mm sieve so that the biochar particles would be a fine size allowing passage through sieves used to estimate aggregate-size distribution (data not presented).

2.2. Characterization of Biochars

Biochar samples were evaluated for physical and chemical properties that included surface area, pH, total negative surface charge, volatile matter, elemental composition, and structural composition using solid-state, cross-polarization, magic-angle spinning and total side-band depression ^{13}C nuclear magnetic resonance (^{13}C NMR). Surface area measurements were obtained from duplicate N_2 adsorption isotherms at 77ºK using a Nova 2000 Surface Area Analyzer (Quantachrome Corp., Boynton Beach, FL). Specific surface areas (S_{BET}) were taken from adsorption isotherms using the Brunauer, Emmett and Teller (BET) equation. The pH of each biochar was measured in triplicate in deionized water from a 1% (w/v) after shaking for 200 rpm for 24 h. The total negative surface charge was measured on duplicate samples based on the Boehm method [25]. While this method also ascertains total titrable surface functional groups, we were interested in the total negative surface charge of the biochars to ascertain their overall ability to retain cationic plant nutrients. Biochar suspensions containing a normalized quantity of C (0.25 g C) were placed in 25 mL of 0.1 M sodium hydroxide (NaOH) and were stirred in a closed vessel for 20 to 24 h. A 10-mL filtered (0.45-µm pore size) aliquot was added to 15 mL of standard 0.1M HCl solution. The HCl neutralized the unreacted base and prevented further reaction between atmospheric CO_2 and the base from occurring. The solution was then back titrated with standard 0.1 M NaOH solution using an automatic titrator (Metrohm Titrando 836, Riverview, FL). The volume of NaOH required to neutralize the sample was converted to titrable neg-ative surface charge, where NaOH was used as titrant. The total negative surface charge was expressed as mmol H^+ eq/g C.

For each raw feedstock and biochar sample, a single estimate of the percentage of volatile material, ash content, and elemental (C, H, O, N, and S) content was determined on an oven dry-weight basis by Hazen Research, Inc. (Golden, CO) following the ASTM D 3172 and 3176 standard methods [26]. In this method, the percentage of O content was determined by difference. These results were used to calculate atomic H/C, O/C and (O+N)/C ratios to evaluate relationships between pyrolysis temperature and the relative degree of hydrophobicity of each biochar. The P and Na contents were also determined in triplicate for each biochar on an oven dry-weight basis using the EPA method 3052 microwave-assisted acid digestion method [27] and were quantified using an inductively coupled plasma mass spectrometer as outlined [10].

For each biochar, the core-structural characteristics were obtained using a Bruker DSX-300 ^{13}C NMR spectrometer (Karlsruhe, Germany) operated at ^{13}C frequency of 75.5 MHz. Operating conditions and spectral, fine-tuning technical parameters are available [28]. Each spectral pattern was integrated using the chemical shift assignments as follows: 0 to 109 ppm, aliphatic and O-alkyl-C; 109 to 163 ppm, aromatic-C; 163 to 190 ppm, carboxyl-C; and 190 to 220 ppm, carbonyl-C. The percent C distribution in each spectral pattern was determined by estimating the area in these chemical shift regions as a percentage of the total area under the spectral curve. The C distributions in these four groups were then normalized to sum the total C distribution to 100%.

[†] Mention of a specific product or vendor does not constitute a guarantee or warranty of a product by the U.S. Department of Agriculture or imply its approval to the exclusion of other products that may be suitable.

2.3. Norfolk Soil and Biochar Incubation

The Norfolk soil used in this study was obtained from the Ap horizon (0 to 15 cm deep) in a field with a long history (20 yrs) of row crop production located at the Clemson University Pee Dee Research and Education Center, Florence, South Carolina. The soil was aired-dried and 2-mm sieved. The Ap horizon was a loamy sand with a particle size distribution of 740, 250, and 10 g kg^{-1}, respectively, of sand, silt, and clay (sedimentation method: Soil Characterization Lab, The Ohio State University, Columbus, OH). X-ray diffraction analysis of the total clay fraction in the Norfolk Ap horizon revealed an abundance of quartz, kaolinite, and rutile with minor amounts of Fe and Al-hydroxy inter-layered chlorite, suggesting that this soil was extensively weathered (X-ray diffraction method; Soil Characterization Laboratory, The Ohio State University, Columbus OH). The pH of the untreated Norfolk Ap soil was measured in a 1:1 soil-to-deionized water mixture [29].

