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Production and characterization of biochars from agricultural by-products for use in soil quality enhancement

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ABSTRACT

Byproducts are produced in significant amounts from crop residues such as pecan shells (PC), peanut shells (PS), and cotton gin (CG) trash. These residues can be used to produce biochar suitable for use in agricultural soil to sequester carbon and enhance plant growth by supplying and retaining nutrients while improving soil physical and biological properties. The objectives of this study were to produce biochars from different byproducts [PC, PS, CG, and switchgrass (*Panicum virgatum* L.)] at different pyrolysis temperatures and residence times, and to evaluate the resulting biochar's physico-chemical properties [yield, ash, pH, total surface area (TSA), surface charge (SC), and electrical conductivity (EC)] and elemental composition. Feedstocks were pyrolyzed under N_2 at 3 temperatures (300, 500, and 750 °C) and residence times each (8, 16, and 24 h), (4, 8, and 12 h), and (1, 2, and 3 h), respectively, depending on the nature of the feedstock. Higher pyrolysis temperatures resulted in lower biochar recovery, greater TSA, higher pH, minimal SC, and higher ash contents. Among the eight biochars, switchgrass-derived biochar produced at 750 °C had the highest TSA (276 $m^2 g^{-1}$) followed by PC biochar (185 $m^2 g^{-1}$). Substantial increase in biochar pH (up to 9.8) occurred at the higher temperatures. Biochars produced at lower temperatures (350 °C) had measurable SC with PS biochar having the highest value (3.16 mmol H^+ eq g^{-1} C). The highest ash content was observed in CG (up to 34%) compared to other biochars which contained <10% ash. These soil-related properties suggest that different biochars types can be produced to selectively improve physicochemical properties of soil through selection of specific feedstocks and pyrolysis conditions.
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1. Introduction

The production and processing of various agricultural commodities yield significant amounts of by-products in the form of crop residues such as nutshells, cotton gin, corn cobs, sugarcane bagasse, rice hulls, and straws, etc. Many of the agricultural residues can be used to produce biochar for its use in agricultural soil applications with the double advantage of sequestering carbon (improve soil structure, nutrient retention, and pH) and increasing the crop productivity [1,2]. In many cases, these agricultural by-products are left as waste materials with little or no economic value while their disposal is sometimes costly and may cause environmental issues. For instance, large amounts (more than 50% of total available agricultural residues in the United States) can be acquired between $40 and $60 per Mg of biomass [3].

Conversion of low value and underutilized agricultural by-products and high volume/low cost industrial biomass (e.g., switchgrass) is ecologically and economically attractive given the fact that energy can be produced at the same time as biochar. Some crop residues such as nut shells (e.g., groundnut, hazelnut, walnut,

Abbreviations: PC, pecan shells; PS, peanut shells; CG, cotton gin; TSA, total surface area; EC, electrical conductivity.

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chestnut, and coconut), bagasse from sugarcane processing, olive or tobacco waste are particularly suitable as precursors for biochar and are often available in large quantities in some locations [4].

Land application of biochar is not a new concept since certain dark earths in the Amazon Basin (so-called Amazonian Dark Earths or "terra preta") are well known as early applications of biochar for soil enhancement. The dark earths result from large amounts of charred materials from biomass burning [5]. These early biochars applications were most likely the result of both habitation activities and deliberate soil application by Amerindian populations before the arrival of Europeans [6].

Today, the emerging interest in the application of biochar to soil is driven by many considerations including environmental sustainability benefits. It is considered as a novel approach to establish a significant and long-term sink for atmospheric CO_2 in terrestrial ecosystems while reducing the need for synthetic fertilizers, and economic benefits through value-added to agricultural production system and higher crop yield resulting from improved soil fertility. In fact, recent studies in the field suggest that the production of biochar and its application to soil can deliver immediate benefits through improved soil fertility and increased crop production [7–9].

Conversion of biomass carbon to biochar carbon leads to sequestration of about 50% of the initial carbon compared to the low amounts retained after burning (3%) and biological decomposition (<10–20% after 5–10 years). Hence, production of biochar yields more stable soil carbon than burning or direct land application of biomass [4].

In a well managed system, biochar could become a key component for a doubly green revolution (sustainable food production and land degradation prevention) while offering one of the best practical ways to counter global warming (GHGs reduction) and counter pollution of streams and groundwater [10].

Many studies have been conducted on the pyrolysis of biomass residues for biochar production [11–13]. However, comparison of the properties of biochars obtained from different biomass residues produced under similar pyrolysis conditions has received limited attention in the literature.

Therefore, this research effort was undertaken to produce agricultural byproducts-based biochars from different biomass residues and compare their potential in soil applications to enhance soil quality, improve plant growth, and help decrease GHGs emissions. The specific objectives of this study were to (1) produce biochars from different byproducts (pecan shell, peanut shell, cotton gin) and switchgrass (a high yield and low cost forage crop) at different pyrolysis temperatures and residence times, and (2) determine specific physicochemical and surface properties of the resulting biochars that serve as predictors of their suitability in soil quality enhancement applications.

2. Materials and methods

2.1. Preparation of biochars

Four agricultural byproducts (pecan shells, peanut shells, cotton gins) and a high yield forage crop (switchgrass) were used as feedstocks to produce biochars. These residues were chosen due to their common and wide availability in the southeast region of the U.S.A. Pecan shells were obtained from Carolina Grains, Lumberton, North Carolina, and peanut shells from Golden Peanuts Company (Alpharetta, GA, USA). Cotton gin and switchgrass were obtained from the USDA-ARS Coastal Plain Research Center, Florence, South Carolina, where cotton, soybeans, and switchgrass were grown for research purposes.

The four precursors were dried overnight at 60 °C using a laboratory oven (Fisher Scientific, USA). The peanut and pecan shells were used as received without any further treatment while the cotton gin and switchgrass were cut into pieces of 0.1 cm long before pyrolysis. A Lindberg box high temperature furnace equipped with a retort (model 51668HR; Lindberg, Watertown, WI) was used for pyrolysis. The sealed furnace retort was purged using N_2 prior to initiation of pyrolysis to prevent carbon losses due to oxidation.

