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Characterization of biochars produced from peanut hulls and pine wood with different pyrolysis conditions

James W. Lee^{1,4*}, Bob Hawkins², Michelle K. Kidder¹, Barbara R. Evans¹, A. C. Buchanan¹ and Danny Day³

Abstract

Background: Application of modern biomass pyrolysis methods for production of biofuels and biochar is potentially a significant approach to enable global carbon capture and sequestration. To realize this potential, it is essential to develop methods that produce biochar with the characteristics needed for effective soil amendment.

Methods: Biochar materials were produced from peanut hulls and pine wood with different pyrolysis conditions, then characterized by cation exchange (CEC) capacity assays, nitrogen adsorption–desorption isotherm measurements, micro/nanostructural imaging, infrared spectra and elemental analyses.

Results: Under a standard assay condition of pH 8.5, the CEC values of the peanut hull-derived biochar materials, ranging from 6.22 to 66.56 cmol kg⁻¹, are significantly higher than those of the southern yellow pine-derived biochar, which are near zero or negative. The biochar produced from peanut hulls with a steam activation process yielded the highest CEC value of 66.56 cmol kg⁻¹, which is about 5 times higher than the cation exchange capacity (12.51 cmol kg⁻¹) of a reference soil sample. Notably, biochar produced from peanut hulls with batch barrel retort pyrolysis also has a much higher CEC value (60.12 cmol kg⁻¹) than that (12.45 cmol kg⁻¹) from Eprida's H₂-producing continuous steam injection process. The CEC values were shown to correlate well with the ratios of oxygen atoms to carbon atoms (O:C ratios) in the biochar materials. The higher O:C ratio in a biochar material may indicate the presence of more hydroxyl, carboxylate, and carbonyl groups that contribute to a higher CEC value for the biochar product. In addition, the increase in surface area can also play a role in increasing the CEC value of biochar, as in the case of the steam activation char.

Conclusion: Comparison of characterization results indicated that CEC value is determined not only by the type of the source biomass materials but also by the pyrolysis conditions. Biochar with the desirable characteristics of extremely high surface area (700 m²/g) and cation exchange capacity (> 60 cmol kg) was created through steam activation.

Keywords: Biochar cation exchange capacity, Biochar surface areas, Biochar O:C ratios, Biomass pyrolysis, Biochar soil amendment, Carbon sequestration

Background

The world currently faces a systematic problem of increased CO₂ emissions, decreased soil-carbon content, and global-climate change (global warming). To solve this massive global energy and environmental sustainability

problem requires a comprehensive portfolio of R and D efforts with multiple energy technologies. Application of modern biomass pyrolysis methods for production of biofuels and biochar is potentially a significant approach to enable global carbon capture and sequestration at GtC scales (Day et al. 2005; Lee and Day 2013). Two of us (Day and Lee) co-initiated this technology concept with biochar as a soil amendment and carbon sequestration agent first in 2002 through a provisional US patent application

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followed by a PCT application (Day and Lee 2004). Using biochar samples produced by Eprida, Inc. (Athens, GA) from peanut hulls and pine wood, we performed certain experimental studies of the biochar materials with an ammonia carbonation process, cation exchange capacity assays, and micro/nanostructural analysis at Oak Ridge National Laboratory (ORNL) (Lee et al. 2013, 2010). This biochar soil amendment approach has received some recognition worldwide (Day and Lee 2004; Marris 2006; Lehmann 2007), especially since certain biochar-related soil (including Terra preta) research results have also indicated the possibility of using biochar as a soil amendment for carbon sequestration (Gundale et al. 2007; Solomon et al. 2007; Lehmann et al. 2006; Downie et al. 2011; Lee et al. 2010). Since the first USA biochar scientific symposium held in 2004 in Athens, Georgia, that was organized by one of us (Day) (Energy with Agricultural Carbon Utilization Symposium 2004), biochar research has increasingly become a wide-spread global scientific effort (Novak and Busscher 2013; Srinivasan et al. 2015; Zhang et al. 2015; Zhao et al. 2015, 2014; Windeatt et al. 2014; Lehmann and Joseph 2009; Bates 2010). Recently, biochar soil application has been discussed at the United Nations Framework Convention on Climate Change for possible consideration as a potential climate mitigation technology in accounting carbon credit (International Biochar Initiative), and a methodology for including biochar soil application as a carbon trading option has been reviewed by the American Carbon Registry (Koper et al. 2013). However, significantly more studies are needed before this approach can be considered for wide-spread commercial implementation (Novak et al. 2014; Baronti et al. 2014; Dai et al. 2013; Singh et al. 2015, 2014; Zhang et al. 2010; Blackwell et al. 2010; Spokas et al. 2010; Beesley et al. 2010; Topoliantz et al. 2005). In this paper, we report the results of a biochar characterization study

performed at ORNL using biochar materials produced from peanut hulls and pine wood under various different pyrolysis conditions as part of the efforts to develop better biochar materials for potential application as a soil amendment and carbon sequestration agent.