The Norfolk soil and biochar incubation experiment was conducted in open-top flower pots that measured 10.3 cm (i.d.) by 8.5 cm tall. Pot drainage holes were sealed using a nylon mesh fabric. Nine g of 0.25-mm biochar was mixed into 450 g of air-dried soil for a 2% mixture (w/w), which equates to a field-application rate of approximately 40 to 44 metric ton ha^{-1}. This application rate was calculated assuming a 15-cm soil depth and bulk density values of 1.3 to 1.4 g cm^{-3}. Previously published results revealed that this biochar application rate resulted in the most significant soil fertility improvements [10]. Each treatment was set up in four replicates. Deionized H_2O was then mixed into each treatment to obtain a soil-moisture content of 10% (w/w) representing the upper range (5 to 10%) of field capacity for a typical Norfolk Ap soil horizon. Soil treatment containers were gently tamped down on a lab bench to obtain a bulk density of 1.3 to 1.4 g cm^{-3}. This left a headspace of 2 to 3 cm above the soil for adding water. The pots were then laboratory incubated for up to 120 d at 10% soil moisture (w/w). The moisture contents were maintained gravimetrically through manual adjustments 2 to 3 times per week. The laboratory room temperature and percent relative humidity, respectively, ranged between 18 to 26ºC and 35 to 83%.

For initial chemical conditions, sub-samples of the treated soils with and without biochar (referred to as T_0), were arbitrarily allowed to incubate for 1-2 h, then were air-dried for 2 to 3 d. Afterwards, these sub-samples were sent to the Clemson University Soil Test laboratory for triplicate measurements of exchangeable P and Na using Mehlich 1 reagent (dilute HCl + H_2SO_4) and pH. On day 28, all pots were leached with 1.2-pore volumes of deionized water; the leachate was collected over a 30 h period and later weighed. The mass of leachate recovered was subtracted from the total volume of water added to determine the water retained by each treatment. The percentage of water retained by each pot was then calculated.

2.4. Statistics

The mean values for soil pH, extractable P, and Na concentrations were found to be non-normally distributed, so median values were tested for significant differences against the control (Norfolk soil + no biochar) using a Student-Newman-Keuls multiple comparison test at a $P = 0.05$ level of significance. The mean values for the percentage by weight of water retained for each biochar treatment against the control were compared using a Holm-Sidek multiple comparison procedure, also at a $P = 0.05$. All statistical tests were performed using SigmaStat v. 3.5 software (SSPS Corp., Chicago, IL).

3. RESULTS AND DISCUSSION

3.1. Biochar Recovery Yields and Physical Characteristics

The yields and physical characteristics of the raw feedstocks and the high and low temperature pyrolyzed biochars are shown in Table 1. More biochar was recovered at the lower pyrolysis temperatures due to minimal condensation of aliphatic compounds, and lower losses of CH_4, H_2 and CO. Below 350ºC, the yield recovery was at least 50%. The yield declined to about 30% as the pyrolysis temperature was increased up to 500 or 700ºC because of dehydration of hydroxyl groups and thermal degradation of ligno-cellulose structures [5,18]. The C recovery efficiency (biochar C/feedstock C) showed a similar pattern with mean C recovery ranging between 44 and 72% for the high and low temperature regimes (Table 1). The 250ºC switchgrass biochar was excluded from the mean (89% C recovery). It is questionable if this low degree of carbonization provides a ‘true-biochar’ or could be considered a torrified product. Torrification involves heating the feedstock to temperatures of 200 to 300ºC at slow heating rates (< 50ºC min^{-1}) under an anoxic atmosphere [18]. These mild conditions cause the torrified biochar to have chemical properties somewhat similar to the original feedstock [30]. The biochar pH values were lower and surface areas smaller at the lower pyrolysis temperatures. Substantial increases in pH occurred at the higher temperatures because of the concentration of non-pyrolyzed inorganic elements in the feedstock. Surface area increases with higher pyrolysis temperatures have been linked to creation of pores and cracking in the biochars basal-structural sheets [17].