A 4 × 3 factorial design with nested residence time within pyrolysis temperature was used in this study with the first factor consisting of four different agricultural precursors (three feedstocks: cotton gin, peanut and pecan shells, and one forage crop: switchgrass), and the second factor consisting of 3 sets of pyrolysis temperatures (300, 500, and 750 °C) and 3 sets of pyrolysis residence time [(8, 16, and 24 h for 300 °C), (4, 8, and 12 h for 500 °C), and (1, 2, and 3 h for 750 °C)]. The choice of this nested design was based on previous results obtained from preliminary range finding experiments conducted in our laboratory in which we observed that no biochar remained when high temperatures were used along with long residence time, especially for soft materials. To account for these observations, we opted to use longer residence time at lower temperatures for soft materials like switchgrass and cotton gin. Hard materials like pecan shells allowed the use of high temperature and short time. Feedstocks were pyrolyzed following the above design under N_2 gas at a flow rate of 0.1 mL min^{-1} using a Lindberg box programmable furnace equipped with retort. Mass yield for biochar recovery was calculated using the following equation [14]:

$$\text{Mass yield}\,(\%) = \left[\frac{W_f}{W_0}\right] \times 100 \quad (1)$$

where W_f is the dry mass (g) of the produced biochars and W_0 is the dry mass (g) of the precursors.

2.2. Measurement of biochars properties with relevance to soil applications

Physical (surface area) and chemical (ash content, pH, surface charge, electrical conductivity, and total elemental analysis) properties of biochars were determined according to the procedures described in previous studies [15–17]. The total elemental analysis was determined using standard EPA method (EPA SW 846 Method 3050B; EPA, 1989) with minor modifications [18].

2.2.1. Ash content

Pre-weighed ceramic crucibles containing approximately 2 g of oven dried biochar were used to measure the ash content of the biochars. The samples were heated in a laboratory muffle furnace (Fisher Scientific, USA) at 760 °C for at least 6 h. After cooling, the remaining solids (ash) were weighed [17]. The percent ash content was calculated as follows:

$$\text{Ash}\,(\%) = \left[\frac{\text{remaining solids wt(g)}}{\text{original carbon wt(g)}}\right] \times 100 \quad (2)$$

2.2.2. pH measurement

The pH measurements of biochar were determined using the method described by Ahmedna [15]. A 1% (w/w) water suspension of each type of biochar was heated to approximately 90 °C and stirred for 20 min then allowed to cool to room temperature before pH measurement with a Corning pH 10 portable pH meter (Acton, MA). The pH meter was calibrated with standard pH 4 and pH 7 buffers [17].

2.2.3. Electrical conductivity

A 1% (w/w) solution of biochar in water was stirred at room temperature for 20 min [19] and electrical conductivity was measured using a Total Dissolved Solids (TDS)/Conductivity meter (Oakton Instruments, Vernon Hills, IL) with values given in microSiemens per centimeter ($\mu S\,cm^{-1}$).

2.2.4. Surface area

A Quantachrome Nova 2200e (Boynton Beach, FL) surface area analyzer was used to determine the surface area of test carbon based on N_2 adsorption at 77 K. Biochar weighing between 0.2 and 0.25 g was previously degassed overnight (for at least 8 h) and placed into the evacuated sample chamber of the surface area analyzer. BET surface area and pore size distribution output was obtained through the Nova 2200e automated software. The BET (Brunauer, Emmett and Teller) equation was used by the software to calculate the specific surface area of the test carbons [20,21].

2.2.5. Surface charge

The total negative surface charge was measured on duplicate samples based on the Boehm method [22–34]. One-tenth mole per liter solution of NaOH was prepared along with a 0.1 mol L^{-1} solution of HCl. A 0.5 g amount of biochar was introduced into a 250 mL flask with a Teflon stirring bar containing 50 mL NaOH solution. A blank (base with no biochar) was run in parallel with the biochar samples. After a 24 h continuous stirring of the samples containing 1% (w/v) carbon slurries along with the blanks, the solutions were filtered using a 0.45 μm Teflon filters. Fifteen mL of 0.1 mol L^{-1} HCl were added to a flask containing 10 mL of the filtrate and then the excess HCl was subsequently determined by titration with 0.1 mol L^{-1} NaOH.

Titrations were carried out using an 836 Titrando Autotitrator (Metrohm USA Inc., Riverview, Florida) equipped with a 50 mL burette and a Corning pH Meter probe. The volume of NaOH necessary to reach the equivalent point was recorded for the blank and the carbon samples. The difference in volume of NaOH consumed by the blank and by the carbon sample was calculated and converted to a titratable negative surface charge with results expressed as mmol H^+ equivalent neutralized by standard base per gram of biochar.

2.3. Total elemental analysis of biochars

The biochar elemental analysis content was determined using standard EPA method (EPA SW 846 Method 3050B; EPA, 1989) with minor modifications [18]. Between 0.1 and 0.3 g of dried biochar was added to 7.5 mL conc. HNO_3 and 2.5 mL of conc. HCL. The mixture was allowed to digest for approximately 30 min in a microwave digestion system. Digested samples were filtered with a 0.45 μm Teflon-filter, then diluted with deionized water to 50 mL, and analyzed for Zn^{2+}, Fe^{2+}, S, P, Mg^{2+}, K^+, and Ca^{2+} using Agilent 710 Series ICP-OES Inductively Coupled Plasma spectrophotometer (Agilent Technologies, Santa Clara, CA, USA). A series of multi-elements standards across a range of concentrations near the expected concentration of analyte in the test solutions were prepared using 1000 μg mL^{-1} stock solutions in 4% HNO_3. Samples containing elements exceeding the working range were diluted to the suitable range and reanalyzed as described above.

3. Results and discussion

3.1. Physicochemical characteristics of biochars

3.1.1. Effect of pyrolysis temperature and residence time on yield of biochars

The physicochemical characteristics of biochars as affected by precursors and pyrolysis temperature are shown in Figs. 1–6 and their elemental analysis is shown in Tables 1 and 2. Pyrolysis of all precursors resulted in higher biochar recovery at lower pyrolysis temperatures. This increase in yield of biochars at lower pyrolysis temperatures was most likely due to minimal condensation of aliphatic compounds, and lower losses of CH_4, H_2 and CO as reported by Amonette and Joseph [23]. The mass yield was at least 50% (Fig. 1) in biochars prepared at pyrolysis temperatures below 500 °C, and decreased to about 30% as the pyrolysis temperature was increased to 750 °C. This decrease in mass yield is likely due to dehydration of hydroxyl groups and thermal degradation of lignocellulosic structures [24].