Methods

Biochar materials

The biochar materials (listed in Table 1) including peanut hull biochar and Southern yellow pine biochar were produced by the biomass pyrolysis process at Eprida and shipped to ORNL for characterization. The peanut hull biochar was produced from pelletized peanut hulls manufactured by Birdsong in Blakely, GA. The Southern yellow pine biochar was produced from pelletized southern yellow pine manufactured by Southern Shavings Co, Cherryville, NC.

Biochar samples #4, 5, 8, 9, and 10 (as listed in Table 1) were generated in Eprida's pilot scale biomass to hydrogen plant located at the University of Georgia's BioConversion Center. Since this was a DOE sponsored project to demonstrate hydrogen from biomass, the equipment and all material produced were under conditions optimized for hydrogen production rather than biochar production (H_2 continuous process). The plant consisted of a pyrolysis unit and a fluidized bed catalytic steam reformer for the production of biochar and hydrogen-rich syngas. The pyrolysis unit consisted of a rotary feeder and a variable speed auger for conveying the feedstock through the reactor. The system was electrically heated and utilized steam as a heated sweep gas and reactant. It typically operated around 15 kg/h biomass throughput with char yields averaging 29–30 %. The average residence time was 12–15 min. The pilot plant has been described in greater detail previously (Das et al. 2009). For all sample production runs, the temperature, rotary feeder, and auger

Table 1 Sample identification (ID) numbers and description: biochars and a control soil sample

Sample ID	Sample description	Biomass pyrolysis condition
4	PNC-EP char; Source: peanut hull	Eprida H2 continuous process char-temp 481 °C, 5.4 psig
5	PNC-M char; Source: peanut hull	Eprida H2 continuous process char-temp 475 °C, 1.4 psig
6	PNC-B char; Source: peanut hull	Batch barrel retort pyrolysis (no temp control/monitoring)
8	PIC-EP char; Source: southern yellow pine	Eprida H2 continuous process char-temp 465 °C, 4.2 psig
9	PIC-M char; Source: southern yellow pine	Eprida H2 continuous process char-temp 474 °C, 1.5 psig
10	PIC-NS char; Source: southern yellow pine	Eprida H2 continuous process no steam char-temp 485 °C, 0.5 psig
12	"High" char; Source: peanut hull	Eprida cross draft process, no steam char-average temp 950 °C
13	"Active" char; Source: peanut hull	Eprida cross-draft process 500C followed steam activation 800 °C Char
14	"Med" char; Source: peanut hull	Eprida cross-draft process, no steam-average temp 600 °C
15	Control soil sample: Milan soil from 0–15 cm deep Source: CSITE, Milan, TN	

speed set-points remained constant and unchanged. Temperatures and pressures listed in Table 1 are measured values, and variances between samples are due to changes in feedstock, sweep gas, and downstream equipment selection. Biochar samples 4 (PNC-EP char) and 8 (PIC-EP char) were produced while the pyrolysis vapors were sent to the catalytic steam reformer and converted to hydrogen-rich syngas. This caused slight restriction in the flow of vapors out of the pyrolysis reactor. Biochar samples 5 (PNC-M char) and 9 (PIC-M char) were run while the pyrolysis vapors were sent directly to flare with none of the vapors being diverted to the steam reforming section and no flow restriction on pyrolysis vapors resulting in lower reactor pressure than samples 4 and 8. Biochar sample 10 (PIC-NS char) was produced with vapors sent directly to flare as with samples 5 and 9; however, no steam was present as a carrier gas in the pyrolysis reactor. Nitrogen was present as required to protect the equipment sensors but it was not present in a quantity significant to be considered a carrier gas.

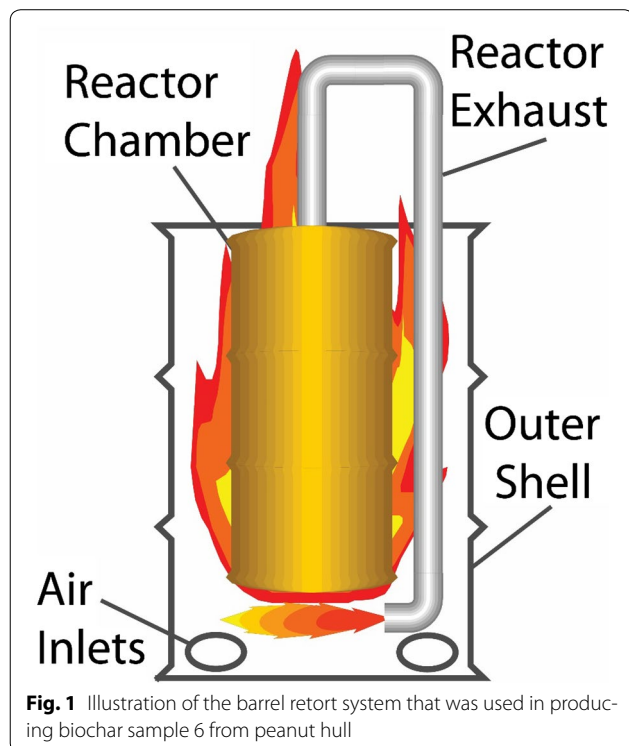
Biochar 6 (PNC-B char) was created by Eprida in a batch retort shown in Fig. 1, which consisted of a 35 gal steel drum reactor placed inside a 55 gal steel drum that was used as an outer shell. The reactor was filled with 100 kg of peanut hull pellets with a char yield of 23 %. The pyrolysis vapors were collected via a single exhaust pipe that ran through the center of the reactor and exited out