Among the feedstocks, biochars produced from poultry litter had the highest pH values of between 8.7 and 10.3. These values measured in the poultry litter biochar were similar to values reported by Chan et al. [11] and Gaskin et al. [19] and were related to Ca and Mg in poultry manure [31]. In Table 2, the percentage of Na in both poultry litter biochars was from 1.88 to 2.69% (w/w), which is somewhat greater than values for poultry litter biochar (1.51 to 1.72%) pyrolyzed between 400 and 500ºC [19]. The increase in poultry litter biochar pH is probably due to the concentration of these nutrients through the pyrolytic process and with higher pyrolysis temperature. Among the eight biochars, pecan shell biochar produced at 700ºC had the highest surface area (222 m^2 g^{-1}), which is explained by its intrinsic higher density and through structural modifications that occurred at higher pyrolysis temperature [17]. Besides the type of feedstock and pyrolysis temperature, the development of porosity during pyrolysis also depends on the residence time and gas-flow rate. These two combined factors determine how biogas forms during pyrolysis, which in turn influences surface area development in the biochar. It is possible that surface area development would increase for both peanut hull and switchgrass feedstocks of pyrolysis temperatures of 700ºC. The surface area for poultry litter biochar produced at 700ºC was much lower than expected. Biochars produced from poultry litter under similar pyrolysis conditions but acid washed for partial removal of ash components displayed a surface area of 238 m^2 g^{-1} [32]. The lower surface areas could possibly be due to plugging of pores by the inorganic compounds in the ash present in high amounts in the biochar (Table 2).

The total surface charge of the biochars was influenced by feedstock selection and pyrolysis temperature (Table 1). Biochars produced at lower temperatures had measurable total surface charge with pecan shell biochar having the highest value (2.46 mmol H^+ eq/g C). Biochars produced between 500 and 700ºC had no measurable total surface charge, except for the 500ºC pyrolyzed switchgrass biochar. Biochars generally have higher charge densities when produced at higher pyrolysis temperatures [6].

Table 1 Percentage mass recovery, C lost, volatile matter, pH, surface area and total acidity contents for biochars from different feedstocks produced at different pyrolysis temperatures.

Feedstock	Pyrolysis T (ºC)	Air-dry Mass Recovered	C Recovered After Pyrolysis[a]	Volatile Matter	pH	Surface Area	Total Negative Surface Charge
		------------ % ------------				m^2 g^{-1}	mmol H^+ eq/g C
Peanut hull	0	---	---	78.1	---	---	---
	400	40	59	38.4	7.9	0.52	1.36
	500	35	56	18.1	8.6	1.22	nd[b]
Pecan shell	0	---	---	78.5	---	---	---
	350	50	62	61.6	5.9	1.01	2.46
	700	30	53	9.7	7.2	222	nd
Poultry litter	0	---	---	67.8	---	---	---
	350	57	72	36.7	8.7	1.10	1.10
	700	36	44	14.1	10.3	9.00	nd
Switchgrass	0	---	---	84.8	---	---	---
	250	78	89	74.4	5.4	0.40	1.19
	500	29	51	13.4	8.0	62.2	0.82

[a]values on an oven-dry basis; [b]nd – non detected

Table 2 Elemental composition and atomic ratios of biochars produced from different feedstocks and at different pyrolysis temperatures.