This trend is in agreement with the findings of McHenry (2009) [25] who reported that at greater than or equal to 400 °C, the biomass material is converted into fused aromatic ring structures with the loss of CO_2, CO, H_2O and H_2 and that the biochar's mass yield depends on the nature of the precursor irrespective of its hardness. Sjostrom [26] stated that the chemical composition of the biomass feedstock has a direct impact upon the physical nature of the biochar produced. At temperatures above 120 °C, organic materials begin to undergo thermal decomposition, losing chemically bound moisture. Hemicelluloses are degraded at 200 °C to 260 °C, cellulose at 240 °C to 350 °C, and lignin at 280 °C to 500 °C. Therefore, the proportions of these components may influence the degree of reactivity and hence, the degree to which the physical structure is modified during processing [27]. This could explain the decrease of the mass yield due to increase in pyrolysis temperature as well as the type of precursor used for biochar preparation.

The effect of pyrolysis residence time on the yields of biochars was significantly ($p < 0.05$) at 300 °C but not at 750 °C (Fig. 1) at which the yield remained almost constant regardless of residence time. At the middle temperature, the yield seems to reach the minimum. This is best illustrated by peanut shells biochar produced at 500 °C for 12 h. It appears that the steepest yield loss occurred within the first hours of residence time during pyrolysis and then continued gradually during residence time. This loss in yield is largely due to the release of volatile matter from the shell structure which increases with pyrolysis temperature and residence time [26].

3.1.2. Effect of pyrolysis temperature and residence time on surface area of biochars

The increase in pyrolysis temperature significantly increased the total surface area of biochars ($p < 0.05$). Study conducted on pistachio nutshells (*Pistacia vera*) by Lua et al. (2004) [28] demonstrated that increasing pyrolysis temperature from 250 °C to 500 °C increases the surface area due to the release of volatiles from pistachio nutshells, resulting in enhanced pore development in biochars.

Among the eight biochars, the switchgrass-derived biochar produced at 750 °C had the highest surface area (276 $m^2\,g^{-1}$) followed by pecan shell-based biochar (185 $m^2\,g^{-1}$). This can be explained by the higher lignin content of these precursors and related structural modifications that occurred at higher pyrolysis temperature following the release of volatiles [29].

The total surface area (TSA) for cotton gin and peanut shells biochars produced at 750 °C was much lower than the TSA of other biochars. The lower surface area exhibited by cotton gin biochar (Fig. 2) could be due to plugging of pores by the inorganic compounds from ash (which is present at the highest amount in cotton gin compared to other biochars), or tars (condensed volatiles), and other amorphous decomposition products. These substances are known to partially block the micropores [30]. Even in a very low ash precursor, such as the hazelnut shells, the surface area was low due to some thermoplastic properties such as particles fusion, melting, and swelling due to high volatile matter [31]. This is in agreement with our results for biochars derived from peanut shells which showed similar thermoplastic properties. These results were

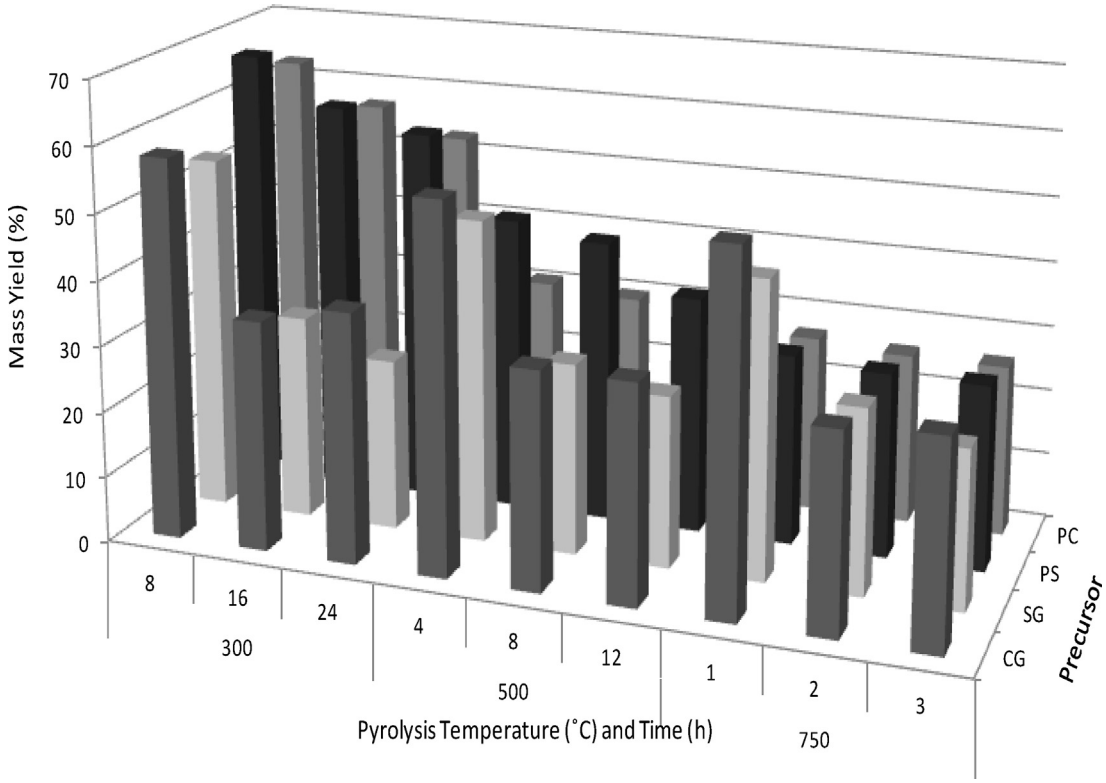

Fig. 1. Effect of pyrolysis temperature and time on mass yield of biochars derived from four agricultural residue feedstocks. *z*-axis represents type of precursor used during pyrolysis, *y*-axis represents the mass yield of different biochars produced, and *x*-axis represents pyrolysis temperatures and times used to produce different biochars. PS: peanut shells; PC: pecan shells; SG: switchgrass; CG: cotton gin.

also similar to those obtained by khezami [32] who reported that the surface area of chars never exceeded 300 $m^2 g^{-1}$ and even decreased with increase in pyrolysis temperature. It was reported that cellulose plays a major role in this process [33] where cellulose microfibrils dominate the mechanism of dimensional change during pyrolysis. This shrinkage is attributed to the formation of graphitic layers resulting from the aromatization process after thermal decomposition of glycosidic chains [27].