the center top and were sent to the underside of the reactor inside the outer shell for combustion. The outer shell, wrapped with a blanket of ceramic insulation, had several 1" holes throughout the bottom to provide air flow. These holes could be individually blocked off by covering with mud. Peanut hulls were placed inside the 35-gal reactor that was sealed except for the exhaust pipe. Hardwood pallet scraps were placed in the bottom of the outer shell to provide the fuel to start the pyrolysis reaction. The pallet scraps were ignited and allowed to combust. The pyrolysis vapors eventually become the main fuel as the wood is consumed and the pyrolysis reaction intensifies. The heat from the combustion in the outer shell is used to provide the heat for pyrolysis inside the reactor. No temperature controls or monitoring equipment were present. The duration and residence time were not measured as the material was left to cool overnight. This method was used to represent low technology charcoal production that is employed throughout the world.

Biochar 12 ("High" char) was made from peanut hull with Day's custom designed cross draft thin bed pyrolysis reactor (50 kg/h). It was designed to produce charcoal for steam activation in a second process. Rotary feed and discharge valves were used to control biomass flow. It utilized a natural gas burner operating at stoichiometric conditions to produce an inert gas stream that passed through a pyrolysis tube reactor with a diameter of 8 cm which also served as a moving bed of pelletized peanut hulls. The pressure was essentially atmospheric as gases were vented to a stack. Material exit temperature was used to control the biomass feed and discharge rates. The biochar of this sample was removed when it reached 950 °C. This was an off-spec product but included for evaluation.

Biochar 13 ("Active" char) was made by Day from a biochar produced in a similar reactor as that which produced Biochar 12 and 14, but the exit temperature was approximately 500 °C, and the biochar material was treated with steam in a novel three-zone 20-ft-long rotary reactor at 800 °C via discharge ports built into the reactor shell on a 18-cm square pattern for approximately 1 h. The hydrogen and carbon monoxide produced by the reaction between the carbon and steam were burned above the bed by injection of air through the same ports to maintain the temperature with additional heat and steam derived from combustion of pyrolysis vapors. The feed rate was maintained at approximately 400 kg/h and discharge rate was 200 kg/h. The material was cooled via a water jacket cooling transport cooler, then ground via a Williams Ring Roller Mill.

Biochar 14 ("Med" char) was made from the same process as that of biochar 12, except the temperature of the biochar when discharged was 600 °C. This is typical of



biochar designed for steam activation. This material was made as part of the DOE hydrogen program where the quantity of gas was more critical than impacts on the biochar. It was made at 600 °C in July 2002 as part of our 100 hour hydrogen production from biomass.

Cation exchange capacity and its assay protocol

A modified barium chloride compulsive exchange method (Skjemstad et al. 2008) was used in this study to determine the CEC for the biochar samples and a soil control from a standard test site located in West Tennessee as described above (University of Tennessee Research and Education Center, Milan, Tennessee, USA). The CEC value for the soil sample was reported previously (Lee et al. 2010). The detailed CEC protocol and data tables S1 and S2 are given in the Additional file 1 (supporting information). The test materials were ground for 4 min in a SPEX CertiPrep 8000-D Mixer mill with 1-cm (diameter) steel balls. Part of each ground sample was subsequently subjected to wet sieving with cutoff of 106 μm followed by oven drying before the CEC assay (Additional file 1: Tables S2 and S3). All samples were assayed in duplicate at ambient temperature (21–25 °C). Following the initial CEC determination for barium loading at pH 8.5, the suspensions were adjusted to lower pH values by addition of 0.010 M H_2SO_4 and the CEC determined again. Milliequivalents of acid required for pH adjustment were determined by weighing the titration containers.

Scanning electron microscopic (SEM) imaging

SEM images were taken with a Hitachi S-4700 at the center for nanophase materials sciences (CNMS) at ORNL. Biochar samples were mixed in water or isopropyl alcohol (IPA) at 5 wt% then placed on top of a 500 μm p-doped silicon wafer (which has very low resistance $<0.005 \Omega\text{-cm}$) and dried to fix the biochar samples onto the wafer. A more detailed description of the biochar SEM imaging method and selected images at three magnifications of samples 4, 5, 6, 8, 9, 12, and 13 are presented as Additional file 1: Figures S1a, S1b, S1c, and S1d in the Supporting Information.

Biochar surface area analysis

Brunauer–Emmett–Teller (BET)-specific surface areas were obtained from nitrogen adsorption–desorption isotherms measured at 77 K on a Quantachrome Autosorb-1 analyzer with all samples outgassed at 200 °C prior to analysis for a minimum of 8 h. Pore size distributions were analyzed by the BJH method, and BET taken from a multipoint plot over a P/P_0 range 0.05–0.35. Isotherms from biochars 4, 5, 6, 8, 9, 12, and 13 are included in the Supporting Information file as Additional file 1: Figures S2, S3, S4, S5, S6, S7, and S8, respectively.