Feedstock	Pyrolysis Temp. (°C)	Elemental composition (%, oven-dry wt. basis) Ash	C	H	O	N	S	Na	P	Atomic ratios H/C	O/C	(O+N)/C
Peanut hull	0	3.3	50.7	6.1	38.1	1.7	0.09	---	---	1.43	0.56	0.59
	400	8.2	74.8	4.5	9.7	2.7	0.09	<0.01	0.26	0.72	0.01	0.13
	500	9.3	81.8	2.9	3.3	2.7	0.10	<0.01	0.26	0.42	0.03	0.06
Pecan shell	0	1.6	51.6	5.7	41	0.30	0.02	---	---	1.32	0.59	0.60
	350	2.4	64.5	5.3	27.6	0.26	0.01	0.01	0.03	0.98	0.32	0.32
	700	5.2	91.2	1.5	1.6	0.51	0.01	0.02	0.05	0.19	0.01	0.02
Poultry litter	0	24.4	36.2	4.8	24.4	4.1	0.32	---	---	1.58	0.51	0.60
	350	35.9	46.1	3.7	8.6	4.9	0.78	1.88	2.94	0.96	0.14	0.23
	700	52.4	44.0	0.3	<0.01	2.8	1.0	2.69	4.28	0.08	<0.01	0.06
Switchgrass	0	2.3	48.3	6.2	42.7	0.51	0.05	---	---	1.53	0.66	0.67
	250	2.6	55.3	6.0	35.6	0.43	0.05	<0.01	0.10	1.29	0.48	0.49
	500	7.8	84.4	2.4	4.3	1.07	0.06	0.01	0.24	0.39	0.04	0.05

These results suggest that, for the most part, biochars produced at higher pyrolysis temperatures could have poorer ability to increase the capacity of Norfolk soils to hold cationic plant nutrients. It is possible, however, that high temperature biochars with large surface areas and aromatic character will eventually be involved in soil nutrient exchange. Abiotic processes are capable of oxidizing surfaces of black carbon compounds, albeit after exposure to soil for months to years [33-35]. Low temperature biochars, on the other hand, may be more readily able to increase soil nutrient retention.

3.2. Biochar Elemental and Structural Characteristics

The ash content, elemental composition and atomic ratios for the raw feedstocks and biochars are shown in Table 2. The ash contents of biochars made from peanut hulls, pecan shells, and switchgrass were < 10%, while biochar made from the poultry litter feedstock ranged from 24 to 52%. For all other materials, ash contents rose with pyrolysis temperature. The high Na and S contents in the poultry litter biochar suggest that raw bedding material may have been treated with an S-containing compound such as sodium-bisulfate ($NaHSO_4$). This supplement is meant to keep the bedding material acidic for ammonia gas emission control. Use of feed supplements and litter treatment varies between different poultry companies, and this constituent can vary in the litter and biochar.

As expected in the pyrolytic process, the C content of the biochar was concentrated while the H and O contents both decreased with increasing temperature. This is a typical feedstock response during the pyrolytic process, where the feedstock loses surface functional –OH groups due to dehydration and at higher temperatures loses C-bound O and H atoms due to structural core degradation [5]. The different mineral content of the various feedstocks also affects the relative C content seen at high temperatures as minerals (Ca, K, etc.) that are not lost during pyrolysis. Pecan shell biochar increased from 52 to 91% C, while poultry litter biochar only increased to 44 from 36% initial C due to the higher ash content from non-volatile minerals. Biochar C contents > 90% from different feed-stocks (wood, corn cob) pyrolyzed at high temper-atures are not unexpected [36].

Among the eight biochars, P was exceptionally concentrated in the poultry litter biochar with high temperature pyrolyzed biochar having the highest %P content (Table 2, 4.28%). Phosphorus is a necessary nutrient in poultry diets for fast animal growth, and excess or unabsorbed P is excreted [31]. As pyrolysis temperature increased, in six of the eight biochars there was an associated increase in %P due to a concentration effect since this element is not lost during volatilization. The N and S contents of the biochars were mixed in terms of their increasing or decreasing concentrations during pyrolysis. Nitrogen levels were also elevated in poultry litter, and this element was partially volatilized during pyrolysis especially for the highest pyrolysis temperature.

The elemental composition of each feedstock was used to calculate atomic ratios as a predictor of their polarity and potential interaction with water. One would expect a biochar possessing higher H/C, O/C and (O+N)/C ratios to be more interactive with polar compounds [28]. The atomic ratios of the biochars, because of dissimilar O and H losses, varied considerably between feedstock and pyrolysis temperatures (Table 2), so that the biochars were most polar (high O/C and O+N/C ratios) at the lower pyrolysis temperatures.