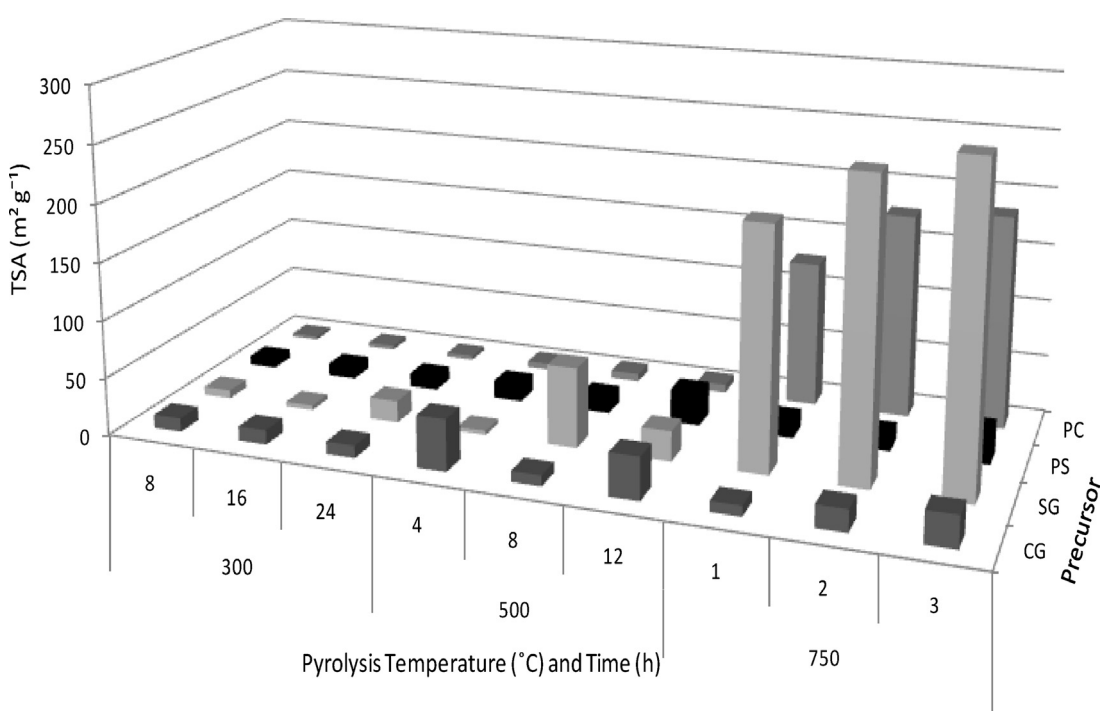

Fig. 2. Effect of pyrolysis temperature and time on surface area of biochars derived from four agricultural residue feedstocks. *z*-axis represents type of precursor used during pyrolysis, *y*-axis represents the total surface area of different biochars produced, and *x*-axis represents pyrolysis temperatures and times used to produce different biochars. PS: peanut shells; PC: pecan shells; SG: switchgrass; CG: cotton gin; TSA: total surface area.

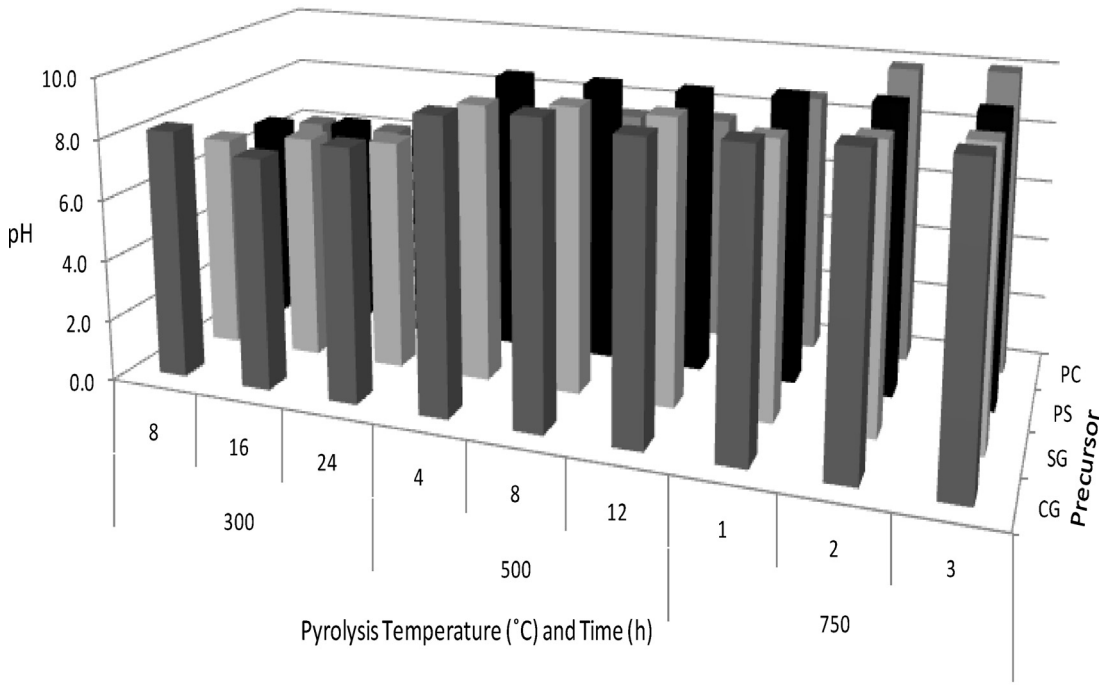

Fig. 3. Effect of pyrolysis temperature and time on pH of biochars derived from four agricultural residue feedstocks. *z*-axis represents type of precursor used during pyrolysis, *y*-axis represents the pH of different biochars produced, and *x*-axis represents pyrolysis temperatures and times used to produce different biochars. PS: peanut shells; PC: pecan shells; SG: switchgrass; CG: cotton gin.