Biochar infrared spectroscopic analysis

Infrared spectra were recorded on a Digilab FTS 7000 FTIR spectrometer, collected in transmittance, resolution of 4 cm^{-1} , 200 scans. Samples were prepared in KBr, 10 wt%, and pressed into a pellet. The spectra are presented in the Additional file 1, with Figure S9 showing the spectra for samples 4, 5, and 6; Additional file 1: Figure S10 those for 8 and 9; and Additional file 1: Figure S11 those for 12 and 13. Waveband assignments for functional groups are marked on the spectra in Additional file 1: Figure S11. Spectra shown are normalized at ca. 1827 cm^{-1} .

Elemental and proximate analysis

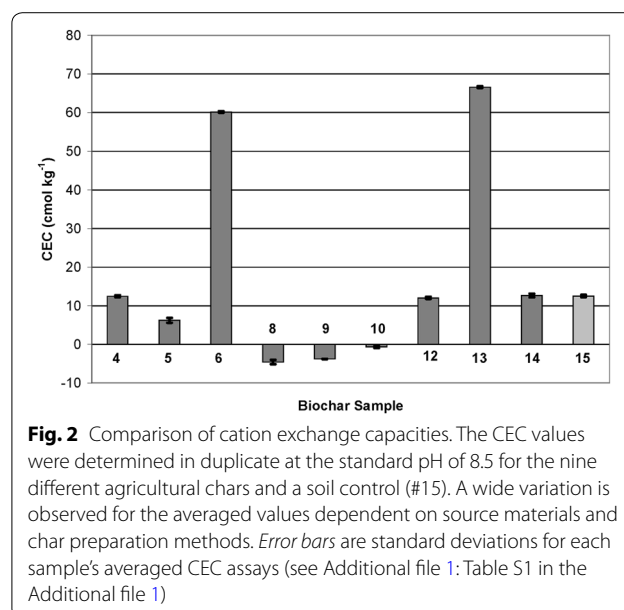
Biochar samples were sent to Galbraith Laboratories, Knoxville, TN for elemental, and proximate analysis.

Results and discussion

Cation exchange capacity (CEC) assay

To test the accuracy of the conductivity assay method for low CEC values, four 20-ml aliquots of 0.010 M MgSO_4 were weighed and titrated to the conductivity of 0.0015 M MgSO_4 . Assuming a simulated sample size of 0.5 g, an average value of $-2.750 \pm 0.2903 \text{ cmol kg}^{-1}$ was obtained.

The observed cation exchange capacity of the biochars varied depending on the type of biomass and the pyrolytic treatment (Fig. 2; Additional file 1: Table S1 in the SI section). At the standard assay pH of 8.5, the CEC values of the peanut hull-derived biochar materials (samples 4, 5, 6, 12, 13, and 14) in a range from 6.22 ± 0.64 to $66.56 \pm 0.22 \text{ cmol kg}^{-1}$ are significantly higher than those (near zero or negative CEC values) of the southern



yellow pine-derived biochars (samples 8, 9, and 10). The PNC-EP biochar (sample 4) produced from the peanut hull through Eprida's continuous steam-injected char-making process (481 °C, 5.4 psig) yielded a CEC value of $12.45 \pm 0.17 \text{ cmol kg}^{-1}$, which is similar to that of a standard soil (sample 15). The PNC-M biochar (sample 5) produced from the peanut hull through Eprida's continuous steam-injected char-making process (475 °C, 1.4 psig) resulted in a CEC value of $6.22 \pm 0.64 \text{ cmol kg}^{-1}$. This result indicates that the pyrolysis condition of PNC-EP (481 °C, 5.4 psig) can produce biochar with a higher CEC value than that of PNC-M (475 °C, 1.4 psig). This improvement in CEC value is probably owing to a higher steam-gas pressure (5.4 psig) used in the PNC-EP process than that (1.4 psig) of PNC-M.

Samples 6 (PNC-B char) and 13 ("Active" char), two of the peanut hull-derived biochar materials, were identified as some of the best biochar materials with the highest CEC values of 60.12 ± 0.19 and $66.56 \pm 0.22 \text{ cmol kg}^{-1}$, which is about five times higher than the cation exchange capacity ($12.51 \pm 0.30 \text{ cmol kg}^{-1}$) of a standard soil (sample 16, Milan top soil). The biochar of sample 6 (PNC-B char) was produced from peanut hull using a batch barrel pyrolysis technique mimicking a traditional char-making process without temperature control/monitoring. The biochar of sample 13 ("Active" char) was produced from the peanut hull with a continuous active char-making process, which resulted in an CEC value of $66.56 \pm 0.22 \text{ cmol kg}^{-1}$. Surprisingly, the PNC-B biochar produced from a batch barrel retort pyrolysis of peanut hull also has much higher CEC value ($60.12 \pm 0.19 \text{ cmol kg}^{-1}$) than that of the PNC-EP biochar from Eprida's H₂-producing continuous steam-injected char-making process ($12.45 \pm 0.26 \text{ cmol kg}^{-1}$). These results indicate that CEC value is determined not only by the type of the source biomass materials but also by the pyrolysis conditions. The CEC value of sample 14 ("medium" char) which was produced by a heat treatment without steam of peanut hulls similar to sample 12, but at a lower temperature (600 °C instead of 950 °C), was close to that of 12. This confirms the presence of steam during the treatment is one of the important process conditions to obtain the high CEC values observed in samples 6 and 13.