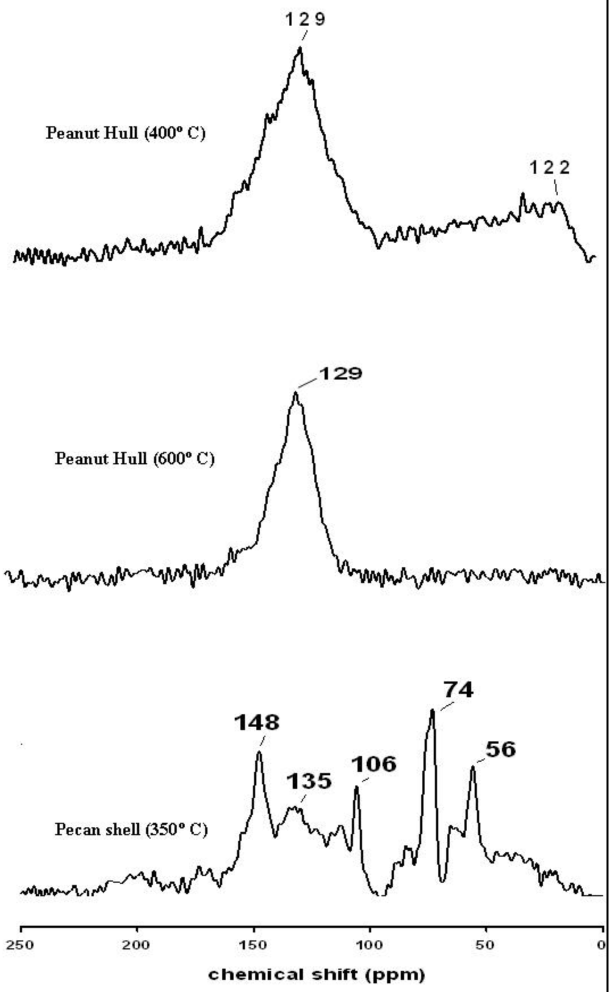

Figure 1 ^{13}C Nuclear magnetic resonance spectral scans of peanut hull (400 and 500ºC); and pecan shell (350ºC) biochar.

Switchgrass biochar (at 250ºC) was the most polar among the eight biochars. Among the four feedstocks, the low temperature switchgrass biochar had chemical properties that suggested it can be the most interactive with water.

The ^{13}C NMR spectral patterns show that the structural make-up of the biochars changed drastically during pyrolysis (Figures 1 and 2). Pecan shell, switchgrass, and poultry litter biochar, which were pyrolyzed in the lower temperature regime (250 to 350ºC) showed sharp, well-defined peaks from 32 to 106 ppm, indicating that O-alkyl and di-O-alkyl compounds that are characteristic of cellulose-type compounds were present [13]. By increasing the pyrolysis temperature to > 350ºC, the spectra were almost devoid of peaks from cellulose-type compounds but were dominated by peaks between 129 and 130 ppm that are assigned to aromatic-C structures.