Fig. 2 shows the effect of pyrolysis residence time on the total surface area of the biochars. The figure suggests that the total surface area increases significantly as the residence time increases ($p < 0.05$), with the highest increase occurring at 750 °C, regardless of the type of precursor. This can be explained by the fact that as the residence time during pyrolysis increases, the rudimentary pore structure within the char improves overtime due accelerated release of the volatile matter [28].

3.1.3. *Effect of pyrolysis temperature and residence time on pH of biochars*

Generally, pH values were lower and surface areas smaller for biochars produced at the lower pyrolysis temperatures. Substantial increase in pH occurred at the higher temperatures because of the increased relative concentration of non-pyrolyzed inorganic elements in the feedstocks and the formation of basic surface oxides under high pyrolysis temperature [34].

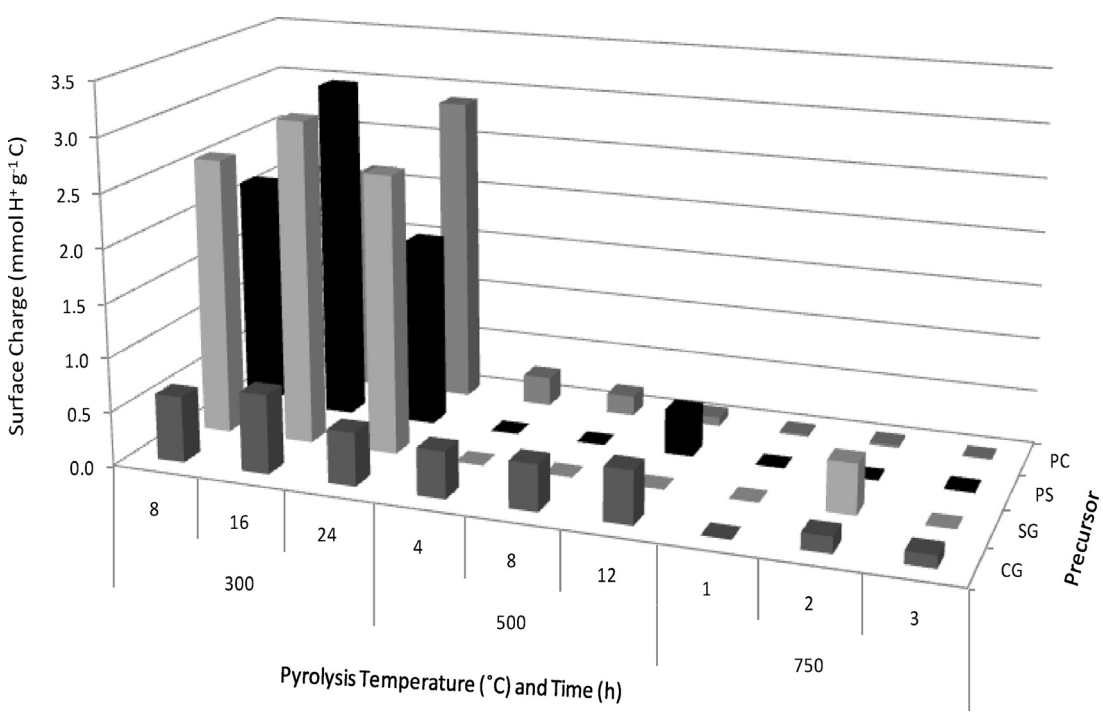

Fig. 4. Effect of pyrolysis temperature and time on surface charge of biochars derived from four agricultural residue feedstocks. *z*-axis represents type of precursor used during pyrolysis, *y*-axis represents the surface charge of different biochars produced, and *x*-axis represents pyrolysis temperatures and times used to produce different biochars. PS: peanut shells; PC: pecan shells; SG: switchgrass; CG: cotton gin.