Negative CEC values (such as -4.582 ± 0.563 , -3.78 ± 0.05 , and $-0.68 \pm 0.26 \text{ cmol kg}^{-1}$) were observed for biochar samples 8 (PIC-EP char), 9 (PIC-M char), and 10 (PIC-NS char) that were produced from pyrolysis of southern yellow pine, and the CEC values generally became more negative for the CEC determination at pH values less than seven (Figs. 2, 3, 4). The pH curves for the CEC show that the chars have ion exchange characteristics similar to those observed for humic substances. Acidification appears to result in release of

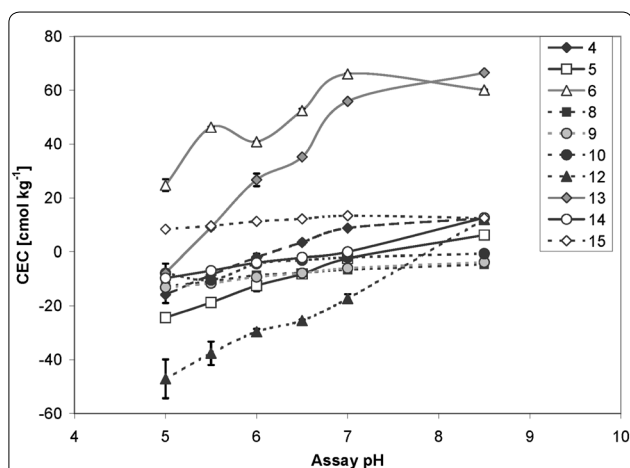


Fig. 3 Cation exchange capacities (CEC) of chars and soil control (#15) that had been ground 4 min were determined for pH values from 8.5 to 5.0. Averages of duplicate assays for each sample are shown. Error bars are standard deviations for each sample's averaged CEC assays (see Additional file 1: Table S1 in the Additional file)

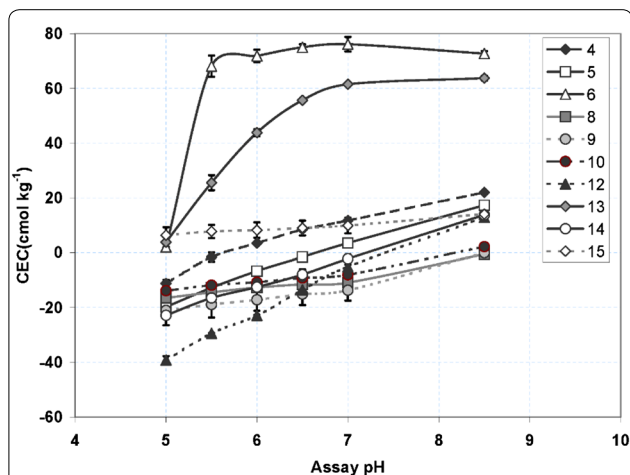


Fig. 4 Cation exchange capacities (CEC) of ground and wet-sieved chars and soil control (#15) were determined for pH values from 8.5 to 5.0. Averages of duplicate assays for each sample are shown. Error bars are standard deviations for each sample's averaged CEC assays (see Additional file 1: Table S2 in the Additional file)

bound cations, probably Ca²⁺, at pH values lower than seven, resulting in negative CEC values. Similar results due to the presence of Ca²⁺ bound to soil organic matter have been reported (Skjemstad et al. 2008). The probable cause of the negative values is the inability of the barium to displace all of the bound cations during the loading at pH 8.5. The char samples may have low binding affinity for Mg²⁺ similar to that reported for humic substances (Manahan 1999), which may also influence the CEC determination by barium chloride-magnesium sulfate displacement. The biochar samples required the addition

of much larger amounts of sulfuric acid to adjust the pH than did the soil control, suggesting that these materials possess an intrinsic buffering capacity. Results obtained from structural determinations of pyrolysis oils derived from biomass indicate that the lignin residues survive pyrolysis largely intact (Fratini et al. 2006), implying that biochars are primarily composed of lignin residues and that their soil amendment benefits stem from chemical properties resembling those of humus composed of lignin residues from biomass degradation.