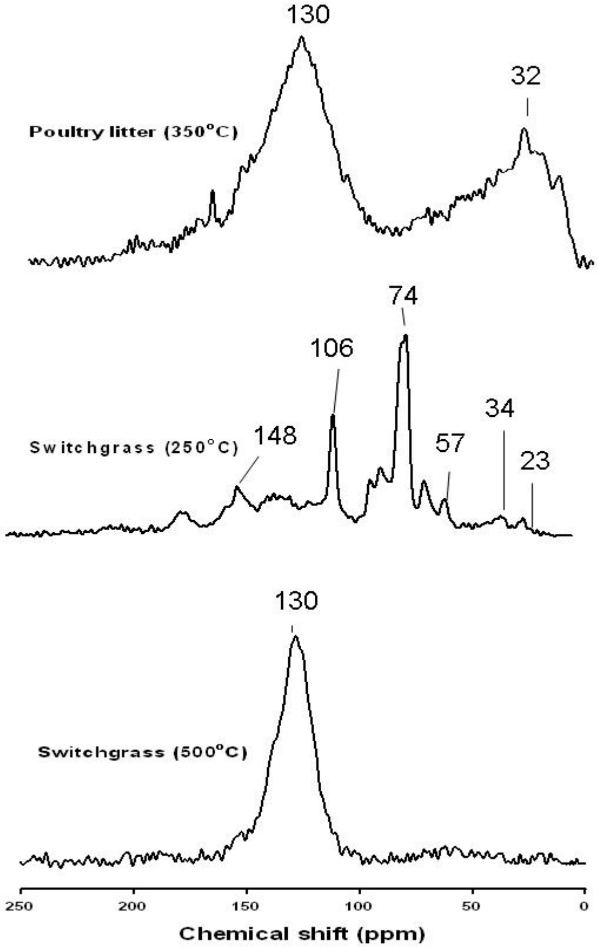

Figure 2 ^{13}C Nuclear magnetic resonance spectral scans of switchgrass (250 and 500ºC); and poultry litter (350ºC) biochar.

Peanut hull biochar made at the intermediate pyrolysis temperature (400ºC) also had a relatively minor peak at 122 ppm, suggesting some aliphatic compound retention. At the higher pyrolysis temperature, peanut hull biochar had lost most of its aliphatic material and exhibited a strong aromatic-C peak at 129 ppm.

Peak integration of the spectral patterns of the biochars confirmed the occurrence of structural modification as a function of pyrolytic temperature (Table 3). Pyrolysis at less than 400ºC caused biochars to retain their volatile material, which is mostly aliphatic-C structures (35 to 63%, Table 3). Raising the pyrolysis temperature to greater than 400ºC caused loss of aliphatic-C moieties and a centralization of C-compounds to mostly poly-condensed aromatic-C type compounds. In fact, the aromatic-C content of all biochars pyrolyzed between 250 and 400ºC was 29 to 57%, and it increased to between 50 and 82% at pyrolytic temperatures greater than 500ºC. Carbon distributed in carboxylate and carbonyl forms changed slightly (except for pecan shell biochar). A poor-quality NMR spectral pattern was obtained from the high temperature poultry litter biochar due to the preponderance of ash (Table 2, 52.4%), so structural analysis was extremely difficult if not impossible.

The NMR results suggest that these biochars may react differently when applied to soils. The literature has shown that biochars with high aromatic-C contents are resistant to microbial mineralization [1,6,10,13], which imparts a large half-life for biochar in soil. Biochar made from ryegrass (*Lolium perenne*) incubated in a Haplic Luvisol (a dark colored, organic-enriched surface horizon over a subsurface argillic horizon) was reported to have a half-life of 1400 yrs [33]. Biochars with high aromatic-C contents are probably appropriate for long-term C sequestration, and could be an ideal biochar trait to sequester soil C for millennia. The lack of surface charge (Table 1) in most of the biochars produced at high temperatures reinforces the premise that these biochars are a poorer choice for increasing a soil's ability to retain nutrients. A preponderance of aromatic structures in the high temperature biochars, however, does not preclude their involvement in cation exchange. Nevertheless, it will take some time for soil processes to oxidize core ring structures in high temperature biochar to form O-containing functional groups [33,34]. Switchgrass biochar produced at the higher temperature is the exception; in fact, it should increase a soil's ability to retain nutrients.

If the goal is to rapidly improve soil quality, then biochar made at low pyrolysis temperatures and from selected feedstocks may be a better option. For instance, the low temperature switchgrass biochar showed the most aliphatic-C character; therefore, it would be expected to contain substrates that may be mineralized by soil microbial communities and improve soil chemical and physical conditions. Furthermore, the low temperature biochars had measurable total surface negative charge, which is ideal for supplementing the soil's ability to retain cationic plant nutrients. However, given the higher C conversion efficiency of biochars produced at lower temperatures (Table 1), a considerable proportion of this C can be mineralized without reducing the C sequestration potential in comparison to the high temperature biochars.