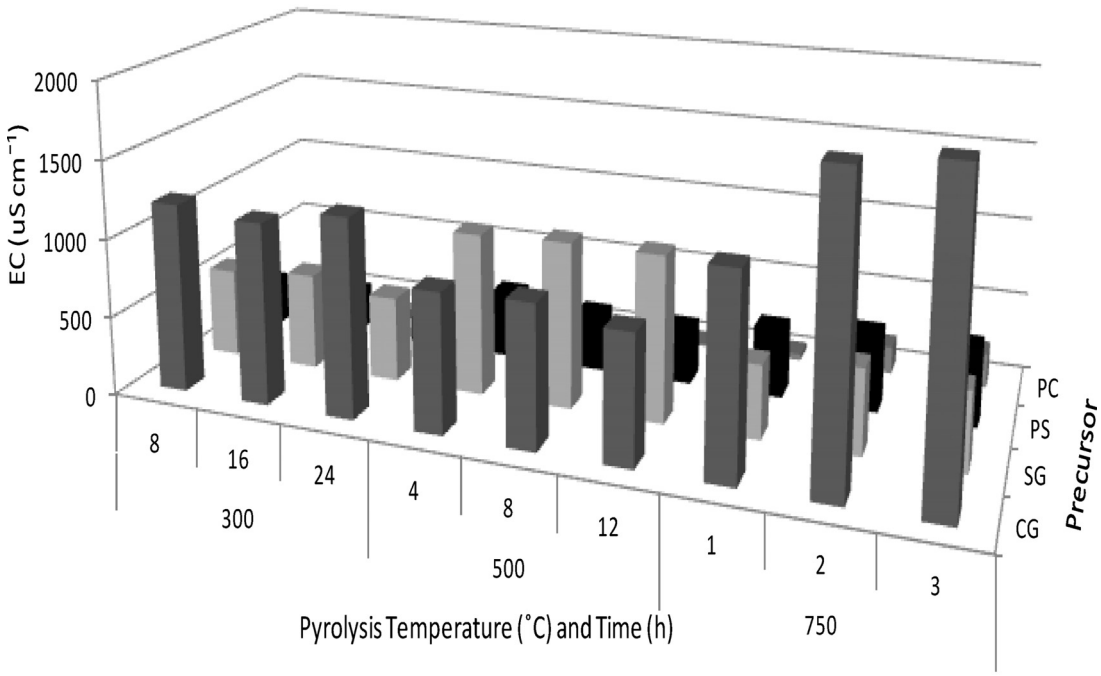

Fig. 5. Effect of pyrolysis temperature and time on the EC of biochars derived from four agricultural residue feedstocks. *z*-axis represents type of precursor used during pyrolysis, *y*-axis represents the electrical conductivity of different biochars produced, and *x*-axis represents pyrolysis temperatures and times used to produce different biochars. PS: peanut shells; PC: pecan shells; SG: switchgrass; CG: cotton gin; EC: electrical conductivity.

Among the feedstocks, biochar produced from cotton gin had the highest pH values ranging from 8.2 to 9.8, followed by pecan shell-based biochar (Fig. 3), probably due to their high Ca^{2+} and Mg^{2+} contents (Tables 1 and 2). The pyrolysis temperature had a significant positive effect on the pH values of biochars. The pH value significantly increased ($p < 0.05$) as pyrolysis temperature increased from 300 °C to 750 °C passing from a value of 6 to almost 10 which can be attributed to the release of the basic cations such as Ca^{2+} and Mg^{2+} during pyrolysis process at higher temperatures. Regardless of the precursor, the pyrolysis residence time appears

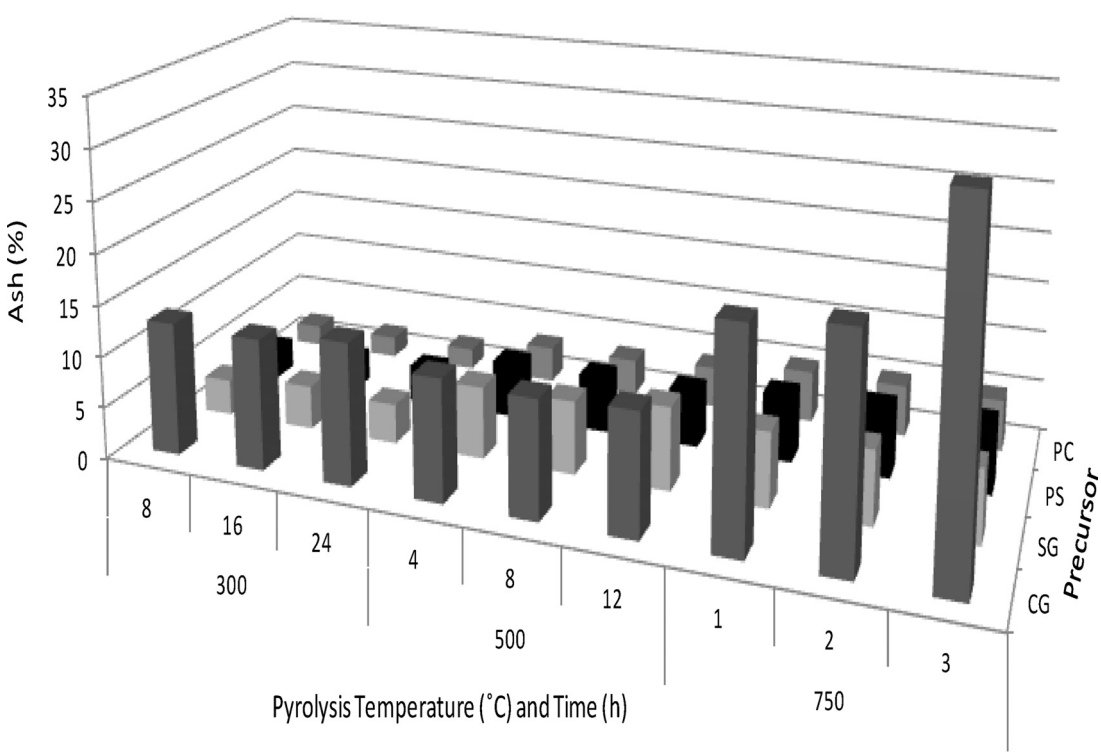

Fig. 6. Effect of pyrolysis temperature and time on ash content of biochars derived from four agricultural residue feedstocks. *z*-axis represents type of precursor used during pyrolysis, *y*-axis represents the ash content of different biochars produced, and *x*-axis represents pyrolysis temperatures and times used to produce different biochars. PS: peanut shells; PC: pecan shells; SG: switchgrass; CG: cotton gin.

Table 1
Total elemental analysis of biochars derived from agricultural residue feedstocks.