The CEC values were determined for the wet-sieved biochar and soil samples (Additional file 1: Table S2). The effect of the wet-sieved treatment on the CEC varied dependent on the sample. The CEC values obtained were similar to those before sieving for chars 4, 5, 6, and 13, but decreased two-fold or greater for chars 8, 9, 10, 12, 14, and soil control 15. The recovery of the char samples and soil control from the wet-sieving procedure was determined by drying and weighing the sieved particles with size less than 106 μm and the residue greater than 106 μm remaining on the sieve (Additional file 1: Table S3). Statistical analysis was carried out with Student's *t* test on the yields obtained by sieving to determine if the proportions of the chars that were smaller in size than 106 μm were correlated with feedstock type, process temperature, steam activation, or high CEC values. Of these, only the feedstock type gave a *P* value <0.05 , with the yield of particles less than 106 μm significantly higher for pine chars compared to peanut chars (see legend of Additional file 1: Table S3 for details of analysis). No correlation between the amount of material lost during sieving due to particle size greater in size than 106 μm following grinding and the CEC values following sieving was apparent. The range of CEC values that were obtained for the char samples and the soil control is similar to but wider than that obtained for the archeological black carbon char samples and adjacent soils (Liang et al. 2006) when the CEC values reported here are converted to mmol kg^{-1} to correspond to the units used for the archeological samples. The range of CEC values that they reported ranged from 26 to 222 mmol kg^{-1} , corresponding to 2.6–22.2 cmol kg^{-1} . They found that the higher CEC values corresponded to higher content of black carbon and higher content of soil nutrients. The results reported here for the CEC values of several modern biochars and a soil control range from -0.5 to 72 cmol kg^{-1} . It is apparent from these results that both the biomass feed stock and the process conditions used to produce a biochar material determine the resultant CEC. This information assists the evaluation of the possible biochar processes for utility in production of soil amendments and carbon sequestration.

As shown in Additional file 1: Table S4, the statistical significance of the differences between the CEC values for the feed stocks and processes (Additional file 1: Table S2) was evaluated using Student's *t* Test with Microsoft Excel 2010 software. The significance of the changes in CEC values for ground samples compared to ground and wet sieved with 106 μm cutoff was also evaluated by calculation of *P* values using Student's *t* Test (Additional file 1: Table S5).

FTIR results

In Additional file 1: Figures S9 and S10, it is seen that samples 4, 5, and 6 of the Eprida peanut hull carry many distinct characteristic OH and C=O frequencies (Socrates 1980), as does samples 8 and 9 of the southern yellow pine. In Additional file 1: Figure S11, the FTIR of samples 12 and 13 show loss of the characteristic OH (3500 cm^{-1}) and CH peaks (several peak intensities missing between $1700\text{--}800\text{ cm}^{-1}$).

Galbraith analysis results

Overall, all biochars (samples 4, 5, 6, 8, 9, 12, and 13) produced from the peanut hull and southern yellow pine samples have relatively similar ash content of 4.5–14.6 %, carbon content of 73 % (samples 4–6, 8–9, and 12–13), and oxygen atom content of 12–20 % (samples 4–6, 8–9 and 13), with exception of sample 12 at 7.5 %, see Table 2. It is also notable that the biochars of southern yellow pine have very little nitrogen <0.5 %, whereas the peanut hull-derived biochars have 0.5–2.0 % nitrogen.

Comparison of samples 4, 5, and 6 show that there is a higher O:C ratio for 6. FTIR analysis also shows that there is also qualitatively stronger C=O and OH absorbance than that of 5. It is also interesting to note that the CEC value for 6 is significantly larger (60.1 cmol kg^{-1}), than for 4 and 5 (12.4 , and 6.2 cmol kg^{-1} , respectively).

Samples 12 and 13 show similar ash content. Sample 13 has a slightly higher % volatile matter (8.86 % vs. 6.15) than 12, but a lower calculated fixed carbon (67.8 vs. 75.1). However, despite that the %C of 12 and 13 are very similar, 13 has a significant amount of more % O, which calculates to a factor of 1.7 times higher O:C ratio for 13 than 12. This correlates again with the CEC ratio, where 13 has a significantly higher CEC of 66.6 cmol kg^{-1} and sample 12 ca. 12.0 cmol kg^{-1} . In addition, sample 13 has a larger surface area, ca. 3.3 times that of 12, see below.

Samples 8 and 9, southern yellow pine, have similar values in all the elemental and proximate analyses, with only the % ash being slightly higher for 8, but the resultant O:C ratios for both samples are 0.15:1. It is notable that the CEC values for 8 and 9 are similar, with negative CEC values of ca. -4.7 to -3.8 .

Table 2 Elemental and proximate analysis of biochars was carried out by Galbraith Laboratories, Knoxville, TN

Sample ID	% Loss on drying	% Volatile matter @950 °C	% Ash	% Fixed carbon (by difference)	C % (mol %)	H % (mol %)	% N (mol %)	O % (mol %)	S % (mol %)	O:C (mol ratio)
#4	5.86	23.13	7.57	65.54	71.54 (0.060)	2.90 (0.03)	2.08	16.59 (0.010)	0.106	0.167:1
#5	6.30	22.25	7.51	67.08	72.33 (0.060)	2.80 (0.028)	1.92	15.00 (0.0094)	0.108	0.156:1
#6	13.31	25.78	7.16	60.41	68.26 (0.057)	2.76 (0.028)	1.97	19.88 (0.012)	660 ppm	0.218:1
#8	4.54	22.60	7.54	67.60	74.78 (0.062)	3.19	<0.5	14.99 (0.0094)	<0.09	0.151:1
#9	5.37	22.55	4.50	70.27	76.59 (0.0638)	2.97	<0.5	15.42 (0.0096)	<0.08	0.151:1
#12	8.14	6.15	14.66	75.12	74.94 (0.062)	0.84 (0.084)	0.95	7.45 (0.0047)	0.16	0.075:1
#13	19.58	8.86	13.60	67.76	72.68 (0.061)	0.71 (0.071)	0.53	12.61 (0.0079)	0.17	0.129:1