3.3. Biochar Modifications to Norfolk Soil Fertility and Water-Holding Capacity

In Table 4, the untreated Norfolk soil (control) exhibits a pH, and extractable P, and Na concentrations typical for a southeastern USA Coastal Plain soil under agricultural management [10]. After a brief (1-2 h) exposure to these biochars, there were some dramatic modifications to a few chemical characteristics in the Norfolk loamy sand. Six of the eight biochars added at 2% (w/w, eq. to 40 to 44 metric t ha^{-1}) significantly increased the Norfolk acidic pH value into the alkaline pH region. While most of the biochars significantly increased Mehlich 1 extractable (plant available) P and Na, the increases were slight compared to the large amount of P and Na extracted after incorporating poultry litter biochar. Application of poultry litter biochars at 2% (w/w) increased Mehlich 1 soil extractable P concentrations between 20- and 28-fold, while extractable Na increased between 99- and 145-fold. Similar property changes occurred to an Australian soil (a Chromosol; a gray-colored sand over mottled clay subsoil) after 10 and 50 metric t ha^{-1} applications of poultry litter biochar [11]. In that report, soil pH, Na, and extractable P concentrations all increased after biochar application. Radish growth, yields, as well as soil microbial biomass were also significantly increased. Although our results showed similar increases in soil pH, Na, and P, it is unknown if these changes would cause harmful effects to crops or soil biota in southeastern Coastal Plain soils treated with poultry litter biochar.

Table 3 Percentage total C distribution among structural groups in biochars pyrolyzed from different feedstocks and at different temperatures.

Feedstock	Pyrolysis Temp (ºC)	Total percentage C as Aliphatic	Aromatic	Carboxylate	Carbonyl	Sum
Peanut hull	400	35	57	5	3	100
	500	12	82	3	3	100
Pecan shell	350	49	42	4	5	100
	700[a]	29	58	14	0	100
Poultry litter	350	36	57	4	3	100
	700	na[b]	na	na	na	na
Switchgrass	250	63	29	5	3	100
	500	12	82	3	3	100

[a]from [10]; [b]na – not available

Table 4 Chemical characteristics of a Norfolk soil after short-term incubation of 2% (w/w) biochars pyrolyzed from different feedstocks and at different temperatures[a].

Norfolk Soil + Biochar Type	Pyrolysis Temp. (ºC)	----------- Median Values for Soil Characteristics ------- pH[b]	P	Na
			------------- (kg ha^{-1})	---------
Control (0% biochar)	---	5.9a	64a	8a
Peanut hull	400	7.7b	104b	20b
	500	7.7b	85c	10a
Pecan shell	350	5.9a	71d	11a
	700	7.5b	71d	11a
Poultry litter	350	8.0c	1280e	791c
	700	9.7d	1812f	1159d
Switchgrass	250	5.9a	74ad	9a
	500	7.0e	94g	9a

[a]Soil incubated with and without biochar for 1-2 h and then air-dried over 2 d for nutrient extraction using Mehlich 1 reagent (dilute HCl + H_2SO_4); [b]Median values followed by a different letter are significantly different using a Student-Newman-Keuls multiple comparisons test at $P = 0.05$

Since both Na and S from a possible $NaHSO_4$ supplement in the raw feedstock become concentrated after pyrolysis, selection of poultry litter feedstock should be done with care. Feed composition selected by the integrator is of proprietary information; therefore, it is not possible to determine the contribution of Na or S coming from either the feed supplement or the application of any treatments to the bedding material. Excess Na in soil is well known to stunt plant growth by limiting water availability due to salt-generated osmotic gradients. The relatively high %P in the poultry litter biochar (Table 2, 2.94 to 4.28%) could be a concern, especially if applied to soils with high runoff potentials. Off-site soluble P and/or P-enriched sediment movement could pose a water quality threat if it is transported into nutrient-sensitive surface water systems and increases soluble P concentrations. Biochar made from poultry litter can still be a viable soil supplement if concentrations of entrained elements are reduced using a supplemental pre-treatment [37]. Szögi et al. [37] reported that an acidic 'quick wash' treatment process removed 60% of the initial total P from poultry litter solids.