Precursor	Pyrolysis temperature (°C)	Pyrolysis time (h)	Ca^{2+} (g kg^{-1})	S (g kg^{-1})	K^+ (g kg^{-1})	Mg^{2+} (g kg^{-1})	P (g kg^{-1})	Fe^{2+} (g kg^{-1})	Zn^{2+} (mg kg^{-1})
Peanut shells		8	5.14 ± 0.16	0.14 ± 0.0[b]	11.44 ± 0.6	1.37 ± 0.0	nd[a]	nd	nd
	300	16	6.29 ± 0.21	0.49 ± 0.0	15.59 ± 0.9	1.80 ± 0.0	nd	nd	1.49 ± 0.0
		24	5.80 ± 0.18	0.26 ± 0.0	13.38 ± 0.7	1.51 ± 0.0	nd	nd	nd
		4	10.67 ± 0.3	1.09 ± 0.0	26.23 ± 1.8	2.90 ± 0.0	nd	0.10 ± 0.0	12.81 ± 0.7
	500	8	10.28 ± 0.4	0.97 ± 0.0	26.25 ± 1.1	2.72 ± 0.0	nd	nd	5.11 ± 0.3
		12	10.46 ± 0.3	0.94 ± 0.0	24.97 ± 1.4	2.68 ± 0.0	nd	nd	11.70 ± 0.5
		1	12.09 ± 0.5	1.10 ± 0.0	29.46 ± 1.3	3.09 ± 0.0	nd	1.34 ± 0.0	5.20 ± 0.1
	750	2	12.35 ± 0.5	1.04 ± 0.0	28.99 ± 1.7	3.11 ± 0.0	nd	1.14 ± 0.0	3.57 ± 0.1
		3	13.25 ± 0.6	1.18 ± 0.0	31.13 ± 2.6	3.30 ± 0.0	nd	1.20 ± 0.0	6.63 ± 0.2
Cotton gin		8	21.19 ± 1.2	2.46 ± 0.0	68.34 ± 4.3	3.84 ± 0.0	0.84 ± 0.0	nd	nd
	300	16	22.00 ± 1.5	2.65 ± 0.0	70.55 ± 3.7	3.90 ± 0.0	1.27 ± 0.0	nd	nd
		24	23.75 ± 1.6	2.75 ± 0.0	71.98 ± 3.1	4.22 ± 0.0	1.26 ± 0.0	nd	nd
		4	19.17 ± 1.1	0.66 ± 0.0	52.66 ± 3.2	5.94 ± 0.1	5.06 ± 0.1	nd	22.85 ± 1.1
	500	8	17.47 ± 1.5	0.68 ± 0.0	50.76 ± 2.1	6.22 ± 0.1	5.44 ± 0.1	nd	24.21 ± 1.8
		12	18.36 ± 1.2	0.53 ± 0.0	52.44 ± 1.8	6.29 ± 0.0	5.97 ± 0.1	nd	29.90 ± 1.4
		1	21.01 ± 1.3	1.14 ± 0.0	60.22 ± 3.8	7.42 ± 0.2	6.96 ± 0.2	0.18 ± 0.0	19.67 ± 0.6
	750	2	18.75 ± 1.4	0.94 ± 0.0	58.01 ± 2.7	7.09 ± 0.1	6.20 ± 0.2	nd	18.67 ± 0.4
		3	23.65 ± 1.8	1.63 ± 0.0	61.62 ± 2.6	7.28 ± 0.3	7.65 ± 0.2	0.34 ± 0.0	27.02 ± 1.2

[a] nd, not detectable.
[b] Values given are means of three estimations and standard deviation.

to have no effect or a statistically non-significant increase on the pH of the biochars (Fig. 3). The latter appears to be impacted mostly by pyrolysis temperature.

3.1.4. *Effect of pyrolysis temperature and residence time on total surface charge of biochars*

The total surface charge of the biochars was significantly influenced by both feedstock and pyrolysis temperature. Biochars produced at lower temperatures had measurable total surface charge with peanut shells biochar having the highest value (3.16 mmol H^+ eq g^{-1} C). Biochars produced between 500 and 750 °C had low or no measurable total surface charge (Fig. 4). The pyrolysis conditions were shown to influence the degree of aromaticity and, therefore, the adsorption characteristics of biochar. The degree of aromaticity increases with increasing pyrolysis temperatures [35] and pyrolysis time [36]. The presence of alkyl aromatic units in the biochars with a variety of oxygen-containing functional groups, including hydroxyl, carboxyl, carbonyl, ether, and lactone structures are gradually lost as the pyrolysis temperature increased. At 500 °C, the OH, C=O, and aliphatic C—H groups are largely lost, and at 750 °C, most of the aromatic C—H groups are decomposed [34].

Our results suggest that, for the most part, biochars produced at higher pyrolysis temperatures could have poorer ability to increase the capacity of soil to hold cationic plant nutrients due to their low surface charge. However, it is possible that high temperature biochars with large surface areas and aromatic characteristics will eventually be involved in soil nutrient exchange.

Cheng et al. [37] reported that abiotic processes are capable of oxidizing surfaces of black carbon compounds, albeit after exposure for months to years to soil. Biochars prepared at low pyrolysis temperatures, on the other hand, may be more readily able to increase soil nutrient retention due to their high surface charge compared to biochars produced at the high pyrolysis temperature.

A positive effect of the residence time on the surface charge was observed at low temperature (300 °C) where the surface charge

Table 2
Total elemental analysis of biochars derived from agricultural residue feedstocks.

Precursor	Pyrolysis temperature (°C)	Pyrolysis time (h)	Ca^{2+} (g kg^{-1})	S (g kg^{-1})	K^+ (g kg^{-1})	Mg^{2+} (g kg^{-1})	P (g kg^{-1})	Fe^{2+} (g kg^{-1})	Zn^{2+} (mg kg^{-1})
Switch grass		8	3.33 ± 0.10[b]	nd[a]	24.15 ± 0.21	3.41 ± 0.12	nd	nd	1.18 ± 0.00
	300	16	3.64 ± 0.11	nd	29.15 ± 0.85	2.89 ± 0.10	nd	nd	4.19 ± 0.12
		24	3.35 ± 0.15	nd	26.35 ± 0.41	3.50 ± 0.14	nd	nd	0.44 ± 0.00
		4	6.61 ± 0.83	nd	43.45 ± 1.44	4.77 ± 0.22	4.28 ± 0.10	nd	12.62 ± 0.54
	500	8	6.60 ± 0.02	nd	43.18 ± 1.15	4.65 ± 0.31	2.25 ± 0.0	nd	13.49 ± 0.32
		12	7.82 ± 0.57	nd	46.41 ± 2.10	5.14 ± 0.17	4.21 ± 0.14	nd	15.16 ± 0.28
		1	8.47 ± 0.06	nd	49.84 ± 1.87	5.67 ± 0.10	4.21 ± 0.18	0.18 ± 0.0	18.19 ± 0.46
	750	2	7.60 ± 0.66	nd	47.62 ± 1.46	5.27 ± 0.21	2.94 ± 0.0	0.19 ± 0.0	15.37 ± 0.39
		3	8.41 ± 0.78	nd	43.42 ± 1.02	5.59 ± 0.30	3.15 ± 0.0	0.26 ± 0.0	23.68 ± 1.02
Pecan shells		8	18.14 ± 1.30	nd	nd	0.37 ± 0.0	nd	nd	nd
	300	16	19.16 ± 1.94	nd	nd	0.38 ± 0.0	nd	nd	nd
		24	18.48 ± 1.21	nd	nd	0.41 ± 0.0	nd	nd	nd
		4	24.62 ± 1.44	nd	1.74 ± 0.0	0.69 ± 0.0	nd	nd	nd
	500	8	26.46 ± 1.05	nd	2.47 ± 0.0	0.76 ± 0.0	nd	nd	nd
		12	28.59 ± 1.11	nd	2.61 ± 0.0	0.82 ± 0.0	nd	nd	nd
		1	32.09 ± 1.42	nd	5.74 ± 0.1	0.91 ± 0.0	nd	nd	nd
	750	2	33.35 ± 1.91	nd	6.87 ± 0.3	1.01 ± 0.0	nd	nd	14.37 ± 0.11
		3	31.81 ± 1.33	nd	4.81 ± 0.2	0.98 ± 0.0	nd	nd	nd