Analysis results are the average of two analyses per sample expressed as % dry weight, except for the percent loss on drying, which is based on a one-time analysis. Standard deviations were <10 % (values given in parentheses)

Table 3 BET measurements of biochar samples

Sample ID	Surface area (multipoint BET): m ² /g
#4	2.52
#5	15.15
#6	7.70
#8	4.64
#9	186
#12	210.3
#13	697.4

Surface analysis

For BET analysis, Table 3 and Additional file 1: Figures S2–S8, all samples were outgassed a minimum of 8 h at 200 °C. In general, the isotherms look like Type I, which indicates microporous solids having relatively small external surfaces, for all samples excluding 9, 12, and 13, surface areas were between 4 and 57 m²/g for ground samples. The limiting uptake of adsorbate is governed by the accessible micropore volume rather than the internal surface area. However, there is some hysteresis, in samples which indicates bottle-neck or slit-shaped pores, and in some cases, the desorption branch closes at very low P/P₀, but sometimes it does not, which is probably an effect of the micropores unable to desorb the N₂ at high pressure. Also, there is no distinct curvature at low relative pressure (P/P₀), or central linear section of the isotherm, which indicates a strong adsorbate–adsorbate (N₂–N₂ gas) interaction rather than adsorbate–adsorbent (N₂–substrate). All of the isotherms except 13 do not close before reaching a relative pressure of <0.3 in the desorption process indicating that microporosity is present. Surprisingly, 12 and 13 have very large surface areas, and 13 exhibits a near closed loop hysteresis above 0.3 P/P₀, indicating possible “ink bottle” pores, but pore analysis indicates that the micropores are <1.5 nm in diameter.

SEM imaging analysis

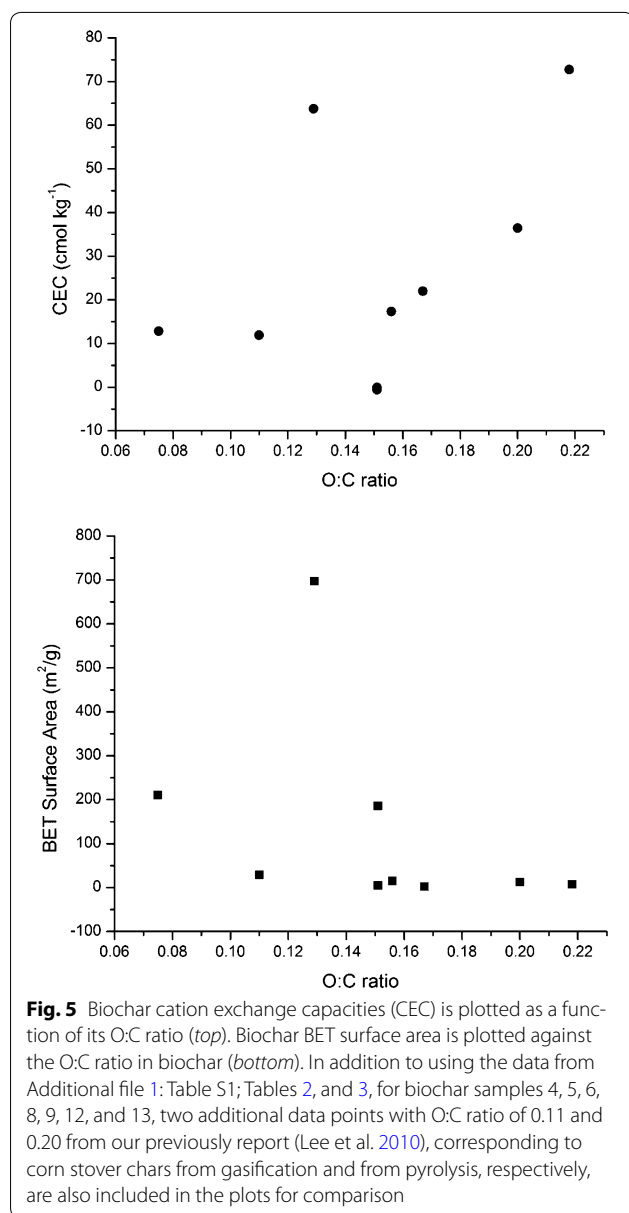
The SEM images of biochar samples 4, 5, 6, 8, 9, 12, and 13 were presented in Additional file 1: Figures S1a–S1d. From left to the right, magnification is 5, 50, and 500K. For each biochar sample, SEM images of three randomly selected spots were presented. According to the SEM images, samples 12 and 13 appear containing more porous or “sponge” type of micro/nanometer structures than samples 4, 5, 6, 8, and 9. This observation seems consistent with the results of the BET analysis, where biochar samples 12 and 13 showed very large surface areas as reported above.

Relationship among biochar cation exchange capacity, O:C ratio, and surface area

When the cation exchange capacities (CEC) measured at pH 8.5 were plotted as a function of the O:C ratio in biochar materials (Fig. 5, top), we noticed a quite clear relationship with the two. As the atomistic O:C ratio increases to above 0.15, biochar cation exchange capacity appears to rise dramatically although there are outliers.