After 28 days of incubation, water retention by the Norfolk soil with and without biochar incorporation varied considerably (Table 5). The Norfolk soil without biochar was able to retain only 35% by wt. of the applied deionized water leachate (mass collected after 30 h of free drainage). In contrast, water leaching of soil treated with the biochars revealed that a few treatments had water retention mass differences. Mixing in switchgrass biochar resulted in the largest, relatively significant shift in water retained; increases from 6.7 to 15.9% occurred relative to the control. This is a significant improvement in the mass of water retained by the Norfolk soil. Water retention increases in a sandy soil treated with soil supplements have also been reported [23,24]. As mentioned previously, these increases required treatment with 4 to 45% charcoal, much higher that the 2% rate employed in this study.

If the goal was to maximize soil water retention, then switchgrass biochar could be chosen. Among the two switchgrass biochars, more water was retained by the Norfolk loamy sand after mixing in the biochar produced at the higher temperature ($P < 0.010$, *t*-test between switchgrass treatment means). Peanut hull biochar produced at the lower pyrolysis temperature also significantly increased water retained by the Norfolk soil, but the relative increase was only 4.6%. While an exact mechanism for more soil water retention is unknown, it is speculated that these results may be a combination of these three biochar types being more polar (Table 2), or having more micropores for physically retaining water, or improved aggregation that created pore space for water storage. Increasing water retention by sandy, Coastal Plain soils after biochar application is an important achievement; more water retained in soil implies less crop moisture stress and potentially higher yields.

4. CONCLUSIONS

A laboratory study was conducted to characterize biochars produced from diverse feedstocks at different pyrolysis temperatures and ascertain their effect on the fertility and water holding capacity in a Norfolk loamy sand. The Norfolk loamy sand used in this study has typical properties of soils used for agricultural production in the Southeastern USA Coastal Plain region; sandy-textures, poor fertility and low water holding capacity.

Table 5 Percentage deionized water retained by Norfolk soil[a] after incubation for 28 days with 2% (w/w) and without biochars pyrolyzed from different feedstocks and at different temperatures.

Norfolk Soil + Biochar Type	Pyrolysis Temp. (°C)	Percentage by Weight of Water Retained Mean[b]	Standard Deviation
Control (0% biochar)	---	35.1a	0.95
Peanut Hull	400	39.7b	1.17
	500	37.9a	2.22
Pecan shell	350	36.9a	0.79
	750	38.3a	1.92
Poultry litter	350	34.1a	1.18
	700	34.8a	1.14
Switchgrass	250	41.8b	2.05
	500	51.0b	2.41

[a] Treatments (n = 4) leached with 1.2 pore volumes of deionized H_2O; water collected after 30 h of free drainage

[b] Means followed by a different letter are significantly different than control using a Holm-Sidek multiple comparison test at $P = 0.05$

Results showed that the structural and physical properties of the biochars varied as a function of feedstock selection and pyrolysis temperatures regimes. Higher pyrolysis temperatures resulted in biochars with lower total surface charges but higher surface areas, pH, and ash contents. These biochars also had higher %C but much lower H and O contents, resulting in a decrease in polar character. The ^{13}C NMR spectral analyses confirmed that losses of volatile materials (mostly aliphatic compounds) occurred at the higher pyrolysis temperatures, resulting in the remaining structures being composed mostly of aromatic-C structures. The high amount of C in aromatic structures explains the lack of total negative surface charges in most high-temperature pyrolyzed biochars. Functional groups, such as –OH and –COOH, that impart these negative charges were lost with volatile material removal. After incubation into the Norfolk soil, the biochars produced at the higher pyrolysis temperatures increased soil pH values. Poultry litter biochar grossly increased Mehlich-1 extractable P and Na concentrations. The Norfolk's water-holding capacity varied with biochar type and feedstock selection; switchgrass biochar produced the largest relative change in water-holding capacity.

This study revealed several interesting aspects of the effects of pyrolysis conditions and feedstock selection on biochar chemical properties and how these biochars influence certain issues in a Norfolk loamy sand. Creation of designer biochars may be possible with distinct quality traits that can improve discrete soil chemical and physical properties.

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