[a] nd, not detectable.
[b] Values given are means of three estimations and standard deviation.

seems to increase as the residence time increases. This could be due to the increase in the degree of the biochar's aromaticity and formation of functional groups on the surface of biochar [34,36].

3.1.5. Effect of pyrolysis temperature and residence time on electrical conductivity and ash content of biochars

The electrical conductivity (EC) of biochars increased with increasing pyrolysis temperature and time, with the highest EC observed in cotton gin biochar at values ranging from 815 to 1971 $\mu S\,cm^{-1}$, depending on the production conditions. Pecan shell-based biochars showed the lowest EC among the four biochars (Fig. 5). This difference in biochar conductivity is likely related to their ash content which is highest for cotton gin and lowest for pecan shells (Tables 1 and 2).

The ash content of biochars made from peanut hulls, pecan shells, and switchgrass were below 10% while the ash content of biochar made from cotton gin was as high as 34%. This high ash content may be partially attributed to the sand/soil contained in the cotton gin during physical collection. Cotton gin residue was laying on the soil surface and silicates could also have been trapped in the condensed bulk of cotton gin balls. The residual sand was difficult to cleanup during preparation for pyrolysis and significant amount may have remained in the feedstock.

For all materials, ash contents increased significantly with pyrolysis temperature but the residence time appears to have no effect on the ash content, except for the cotton gin biochars produced at high temperature (750 °C) where the ash content significantly increased overtime (Fig. 6). This is expected since additional burn off over time at this high temperature leads to loss of yield primarily due to organic matter loss.

A strong positive correlation was observed between the pH, EC, and the ash content of the biochars. This correlation is due to the fact that increase of ash content or EC affects the biochar's pH. Furthermore, all the three variables increased as the pyrolysis temperature was increased.

The type of feedstock and conditions are important factors controlling the properties of the resulting biochar [38]. Firstly, the chemical and structural composition of the biomass feedstock relates to the chemical and structural composition of the resulting biochars. Secondly, the extent of the physical and chemical alterations undergone by the biomass during pyrolysis (e.g., attrition, cracking, micro-structural rearrangements) is dependent on the processing conditions (mainly temperature and residence times).

Cellulose and lignin undergo thermal degradation at pyrolysis temperatures ranging between 240–350 °C and 280–500 °C, respectively [38]. The relative proportion of each component will, therefore, determine the extent to which the biomass structure is retained during pyrolysis, at any given temperature. For example, pyrolysis of wood-based feedstocks generates coarser and more resistant biochars with carbon contents of up to 80%, as the rigid ligninolytic nature of the source material is retained in the biochar residue [39]. Biomass with high ligno-cellulosic contents (such as pecan shells) is shown to produce the highest biochar mass yields, given the stability of lignin and cellulose to thermal degradation. Therefore, at comparable temperatures and residence times, lignin loss is typically less than half of cellulose loss [38]. Whereas woody feedstock generally contains low proportions (<1% by weight) of ash, biomass with high mineral contents such as grass (switchgrass), and straw residues (cotton gin) generally produce ash-rich biochars [38].

The mineral content of the feedstock is largely retained in the resulting biochar, where it concentrates due to the gradual loss of carbon (C), hydrogen (H) and oxygen (O) during processing [40]. The mineral ash content of the feedstock can vary widely and evidence seems to suggest a relationship between that and biochar mass yield [23].

3.1.6. Effect of pyrolysis temperature and residence time on elemental composition of biochars

The elemental composition of the four types of biochars is shown in Tables 1 and 2. The biochars show dissimilarities in terms of elemental composition. This variability can be attributed to the different feedstocks and different conditions under which the four biochars were produced. K^+ and Mg^{2+} were most concentrated in cotton gin-based biochar, with biochar produced at high pyrolysis temperatures exhibiting the highest Mg^{2+}/K^+ concentration followed by switchgrass. On the other hand, pecan shells showed a very high concentration of Ca^{2+} compared to other biochars followed by cotton gin (Tables 1 and 2).

Unlike biochars from cotton gin and peanut shells, pecan shells and switchgrass derived biochars did not contain sulfur. This high variability in inorganic nutrient content and availability is likely to affect plant and soil responses following addition of these biochars. Accordingly, it would be difficult to adopt an optimum rate of soil application for all biochars due to the large variability in biochars nutrient composition. Hence, optimal application rates of a specific biochar can be accurately determined only for each soil type and plant species.

The above-discussed physicochemical properties of biochars from agricultural residues suggest that the complex and varying changes in biomass during pyrolysis affect both the composition and chemical structure of the resulting biochars, with significant implications on nutrients contents, especially nutrients availability to plants. Therefore, care must be taken to identify and use the right combination of pyrolysis conditions and precursor type for the target soil and even the type of plants to be used.

4. Conclusion

Biochars produced from different biomass under a range of pyrolysis process conditions exhibited major differences in their physical, chemical and adsorption properties. These dissimilarities were caused by differences among precursors and the effect of the pyrolysis conditions. However, the choice of feedstock and pyrolysis conditions can be made and adjusted to yield desirable properties for the intended soil application.

This study demonstrated the feasibility of developing biochars that possess specific properties with the potential to effectively alter the physicochemical properties of the soil and even target specific soil properties such as pH. Accordingly, designer biochars can be produced from agricultural by-products for specific soil applications such as pH buffering, nutrient enrichment, soil aggregation and moisture retention.

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