One of the outliers is the cation exchange capacity value of 63.78 cmol kg⁻¹ with an O:C ratio of 0.129 from sample #13 which is the “active” char that was produced from peanut hull through the Eprida Cross-Draft Process at 500 °C followed by an 800 °C steam activation. As shown in Fig. 5 (bottom), this steam-activated biochar has much larger surface area (about 700 m²/g) than any of the other biochars. This explains why its cation exchange capacity is so high (63.78 cmol kg⁻¹); apparently because CEC in some extent is also dependent on biochar surface area.

When biochar BET surface area was plotted against the O:C ratio (Fig. 5, bottom), we noticed, these two properties seem somewhat inversely related. As the atomistic O:C ratio decreases, biochar BET surface area has a trend to increase. This observation is consistent with the understanding that the low O:C ratio (such as 0.075 in biochar



sample #12) was likely resulted from a high pyrolysis temperature (e.g., 950 °C) that favors deoxygenation and gasification of biomass, producing a biochar with somewhat higher surface area (Jindo et al. 2014; Budai et al. 2014; Wang et al. 2013). However, a moderate increase in biochar surface area under this condition apparently does not outweigh (overbalance) the loss of oxygen-containing functional groups due to the thermal deoxygenation of biochar products. Except in the case of steam activation, use of a moderate biomass pyrolysis temperature and/or condition that can retain a relatively higher O:C ratio is more likely to produce a desirable biochar with a higher cation exchange capacity. A similar relationship

(trend) between O:C ratio and cation exchange capacity was recently noticed also in a separate study with biochars from a hydrothermal biomass conversion process (Huff et al. 2014).

Summary

Under a standard assay condition of pH 8.5, the CEC values of the peanut hull-derived biochar materials (samples 4, 5, 6, 12, 13, and 14) in a range from 6.22 ± 0.64 to 66.56 ± 0.22 cmol kg^{-1} are significantly higher than those (near zero or negative CEC values) of the southern yellow pine-derived biochars (samples 8, 9, and 10). The biochar (sample 4) produced from the peanut hull through a continuous steam-gasified biochar-making process yielded a CEC value of 12.45 ± 0.17 cmol kg^{-1} , which is similar to that of a standard soil (sample 15). The biochar (sample 5) produced from the peanut hull through Eprida's H₂ continuous feed steam injection biochar-making process resulted in a CEC value of 6.22 ± 0.64 cmol kg^{-1} . Samples 6 and 13, two of the peanut hull-derived biochar materials, were identified as some of the best biochar materials with the highest CEC values of 60.12 ± 0.19 and 66.56 ± 0.22 cmol kg^{-1} , which is about five times higher than the cation exchange capacity (12.51 ± 0.30 cmol kg^{-1}) of a standard soil (sample 15, Milan top soil). The biochar of sample 6 (PNC-B char) was produced from the peanut hull using a batch barrel slow pyrolysis technique mimicking a traditional char-making process without temperature control/monitoring. The biochar of sample 13 ("Active" char) was produced from the peanut hull with a continuous active char-making process, which resulted in an CEC value of 66.56 ± 0.22 cmol kg^{-1} . Surprisingly, the PNC-B biochar produced from a batch barrel retort pyrolysis of peanut hull has much a higher CEC value (60.12 ± 0.19 cmol kg^{-1}) than that (12.45 ± 0.17 cmol kg^{-1}) of the PNC-EP biochar from Eprida's H₂-producing continuous steam-injected char-making process.

These results indicate that CEC value is determined not only by the type of the source biomass materials but also by the pyrolysis conditions. It was also found that the CEC values correlate well with the ratios of the oxygen atoms to the carbon atoms (O:C ratios) in the biochar materials. That is, the higher the O:C, the higher the CEC value. The higher O:C ratio in a biochar material may indicate the presence of more hydroxyl, carboxylate, and carbonyl groups that could contribute to a higher CEC value for the biochar product. In addition, the increase in surface area can also play a role in the increased CEC value of biochar. Although sample 13 ("Active" char) has a smaller O:C ratio than biochar 6 (PNC-B), the increase in surface area apparently also plays a role in increasing its CEC value.

Additional file

Additional file 1. Supporting information for this article is available online at the journal website. The supporting information describes: (1) Reference Soil Sample; (2) Detailed protocol for biochar sample grinding, sieving, and cation exchange capacity (CEC) determination and includes CEC data tables, calculation equations, and statistical analysis of CEC results; (3) Detailed description of scanning electron microscopic (SEM) sample preparation and imaging procedures; (4) Nitrogen adsorption-desorption isotherms from biochar surface area (BET) analysis; (5) Fourier transform infrared spectroscopy (FTIR) of biochar materials.

Authors' contributions

JWL conducted the overall biochar research project, analyzed data, and drafted the manuscript. BH and DD conducted the biochar production processes and co-wrote the description of biochar product samples and their associated production processes. BRE carried out CEC assays, biochar wet sieving, and statistical analysis and co-wrote the manuscript. MKK and ACB conducted the biochar elemental analysis, BET and FTIR measurements and co-wrote the manuscript. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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